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(54) Titre : **Processing and transforming biomass.**

(57) **Abrégé :**

Biomass (e.g., plant biomass, animal biomass, and municipal waste biomass) is processed to produce useful intermediates and products, such as energy, fuels, foods or materials. The saccharified biomass is fermented in two steps to form two separate products. The second product can be a carboxylic acid which is reacted with an alcohol to form an ester. The alcohol used for the esterification may be obtained from the biomass. The ester is hydrogenated to alcohols with catalysts.

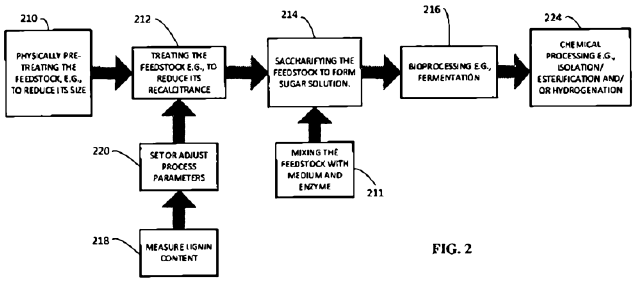

FIG. 2

17470

ORIGINAL

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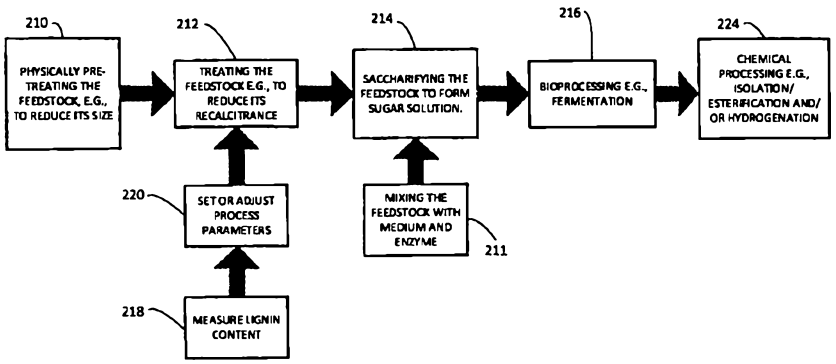
FIG. 2



(57) Abstract: Biomass (e.g., plant biomass, animal biomass, and municipal waste biomass) is processed to produce useful intermediates and products, such as energy, fuels, foods or materials. The saccharified biomass is fermented in two steps to form two separate products. The second product can be a carboxylic acid which is reacted with an alcohol to form an ester. The alcohol used for the esterification may be obtained from the biomass. The ester is hydrogenated to alcohols with catalysts.

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PROCESSING AND TRANSFORMING BIOMASS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application incorporates by reference the full disclosure of the following co-pending provisional applications: the co-pending provisionals filed March 8, 2013: USSN 61/774,684; USSN 61/774,773; USSN 61/774,731; USSN 61/774,735; USSN 61/774,740; USSN 61/774,744; USSN 61/774,746; USSN 61/774,750; USSN 61/774,752; USSN 61/774,754; USSN 61/774,775; USSN 61/774,780; USSN 61/774,761; USSN 61/774,723; and USSN 61/793,336, filed March 15, 2013.

BACKGROUND OF THE INVENTION

[0002] As demand for petroleum increases, so too does interest in renewable feedstocks for manufacturing biofuels and biochemicals. The use of lignocellulosic biomass as a feedstock for such manufacturing processes has been studied since the 1970s. Lignocellulosic biomass is attractive because it is abundant, renewable, domestically produced, and does not compete with food industry uses.

[0003] Many potential lignocellulosic feedstocks are available today, including agricultural residues, woody biomass, municipal waste, oilseeds/cakes and sea weeds, to name a few. At present these materials are either used as animal feed, biocompost materials, burned in a co-generation facility or are landfilled.

[0004] Lignocellulosic biomass comprises crystalline cellulose fibrils embedded in a hemicellulose matrix, surrounded by lignin. This produces a compact matrix that is difficult to access by enzymes and other chemical, biochemical and/or biological processes. Cellulosic biomass materials (*i.e.*, biomass material from which the lignin has been removed) is more accessible to enzymes and other conversion processes, but even so, naturally-occurring cellulosic materials often have low yields (relative to theoretical yields) when contacted with hydrolyzing enzymes. Lignocellulosic biomass is even more recalcitrant to enzyme attack. Furthermore, each type of lignocellulosic biomass has its own specific composition of cellulose, hemicellulose and lignin.

SUMMARY

[0005] Generally, this invention relates to systems, methods and processes for converting a biomass feedstock, e.g., cellulosic, starchy or lignocellulosic materials, to useful primary products, for example, alcohols, acids, esters, and sugars. The invention also relates to equipment, methods and systems to convert these primary products to useful secondary products, for example, converting esters by hydrogenolysis to alcohols (e.g., n-butanol, sec-butanol, iso-butanol, t-butanol, ethanol, and mixtures of any of these).

[0006] In one aspect the invention relates to methods of making products. The method includes producing one or more acids (e.g., acetic acid, n-butyric acid, iso-butyric acid) from biomass, e. g., saccharified biomass, sugars e. g., sugar in a saccharified biomass, the sugar fraction of a saccharified biomass, and converting the one or more acids into one or more esters. The method further includes hydrogenating the one or more esters utilizing a catalyst and hydrogen to produce one or more products, such as alcohols. Optionally, the one or more acids are produced by fermentation of the saccharified biomass sugars. Optionally, the saccharified biomass sugars are produced by saccharification of a cellulosic or lignocellulosic biomass material with one or more enzymes and/or one or more acids, such as by first using an acid and then using the one or more enzymes. The method can also further include recalcitrance reducing the cellulosic or lignocellulosic material e. g., by electron beam irradiation, e.g., delivering a dose of irradiation is between 10 and 200 Mrad to the material. Optionally, the catalyst can include a metal such as Pt, Pd, Re, Os, Ru, Rb, Ni, Co, Mo, W, Zn, Cr, Cu oxides of these and combinations of these. During the hydrogenation, a hydrogen pressure between about 5 and 120 atm. while utilizing the catalyst to produce one or more alcohols. Optionally, the method includes isolating at least one of the carboxylic acids (e.g., butyric acid) prior to converting the one or more acids into one or more esters (e.g., ethyl butyrate). Optionally, the method can be used to produce esters including ethyl butyrate, butyl butyrate, hexyl butyrate, and octyl butyrate. The alcohol portion of the ester maybe derived from biomass processing or by petrochemical processing. The carboxylic acid and alcohol can be reacted by known chemical processes to obtain the ester.

[0007] Another aspect of the invention features a method for making a product including converting the product of the fermentation of a saccharified treated lignocellulosic material to an ester, and producing an alcohol by passing the ester over a first catalyst e. g., a catalyst in the presence of hydrogen. The method can further include passing the ester over a second catalyst e. g., a catalyst. The first and the second catalysts can be different kinds of catalysts,

for example they can have different compositions (e.g., including supports such as silica and Al_2O_3). Alternatively, the first and second catalyst can be the same kind of catalysts.

[0008] In some implementations the method includes applying a first pressure of hydrogen while passing the ester over the first catalyst and applying a second pressure of hydrogen while passing the ester over the second catalyst, wherein the first pressure is higher than the second pressure by at least 0.5 atm. Optionally, the method can further include heating the first catalyst to a first temperature while passing the ester over the first catalyst and heating the second catalyst to a second temperature while passing the ester over the second catalyst, wherein the first temperature is higher than the second temperature by at least 10 ° C. Alternatively, the temperature of the second reactor can be higher than the first and the pressure can be increased between the two reactors. Optionally, the first and second catalysts can include metals in their compositions that include Pt, Pd, Re, Os, Ru, Rb, Ni, Co, Mo, W, Zn, Cr, Cu, oxides of these and combinations of these. Optionally, the method can include applying a hydrogen pressure between about 5 and 120 atm. Alternatively, the first and/or second catalyst is classified as a reforming catalyst.

[0009] In other implementations, the product of the fermentation comprises a carboxylic acid. Optionally, the carboxylic acid can have from 1 to 20 carbons and 1 to 5 carboxylic acid group (e.g., butyric acid, aspartic acid). Optionally, the product of the fermentation comprises an alcohol. Optionally, the ester can be, for example, ethyl butyrate, propyl butyrate, butyl butyrate, hexyl butyrate and octyl butyrate and the isomers of the alcohol and the carboxylic acid portion of the ester. That is, butyric acid and butyrate esters can refer to both the normal (n-) and iso isomer. The method can further include fermenting the biomass to at least two products and converting comprises condensing the products to the ester. For example, butyric acid and butanol can be converted to the butyl butyrate and then in turn hydrogenated to 2 moles of butanol.

[0010] In some implementations the method includes isolating the fermentation product prior to converting the product. Optionally, the fermentation product can be contacted with a resin and bonding the fermentation product to the resin. In addition the fermentation product can be removed from the resin by acidifying the fermentation product and extracting the acidified product with a solvent (e.g., alcohol).

[0011] Some implementations of the method include producing the treated lignocellulosic material by irradiating a lignocellulosic material with an electron beam. For example, irradiation can be done to accomplish a dose of about between 10 and 150 Mrad.

[0012] In some implementations the treated biomass is saccharified by contacting the treated biomass with an enzyme. The method can include that the saccharification produces a mixture comprising glucose and xylose and that the fermenting can include fermenting the xylose. In addition, the glucose can be fermented to an alcohol (e.g., selectively without fermenting the xylose), and optionally the alcohol can be distilled, prior to fermenting the xylose. Optionally, xylose can be added to the saccharified treated material (e.g., xylose in addition to that available from the treated saccharified material).

[0013] In another aspect the invention relates to a method of producing a product including fermenting a first sugar produced from the saccharification of a treated lignocellulosic material with a first organism and fermenting a second sugar produced from the saccharified treated lignocellulosic material with a second organism. Also, optionally distilling the product of the fermentation of the first sugar prior to fermenting the second sugar. For example, the first sugar can be glucose and the second sugar can be xylose. In some implementations the product of fermenting the first sugar is an alcohol (e.g., ethanol) and the product of fermenting the second sugar is a carboxylic acid (e.g., butyric acid).Optionally, the method can further include adding xylose to the saccharified material. Optionally, the following can be added to the saccharified material: acids, bases, buffers, amino acids, vitamins, blackstrap molasses, reinforced clostridia media, metal ions, yeast extract, meat extracts, vegetable extracts, peptones, carbon sources, proteins, Fe, Mn, Mg, Na, Cu, Zn, p-aminobenzoic acids, choline, thiamin, albumin, inositol and combinations of these. Optionally, the treated lignocellulosic material is produced by irradiating a lignocellulosic material with an electron beam, for example, with a dose of between about 10 and 200 Mrad.

[0014] In some implementations, the method further includes converting the product from the fermentation of the second sugar to an ester. Optionally, the ester can be hydrogenated to produce an alcohol.

[0015] In some implementations the method includes extracting the product of fermenting the second sugar utilizing an alcohol which include n-hexanol, n-octanol, n-decanol, n-dodecanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol, isomers of these alcohols and combinations of these.

[0016] Some of the possible advantages of the methods will now be discussed. Some fermentations are product inhibited so that the amount of a desired fermentation product that can be produced can be limited. For example, the fermentation of sugars to n-butanol by some species of *Clostridia* is often limited to one or two percent because above these levels it

is inhibitory or toxic to the organism. It can be challenging to remove this small amount of n-butanol from the aqueous spent fermentation broth. An intermediate to n-butanol in the fermentation is butyric acid, produced in the acidogenic phase of the fermentation. Butyric acid is generally less inhibitory or less toxic to Clostridia species and thus can be accumulated in higher concentrations than butanol, e.g., 4-7%. Butyric acid also can be less challenging to isolate from the fermentation broth due in part to its higher molecular weight and its partially ionic nature. Butyric acid is a useful product, for example, used in the chemical, food, flavor, fragrances and pharmaceutical industries. Butyric acid can also be directly hydrogenated to n-butanol. Alternatively, butyric acid can be esterified, for example, to ethyl butyrate and this product can be hydrogenated to n-butanol and ethanol under milder conditions than the direct hydrogenation. In addition to these advantages, deriving products, e.g., n-butanol, from biomass as described herein does not require as many high energy catalytic steps as required in the processing of fossil fuels. For example, fossil fuels can have a high concentration of compounds that must be removed prior to or during cracking, for example sulfur compounds that must be removed by hydrodesulfurization. By using the methods described herein, a clean biomass-derived feedstock is provided to catalysts (e.g., reforming catalysts) used in the processes and lower temperatures and pressures can be utilized.

[0017] Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

DESCRIPTION OF THE DRAWING

[0018] The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating embodiments of the present invention.

[0019] FIG. 1 is a diagram illustrating exemplary enzymatic hydrolysis of biomass.

[0020] FIG. 2 is a flow diagram showing processes for manufacturing sugar solutions from a feedstock.

[0021] FIG. 3 is a flow diagram showing processes for manufacturing sugar solutions from a feedstock showing a second fermentation.

[0022] FIG. 4 is a diagram illustrating a reaction scheme for converting a sugar to an alcohol with ethyl butyrate as the ester.

DETAILED DESCRIPTION

[0023] Using the methods and systems described herein, cellulosic and lignocellulosic feedstock materials, for example that can be sourced from biomass (e.g., plant biomass, animal biomass, paper, and municipal waste biomass) and that are often readily available but difficult to process, can be turned into useful products. Included are methods and systems to produce useful primary products, for example, alcohols, acids, and sugars. The invention also relates to methods and systems to convert these primary products to useful secondary products, for example, esters and alcohols (e.g., butanol, ethanol, esters and mixtures of these).

[0024] Enzymes and biomass-destroying organisms that break down biomass, such as the cellulose, hemicellulose and/or the lignin portions of the biomass, contain or manufacture various cellulolytic enzymes (cellulases), ligninases, xylanases, hemicellulases or various small molecule biomass-destroying metabolites. FIG. 1 provides some examples of these biomass-destroying processes. A cellulosic substrate is initially hydrolyzed by endoglucanases at random locations producing oligomeric intermediates. These intermediates are then substrates for exo-splitting glucanases such as cellobiohydrolase to produce cellobiose from the ends of the cellulose polymer. Cellobiose is a water-soluble 1,4-linked dimer of glucose. Finally cellobiase cleaves cellobiose to yield glucose. In the case of hemicellulose, a xylanase (e.g., hemicellulase) acts on this biopolymer and releases Xylo-oligosaccharides and xylose as possible products.

[0025] FIG. 2 shows processes for manufacturing sugars and fermentation products from a feedstock (e.g., cellulosic or lignocellulosic materials). In an initial step (**210**) the method includes, optionally, mechanically treating a cellulosic and/or lignocellulosic feedstock. Before and/or after this treatment, the feedstock can be treated with another physical treatment (**212**), for example irradiation, sonication, steam explosion, oxidation, pyrolysis or combinations of these, to reduce or further reduce its recalcitrance. A sugar solution e.g., including glucose, xylose and combinations of these, is formed by saccharifying the feedstock (**214**). The saccharification can be, for example, accomplished efficiently by the addition of one or more enzymes, e.g., cellulases and xylanases (**211**) or one or more enzymes and one or more acids in any order. The sugar solution can be bioprocessed (**216**),

for example by utilizing an organism to ferment the sugars to a primary product, e.g., an alcohol, a carboxylic acid, a ketone, hydrogen and combinations of these. Optionally, the fermentation can include more than one organism and comprises more than one fermentation step, for example producing one or more product simultaneously or sequentially. Optionally, the fermentation can be selective to one sugar. The primary product of the bioprocessing step can be chemically processed (**224**). For example, a carboxylic acid can be hydrogenated to an alcohol, esterified and/or esterified and then hydrogenated. Hydrogenation can occur in a batch reactor, or, in a continuous reactor. Optionally, the chemically processing can include isolation of the product, for example by a column extraction, solvent extraction and/or by distillation. If desired, the steps of measuring lignin content (**218**) and setting or adjusting process parameters based on this measurement (**220**) can be performed at various stages of the process, for example, as described in U.S. Application Number 12/704,519, filed on February 11, 2011, the complete disclosure of which is incorporated herein by reference.

[0026] In an analogous embodiment. Fig. 3 which is similar to Fig. 2, but with a different naming scheme. After saccharification the mixture is fermented at step **217** such that only one of the sugars is fermented to form a first product within a mixture of at least a second (unfermented) sugar, and fermentation solids. The first product at step **225** is isolated by any of the isolation means described herein. Optionally, the fermentation solids may be separated from at least the second (unfermented) sugar at step **232**. A second fermentation process at step **227** will convert the second sugar to a second product which can be isolated by any of the isolation means described herein at step **230**. Examples of the first and second sugar can be glucose and xylose, respectively, with the glucose being converted in the first fermentation step. For example, depending on the fermentation organism and/or fermentation conditions the glucose can be converted to ethanol or lactic acid. Alternately, the first sugar can be xylose and the second sugar can be glucose. In this case, the xylose fermentation product is the first product.

[0027] FIG. 4 shows an example of a reaction scheme for converting a sugar to an alcohol, specifically butanol. In a first step, for example, xylose is fermented to n-butyric acid. It should be understood that the iso-butyric acid may also undergo a similar reaction scheme. In a second step the butyric acid is contacted with the quaternary amine functionalized resin Amberlite™ 400. Butyrate becomes associated with the quaternary amine groups and is extracted from solution in this second step. In a third step the resin and bound butyrate is contacted with a strong acid, e.g., aqueous sulfuric acid, with the effect of protonating the butyrate and forming free butyric acid. The butyric acid can then be extracted

by ethanol or other alcohol providing butyric acid in an alcoholic solution. In a fourth step the butyric acid and ethanol (optionally additional ethanol can be added) is contacted with an optionally catalyst and heated (e.g., to refluxing temperatures around 80 to 90° C at atmospheric pressure) so that an esterification reaction occurs producing ethyl butyrate. In a fifth step, the ethyl butyrate is hydrogenated to butanol and ethanol utilizing hydrogen and a catalyst (e.g., Re/Al_2O_3). The hydrogenation step can be carried out in any reactor suited for hydrogenations.

[0028] The fermentation can produce a carboxylic acid, for example, as described in US APPN 13/177827 filed on July 7, 2011 and US APPN 13/668358 filed on November 5, 2012, the entire disclosure of which are incorporated herein by reference. The carboxylic acid can be, for example any carboxylic acid with between 1 to 20 carbons and 1 to 5 carboxylic acid ($-CO_2H$) groups (e.g., 1 to 10 carbons and 1 to 4 carboxylic acid groups, 1 to 5 carbons and 1 to 3 carboxylic acid groups). For example some carboxylic acids that can be utilized in the methods described herein are acetic acid, propionic acid, tartaric acid, malonic acid, succinic acid, glutaric acid, adipic acid, benzoic acid, phthalic acid, maleic acid, gluconic acid, traumatic acid, muconic acid, butyric acid (e.g., n-butyric acid, isobutyric acid), valeric acid, caproic acid, lauric acid, palmitic acid, stearic acid and arachidic acid.

[0029] Sugars from biomass can include one or more sugars. For example, some fermenting species can consume more than one sugar simultaneously or sequentially. Some fermenting species prefer one sugar. For example, some organisms may prefer the fermentation of fructose as described in PCT application No. PCT/US12/71097 filed Dec 20, 2012, designating the US and published in English. Optionally, the sugar solution can be processed prior to any fermentation step. For example, a saccharified solution as prepared by the methods described herein can be purified and/or processed by filtration (e.g., including rotary vacuum drum filtration), chromatography (e.g., simulated moving bed chromatography), electrodialysis including bipolar electrodialysis, crystallization and combinations of these. Optionally, processing can include fermenting one sugar in a mixture of two sugars and removal of the fermentation product, leaving a sugar solution of substantially the second sugar which can be more easily utilized, for example isolated and/or fermented (e.g. to a carboxylic acid). Some exemplary methods for purification and/or processing that can be utilized are discussed in co-pending U. S. Provisional Application Serial No's. 61/774,775, 61/774,780 and 61/774,761, the disclosures of which are incorporated herein by reference. In some cases, a biomass source can provide a higher amount of essentially only one sugar, for example some paper products, cotton and other

biomass that is almost entirely a glucose source with little if any xylose. Other biomass sources may provide mostly xylose and/or lignin.

[0030] Some suitable microorganisms to produce butyrate can include *C. saccharobutylacetonicum*, *C. saccharoperbutylacetonicum*, *C. saccharobutylicum*, *C. Puniceum*, *C. beijernckii*, *C. acetobutylicum*, *C. acetobutylicum*, *C. roseum*, *C. aurantibutyricum*, *C. felsineum* and *C. tyrobutyricum*. It can be beneficial to supply additives during fermentation, for example acids, bases, buffers, amino acids, vitamins, blackstrap molasses, reinforced clostridia media (RCM), metal ions, yeast extract, distillate bottoms, meat extracts, vegetable extracts, peptones, carbon sources and proteins. For example the addition of metal ions of Fe, Mn, Mg, Na, Cu, Zn and combinations of these can be beneficial. Other additives, for example, p-aminobenzoic acids, choline, inositol, thiamin, and albumin can be beneficial.

[0031] A preferred additive that can be utilized is the distillate bottom from a fermented saccharified lignocellulosic or cellulosic material (e.g., biomass). For example the yeast fermentation of a saccharified material as described herein producing ethanol can be distilled to produce a distillation bottom. The distillate bottom containing yeast cells and spent biomass (e.g., lignin, non-fermented sugars, proteins) can be used as an additive to a second fermentation. The distillate bottom can be optionally purified prior to use, for example, by methods described herein (e.g., rotary vacuum drum filters, simulated moving bed chromatography and improvements to simulated moving bed chromatography, filtration, precipitation). The concentration of solids (e.g., dissolved and/or suspended solids) can be at least about 5 wt.% (e.g., at least about 10 wt.%, at least about 20 wt.%, at least about 20 wt.%, at least about 30 wt.%, at least about 40 wt.%, at least about 50 wt.%, at least about 60 wt.%, between about 10 and 90 wt.%, between about 20 and 60 wt.%). The distillate bottom be used directly in the distillation or it can be diluted with a solvent (e.g., water) and used as at least 5 wt.% distillate bottom to solvent (e.g., at least 10 wt.%, at least 20 wt.%, at least 30 wt.%, at least 40 wt.%, between about 10 and 80 wt.%, between about 10 and 60 wt.%, between about 10 and 50 wt.%, between about 20 and 50 wt.%, between about 20 and 40 wt.%). The distillation bottom additive can be used in combination with other additive as herein described and additional sugars (e.g., glucose and/or xylose).

[0032] During fermentation, the pH of the fermentation media can be an important parameter to control. Buffers, for example, phosphate, sulfate and acetate buffers can help maintain a target pH. Addition of acids and bases (e. g., ammonium hydroxide, sodium and potassium hydroxides, acetic acid, sulfuric acid, phosphoric acid, nitric acids) can also be

added before, after and during the fermentation to maintain and or change or control the pH. During fermentation, the pH is optimally between about 2 and 8 (e.g., between about 3 and 8, between about 4 and 8, between about 4 and 7). Maintaining the pH above a critical value, for example above about 3 (e.g., above about 3.5, above about 4) by the addition of a base can often improve the fermentation. This control can be particularly important while using acidogenic bacteria since the acid products can lower the pH during the fermentation to values that are toxic to the organisms.

[0033] The temperature can also be a controlling and important parameter during fermentation. Optimally the temperature is maintained between about 20 and 50 °C (e.g., between about 20 and 40 °C, between about 30 and 40 °C). In some instances lower or higher temperatures from an optimal temperature can be utilized to induce a desired fermentation phase, e.g., acidogenisis, solventogenisis, log growth, sporulation.

[0034] For anaerobic organisms it is preferable to conduct the fermentation in the absence of oxygen e.g., under a blanket of an inert gas such as N_2, Ar, He, CO_2 or mixtures thereof. Additionally, the mixture may have a constant purge of an inert gas flowing through the tank or bioreactor during part of or all of the fermentation.

[0035] The fermenting or saccharifying organism can be immobilized on a support. For example an application of this process is described in U.S. Patent 5,563,069. The organism can be supported on a cellulosic or lignocellulosic material as describe in U.S Patent serial No 12/782,543 the entire disclosure of which is herein incorporated by reference.

[0036] The product of fermentation can be removed from the fermentation media by any useful means. For example, butyric acid and other fermentation products can be removed/purified by adding base to the fermentation solution, adding acid to the fermented solution, extraction, filtration, centrifugation, distillation, cross flow filtration, membrane filtration, pertraction, electrodialysis, adsorption and/or bonding to a resin or other solid, and combinations of these methods. Optionally, after purification, if the product is wet, the product can be dried, for example by contacting the product with molecular sieves or other drying agents (e.g., sodium sulfate, magnesium sulfate). An extraction method for organic acids including formation of an alkyl amine adduct in an aqueous solution that can be subsequently extracted from the aqueous phase is described in US Application Serial No. 12935075 filed March 27, 2009, the entire disclosure of which is incorporated herein by reference. In one preferred embodiment, organic acids (e.g., butyric acid) can be extracted by adsorption/adduct formation/bonding to on a solid support, for example a resin, solid and/or polymer support.

[0037] In some embodiments the fermented product can be extracted directly from the fermentation solution or from a solution that has been distilled. The extracting solvent can be, for example, an alcohol, an ether, an oil (e.g., castor oil, coconut oil, palm oil). For example, for the extraction of carboxylic acid (e.g., butyric acid) some particularly useful alcohols are fatty alcohols, for example, having between 6 and 20 carbons and 1 to 5 alcoholic functional groups (e.g., n-hexanol, n-octanol, n-decanol, n-dodecanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol, isomers of these and combinations of these). The acid can be protonated by treating the solution containing the acid with a mineral acid to adjust the pH to about pH 3 (e.g., between about pH 2 and 4) prior to extraction.

[0038] The acid can be esterified as discussed herein to the ester. The alcohols listed herein can be also utilized to esterify the fermentation derived acid. The esterification can be done in the extraction solution. For example, an alcohol can be added to the extracting solvent. If the extracting solvent is an alcohol then the alcohol can be directly utilized for esterification with or without concentration or dilution of the alcohol. For example, butyric acid derived from the fermentation of a biomass can be protonated by the addition of sulfuric acid to the fermented solution. The butyric acid can be subsequently distilled away from the acidified solution. The distillate can then be extracted in an alcohol (e.g., n-octanol). An acid catalyst can be added to the extracted acid and alcohol and the solution heated to produce an ester. Alternatively, fermented solution can be acidified and then directly extracted with an alcohol (e.g., octanol). The mixture can then be esterified.

[0039] In some embodiments the resins utilized to adsorb organic acids (e.g., butyric acid) can be polymers with ion exchange properties, for example having quaternary amine functional groups that can ion exchange with the acidic proton of the acid. For example Amberlite™ IRA 410, Amberlite™ IRA-67, Amberlite™ 96, Amberlite™ XAD-1180M, Amberlite™ XAD-2, Amberlite™ 400 and Amberlite™ IRN150. A solution containing the organic acid can be contacted with the ion exchange resin by passing the solution through a packed column (e.g., glass, metal, plastic) of the resin. Optionally, the solution containing the organic acid can be combined with the resin in a vessel (e.g., in a batch mode) and agitated (e.g., shaken, stirred) for several minutes to several hours (e.g., 1 min to 24 hours, 1 min to 12 hours, 1 min to 8 hours, 1 min to 4 hours, 1 min to 1 hour, 1 hour to 4 hours, 1 hour to 12 hours). In batch mode the organic acid depleted solution can be decanted or filtered from the resin after a sufficient time to adsorb/bond at least some of the organic acid. The amount of

butyric acid in the batch separation or column separation methods can be monitored by any useful method, for example, head space analysis, titrations and HPLC.

[0040] A resin for adsorbing an organic acid can be contacted with the fermenting solution while the fermentation is still processing or after the fermentation is complete. For example the active fermentation media can be pumped through a column of the resin or the resin can be added to the fermentation broth.

[0041] The organic acid can, for example, be removed from the resin by contacting the resin and bound organic acid with an acid solution. For example the acid solution can include a mineral acid (e.g., hydrochloric, sulfuric, phosphoric, nitric) or the acid can be an organic acid (acetic acid, trifluoroacetic acid). It is generally preferable to use an acid with a low pKa, e.g., about lower than the pKa of butyric acid e.g., a pKa of less than about 4, less than about 3, less than about 2. The pH of the solution after acidification is optimally between about 1 and 6 (e.g., between about 2 and 5, between about 2 and 4). It can be advantageous to utilize a solvent with or without water to aid in extracting the organic acid or organic acid salt from the resin. For example the solvent can be an alcohol (e.g., methanol, ethanol, propanol, butanol or the fatty acid alcohols previously described), an ether (e.g., diethyl ether, tetrahydrofuran, methyl tert-butyl ether, di-isopropyl ether), acetonitrile, acetone, butyl acetate, dimethylformamide, ethyl acetate and combinations of these. These can be combined in any percentage with water and each other. A preferred method of removing adsorbed organic acid from a resin packed column is elution with acidified alcohol (e.g. ethanol and/or methanol with and added acid) or an acidified alcohol/water solution (e.g., ethanol/water, methanol/water with and added acid). Resins can be recycled after removal of the acid, for example by flushing with excess of the acidified solution followed by flushing with water, optionally deionized water.

[0042] The acidified eluent/extracting solution from the resin processing containing the carboxylic acid can be neutralized by addition of a base. This can produce the salt of the carboxylic acid. The salts of the carboxylic acid can be evaporated to dryness and then oven dried (e.g. at 80 to 100 ° C). The salts can be subsequently utilized in esterification reactions, with optionally re-acidification prior to the reaction.

[0043] In an alternative to acidification to remove the organic acid from the resin, the acidic proton of the organic acid can be removed by ion exchange with a cation to form the salt of an organic acid. Some useful exchanging ions include, for example, quaternary ammonium ions, alkali metal ions and alkali earth metal ions, transition metal ion and

combinations of these. The salt of the carboxylic acid thus produced can be further processed as previously discussed.

[0044] The formation of esters as discussed herein from carboxylic acids can be done by utilizing any alcohol, for example, alcohols containing 1 to 20 carbon atoms and 1 to 5 alcohol groups (e.g., 1 to 10 carbon atoms and 1-4 alcohol groups, 1 to 10 carbon atoms and 1-2 alcohol groups). Some exemplary alcohols are methanol, ethanol, propanol, n-butanol, n-hexanol, n-octanol, n-decanol, n-dodecanol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, linoleyl alcohol, diols (e.g., ethylene glycol), triols (e.g., glycerol), polyols, isomers of these and combinations of these. Esterification can be done with an excess of the alcohol, for example in a molar ratio of between about 1 to 50, with or without a diluting solvent. The esterification reaction can be carried out at temperatures between about 80 and 300 ° C (e.g., between about 80 and 200 ° C, between about 80 and 150 ° C) and under pressures of between about 1 to 30 atm. (e.g.. between about 1 and 20 atm., between about 1 and 10 atm.). In some implementations the alcohol that is utilized includes alcohol that is derived from the fermentation of saccharified lignocellulosic or cellulosic feeds, for example, as described herein, ethanol and or butanol can be utilized. The alcohol can also be derived from other renewable sugar sources and methods, for example the sources can include, starch and sugars from corn kernels, sugar cane, fruits, legumes and/or beets. Ethanol and butanol are particularly useful alcohols that can be generated by the method described herein. The alcohol may also be obtained from hydrocarbon sources.

[0045] The esterification reaction is facilitated by utilizing a catalyst, e.g., an acid catalyst. The acid catalyst can be homogeneous or heterogeneous. Some useful homogeneous acid catalysts include sulfuric, phosphoric, nitric, hydrochloric and trifluoroacetic acid. Heterogeneous acid catalysts include resins or functionalized polymers, for example, sulfonated polystyrene resins. The acids can be solid catalysts e.g., as zeolites, sulfonated carbons, alumina, clays, aluminosilicates, heteropolyacids, silica and combinations of these. Dehydrating agents, e.g., molecular sieves can be used in addition to the catalysts or after the esterification to remove water formed during the esterification. Other methods, for example distillation as a low-boiling azeotrope with toluene can be used to remove water.

[0046] In some embodiments an acid (e.g., butyric acid) can be esterified while it is bound to a resins utilized to adsorb organic acids. The ester can then be extracted into a solvent, for example, the solvents previously discussed for removing the protonated acid from a resin.

[0047] In some optional embodiments esters can be prepared utilizing an organism. For example *Staphylococci* can be combined with carboxylic acids (e.g., butyric acid) and alcohols (e.g., ethyl alcohol) to produce ethyl butyrate. Other carboxylic acids, alcohols and organism combinations can also be utilized. Other esters that can be formed from acids and alcohols derived from sugars by organisms (e.g., *S. cerevisiae*) include isoamyl acetate, ethyl caproate, ethyl caprylate, ethyl caproate, phenylethyl acetate, ethyl laurate, ethyl myristate, and ethyl palmitate.

[0048] The ester can be separated from excess alcohol, unreacted acid and impurities by any useful method. For example distillation, chromatography, filtration can be useful. If there is any excess acid it can also be removed by passing over/through ion exchange material, for example as previously described. The ester can also be simply utilized as a mixture, mostly of excess alcohol, for example as a direct fuel or fuel additive, e.g., distributed to reformulators, for high octane fuel and/or fuel additive. Other uses as a mixture to the chemical, food, flavor, fragrances and pharmaceutical industries are evident to those skilled in the art.

[0049] The organic acids produced by the methods herein described can be hydrogenated directly to an alcohol. However, direct hydrogenation requires very high pressures and the catalysts are often quickly deactivated. The esterification is advantageous in allowing more mild conditions to be utilized for a hydrogenolysis. For example direct hydrogenation can require pressures in excess of 100 atm., temperatures above 300 ° C and catalysts lifetimes of only a few hours before the catalysts need to be regenerated or replaced. The hydrogenolysis of esters can be done at temperatures between about 100 to 300 ° C (e.g., 120 to 250 ° C, 150 to 300 ° C), hydrogen pressures less than about 120 atm. (e.g., between about 5 and 120 atm., between about 5 and 60 atm.) and catalysts can last for at least an hour (e.g., at least two hours, at least 5 hours, at least 8 hours, at least 16 hours, more than a day, two days, a week, a month, a year) before needing to be regenerated and/or replaced.

[0050] Important parameters to consider during the hydrogenolysis of the ester are the conversion and selectivity to the products. The conversion can be expressed as a percentage of the product reacted (e.g., initial product/final product times 100%). The conversion can also be expressed as the rate of consumption of the staring material (e.g., the ester). The selectivity is a measure of the amount of the desired product that is obtained, in comparison to unwanted products (e.g., side products, decomposition products). The selectivity can be expressed as a percentage, for example a percent purity, or as a rate of formation of a desired product *vs.* the rate of formation of undesired products (or the rate of formation of desired product to the rate of consumption of the starting material). Some unwanted products can be

partial reduction products, oligomers and/or thermal decomposition products. Although not always the case, it is often found that there is an inverse relation between the conversion rates and selectivity, so that it can be difficult to drive the reaction quickly to completion with a high selectivity.

[0051] Catalysts are utilized during the hydrogenolysis. Catalysts can include the metals Pd, Pt, Os, Ru, Rb, Re, Ir, Rh, Ni, Co, Mo, W, Cu, Zn, Cr, oxides of these and combinations of these. In some cases promoter or moderators species are added/combined including Cr, Mn, Pb, Zn, Cd, Ag, Ba, Ca, Mg, Sn, Ni, Co, U, As and Ge oxides of these and combinations of these. One or more catalyst and one or more promoter can be combined in any concentration and ratio. The promoters increase the performance of the catalyst, for example increasing the conversion and selectivity.

[0052] The catalysts and promoters can be used as bulk catalysts (e.g., not on a support). Bulk catalysts can be formed into shapes to increase surface area and allow flow of reactants over its surface. For example in the form of: wool, a mesh, a grid, a wire, a perforated solid with channels, a sponge, beads and/or a powder. The catalysts and promoters can be mixed when utilized in bulk, for example powers of one or more catalyst and powders of one or more promoters can be combined/mixed. The metals or metal with promoter species can be advantageously adsorbed and or bonded onto a support. The support can be, for example, alumina, silica, aluminosilicates, clays, zeolites (e.g., USY and beta zeolite) or other inorganic materials. The supported catalysts typically have between about 0.1 wt. % and 10 wt. % of each metal (e.g., between 0.1 and 1 wt. %), although higher amounts can be used. One or more metal and one or more promoter can be combined with one or more support in all combinations. These supported catalyst may be formed into any convenient form.

[0053] The catalysts can be homogeneous catalysts, for example tris(triphenylphosphine)rhodium(I) chloride, and similar catalysts wherein the metal is complexed with stabilizing ligand(s) (e.g., amines, phosphines, alcohols, ethers, ketones, carboxylates, acetylacetonates, optionally bis, tri or tetrakis chelating ligands, combinations of these). The catalyst can be the polymer supported analog of a homogeneous catalyst, for example, wherein the ligands are attached to a polymer, e.g., functionalized polystyrenes wherein the functional groups are the ligands previously mentioned.

[0054] Supported catalysts can be prepared by any useful means, for example, by using the incipient wetness method, a decomposition precipitation method, a solution self-assembly method, and/or by vapor phase deposition/decomposition. For example, utilizing the incipient wetness method, a desired metal precursor can be dissolved or suspended in a volume of

solvent similar to the pore volume of the support and it is combined with the support. The catalyst can be activated. Activation can include removal of the solvent under vacuum, calcination, for example in the presence of oxygen, nitrogen, hydrogen or other gasses, in any order and repeatedly. The catalysts can be added before the promoter, with the promoter, after the promoter or in combinations of addition steps. The supported catalysts can be formed into beads, or extruded into rods and other shapes. Often these are combined with binders (e.g., inert ceramic material, porous binders).

[0055] Some catalysts, conditions, equipment and systems that can be utilized herein for the hydrogenolysis and esterification reaction are described in: "Catalysis of Organic Reactions" edited John R. Sowa, Jr., CRC Press (2005); "Catalytic Naphtha Reforming Second Edition, Revised and Expanded" edited George J. Antos and Abdullah M. Aitani, Marcel Dekker (2005) chapters 6, 8 and 9; and "Steam reforming catalysts Natural gas, associated gas and LPG" Johnson Matthey, pages 1-15; For example bi and tri metallic supported catalysts of SnRu and SnRePt can be utilized for the hydrogenolysis of ethyl butyrate.

[0056] Catalysts can be utilized for hydrogenolysis in a batch mode. For example the ester is combined, often with a solvent, in a vessel (e.g., a Parr™ reactor). The vessel can be sparged with hydrogen and/or pressurized with hydrogen. The vessels can be equipped with heaters, (e.g., heating jackets) and agitators (e.g., propellers, impellers). The catalysts can also be utilized in a fluidized bed reactor. These require a high gas flow rate, e.g., of an inert gas (e.g., nitrogen, He, Ar) in addition to hydrogen and the ester. The catalyst is fluidized by the rapid flow of gases through the reactor. One or more catalysts can be utilized sequentially or in combination (e.g., mixed together). A loop reactor may be used as it is a design option of a batch reactor, except the liquid in the vessel is recirculated outside of the reactor. If utilized sequentially, the catalysts can be utilized under different reaction conditions, e.g., temperatures, pressures (e.g., hydrogen pressures) and/or agitation (e.g., stirring rates). These combinations can, for example, optimize throughputs and combined conversion/selectivity.

[0057] Optionally, the catalysts are utilized in a fixed bed flow reactors (e.g., a flow reactor, packed bed reactor, trickle bed reactor). These reactors are configured as a column packed with the catalysts (e.g., bulk or supported catalyst) through which the reactants (e.g., esters and hydrogen) are flowed. The columns can be heated, for example, by a heating jacket charged with a heating fluid (e.g., water, high pressure water, oil), steam, electric heaters (e.g., resistive heating), or any other heating means. The columns can also be designed to withstand high pressures e.g., at least about 50 psi, at least about 100 psi, at least about 150

psi, at least about 200 psi, at least about 300 psi, at least about 500 psi. The columns can also be equipped with safety equipment e.g., pressure release valves, and high temperature process shut off (e.g., flow shut off, venting). Optionally, two or more fixed bed reactors can be utilized in series for one flow stream of reactants (e.g., up to 20, up to 10, 2 to 5, 3 to 10, 1 to 3). In some optional configurations some of the reactors are by-passed, for example, to keep them as a backup. Having available backups is particularly useful to avoid down time when one or more of the flow reactors are not operating within acceptable parameters e.g., if catalysts in the reactor are deactivated. Another advantage of utilizing reactors in series is that the reactors can be charged with different catalysts, for example having different selectivity and conversion rates, for optimal throughputs and combined conversion/selectivity. The columns can also be run under different conditions, e.g., flow rates, pressures and temperatures. For example two or more columns can be utilized wherein the difference in temperatures can be about 0 to 10 ° C (e.g., about 10 to 200 ° C, about 50 to 200 ° C, about 50 to 150 ° C, about 50 to 100 ° C). In addition to or alternatively the difference in pressure (e.g., hydrogen pressure) when using at least more than one column, can be between about 0 to 5 atm. (e.g. between about 5 and 50 atm., between about 10 and 50 atm., between about 30 and 50 atm.).

[0058] The hydrogenolysis catalysts as described can be recycled / regenerated. For example often the catalysts are oxidized by heating to high temperature in an oxidizing environment (e.g., in the presence of oxygen) e.g., between about 200 and 800 ° C (e.g., 400 to 600 ° C). After purging with an inert gas (e.g., nitrogen, argon, helium) the catalysts are reduced at a high temp e.g., between about 200 and 800 ° C. The reducing agent, for example, can be hydrogen gas made to flow over the catalyst.

[0059] The hydrogen that is utilized in the processes described herein can be supplied by biogas, for example from the anaerobic digestion of biomass, e.g., treated biomass as described herein. The hydrogen may be cleaned prior to its use for hydrogenation. Contaminants such as carbon monoxide, should be removed. Other sources of hydrogen include locating the hydrogenolysis reactor system close to a hydrogen source, including a pipeline and steam reformer of methane, natural gas or the like.

[0060] Using the catalysts, overall selectivity of greater than about 90 % can be achieved (e.g., greater than 95%, greater than 98%, greater than 99%) can be achieved. The overall conversion rates are above 80% (e.g., greater than about 90%, greater than about 95%, greater than about 99%).

[0061] The alcohols produced by the hydrogenolysis can be separated, for example, by distillation if the boiling point is different enough. For example the hydrogenolysis product of ethyl butyrate, ethanol and butanol, can be separated by distillation. The ethanol that is recovered can be re-used for esterification. The mixture of alcohols can even be utilized without separation, for example as a direct fuel or fuel additive. Other uses as a mixture or purified separated products applicable to the chemical, food, flavor, fragrances and pharmaceutical industries will be recognized by those skilled in the art. In the case of some esters, for example butyl butyrate, the hydrogenolysis product is butanol and separation schemes can be used to improve impurities.

RADIATION TREATMENT

[0062] The feedstock can be treated with electron bombardment to modify its structure to reduce its recalcitrance. Such treatment can, for example, reduce the average molecular weight of the feedstock, change the crystalline structure of the feedstock, and/or increase the surface area and/or porosity of the feedstock.

[0063] Electron bombardment via an electron beam is generally preferred, because it provides very high throughput. Electron beam accelerators are available, for example, from IBA, Belgium, and NHV Corporation, Japan.

[0064] Electron bombardment may be performed using an electron beam device that has a nominal energy of less than 10 MeV, *e.g.*, less than 7 MeV, less than 5 MeV, or less than 2 MeV, *e.g.*, from about 0.5 to 1.5 MeV, from about 0.8 to 1.8 MeV, or from about 0.7 to 1 MeV. In some implementations the nominal energy is about 500 to 800 keV.

[0065] The electron beam may have a relatively high total beam power (the combined beam power of all accelerating heads, or, if multiple accelerators are used, of all accelerators and all heads), *e.g.*, at least 25 kW, *e.g.*, at least 30, 40, 50, 60, 65, 70, 80, 100, 125, or 150 kW. In some cases, the power is even as high as 500 kW, 750 kW, or even 1000 kW or more. In some cases the electron beam has a beam power of 1200 kW or more, e.g., 1400, 1600, 1800, or even 3000 kW.

[0066] This high total beam power is usually achieved by utilizing multiple accelerating heads. For example, the electron beam device may include two, four, or more accelerating heads. The use of multiple heads, each of which has a relatively low beam power, prevents excessive temperature rise in the material, thereby preventing burning of the material, and also increases the uniformity of the dose through the thickness of the layer of material.

[0067] It is generally preferred that the bed of biomass material has a relatively uniform thickness. In some embodiments the thickness is less than about 1 inch (e.g., less than about 0.75 inches, less than about 0.5 inches, less than about 0.25 inches, less than about 0.1 inches, between about 0.1 and 1 inch, between about 0.2 and 0.3 inches).

[0068] In some implementations, it is desirable to cool the material during and between dosing the material with electron bombardment. For example, the material can be cooled while it is conveyed, for example by a screw extruder, vibratory conveyor or other conveying equipment. For example cooling while conveying is described in U. S. Provisional Patent Application Nos. 61/774,735, and 61/774,752 the entire description therein is herein incorporated by reference.

[0069] To reduce the energy required by the recalcitrance-reducing process, it is desirable to treat the material as quickly as possible. In general, it is preferred that treatment be performed at a dose rate of greater than about 0.25 Mrad per second, *e.g.*, greater than about 0.5, 0.75, 1, 1.5, 2, 5, 7, 10, 12, 15, or even greater than about 20 Mrad per second, *e.g.*, about 0.25 to 2 Mrad per second. Higher dose rates allow a higher throughput for a target (e.g., the desired) dose. Higher dose rates generally require higher line speeds, to avoid thermal decomposition of the material. In one implementation, the accelerator is set for 3 MeV, 50 mA beam current, and the line speed is 24 feet/minute, for a sample thickness of about 20 mm (*e.g.*, comminuted corn cob material with a bulk density of 0.5 g/cm^3).

[0070] In some embodiments, electron bombardment is performed until the material receives a total dose of at least 0.1 Mrad, 0.25 Mrad, 1 Mrad, 5 Mrad, *e.g.*, at least 10, 20, 30 or at least 40 Mrad. In some embodiments, the treatment is performed until the material receives a dose of from about 10 Mrad to about 50 Mrad, *e.g.*, from about 20 Mrad to about 40 Mrad, or from about 25 Mrad to about 30 Mrad. In some implementations, a total dose of 25 to 35 Mrad is preferred, applied ideally over a couple of seconds, *e.g.*, at 5 Mrad/pass with each pass being applied for about one second. Applying a dose of greater than 7 to 8 Mrad/pass can in some cases cause thermal degradation of the feedstock material. Cooling can be applied before, after, or during irradiation. For example, the cooling methods, systems and equipment as described in the following applications can be utilized: US Provisional Application No. 61/774,735, and US Provisional Application No. 61/774,754, the entire disclosures of which are herein incorporated by reference.

[0071] Using multiple heads as discussed above, the material can be treated in multiple passes, for example, two passes at 10 to 20 Mrad/pass, *e.g.*, 12 to 18 Mrad/pass, separated by a few seconds of cool-down, or three passes of 7 to 12 Mrad/pass, *e.g.*, 5 to 20 Mrad/pass, 10

to 40 Mrad/pass, 9 to 11 Mrad/pass. As discussed herein, treating the material with several relatively low doses, rather than one high dose, tends to prevent overheating of the material and also increases dose uniformity through the thickness of the material. In some implementations, the material is stirred or otherwise mixed during or after each pass and then smoothed into a uniform layer again before the next pass, to further enhance treatment uniformity.

[0072] In some embodiments, electrons are accelerated to, for example, a speed of greater than 75 percent of the speed of light, *e.g.*, greater than 85, 90, 95, or 99 percent of the speed of light.

[0073] In some embodiments, any processing described herein occurs on lignocellulosic material that remains dry as acquired or that has been dried, *e.g.*, using heat and/or reduced pressure. For example, in some embodiments, the cellulosic and/or lignocellulosic material has less than about 25 wt. % retained water, measured at 25°C and at fifty percent relative humidity (e.g., less than about 20 wt.%, less than about 15 wt.%, less than about 14 wt.%, less than about 13 wt.%, less than about 12 wt.%, less than about 10 wt.%, less than about 9 wt.%, less than about 8 wt.%, less than about 7 wt.%, less than about 6 wt.%, less than about 5 wt.%, less than about 4 wt.%, less than about 3 wt.%, less than about 2 wt.%, less than about 1 wt.%, less than about 0.5 wt.%, less than about 15 wt.%.

[0074] In some embodiments, two or more electron sources are used, such as two or more ionizing sources. For example, samples can be treated, in any order, with a beam of electrons, followed by gamma radiation and UV light having wavelengths from about 100 nm to about 280 nm. In some embodiments, samples are treated with three ionizing radiation sources, such as a beam of electrons, gamma radiation, and energetic UV light. The biomass is conveyed through the treatment zone where it can be bombarded with electrons.

[0075] It may be advantageous to repeat the treatment to more thoroughly reduce the recalcitrance of the biomass and/or further modify the biomass. In particular the process parameters can be adjusted after a first (*e.g.*, second, third, fourth or more) pass depending on the recalcitrance of the material. In some embodiments, a conveyor can be used which includes a circular system where the biomass is conveyed multiple times through the various processes described above. In some other embodiments multiple treatment devices (*e.g.*, electron beam generators) are used to treat the biomass multiple (*e.g.*, 2, 3, 4 or more) times. In yet other embodiments, a single electron beam generator may be the source of multiple beams (*e.g.*, 2, 3, 4 or more beams) that can be used for treatment of the biomass.

[0076] The conveyors (e.g., vibratory conveyor) can be made of corrosion resistant materials. The conveyors can utilize structural materials that include stainless steel (e.g., 304, 316 stainless steel, HASTELLOY® ALLOYS and INCONEL® Alloys). For example, HASTELLOY® Corrosion-Resistant alloys from Hynes (Kokomo, Indiana, USA) such as HASTELLOY® B-3® ALLOY, HASTELLOY® HYBRID-BC1® ALLOY, HASTELLOY® C-4 ALLOY, HASTELLOY® C-22® ALLOY, HASTELLOY® C-22HS® ALLOY, HASTELLOY® C-276 ALLOY, HASTELLOY® C-2000® ALLOY, HASTELLOY® G-30® ALLOY, HASTELLOY® G-35® ALLOY, HASTELLOY® N ALLOY and HASTELLOY® ULTIMET® alloy.

[0077] The vibratory conveyors can include non-stick release coatings, for example TEFLON™ (DuPont, Delaware, USA). The vibratory conveyors can also include corrosion resistant coatings. For example coatings that can be supplied from Metal Coatings Corp (Houston, Texas, USA) and others such as Fluoropolymer, XYLAN®, Molybdenum Disulfide, Epoxy Phenolic, Phosphate- ferrous metal coating, Polyurethane- high gloss topcoat for epoxy, inorganic zinc, Poly Tetrafluoroethylene, PPS/RYTON®, fluorinated ethylene propylene, PVDF/DYKOR®, ECTFE/HALAR® and Ceramic Epoxy Coating. The coatings can improve resistance to process gases (e.g., ozone), chemical corrosion, pitting corrosion, galling corrosion and oxidation.

[0078] The effectiveness in changing the molecular/supermolecular structure and/or reducing the recalcitrance of the carbohydrate-containing biomass depends on the electron energy used and the dose applied, while exposure time depends on the power and dose. Optionally, the dose rate and total dose are adjusted so as not to destroy (e.g., char or burn) the biomass material. For example, the carbohydrates should not be damaged in the processing so that they can be released from the biomass intact, e.g. as monomeric sugars.

[0079] In some embodiments, the treatment (with any electron source or a combination of sources) is performed until the material receives a dose of at least about 0.05 Mrad, *e.g.*, at least about 0.1, 0.25, 0.5, 0.75, 1.0, 2.5, 5.0, 7.5, 10.0, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, or 200 Mrad. In some embodiments, the treatment is performed until the material receives a dose of between 0.1-100 Mrad, 1-200, 5-200, 10-200, 5-150, 50-150 Mrad, 5-100, 5-50, 5-40, 10-50, 10-75, 15-50, 20-35 Mrad.

RADIATION OPAQUE MATERIALS

[0080] The invention can include processing the material in a vault and/or bunker that is constructed using radiation opaque materials. In some implementations, the radiation opaque

materials are selected to be capable of shielding the components from X-rays with high energy (short wavelength), which can penetrate many materials. One important factor in designing a radiation shielding enclosure is the attenuation length of the materials used, which will determine the required thickness for a particular material, blend of materials, or layered structure. The attenuation length is the penetration distance at which the radiation is reduced to approximately 1/e (e = Euler's number) times that of the incident radiation. Although virtually all materials are radiation opaque if thick enough, materials containing a high compositional percentage (e.g., density) of elements that have a high Z value (atomic number) have a shorter radiation attenuation length and thus if such materials are used a thinner, lighter shielding can be provided. Examples of high Z value materials that are used in radiation shielding are tantalum and lead. Another important parameter in radiation shielding is the halving distance, which is the thickness of a particular material that will reduce gamma ray intensity by 50%. As an example for X-ray radiation with an energy of 0.1 MeV the halving thickness is about 15.1 mm for concrete and about 0.2.7 mm for lead, while with an X-ray energy of 1 MeV the halving thickness for concrete is about 44.45 mm and for lead is about 7.9 mm. Radiation opaque materials can be materials that are thick or thin so long as they can reduce the radiation that passes through to the other side. Thus, if it is desired that a particular enclosure have a low wall thickness, e.g., for light weight or due to size constraints, the material chosen should have a sufficient Z value and/or attenuation length so that its halving length is less than or equal to the desired wall thickness of the enclosure.

[0081] In some cases, the radiation opaque material may be a layered material, for example having a layer of a higher Z value material, to provide good shielding, and a layer of a lower Z value material to provide other properties (e.g., structural integrity, impact resistance, etc.). In some cases, the layered material may be a "graded-Z" laminate, e.g., including a laminate in which the layers provide a gradient from high-Z through successively lower-Z elements. In some cases the radiation opaque materials can be interlocking blocks, for example, lead and/or concrete blocks can be supplied by NELCO Worldwide (Burlington, MA), and reconfigurable vaults can be utilized as described in US Provisional Application No.61/774,744.

[0082] A radiation opaque material can reduce the radiation passing through a structure (e.g., a wall, door, ceiling, enclosure, a series of these or combinations of these) formed of the material by about at least about 10 %, (e.g., at least about 20%, at least about 30%, at least about 40%, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at

least about 90%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, at least about 99%, at least about 99.9%, at least about 99.99%, at least about 99.999%) as compared to the incident radiation. Therefore, an enclosure made of a radiation opaque material can reduce the exposure of equipment/system/components by the same amount. Radiation opaque materials can include stainless steel, metals with Z values above 25 (e.g., lead, iron), concrete, dirt, sand and combinations thereof. Radiation opaque materials can include a barrier in the direction of the incident radiation of at least about 1 mm (e.g., 5 mm, 10 mm, 5 cm, 10 cm, 100 cm, 1 m, 10 m).

RADIATION SOURCES

[0083] The type of radiation determines the kinds of radiation sources used as well as the radiation devices and associated equipment. The methods, systems and equipment described herein, for example for treating materials with radiation, can utilized sources as described herein as well as any other useful source.

[0084] Sources of gamma rays include radioactive nuclei, such as isotopes of cobalt, calcium, technetium, chromium, gallium, indium, iodine, iron, krypton, samarium, selenium, sodium, thallium, and xenon.

[0085] Sources of X-rays include electron beam collision with metal targets, such as tungsten or molybdenum or alloys, or compact light sources, such as those produced commercially by Lyncean.

[0086] Alpha particles are identical to the nucleus of a helium atom and are produced by the alpha decay of various radioactive nuclei, such as isotopes of bismuth, polonium, astatine, radon, francium, radium, several actinides, such as actinium, thorium, uranium, neptunium, curium, californium, americium, and plutonium.

[0087] Sources for ultraviolet radiation include deuterium or cadmium lamps.

[0088] Sources for infrared radiation include sapphire, zinc, or selenide window ceramic lamps.

[0089] Sources for microwaves include klystrons, Slevin type RF sources, or atom beam sources that employ hydrogen, oxygen, or nitrogen gases.

[0090] Accelerators used to accelerate the particles (e.g., electrons or ions) can be DC (e.g., electrostatic DC or electrodynamic DC), RF linear, magnetic induction linear or continuous wave. For example, various irradiating devices may be used in the methods disclosed herein, including field ionization sources, electrostatic ion separators, field ionization generators, thermionic emission sources, microwave discharge ion sources,

recirculating or static accelerators, dynamic linear accelerators, van de Graaff accelerators, Cockroft Walton accelerators (e.g., PELLETRON® accelerators), LINACS, Dynamitrons (e.g., DYNAMITRON® accelerators), cyclotrons, synchrotrons, betatrons, transformer-type accelerators, microtrons, plasma generators, cascade accelerators, and folded tandem accelerators. For example, cyclotron type accelerators are available from IBA, Belgium, such as the RHODOTRON™ system, while DC type accelerators are available from RDI, now IBA Industrial, such as the DYNAMITRON®. Other suitable accelerator systems include, for example: DC insulated core transformer (ICT) type systems, available from Nissin High Voltage, Japan; S-band LINACs, available from L3-PSD (USA), Linac Systems (France), Mevex (Canada), and Mitsubishi Heavy Industries (Japan); L-band LINACs, available from Iotron Industries (Canada); and ILU-based accelerators, available from Budker Laboratories (Russia). Ions and ion accelerators are discussed in Introductory Nuclear Physics, Kenneth S. Krane, John Wiley & Sons, Inc. (1988), Krsto Prelec, FIZIKA B 6 (1997) 4, 177–206, Chu, William T., "Overview of Light-Ion Beam Therapy", Columbus-Ohio, ICRU-IAEA Meeting, 18-20 March 2006, Iwata, Y. et al., "Alternating-Phase-Focused IH-DTL for Heavy-Ion Medical Accelerators", Proceedings of EPAC 2006, Edinburgh, Scotland, , and Leitner, C.M. et al., "Status of the Superconducting ECR Ion Source Venus", Proceedings of EPAC 2000, Vienna, Austria. Some particle accelerators and their uses are disclosed, for example, in U.S. Pat. No. 7,931,784 to Medoff, the complete disclosure of which is incorporated herein by reference.

[0091] Electrons may be produced by radioactive nuclei that undergo beta decay, such as isotopes of iodine, cesium, technetium, and iridium. Alternatively, an electron gun can be used as an electron source via thermionic emission and accelerated through an accelerating potential. An electron gun generates electrons, which are then accelerated through a large potential (e.g., greater than about 500 thousand, greater than about 1million, greater than about 2 million, greater than about 5 million, greater than about 6 million, greater than about 7 million, greater than about 8 million, greater than about 9 million, or even greater than 10 million volts) and then scanned magnetically in the x-y plane, where the electrons are initially accelerated in the z direction down the accelerator tube and extracted through a foil window. Scanning the electron beams is useful for increasing the irradiation surface when irradiating materials, e.g., a biomass, that is conveyed through the scanned beam. Scanning the electron beam also distributes the thermal load homogenously on the window and helps reduce the foil window rupture due to local heating by the electron beam. Window foil

rupture is a cause of significant down-time due to subsequent necessary repairs and re-starting the electron gun.

[0092] A beam of electrons can be used as the radiation source. A beam of electrons has the advantages of high dose rates (e.g., 1, 5, or even 10 Mrad per second), high throughput, less containment, and less confinement equipment. Electron beams can also have high electrical efficiency (e.g., 80%), allowing for lower energy usage relative to other radiation methods, which can translate into a lower cost of operation and lower greenhouse gas emissions corresponding to the smaller amount of energy used. Electron beams can be generated, e.g., by electrostatic generators, cascade generators, transformer generators, low energy accelerators with a scanning system, low energy accelerators with a linear cathode, linear accelerators, and pulsed accelerators.

[0093] Electrons can also be more efficient at causing changes in the molecular structure of carbohydrate-containing materials, for example, by the mechanism of chain scission. In addition, electrons having energies of 0.5-10 MeV can penetrate low density materials, such as the biomass materials described herein, e.g., materials having a bulk density of less than 0.5 g/cm3, and a depth of 0.3-10 cm. Electrons as an ionizing radiation source can be useful, e.g., for relatively thin piles, layers or beds of materials, e.g., less than about 0.5 inch, e.g., less than about 0.4 inch, 0.3 inch, 0.25 inch, or less than about 0.1 inch. In some embodiments, the energy of each electron of the electron beam is from about 0.3 MeV to about 2.0 MeV (million electron volts), e.g., from about 0.5 MeV to about 1.5 MeV, or from about 0.7 MeV to about 1.25 MeV. Methods of irradiating materials are discussed in U.S. Pat. App. Pub. 2012/0100577 A1, filed October 18, 2011, the entire disclosure of which is herein incorporated by reference.

[0094] Electron beam irradiation devices may be procured commercially or built. For example, elements or components such inductors, capacitors, casings, power sources, cables, wiring, voltage control systems, current control elements, insulating material, microcontrollers and cooling equipment can be purchased and assembled into a device. Optionally, a commercial device can be modified and/or adapted. For example, devices and components can be purchased from any of the commercial sources described herein including Ion Beam Applications (Louvain-la-Neuve, Belgium), Wasik Associates Inc. (Dracut, MA), NHV Corporation (Japan), the Titan Corporation (San Diego, CA), Vivirad High Voltage Corp (Billerica, MA) and/or Budker Laboratories (Russia). Typical electron energies can be 0.5 MeV, 1 MeV, 2 MeV, 4.5 MeV, 7.5 MeV, or 10 MeV. Typical electron beam irradiation device power can be 1 kW, 5 kW, 10 kW, 20 kW, 50 kW, 60 kW, 70 kW, 80 kW, 90 kW,

100 kW, 125 kW, 150 kW, 175 kW, 200 kW, 250 kW, 300 kW, 350 kW, 400 kW, 450 kW, 500 kW, 600 kW, 700 kW, 800 kW, 900 kW or even 1000 kW. Accelerators that can be used include NHV irradiators medium energy series EPS-500 (e.g., 500 kV accelerator voltage and 65, 100 or 150 mA beam current), EPS-800 (e.g., 800 kV accelerator voltage and 65 or 100 mA beam current), or EPS-1000 (e.g., 1000 kV accelerator voltage and 65 or 100 mA beam current). Also, accelerators from NHV's high energy series can be used such as EPS-1500 (e.g., 1500 kV accelerator voltage and 65 mA beam current), EPS-2000 (e.g., 2000 kV accelerator voltage and 50 mA beam current), EPS-3000 (e.g., 3000 kV accelerator voltage and 50 mA beam current) and EPS-5000 (e.g., 5000 and 30 mA beam current).

[0095] Tradeoffs in considering electron beam irradiation device power specifications include cost to operate, capital costs, depreciation, and device footprint. Tradeoffs in considering exposure dose levels of electron beam irradiation would be energy costs and environment, safety, and health (ESH) concerns. Typically, generators are housed in a vault, e.g., of lead or concrete, especially for production from X-rays that are generated in the process. Tradeoffs in considering electron energies include energy costs.

[0096] The electron beam irradiation device can produce either a fixed beam or a scanning beam. A scanning beam may be advantageous with large scan sweep length and high scan speeds, as this would effectively replace a large, fixed beam width. Further, available sweep widths of 0.5 m, 1 m, 2 m or more are available. The scanning beam is preferred in most embodiments describe herein because of the larger scan width and reduced possibility of local heating and failure of the windows.

ELECTRON GUNS - WINDOWS

[0097] The extraction system for an electron accelerator can include two window foils. Window foils are described in International App. No. PCT/US2013/064332 (which was filed October 10, 2013the complete disclosure of which is herein incorporated by reference. The cooling gas in the two foil window extraction system can be a purge gas or a mixture, for example air, or a pure gas. In one embodiment the gas is an inert gas such as nitrogen, argon, helium and or carbon dioxide. It is preferred to use a gas rather than a liquid since energy losses to the electron beam are minimized. Mixtures of pure gas can also be used, either pre-mixed or mixed in line prior to impinging on the windows or in the space between the windows. The cooling gas can be cooled, for example, by using a heat exchange system (*e.g.*, a chiller) and/or by using boil off from a condensed gas (*e.g.*, liquid nitrogen, liquid helium).

[0098] When using an enclosure, the enclosed conveyor can also be purged with an inert gas so as to maintain an atmosphere at a reduced oxygen level. Keeping oxygen levels low avoids the formation of ozone which in some instances is undesirable due to its reactive and toxic nature. For example the oxygen can be less than about 20% (*e.g.*, less than about 10%, less than about 1%, less than about 0.1%, less than about 0.01%, or even less than about 0.001% oxygen). Purging can be done with an inert gas including, but not limited to, nitrogen, argon, helium or carbon dioxide. This can be supplied, for example, from a boil off of a liquid source (*e.g.*, liquid nitrogen or helium), generated or separated from air *in situ*, or supplied from tanks. The inert gas can be recirculated and any residual oxygen can be removed using a catalyst, such as a copper catalyst bed. Alternatively, combinations of purging, recirculating and oxygen removal can be done to keep the oxygen levels low.

[0099] The enclosure can also be purged with a reactive gas that can react with the biomass. This can be done before, during or after the irradiation process. The reactive gas can be, but is not limited to, nitrous oxide, ammonia, oxygen, ozone, hydrocarbons, aromatic compounds, amides, peroxides, azides, halides, oxyhalides, phosphides, phosphines, arsines, sulfides, thiols, boranes and/or hydrides. The reactive gas can be activated in the enclosure, *e.g.*, by irradiation (*e.g.*, electron beam, UV irradiation, microwave irradiation, heating, IR radiation), so that it reacts with the biomass. The biomass itself can be activated, for example by irradiation. Preferably the biomass is activated by the electron beam, to produce radicals which then react with the activated or unactivated reactive gas, *e.g.*, by radical coupling or quenching.

[00100] Purging gases supplied to an enclosed conveyor can also be cooled, for example below about 25°C, below about 0°C, below about -40°C, below about -80°C, below about -120°C. For example, the gas can be boiled off from a compressed gas such as liquid nitrogen or sublimed from solid carbon dioxide. As an alternative example, the gas can be cooled by a chiller or part of or the entire conveyor can be cooled.

HEATING AND THROUGHPUT DURING RADIATION TREATMENT

[00101] Several processes can occur in biomass when electrons from an electron beam interact with matter in inelastic collisions. For example, ionization of the material, chain scission of polymers in the material, cross linking of polymers in the material, oxidation of the material, generation of X-rays ("Bremsstrahlung") and vibrational excitation of molecules (e.g. phonon generation). Without being bound to a particular mechanism, the reduction in

recalcitrance can be due to several of these inelastic collision effects, for example ionization, chain scission of polymers, oxidation and phonon generation. Some of the effects (e.g., especially X-ray generation), necessitate shielding and engineering barriers, for example, enclosing the irradiation processes in a concrete (or other radiation opaque material) vault. Another effect of irradiation, vibrational excitation, is equivalent to heating up the sample. Heating the sample by irradiation can help in recalcitrance reduction, but excessive heating can destroy the material, as will be explained below.

[00102] The adiabatic temperature rise (ΔT) from adsorption of ionizing radiation is given by the equation: $\Delta T = D/Cp$: where D is the average dose in kGy, Cp is the heat capacity in J/g °C, and ΔT is the change in temperature in °C. A typical dry biomass material will have a heat capacity close to 2. Wet biomass will have a higher heat capacity dependent on the amount of water since the heat capacity of water is very high (4.19 J/g °C). Metals have much lower heat capacities, for example 304 stainless steel has a heat capacity of 0.5 J/g °C. The temperature change due to the instant adsorption of radiation in a biomass and stainless steel for various doses of radiation is shown below.

[00103]

Calculated Temperature Increase for Biomass and Stainless Steel.

Dose (Mrad)	**Estimated Biomass ΔT (°C)**	**Steel ΔT (°C)**
10	50	200
50	250, Decomposition	1000
100	500, Decomposition	2000
150	750, Decomposition	3000
200	1000, Decomposition	4000

[00104] High temperatures can destroy and or modify the biopolymers in biomass so that the polymers (e.g., cellulose) are unsuitable for further processing. A biomass subjected to high temperatures can become dark, sticky and give off odors indicating decomposition. The stickiness can even make the material hard to convey. The odors can be unpleasant and be a safety issue. In fact, keeping the biomass below about 200°C has been found to be beneficial in the processes described herein (e.g., below about 190°C, below about 180°C, below about 170°C, below about 160°C, below about 150°C, below about 140°C, below about 130°C, below about 120°C, below about 110°C, between about 60°C and 180°C, between about 60°C and 160°C, between about 60°C and 150°C, between about 60°C and 140°C, between

about 60°C and 130°C, between about 60°C and 120°C, between about 80°C and 180°C, between about 100°C and 180°C, between about 120°C and 180°C, between about 140°C and 180°C, between about 160°C and 180°C, between about 100°C and 140°C, between about 80°C and 120°C).

[00105] It has been found that irradiation above about 10 Mrad is desirable for the processes described herein (e.g., reduction of recalcitrance). A high throughput is also desirable so that the irradiation does not become a bottle neck in processing the biomass. The treatment is governed by a Dose rate equation: M = FP/D * time, where M is the mass of irradiated material (Kg), F is the fraction of power that is adsorbed (unit less), P is the emitted power (KW=Voltage in MeV * Current in mA), time is the treatment time (sec) and D is the adsorbed dose (KGy). In an exemplary process where the fraction of adsorbed power is fixed, the Power emitted is constant and a set dosage is desired, the throughput (e.g., M, the biomass processed) can be increased by increasing the irradiation time. However, increasing the irradiation time without allowing the material to cool, can excessively heat the material as exemplified by the calculations shown above. Since biomass has a low thermal conductivity (less than about 0.1 $Wm^{-1}K^{-1}$), heat dissipation is slow, unlike, for example metals (greater than about 10 $Wm^{-1}K^{-1}$) which can dissipate energy quickly as long as there is a heat sink to transfer the energy to.

ELECTRON GUNS – BEAM STOPS

[00106] In some embodiments the systems and methods include a beam stop (*e.g.*, a shutter). For example, the beam stop can be used to quickly stop or reduce the irradiation of material without powering down the electron beam device. Alternatively the beam stop can be used while powering up the electron beam, *e.g.*, the beam stop can stop the electron beam until a beam current of a desired level is achieved. The beam stop can be placed between the primary foil window and a secondary foil window. For example the beam stop can be mounted so that it is movable, that is, so that it can be moved into and out of the beam path. Even partial coverage of the beam can be used, for example, to control the dose of irradiation. The beam stop can be mounted to the floor, to a conveyor for the biomass, to a wall, to the radiation device (*e.g.*, at the scan horn), or to any structural support. Preferably the beam stop is fixed in relation to the scan horn so that the beam can be effectively controlled by the beam stop. The beam stop can incorporate a hinge, a rail, wheels, slots, or other means allowing for its operation in moving into and out of the beam. The beam stop can be made of

any material that will stop at least 5% of the electrons, *e.g.*, at least 10%, 20%, 30%, 40%, 50%, 60%, 70%, at least 80%, 85%, 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99% or even about 100% of the electrons.

[00107] The beam stop can be made of a metal including, but not limited to, stainless steel, lead, iron, molybdenum, silver, gold, titanium, aluminum, tin, or alloys of these, or laminates (layered materials) made with such metals (*e.g.*, metal-coated ceramic, metal-coated polymer, metal-coated composite, multilayered metal materials).

[00108] The beam stop can be cooled, for example, with a cooling fluid such as an aqueous solution or a gas. The beam stop can be partially or completely hollow, for example with cavities. Interior spaces of the beam stop can be used for cooling fluids and gases. The beam stop can be of any shape, including flat, curved, round, oval, square, rectangular, beveled and wedged shapes.

[00109] The beam stop can have perforations so as to allow some electrons through, thus controlling (*e.g.*, reducing) the levels of radiation across the whole area of the window, or in specific regions of the window. The beam stop can be a mesh formed, for example, from fibers or wires. Multiple beam stops can be used, together or independently, to control the irradiation. The beam stop can be remotely controlled, *e.g.*, by radio signal or hard wired to a motor for moving the beam into or out of position.

BIOMASS MATERIALS

[00110] Lignocellulosic materials include, but are not limited to, wood, particle board, forestry wastes (*e.g.*, sawdust, aspen wood, wood chips), grasses, (*e.g.*, switchgrass, miscanthus, cord grass, reed canary grass), grain residues, (*e.g.*, rice hulls, oat hulls, wheat chaff, barley hulls), agricultural waste (*e.g.*, silage, canola straw, wheat straw, barley straw, oat straw, rice straw, jute, hemp, flax, bamboo, sisal, abaca, corn cobs, corn stover, soybean stover, corn fiber, alfalfa, hay, coconut hair), sugar processing residues (*e.g.*, bagasse, beet pulp, agave bagasse), , algae, seaweed, manure, sewage, and mixtures of any of these.

[00111] In some cases, the lignocellulosic material includes corncobs. Ground or hammer milled corncobs can be spread in a layer of relatively uniform thickness for irradiation, and after irradiation are easy to disperse in the medium for further processing. To facilitate harvest and collection, in some cases the entire corn plant is used, including the corn stalk, corn kernels, and in some cases even the root system of the plant.

[00112] Advantageously, no additional nutrients (other than a nitrogen source, *e.g.*, urea or ammonia) are required during fermentation of corncobs or cellulosic or lignocellulosic materials containing significant amounts of corncobs.

[00113] Corncobs, before and after comminution, are also easier to convey and disperse, and have a lesser tendency to form explosive mixtures in air than other cellulosic or lignocellulosic materials such as hay and grasses.

[00114] Cellulosic materials include, for example, paper, paper products, paper waste, paper pulp, pigmented papers, loaded papers, coated papers, filled papers, magazines, printed matter (*e.g.*, books, catalogs, manuals, labels, calendars, greeting cards, brochures, prospectuses, newsprint), printer paper, polycoated paper, card stock, cardboard, paperboard, materials having a high α-cellulose content such as cotton, and mixtures of any of these. For example paper products as described in U.S. App. No. 13/396,365 ("Magazine Feedstocks" by Medoff *et al.*, filed February 14, 2012), the full disclosure of which is incorporated herein by reference.

[00115] Cellulosic materials can also include lignocellulosic materials which have been partially or fully de-lignified.

[00116] In some instances other biomass materials can be utilized, for example starchy materials. Starchy materials include starch itself, *e.g.*, corn starch, wheat starch, potato starch or rice starch, a derivative of starch, or a material that includes starch, such as an edible food product or a crop. For example, the starchy material can be arracacha, buckwheat, banana, barley, cassava, kudzu, oca, sago, sorghum, regular household potatoes, sweet potato, taro, yams, or one or more beans, such as favas, lentils or peas. Blends of any two or more starchy materials are also starchy materials. Mixtures of starchy, cellulosic and or lignocellulosic materials can also be used. For example, a biomass can be an entire plant, a part of a plant or different parts of a plant, *e.g.*, a wheat plant, cotton plant, a corn plant, rice plant or a tree. The starchy materials can be treated by any of the methods described herein.

[00117] Microbial materials include, but are not limited to, any naturally occurring or genetically modified microorganism or organism that contains or is capable of providing a source of carbohydrates (*e.g.*, cellulose), for example, protists, *e.g.*, animal protists (*e.g.*, protozoa such as flagellates, amoeboids, ciliates, and sporozoa) and plant protists (*e.g.*, algae such alveolates, chlorarachniophytes, cryptomonads, euglenids, glaucophytes, haptophytes, red algae, stramenopiles, and viridaeplantae). Other examples include seaweed, plankton (*e.g.*, macroplankton, mesoplankton, microplankton, nanoplankton, picoplankton, and

femtoplankton), phytoplankton, bacteria (*e.g.*, gram positive bacteria, gram negative bacteria, and extremophiles), yeast and/or mixtures of these. In some instances, microbial biomass can be obtained from natural sources, *e.g.*, the ocean, lakes, bodies of water, *e.g.*, salt water or fresh water, or on land. Alternatively or in addition, microbial biomass can be obtained from culture systems, *e.g.*, large scale dry and wet culture and fermentation systems.

[00118] In other embodiments, the biomass materials, such as cellulosic, starchy and lignocellulosic feedstock materials, can be obtained from transgenic microorganisms and plants that have been modified with respect to a wild type variety. Such modifications may be, for example, through the iterative steps of selection and breeding to obtain desired traits in a plant. Furthermore, the plants can have had genetic material removed, modified, silenced and/or added with respect to the wild type variety. For example, genetically modified plants can be produced by recombinant DNA methods, where genetic modifications include introducing or modifying specific genes from parental varieties, or, for example, by using transgenic breeding wherein a specific gene or genes are introduced to a plant from a different species of plant and/or bacteria. Another way to create genetic variation is through mutation breeding wherein new alleles are artificially created from endogenous genes. The artificial genes can be created by a variety of ways including treating the plant or seeds with, for example, chemical mutagens (*e.g.*, using alkylating agents, epoxides, alkaloids, peroxides, formaldehyde), irradiation (*e.g.*, X-rays, gamma rays, neutrons, beta particles, alpha particles, protons, deuterons, UV radiation) and temperature shocking or other external stressing and subsequent selection techniques. Other methods of providing modified genes is through error prone PCR and DNA shuffling followed by insertion of the desired modified DNA into the desired plant or seed. Methods of introducing the desired genetic variation in the seed or plant include, for example, the use of a bacterial carrier, biolistics, calcium phosphate precipitation, electroporation, gene splicing, gene silencing, lipofection, microinjection and viral carriers. Additional genetically modified materials have been described in U.S. Application Serial No 13/396,369 filed February 14, 2012 the full disclosure of which is incorporated herein by reference.

Any of the methods described herein can be practiced with mixtures of any biomass materials described herein.

BIOMASS MATERIAL PREPARATION – MECHANICAL TREATMENTS

[00119] The biomass can be in a dry form, for example with less than about 35% moisture content (*e.g.*, less than about 20 %, less than about 15 %, less than about 10 % less than about

5 %, less than about 4%, less than about 3 %, less than about 2 % or even less than about 1 %). The biomass can also be delivered in a wet state, for example as a wet solid, a slurry or a suspension with at least about 10 wt. % solids (*e.g.*, at least about 20 wt.%, at least about 30 wt. %, at least about 40 wt.%, at least about 50 wt.%, at least about 60 wt.%, at least about 70 wt.%).

[00120] The processes disclosed herein can utilize low bulk density materials, for example cellulosic or lignocellulosic feedstocks that have been physically pretreated to have a bulk density of less than about 0.75 g/cm^3, *e.g.*, less than about 0.7, 0.65, 0.60, 0.50, 0.35, 0.25, 0.20, 0.15, 0.10, 0.05 or less, *e.g.*, less than about 0.025 g/cm^3. Bulk density is determined using ASTM D1895B. Briefly, the method involves filling a measuring cylinder of known volume with a sample and obtaining a weight of the sample. The bulk density is calculated by dividing the weight of the sample in grams by the known volume of the cylinder in cubic centimeters. If desired, low bulk density materials can be densified, for example, by methods described in US. Pat. No. 7,971,809 to Medoff, the full disclosure of which is hereby incorporated by reference.

[00121] In some cases, the pre-treatment processing includes screening of the biomass material. Screening can be through a mesh or perforated plate with a desired opening size, for example, less than about 6.35 mm (1/4 inch, 0.25 inch), (*e.g.*, less than about 3.18 mm (1/8 inch, 0.125 inch), less than about 1.59 mm (1/16 inch, 0.0625 inch), is less than about 0.79 mm (1/32 inch, 0.03125 inch), *e.g.*, less than about 0.51 mm (1/50 inch, 0.02000 inch), less than about 0.40 mm (1/64 inch, 0.015625 inch), less than about 0.23 mm (0.009 inch), less than about 0.20 mm (1/128 inch, 0.0078125 inch), less than about 0.18 mm (0.007 inch), less than about 0.13 mm (0.005 inch), or even less than about 0.10 mm (1/256 inch, 0.00390625 inch)). In one configuration the desired biomass falls through the perforations or screen and thus biomass larger than the perforations or screen are not irradiated. These larger materials can be re-processed, for example by comminuting, or they can simply be removed from processing. In another configuration material that is larger than the perforations is irradiated and the smaller material is removed by the screening process or recycled. In this kind of a configuration, the conveyor itself (for example a part of the conveyor) can be perforated or made with a mesh. For example, in one particular embodiment the biomass material may be wet and the perforations or mesh allow water to drain away from the biomass before irradiation.

[00122] Screening of material can also be by a manual method, for example by an operator or mechanoid (*e.g.*, a robot equipped with a color, reflectivity or other sensor) that removes

unwanted material. Screening can also be by magnetic screening wherein a magnet is disposed near the conveyed material and the magnetic material is removed magnetically.

[00123] Optional pre-treatment processing can include heating the material. For example a portion of the conveyor can be sent through a heated zone. The heated zone can be created, for example, by IR radiation, microwaves, combustion (*e.g.*, gas, coal, oil, biomass), resistive heating and/or inductive coils. The heat can be applied from at least one side or more than one side, can be continuous or periodic and can be for only a portion of the material or all the material. For example, a portion of the conveying trough can be heated by use of a heating jacket. Heating can be, for example, for the purpose of drying the material. In the case of drying the material, this can also be facilitated, with or without heating, by the movement of a gas (*e.g.*, air, oxygen, nitrogen, He, CO_2, Argon) over and/or through the biomass as it is being conveyed.

[00124] Optionally, pre-treatment processing can include cooling the material. Cooling material is described in US Pat. No. 7,900,857 to Medoff, the disclosure of which in incorporated herein by reference. For example, cooling can be by supplying a cooling fluid, for example water (*e.g.*, with glycerol), or nitrogen (*e.g.*, liquid nitrogen) to the bottom of the conveying trough. Alternatively, a cooling gas, for example, chilled nitrogen can be blown over the biomass materials or under the conveying system.

[00125] Another optional pre-treatment processing method can include adding a material to the biomass. The additional material can be added by, for example, by showering, sprinkling and or pouring the material onto the biomass as it is conveyed. Materials that can be added include, for example, metals, ceramics and/or ions as described in U.S. Pat. App. Pub. 2010/0105119 A1 (filed October 26, 2009) and U.S. Pat. App. Pub. 2010/0159569 A1 (filed December 16, 2009), the entire disclosures of which are incorporated herein by reference. Optional materials that can be added include acids and bases. Other materials that can be added are oxidants (*e.g.*, peroxides, chlorates), polymers, polymerizable monomers (*e.g.*, containing unsaturated bonds), water, catalysts, enzymes and/or organisms. Materials can be added, for example, in pure form, as a solution in a solvent (*e.g.*, water or an organic solvent) and/or as a solution. In some cases the solvent is volatile and can be made to evaporate *e.g.*, by heating and/or blowing gas as previously described. The added material may form a uniform coating on the biomass or be a homogeneous mixture of different components (*e.g.*, biomass and additional material). The added material can modulate the subsequent irradiation step by increasing the efficiency of the irradiation, damping the irradiation or changing the effect of the irradiation (*e.g.*, from electron beams to X-rays or

heat). The method may have no impact on the irradiation but may be useful for further downstream processing. The added material may help in conveying the material, for example, by lowering dust levels.

[00126] Biomass can be delivered to the conveyor (e.g., the vibratory conveyors used in the vaults herein described) by a belt conveyor, a pneumatic conveyor, a screw conveyor, a hopper, a pipe, manually or by a combination of these. The biomass can, for example, be dropped, poured and/or placed onto the conveyor by any of these methods. In some embodiments the material is delivered to the conveyor using an enclosed material distribution system to help maintain a low oxygen atmosphere and/or control dust and fines. Lofted or air suspended biomass fines and dust are undesirable because these can form an explosion hazard or damage the window foils of an electron gun (if such a device is used for treating the material).

[00127] The material can be leveled to form a uniform thickness between about 0.0312 and 5 inches (*e.g.*, between about 0.0625 and 2.000 inches, between about 0.125 and 1 inches, between about 0.125 and 0.5 inches, between about 0.3 and 0.9 inches, between about 0.2 and 0.5 inches between about 0.25 and 1.0 inches, between about 0.25 and 0.5 inches,

[00128] Generally, it is preferred to convey the material as quickly as possible through the electron beam to maximize throughput. For example the material can be conveyed at rates of at least 1 ft./min, *e.g.*, at least 2 ft./min, at least 3 ft./min, at least 4 ft./min, at least 5 ft./min, at least 10 ft./min, at least 15 ft./min, 20, 25, 30, 35, 40, 45, 50 ft./min. The rate of conveying is related to the beam current, for example, for a ¼ inch thick biomass and 100 mA, the conveyor can move at about 20 ft./min to provide a useful irradiation dosage, at 50 mA the conveyor can move at about 10 ft./min to provide approximately the same irradiation dosage.

[00129] After the biomass material has been conveyed through the radiation zone, optional post-treatment processing can be done. The optional post-treatment processing can, for example, be a process described with respect to the pre-irradiation processing. For example, the biomass can be screened, heated, cooled, and/or combined with additives. Uniquely to post-irradiation, quenching of the radicals can occur, for example, quenching of radicals by the addition of fluids or gases (*e.g.*, oxygen, nitrous oxide, ammonia, liquids), using pressure, heat, and/or the addition of radical scavengers. For example, the biomass can be conveyed out of the enclosed conveyor and exposed to a gas (*e.g.*, oxygen) where it is quenched, forming carboxylated groups. In one embodiment the biomass is exposed during irradiation to the reactive gas or fluid. Quenching of biomass that has been irradiated is described in

U.S. Pat. No. 8,083,906 to Medoff, the entire disclosure of which is incorporate herein by reference.

[00130] If desired, one or more mechanical treatments can be used in addition to irradiation to further reduce the recalcitrance of the carbohydrate-containing material. These processes can be applied before, during and or after irradiation.

[00131] In some cases, the mechanical treatment may include an initial preparation of the feedstock as received, *e.g.*, size reduction of materials, such as by comminution, *e.g.*, cutting, grinding, shearing, pulverizing or chopping. For example, in some cases, loose feedstock (*e.g.*, recycled paper, starchy materials, or switchgrass) is prepared by shearing or shredding. Mechanical treatment may reduce the bulk density of the carbohydrate-containing material, increase the surface area of the carbohydrate-containing material and/or decrease one or more dimensions of the carbohydrate-containing material.

[00132] Alternatively, or in addition, the feedstock material can be treated with another treatment, for example chemical treatments, such as with an acid (HCl, H_2SO_4, H_3PO_4), a base (e.g., KOH and NaOH), a chemical oxidant (e.g., peroxides, chlorates, ozone), irradiation, steam explosion, pyrolysis, sonication, oxidation, chemical treatment. The treatments can be in any order and in any sequence and combinations. For example, the feedstock material can first be physically treated by one or more treatment methods, *e.g.*, chemical treatment including and in combination with acid hydrolysis (e.g., utilizing HCl, H_2SO_4, H_3PO_4), radiation, sonication, oxidation, pyrolysis or steam explosion, and then mechanically treated. This sequence can be advantageous since materials treated by one or more of the other treatments, *e.g.*, irradiation or pyrolysis, tend to be more brittle and, therefore, it may be easier to further change the structure of the material by mechanical treatment. As another example, a feedstock material can be conveyed through ionizing radiation using a conveyor as described herein and then mechanically treated. Chemical treatment can remove some or all of the lignin (for example chemical pulping) and can partially or completely hydrolyze the material. The methods also can be used with pre-hydrolyzed material. The methods also can be used with material that has not been pre hydrolyzed The methods can be used with mixtures of hydrolyzed and non-hydrolyzed materials, for example with about 50% or more non-hydrolyzed material, with about 60% or more non- hydrolyzed material, with about 70% or more non-hydrolyzed material, with about 80% or more non-hydrolyzed material or even with 90% or more non-hydrolyzed material.

[00133] In addition to size reduction, which can be performed initially and/or later in processing, mechanical treatment can also be advantageous for "opening up," "stressing,"

breaking or shattering the carbohydrate-containing materials, making the cellulose of the materials more susceptible to chain scission and/or disruption of crystalline structure during the physical treatment.

[00134] Methods of mechanically treating the carbohydrate-containing material include, for example, milling or grinding. Milling may be performed using, for example, a hammer mill, ball mill, colloid mill, conical or cone mill, disk mill, edge mill, Wiley mill, grist mill or other mill. Grinding may be performed using, for example, a cutting/impact type grinder. Some exemplary grinders include stone grinders, pin grinders, coffee grinders, and burr grinders. Grinding or milling may be provided, for example, by a reciprocating pin or other element, as is the case in a pin mill. Other mechanical treatment methods include mechanical ripping or tearing, other methods that apply pressure to the fibers, and air attrition milling. Suitable mechanical treatments further include any other technique that continues the disruption of the internal structure of the material that was initiated by the previous processing steps.

[00135] Mechanical feed preparation systems can be configured to produce streams with specific characteristics such as, for example, specific maximum sizes, specific length-to-width, or specific surface areas ratios. Physical preparation can increase the rate of reactions, improve the movement of material on a conveyor, improve the irradiation profile of the material, improve the radiation uniformity of the material, or reduce the processing time required by opening up the materials and making them more accessible to processes and/or reagents, such as reagents in a solution.

[00136] The bulk density of feedstocks can be controlled (*e.g.*, increased). In some situations, it can be desirable to prepare a low bulk density material, *e.g.*, by densifying the material (*e.g.*, densification can make it easier and less costly to transport to another site) and then reverting the material to a lower bulk density state (*e.g.*, after transport). The material can be densified, for example from less than about 0.2 g/cc to more than about 0.9 g/cc (*e.g.*, less than about 0.3 to more than about 0.5 g/cc, less than about 0.3 to more than about 0.9 g/cc, less than about 0.5 to more than about 0.9 g/cc, less than about 0.3 to more than about 0.8 g/cc, less than about 0.2 to more than about 0.5 g/cc). For example, the material can be densified by the methods and equipment disclosed in U.S. Pat. No. 7,932,065 to Medoff and International Publication No. WO 2008/073186 (which was filed October 26, 2007, was published in English, and which designated the United States), the full disclosures of which are incorporated herein by reference. Densified materials can be processed by any of the

methods described herein, or any material processed by any of the methods described herein can be subsequently densified.

[00137] In some embodiments, the material to be processed is in the form of a fibrous material that includes fibers provided by shearing a fiber source. For example, the shearing can be performed with a rotary knife cutter.

[00138] For example, a fiber source, *e.g.*, that is recalcitrant or that has had its recalcitrance level reduced, can be sheared, *e.g.*, in a rotary knife cutter, to provide a first fibrous material. The first fibrous material is passed through a first screen, *e.g.*, having an average opening size of 1.59 mm or less (1/16 inch, 0.0625 inch), provide a second fibrous material. If desired, the fiber source can be cut prior to the shearing, *e.g.*, with a shredder. For example, when a paper is used as the fiber source, the paper can be first cut into strips that are, *e.g.*, 1/4- to 1/2-inch wide, using a shredder, *e.g.*, a counter-rotating screw shredder, such as those manufactured by Munson (Utica, N.Y.). As an alternative to shredding, the paper can be reduced in size by cutting to a desired size using a guillotine cutter. For example, the guillotine cutter can be used to cut the paper into sheets that are, *e.g.*, 10 inches wide by 12 inches long.

[00139] In some embodiments, the shearing of the fiber source and the passing of the resulting first fibrous material through a first screen are performed concurrently. The shearing and the passing can also be performed in a batch-type process.

[00140] For example, a rotary knife cutter can be used to concurrently shear the fiber source and screen the first fibrous material. A rotary knife cutter includes a hopper that can be loaded with a shredded fiber source prepared by shredding a fiber source.

[00141] In some implementations, the feedstock is physically treated prior to saccharification and/or fermentation. Physical treatment processes can include one or more of any of those described herein, such as mechanical treatment, chemical treatment, irradiation, sonication, oxidation, pyrolysis or steam explosion. Treatment methods can be used in combinations of two, three, four, or even all of these technologies (in any order). When more than one treatment method is used, the methods can be applied at the same time or at different times. Other processes that change a molecular structure of a biomass feedstock may also be used, alone or in combination with the processes disclosed herein.

[00142] Mechanical treatments that may be used, and the characteristics of the mechanically treated carbohydrate-containing materials, are described in further detail in U.S. Pat. App. Pub. 2012/0100577 A1, filed October 18, 2011, the full disclosure of which is hereby incorporated herein by reference.

SONICATION, PYROLYSIS, OXIDATION, STEAM EXPLOSION

[00143] If desired, one or more sonication, pyrolysis, oxidative, or steam explosion processes can be used instead of or in addition to irradiation to reduce or further reduce the recalcitrance of the carbohydrate-containing material. For example, these processes can be applied before, during and or after irradiation. These processes are described in detail in U.S. Pat. No. 7,932,065 to Medoff, the full disclosure of which is incorporated herein by reference.

USE OF TREATED BIOMASS MATERIAL

[00144] Using the methods described herein, a starting biomass material (*e.g.*, plant biomass, animal biomass, paper, and municipal waste biomass) can be used as feedstock to produce useful intermediates and products such as organic acids, salts of organic acids, anhydrides, esters of organic acids and fuels, *e.g.*, fuels for internal combustion engines or feedstocks for fuel cells. Systems and processes are described herein that can use as feedstock cellulosic and/or lignocellulosic materials that are readily available, but often can be difficult to process, *e.g.*, municipal waste streams and waste paper streams, such as streams that include newspaper, kraft paper, corrugated paper or mixtures of these.

[00145] In order to convert the feedstock to a form that can be readily processed, the glucan- or xylan-containing cellulose in the feedstock can be hydrolyzed to low molecular weight carbohydrates, such as sugars, by a saccharifying agent, *e.g.*, an enzyme or acid, a process referred to as saccharification. The low molecular weight carbohydrates can then be used, for example, in an existing manufacturing plant, such as a single cell protein plant, an enzyme manufacturing plant, or a fuel plant, *e.g.*, an ethanol manufacturing facility.

[00146] The feedstock can be hydrolyzed using an enzyme, *e.g.*, by combining the materials and the enzyme in a solvent, *e.g.*, in an aqueous solution.

[00147] Alternatively, the enzymes can be supplied by organisms that break down biomass, such as the cellulose and/or the lignin portions of the biomass, contain or manufacture various cellulolytic enzymes (cellulases), ligninases or various small molecule biomass-degrading metabolites. These enzymes may be a complex of enzymes that act synergistically to degrade crystalline cellulose or the lignin portions of biomass. Examples of cellulolytic enzymes include: endoglucanases, cellobiohydrolases, and cellobiases (beta-glucosidases).

[00148] During saccharification a cellulosic substrate can be initially hydrolyzed by endoglucanases at random locations producing oligomeric intermediates. These intermediates are then substrates for exo-splitting glucanases such as cellobiohydrolase to produce cellobiose from the ends of the cellulose polymer. Cellobiose is a water-soluble 1,4-linked dimer of glucose. Finally, cellobiase cleaves cellobiose to yield glucose. The efficiency (*e.g.*, time to hydrolyze and/or completeness of hydrolysis) of this process depends on the recalcitrance of the cellulosic material.

INTERMEDIATES AND PRODUCTS

[00149] Using the processes described herein, the biomass material can be converted to one or more products, such as energy, fuels, foods and materials. Specific examples of products include, but are not limited to, hydrogen, sugars (*e.g.*, glucose, xylose, arabinose, mannose, galactose, fructose, disaccharides, oligosaccharides and polysaccharides), alcohols (*e.g.*, monohydric alcohols or dihydric alcohols, such as ethanol, n-propanol, isobutanol, *sec*-butanol, tert-butanol or n-butanol), hydrated or hydrous alcohols (*e.g.*, containing greater than 10%, 20%, 30% or even greater than 40% water), biodiesel, organic acids, hydrocarbons (*e.g.*, methane, ethane, propane, isobutene, pentane, n-hexane, biodiesel, bio-gasoline and mixtures thereof), co-products (*e.g.*, proteins, such as cellulolytic proteins (enzymes) or single cell proteins), and mixtures of any of these in any combination or relative concentration, and optionally in combination with any additives (*e.g.*, fuel additives). Other examples include carboxylic acids, salts of a carboxylic acid, a mixture of carboxylic acids and salts of carboxylic acids and esters of carboxylic acids (*e.g.*, methyl, ethyl and n-propyl esters), ketones (*e.g.*, acetone), aldehydes (*e.g.*, acetaldehyde), alpha and beta unsaturated acids (*e.g.*, acrylic acid) and olefins (*e.g.*, ethylene). Other alcohols and alcohol derivatives include propanol, propylene glycol, 1,4-butanediol, 1,3-propanediol, sugar alcohols (*e.g.*, erythritol, glycol, glycerol, sorbitol threitol, arabitol, ribitol, mannitol, dulcitol, fucitol, iditol, isomalt, maltitol, lactitol, xylitol and other polyols), and methyl or ethyl esters of any of these alcohols. Other products include methyl acrylate, methyl methacrylate, D- or L-lactic acid, citric acid, formic acid, acetic acid, propionic acid, butyric acid, succinic acid, valeric acid, caproic acid, 3-hydroxypropionic acid, palmitic acid, stearic acid, oxalic acid, malonic acid, glutaric acid, oleic acid, linoleic acid, glycolic acid, gamma-hydroxybutyric acid, and mixtures thereof, salts of any of these acids, mixtures of any of the acids and their respective salts.

[00150] Any combination of the above products with each other, and/or of the above products with other products, which other products may be made by the processes described herein or otherwise, may be packaged together and sold as products. The products may be combined, *e.g.*, mixed, blended or co-dissolved, or may simply be packaged or sold together.

[00151] Any of the products or combinations of products described herein may be sanitized or sterilized prior to selling the products, *e.g.*, after purification or isolation or even after packaging, to neutralize one or more potentially undesirable contaminants that could be present in the product(s). Such sanitation can be done with electron bombardment, for example, be at a dosage of less than about 20 Mrad, *e.g.*, from about 0.1 to 15 Mrad, from about 0.5 to 7 Mrad, or from about 1 to 3 Mrad.

[00152] The processes described herein can produce various by-product streams useful for generating steam and electricity to be used in other parts of the plant (co-generation) or sold on the open market. For example, steam generated from burning by-product streams can be used in a distillation process. As another example, electricity generated from burning by-product streams can be used to power electron beam generators used in pretreatment.

[00153] The by-products used to generate steam and electricity are derived from a number of sources throughout the process. For example, anaerobic digestion of wastewater can produce a biogas high in methane and a small amount of waste biomass (sludge). As another example, post-saccharification and/or post-distillate solids (*e.g.*, unconverted lignin, cellulose, and hemicellulose remaining from the pretreatment and primary processes) can be used, *e.g.*, burned, as a fuel.

[00154] Other intermediates and products, including food and pharmaceutical products, are described in U.S. Pat. App. Pub. 2010/0124583 A1, published May 20, 2010, to Medoff, the full disclosure of which is hereby incorporated by reference herein.

LIGNIN DERIVED PRODUCTS

[00155] The spent biomass (e.g., spent lignocellulosic material) from lignocellulosic processing by the methods described are expected to have a high lignin content and in addition to being useful for producing energy through combustion in a Co-Generation plant, may have uses as other valuable products. For example, the lignin can be used as captured as a plastic, or it can be synthetically upgraded to other plastics. In some instances, it can also be converted to lignosulfonates, which can be utilized as binders, dispersants, emulsifiers or as sequestrants.

[00156] When used as a binder, the lignin or a lignosulfonate can, e.g., be utilized in coal briquettes, in ceramics, for binding carbon black, for binding fertilizers and herbicides, as a dust suppressant, in the making of plywood and particle board, for binding animal feeds, as a binder for fiberglass, as a binder in linoleum paste and as a soil stabilizer.

[00157] As a dispersant, the lignin or lignosulfonates can be used, e.g., concrete mixes, clay and ceramics, dyes and pigments, leather tanning and in gypsum board.

[00158] As an emulsifier, the lignin or lignosulfonates can be used, e.g., in asphalt, pigments and dyes, pesticides and wax emulsions.

[00159] As a sequestrant, the lignin or lignosulfonates can be used, e.g., in micro-nutrient systems, cleaning compounds and water treatment systems, e.g., for boiler and cooling systems.

[00160] For energy production lignin generally has a higher energy content than holocellulose (cellulose and hemicellulose) since it contains more carbon than holocellulose. For example, dry lignin can have an energy content of between about 11,000 and 12,500 BTU per pound, compared to 7,000 an 8,000 BTU per pound of holocellulose. As such, lignin can be densified and converted into briquettes and pellets for burning. For example, the lignin can be converted into pellets by any method described herein. For a slower burning pellet or briquette, the lignin can be crosslinked, such as applying a radiation dose of between about 0.5 Mrad and 5 Mrad. Crosslinking can make a slower burning form factor. The form factor, such as a pellet or briquette, can be converted to a "synthetic coal" or charcoal by pyrolyzing in the absence of air, e.g., at between 400 and 950 °C. Prior to pyrolyzing, it can be desirable to crosslink the lignin to maintain structural integrity.

[00161] Co-generation using spent biomass is described in U.S. Provisional Application 61/774,773, filed March 8, 2013 the entire disclosure therein is herein incorporated by reference.

BIOMASS PROCESSING AFTER IRRADIATION

[00162] After irradiation the biomass may be transferred to a vessel for saccharification. Alternately, the biomass can be heated after the biomass is irradiated prior to the saccharification step. The heated means can be created, for example, by IR radiation, microwaves, combustion (e.g., gas, coal, oil, biomass), resistive heating and/or inductive coils. The heat can be applied from at least one side or more than one side, can be continuous or periodic and can be for only a portion of the material or all the material. The biomass may

be heated to temperatures above 90°C in an aqueous liquid that may have an acid or a base present. For example, the aqueous biomass slurry may be heated to 90 to 150°C, alternatively, 105 to 145°C, optionally 110 to 140°C or further optionally from 115 to 135°C. The time that the aqueous biomass mixture is held at the peak temperature is 1 to 12 hours, alternately, 1 to 6 hours, optionally 1 to 4 hours at the peak temperature. In some instances, the aqueous biomass mixture is acidic, and the pH is between 1 and 5, optionally 1 to 4, or alternately, 2 to 3. In other instances, the aqueous biomass mixture is alkaline and the pH is between 6 and 13, alternately, 8 to 12, or optionally, 8 to 11.

SACCHARIFICATION

[00163] The treated biomass materials can be saccharified, generally by combining the material and a cellulase enzyme in a fluid medium, *e.g.*, an aqueous solution. In some cases, the material is boiled, steeped, or cooked in hot water prior to saccharification, as described in U.S. Pat. App. Pub. 2012/0100577 A1 by Medoff and Masterman, published on April 26, 2012, the entire contents of which are incorporated herein.

[00164] The saccharification process can be partially or completely performed in a tank (*e.g.*, a tank having a volume of at least 4000, 40,000, or 500,000 L) in a manufacturing plant, and/or can be partially or completely performed in transit, *e.g.*, in a rail car, tanker truck, or in a supertanker or the hold of a ship. The time required for complete saccharification will depend on the process conditions and the carbohydrate-containing material and enzyme used. If saccharification is performed in a manufacturing plant under controlled conditions, the cellulose may be substantially entirely converted to sugar, *e.g.*, glucose in about 12-96 hours. If saccharification is performed partially or completely in transit, saccharification may take longer.

[00165] It is generally preferred that the tank contents be mixed during saccharification, *e.g.*, using jet mixing as described in International App. No. PCT/US2010/035331, filed May 18, 2010, which was published in English as WO 2010/135380 and designated the United States, the full disclosure of which is incorporated by reference herein.

[00166] The addition of surfactants can enhance the rate of saccharification. Examples of surfactants include non-ionic surfactants, such as a Tween® 20 or Tween® 80 polyethylene glycol surfactants, ionic surfactants, or amphoteric surfactants.

[00167] It is generally preferred that the concentration of the sugar solution resulting from saccharification be relatively high, *e.g.*, greater than 40%, or greater than 50, 60, 70, 80, 90 or

even greater than 95% by weight. Water may be removed, *e.g.*, by evaporation, to increase the concentration of the sugar solution. This reduces the volume to be shipped, and also inhibits microbial growth in the solution.

[00168] Alternatively, sugar solutions of lower concentrations may be used, in which case it may be desirable to add an antimicrobial additive, *e.g.*, a broad spectrum antibiotic, in a low concentration, *e.g.*, 50 to 150 ppm. Other suitable antibiotics include amphotericin B, ampicillin, chloramphenicol, ciprofloxacin, gentamicin, hygromycin B, kanamycin, neomycin, penicillin, puromycin, streptomycin. Antibiotics will inhibit growth of microorganisms during transport and storage, and can be used at appropriate concentrations, *e.g.*, between 15 and 1000 ppm by weight, *e.g.*, between 25 and 500 ppm, or between 50 and 150 ppm. If desired, an antibiotic can be included even if the sugar concentration is relatively high. Alternatively, other additives with anti-microbial of preservative properties may be used. Preferably the antimicrobial additive(s) are food-grade.

[00169] A relatively high concentration solution can be obtained by limiting the amount of water added to the carbohydrate-containing material with the enzyme. The concentration can be controlled, *e.g.*, by controlling how much saccharification takes place. For example, concentration can be increased by adding more carbohydrate-containing material to the solution. In order to keep the sugar that is being produced in solution, a surfactant can be added, *e.g.*, one of those discussed above. Solubility can also be increased by increasing the temperature of the solution. For example, the solution can be maintained at a temperature of 40-50°C, 60-80°C, or even higher.

SACCHARIFYING AGENTS

[00170] Suitable cellulolytic enzymes include cellulases from species in the genera *Bacillus*, *Coprinus*, *Myceliophthora*, *Cephalosporium*, *Scytalidium*, *Penicillium*, *Aspergillus*, *Pseudomonas*, *Humicola*, *Fusarium*, *Thielavia*, *Acremonium*, *Chrysosporium* and *Trichoderma*, especially those produced by a strain selected from the species *Aspergillus* (see, *e.g.*, EP Pub. No. 0 458 162), *Humicola insolens* (reclassified as *Scytalidium thermophilum*, see, *e.g.*, U.S. Pat. No. 4,435,307), *Coprinus cinereus*, *Fusarium oxysporum*, *Myceliophthora thermophila*, *Meripilus giganteus*, *Thielavia terrestris*, *Acremonium sp.* (including, but not limited to, *A. persicinum*, *A. acremonium*, *A. brachypenium*, *A. dichromosporum*, *A. obclavatum*, *A. pinkertoniae*, *A. roseogriseum*, *A. incoloratum*, and *A. furatum*). Preferred strains include *Humicola insolens* DSM 1800, *Fusarium oxysporum*

DSM 2672, *Myceliophthora thermophila* CBS 117.65, *Cephalosporium sp.* RYM-202, *Acremonium sp.* CBS 478.94, *Acremonium sp.* CBS 265.95, *Acremonium persicinum* CBS 169.65, *Acremonium acremonium* AHU 9519, *Cephalosporium sp.* CBS 535.71, *Acremonium brachypenium* CBS 866.73, *Acremonium dichromosporum* CBS 683.73, *Acremonium obclavatum* CBS 311.74, *Acremonium pinkertoniae* CBS 157.70, *Acremonium roseogriseum* CBS 134.56, *Acremonium incoloratum* CBS 146.62, and *Acremonium furatum* CBS 299.70H. Cellulolytic enzymes may also be obtained from *Chrysosporium*, preferably a strain of *Chrysosporium lucknowense*. Additional strains that can be used include, but are not limited to, *Trichoderma* (particularly *T. viride*, *T. reesei*, and *T. koningii*), alkalophilic *Bacillus* (see, for example, U.S. Pat. No. 3,844,890 and EP Pub. No. 0 458 162), and *Streptomyces* (see, *e.g.*, EP Pub. No. 0 458 162).

[00171] In addition to or in combination to enzymes, acids, bases and other chemicals (e.g., oxidants) can be utilized to saccharify lignocellulosic and cellulosic materials. These can be used in any combination or sequence (e.g., before, after and/or during addition of an enzyme). For example strong mineral acids can be utilized (e.g. HCl, H_2SO_4, H_3PO_4) and strong bases (e.g., NaOH, KOH).

SUGARS

[00172] In the processes described herein, for example after saccharification, sugars (*e.g.*, glucose and xylose) can be isolated. For example sugars can be isolated by precipitation, crystallization, chromatography (*e.g.*, simulated moving bed chromatography, high pressure chromatography), centrifugation, extraction, any other isolation method known in the art, and combinations thereof.

HYDROGENATION AND OTHER CHEMICAL TRANSFORMATIONS

[00173] The processes described herein can include hydrogenation. For example glucose and xylose can be hydrogenated to sorbitol and xylitol respectively. Hydrogenation can be accomplished by use of a catalyst (*e.g.*, Pt/gamma-Al_2O_3, Ru/C, Raney Nickel, or other catalysts know in the art) in combination with H_2 under high pressure (*e.g.*, 10 to 12000 psi). Other types of chemical transformation of the products from the processes described herein can be used, for example production of organic sugar derived products such (*e.g.*, furfural and furfural-derived products). Chemical transformations of sugar derived products are described in US Prov. App. No. 61/667,481, filed July 3, 2012, the disclosure of which is incorporated herein by reference in its entirety.

FERMENTATION

[00174] Yeast and *Zymomonas* bacteria, for example, can be used for fermentation or conversion of sugar(s) to alcohol(s). Other microorganisms are discussed below. The optimum pH for fermentations is about pH 4 to 7. For example, the optimum pH for yeast is from about pH 4 to 5, while the optimum pH for *Zymomonas* is from about pH 5 to 6. Typical fermentation times are about 24 to 168 hours (*e.g.*, 24 to 96 hrs.) with temperatures in the range of 20°C to 40°C (*e.g.*, 26°C to 40°C), however thermophilic microorganisms prefer higher temperatures.

[00175] In some embodiments, *e.g.*, when anaerobic organisms are used, at least a portion of the fermentation is conducted in the absence of oxygen, *e.g.*, under a blanket of an inert gas such as N_2, Ar, He, CO_2 or mixtures thereof. Additionally, the mixture may have a constant purge of an inert gas flowing through the tank during part of or all of the fermentation. In some cases, anaerobic condition, can be achieved or maintained by carbon dioxide production during the fermentation and no additional inert gas is needed.

[00176] In some embodiments, all or a portion of the fermentation process can be interrupted before the low molecular weight sugar is completely converted to a product (*e.g.*, ethanol). The intermediate fermentation products include sugar and carbohydrates in high concentrations. The sugars and carbohydrates can be isolated via any means known in the art. These intermediate fermentation products can be used in preparation of food for human or animal consumption. Additionally or alternatively, the intermediate fermentation products can be ground to a fine particle size in a stainless-steel laboratory mill to produce a flour-like substance. Jet mixing may be used during fermentation, and in some cases saccharification and fermentation are performed in the same tank.

[00177] Nutrients for the microorganisms may be added during saccharification and/or fermentation, for example the food-based nutrient packages described in U.S. Pat. App. Pub. 2012/0052536, filed July 15, 2011, the complete disclosure of which is incorporated herein by reference.

[00178] Fermentation" includes the methods and products that are disclosed in International App. No. PCT/US2012/071097 (which was filed December 20, 2012, was published in English as WO 2013/096700 and designated the United States) and International App. No. PCT/US2012/071083 (which was filed December 20, 2012, was published in English as WO 2013/096693 and designated the United States) the contents of both of which are incorporated by reference herein in their entirety.

[00179] Mobile fermenters can be utilized, as described in International App. No. PCT/US2007/074028 (which was filed July 20, 2007, was published in English as WO 2008/011598 and designated the United States) and has a US issued Patent No. 8,318,453, the contents of which are incorporated herein in its entirety. Similarly, the saccharification equipment can be mobile. Further, saccharification and/or fermentation may be performed in part or entirely during transit.

FERMENTATION AGENTS

[00180] The microorganism(s) used in fermentation can be naturally-occurring microorganisms and/or engineered microorganisms. For example, the microorganism can be a bacterium (including, but not limited to, *e.g.*, a cellulolytic bacterium), a fungus, (including, but not limited to, *e.g.*, a yeast), a plant, a protist, *e.g.*, a protozoa or a fungus-like protest (including, but not limited to, *e.g.*, a slime mold), or an alga. When the organisms are compatible, mixtures of organisms can be utilized.

[00181] Suitable fermenting microorganisms have the ability to convert carbohydrates, such as glucose, fructose, xylose, arabinose, mannose, galactose, oligosaccharides or polysaccharides into fermentation products. Fermenting microorganisms include strains of the genus *Sacchromyces spp.* (including, but not limited to, *S. cerevisiae* (baker's yeast), *S. distaticus*, *S. uvarum*), the genus *Kluyveromyces*, (including, but not limited to, *K. marxianus*, *K. fragilis*), the genus *Candida* (including, but not limited to, *C. pseudotropicalis*, and *C. brassicae*), *Pichia stipitis* (a relative of *Candida shehatae*), the genus *Clavispora* (including, but not limited to, *C. lusitaniae* and *C. opuntiae*), the genus *Pachysolen* (including, but not limited to, *P. tannophilus*), the genus *Bretannomyces* (including, but not limited to, *e.g.*, *B. clausenii* (Philippidis, G. P., 1996, Cellulose bioconversion technology, in Handbook on Bioethanol: Production and Utilization, Wyman, C.E., ed., Taylor & Francis, Washington, DC, 179-212)). Other suitable microorganisms include, for example, *Zymomonas mobilis, Clostridium spp.* (including, but not limited to, *C. thermocellum* (Philippidis, 1996, *supra*), *C. saccharobutylacetonicum*, *C. tyrobutyricum C. saccharobutylicum*, *C. Puniceum*, *C. beijernckii*, and *C. acetobutylicum*), *Moniliella spp. (including but not limited to M. pollinis,M. tomentosa, M. madida, M. nigrescens, M. oedocephali, M. megachiliensis), Yarrowia lipolytica, Aureobasidium sp., Trichosporonoides sp., Trigonopsis variabilis, Trichosporon sp., Moniliellaacetoabutans sp., Typhula variabilis, Candida magnoliae, Ustilaginomycetes sp., Pseudozyma tsukubaensis*, yeast species of genera

Zygosaccharomyces, Debaryomyces, Hansenula and Pichia, and fungi of the dematioid genus *Torula (e.g., T.corallina).*

[00182] Additional microorganisms include the *Lactobacillus* group. Examples include *Lactobacillus casei, Lactobacillus rhamnosus, Lactobacillus delbrueckii, Lactobacillus plantarum, Lactobacillus coryniformis*, e.g., *Lactobacillus coryniformis subspecies torquens, Lactobacillus pentosus, Lactobacillus brevis*. Other microorganisms include *Pediococus penosaceus, Rhizopus oryzae.*

[00183] Several organisms, such as bacteria, yeasts and fungi, can be utilized to ferment biomass derived products such as sugars and alcohols to succinic acid and similar products. For example, organisms can be selected from; *Actinobacillus succinogenes, Anaerobiospirillum succiniciproducens, Mannheimia succiniciproducens, Ruminococcus flaverfaciens, Ruminococcus albus, Fibrobacter succinogenes, Bacteroides fragilis, Bacteroides ruminicola, Bacteroides amylophilus,Bacteriodes succinogenes, Mannheimia succiniciproducens, Corynebacterium glutamicum, Aspergillus niger, Aspergillus fumigatus, Byssochlamys nivea, Lentinus degener, Paecilomyces varioti, Penicillium viniferum, Saccharomyces cerevisiae, Enterococcus faecali, Prevotella ruminicolas, Debaryomyces hansenii, Candida catenulata* VKM Y-5, *C. mycoderma* VKM Y-240, *C. rugosa* VKM Y-67, *C. paludigena* VKM Y-2443, *C. utilis* VKM Y-74, *C. utilis* 766, *C. zeylanoides* VKM Y-6, *C. zeylanoides* VKM Y-14, *C. zeylanoides* VKM Y-2324, *C. zeylanoides* VKM Y-1543, *C. zeylanoides* VKM Y-2595, *C. valida* VKM Y-934, *Kluyveromyces wickerhamii* VKM Y-589, *Pichia anomala* VKM Y-118, P. *besseyi* VKM Y-2084, *P. media* VKM Y-1381, *P. guilliermondii* H-P-4, *P. guilliermondii* 916, *P. inositovora* VKM Y-2494, *Saccharomyces cerevisiae* VKM Y-381, *Torulopsis candida* 127, *T. candida* 420, *Yarrowia lipolytica* 12a, *Y. lipolytica* VKM Y-47, *Y. lipolytica* 69, *Y. lipolytica* VKM Y-57, *Y. lipolytica* 212, *Y. lipolytica* 374/4, *Y. lipolytica* 585, *Y. lipolytica* 695, *Y. lipolytica* 704, and mixtures of these organisms.

[00184] Many such microbial strains are publicly available, either commercially or through depositories such as the ATCC (American Type Culture Collection, Manassas, Virginia, USA), the NRRL (Agricultural Research Service Culture Collection, Peoria, Illinois, USA), or the DSMZ (Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Braunschweig, Germany), to name a few.

[00185] Commercially available yeasts include, for example, RED STAR®/Lesaffre Ethanol Red (available from Red Star/Lesaffre, USA), FALI® (available from Fleischmann's Yeast, a division of Burns Philip Food Inc., USA), SUPERSTART® (Lallemand Biofuels

and Distilled Spirits, Canada), EAGLE C6 FUELTM or C6 FUELTM (available from Lallemand Biofuels and Distilled Spirits, Canada), GERT STRAND® (available from Gert Strand AB, Sweden) and FERMOL® (available from DSM Specialties).

DISTILLATION

[00186] After fermentation, the resulting fluids can be distilled using, for example, a "beer column" to separate ethanol and other alcohols from the majority of water and residual solids. The vapor exiting the beer column can be, *e.g.*, 35% by weight ethanol and can be fed to a rectification column. A mixture of nearly azeotropic (92.5%) ethanol and water from the rectification column can be purified to pure (99.5%) ethanol using vapor-phase molecular sieves. The beer column bottoms can be sent to the first effect of a three-effect evaporator. The rectification column reflux condenser can provide heat for this first effect. After the first effect, solids can be separated using a centrifuge and dried in a rotary dryer. A portion (25%) of the centrifuge effluent can be recycled to fermentation and the rest sent to the second and third evaporator effects. Most of the evaporator condensate can be returned to the process as fairly clean condensate with a small portion split off to waste water treatment to prevent build-up of low-boiling compounds.

HYDROCARBON-CONTAINING MATERIALS

[00187] In other embodiments utilizing the methods and systems described herein, hydrocarbon-containing materials can be processed. Any process described herein can be used to treat any hydrocarbon-containing material herein described. "Hydrocarbon-containing materials," as used herein, is meant to include oil sands, oil shale, tar sands, coal dust, coal slurry, bitumen, various types of coal, and other naturally-occurring and synthetic materials that include both hydrocarbon components and solid matter. The solid matter can include rock, sand, clay, stone, silt, drilling slurry, or other solid organic and/or inorganic matter. The term can also include waste products such as drilling waste and by-products, refining waste and by-products, or other waste products containing hydrocarbon components, such as asphalt shingling and covering, asphalt pavement, etc.

CONVEYING SYSTEMS

[00188] Various conveying systems can be used to convey the biomass material, for example, as previously discussed, to a vault, and under an electron beam in a vault. Exemplary conveyors are belt conveyors, pneumatic conveyors, screw conveyors, carts,

trains, trains or carts on rails, elevators, front loaders, backhoes, cranes, various scrapers and shovels, trucks, and throwing devices can be used. For example, vibratory conveyors can be used in various processes described herein. Vibratory conveyors are described in PCT/US2013/64289 filed October 10, 2013 the full disclosure of which is incorporated by reference herein.

[00189] Vibratory conveyors are particularly useful for spreading the material and producing a uniform layer on the conveyor trough surface. For example the initial feedstock can form a pile of material that can be at least four feet high (e.g., at least about 3 feet, at least about 2 feet, at least about 1 foot, at least about 6 inches, at least about 5 inches, at least about, 4 inches, at least about 3 inches, at least about 2 inches, at least about 1 inch, at least about ½ inch) and spans less than the width of the conveyor (e.g., less than about 10%, less than about 20%, less than about 30%, less than about 40%, less than about 50%, less than about 60%, less than about 70%, less than about 80%, less than about 90%, less than about 95%, less than about 99%). The vibratory conveyor can spread the material to span the entire width of the conveyor trough and have a uniform thickness, preferably as discussed above. In some cases, an additional spreading method can be useful. For example, a spreader such as a broadcast spreader, a drop spreader (e.g., a CHRISTY SPREADER™) or combinations thereof can be used to drop (e.g., place, pour, spill and/or sprinkle) the feedstock over a wide area. Optionally, the spreader can deliver the biomass as a wide shower or curtain onto the vibratory conveyor. Additionally, a second conveyor, upstream from the first conveyor (e.g., the first conveyor is used in the irradiation of the feedstock), can drop biomass onto the first conveyor, where the second conveyor can have a width transverse to the direction of conveying smaller than the first conveyor. In particular, when the second conveyor is a vibratory conveyor, the feedstock is spread by the action of the second and first conveyor. In some optional embodiments, the second conveyor ends in a bias cross cut discharge (e.g., a bias cut with a ratio of 4:1) so that the material can be dropped as a wide curtain (e.g., wider than the width of the second conveyor) onto the first conveyor. The initial drop area of the biomass by the spreader (e.g., broadcast spreader, drop spreader, conveyor, or cross cut vibratory conveyor) can span the entire width of the first vibratory conveyor, or it can span part of this width. Once dropped onto the conveyor, the material is spread even more uniformly by the vibrations of the conveyor so that, preferably, the entire width of the conveyor is covered with a uniform layer of biomass. In some embodiments combinations of spreaders can be used. Some methods of spreading a feed stock are described in U.S. Patent

No. 7,153,533, filed July 23, 2002 and published December 26, 2006, the entire disclosure of which is incorporated herein by reference.

[00190] Generally, it is preferred to convey the material as quickly as possible through an electron beam to maximize throughput. For example, the material can be conveyed at rates of at least 1 ft/min, e.g., at least 2 ft/min, at least 3 ft/min, at least 4 ft/min, at least 5 ft/min, at least 10 ft/min, at least 15 ft/min, at least 20 ft/min, at least 25 ft/min, at least 30 ft/min, at least 40 ft/min, at least 50 ft/min, at least 60 ft/min, at least 70 ft/min, at least 80 ft/min, at least 90 ft/min. The rate of conveying is related to the beam current and targeted irradiation dose, for example, for a ¼ inch thick biomass spread over a 5.5 foot wide conveyor and 100 mA, the conveyor can move at about 20 ft/min to provide a useful irradiation dosage (e.g. about 10 Mrad for a single pass), at 50 mA the conveyor can move at about 10 ft/min to provide approximately the same irradiation dosage.

[00191] The rate at which material can be conveyed depends on the shape and mass of the material being conveyed, and the desired treatment. Flowing materials e.g., particulate materials, are particularly amenable to conveying with vibratory conveyors. Conveying speeds can, for example be, at least 100 lb/hr (e.g., at least 500 lb/hr, at least 1000 lb/hr, at least 2000 lb/hr, at least 3000 lb/hr, at least 4000 lb/hr, at least 5000 lb/hr, at least 10,000 lb/hr, at least 15, 000 lb/hr, or even at least 25,000 lb/hr). Some typical conveying speeds can be between about 1000 and 10,000 lb/hr, (e.g., between about 1000 lb/hr and 8000 lb/hr, between about 2000 and 7000 lb/hr, between about 2000 and 6000 lb/hr, between about 2000 and 5000lb/hr, between about 2000 and 4500 lb/hr, between about 1500 and 5000 lb/hr, between about 3000 and 7000 lb/hr, between about 3000 and 6000 lb/hr, between about 4000 and 6000 lb/hr and between about 4000 and 5000 lb/hr). Typical conveying speeds depend on the density of the material. For example, for a biomass with a density of about 35 lb/ft3, and a conveying speed of about 5000 lb/hr, the material is conveyed at a rate of about 143 ft3/hr, if the material is ¼" thick and is in a trough 5.5 ft wide, the material is conveyed at a rate of about 1250 ft/hr (about 21 ft/min). Rates of conveying the material can therefore vary greatly. Preferably, for example, a ¼" thick layer of biomass, is conveyed at speeds of between about 5 and 100 ft/min (e.g. between about 5 and 100 ft/min, between about 6 and 100 ft/min, between about 7 and 100 ft/min, between about 8 and 100 ft/min, between about 9 and 100 ft/min, between about 10 and 100 ft/min, between about 11 and 100 ft/min, between about 12 and 100 ft/min, between about 13 and 100 ft/min, between about 14 and 100 ft/min, between about 15 and 100 ft/min, between about 20 and 100 ft/min, between about 30 and 100 ft/min, between about 40 and 100 ft/min, between about 2 and 60 ft/min, between about 3 and 60

ft/min, between about 5 and 60 ft/min, between about 6 and 60 ft/min, between about 7 and 60 ft/min, between about 8 and 60 ft/min, between about 9 and 60 ft/min, between about 10 and 60 ft/min, between about 15 and 60 ft/min, between about 20 and 60 ft/min, between about 30 and 60 ft/min, between about 40 and 60 ft/min, between about 2 and 50 ft/min, between about 3 and 50 ft/min, between about 5 and 50 ft/min, between about 6 and 50 ft/min, between about 7 and 50 ft/min, between about 8 and 50 ft/min, between about 9 and 50 ft/min, between about 10 and 50 ft/min, between about 15 and 50 ft/min, between about 20 and 50 ft/min, between about 30 and 50 ft/min, between about 40 and 50 ft/min). It is preferable that the material be conveyed at a constant rate, for example, to help maintain a constant irradiation of the material as it passes under the electron beam (e.g., shower, field).

[00192] The vibratory conveyors described can include screens used for sieving and sorting materials. Port openings on the side or bottom of the troughs can be used for sorting, selecting or removing specific materials, for example, by size or shape. Some conveyors have counterbalances to reduce the dynamic forces on the support structure. Some vibratory conveyors are configured as spiral elevators, are designed to curve around surfaces and/or are designed to drop material from one conveyor to another (e.g., in a step, cascade or as a series of steps or a stair). Along with conveying materials conveyors can be used, by themselves or coupled with other equipment or systems, for screening, separating, sorting, classifying, distributing, sizing, inspection, picking, metal removing, freezing, blending, mixing, orienting, heating, cooking, drying, dewatering, cleaning, washing, leaching, quenching, coating, de-dusting and/or feeding. The conveyors can also include covers (e.g., dust-tight covers), side discharge gates, bottom discharge gates, special liners (e.g., anti-stick, stainless steel, rubber, custom steal, and or grooved), divided troughs, quench pools, screens, perforated plates, detectors (e.g., metal detectors), high temperature designs, food grade designs, heaters, dryers and or coolers. In addition, the trough can be of various shapes, for example, flat bottomed, vee shaped bottom, flanged at the top, curved bottom, flat with ridges in any direction, tubular, half pipe, covered or any combinations of these. In particular, the conveyors can be coupled with an irradiation systems and/or equipment.

[00193] The conveyors (e.g., vibratory conveyor) can be made of corrosion resistant materials. The conveyors can utilize structural materials that include stainless steel (e.g., 304, 316 stainless steel, HASTELLOY® ALLOYS and INCONEL® Alloys). For example, HASTELLOY® Corrosion-Resistant alloys from Hynes (Kokomo, Indiana, USA) such as HASTELLOY® B-3® ALLOY, HASTELLOY® HYBRID-BC1® ALLOY, HASTELLOY® C-4 ALLOY, HASTELLOY® C-22® ALLOY, HASTELLOY® C-22HS®

ALLOY, HASTELLOY® C-276 ALLOY, HASTELLOY® C-2000® ALLOY, HASTELLOY® G-30® ALLOY, HASTELLOY® G-35® ALLOY, HASTELLOY® N ALLOY and HASTELLOY® ULTIMET® alloy.

[00194] The vibratory conveyors can include non-stick release coatings, for example, TUFFLON™ (Dupont, Delaware, USA). The vibratory conveyors can also include corrosion resistant coatings. For example, coatings that can be supplied from Metal Coatings Corp (Houston, Texas, USA) and others such as Fluoropolymer, XYLAN®, Molybdenum Disulfide, Epoxy Phenolic, Phosphate- ferrous metal coating, Polyurethane- high gloss topcoat for epoxy, inorganic zinc, Poly Tetrafluoro ethylene, PPS/RYTON®, fluorinated ethylene propylene, PVDF/DYKOR®, ECTFE/HALAR® and Ceramic Epoxy Coating. The coatings can improve resistance to process gases (e.g., ozone), chemical corrosion, pitting corrosion, galling corrosion and oxidation.

[00195] Optionally, in addition to the conveying systems described herein, one or more other conveying systems can be enclosed. When using an enclosure, the enclosed conveyor can also be purged with an inert gas so as to maintain an atmosphere at a reduced oxygen level. Keeping oxygen levels low avoids the formation of ozone which in some instances is undesirable due to its reactive and toxic nature. For example, the oxygen can be less than about 20% (e.g., less than about 10%, less than about 1%, less than about 0.1%, less than about 0.01%, or even less than about 0.001% oxygen). Purging can be done with an inert gas including, but not limited to, nitrogen, argon, helium or carbon dioxide. This can be supplied, for example, from a boil off of a liquid source (e.g., liquid nitrogen or helium), generated or separated from air in situ, or supplied from tanks. The inert gas can be recirculated and any residual oxygen can be removed using a catalyst, such as a copper catalyst bed. Alternatively, combinations of purging, recirculating and oxygen removal can be done to keep the oxygen levels low.

[00196] The enclosed conveyor can also be purged with a reactive gas that can react with the biomass. This can be done before, during or after the irradiation process. The reactive gas can be, but is not limited to, nitrous oxide, ammonia, oxygen, ozone, hydrocarbons, aromatic compounds, amides, peroxides, azides, halides, oxyhalides, phosphides, phosphines, arsines, sulfides, thiols, boranes and/or hydrides. The reactive gas can be activated in the enclosure, e.g., by irradiation (e.g., electron beam, UV irradiation, microwave irradiation, heating, IR radiation), so that it reacts with the biomass. The biomass itself can be activated, for example by irradiation. Preferably the biomass is activated by the electron beam, to

produce radicals which then react with the activated or unactivated reactive gas, e.g., by radical coupling or quenching.

[00197] Purging gases supplied to an enclosed conveyor can also be cooled, for example below about 25°C, below about 0°C, below about -40°C, below about -80°C, below about -120°C. For example, the gas can be boiled off from a compressed gas such as liquid nitrogen or sublimed from solid carbon dioxide. As an alternative example, the gas can be cooled by a chiller or part of or the entire conveyor can be cooled.

OTHER EMBODIMENTS

[00198] Any material, processes or processed materials described herein can be used to make products and/or intermediates such as composites, fillers, binders, plastic additives, adsorbents and controlled release agents. The methods can include densification, for example, by applying pressure and heat to the materials. For example composites can be made by combining fibrous materials with a resin or polymer. For example radiation cross-linkable resin, e.g., a thermoplastic resin can be combined with a fibrous material to provide a fibrous material/cross-linkable resin combination. Such materials can be, for example, useful as building materials, protective sheets, containers and other structural materials (e.g., molded and/or extruded products). Absorbents can be, for example, in the form of pellets, chips, fibers and/or sheets. Adsorbents can be used, for example, as pet bedding, packaging material or in pollution control systems. Controlled release matrices can also be the form of, for example, pellets, chips, fibers and or sheets. The controlled release matrices can, for example, be used to release drugs, biocides, fragrances. For example, composites, absorbents and control release agents and their uses are described in U.S. Serial No. PCT/US2006/010648, filed March 23, 2006, and US Patent No. 8,074,910 filed November 22, 2011, the entire disclosures of which are herein incorporated by reference.

[00199] In some instances the biomass material is treated at a first level to reduce recalcitrance, e.g., utilizing accelerated electrons, to selectively release one or more sugars (e.g., xylose). The biomass can then be treated to a second level to release one or more other sugars (e.g., glucose). Optionally the biomass can be dried between treatments. The treatments can include applying chemical and biochemical treatments to release the sugars. For example, a biomass material can be treated to a level of less than about 20 Mrad (e.g., less than about 15 Mrad, less than about 10 Mrad, less than about 5 Mrad, less than about 2 Mrad) and then treated with a solution of sulfuric acid, containing less than 10% sulfuric acid

(e.g., less than about 9%, less than about 8%, less than about 7%, less than about 6%, less than about 5%, less than about 4%, less than about 3%, less than about 2%, less than about 1%, less than about 0.75%, less than about 0.50 %, less than about 0.25%) to release xylose. Xylose, for example that is released into solution, can be separated from solids and optionally the solids washed with a solvent/solution (e.g., with water and/or acidified water). Optionally, the solids can be dried, for example in air and/or under vacuum optionally with heating (e.g., below about 150 ° C, below about 120 ° C) to a water content below about 25 wt. % (below about 20 wt. %, below about 15 wt. %, below about 10 wt. %, below about 5 wt. %). The solids can then be treated with a level of less than about 30 Mrad (e.g., less than about 25 Mrad, less than about 20 Mrad, less than about 15 Mrad, less than about 10 Mrad, less than about 5 Mrad, less than about 1 Mrad or even not at all) and then treated with an enzyme (e.g., a cellulase) to release glucose. The glucose (e.g., glucose in solution) can be separated from the remaining solids. The solids can then be further processed, for example utilized to make energy or other products (e.g., lignin derived products).

EXAMPLES

[00200] Concentrations were determined by HPLC in aqueous diluted and filtered solutions with appropriate standards. Unless otherwise noted the reactants were obtained from Sigma/Aldrich, St. Louis MO, Fisher Scientific, Waltham MA or equivalent reactant supply house.

Saccharification

[00201] A cylindrical tank with a diameter of 32 Inches, 64 Inches in height and fit with ASME dished heads (top and bottom) was used in the saccharification. The tank was also equipped with a hydrofoil mixing blade 16" wide. Heating was provided by flowing hot water through a half pipe jacket surrounding the tank.

[00202] The tank was charged with 200 kg water, 80 kg of biomass, and 18 kg of Duet™ Cellulase enzyme available from Genencor, Palo Alto, and CA. Biomass was corn cob that had been hammer milled and screened to a size of between 10 and 40 mesh. The biomass was irradiated with an electron beam to a total dosage of 35 Mrad. The pH of the mixture was adjusted and maintained automatically throughout the saccharification at 4.8 using $Ca(OH)_2$. This combination was heated to 53 °C, stirred at 180 rpm for about 24 hours after which the saccharification was considered completed.

[00203] A portion of this material was screened through a 20 mesh screen and the solution stored in an 8 gal carboy at 4 °C.

Fermentation of Glucose to Ethanol

[00204] About 400mL of the saccharified material was decanted into a 1L New Brunswick BioFlow 115 Bioreactor. The material was aerated and heated to 30 °C prior to inoculation. Stirring was set at 50 rpm. The pH was measured at 5.2, which is acceptable for fermentation so it was not adjusted. Aeration was discontinued and the contents of the bioreactor were inoculated with 5 mg of Thermosacc Dry Yeast (Lallemand, Inc., Memphis TN) (*Saccharomyces cerevisiae*). Fermentation was allowed to proceed for about 24 hours.

[00205] After fermentation the glucose concentration was below the detection limit, the ethanol concentration was about 25 g/L, and the xylose concentration was about 30g/L.

Preparation of Distillate Bottoms

[00206] Distillate bottoms were prepared by distilling the ethanol from fermented material as described above. In addition, solids were removed by centrifugation. The final amount of dissolved solids was 5 to 10 wt. %. There also were fines in the suspended solid. After the distillation the xylose concentration was about 40 g/L. These bottoms were designated as Distillate Bottoms Lot A. A similarly prepared batch was designated as Lot R.

Fermentation of Xylose to Butyric Acid:

Distillate Bottoms Experiment (A)

[00207] Seven 1L New Brunswick BioFlow 115 Bioreactor were utilized in the experiment. All seven reactors were initially filled with 200 mL of 3x concentrate of P2 media (described below) and of 72 g Xylose (Danisco, Copenhagen, DE), Two of the reactors (BR2 and BR4) were charged with 120 mL of distillate bottom prepared as described above (Lot A). Two reactors (BR6 and BR8) were charged with 240 mL of distillate bottom (Lot A). Two (BR18 and BR20) were charged with 360mL of distillate bottom (Lot A). One reactor (BR22) was charged with 240 mL of distillate bottom (Lot R). All the bioreactors were brought to total volume of 600mL with DI water. For example, BR2 had 200 mL of P2 media, 120 mL of Distillate Bottoms Lot A, ~72 grams of xylose and DI water to make up to 600 mL. The Xylose concentration was 72 grams plus ~ 4.8 g from the Distillate Bottoms for a concentration of about 128 g/L. The reactors were sparged with N_2 gas and inoculated with 7% (45mL of *C.tyrobutyricum* (ATCC 25755). The seed was grown overnight at 37 ° C in 300mL of reinforced clostridia media from 1 mL freezer stocks. The bioreactors were sampled periodically submitted for GC and HPLC analysis. The fermentations were

maintained above 6.0 using 3.7N ammonium hydroxide. Table 1 shows data collected for these experiments.

[00208] P2 based medium was made as described in US 6,358,717 but as a 3 fold concentrate (3X), that is only 1/3 of the water was used to make the solutions. P2 medium is made as follows. The medium is composed of the following separately prepared solutions (in grams per 100 ml of distilled water, unless indicated otherwise): 790 ml of distilled water (solution I), 0.5 g of K_2HPO_4, 0.5 g of KH_2PO_4, 2.2 g of CH_3COONH_4 (solution II), 2.0 g of $MgSO_4 \cdot 7H_2O$, 0.1 g of $MnSO_4 \cdot H_2O$, 0.1 g of NaCl, 0.1 g of $FeSO_4 \cdot 7H_2O$ (solution III), and 100 mg of p-aminobenzoic acid, 100 mg of thiamine, 1 mg of biotin (solution IV). Solutions I and II were filter sterilized and subsequently mixed to form a buffer solution. Solutions III and IV were filter sterilized. Portions (10 and 1 ml) of solutions III and IV, respectively, were added aseptically to the buffer solution. The final pH of the P2 medium was 6.6.

Table 1

Sample	Time (hr)	Distillate bottom	Butyric Acid (g/L)	Xylose (g/L)
A-BR2	17	20% Lot A	8.5	95.1
A-BR4	17	20% Lot A	9.7	93.4
A-BR6	17	40% Lot A	7.9	90.4
A-BR8	17	40% Lot A	4.9	106.4
A-BR18	17	60% Lot A	4.8	94.8
A-BR20	17	60% Lot A	5.5	94.6
A-BR22	17	60% Lot R	7.8	115.4
A-BR2	24	20% Lot A	15.6	81.4
A-BR4	24	20% Lot A	16.3	79.1
A-BR6	24	40% Lot A	16.3	78.9
A-BR8	24	40% Lot A	8	91.5
A-BR18	24	60% Lot A	9.5	83.8
A-BR20	24	60% Lot A	11.2	81.9
A-BR22	24	60% Lot R	12.7	102
A-BR2	41	20% Lot A	29.6	40.4
A-BR4	41	20% Lot A	30.8	35.1
A-BR6	41	40% Lot A	31.3	44.4
A-BR8	41	40% Lot A	20.9	55.8
A-BR18	41	60% Lot A	27	54.5
A-BR20	41	60% Lot A	27.6	52.2
A-BR22	41	60% Lot R	28.7	60.9
A-BR2	48	20% Lot A	34	28.5
A-BR4	48	20% Lot A	36	22.4
A-BR6	48	40% Lot A	34.7	35.7
A-BR8	48	40% Lot A	27.5	44.8

A-BR18	48	60% Lot A	32.7	46.9
A-BR20	48	60% Lot A	33.2	44.6
A-BR22	48	60% Lot R	30.8	48.7
A-BR2	66	20% Lot A	48	5.6
A-BR4	66	20% Lot A	48.1	0.5
A-BR6	66	40% Lot A	39.1	19.1
A-BR8	66	40% Lot A	36.4	23.1
A-BR18	66	60% Lot A	38.1	28.7
A-BR20	66	60% Lot A	36.1	27.7
A-BR22	66	60% Lot R	38.1	25.2
A-BR2	72	20% Lot A	43.5	1.8
A-BR4	72	20% Lot A	42.8	NF
A-BR6	72	40% Lot A	41.3	14.9
A-BR8	72	40% Lot A	41	16.4
A-BR18	72	60% Lot A	39.3	23.6
A-BR20	72	60% Lot A	39	23.1
A-BR22	72	60% Lot R	48.9	18.2
A-BR2	138	20% Lot A	47.4	NF
A-BR4	138	20% Lot A	43.2	NF
A-BR6	138	40% Lot A	49	2.1
A-BR8	138	40% Lot A	46.1	0.5
A-BR18	138	60% Lot A	48.4	3
A-BR20	138	60% Lot A	47.5	3.9
A-BR22	138	60% Lot R	47.9	0.7
NF: not found, below detection limit				

Distillate Bottoms Experiment (B)

[00209] Six bioreactors were used in this experiment. For a 600 mL reactor charge, two reactors (B-BR2 and B-BR4) were filled with 72 g of xylose, 5ppm $FeSO_4x7H_2O$, and 6g/L Fluka brand yeast extract and DI water added to obtain 600 mL. Two other reactors (B-BR6 and B-BR8) were filled with 72 g of xylose, 5ppm $FeSO_4x7H_2O$, 40%240 mL distillate bottom and DI water added to obtain 600 mL. One reactor (B-BR 18) was filled with 72g xylose. 2oo mL of modified P2 supplemented with 240 mL distillate bottom and DI water added to obtain 600 mL. Another reactor (B-BR20) was filled with 72 g of xylose, 200 mL of modified P2 supplemented (as described above, but not as the 3X concentrate) with 60g/L yeast extract and DI water added to obtain 600 mL. All six reactors were sparged with N2 gas and then inoculated with 5% (30ml) of *C. tyrobutyricum* (ATCC 25755)). Table 2 shows this data.

[00210] The seed was grown overnight in a modified reinforced clostridia media consisting per liter of 10g peptone, 10g beef extract, 5g NaCl, .5g of L cysteine, 3g of sodium

acetate, .5g of anhydrous agar and 5g of xylose. The media was made up in 900ml of di water without xylose; 270ml was aliquoted into 500ml bottles. The bottles were sparged, autoclaved, and 30ml of 50g/L xylose was injected through a .22 micron filter into each bottle. The xylose solution was sparged with N_2 gas prior to injection. A 1ml freezer stock was used per 300ml bottle.

[00211] The pH of the fermentation was maintained above 6.0 using 3.7N NH_4OH. Samples were taken periodically and analyzed with GC and HPLC.

Table 2

Sample	Time (hr)	Media	Butyric Acid (g/L)	Xylose (g/L)
B-BR2	17	6g/L YE + 5mg/L $FeSO_4$	NF	94
B-BR4	17	6g/L YE + 5mg/L $FeSO_4$	NF	95.4
B-BR6	17	40% DB + 5mg/L $FeSO_4$	NF	117.8
B-BR8	17	40% DB+ 5mg/L $FeSO_4$	NF	119.2
B-BR18	17	P2 + 40% DB	0.3	104.4
B-BR20	17	P2 + 60g/L YE	NF	98.2
B-BR2	24	6g/L YE + 5mg/L $FeSO_4$	0.8	84.4
B-BR4	24	6g/L YE + 5mg/L $FeSO_4$	1.2	83.1
B-BR6	24	40% DB + 5mg/L $FeSO_4$	0.8	113.2
B-BR8	24	40% DB+ 5mg/L $FeSO_4$	0.7	113
B-BR18	24	P2 + 40% DB	0.9	101
B-BR20	24	P2 + 60g/L YE	1.7	99
B-BR2	41	6g/L YE + 5mg/L $FeSO_4$	5.5	51.9
B-BR4	41	6g/L YE + 5mg/L $FeSO_4$	9.3	48.5
B-BR6	41	40% DB + 5mg/L $FeSO_4$	14.8	88
B-BR8	41	40% DB+ 5mg/L $FeSO_4$	14	91.4
B-BR18	41	P2 + 40% DB	7.9	73.7
B-BR20	41	P2 + 60g/L YE	32.5	3.8
B-BR2	48	6g/L YE + 5mg/L $FeSO_4$	7.1	44.1
B-BR4	48	6g/L YE + 5mg/L $FeSO_4$	11	41.9
B-BR6	48	40% DB + 5mg/L $FeSO_4$	18.8	77.3
B-BR8	48	40% DB+ 5mg/L $FeSO_4$	19.2	81.9
B-BR18	48	P2 + 40% DB	16.8	66.2
B-BR20	48	P2 + 60g/L YE	37.1	NF
B-BR2	66	6g/L YE + 5mg/L $FeSO_4$	9.5	31.5
B-BR4	66	6g/L YE + 5mg/ $FeSO_4$	15.2	30.1
B-BR6	66	40% DB + 5mg/L $FeSO_4$	27.4	53.6
B-BR8	66	40% DB+ 5mg/L $FeSO_4$	25.2	61
B-BR18	66	P2 + 40% DB	28.7	43.9
B-BR20	66	P2 + 60g/L YE	41.3	NF

B-BR2	72	6g/L YE + 5mg/L $FeSO_4$	9.5	29
B-BR4	72	6g/L YE + 5mg/L $FeSO_4$	17.8	27.8
B-BR6	72	40% DB + 5mg/L $FeSO_4$	27.6	47.8
B-BR8	72	40% DB+ 5mg/L $FeSO_4$	26.7	52.4
B-BR18	72	P2 + 40% DB	30.6	36.5
B-BR20	72	P2 + 60g/L YE	36.2	NF
B-BR2	137	6g/L YE + 5mg/L $FeSO_4$	9.8	19.4
B-BR4	137	6g/L YE + 5mg/L $FeSO_4$	20.6	16.6
B-BR6	137	40% DB + 5mg/L $FeSO_4$	41.9	24.1
B-BR8	137	40% DB+ 5mg/L $FeSO_4$	42.6	16.6
B-BR18	137	P2 + 40% DB	40.2	4.3
B-BR20	137	P2 + 60g/L YE	36.3	NF
NF: not found, below detection limit				
YE: yeast extract				
DB: distillate bottom				
P2: modified P2 media				

Isolation of Butyrate Using an Acidic Resin

[00212] Amberlite™ IRA 400 resin (500 g) was washed with water (2 x 500 mL) in a 5 L round bottom flask. Excess water was removed carefully with a pipette before adding a fermentation broth to the wet resin. Fermentation broth (2 L) containing 44.7g/L butyric acid was added and the resulting mixture was stirred using a magnetic stirrer for 1.5 h. A small analytical sample was removed and was found to contain 32.5 g/L butyric acid (27 % loss) by GC head space analysis. This indicated that 24.5 g of butyric acid was adsorbed onto the resin.

[00213] The supernatant solution was poured off and the wet resin was loaded onto a glass column with a wire sieve at the bottom to prevent clogging. Fermentation broth was rinsed off the resin with a flow of water (2 L) until the eluent was clear. The resin was then transferred to a 2 L round bottom flask containing a magnetic stirring bar and then treated with 100 mL of 1 N HCl followed by 8 mL of 6 N HCl. The resulting mixture was stirred for 5 minutes and the pH was found to be 2.5, which was then subjected to distillation. A total of five bulb to bulb distillations gave 150-250 mL fractions. In between distillations more water and 1 N HCl was added to the resin. Fractions were made basic with 20 % aqueous NaOH and concentrated by rotary evaporation. Drying *in vacuo* at 120 ° C overnight gave 16.23 g as a combined crude solid or 14.13 g of sodium butyrate in the sample. This amounts to a 57.7 % recovery for the five distillations. Additional distillations would lead to a higher recovery.

Isolation of Butyrate using a Basic Resin

[00214] To 400 mL of butyric acid fermentation broth (44.58 g/L) in a 1 L round bottom flask 100 mL of Amberlite™ IRN 150 (basic component) wet resin was added. The resulting mixture was stirred at room temperature for 2 hours and then allowed to stand for 10 minutes. A small analytical sample (1/2 mL) was removed and placed in a vial. This was found to have 24.29 g/L butyric acid (54.49 % reduction) by GC head space analysis. This indicated that 9.72 g was adsorbed onto the resin.

[00215] The supernatant solution was poured off and the remaining broth was removed with a 50 mL pipette. The resin was rinsed with water (8 x 25 mL) and then treated with a 10 % solution of H_2SO_4 in EtOH (50 mL). The resulting mixture was stirred at room temperature for 5 minutes and then the ethanolic solution was removed by pipette. The resin was then rinsed with EtOH (10 x 25 mL), followed by water (10 x 25 mL). The EtOH rinse solutions were combined and basified with 20 % NaOH (pH 11) and then concentrated by rotary evaporation. The water rinse solutions were treated similarly and both solids were dried further *in vacuo* at 120 ° C to give 6.74 g (72.57 % sodium butyrate by LC analysis) from ethanol and 1.90 g (80.44 % sodium butyrate by LC analysis) from water. The total recovery from the resin was 66.1 %.

Conversion of Butyrate to Ethyl Butyrate

[00216] A crude mixture of solids containing a total of 8.9 g of sodium butyrate was treated with 50 mL of ethanol in a 250 mL round bottom flask and the resulting mixture was cooled in a water bath and slowly treated with concentrated sulfuric acid (16 g) while stirring with a magnetic stirring bar. The round bottom flask was fitted with a reflux condenser and the reaction mixture was boiled for 4 hours under N_2. After cooling to room temperature the reaction mixture was poured into a separatory funnel containing a 150 mL aqueous solution of Na_2HPO_4 (40 g). The final pH of the solution after mixing was 7. The top layer was separated out and filtered through glass wool to remove sludge giving 4.5 mL of ethyl butyrate. This sample was combined with other similar samples to give about 29 g of a crude liquid that was distilled to give 23.6 g (88 % purity by LC analysis) ethyl butyrate. The impurities were mostly ethanol (9.2 %) and ethyl acetate (2 %).

Hydrogenolysis of Ethyl Butyrate

[00217] Ethyl butyrate (20.8 g, 0.176 mol) in 225 mL of dry ethanol was added to 0.5 % Re on alumina (8.1 g, reduced) in a 1 L stainless steel autoclave. After purging with N_2 and evacuating, the resulting mixture was filled with 116 psi H_2 and then stirred at 600 rpm and

heated at 270 °C for a total of 25.5 hours over a 4 day period. The autoclave was depressurized to room temperature each morning and then more H_2 was added (108-112 psi). Pressures ranging from 1400-1500 psi were used for the hydrogenation. Gas chromatography head space analysis indicated a greater than 65 % molar conversion of ethyl butyrate with a greater than 90 %selectivity to n-butanol.

[00218] Other than in the examples herein, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages, such as those for amounts of materials, elemental contents, times and temperatures of reaction, ratios of amounts, and others, in the following portion of the specification and attached claims may be read as if prefaced by the word "about" even though the term "about" may not expressly appear with the value, amount, or range. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00219] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains error necessarily resulting from the standard deviation found in its underlying respective testing measurements. Furthermore, when numerical ranges are set forth herein, these ranges are inclusive of the recited range end points (e.g., end points may be used). When percentages by weight are used herein, the numerical values reported are relative to the total weight.

[00220] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of "1 to 10" is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. The terms "one," "a," or "an" as used herein are intended to include "at least one" or "one or more," unless otherwise indicated.

[00221] Any patent, publication, or other disclosure material, in whole or in part, that is said to be incorporated by reference herein is incorporated herein only to the extent that the

incorporated material does not conflict with existing definitions, statements, or other disclosure material set forth in this disclosure. As such, and to the extent necessary, the disclosure as explicitly set forth herein supersedes any conflicting material incorporated herein by reference. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material set forth herein will only be incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material.

[00222] While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

WHAT IS CLAIMED IS:

1. A method of making a product, the method comprising:

producing one or more acids from saccharified biomass sugars;

converting the one or more acids into one or more esters; and

hydrogenating the one or more esters utilizing a catalyst and hydrogen to produce one or more products including alcohols.

2. The method of claim 1 wherein the one or more acids are produced by fermentation of the saccharified biomass sugars.

3. The method of claim 1 or 2 wherein the one or more acids comprise butyric acid or acetic acid.

4. The method of claim 1 wherein the saccharified biomass sugars are produced by saccharification of a cellulosic or lignocellulosic biomass material with a method selected from the following group consisting of one or more enzymes, one or more acids, and combinations of these.

5. The method of claim 4 further comprising recalcitrance reducing the cellulosic or lignocellulosic material by electron beam irradiation.

6. The method of claim 5 wherein the dose of irradiation is between 10 and 200 Mrad.

7. The method of claim 1 wherein the catalyst includes a metal selected from the group consisting of Pt, Os, Re, Ru, Rb, Ni, Co, Mo, W, Zn, Cr, Cu, oxides of these and combinations of these.

8. The method of claim 7 further comprising applying a hydrogen pressure between about 5 and 120 atm. while utilizing catalyst to produce alcohols.

9. The method of claim 1 further comprising isolating at least one of the acids prior to converting the one or more acids into one or more esters.

10. The method of claim 1 wherein the ester is selected from the group consisting of ethyl butyrate, butyl butyrate, hexyl butyrate and octyl butyrate.

11. A method of making a product, the method comprising:

converting the product of the fermentation of a saccharified treated lignocellulosic material to an ester, and

producing an alcohol by passing the ester over a first catalyst in the presence of hydrogen.

12. The method of claim 11 further comprising passing the ester over a second catalyst.

13. The method of claim 12 wherein the first and second catalyst are different catalysts.

14. The method of claim 12 wherein the first and second catalyst are the same catalyst.

15. The method of claims 12 further comprising applying a first pressure of hydrogen while passing the ester over the first catalyst and applying a second pressure of hydrogen while passing the ester over the second catalyst, wherein the first pressure is higher than the second pressure by at least 10 psi.

16. The method claim 12 further comprising heating the first catalyst to a first temperature while passing the ester over the first catalyst and heating the second catalyst to a second temperature while passing the ester over the second catalyst, wherein the first temperature is higher than the second temperature by at least 10 ° C.

17. The method of claim 12 wherein the first and second catalyst comprise metals selected from the group consisting of Pt, Re, Os, Ru, Rb, Ni, Co, Mo, W, Zn, Cr, oxides of these and combinations of these.

18. The method of claim 12 further comprising applying a hydrogen pressure between about 5 and 100 atm. while passing the hydrogen over the first and/or second catalyst.

19. The method of claim 12 wherein the product of the fermentation comprises a carboxylic acid.

20. The method of claim 19 wherein the carboxylic acid has from 1 to 20 carbons and 1 to 5 carboxylic acid groups.

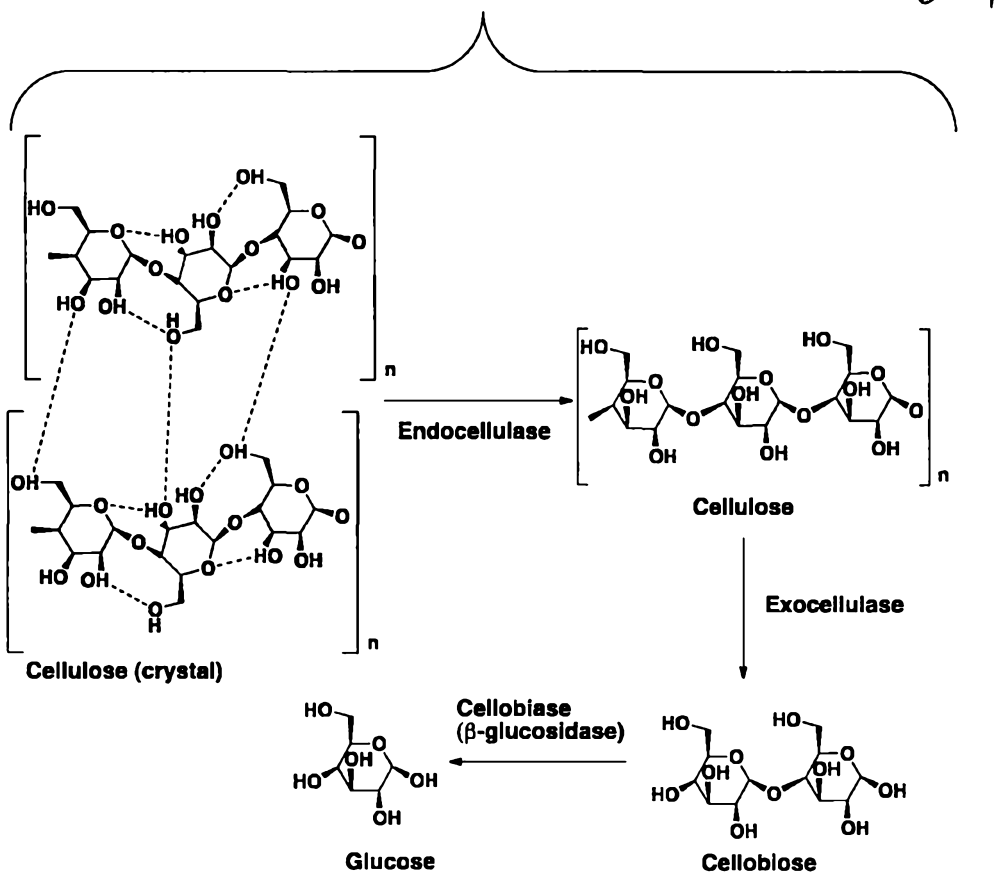
21. The method of claim 19 or 20 wherein the carboxylic acid is butyric acid.

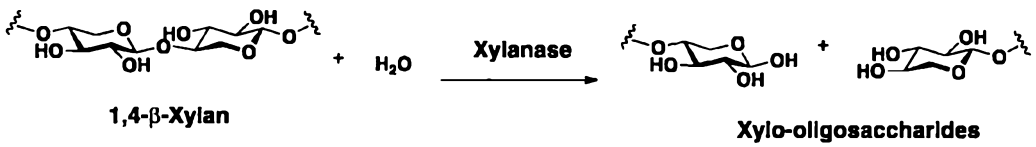
22. The method of claims 11 wherein the fermentation product comprises an alcohol.

23. The method claim 11 wherein the ester is selected from the group consisting of ethyl butyrate, butyl butyrate, hexyl butyrate and octyl butyrate.

24. The method claim 1 further comprising fermenting the biomass to at least two fermentation products where the two of the products are the acid and an alcohol which are, in turn, reacted to form an ester.

FIG. 1





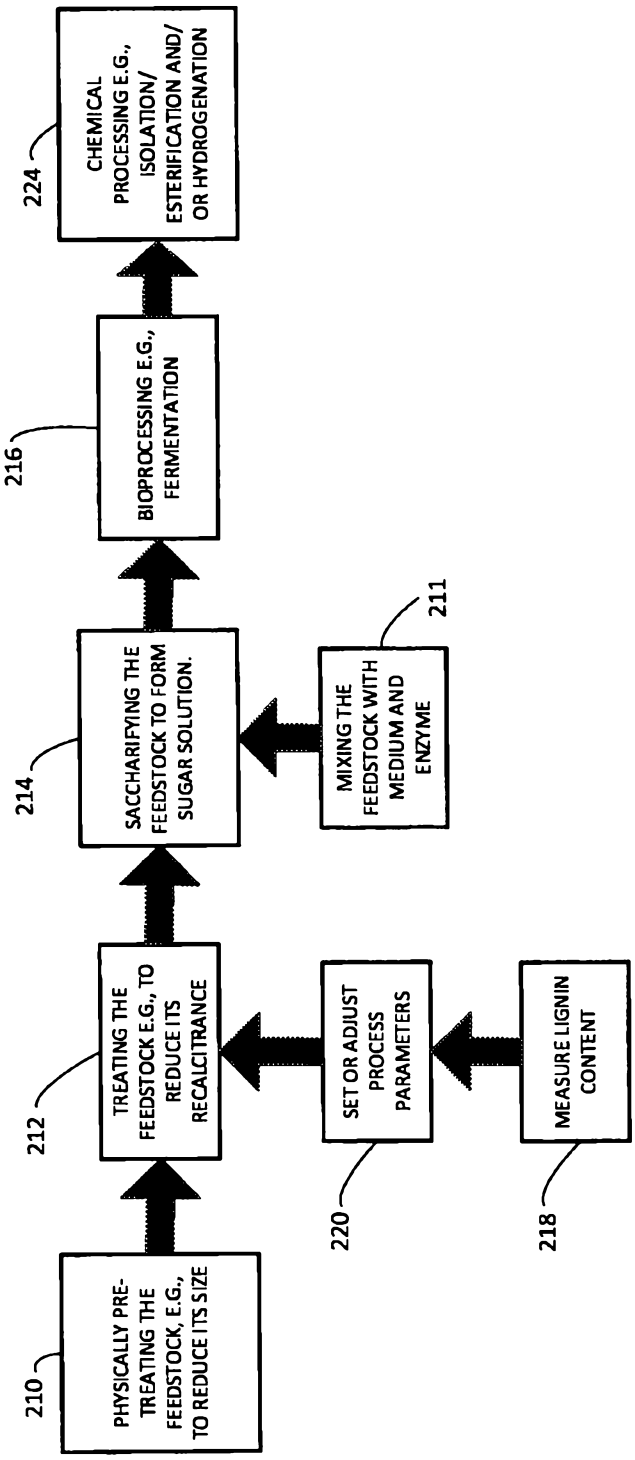
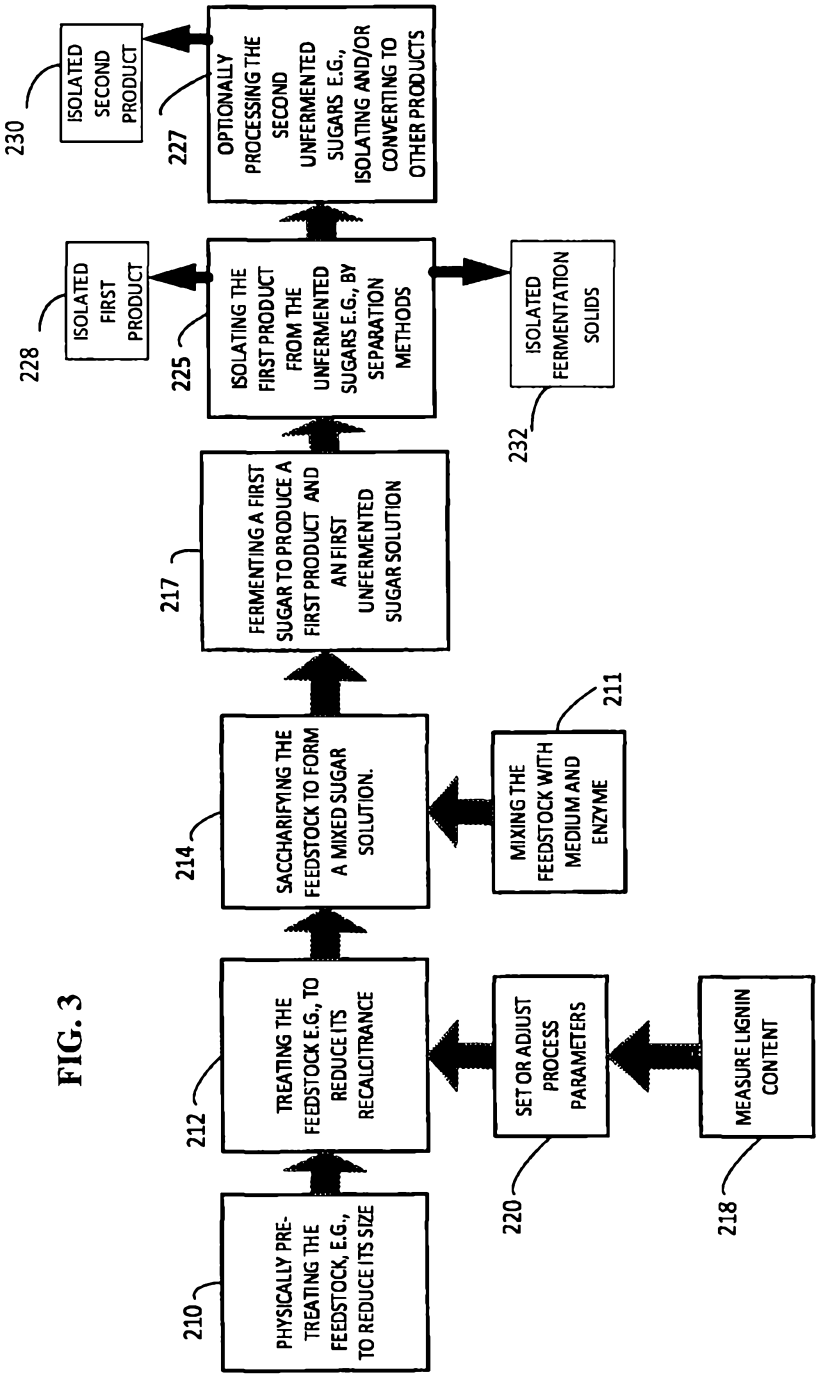

PHYSICALLY PRE-TREATING THE FEEDSTOCK, E.G., TO REDUCE ITS SIZE
210
TREATING THE FEEDSTOCK E.G., TO REDUCE ITS RECALCITRANCE
212
SET OR ADJUST PROCESS PARAMETERS
220
MEASURE LIGNIN CONTENT
218
SACCHARIFYING THE FEEDSTOCK TO FORM SUGAR SOLUTION.
214
MIXING THE FEEDSTOCK WITH MEDIUM AND ENZYME
211
BIOPROCESSING E.G., FERMENTATION
216
CHEMICAL PROCESSING E.G., ISOLATION/ ESTERIFICATION AND/ OR HYDROGENATION
224

FIG. 2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SET OR ADJUST PROCESS PARAMETERS
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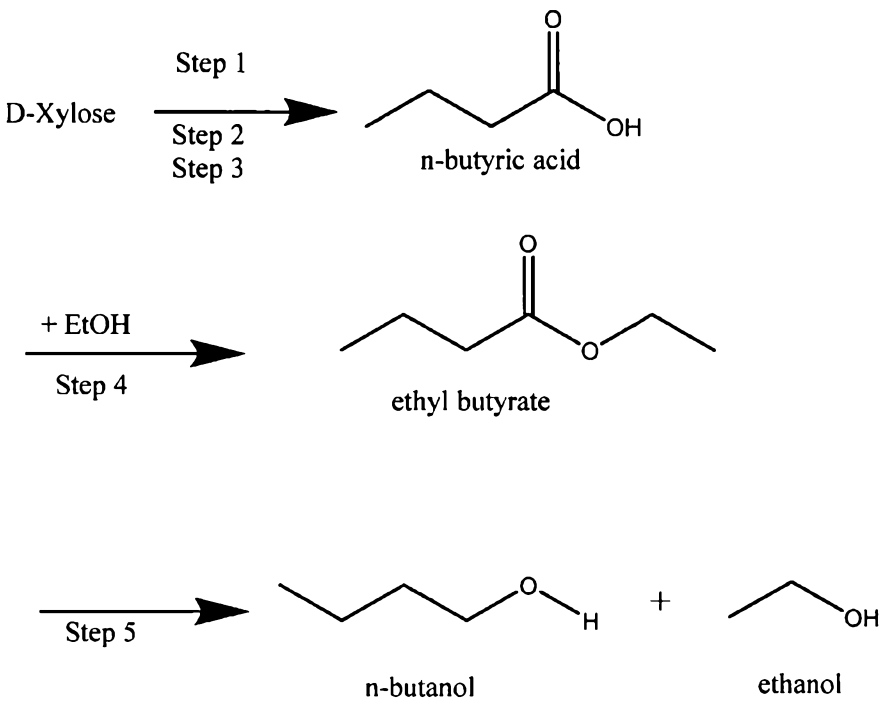
MEASURE LIGNIN CONTENT
PHYSICALLY PRE-TREATING THE FEEDSTOCK, E.G., TO REDUCE ITS SIZE
210
TREATING THE FEEDSTOCK E.G., TO REDUCE ITS RECALCITRANCE
212
SET OR ADJUST PROCESS PARAMETERS
MIXING THE FEEDSTOCK WITH MEDIUM AND ENZYME
211
SACCHARIFYING THE FEEDSTOCK TO FORM A MIXED SUGAR SOLUTION.
214
FERMENTING A FIRST SUGAR TO PRODUCE A FIRST PRODUCT AND AN FIRST UNFERMENTED SUGAR SOLUTION
217
ISOLATING THE FIRST PRODUCT FROM THE UNFERMENTED SUGARS E.G., BY SEPARATION METHODS
225
ISOLATED FERMENTATION SOLIDS
232
ISOLATED FIRST PRODUCT
228
OPTIONALLY PROCESSING THE SECOND UNFERMENTED SUGARS E.G., ISOLATING AND/OR CONVERTING TO OTHER PRODUCTS
227
ISOLATED SECOND PRODUCT
230

FIG. 3

FIG. 4


Step 1
D-Xylose
Step 2
Step 3
O
OH
n-butyric acid
+ EtOH
Step 4
O
O
ethyl butyrate
Step 5
O
H
+
OH
n-butanol
ethanol

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/021796

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C12P 7/52 (2014.01)
USPC - 435/141
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)
IPC(8) - C07C 29/136, 31/08; C10J 1/00, 3/00; C10L 3/10; C12P 7/00, 7/02, 7/04, 7/06, 7/16, 7/40, 7/42, 7/46, 7/52, 7/54, 7/56, 7/62 (2014.01)
USPC - 435/135, 136, 139, 140, 141, 145, 146, 155, 157, 160

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
CPC - C10J 2300/1612, 2300/1665, 2300/1681; C13K 1/02, 1/06; C12P 7/04, 7/065, 7/54, 7/56; Y02E 50/17 (2014.02)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X – Y	US 2011/0287498 A1 (MEDOFF et al) 24 November 2011 (24.11.2011) entire document	1-10, 24 – 21, 23
X – Y	WO 2012/006438 A2 (WARNER et al) 12 January 2012 (12.01.2012) entire document	11-20, 22 – 21, 23
A	US 2008/0248540 A1 (YANG) 09 October 2008 (09.10.2008) entire document	1-24
A	US 2012/0322117 A1 (ANTON et al) 20 December 2012 (20.12.2012) entire document	1-24
P, X	US 2013/0158302 A1 (DUFF et al) 20 June 2013 (20.06.2013) entire documen	1-24

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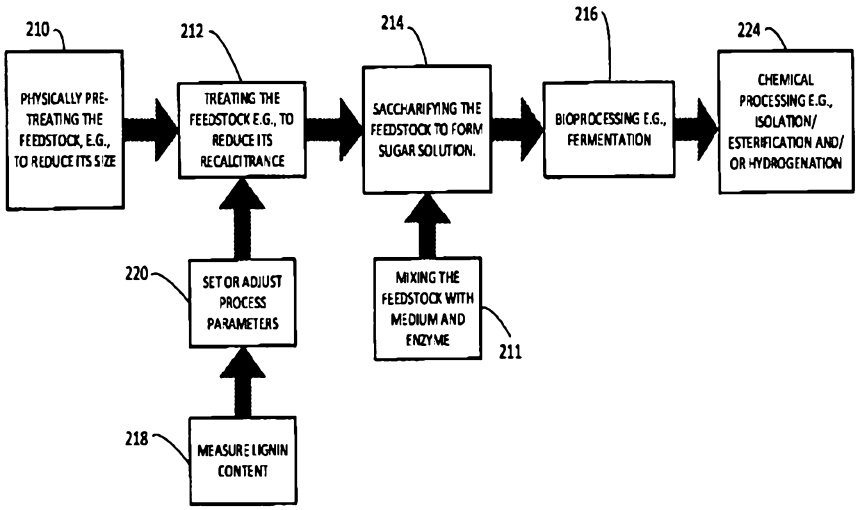
Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2014	21 MAY 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

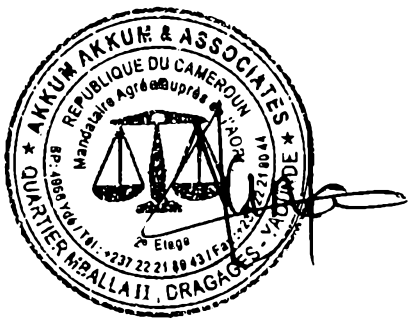
Form PCT/ISA/210 (second sheet) (July 2009)

Abstract

Biomass (e.g., plant biomass, animal biomass, and municipal waste biomass) is processed to produce useful intermediates and products, such as energy, fuels, foods or materials. The saccharified biomass is fermented in two steps to form two separate products. The second product can be a carboxylic acid which is reacted with an alcohol to form an ester. The alcohol used for the esterification may be obtained from the biomass. The ester is hydrogenated to alcohols with catalysts.

FIG. 2





27/08/2015