METHODS AND SYSTEMS FOR PROCESSING SUGAR MIXTURES AND RESULTANT COMPOSITIONS

Abstract: A method including: (a) selectively reacting a first sugar in a mixture which includes at least one second sugar to form a product mixture comprising a product of said first sugar; (b) separating said product of said first sugar from said product mixture; and (c) separating at least one of said at least one second sugar from said product mixture.

Published:
— with international search report (Art. 21(3))
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
METHODS AND SYSTEMS FOR PROCESSING SUGAR MIXTURES AND RESULTANT COMPOSITIONS

RELATED APPLICATIONS

In accord with the provisions of 35 U.S.C. §119(a) and/or §365(b), this application claims priority from:

prior Israeli application IL207945 filed on 2 September 2010 by Robert JANSEN et al. and entitled "Method for the Production of Carbohydrates"; and

prior PCT Application IL1 1/000424 filed on 1 June 2011 by Robert JANSEN et al. and entitled "Lignin Compositions, Systems and Methods for Producing Lignin and/or HCL"; and

prior PCT application IL1 1/000509 filed on June 26, 2011 by Aharon EYAL et al. and entitled "Sugar Mixtures and Methods for Production and Use thereof; and

prior PCT application IL1 1/000517 filed on June 28, 2011 by Aharon EYAL et al. and entitled "Methods and Systems for Processing a Sucrose Crop and Sugar Mixtures"

prior PCT application US11/46153 filed on 1 August 2011 by Robert JANSEN et al. and entitled "Methods and Systems for Solvent Purification";

the contents of each of which is fully incorporated herein by reference.

In accord with the provisions of 35 U.S.C. §119(e) and §363, this application claims the benefit of:

US 61/529277 filed on 31 August, 2011 by Aharon EYAL et al. and entitled "Methods and Systems for Processing Sugar Mixtures and Resultant Compositions"

the contents of which is fully incorporated herein by reference.

In addition, this application is related to the following co-pending applications, each of which is fully incorporated herein by reference:

US 61/483,777 filed on 9 May, 2011 by Robert JANSEN et al. and entitled "Hydrolysis Systems and Methods";

US 61/487,319 filed on 18 May, 2011 by Robert JANSEN et al. and entitled "Hydrolysis Systems and Methods"; and


FIELD OF THE INVENTION

This invention relates to processing of sugars.
BACKGROUND OF THE INVENTION

Plants are composed in large part of lignocellulosic material and smaller amounts of lipophilic materials (often referred to as "extractives") and minerals (i.e. ash).

The lignocellulosic material includes lignin, cellulose and hemicellulose.

Cellulose and hemicellulose are each polymeric saccharides (i.e. polysaccharides) of monomeric saccharides (i.e. monosaccharides). Although cellulose and hemicellulose are carbohydrates in a strict chemical sense, the bond types used to connect the monomeric saccharides, and/or the specific monosaccharides in the polymer, make them less physiologically available than other polymeric carbohydrates such as amylase (starch).

Cellulose is rich in six-carbon sugars (hexoses), such as glucose, mannose and galactose. Hemicellulose includes a significant amount of five-carbon sugars (pentoses), such as xylose and arabinose.

Some of these monosaccharides form a large fraction of the total saccharides (e.g. glucose) in the lignocellulosic material, while others are present in relatively low amounts.

Lignocellulosic material is available in a wide variety of forms. In many cases lignocellulosic material is a by-product or waste product. For example, corn stover is a by-product of the corn industry. Alternatively or additionally, the bagasse remaining after initial extraction of sucrose from sugar cane is primarily lignocellulosic. When lignocellulosic material is the by-product, it is often present in a greater quantity by weight than the primary product, as in the case of corn stover and sugar cane bagasse.

In other cases, the primary product is lignocellulosic (e.g. wood produced from timber).

SUMMARY OF THE INVENTION

A broad aspect of the invention relates to sugar processing. More specifically the various exemplary embodiments of the invention described in this application relate to methods of processing a mixture containing more than one sugar.

As used in this specification and the accompanying claims the term "sugar" indicates a monosaccharide or an oligosaccharide containing at least two monosaccharide sub-units and having a solubility greater than 5% in water at 25 degrees centigrade.

In some exemplary embodiments of the invention, one or more of the sugars in the mixture is provided as a "precursor".

As used in this specification and the accompanying claims a "precursor" of a sugar indicates any molecule that can be transformed to the corresponding sugar in one or two chemical reactions. For example, a monosaccharide or an oligosaccharide can be a precursor of another monosaccharide, of a disaccharide or of a longer polysaccharide. For example, glucose
can be a precursor of fructose. Alternatively or additionally, an oligosaccharide (e.g. disaccharide) can be a precursor of a different disaccharide or a longer polysaccharide. Alternatively or additionally, esters or ethers of sugars can be precursors of the corresponding sugars.

One aspect of some embodiments of the invention relates to selectively reacting a first sugar in the presence of a second (different) sugar (or a precursor of the second sugar) to form a product mixture including a product produced from the first sugar followed by separating that product from the mixture. In some exemplary embodiments of the invention, the first sugar is glucose and the product produced from the first sugar is ethanol. Optionally, removal of the product produced from the first sugar can be via distillation.

Alternatively or additionally, according to various exemplary embodiments of the invention the selective reaction includes fermentation via a suitable micro-organism for the first sugar in question. In some exemplary embodiments of the invention, selection of a micro-organism with a specific ability to ferment a desired first sugar contributes to selectivity of the reaction.

In some exemplary embodiments of the invention, the second sugar is present as a sugar \textit{per se}. The second sugar is optionally removed from the reaction mixture as a sugar. Alternatively or additionally, the second sugar is processed to a product produced from the second sugar. According to various exemplary embodiments of the invention, this processing occurs in the mixture or after removal of the second sugar from the mixture.

In some exemplary embodiments of the invention, the product produced from the second sugar is removed from the mixture. Removal techniques for the product include, but are not limited to crystallization, microfiltration and chromatographic separation. Optionally, the product produced from the second sugar is modified to produce a modified product.

In some exemplary embodiments of the invention, the second sugar is present as a sugar precursor. In some exemplary embodiments of the invention, the second sugar precursor is removed from the reaction mixture as a sugar precursor.

In those exemplary embodiments of the invention in which the second sugar is processed to a product produced from the second sugar, this processing can occur in the mixture or after removal of the second sugar from the mixture.

In some exemplary embodiments of the invention, the product produced from the second sugar is removed from the mixture. Removal techniques for the product include, but are not limited to crystallization, microfiltration and chromatographic separation. Optionally, the product produced from the second sugar is modified to produce a modified product.
Another aspect of some exemplary embodiments of the invention relates to increasing a relative concentration of a second sugar in a mixture by removing a first sugar. In some exemplary embodiments of the invention, removal of the first sugar includes conversion of the first sugar to a first sugar product.

Some exemplary embodiments of the invention, relate to preparation of the mixture. Optionally, this preparation includes hydrolysis of a lignocellulosic substrate. In some exemplary embodiments of the invention, this hydrolysis employs a strong acid, for example HCl or H₂SO₄. According to various exemplary embodiments of the invention the acid is applied to the substrate at a concentration of 30, 32, 34, 36, 38, 40, 42, 44 or 46 %, or intermediate or greater percentages, as calculated by wt of acid/ [wt of acid + water].

Some exemplary embodiments of the invention relate to further processing of a product of the first sugar and/or a second sugar to a conversion product.

One aspect of some embodiments of the invention relates to selectively removing at least two monomeric sugars from a sugar mixture containing oligomeric sugars and processing at least a portion of the oligomeric sugars to produce additional monomeric sugars. In some exemplary embodiments of the invention, at least one of the two monomeric sugars is converted to a product and the product is removed from the mixture. Alternatively or additionally, at least one of the two monomeric sugars is crystallized and the crystals are removed from the mixture. In some exemplary embodiments of the invention, processing of the oligomeric sugars includes hydrolysis. Optionally, this hydrolysis is in a dilute acid solution. Optionally, the dilute acid solution includes at least 4, optionally at least 6, optionally at least 9%, or intermediate or greater percentages of acid. Optionally, the dilute acid solution includes less than 15, optionally less than 12, optionally less than 11%, or intermediate or lower percentages of acid. In some exemplary embodiments of the invention, the dilute acid solution includes 4 to 15%, optionally 6 to 12%, optionally 9 to 11% acid. In some exemplary embodiments of the invention, HCl is employed for this hydrolysis.

One aspect of some embodiments of the invention relates to fermentation of glucose in a sugar mixture to produce ethanol and use of at least a portion of the produced ethanol in crystallization of a non-glucose sugar from the mixture. According to various exemplary embodiments of the invention the non-glucose sugar can be monomeric or oligomeric (disaccharide; trisacchararide or longer oligomer). In some exemplary embodiments of the invention, two or more rounds of crystallization are conducted to separate a series of different sugars from the mixture.
Another aspect of some embodiments of the invention relates to a system designed and configured to separate sugars from a mixture using a combination of fermentation to produce an alcohol from one sugar followed by crystallization of at least one additional sugar using the alcohol.

It will be appreciated that the various aspects described above relate to the solution of technical problems associated with harvest of minor components of a mixture in an industrial context.

Alternatively or additionally, it will be appreciated that the various aspects described above relate to the solution of technical problems related to re-arrangement of a sequence of monosaccharide units within an oligosaccharide.

Alternatively or additionally, it will be appreciated that the various aspects described above relate to solution of technical problems related to exploitation of multiple components in a sugar mixture.

In some exemplary embodiments of the invention, there is provided a method including:

- (a) selectively reacting a first sugar in a mixture which includes at least one second sugar to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) separating at least one of the at least one second sugar from the product mixture.

In some exemplary embodiments of the invention, there is provided a method including:

- (a) selectively reacting a first sugar in a mixture which includes at least one second sugar, to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) reacting at least one of the at least one second sugar to form a second sugar product.

In some exemplary embodiments of the invention, there is provided a method including:

- (a) selectively reacting a first sugar in a mixture which includes at least one second sugar precursor, to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) reacting at least one of the at least one second sugar precursor to form a second sugar product.

- Optionally, the method includes separating at least one of the at least one second sugar from the product mixture.

- Optionally, the method includes separating at least one second sugar product from the product mixture.

- Optionally, the first sugar includes glucose and wherein the selectively reacting includes fermenting.
Optionally, the at least one second sugar precursor includes a pentose.

Optionally, the at least one second sugar includes a pentose.

Optionally, the pentose is selected from the group consisting of xylose, xylulose, lyxose, ribulose and arabinose.

Optionally, the at least one second sugar includes a disaccharide.

Optionally, the at least one second sugar precursor includes a disaccharide.

Optionally, the disaccharide is selected from the group consisting of trehalose, gentiobiose, kojibiose, nigerose, sophorose and laminarobiose.

Optionally, the second sugar is xylose.

Optionally, the method includes reacting the second sugar to form a second sugar product.

Optionally, the method includes reacting the second sugar precursor to form a second sugar product.

Optionally, the second sugar is xylose and the second sugar product is selected from xylitol and a rumen bypass protein.

Optionally, the weight ratio between the second sugar to the first sugar prior to the selectively reacting is R1;

the weight ratio between the second sugar to the first sugar in the product mixture is R2; and

the ratio of R2 to R1 is greater than 5.

Optionally, the weight ratio between the second sugar precursor to the first sugar prior to the selectively reacting is R1;

the weight ratio between the second sugar precursor to the first sugar in the product mixture is R2; and

the ratio of R2 to R1 is greater than 5.

Optionally, the total weight of the second sugar includes at least 50% of the total sugars in the product mixture.

Optionally, the total weight of the second sugar precursor is equal to at least 50% of the total sugars in the product mixture.

Optionally, the product of the first sugar is selected from the group consisting of ethanol, higher alcohols, organic acids and organic acid ester of 3 to 22 carbon atoms, amino acids, yeast and proteins.

Optionally, the separating includes at least one of distillation, membrane filtration, solvent extraction and chromatographic separation.
Optionally, the product of the first sugar has an atmospheric-pressure boiling point of less than 100°C.

Optionally, the product of the first sugar forms an azeotrope with water.

In some exemplary embodiments of the invention, there is provided a method including:

(a) providing a mixture including a first sugar and at least one second sugar precursor; (b) selectively reacting the first sugar to form a product mixture including a product of the first sugar; (c) selectively reacting the precursor to form the second sugar; and (d) separating the product of the first sugar.

Optionally, the method includes separating at least one of the at least one second sugar precursor from the product mixture.

Optionally, selectively reacting the precursor to form the second sugar occurs after separating the product of the first sugar.

Optionally, separating the product of the first sugar from the second sugar includes separating each of the product of the first sugar and the second sugar from the product mixture.

Optionally, separating the product of the first sugar is followed by separating the second sugar precursor.

Optionally, separating the product of the first sugar is followed by selectively reacting the precursor to form the second sugar.

Optionally, selectively reacting the precursor includes acid catalysis.

Optionally, selectively reacting the precursor includes enzymatic catalysis.

Optionally, selectively reacting the first sugar includes fermentation.

Optionally, selectively reacting the precursor includes hydrolysis.

Optionally, selectively reacting the precursor includes transglucosidation.

Optionally, selectively reacting the precursor includes oligomerization.

Optionally, the method includes reacting the second sugar to form a second sugar product.

Optionally, the method includes preparing the mixture.

Optionally, the preparing includes:

- providing a lignocellulosic material feed;
- hydrolyzing the lignocellulosic material feed to form a hydrolyzate including at least one first sugar and at least one of at least one second sugar and at least one second sugar precursor.

Optionally, the method includes de-acidifying the hydrolyzate.

Optionally, the hydrolyzing is performed in a counter-current mode.
Optionally, the lignocellulosic material feed includes at least 5% hemicellulose.

Optionally, the hydrolyzing employs a hydrolysis medium with a wt/wt ratio of HCl to (HCl+water) of at least 0.35.

Optionally, the de-acidifying includes selective extraction of HCl with an alcohol.

Optionally, an amount of at least one of the at least one second sugars in the mixture, optionally present as a precursor, is at least 85% of a theoretical yield of the same second sugar in the lignocellulosic material feed.

Optionally, the combined concentration of the second sugar and the second sugar precursor in the mixture is CI;

wherein the combined concentration of the second sugar and the second sugar precursor in the product mixture after removal of the first sugar product is C2 and C2/C1 is greater than 1.5.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing a fermentor; and (b) fermenting a medium including a second sugar according as described above in the fermentor to produce a conversion product.

In some exemplary embodiments of the invention, there is provided a method including: (a) providing an input stream including at least one member of the group consisting of:

the second sugars as described above; and

the product of the first sugar as described above; and (b) converting at least a portion of the input stream to produce a conversion product.

Optionally, the conversion product includes at least one member selected from the group consisting of alcohols, carboxylic acids, amino acids, monomers for the polymer industry and proteins.

Optionally, the method includes processing the conversion product to produce a consumer product selected from the group consisting of detergent, polyethylene-based products, polypropylene-based products, polyolefin-based products, polylactic acid (polylactide)- based products, polyhydroxyalkanoate-based products and polyacrylic-based products.

Optionally, the detergent includes a sugar-based surfactant, a fatty acid-based surfactant, a fatty alcohol-based surfactant, or a cell-culture derived enzyme.

Optionally, the polyacrylic-based product is selected from plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.
Optionally, the polyolefin-based products are selected from milk jugs, detergent bottles, margarine tubs, garbage containers, water pipes, absorbent articles, diapers, non-wovens, high density polyethylene (HDPE) toys and HDPE detergent packagings.

Optionally, the polypropylene based products are selected from absorbent articles, diapers and non-wovens.

Optionally, the polylactic acid based products are selected from packaging of agriculture products and of dairy products, plastic bottles, biodegradable products and disposables.

Optionally, the polyhydroxyalkanoate based products are selected from packaging of agriculture products, plastic bottles, coated papers, molded or extruded articles, feminine hygiene products, tampon applicators, absorbent articles, disposable nonwovens and wipes, medical surgical garments, adhesives, elastomers, films, coatings, aqueous dispersants, fibers, intermediates of pharmaceuticals and binders.

Optionally, the conversion product includes at least one member of the group consisting of ethanol, butanol, isobutanol, a fatty acid, a fatty acid ester, a fatty alcohol and biodiesel.

Optionally, the method includes processing of the conversion product to produce at least one product selected from the group consisting of an isobutene condensation product, jet fuel, gasoline, gasohol, diesel fuel, drop-in fuel, a diesel fuel additive, and a precursor thereof.

Optionally, the gasohol is ethanol-enriched gasoline or butanol-enriched gasoline.

Optionally, the product is selected from the group consisting of diesel fuel, gasoline, jet fuel and drop-in fuels.

In some exemplary embodiments of the invention, there is provided a consumer product, a precursor of a consumer product, or an ingredient of a consumer product produced from a conversion product as described above.

In some exemplary embodiments of the invention, there is provided a consumer product, a precursor of a consumer product, or an ingredient of a consumer product including at least one conversion product produced by a method as described above, wherein the conversion product is selected from carboxylic and fatty acids, dicarboxylic acids, hydroxycarboxylic acids, hydroxyl di-carboxylic acids, hydroxyl-fatty acids, methylglyoxal, mono-, di-, or poly-alcohols, alkanes, alkenes, aromatics, aldehydes, ketones, esters, biopolymers, proteins, peptides, amino acids, vitamins, antibiotics, and pharmaceuticals.

Optionally, the consumer product is ethanol-enriched gasoline, jet fuel, or biodiesel.

Optionally, the consumer product, a precursor of a consumer product, or an ingredient of a consumer product as described above, wherein the consumer product has a ratio of carbon-14 to carbon-12 of at least about $2.0 \times 10^{-13}$.
In some exemplary embodiments of the invention, relate to a consumer product including an ingredient as described above, and an additional ingredient produced from a raw material other than a lignocellulosic material.

Optionally, the conversion product includes xylitol.

Optionally, the method includes incorporating the xylitol into an edible product.

Optionally, the conversion product includes rumen bypass protein.

Optionally, the method includes incorporating the rumen bypass protein into a livestock feed.

Optionally, the ingredient and the additional ingredient produced from a raw material other than a lignocellulosic material are essentially of the same chemical composition.

Optionally, the consumer product as described above includes a marker molecule at a concentration of at least 100ppb.

According to various exemplary embodiments of the invention the the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy- methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms betaine, amino acids, proteins phosphate and glycerol.

In some exemplary embodiments of the invention, there is provided a method including:

(a) selectively reacting a first sugar in an initial mixture which includes at least one oligosaccharide to form a product mixture including a product of the first sugar; (b) producing an oligosaccharide rich sugar fraction with a ratio of at least one of the at least one oligosaccharide to a total sugar concentration greater than a same ratio in the product mixture; and (c) hydrolyzing the oligosaccharide rich sugar fraction to produce monomeric sugars.

Optionally, the first sugar is a monomeric sugar.

Optionally, the initial mixture includes at least one additional monomeric sugar.

In some exemplary embodiments of the invention, there is provided a method including:

(a) selectively reacting a first sugar in an initial mixture which includes a first sugar and at least one oligosaccharide to form a product mixture including a product of the first sugar; (b) separating the product of the first sugar from the product mixture; and (c) hydrolyzing the oligosaccharide to produce additional first sugar.

Optionally, the initial mixture includes a second sugar.

Optionally, the method includes separating the second sugar.

Optionally, the method includes separating the product of the first sugar from the product mixture.
Optionally, the method includes separating at least one monomeric sugar from the product mixture.

Optionally, the selectively reacting produces an alcohol.

Optionally, the initial mixture includes a second sugar, and includes use of the alcohol to aid in crystallization of the second sugar.

Optionally, the method includes: distilling the alcohol from the product mixture; and re-introducing the alcohol during the crystallization.

Optionally, the method includes crystallizing the second sugar; and distilling the alcohol from the product mixture.

Optionally, the producing an oligomer rich sugar fraction includes crystallization of at least one of the at least one oligosaccharide from the product mixture.

Optionally, the selectively reacting the first sugar produces an alcohol.

Optionally, the method includes use of the alcohol to aid in the crystallization.

In some exemplary embodiments of the invention, there is provided a method including:

(a) fermenting glucose in a portion of an initial mixture which includes at least one additional monomeric sugar and at least one oligosaccharide to form a product mixture including ethanol; and (b) using the ethanol to aid in crystallization of at least one non-glucose sugar in the product mixture.

Optionally, crystallization of at least one non-glucose sugar produces crystals including primarily at least one of the at least one additional monomeric sugar and an oligosaccharide enriched mother liquor.

Optionally, the method includes hydrolyzing the oligosaccharide enriched mother liquor to produce additional monomeric sugars.

Optionally, crystallization of at least one non-glucose sugar produces crystals including primarily at least one of the at least one oligosaccharide and a monomeric sugar enriched mother liquor.

Optionally, the method includes crystallizing at least one monomeric sugar from the monomeric sugar enriched mother liquor.

Optionally, the method includes using ethanol to aid in crystallization of the at least one monomeric sugar.

In some exemplary embodiments of the invention, there is provided a system including:

(a) a fermentor adapted to deliver a stream of spent media to a separation unit; (b) the separation unit adapted to separate solids from the spent media and deliver a supernatant stream; (c) a still adapted to distill an alcohol from the supernatant stream to produce a modified
supernatant; (d) a primary crystallization module adapted to receive at least a portion of the alcohol from the distillation unit and crystallize at least one sugar from the modified supernatant to produce a mother liquor.

Optionally, the system includes a secondary crystallization module adapted to receive at least a portion of the alcohol from the distillation unit and crystallize at least one additional sugar from the mother liquor to produce a spent mother liquor.

Optionally, the system includes an alcohol recovery module adapted to distill the alcohol from at least one of the mother liquor and the spent mother liquor.

Optionally, the system includes a hydrolysis module adapted to:
receive a material selected from the group consisting of: crystals produced by the primary crystallization module; the mother liquor; crystals produced by the secondary crystallization module and the spent mother liquor; and
hydrolyze the received material to produce additional monomeric sugars.

Optionally, the system includes: a recycling module adapted to deliver the additional monomeric sugars to the fermentor.

Optionally, the system includes at least one pump to control flows among and between components of the system.

Optionally, the system includes a controller adapted to control at least one of the at least one pumps.

Optionally, the system includes at least one detector configured to provide data pertaining to at least one system parameter to the controller, wherein the controller is responsive to the data. In some exemplary embodiments of the invention, there is provided a sugar composition including:

(a) at least 25% xylose by weight relative to total sugar concentration;
(b) at least one alpha-bonded di-glucose; and
(c) at least one beta-bonded di-glucose.

Optionally, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 40% total sugars.

Optionally, the composition is provided as a solution.

Optionally, the composition includes less than 90% xylose of total sugars on a weight basis.
Optionally, the composition includes glucose between 0.001% and 5% of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% arabinose of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, there is provided a sugar composition including (by weight relative to total sugar concentration):

(a) at least 60% xylose;
(b) at least 100 PPB of a marker molecule; and
(c) 0.001% to 10% oligosaccharides.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy- methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Optionally, the composition includes at least two marker molecules.

Optionally, the composition includes at least three marker molecules.

Optionally, the composition includes at least one fermentation residue.

Optionally, the at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

Optionally, the composition includes at least two fermentation residues.

Optionally, the composition includes at least three fermentation residues.

Optionally, the composition includes glucose between 0.001% and 5% of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% arabinose of total sugars on a weight basis.

Optionally, the oligosaccharides include at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the oligosaccharides include at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

Optionally, a concentration of the marker molecule does not exceed 0.5%.
Optionally, the composition includes at least 60% total sugars.

Optionally, the composition includes at least one sugar selected from the group consisting of mannose, galactose and arabinose.

Optionally, the composition includes at least 3% mannose relative to total monosaccharides by weight.

Optionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Optionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

In some exemplary embodiments of the invention, there is provided a sugar composition including: (a) at least one of alpha-bonded di-glucose, beta-bonded di-glucose and arabinose; (b) 0.01% - 20% xylose by weight relative to total sugar concentration; and (c) at least 100 PPB of a marker molecule.

Optionally, the composition is provided as a solution.

Optionally, the composition includes glucose between 0.001%> and 5% (3, 1) of total sugars on a weight basis.

Optionally, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

Optionally, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

Optionally, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

Optionally, the composition includes at least 40%> total sugars.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy- methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Optionally, the composition includes at least two marker molecules.

Optionally, the composition includes at least three marker molecules.

Optionally, the composition includes at least one fermentation residue.

Optionally, at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

Optionally, a concentration of the marker molecule does not exceed 0.5%.
Optionally, the composition includes a sugar selected from the group consisting of mannose and galactose.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although suitable methods and materials are described below, methods and materials similar or equivalent to those described herein can be used in the practice of the various embodiments of the invention. In case of conflict, the patent specification, including definitions, will control. All materials, methods, and examples are illustrative only and are not intended to be limiting.

As used herein, the terms "comprising" and "including" or grammatical variants thereof are to be taken as specifying inclusion of the stated features, integers, actions or components without precluding the addition of one or more additional features, integers, actions, components or groups thereof. This term is broader than, and includes the terms "consisting of" and "consisting essentially of" as defined by the Manual of Patent Examination Procedure of the United States Patent and Trademark Office.

The term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from, known manners, means, techniques and procedures by practitioners of chemistry and/or engineering.

Percentages (%) of chemicals typically supplied as powders or crystals (e.g. sugars) are W/W (weight per weight) unless otherwise indicated. Percentages (%) of chemicals typically supplied as liquids (e.g. alcohols) are W/W (weight per weight) unless otherwise indicated.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In order to understand the invention and to see how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying figures. In the figures, identical and similar structures, elements or parts thereof that appear in more than one figure are generally labeled with the same or similar references in the figures in which they appear. Dimensions of components and features shown in the figures are chosen primarily for convenience and clarity of presentation and are not necessarily to scale.

In the attached figures:

**Fig. 1** is a schematic representation of a hydrolysis system which can be used to produce a sugar mixture according to some exemplary embodiments of the invention;

**Fig. 2a** is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;
**Fig. 2b** is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;

**Fig. 2c** is a simplified flow scheme depicting events associated with practice of exemplary methods according to some embodiments of the invention;

**Fig. 3** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 4** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 5** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 6a** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 6b** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 7a** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 7b** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 8a** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 8b** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 8c** is a simplified flow diagram of exemplary methods according to some embodiments of the invention;

**Fig. 9** is a schematic representation of an exemplary system according to some embodiments of the invention;

**Fig. 10** is a simplified flow diagram of exemplary methods according to some embodiments of the invention; and

**Fig. 11** is a logic hierarchy illustrating approaches to separating products of value from lignocelluloses.

**DETAILED DESCRIPTION OF EMBODIMENTS**

Embodiments of the invention relate to systems and methods for processing mixtures of sugars as well as to modified sugar mixtures found at various stages during this processing. In
many exemplary embodiments of the invention, the mixture contains two or more monomeric sugars (e.g. glucose and xylose) and one or more disaccharides or longer oligosaccharide sugars.

Specifically, some embodiments of the invention can be used to process hydrolyzates of lignocellulosic substrates. Optionally, these hydrolyzates result from acid hydrolysis (e.g. with concentrated HCl).

The principles and operation of a system and/or method according to exemplary embodiments of the invention may be better understood with reference to the drawings and accompanying descriptions.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

**Exemplary source of sugar mixtures**

Fig. 1 is a simplified schematic diagram of a system for acid hydrolysis of a lignocellulosic substrate indicated generally as 100. Depicted system 100 includes a main hydrolysis reactor 110 adapted to receive a lignocellulosic substrate input 112. Optionally, substrate 112 is provided as wood chips, although any "woody material" can be used instead of wood. Additional exemplary woody materials include, but are not limited to, sugar cane bagasse, sugar beets and/or their cossettes, corn stover, post harvest plants (e.g. cotton, soybean or rapeseed), switchgrass and broomgrass.

In the depicted exemplary system, substrate 112 is brought into contact with a concentrated HCl solution in reactor 110 and hemicellulose and/or cellulose in the substrate are hydrolyzed to produce a mixture of soluble sugars and residual lignin. These materials are collected separately as lignin stream 120 and sugar mixture 130, each of which contains a large amount of HCl.

Since the acid acts as a catalyst, it is not consumed in the process. In addition, residual acid content of the product and the co-products should be low in order to enable their use. Acid recovery from the hydrolyzate should be conducted under conditions minimizing thermal degradation. Alternatively or additionally, the high concentration of monomeric sugars in the presence of the HCl catalyst can cause re-oligomerization. Cellulose in substrate 112 typically contains primarily beta bonds between the saccharide sub-units of the polymer chain. Dimers and longer oligosaccharides resulting from re-oligomerization can contain alpha bonds.
Details of exemplary hydrolysis methods and systems are described in detail in co-pending US provisional applications 61/483,777 and 61/487,319; each of which is fully incorporated herein by reference. According to various exemplary embodiments of the invention the way in which hydrolysis is conducted in reactor 110 contributes to the composition of sugar mixture 130 and/or lignin stream 120. Contribution to the composition of sugar mixture 130 and/or lignin stream 120 may be, for example, a reduction in the amount of sugar degradation products in the mixture and/or an increase in yield of intact pentoses such as xylose.

Sugar mixture 130 is processed to remove HC1 and/or adjust the mixture to achieve one or more desired ratios of mixture components (e.g. disaccharides and/or monosaccharides). This processing is conducted in a sugar refining module, designated here generically as 201.

Optionally, additional sugar mixture is recovered from lignin stream 120 as described in co-pending PCT application IL11/000424 which is fully incorporated herein by reference. In some exemplary embodiments of the invention, this additional sugar mixture is routed to refining module 201. According to various exemplary embodiments of the invention this additional sugar mixture increases a total sugar yield and/or changes a composition of the mixture.

In depicted system 100, refining module 201 employs a flow of organic solvent 155 (solid arrows) to extract HC1 140 (dashed arrows) from sugar mixture 130.

De-acidified sugars 230 are the primary product of refining module 201. Module 201 also produces a stream of HC1 140 mixed with solvent 155 (depicted as parallel dashed and solid arrows respectively for clarity) which is routed to a solvent/HC1 recovery module 150. Recovery module 150 separates HC1 140 from solvent 155. In some exemplary embodiments of the invention, separation is by distillation. HC1 140 is recycled to hydrolysis reactor 110 and solvent 155 is recycled to refining module 201.

De-acidified sugars 230 are present as a mixture. Various components of the mixture can be harvested and/or converted as described hereinbelow. Each strategy for harvest and/or conversion of specific sugars and/or sugar products represents an exemplary embodiment of the invention. In some cases, implementation of specific embodiments will be influenced by an initial composition of sugar mixture 230. In many cases, sugar mixture 230 will contain glucose as a primary component since glucose is a primary component of lignocellulosic substrate 112. Alternatively or additionally, in many cases, sugar mixture 230 will contain a significant amount of xylose since xylose is typically the most prevalent saccharide component of hemicellulose in lignocellulosic substrate 112.

Although HC1 hydrolysis of substrate 112 is described by way of example, sugar mixtures resulting from other processes are also amenable to use in various exemplary embodiments of the
invention. These other processes include any procedure which converts a large portion of the biomass in substrate 112 to soluble sugars. Such procedures include, but are not limited to, enzymatic hydrolysis, hydrolysis with other acids (e.g. H\textsubscript{2}SO\textsubscript{4}) and hydrolysis with "reactive fluids" (e.g. super critical or near critical water) as described in WO 2010/009343; which is fully incorporated herein by reference.

**Process overview**

Figs. 2a, 2b and 2c are simplified flow schemes depicting events associated with practice of exemplary methods according to various embodiments of the invention.

Fig. 2a is a flow scheme indicated generally as scheme 200 depicting an exemplary sugar mixture 230 (Fig. 1). For simplicity, mixture 230 is depicted as containing a first sugar 231 and a second sugar 232 which is optionally present (at least in part) as a precursor 233. In actuality, mixture 230 typically contains a large number of different sugars, which are not depicted. Each of these different sugars could potentially be treated as a first sugar or a second sugar.

According to scheme 200, mixture 230 is subjected to a selective reaction 240 to produce a product mixture 250. As a result of reaction 240, product mixture 250 includes a product 251 of the first sugar. By way of example, if the first sugar is glucose reaction 240 can be a fermentation reaction (e.g. with yeast or another microorganism capable of using glucose as a substrate) and product 251 can be ethanol and/or yeast. In some exemplary embodiments of the invention, first sugar 231 is substantially completely converted to product 251.

According to depicted flow scheme 200, product 251 is separated 260 from 2\textsuperscript{nd} sugar 232 at this stage. Continuing with the example begun above, if product 251 includes ethanol, separation 260 can be by distillation. Alternatively or additionally, if product 251 includes yeast, separation can be via filtration and/or centrifugation. Second sugar 232, optionally as precursor 233 is depicted here alone for clarity but will often be present as part of a mixture similar to mixture 250 except that it has no first sugar product 251.

Fig. 2b is a flow scheme indicated generally as scheme 202 depicting an additional processing of first sugar product 251. According to flow scheme 202, product 251 is subjected to an additional reaction 272. Reaction 272 can be biological or chemical. Since product 251 is provided in isolation, the specificity of reaction 272 is assured. The result of reaction 272 is a modified product 282 of first sugar product 251. Continuing the example begun above, if product 251 is ethanol, modified product 282 may be, for example, ethylene.

According to flow scheme 202, modified product 282 is next subjected to a manufacturing process 292 to produce a manufactured product 293. For example, process 293 could include polymerization of ethylene to polyethylene and formation of a film as...
manufactured product 293. Optionally, manufactured product 293 could be converted to one or more consumer products 295. In the case of polyethylene, consumer products 295 might include one or more of packaging materials, carrier bags and trash-bags.

It is stressed that the flow scheme of Figs. 2a and 2b is very versatile, even if only one first sugar is considered. For example, if first sugar 231 is glucose it can be subject to selective reaction 240 in the form of homolactic acid fermentation to produce lactic acid as product 251. In this case, reaction 272 might include polymerization as part of manufacturing process 292 to produce a manufactured product 293 in the form of polylactide (PLA). PLA can be used in a wide variety of consumer products 295 including, but not limited to, woven fabrics with improved ironability, microwavable trays, sutures, stents, dialysis media, drug delivery devices, bioplastics, compost bags, food packaging, disposable tableware, non woven textiles, upholstery, disposable garments, awnings, feminine hygiene products, and diapers.

Fig. 2c is a flow scheme indicated generally as scheme 204 depicting additional processing of second sugar 232 and/or second sugar precursor 233. According to various exemplary embodiments of the invention, portions, optionally all of, scheme 204 can be conducted before or after separation 260.

In those exemplary embodiments of the invention, in which second sugar 232 is initially provided as precursor 233, there are two possibilities for scheme 204.

According to the first depicted possibility, 2nd sugar 232 is realized 234 from precursor 233.

According to the second possibility, precursor 233 is converted 275 directly to product 284 of second sugar 232.

As used in this specification and the accompanying claims the term "realization" indicates a reaction which has a desired sugar as a product.

Realization 234 can include, for example, a chemical reaction (e.g. hydrolysis, oligomerization) and/or an enzymatic reaction (e.g. transglucosidation, oligomerization). When realization 234 is conducted, 2nd sugar 232 is then reacted 274 to produce product 284 of second sugar 232.

Various ways to accomplish realization 234 and/or reaction 274 and/or conversion 275 are described below.

According to depicted exemplary scheme 204, product 284 is subjected to a manufacturing process 294 to produce a manufactured product 296 which can optionally be incorporated into one or more consumer products 298.
For example, if second sugar 232 is xylose, realization 232 can optionally include release of xylose from an oligomeric precursor 233 containing xylose. Optionally, reaction 274 could include hydrogenation to produce xylitol as product 284. According to this exemplary embodiment, manufacturing process 294 might include concentration to produce a product that is 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of total sugars by weight. Optionally, these sugars could be 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of xylose. Optionally, manufacturing process 294 includes crystallization to produce crystals that are 65, optionally 70, optionally 75, optionally 80, optionally 85% or intermediate or greater percentages of xylose as manufactured product 296. In some exemplary embodiments of the invention, these crystals are incorporated into edible products (e.g. chewing gum and/or candy) which serve as consumer products 298.

Exemplary realization and/or reaction and/or direct conversion

In some exemplary embodiments of the invention, precursor 233 can be an oligosaccharide comprising second sugar 232 (e.g. if second sugar 232 is xylose, precursor 233 can be a xylose-comprising disaccharide or gentiobiose-comprising trisaccharide). In other exemplary embodiments of the invention, second sugar 232 is a disaccharide and/or precursor 233 includes at least two sugars, each of which includes a component of second sugar 232, e.g. as in the case where second sugar 232 is gentiobiose and the precursor includes maltose and/or isomaltose.

According to various exemplary embodiments of the invention realization 234 and/or reaction 274 and/or conversion 275 can each independently include hydrolysis and/or oligomerization, and/or transglucosidation. As used in this specification and the accompanying claims the term "oligomerization" means combining monosaccharides and/or oligosaccharides to form an oligosaccharide of a higher degree of polymerization (e.g. combining two glucose molecules to form sophorose).

As used in this specification and the accompanying claims the term "transglucosidation" means transfer of at least one carbohydrate between oligosaccharide s, e.g. as in

\[ A-A + B-B \rightarrow 2A-B; \text{ or} \]

\[ A-A + B-B \rightarrow A-A-B + B \]

Such reacting of the precursor may comprise a combination, e.g. of hydrolysis followed by oligomerization, as in

A-x-A \[ \rightarrow 2A \]
2A \[ \rightarrow A-y-A \]
where A-x-A and A-y-A are disaccharides composed of the same monosaccharides, but bound by a different bond, e.g. cellobiose and gentiobiose.

Alternatively or additionally, realization 234 and/or reaction 274 and/or conversion 275 can each independently include acid catalysis and/or enzymatic catalysis. Optionally, precursor 233 is catalyzed by HC1. Optionally, temperature influences kinetics of such catalysis. Optionally, the catalysis is enzymatically catalyzed. According to various exemplary embodiments of the invention enzymes such as alpha-glucosidase and/or beta-glucosidase and/or transglucosidases can be employed for this purpose. Optionally, enzymatic catalysis includes fermentation.

According to various exemplary embodiments of the invention realization 234 and/or reaction 274 and/or conversion 275 can each independently include simulated moving bed hydrolysis, sequential simulated moving bed hydrolysis, and ion exchange ISEP® and/or CSEP® (Calgon Carbon Corporation; Pittsburgh, PA; USA).

**First Exemplary method**

Fig. 3 is a simplified flow diagram of an exemplary method for producing value from at least two sugars from within a complex mixture of sugars, indicated generally as 300. Depicted exemplary method 300, includes selectively reacting 310 a first sugar in an initial mixture which includes at least one second sugar and/or at least one second sugar precursor, to form a product mixture 320 including a product of the first sugar and separating 330 the product of the first sugar from product mixture 320.

Optionally, the first sugar can be glucose; selective reaction 310 can be fermentation with a micro-organism with a strong preference for glucose, to produce ethanol as a product. In this case, separation 330 can be, for example, by distillation of ethanol from product mixture 320.

Alternatively or additionally, the second sugar can be a pentose.

In some exemplary embodiments of the invention, method 300 includes separating 340 at least one of the at least one second sugar from product mixture 320.

Optionally, at least one of said at least one second sugar is at least partly present as a second sugar precursor. In some exemplary embodiments of the invention, method 300 includes separating 342 at least one of the at least one second sugar precursor from product mixture 320.

According to these exemplary embodiments of method 300, the method includes reacting 350 the precursor to produce the second sugar.

In other exemplary embodiments of the invention, reacting of the precursor to produce the second sugar occurs in product mixture 320 or in the initial mixture prior to selectively reacting 310 (not depicted).
According to various exemplary embodiments of the invention reacting 350 the precursor includes acid catalysis and/or enzymatic catalysis.

Optionally, the second sugar is reacted to form a second sugar product (not depicted). Alternatively a second sugar precursor can be reacted to form a second sugar product directly without forming the second sugar as an intermediate (not depicted).

In those exemplary embodiments of the invention where the second sugar is xylose the second sugar product can be, for example, xylitol or a rumen bypass protein. Conversion of xylose to xylitol can be, for example, via hydrogenation.

Exemplary ratios

Method 300 can be conducted with a high degree of efficiency. This efficiency can be expressed as one or more ratios. Optionally, such ratios can be used to characterize additional exemplary embodiments of the invention.

For example, if a weight ratio between the total amount of (second sugar and second sugar precursor) to the first sugar prior to selectively reacting 310 is defined as R1 and a ratio between the total amount of (second sugar and second sugar precursor) to the first sugar in product mixture 320 is defined as R2: in some exemplary embodiments of the invention the ratio of R2 to R1 is optionally greater than 4, optionally greater than 5, optionally greater than 6, optionally greater than 7, optionally greater than 10 or intermediate or larger numbers.

Alternatively or additionally, in some exemplary embodiments of the invention, a total weight of (the second sugar and the second sugar precursor) is at least 40; optionally 50; optionally 60; optionally 70% or intermediate or greater percentages of the total sugars in product mixture 320 by weight.

Exemplary second sugars

In some exemplary embodiments of the invention, the second sugar includes a pentose.

Exemplary pentoses include, but are not limited to xylose and/or xylulose and/or lyxose and/or ribulose and/or arabinose. Optionally the second sugar is xylose.

In some exemplary embodiments of the invention, the at least one second sugar includes a disaccharide. Optionally, the disaccharide includes trehalose and/or gentiobiose and/or kojibiose and/or nigerose and/or sophorose and laminaribiose.

Exemplary first sugar products

In some exemplary embodiments of the invention, the first sugar product has an atmospheric-pressure boiling point of less than 100°C. Alternatively or additionally, in some exemplary embodiments of the invention, the first sugar product forms an azeotrope with water.
According to various exemplary embodiments of the invention the first sugar product includes an alcohol (e.g. ethanol or a higher alcohol) and/or an organic acid and/or an organic acid ester of 3 to 22 carbon atoms and/or an amino acid and/or yeast and/or a protein. Optionally, a single first sugar (e.g. glucose) can yield more than one first sugar product. For example, yeast and ethanol are two separate products produced when glucose serves as the first sugar and selective reaction 310 includes fermentation with yeast. According to various exemplary embodiments of the invention yeast and ethanol can be removed by different methods (e.g. centrifugation and distillation respectively) and/or at different points in the process (e.g. yeast may be removed prior to separation 340 and/or 342 and ethanol may be removed after separation 340 and/or 342).

**Exemplary separation methods**

According to various exemplary embodiments of the invention each of separation 330, separation 340 and separation 342 can include one or more of distillation, membrane filtration (optionally ultrafiltration), chromatographic separation, crystallization, selective precipitation, centrifugation and solvent extraction. These separation techniques can also be applied to additional separations indicated in other methods hereinbelow.

**Second exemplary method**

Fig. 4 is a simplified flow diagram of an exemplary method for realization of value from a first sugar and a second sugar precursor from within a complex mixture of sugars, indicated generally as 400. Depicted exemplary method 400 includes providing 410 a mixture including a first sugar and at least one second sugar precursor and selectively reacting 420 the first sugar to form a product of the first sugar in product mixture 422. Depicted exemplary method 400 also includes selectively reacting 430 the second sugar precursor 424 to form the second sugar and separating 440 the product of the first sugar. Optionally, second sugar precursor 424 is separated from product mixture 422 prior to selective reaction 430. Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting precursor 430 occurs after separating 440.

In some exemplary embodiments of the invention, separating 440 includes separating the product of the first sugar and separating the second sugar from product mixture 422.

In other exemplary embodiments of the invention, separating 440 includes separating the product of the first sugar from the reaction mixture followed by separating the second sugar precursor from the mixture prior to the selectively reacting 430 the precursor to form the second sugar.
In other exemplary embodiments of the invention, separating 440 the product of the first sugar is followed by separating second sugar precursor 424 from product mixture 422.

In still other exemplary embodiments of the invention, separating 440 includes separating the product of the first sugar from the mixture followed by selectively reacting the precursor of the second sugar to form the second sugar and separating the second sugar from the mixture.

In some exemplary embodiments of the invention, selectively reacting 420 the first sugar includes fermentation. Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting 430 the precursor includes hydrolysis, optionally acid hydrolysis and/or enzymatic hydrolysis.

Alternatively or additionally, selectively reacting 430 the precursor includes acid catalysis and/or enzymatic catalysis.

Alternatively or additionally, in some exemplary embodiments of the invention, selectively reacting 430 the precursor includes transglucosidation. Optionally, method 400 includes reacting 450 the second sugar to form a second sugar product.

Alternatively or additionally, selective reaction 430 and/or reaction 450 can include oligomerization. Optionally, combination of catalysis with oligomerization produces a similar oligomer chain but with different bonds between the saccharide links. In some exemplary embodiments of the invention, enzymatic catalysis is via fermentation.

Exemplary mixture preparation

Fig. 5 is a simplified flow diagram of an exemplary method for preparing a mixture of sugars as described above, indicated generally as 500. Depicted exemplary method 500 includes providing 510 a lignocellulosic material feed, hydrolyzing 520 the lignocellulosic material feed to form a hydrolyzate 540. If the hydrolysis is conducted in an acid, method 500 can include deacidifying 530 the hydrolyzate. Hydrolyzate 540 includes at least one first sugar and at least one second sugar. Optionally, the second sugar is at least partially present as a precursor and hydrolyzing 520 is performed in a counter-current mode. Optionally, at least 5%, optionally at least 10%, optionally at least 15% or intermediate or greater percentages of said lignocellulosic material feed is hemicellulose.

In some exemplary embodiments of the invention, hydrolyzing 520 employs a hydrolysis medium with a wt/wt ratio of mineral acid to (mineral acid + water) of at least 0.35; optionally at least 0.37; optionally at least 0.39; optionally at least 0.41; optionally at least 0.43; optionally at least 0.45 or intermediate or greater ratios. Exemplary mineral acids include, but are not limited to HCl and H₂SO₄.
In other exemplary embodiments of the invention, hydrolyzing 520 employs one or more enzymes to breakdown the lignocellulose provided at 510. According to various exemplary embodiments of the invention the enzymes can be provided as purified enzymes, cellular extracts, cell supernatants, or a culture containing living cells.

In some exemplary embodiments, hydrolysis 520 employs at least one reactive fluid, to produce soluble sugars from the lignocellulose provided at 510.

As used in this specification and the accompanying claims the term "reactive fluid" has the meaning ascribed to it in WO 2010/009343; paragraph [0058]. WO 2010/009343 is fully incorporated herein by reference. Alternatively or additionally, one of ordinary skill in the art will be familiar with the contents of WO 2010/009343.

In some exemplary embodiments of the invention, de-acidifying 530 includes selective extraction of HC1 with a first extractant comprising a first solvent (SI) characterized by a water solubility of less than 10% and by at least one of: having a delta-P between 5 and 10 MPa\(^{1/2}\); and having a delta-H between 5 and 20 MPa\(^{1/2}\), whereupon HC1 selectively transfers to the first extractant to form an HCl-carrying first extract and an HCl-depleted aqueous feed.

As used herein Delta-P is the polarity related component of Hoy's cohesion parameter and delta-H is the hydrogen bonding related component of Hoy's cohesion parameter.

The cohesion parameter, or, solubility parameter, was defined by Hildebrand as the square root of the cohesive energy density:

\[
\delta = \sqrt{\frac{\Delta E_{vap}}{V}}
\]

in which \(\Delta E_{vap}\) and \(V\) are the energy or heat of vaporization and molar volume of the liquid, respectively. Hansen extended the original Hildebrand parameter to three-dimensional cohesion parameter. According to this concept, the total solubility parameter delta is separated into three different components, or, partial solubility parameters relating to the specific intermolecular interactions:

\[
\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2
\]

in which delta-D, delta-P and delta-H are the dispersion, polarity, and Hydrogen bonding components, respectively. Hoy proposed a system to estimate total and partial solubility parameters. The unit used for those parameters is MPa\(^{1/2}\). A detailed explanation of that parameter and its components could be found in "CRC Handbook of Solubility Parameters and Other Cohesion Parameters", second edition, pages 122-138. That and other references provide tables.

- 26 -
with the parameters for many compounds. In addition, methods for calculating those parameters are provided.

In some exemplary embodiments of the invention, de-acidifying 530 includes selective extraction of HCl with an alcohol, optionally hexanol and/or 2-ethylhexanol.

Optionally, an amount of at least one of said at least one second sugars, optionally as a precursor, in the product mixture is at least 80; optionally 85; optionally 90%, or intermediate or greater percentages, of a theoretical yield of the same second sugar in the lignocellulosic material feed provided at 510.

Considering for a moment the concentration of the second sugar and/or its precursor relative to the total amount of sugars present in the mixture, in some cases: if a combined concentration of (the second sugar and its precursor) in the hydrolyzate at 520 is C1 and the combined concentration of (the second sugar and its precursor) in the product mixture 320 after removal of the first sugar product is C2; then C2/C1 is greater than 1.5, optionally greater than 2 and optionally greater than 3. Alternatively or additionally, in some exemplary embodiments of the invention, C2 is at least 30% of saturation concentration at 25°C, optionally at least 50% and optionally at least 70%.

According to various exemplary embodiments of the invention water may be removed at different stages. Optionally, water removal increases a concentration of one or more sugars in the solution. In some exemplary embodiments of the invention, increasing a sugar concentration brings it closer to its saturation point. Optionally, crystallization is more easily accomplished in proximity to the saturation point.

**Exemplary downstream processing**

Fig. 6a is a simplified flow diagram of an exemplary method for preparing a conversion product from a second sugar, indicated generally as 601.

Depicted exemplary method 601 includes providing 610 a fermentor and fermenting 620 a medium comprising a second sugar (e.g. 232; 233; 250; 424; or steps 340; 350; 540) the fermentor to produce a conversion product 630.

Fig. 6b is a simplified flow diagram of an exemplary method for preparing a conversion product from a second sugar and/or a first sugar product indicated generally as 602.

Depicted exemplary method 602 includes providing an input stream comprising at least one of a second sugar (e.g. 232; 233; 250; 424; or steps 340; 350; 540) and a product of a first sugar (e.g. 251; 422; or step 330) and converting 621 at least a portion of said input stream to produce a conversion product 631.
In some exemplary embodiments of the invention, conversion product 631 includes at least one member selected from the group consisting of alcohols, carboxylic acids, amino acids, monomers for the polymer industry and proteins.

Optionally, the method includes processing conversion product 631 to produce a consumer product such as a detergent, a polyethylene-based product, a polypropylene-based product, a polyolefin-based product, a polylactic acid (polylactide)-based product, a polyhydroxyalkanoate-based product and a polyacrylic-based products.

Optionally, the detergent includes a sugar-based surfactant, a fatty acid-based surfactant, a fatty alcohol-based surfactant, or a cell-culture derived enzyme.

Optionally, the polyacrylic-based product is selected from plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.

Optionally, the polyolefin-based products are selected from milk jugs, detergent bottles, margarine tubs, garbage containers, water pipes, absorbent articles, diapers, non wovens, high density polyethylene (HDPE) toys and HDPE detergent packagings.

Optionally, the polypropylene based products are selected from absorbent articles, diapers and non wovens.

Optionally, the polylactic acid based products are selected from packaging of agriculture products and of dairy products, plastic bottles, biodegradable products and disposables.

Optionally, the polyhydroxyalkanoate based products are selected from packaging of agriculture products, plastic bottles, coated papers, molded or extruded articles, feminine hygiene products, tampon applicators, absorbent articles, disposable nonwovens and wipes, medical surgical garments, adhesives, elastomers, films, coatings, aqueous dispersants, fibers, intermediates of pharmaceuticals and binders.

In some exemplary embodiments of the invention, conversion product 631 includes at least one member of the group consisting of ethanol, butanol, isobutanol, a fatty acid, a fatty acid ester, a fatty alcohol and biodiesel.

In some exemplary embodiments of the invention, the method includes processing of conversion product 631 to produce at least one product selected from the group consisting of an isobutene condensation product, jet fuel, gasoline, gasohol, diesel fuel, drop-in fuel, diesel fuel additive, and a precursor thereof.

Optionally, the gasohol is ethanol-enriched gasoline or butanol-enriched gasoline.
Optionally, the product is selected from the group consisting of diesel fuel, gasoline, jet fuel and drop-in fuels. US patent application publication 2009/0035842 describes technology relevant to these applications and is fully incorporated herein by reference.

Some exemplary embodiments of the invention relate to a consumer product, a precursor of a consumer product, or an ingredient of a consumer product produced from a conversion product 631.

Optionally, the consumer product, precursor of a consumer product, or ingredient of a consumer product includes a conversion product 631 selected from carboxylic and fatty acids, dicarboxylic acids, hydroxylcarboxylic acids, hydroxyl di-carboxylic acids, hydroxyl-fatty acids, methylglyoxal, mono-, di-, or poly-alcohols, alkanes, alkenes, aromatics, aldehydes, ketones, esters, biopolymers, proteins, peptides, amino acids, vitamins, antibiotics, and pharmaceuticals.

Optionally, the product is ethanol-enriched gasoline, jet fuel, or biodiesel.

Optionally, the consumer product, precursor of a consumer product, or ingredient of a consumer product has a ratio of carbon-14 to carbon-12 of about 2.0 \times 10^{-13} or greater.

In some exemplary embodiments of the invention, the consumer product includes an ingredient and an additional ingredient produced from a raw material other than lignocellulosic material. Optionally, the ingredient and said additional ingredient produced from a raw material other than lignocellulosic material are essentially of the same chemical composition.

Optionally, the consumer product includes a marker molecule at a concentration of at least 1000ppb. Marker molecules suitable for use in this context include, but are not limited to, furfural, hydroxy-methyl furfural, products of fufural or hydroxy-methylfurfural condensation, color compounds derived from sugar carmelization, levulinic acid, acetic acid, methanol, galacturonic acid, and glycerol.

In some exemplary embodiments of the invention, conversion product 631 includes xylitol. In some exemplary embodiments of the invention, method 601 and/or 602 includes incorporating the xylitol into an edible product. Edible products include, but are not limited to, chewing gum, candy, energy bars, energy gels, energy drinks, cookies and other food products.

In some exemplary embodiments of the invention, conversion product 631 includes rumen bypass protein. In some exemplary embodiments of the invention, method 601 and/or 602 includes incorporating the rumen bypass protein into a livestock feed. Livestock feeds include, but are not limited to hay, straw, silage compressed feed, pelleted feed, oils, mixed rations and crumbled pellets.
Additional exemplary method

Fig. 7a is a simplified flow diagram of an exemplary method for recovering sugars (optionally monomeric sugars) and/or their products from a complex sugar mixture including oligosaccharides, indicated generally as 700.

Depicted exemplary method 700 includes selectively reacting 710 a first sugar in a portion of an initial mixture which includes and at least one oligosaccharide to form a product mixture 720 comprising a product 721 of the first sugar. Optionally, the initial mixture includes one or more monomeric sugars. Depicted exemplary method 700 also includes producing 730 an oligomer rich sugar fraction with a ratio of at least one of said at least one oligosaccharide to a total sugar concentration greater than a ratio of the same components in product mixture 720. Optionally, method 700 includes hydrolyzing 740 the oligomer rich sugar fraction to produce additional monomeric sugars 750. Exemplary ways to perform hydrolysis 740 are described in co-pending provisional patent application US 61/524,839 which is fully incorporated herein by reference.

Depicted exemplary method 700 includes separating 760 product 721 of the first sugar from product mixture 720. Optionally, method 700 includes separating 770 at least one of the at least one additional monomeric sugars from product mixture 720. In some exemplary embodiments of the invention, separation 770 includes crystallization. Optionally, xylose is crystallized during separation 770.

In some exemplary embodiments of the invention, selectively reacting 710 the first monomeric sugar yields an alcohol 790 as a reaction product. Optionally, the first monomeric sugar is glucose and the alcohol includes ethanol.

In the depicted exemplary embodiment, method 700 includes use of alcohol 790 to aid in crystallization 795 of at least one of said at least one additional monomeric sugars. In some exemplary embodiments of the invention, the monomeric sugar to be crystallized is xylose. In some exemplary embodiments of the invention, separation 770 includes removal of water to increases a concentration of each sugar in the mixture. Alternatively or additionally, separation 770 includes addition of alcohol 790 at a higher concentration than that which was present in the mixture prior to separation 760 by distillation 797. Optionally, separation 770 by crystallization employs alcohol 790 at a concentration of 15; 20; 25; 30; 35; 40; 45; 50; 55; 60; 65; 70; 75; 80; 85; 90% or intermediate concentrations (W/W).

In some exemplary embodiments of the invention, alcohol 790 is distilled 797 from product mixture 720 as a means of separation 760 of product 721 and re-introduced during crystallization 795 at a desired concentration. Optionally, these embodiments include a repetition...
of separation 760 (indicated by double headed arrow) to recover alcohol 790. These embodiments are advantageous in that they can achieve a high alcohol concentration which makes it feasible to crystallize sugars that are relatively far from their saturation point. However, there is an energy cost to re-distilling the alcohol for recovery.

In other exemplary embodiments of the invention (not depicted), separation 770 by crystallizing 795 at least one of the at least one additional monomeric sugars is followed by distilling 797 of alcohol 790 from the product mixture. These embodiments are advantageous in that they involve only a single distillation, but cannot achieve the high alcohol concentrations during crystallization which are possible if distillation is conducted prior to crystallization unless alcohol is introduced from an outside source, or from a previous round of purification.

In some exemplary embodiments of the invention, producing 730 an oligomer rich sugar fraction includes crystallization 795 of at least one of said at least one oligosaccharide from product mixture 720. Optionally, this crystallization employs an alcohol 790 produced by selectively reacting 710. Alcohol 790 can be used to aid in crystallization of an oligosaccharide as described above for monomeric sugars.

According to various exemplary embodiments of the invention separation 770 produces either crystals of oligosaccharide, or a liquid mixture enriched in oligosaccharides. In either case, these oligomeric sugars can be used to produce 730 the oligomer rich sugar fraction which can subsequently be hydrolyzed 740 to produce additional monomeric sugars.

Fig. 7b is a simplified flow diagram of another exemplary method for recovering sugars (optionally monomeric sugars) and/or their products from a complex sugar mixture including oligosaccharides, indicated generally as 701.

Depicted Exemplary method 701 includes selectively reacting 710 a first sugar in an initial mixture which includes a first sugar and at least one oligosaccharide 722 to form a product mixture 720 comprising a product 721 of the first sugar. Depicted method 701 also includes separating 761 product 721 from product mixture 720 and hydrolyzing 741 oligosaccharide 722 to produce additional first sugar 751.

Optionally, the initial mixture includes a second sugar. In some exemplary embodiments of the invention, the method includes separating the second sugar.

Another additional exemplary method

Fig. 8a is a simplified flow diagram of an exemplary method for recovering ethanol and a crystallized non-glucose sugar from a complex sugar mixture including oligosaccharides, indicated generally as 801.
Depicted exemplary method 801 includes fermenting 810 glucose in a portion of an
initial mixture which includes at least one additional monomeric sugar and at least one
oligosaccharide to form a product mixture 812 including ethanol and using 820 the ethanol to aid
in crystallization of at least one non-glucose sugar in the product mixture to produce crystals
821. Optionally, the non-glucose sugar is xylose.

Fig. 8b is a simplified flow diagram of an exemplary method according to Fig 8a in
which crystals 821 are monomeric sugar crystals indicated generally as method 802.

Depicted exemplary method 802 begins with separation 830 of at least one non-glucose
sugar as crystals 821a comprising primarily at least one of the at least one additional monomeric
sugar and an oligosaccharide enriched mother liquor 822a.

Optionally, method 802 includes hydrolyzing 840 oligosaccharide enriched mother liquor
822a to produce additional monomeric sugars 841a.

Fig. 8c is a simplified flow diagram of an exemplary method according to Fig 8a in
which crystals 821 are oligosaccharide crystals indicated generally as method 804.

Depicted exemplary method 804 begins with separation 830 of crystals 821b comprising
primarily one or more oligosaccharides and a monomeric sugar enriched mother liquor 822b.

In the depicted embodiment, method 804 includes crystallizing 850 at least one
monomeric sugar from monomeric sugar enriched mother liquor 822b. Optionally, an alcohol,
such as ethanol 860 is used to aid in crystallization 850.

In some exemplary embodiments of the invention, crystals 821b are hydrolyzed 824 to
produce additional monomeric sugars 841b. In some exemplary embodiments of the invention,
these additional monomeric sugars include glucose.

**Exemplary system**

Fig. 9 is schematic diagram of an exemplary system for processing a sugar mixture
indicated generally system 900. Depicted exemplary system 900 includes a fermentor 910
adapted to deliver a stream of spent media 912 to a separation unit 920 adapted to separate solids
922 from spent media 912 and deliver a supernatant stream 924. According to various exemplary
embodiments of the invention separation unit 920 includes centrifugation components and/or
filtration components.

Depicted exemplary system 900 also includes a distillation unit 930 adapted to distill an
alcohol 932 from supernatant stream 924 to produce a modified supernatant 934. Adaptation to
distill an alcohol can include implementation of one or more design changes which take into
account the alcohol to be distilled and/or the composition of supernatant stream 924. For
example, if the alcohol to be distilled has a high boiling point, a stronger heat source may be
provided. Alternatively or additionally, if there are components in stream 924 with a boiling point close to that of the alcohol in question, a long distillation column, or two or more distillation columns in series, may be incorporated into distillation unit 930 to improve separation of the alcohol from other components. In some exemplary embodiments of the invention, the alcohol is ethanol which can be recovered at up to 95% purity.

Depicted exemplary system 900 also includes a primary crystallization module 940 adapted to receive at least a portion of modified supernatant 934 from distillation unit 930 and crystallize at least one sugar (crystals 942) therefrom to produce a mother liquor 944. Optionally, distillation unit 930 also delivers at least a portion of alcohol 932 to crystallization module 940. Alternatively or additionally, crystallization module 940 receives alcohol from an independently provided alcohol reservoir (not depicted). Optionally, separation of alcohol 932 from stream 934 followed by re-mixing of these components contributes to an ability to increase the alcohol concentration in stream 934. In some exemplary embodiments of the invention, increasing the alcohol concentration improves one or more crystallization parameters. Crystallization parameters include, but are not limited to, yield and purity of crystals. Alcohol concentrations during crystallization are optionally as described above in the context of Fig. 7a.

In some exemplary embodiments of the invention, fermentor 910 converts glucose to ethanol which is distilled by distillation unit 930 so that modified supernatant 934 is substantially free of glucose. According to these exemplary embodiments of the invention crystals 942 are of a non-glucose sugar. According to various exemplary embodiments of the invention this sugar can be monomeric or oligomeric (e.g. disaccharide or higher).

Optionally, system 900 includes a secondary crystallization module 950 adapted to receive at least a portion of alcohol 932 from distillation unit 930 and crystallize at least one additional sugar (crystals 952) from mother liquor 944 to produce a spent mother liquor 954. Alternatively or additionally, secondary crystallization module 950 receives alcohol from an independently provided alcohol reservoir (not depicted).

Depicted exemplary system 900 also includes an alcohol recovery module 960 adapted to distill alcohol 962 from mother liquor 944 and/or spent mother liquor 954. Module 960 also produces a liquor residue 964. In some exemplary embodiments of the invention, residue 964 is subject to anaerobic fermentation in an anaerobic fermentation module (not depicted). Optionally, this anaerobic fermentation produces a usable energy source such as methane. In some exemplary embodiments of the invention, methane produced in this manner is used to
provide heat energy for various system components (e.g. distillation module 930 and/or alcohol recovery module 960).

In some exemplary embodiments of the invention, exemplary system 900 also includes a hydrolysis module 970. Hydrolysis module 970 produces additional monomeric sugars 972 from an input material including dimeric sugars and other soluble oligomeric sugars. According to various exemplary embodiments of the invention the input material includes one or more of crystals 942 produced by primary crystallization module 940; mother liquor 944; crystals 952 produced by secondary crystallization module 950 and spent mother liquor 954. Optionally, additional monomeric sugars 972 are delivered to fermentor 910 (as depicted) and/or to crystallization module 940 and/or 950 (not shown) by a recycling pump (not depicted).

According to various exemplary embodiments of the invention system 900 includes one or more pumps (not depicted) to control flows among and between components of the system.

Depicted exemplary system 900 includes a controller 990 adapted to control at least one of the at least one pumps. Optionally, system 900 includes one or more detectors (not shown) configured to provide data pertaining to at least one system parameter to controller 990. In some exemplary embodiments of the invention, controller 990 is responsive to the data. System parameters include, but are not limited to, concentration of specific sugars at specific points, total sugar concentration at specific points, alcohol concentration, temperatures, flow rates and acid concentration.

**Additional Exemplary method**

Fig. 10 is a simplified flow diagram of an exemplary method according to some embodiments of the invention depicted generally as 1000. Depicted exemplary method 1000 produces a first sugar product 101 I and a product of a second sugar from a mixture 1010 of sugars. Optionally, the product of the second sugar is xylitol.

According to depicted exemplary method 1000, separation of 1st sugar product 101 I from mixture 1010 produces a modified mixture 1020. In some exemplary embodiments of the invention, mixture 1010 is provided as an aqueous solution of sugars. In some exemplary embodiments of the invention, mixture 1020 is at least 35, optionally at least 40, optionally 45, optionally 50% or intermediate or greater percentages of xylose on a weight basis relative to total sugars. In the depicted exemplary embodiment, ultrafiltration 1022 of modified mixture 1020 produces a concentrated mixture 1024. In some exemplary embodiments of the invention, mixture 1024 includes 45, optionally 50, optionally 55, optionally 60% or intermediate or greater percentages of total sugars on a weight basis.
In the depicted exemplary embodiment, concentrated mixture 1024 is subject to chromatographic separation 1030. Chromatographic separation enriches the mixture for xylose, but may also dilute the mixture. In the depicted exemplary embodiment, xylose fraction 1040 includes 65, optionally 70, optionally 80, optionally 85% or intermediate or greater percentages of xylose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction 1040 may include 2, optionally 3, optionally 4% or intermediate or greater percentages of mannose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction 1040 may include 4, optionally 5, optionally 6% or intermediate or greater percentages of galactose on a weight basis relative to total sugars in the solution. Alternatively or additionally, fraction 1040 may include 1, optionally 2, optionally 3% or intermediate or greater percentages of arabinose on a weight basis relative to total sugars in the solution.

In the depicted exemplary embodiment, concentration 1050 increases the total sugar concentration to 65, optionally 70, optionally 75, optionally 80% or intermediate or greater percentages. Concentration 1050 brings xylose closer to its saturation point.

Crystallization 1060 produces crystals 1062 of a second sugar (e.g. xylose) and a mother liquor 1070. Optionally, an organic solvent, such an alcohol (e.g. ethanol or methanol) is added to the solution during crystallization 1060 to aid in precipitation of sugar crystals. Exemplary alcohol concentrations are provided above in the context of Fig. 7a.

Crystals 1062, which are substantially pure, can be subjected to hydrogenation 1124 to produce a corresponding alcohol. For example, if crystals 1062 are xylose crystals, hydrogenation will produce xylitol. Since hydrogenation is not typically a selective reaction, crystallization 1060 contributes to an ability to produce a desired sugar-alcohol at relatively high purity.

Returning now to crystallization 1060, the resultant mother liquor 1070 can be subject to additional chromatographic separation together with an additional amount of concentrated mixture 1024. Optionally, this allows at least a portion of xylose in mother liquor 1070 to be recovered by an additional round of crystallization 1060. Optionally, remaining sugars 1042 can be sent to anaerobic fermentation 1044 to produce an energy source, such as methane.

**Exemplary sugar compositions**

Some exemplary embodiments of the invention relate to sugar compositions which exist as production intermediates in various methods described herein.

For example, practice of the procedure outlined in Fig 10 might produce, as an intermediate product, a sugar composition including at least 25; optionally 30; optionally 35 % xylose by weight relative to total sugar concentration with a detectable amount of at least one
alpha-bonded di-glucose and a detectable amount of at least one beta-bonded di-glucose. Optionally, the alpha-bonded di-glucose includes maltose and/or isomaltose and/or trehalose. Optionally, the beta-bonded di-glucose includes gentiobiose and/or sophorose and/or cellobiose. Compositions of this general type might occur at, for example, 1020 in Fig. 10. According to various exemplary embodiments of the invention the alpha bonded di-glucose is optionally present at a level of at least 10, optionally at least 50, optionally at least 100, optionally at least 500, optionally at least 1000 PPM or intermediate or greater levels. Alternatively or additionally, according to various exemplary embodiments of the invention the beta bonded di-glucose is optionally present at a level of at least 10, optionally at least 50, optionally at least 100, optionally at least 500, optionally at least 1000 PPM or intermediate or greater levels.

Optionally, the composition includes at least 40; optionally at least 42; optionally at least 45; optionally at least 47; optionally at least 50% total sugars. Compositions of this general type might occur at, for example, 1024 in Fig. 10.

Optionally, the composition is provided as a solution, for example an aqueous solution.

In some exemplary embodiments of the invention, the composition includes less than 90; optionally 80; optionally 70%> xylose of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes glucose at a concentration of at least 0.001; optionally at least 0.01; optionally at least 0.1 % of total sugars on a weight basis. Alternatively or additionally, in some exemplary embodiments of the invention the composition includes glucose at a concentration of less than 5; optionally 3; optionally 1% of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes at least 0.001; optionally 0.01; optionally 0.1% arabinose of total sugars on a weight basis.

Alternatively or additionally, in some exemplary embodiments of the invention the composition includes at least 0.001; optionally 0.0005; optionally 0.0001%> non-volatile fermentation product on a weight basis. As used in this specification and the accompanying claims the term “non volatile fermentation products” includes but is not limited to: lactic acid, succinic acid, fatty acids, esters of fatty acids and proteins.

Alternatively or additionally, practice of the procedure outlined in Fig 10 might produce, as an intermediate product, a sugar solution comprising (by weight relative to total sugar concentration) at least 60% xylose, at least 100 PPB of a marker molecule and 0.001% to 10%
oligosaccharides. Optionally, the oligosaccharides include maltose and/or isomaltose and/or trehalose. Optionally, the oligosaccharides include gentiobiose, sophorose and cellobiose.

According to various exemplary embodiments of the invention the marker molecule includes at least one, optionally at least two, optionally at least three of furfural, hydroxy-methyl furfural, products of furfural or hydroxy- methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

Alternatively or additionally, the composition includes at least one; optionally at least two; optionally at least three fermentation residue(s). According to various exemplary embodiments of the invention the fermentation residue includes a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor. Optionally, fermentation residues can serve as marker molecules. Thus, there are marker molecules indicative of hydrolysis of a lignocellulosic substrate, and additional marker molecules indicative of fermentation of sugars in the resultant hydrolyzate.

Optionally, the composition includes glucose at a concentration of 0.001; optionally 0.01; optionally 0.1% of total sugars on a weight basis. Alternatively or additionally, the composition optionally includes glucose at a concentration of not more than 5; optionally 3; optionally 1% of total sugars on a weight basis.

Alternatively or additionally, the composition optionally includes arabinose at a concentration of at least 0.001; optionally 0.01; optionally 0.1% of total sugars on a weight basis.

Alternatively or additionally, the composition optionally includes 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, the concentration of marker molecule does not exceed 0.5%. Optionally, a total concentration of the two, optionally the three, marker molecules does not exceed 0.5%.

Optionally, the composition includes at least 60% total sugars.

Optionally, the composition includes mannose and/or galactose and/or arabinose.

In some exemplary embodiments of the invention, the solution includes at least 3% mannose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

Compositions of this general type might occur at, for example, 1040 or 1050 in Fig. 10.
Additional exemplary composition

Some exemplary embodiments of the invention relate to sugar compositions which remain after glucose and xylose have been removed from an initial mixture 1010. These embodiments correspond, for example, to mother liquor 1070 in Fig. 10. This type of sugar composition includes at least one of:

- alpha-bonded di-glucose;
- beta-bonded di-glucose; and
- arabinose;

together with 0.01% - 20% xylose by weight relative to total sugar concentration and at least 100 PPB of a marker molecule.

Optionally, the composition is provided as a solution, for example an aqueous solution.

In some exemplary embodiments of the invention, the composition includes glucose at a concentration of at least 0.001% but not more than and 5%; optionally 3; optionally 1% of total sugars on a weight basis.

In some exemplary embodiments of the invention, the composition includes at least 0.001% non-volatile fermentation product on a weight basis.

In some exemplary embodiments of the invention, the alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose. Alternatively or additionally, in some exemplary embodiments of the invention, the beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

In some exemplary embodiments of the invention, the composition includes at least 40% total sugars.

Optionally, the marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy- methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol. Optionally, the composition includes at least two, optionally at least three, marker molecules.

Alternatively or additionally, the composition includes at least one fermentation residue. Optionally, the fermentation residue includes a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.
In some exemplary embodiments of the invention, the concentration of marker molecule does not exceed 0.5%. Optionally, a total concentration of the two, optionally the three, marker molecules does not exceed 0.5%.

Optionally, the composition includes mannose and/or galactose and/or arabinose.

In some exemplary embodiments of the invention, the solution includes at least 3% mannose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 5% galactose relative to total monosaccharides by weight.

Alternatively or additionally, the composition includes at least 2% arabinose relative to total monosaccharides by weight.

**Exemplary logic hierarchy**

Fig. 11 is a logic hierarchy illustrating approaches to separating products of value from lignocelluloses according to various exemplary embodiments of the invention indicated generally as 1100.

Exemplary embodiments depicted by method 1100 feature a one stage hydrolysis 1130 as described hereinabove in the context of Fig. 1. Such a hydrolysis produces a sugar mixture 1132. Without considering the quantitative yield of any specific sugars in mixture 1132, logic hierarchy 1100 includes various strategies for exploiting two or more sugar components in the mixture.

The depicted exemplary embodiments of the invention implement a selective conversion 1140 of one sugar to produce a conversion product 1142. In some exemplary embodiments of the invention, conversion 1140 includes a fermentation reaction. Optionally, conversion 1140 includes a chemical reaction and/or an enzymatic reaction not mediated by a microorganism. In some exemplary embodiments of the invention, conversion 1140 includes fermentation of glucoses and conversion product 1142 includes ethanol.

A simplified sugar mixture 1150 remains following separation of conversion product 1142. According to various exemplary embodiments of the invention it is possible to perform a selective conversion 1180 of a second sugar to form an additional product and/or to crystallize 1170 one or more second sugar(s). In one exemplary embodiment of the invention, xylose serves as a second sugar in simplified sugar mixture 1150. According to this embodiment, xylose can be crystallized 1170 and then selectively converted 1180 by hydrogenation to xylitol.

Regardless of the first sugar and second sugar employed, selective conversion 1140 followed by removal of conversion product 1142 contributes to an ability to selectively convert 1180 the second sugar by providing a simplified sugar mixture 1150.
In some exemplary embodiments of the invention, crystallization 1170 is performed to remove an interfering sugar from mixture 1150 and permit selective conversion 1180 of a desired second sugar to form a desired product.

It is expected that during the life of this patent many chromatographic separation techniques will be developed and the scope of the invention is intended to include all such new technologies apriori.

As used herein the term "about" refers to ± 10%; optionally ±5%; optionally ±1%, optionally ±0.1%.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

Specifically, a variety of numerical indicators have been utilized. It should be understood that these numerical indicators could vary even further based upon a variety of engineering principles, materials, intended use and designs incorporated into the invention. Additionally, components and/or actions ascribed to exemplary embodiments of the invention and depicted as a single unit may be divided into subunits. Conversely, components and/or actions ascribed to exemplary embodiments of the invention and depicted as sub-units/individual actions may be combined into a single unit/action with the described/depicted function.

Alternatively, or additionally, features used to describe a method can be used to characterize an apparatus and features used to describe an apparatus can be used to characterize a method.

It should be further understood that the individual features described herein/above can be combined in all possible combinations and sub-combinations to produce additional embodiments of the invention. The examples given above are exemplary in nature and are not intended to limit the scope of the invention which is defined solely by the following claims. Specifically, the invention has been described in the context of sugar mixtures resulting from acid hydrolysis of a lignocellulosic substrate but might also be used in the context of sugar mixtures formed by other processes.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any
reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

The terms "include", and "have" and their conjugates as used herein mean "including but not necessarily limited to".

Additional objects, advantages, and novel features of various embodiments of the invention will become apparent to one ordinarily skilled in the art upon examination of the following example, which is not intended to be limiting. Additionally, various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below finds experimental support in the following examples.

EXAMPLE

Reference is now made to the following example, which together with the above descriptions, illustrates some embodiments of the invention in a non limiting fashion.

EXAMPLE:

Projected compositions of sugar mixtures after removal of glucose by fermentation and distillation of ethanol

This example projects expected relative concentrations of monosaccharides in de-acidified hydrolyzates described in PCT IL 201 1/000509, which is fully incorporated herein by reference, following removal of substantially all glucose by fermentation and distillation. This example also presumes that the fermentation reaction is specific and that other monosaccharides are not fermented to any significant degree.

In order to prepare the initial sugar mixtures, which would serve as the fermentation substrate, various lignocellulosic materials were introduced into a six stage hydrolysis reactor series in a counter-current operation as described in co-pending US provisional application 61/483,777 filed May 9, 201 1 and entitled "Hydrolysis systems and methods". This application is fully incorporated herein by reference.

Briefly, an aqueous solution of 42% HC1 was introduced continually at a temperature of 10-15°C for 24 hours. The hydrolyzate was collected, HC1 was removed by extraction and the de-acidified hydrolyzate was concentrated to give a sugar composition. Analysis of actual results of monosaccharides are summarized in Table 1 (before). Disaccharide data is not presented but may be found in PCT IL 201 1/000509. These actual results are calculated as % from sample's refractive total saccharides (%/RTS).
Table 1 also includes a calculated projection of relative sugar concentrations (as a % of total monosaccharides) following removal of glucose by fermentation/distillation (after).

The assayed substrates included two samples of pine wood, sugar cane bagasse and eucalyptus wood.

Results presented in Table 1 indicate that selective fermentation of glucose (optionally followed by removal of the resultant ethanol from the hydrolyzate mixture) increases the relative proportion of xylose. In the case of pine wood, xylose is the major monosaccharide component after glucose is eliminated.

Although di-saccharides and higher oligosaccharides account for a significant proportion of total sugars in the mixture, they are divided among a large number of different molecules. Alternatively or additionally, di-saccharides and higher oligosaccharides can be separated from a mixture of monosaccharides using chromatographic techniques. For this reason it seems that selective precipitation of xylose from glucose depleted mixtures will be feasible. It is envisioned that selective precipitation can be aided by cooling and/or addition of a non-aqueous solvent, such as ethanol. Optionally, ethanol produced by glucose fermentation can be used for this purpose.

**Table 1**: Monosaccharides in hydrolyzates of various substrates before and after selective removal of glucose

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Status</th>
<th>Other</th>
<th>Arabinose</th>
<th>Galactose</th>
<th>Glucose</th>
<th>Xylose</th>
<th>Mannose</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine 1</td>
<td>before</td>
<td>0.1 (Rhamnose)</td>
<td>1.6</td>
<td>2.7</td>
<td>27.7</td>
<td>7.0</td>
<td>7.4</td>
<td>46.5</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>0.5</td>
<td>8.5</td>
<td>14.3</td>
<td>NA</td>
<td>37.2</td>
<td>39.3</td>
<td>NA</td>
</tr>
<tr>
<td>Pine 2</td>
<td>before</td>
<td>NA*</td>
<td>0.3</td>
<td>0.8</td>
<td>36.0</td>
<td>8.0</td>
<td>1.0</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>NA*</td>
<td>3.0</td>
<td>7.9</td>
<td>NA</td>
<td>79.2</td>
<td>9.9</td>
<td>NA</td>
</tr>
<tr>
<td>Bagasse</td>
<td>before</td>
<td>2.4 (fructose)</td>
<td>2.2</td>
<td>7.2</td>
<td>48.7</td>
<td>4.9</td>
<td>4.8</td>
<td>70.2</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>11.2</td>
<td>10.2</td>
<td>33.5</td>
<td>NA</td>
<td>22.8</td>
<td>22.3</td>
<td>NA</td>
</tr>
<tr>
<td>Eucalyptus</td>
<td>before</td>
<td>3.38 (fructose)</td>
<td>2.6</td>
<td>7.24</td>
<td>46.1</td>
<td>8.27</td>
<td>5.83</td>
<td>73.42</td>
</tr>
<tr>
<td></td>
<td>after</td>
<td>12.4</td>
<td>9.5</td>
<td>26.5</td>
<td>NA</td>
<td>30.3</td>
<td>5.83</td>
<td>21.33</td>
</tr>
</tbody>
</table>

*NA indicates not applicable

In those cases where crystallization of xylose proves difficult due to the presence of another sugar in a large amount (e.g. bagasse or eucalyptus where a large amount of galactoses is present) the interfering sugar can be removed prior to such crystallization if necessary. For example galactose has a solubility of 683 g/L (Wikipedia) in water while xylose has a solubility of 1250 g/L in water (Merck index). This suggests that galactose could be removed prior to xylose via selective crystallization of galactose.
CLAIMS:

1. A method comprising:
   (a) selectively reacting a first sugar in a mixture which includes at least one second sugar to form a product mixture comprising a product of said first sugar;
   (b) separating said product of said first sugar from said product mixture; and
   (c) separating at least one of said at least one second sugar from said product mixture.

2. A method comprising:
   (a) selectively reacting a first sugar in a mixture which includes at least one second sugar, to form a product mixture comprising a product of said first sugar;
   (b) separating said product of said first sugar from said product mixture; and
   (c) reacting at least one of said at least one second sugar to form at least one second sugar product.

3. A method comprising:
   (a) selectively reacting a first sugar in a mixture which includes at least one second sugar precursor, to form a product mixture comprising a product of said first sugar;
   (b) separating said product of said first sugar from said product mixture; and
   (c) reacting at least one of said at least one second sugar precursor to form at least one second sugar product.

4. A method according to claim 2, comprising separating at least one of said at least one second sugar from said product mixture.

5. A method according to claim 2 or claim 3, comprising separating at least one of said at least one second sugar product from said product mixture.

6. A method according to any one of claims 1 to 5, wherein said first sugar comprises glucose and wherein said selectively reacting comprises fermenting.

7. A method according to claim 3, wherein said at least one second sugar precursor comprises a pentose.
8. A method according to claim 1 or 2, wherein said at least one second sugar comprises a pentose.

9. A method according to claim 7 or 8, wherein said pentose is selected from the group consisting of xylose, xylulose, lyxose, ribulose and arabinose.

10. A method according to claim 1 or 2, wherein said at least one second sugar comprises a disaccharide.

11. A method according to claim 3, wherein said at least one second sugar precursor comprises a disaccharide.

12. A method according to claim 10 or 11, wherein said disaccharide is selected from the group consisting of trehalose, gentiobiose, kojibiose, nigerose, sophorose and laminarobiose.

13. A method according to any one of claims 1 to 3, wherein said at least one second sugar is xylose.

14. A method according to claim 1, comprising reacting at least one of said second sugar to form a second sugar product.

15. A method according to claim 3, comprising reacting at least two of said at least one second sugar precursor to form at least one second sugar product.

16. A method according to claim 14 or claim 15, wherein said at least one second sugar is xylose and wherein said second sugar product is selected from xylitol and a rumen bypass protein.

17. A method according to claim 1 or claim 2, wherein:
   the weight ratio between said at least one second sugar to said first sugar prior to said selectively reacting is R1;
   the weight ratio between said at least one second sugar to said first sugar in said product mixture is R2; and
   the ratio of R2 to R1 is greater than 5.
18. A method according to claim 3, wherein:
the weight ratio between said at least one second sugar precursor to said first sugar prior to said selectively reacting is R1;
the weight ratio between said at least one second sugar precursor to said first sugar in said product mixture is R2; and
the ratio of R2 to R1 is greater than 5.

19. A method according to claim 1 or claim 2, wherein the total weight of said at least one second sugar comprises at least 50% of the total sugars in said product mixture.

20. A method according to claim 3, wherein the total weight of said at least one second sugar precursor is equal to at least 50% of the total sugars in said product mixture.

21. A method according to any one of claims 1 to 3, wherein said product of said first sugar is selected from the group consisting of ethanol, higher alcohols, organic acids and organic acid ester of 3 to 22 carbon atoms, amino acids, yeast and proteins.

22. A method according any one of claims 1 to 3, wherein said separating comprises at least one of distillation, membrane filtration, solvent extraction and chromatographic separation.

23. A method according to any one of claims 1 to 3, wherein said product of said first sugar has an atmospheric-pressure boiling point of less than 100°C.

24. A method according to any one of claims 1 to 3, wherein said product of said first sugar forms an azeotrope with water.

25. A method comprising:
(a) providing a mixture including a first sugar and at least one second sugar precursor;
(b) selectively reacting said first sugar to form a product mixture comprising a product of said first sugar;
(c) selectively reacting said at least one second sugar precursor to form said second sugar; and
(d) separating said product of said first sugar.
26. A method according to claim 25, comprising separating at least one of said at least one second sugar precursor from said product mixture.

27. A method according to claim 25, wherein selectively reacting said at least one second sugar precursor to form said at least one second sugar occurs after separating said product of said first sugar.

28. A method according to claim 25, wherein said separating said product of said first sugar from said at least one second sugar includes separating each of said product of said first sugar and said at least one second sugar from said product mixture.

29. A method according to claim 26, wherein said separating said product of said first sugar is followed by separating said at least one second sugar precursor.

30. A method according to claim 25, wherein said separating said product of said first sugar is followed by selectively reacting said precursor to form said second sugar.

31. A method according to claim 25, wherein said selectively reacting said at least one second sugar precursor comprises acid catalysis.

32. A method according to claim 25, wherein said selectively reacting said at least one second sugar precursor comprises enzymatic catalysis.

33. A method according to claim 25, wherein said selectively reacting said first sugar comprises fermentation.

34. A method according to claim 25, wherein said selectively reacting said at least one second sugar precursor comprises hydrolysis.

35. A method according to claim 25, wherein said selectively reacting said at least one second sugar precursor comprises transglucosidation.
36. A method according to claim 25, wherein said selectively reacting said at least one second sugar precursor, comprises oligomerization.

37. A method according to claim 25, comprising reacting said second sugar to form a second sugar product.

38. A method according to any one of claims 1, 2, 3 or 25, comprising preparing said mixture.

39. A method according to claim 38, wherein said preparing comprises:
  providing a lignocellulosic material feed;
  hydrolyzing said lignocellulosic material feed to form a hydrolyzate comprising at least one first sugar and at least one of at least one second sugar and at least one second sugar precursor.

40. A method according to claim 39, comprising de-acidifying said hydrolyzate.

41. A method according to claim 39, wherein said hydrolyzing is performed in a counter-current mode.

42. A method according to claim 39, wherein said lignocellulosic material feed comprises at least 5% hemicellulose.

43. A method according to claim 39, wherein said hydrolyzing employs a hydrolysis medium with a wt/wt ratio of HCl to (HCl+water) of at least 0.35.

44. A method according to claim 40, wherein said de-acidifying comprises selective extraction of HCl with an alcohol.

45. A method according to claim 39, wherein an amount of at least one of said at least one second sugars in said mixture, optionally present as a precursor, is at least 85% of a theoretical yield of the same second sugar in said lignocellulosic material feed.
46. A method according to claim 38, wherein:
   the combined concentration of said second sugar and said second sugar precursor in said mixture is C1;
   wherein the combined concentration of said second sugar and said second sugar precursor in said product mixture after removal of said first sugar product is C2 and C2/C1 is greater than 1.5.

47. A method comprising:
   (a) providing a fermentor; and
   (b) fermenting a medium comprising a second sugar according to any one of claims 1 to 46 in said fermentor to produce a conversion product.

48. A method comprising:
   (a) providing an input stream comprising at least one member of the group consisting of:
       said second sugars according to any one of claims 1 to 46; and
       said product of said first sugar according to any one of claims 1 to 46; and
   (b) converting at least a portion of said input stream to produce a conversion product.

49. A method according to claim 47 or 48, wherein said conversion product includes at least one member selected from the group consisting of alcohols, carboxylic acids, amino acids, monomers for the polymer industry and proteins.

50. A method according to claim 47 or 48, comprising processing said conversion product to produce a consumer product selected from the group consisting of detergent, polyethylene-based products, polypropylene-based products, polyolefin-based products, polylactic acid (polylactide)-based products, polyhydroxyalkanoate-based products and polyacrylic-based products.

51. A method according to claim 50, wherein said detergent comprises a sugar-based surfactant, a fatty acid-based surfactant, a fatty alcohol-based surfactant, or a cell-culture derived enzyme.
52. A method according to claim 50, wherein said polyacrylie-based product is selected from plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.

53. A method according to claim 50, wherein said polyolefin-based products are selected from milk jugs, detergent bottles, margarine tubs, garbage containers, water pipes, absorbent articles, diapers, non-wovens, high density polyethylene (HDPE) toys and HDPE detergent packagings.

54. A method according to claim 50, wherein said polypropylene based products are selected from absorbent articles, diapers and non-wovens.

55. A method according to claim 50, wherein said polylactic acid based products are selected from packaging of agriculture products and of dairy products, plastic bottles, biodegradable products and disposables.

56. A method according to claim 50, wherein said polyhydroxyalkanoate based products are selected from packaging of agriculture products, plastic bottles, coated papers, molded or extruded articles, feminine hygiene products, tampon applicators, absorbent articles, disposable nonwovens and wipes, medical surgical garments, adhesives, elastomers, films, coatings, aqueous dispersants, fibers, intermediates of pharmaceuticals and binders.

57. A method according to claim 49, wherein said conversion product includes at least one member of the group consisting of ethanol, butanol, isobutanol, a fatty acid, a fatty acid ester, a fatty alcohol and biodiesel.

58. A method according to 57, comprising processing of said conversion product to produce at least one product selected from the group consisting of an isobutene condensation product, jet fuel, gasoline, gasohol, diesel fuel, drop-in fuel, a diesel fuel additive, and a precursor thereof.

59. A method according to claim 58, wherein said gasohol is ethanol-enriched gasoline or butanol-enriched gasoline.
60. A method according to claim 58, wherein said product is selected from the group consisting of diesel fuel, gasoline, jet fuel and drop-in fuels.

61. A consumer product, a precursor of a consumer product, or an ingredient of a consumer product produced from a conversion product according to claim 47 or 48.

62. A consumer product, a precursor of a consumer product, or an ingredient of a consumer product comprising at least one conversion product produced by a method according to claim 47 or 48, wherein said conversion product is selected from carboxylic and fatty acids, dicarboxylic acids, hydroxylcarboxylic acids, hydroxyl di-carboxylic acids, hydroxyl-fatty acids, methylglyoxal, mono-, di-, or poly-alcohols, alkanes, alkenes, aromatics, aldehydes, ketones, esters, biopolymers, proteins, peptides, amino acids, vitamins, antibiotics, and pharmaceuticals.

63. A consumer product according to claim 62, wherein said consumer product is ethanol-enriched gasoline, jet fuel, or biodiesel.

64. The consumer product, a precursor of a consumer product, or an ingredient of a consumer product according to claim 62, wherein said consumer product has a ratio of carbon-14 to carbon-12 of at least about 2.0 x 10^{-13}.

65. A consumer product comprising an ingredient according to claim 61, and an additional ingredient produced from a raw material other than a lignocellulosic material.

66. The consumer product according to claim 65, wherein said ingredient and said additional ingredient produced from a raw material other than a lignocellulosic material are essentially of the same chemical composition.

67. A consumer product according to claim 61, comprising a marker molecule at a concentration of at least 100ppb.

68. A consumer product according to claim 67, wherein said marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurufural condensation, color compounds formed on heating a sugar, levulinic acid, acetic
acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms betaine, amino acids, proteins phosphate and glycerol.

69. A method comprising:
(a) selectively reacting a first sugar in an initial mixture which includes at least one oligosaccharide to form a product mixture comprising a product of said first sugar;
(b) producing an oligosaccharide rich sugar fraction with a ratio of at least one of said at least one oligosaccharide to a total sugar concentration greater than a same ratio in said product mixture; and
(c) hydrolyzing said oligosaccharide rich sugar fraction to produce monomeric sugars.

70. A method according to claim 69, wherein said first sugar is a monomeric sugar.

71. A method according to claim 70, wherein said initial mixture includes at least one additional monomeric sugar.

72. A method comprising:
(a) selectively reacting a first sugar in an initial mixture which includes a first sugar and at least one oligosaccharide to form a product mixture comprising a product of said first sugar;
(b) separating said product of said first sugar from said product mixture; and
(c) hydrolyzing said oligosaccharide to produce additional first sugar.

73. A method according to claim 72, wherein said initial mixture comprises a second sugar.

74. A method according to claim 73, comprising separating said second sugar.

75. A method according to any one of claims 69 to 74, comprising separating said product of said first sugar from said product mixture.

76. A method according to claim 71, comprising separating at least one monomeric sugar from said product mixture.

77. A method according to claim 69 or 72, wherein said selectively reacting produces an alcohol.
78. A method according to claim 77, wherein said initial mixture comprises a second sugar, and comprising use of said alcohol to aid in crystallization of said second sugar.

79. A method according to claim 78, comprising: distilling said alcohol from said product mixture; and re-introducing said alcohol during said crystallization.

80. A method according to claim 78, comprising: crystallizing said second sugar; and distilling said alcohol from said product mixture.

81. A method according to any one of claims 69 to 74, wherein said producing an oligomer rich sugar fraction includes crystallization of at least one of said at least one oligosaccharide from said product mixture.

82. A method according to claim 81, wherein said selectively reacting said first sugar produces an alcohol.

83. A method according to claim 82, comprising use of said alcohol to aid in said crystallization.

84. A method comprising:
(a) fermenting glucose in a portion of an initial mixture which includes at least one additional monomeric sugar and at least one oligosaccharide to form a product mixture comprising ethanol; and
(b) using said ethanol to aid in crystallization of at least one non-glucose sugar in said product mixture.

85. A method according to claim 84, wherein crystallization of at least one non-glucose sugar produces crystals comprising primarily at least one of said at least one additional monomeric sugar and an oligosaccharide enriched mother liquor.

86. A method according to claim 85, comprising:
hydrolyzing said oligosaccharide enriched mother liquor to produce additional monomeric sugars.

87. A method according to claim 84, wherein crystallization of at least one non-glucose sugar produces crystals comprising primarily at least one of said at least one oligosaccharide and a monomeric sugar enriched mother liquor.

88. A method according to claim 87, comprising crystallizing at least one monomeric sugar from said monomeric sugar enriched mother liquor.

89. A method according to claim 88, comprising using ethanol to aid in crystallization of said at least one monomeric sugar.

90. A system comprising:
   (a) a fermentor adapted to deliver a stream of spent media to a separation unit;
   (b) said separation unit adapted to separate solids from said spent media and deliver a supernatant stream;
   (c) a still adapted to distill an alcohol from said supernatant stream to produce a modified supernatant;
   (d) a primary crystallization module adapted to receive at least a portion of said alcohol from said distillation unit and crystallize at least one sugar from said modified supernatant to produce a mother liquor.

91. A system according to claim 90, comprising:
   a secondary crystallization module adapted to receive at least a portion of said alcohol from said distillation unit and crystallize at least one additional sugar from said mother liquor to produce a spent mother liquor.

92. A system according to claim 90 or claim 91, comprising:
   an alcohol recovery module adapted to distill said alcohol from at least one of said mother liquor and said spent mother liquor.

93. A system according to claim 91, comprising:
   a hydrolysis module adapted to:
receive a material selected from the group consisting of: crystals produced by said primary crystallization module; said mother liquor; crystals produced by said secondary crystallization module and said spent mother liquor; and hydrolyze said received material to produce additional monomeric sugars.

94. A system according to claim 93, comprising:
a recycling module adapted to deliver said additional monomeric sugars to said fermentor.

95. A system according to any one of claims 90 to 94, comprising at least one pump to control flows among and between components of the system.

96. A system according to claim 95, comprising a controller adapted to control at least one of said at least one pumps.

97. A system according to claim 96, comprising at least one detector configured to provide data pertaining to at least one system parameter to said controller, wherein said controller is responsive to said data.

98. A method according to claim 47 or claim 48, wherein said conversion product includes xylitol.

99. A method according to claim 98, comprising incorporating said xylitol into an edible product.

100. A method according to claim 47 or claim 48, wherein said conversion product includes rumen bypass protein.

101. A method according to claim 100, comprising incorporating said rumen bypass protein into a livestock feed.

102. A sugar composition comprising:
(a) at least 25% xylose by weight relative to total sugar concentration;
(b) at least one alpha-bonded di-glucose; and
(c) at least one beta-bonded di-glucose.
103. A composition according to Claim 102, wherein said alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

104. A composition according to Claim 102, wherein said beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

105. A composition according to any one of claims 102-104, comprising at least 40% total sugars.

106. A composition according to any one of claims 102-105, provided as a solution.

107. A composition according to any one of claims 102-106, comprising less than 90% xylose of total sugars on a weight basis.

108. A composition according to any one of claims 102-107, wherein glucose comprises between 0.001% and 5% of total sugars on a weight basis.

109. A composition according to any one of claims 102-108, comprising at least 0.001% arabinose of total sugars on a weight basis.

110. A composition according to any one of claims 102-108, comprising at least 0.001% non-volatile fermentation product on a weight basis.

111. A sugar composition comprising (by weight relative to total sugar concentration):
   (a) at least 60% xylose;
   (b) at least 100 PPB of a marker molecule; and
   (c) 0.001% to 10% oligosaccharides.

112. A composition according to claim 111, wherein said marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.
113. A composition according to claim 111 or 112, comprising at least two marker molecules.

114. A composition according to claim 111 or 112, comprising at least three marker molecules.

115. A composition according to claim 111, comprising at least one fermentation residue.

116. A composition according to claim 115, wherein said at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

117. A composition according to claim 115 or 116, comprising at least two fermentation residues.

118. A composition according to claim 113, comprising at least three fermentation residues.

119. A composition according to claim 111, wherein glucose comprises between 0.001% and 5% of total sugars on a weight basis.

120. A composition according to claim 111, comprising at least 0.001% arabinose of total sugars on a weight basis.

121. A composition according to Claim 111, wherein oligosaccharides include at least one member of the group consisting of maltose, isomaltose and trehalose.

122. A composition according to Claim 111, wherein said oligosaccharides include at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.

123. A composition according to any one of claims 111-122, comprising at least 0.001% non-volatile fermentation product on a weight basis.

124. A composition according to any one of claims 111-123, wherein a concentration of said marker molecule does not exceed 0.5%.>
125. A composition according to claim 111, comprising at least 60% total sugars.

126. A composition according to any one of claims 111 to 125, comprising at least one sugar selected from the group consisting of mannose, galactose and arabinose.

127. A composition according to claim 111, comprising at least 3% mannose relative to total monosaccharides by weight.

128. A composition according to claim 111, comprising at least 5% galactose relative to total monosaccharides by weight.

129. A composition according to any one of claims 111 to 128, comprising at least 2% arabinose relative to total monosaccharides by weight.

130. A sugar composition comprising:
(a) at least one of alpha-bonded di-glucose, beta-bonded di-glucose and arabinose;
(b) 0.01% - 20% xylose by weight relative to total sugar concentration; and
(c) at least 100 PPB of a marker molecule.

131. A composition according to claim 130, provided as a solution.

132. A composition according to claim 130, wherein glucose comprises between 0.00 1% and 5%, (3, 1) of total sugars on a weight basis.

133. A composition according to claim 130, comprising at least 0.001% non-volatile fermentation product on a weight basis.

134. A composition according to claim 130, wherein said alpha-bonded di-glucose includes at least one member of the group consisting of maltose, isomaltose and trehalose.

135. A composition according to claim 130, wherein said beta-bonded di-glucose includes at least one member selected from the group consisting of gentiobiose, sophorose and cellobiose.
136. A composition according to any one of claims 130-135, comprising at least 40% total sugars.

137. A composition according to claim 130, wherein said marker molecule is selected from the group consisting of furfural, hydroxy-methyl furfural, products of furfural or hydroxy-methylfurfural condensation, color compounds formed on heating a sugar, levulinic acid, acetic acid, methanol, galacturonic acid, an alcohol of more than four carbon atoms, betaine, amino acids, proteins phosphate and glycerol.

138. A composition according to claim 130 or 137, comprising at least two marker molecules.

139. A composition according to claim 130 or 138, comprising at least three marker molecules.

140. A composition according to claim 130, comprising at least one fermentation residue.

141. A composition according to claim 140, wherein said at least one fermentation residue is a component of an ingredient selected from the group consisting of sugar molasses, yeast extract and corn steep liquor.

142. A composition according to claim 130, wherein a concentration of said marker molecule does not exceed 0.5%.

143. A composition according to claim 130, comprising a sugar selected from the group consisting of mannose and galactose.
Product of 1st sugar (251) → reaction (272) → Modified product of 1st sugar product (282) → Manufacturing process (292) → Manufactured product (293) → Consumer product (295)
selectively react first sugar in initial mixture containing at least 1 second sugar (310)

product mixture with product of first sugar (320)

separate product of first sugar from product mixture (330)

separate at least one second sugar from product mixture (340)

separate at least one second sugar precursor from product mixture (342)

react precursor to produce second sugar (350)
provide mixture including first sugar and second sugar precursor (410)

selectively react first sugar to form product of first sugar (420)

selectively react precursor to form second sugar (430)

separate product of first sugar (440)

react second sugar to form second sugar product (450)
provide lignocellulosic material feed (510)

hydrolyze (520)

deacidify hydrolyzate (530)

hydrolyzate with at least one first sugar and at least one second sugar, the second sugar optionally as a precursor (540)
Fig. 6a

provide a fermentor (610)

ferment medium comprising a second sugar (620)

conversion product (630)

Fig. 6b

provide input stream with a second sugar and/or a product of a first sugar (611)

convert at least a portion of input stream (621)

conversion product (631)
selectively react first sugar in portion of initial mixture which includes at least one at one oligosaccharide (710)

Product mixture (720)

Product of first sugar (721)

produce oligomer rich sugar fraction (730)

Hydrolyze (740)

Additional monomeric sugars (750)

separate (760)

separate at least one additional monomeric sugar from product mixture (770)

Alcohol (790)

Crystallization (795)

Distillation (797)
selectively react first sugar in portion of initial mixture which includes at least one oligosaccharide (710)

Product mixture (720)

Product of first sugar (721)

oligosaccharide (722)

Hydrolyze (741)

separate (761)

Additional first sugar (751)

Product of first sugar (721)
ferment glucose in portion of initial mixture including additional monomeric sugar and at least one non-monomeric sugar (810)

Product mixture including ethanol (812)

use ethanol to aid in crystallization of at least one non-glucose sugar in product mixture (820)

Crystals (821)
Separation (830)

crystals of at least one additional monomeric sugar (821a)

oligosaccharide enriched mother liquor (822a)

hydrolyze oligosaccharide enriched mother liquor (840)

additional monomeric sugars (841a)
Separation (830)

- crystals including primarily oligosaccharides (821b)
- ethanol (860)

monomeric sugar enriched mother liquor (822b)

Hydrolyze 824

- additional monomeric sugars (841b)

crystallize at least one monomeric sugar (850)
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(8) - C07D 41/00 (201 1.01)  
USPC - 546/269.7  
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) - C07D 417/00 (201 1.01)  
USPC 7 546/269.7 subclass 7 546/269.7; 548/146

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Dialog, Google Patent, Google Scholar, WIPO (sugar, second, separating, first, precursor, react, mixture, pentose, xylose, dissacharide, oligosaccharide, maker, furfural, fermentation, molasses, yeast, liquor, by-product, residue, glucose, billion, weight, ppb, marker, maltose, trehalose, concentration, cellobiose, composition, diglucose, molecule,

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Y</td>
<td>119, 121, 122, 134-136</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>121, 122, 127, 128, 130-137, 140, 141, 142</td>
</tr>
<tr>
<td>Y</td>
<td>US 7,498,430 B2 (HOLLINGSWORTH) 03 March 2009 (03.03.2009) entire document, especially col 1, In 57-65 and col 2, In 34; 44-49.</td>
<td>1-5, 7, 8, 10, 11, 13-46, 72-75, 77-83</td>
</tr>
<tr>
<td>Y</td>
<td>US 2,842,591 A (SHELTON) 08 July 1958 (08.07.1958) entire document, especially col 1, In 49-55.</td>
<td>3, 5, 7, 11, 13, 15, 16, 18, 20-46</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

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

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

Date of the actual completion of the international search: 30 December 2011 (30.12.2001 1)

Date of mailing of the international search report: **10 FEB 2012**

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: Lee W. Young  
PCT Helpdesk: 571-272-4300  
PCT OBP: 571-272-7774

Form PCT/ISA/2 10 (second sheet) (July 2009)
As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims. As only some of the required additional search fees were timely paid by the applicant, the international search report covers only those claims for which fees were paid specifically.

The International Searching Authority found multiple inventions in this international application, as follows:

<table>
<thead>
<tr>
<th>No.</th>
<th>Observation where unity of invention is lacking (Continuation of item 3 of first sheet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Claims Nos.: 6, 9, 12-17, 20, 25-26, 33-49, 101, 106-109, 112-123, 124, 126, 129, 139</td>
</tr>
<tr>
<td>2</td>
<td>Claims Nos.: 10, 123-124, 126, 129, 139</td>
</tr>
</tbody>
</table>

No protest accompanied the payment of additional search fees.

No protest accompanied the payment of additional search fees.

Remark on Protest:

The additional search fees were timely paid by the applicant. Consequently, this international search report is not subject to any protest.

Claims Nos.: 6, 9, 12-17, 20, 25-26, 33-49, 101, 106-109, 112-123, 124, 126, 129, 139

Claims Nos.: 10, 123-124, 126, 129, 139

This international search report has not been established in respect of certain claims under Article 15(2)(a) for the following reasons:

1. Because they are subject matter not required to be searched by this Authority.

2. Claims Nos.: 10, 123-124, 126, 129, 139 because they relate to subject matter not required to be searched by this Authority.
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

--- Please See Continuation Sheet ---
Continuation of Documents Considered to Be Relevant:

Y US 5,176,832 A (DORTA, et al.) 05 January 1993 (05.01.1993) entire document, especially col 2, ln 45-69. 74, 75, 81-83, 86
Y US 4,710,567 A (KEA, et al.) 01 December 1987 (01.12.1987) entire document, especially col 1, ln 38-44. 21
Y US 3,251,716 A (PORTER, et al.) 17 May 1966 (17.05.1966) entire document, especially col 1, ln 55-56. 43

Form PCT/ISA/2 10 (patent family annex) (July 2009)