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(54) METHODS AND SYSTEMS FOR SOLVENT PURIFICATION

VERFAHREN UND SYSTEME ZUR LÖSUNGSMITTELREINIGUNG

PROCÉDÉS ET SYSTÈMES DE PURIFICATION DE SOLVANT

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Description**FIELD OF THE INVENTION**

[0001] This invention relates to methods and systems for solvent purification.

BACKGROUND OF THE INVENTION

[0002] Organic solvents are used in many industrial processes.

[0003] Some solvents can be environmentally hazardous. Factories using hazardous solvents may be subject to regulations concerning solvent disposal.

[0004] Alternatively or additionally, some solvents can be expensive. Factories using expensive solvents may attempt to reduce the amount of solvent consumed in production as a cost saving measure.

SUMMARY OF THE INVENTION

[0005] A broad aspect of the invention relates to recovery of extractant including an S1 solvent from an extract including extractant carrying a contaminant load and acid (e.g. HCl) and/or water. In some exemplary embodiments of the invention, the contaminant load originates from contact with an acid hydrolyzate of a lignocellulosic substrate and/or from contact with acidified lignin and associated sugars separated from such a hydrolyzate.

[0006] As used in this specification and the accompanying claims the term "S1" or "S1 solvent" indicates an organic solvent (in some embodiments a "first" organic solvent) which is less than 15% soluble in water and has a polarity related component of Hoy's cohesion parameter (δ_P) between 5 and 10 MPa^{1/2} and/or a hydrogen-bond related component of Hoy's cohesion parameter (δ_H) between 5 and 20 MPa^{1/2}. S1 includes an alcohol, ketone or aldehyde with 5, optionally 6, or 8 or more carbon atoms. Optionally, S1 includes a hexanol, a heptanol or an octanol such as 2-ethylhexanol and combinations thereof.

[0007] As used in this specification and the accompanying claims the term "S2" or "S2 solvent" or "second organic solvent" indicates an organic solvent characterized by water solubility of at least 30% and a δ_P greater than 8 MPa^{1/2} and/or a δ_H greater than 12 MPa^{1/2}.

[0008] For example, S2 may include methanol and/or ethanol.

[0009] δ_P is the polarity related component of Hoy's cohesion parameter and δ_H is the hydrogen bonding related component of Hoy's cohesion parameter.

[0010] The cohesion parameter, as referred to above or, solubility parameter, was defined by Hildebrand as the square root of the cohesive energy density:

$$\delta = \sqrt{\frac{\Delta E_{\text{vap}}}{V}}$$

where ΔE_{vap} and V are the energy or heat of vaporization and molar volume of the liquid, respectively. Hansen extended the original Hildebrand parameter to a three-dimensional cohesion parameter. According to this concept, the total solubility parameter, δ , is composed of 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 δ_D , δ_P and δ_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 can be found in "CRC Handbook of Solubility Parameters and Other Cohesion Parameters", second edition, pages 122-138. That and other references provide tables with the parameters for many compounds. In addition, methods for calculating those parameters are provided.

[0011] In some exemplary embodiments of the invention, S1 has a boiling point at 1atm between 100°C and 200°C and forms a heterogeneous azeotrope with water having a boiling point at 1 atm of less than 100 °C.

[0012] The S1 solvent includes alcohols and/or ketones and/or aldehydes having at least 5 carbon atoms. Optionally,

the S1 solvent includes only alcohols. In some exemplary embodiments of the invention, the alcohols include hexanol and/or 2-ethyl-hexanol.

[0013] As used in this specification and the accompanying claims the term "extractant" refers to a composition including an S1 solvent capable of selectively extracting an acid from an aqueous solution. In some exemplary embodiments of the invention, the "extractant" carries a contaminant load. In some exemplary embodiments of the invention, the aqueous solution is provided as an acidic aqueous substrate containing sugars. In some exemplary embodiments of the invention, contact between the extractant and the acidic aqueous substrate increases a concentration of sugars and decreases a concentration of acid in the substrate. According to various exemplary embodiments of the invention the substrate includes one or more impurities. Each of these impurities transfers, or fails to transfer, to the extractant with characteristic kinetics.

[0014] According to various exemplary embodiments of the invention the kinetics of transfer of each specific impurity can be influenced by the nature of the specific impurity, and/or reaction conditions (e.g. concentration and/or temperature and/or contact time and/or pH) and/or by the specific extractant employed.

[0015] The relative affinity of any specific impurity can be summarized as an S1/water distribution coefficient. The S1/water distribution coefficient is determined by generating a 1% solution of the impurity in S1, contacting that solution with an equivalent amount of water, equilibrating the two phases (mixing them until there is no further change in composition) to form an impurity-comprising organic phase (S1 rich) and an impurity-comprising aqueous phase, separating the two phases, analyzing each one of them for the impurity and dividing the concentration of the impurity in the organic phase by the concentration of the impurity in the aqueous phase.

[0016] According to various exemplary embodiments of the invention specific impurities may be characterized by an S1/water distribution coefficient greater than 1, optionally greater than 2, optionally greater than 3 and optionally greater than 5.

[0017] According to various exemplary embodiments of the invention a contribution of any specific impurity to the contaminant load in the extract will increase in proportion to its concentration in the substrate and/or in proportion to its S1/water distribution coefficient.

[0018] As used in this specification and the accompanying claims the term "extract" or "initial extract" refers to extractant which has been brought into contact with a substrate as described above and then separated. The extract includes extractant, acid and a portion of the impurities which have transferred to the S1 solvent and become part of the contaminant load.

[0019] In some exemplary embodiments of the invention, extractant from the extract is reused as extractant for additional extractions (e.g., to extract an additional portion of the substrate). In order to facilitate this reuse, an acid is separated from the extract to produce de-acidified extractant. Each time that de-acidified extractant is brought into contact with an additional portion of substrate, additional impurities migrate to the S1 extractant so that the contaminant load increases with each successive round of contact if no action is taken to reduce the load. If the contaminant load is allowed to increase indefinitely, it eventually contributes to loss of extraction capacity and/or hindrance to phase contact/separation. Some exemplary embodiments of the invention relate to systems and/or methods to maintain the contaminant load in an acceptable range. Optionally, the acceptable range is determined by considering extraction capacity and/or hindrance to phase contact/separation. According to various exemplary embodiments of the invention specific impurities are considered separately when determining the acceptable range. Alternatively or additionally, groups of impurities are considered separately when determining the acceptable range.

[0020] As used in this specification and the accompanying claims the term "contaminant load" refers to the sum total of impurities present in an S1 extract and/or S1 extractant at any given point. These impurities may include undesired materials present in the lignocellulosic substrate and/or breakdown products of sugars (e.g. furfurals) and/or solvent derivatives (e.g. esters or salts). The contaminant load includes one or more impurities selected from the group consisting of mineral acids, organic acids, anionic chloride complexes of heavy metals, alkyl chlorides, alkyl acetates and hydrophobic organic compounds, wherein "hydrophobic organic compounds" include one or more of phenolic compounds, aldehydes, furfural, hydroxymethylfurfural, tall oils, wood extractives and products of their reaction. In some exemplary embodiments of the invention, the viscosity of a solution containing 95% S1 and 5% contaminant load is greater by at least 1% compared with 100% S1. Optionally, various impurities contributing to the contaminant load have absorption in the visible spectrum.

[0021] One aspect of some embodiments of the invention relates to separating acid from the initial extract to produce de-acidified extract. Optionally, the initial extract is washed with acid. In some exemplary embodiments of the invention, this acid wash removes sugars, which can be recycled (e.g. to an upstream hydrolytic reaction). In some exemplary embodiments of the invention, this acid wash contributes to a reduction in sugar degradation. This reduction in degradation can contribute to a reduction in unwanted degradation products such as, for example, furfural from degradation of pentoses (e.g. xylose and arabinose) and hydroxymethylfurfural from degradation of hexoses (e.g. glucose, galactose and mannose). Alternatively or additionally, this acid wash contributes to a reduction in hydrophilic impurities in the initial extract. In some exemplary embodiments of the invention, acid is separated from the initial extract by distillation under

vacuum and a slightly elevated temperature to produce de-acidified extract which includes S1 solvent and a contaminant load.

[0022] One aspect of some embodiments of the invention relates to reducing a contaminant load in the de-acidified extract by refining. In some exemplary embodiments of the invention, refining is conducted so that a desired degree of extraction capacity and/or phase contact/separation of the S1 extractant is maintained.

[0023] In some exemplary embodiments of the invention, refining is conducted without distillation. Optionally, mineral acids and/or heavy metal complexes and/or acetic acid and/or acetates formed therefrom and/or hydrophobic impurities are at least partially removed from the de-acidified extract by the refining.

[0024] The refining involves treatment of the de-acidified extract with lime to produce limed extract. Optionally, lime is contacted with the de-acidified extract as a slurry (e.g. 2, 5, 10, 20 or 30% wt or intermediate or greater percentages) of solid lime suspended in water or an aqueous solution of lime. In some exemplary embodiments of the invention, addition of carbon dioxide to the limed extract causes precipitation of calcium carbonate. In some exemplary embodiments of the invention, the calcium carbonate is removed by filtration. In some exemplary embodiments of the invention, the filtered limed extract is washed with water to remove remaining calcium salts.

[0025] As used in this specification and the accompanying claims the term "carbonatation" indicates contacting a solution with CO₂ gas, either as a pure stream, or as part of a gaseous mixture containing CO₂.

[0026] As used in this specification and the accompanying claims the term "lime" indicates calcium oxide (also known as quicklime) and/or calcium hydroxide and/or calcium carbonate. According to various exemplary embodiments of the invention, lime is provided as a solid or in solution.

[0027] It will be appreciated that the various aspects described above relate to solution of technical problems related to reducing a requirement for solvent disposal in an industrial setting.

[0028] Alternatively or additionally, it will be appreciated that the various aspects described above relate to solution of technical problems related to reducing a concentration of one or more impurities which contribute to a contaminant load in a solvent recycling loop.

[0029] Specifically, there is provided by the present invention a method comprising: (a) contacting lime with an extract comprising an S1 solvent carrying a contaminant load to form a lime treated extract; and (b) reducing said contaminant load by removing solids; wherein said S1 solvent is an organic solvent selected from the group consisting of alcohols, ketones, and aldehydes having at least 5 carbon atoms, and further wherein said contaminant load comprises one or more impurities selected from the group consisting of mineral acids, organic acids, anionic chloride complexes of heavy metals, alkyl chlorides, alkyl acetates, phenolic compounds, aldehydes, furfural, hydroxymethylfurfural, tall oils, wood extractives and products of their reaction.

[0030] Optionally, at least 35% of the lime is recycled lime.

[0031] Optionally, the method includes carbonatating the removed solids with CO₂ gas to form a slurry including calcium carbonate. Optionally, the method includes carbonatating the lime treated extract with CO₂ gas to form a slurry including calcium carbonate.

[0032] Optionally, the method includes contacting the slurry with additional lime.

[0033] Optionally, the method includes washing the lime treated extract with water.

[0034] Optionally, the S1 solvent is n-hexanol. Optionally, the S1 solvent is 2-ethyl-1-hexanol. Optionally, the contaminant load is reduced by more than 20%.

[0035] Optionally, the method includes contacting an extractant including the S1 solvent with an acid hydrolyzate of a lignocellulosic substrate to produce an acid-carrying extract; and de-acidifying the acid carrying extract to produce the extract. Optionally, the method includes contacting an extractant including the S1 solvent with an acid including lignin composition to produce the extract.

[0036] Optionally, the apparent pH of the lime treated extract is at least 6.5.

[0037] Optionally, the apparent pH of the lime treated extract is not more than 8.5.

[0038] In some exemplary embodiments of the invention, there is provided a method including:

(a) contacting an acid hydrolyzate of a lignocellulosic substrate with a first extractant including an S1 solvent to produce an acid-reduced hydrolyzate containing sugars and a first extract containing S1 solvent carrying a contaminant load; (b) contacting the acid-reduced hydrolyzate with a second extractant including an S1 solvent and an S2 solvent to produce a de-acidified hydrolyzate containing sugars and a second extract including S1 solvent, S2 solvent, acid and water; (c) treating the first extract by the method of the invention to produce a first extract with a reduced contaminant load; and (d) recycling at least a portion of the first extract with a reduced contaminant load.

[0039] Optionally, the recycling includes use of the first extract with a reduced contaminant load as part of the first extractant.

[0040] Optionally, the recycling includes use of the first extract with a reduced contaminant load as part of the second extractant.

[0041] Optionally, the recycling includes use of the first extract with a reduced contaminant load to deacidify a lignin stream.

[0042] In some exemplary embodiments of the invention, there is provided a method including:

(a) cyclically contacting a first portion of an extractant including S1 solvent in a system with an acid hydrolyzate of a lignocellulosic substrate to produce an acid reduced hydrolyzate and an extract including acid and S1 solvent carrying a contaminant load; (b) de-acidifying the extract to form de-acidified extract with S1 solvent carrying the contaminant load; and (c) cyclically routing a second portion of the extractant including S1 solvent carrying a contaminant load to a decontamination module which applies a contaminant reduction process to the second portion to produce extractant with a reduced contaminant load, wherein the "contaminant reduction process" is the method of the present invention.

[0043] Optionally, the method includes cyclically contacting a third portion of an extractant including S1 solvent in a system with an acid including lignin stream from hydrolysis of a lignocellulosic substrate to produce an acid reduced lignin stream and an extract including S1 solvent and a contaminant load.

[0044] Optionally, a size of the first portion is larger than a size of the second portion.

[0045] Optionally, a size of the third portion is larger than a size of the second portion.

[0046] Optionally, the method includes coordinating the cyclically contacting and the cyclically routing so that a contaminant load in the first portion is maintained in a desired range.

[0047] Optionally, the S 1 solvent is n-hexanol.

[0048] Optionally, the S1 solvent is 2-ethyl-1-hexanol.

[0049] Optionally, the contaminant reduction process includes carbonatation with a gas stream including CO₂.

[0050] Optionally, carbonatation is conducted without removal of S 1 solvent.

[0051] Optionally, carbonatation is conducted following removal of S1 solvent.

[0052] In some exemplary embodiments of the invention, there is provided an apparatus comprising: (a) a decontamination module adapted to contact lime with an extract comprising an S1 solvent carrying a contaminant load to produce limed extract; (b) a solids removal mechanism adapted to remove solids from said limed extract; (c) an acidulating mechanism adapted to acidify said limed extract; and (d) a washing mechanism adapted to wash said acidulated extract; wherein said S 1 solvent is an organic solvent selected from the group consisting of alcohols, ketones, and aldehydes having at least 5 carbon atoms, and further wherein said contaminant load comprises one or more impurities selected from the group consisting of mineral acids, organic acids, anionic chloride complexes of heavy metals, alkyl chlorides, alkyl acetates, phenolic compounds, aldehydes, furfural, hydroxymethylfurfural, tall oils, wood extractives and products of their reaction.

[0053] Optionally, the apparatus includes a de-acidification module adapted to separate acid from an extract including acid and S 1 solvent carrying a contaminant load and output a de-acidified extract.

[0054] Optionally, the apparatus includes a carbonatation mechanism adapted to bubble a stream of gas including CO₂ through the limed extract.

[0055] Optionally, the apparatus includes a carbonatation mechanism adapted to bubble a stream of gas including CO₂ through the removed solids.

[0056] Optionally, the apparatus includes a controller designed and configured to coordinate activity of the modules and mechanism so that a contaminant load in the limed extract after solids removal is less than 80% of a contaminant load in the extract introduced into the de-acidification module.

[0057] Optionally, the apparatus includes a controller designed and configured to coordinate activity of the modules and mechanism so that a contaminant load in the extract is maintained in a desired range.

[0058] By carrying out the methods of the invention, there can be provided a calcium composition including (on a dry weight basis) at least 1% calcium carbonate; and at least 1% furfurals.

[0059] Optionally, the composition includes at least 5 % furfurals.

[0060] Optionally, the composition includes at least 5% phenolic compounds.

[0061] Optionally, the composition includes at least 0.1% calcium acetate.

[0062] Optionally, the composition includes at least 0.5% of calcium formate.

[0063] Optionally, the composition includes hexanol.

[0064] Optionally, the composition includes 2-ethyl hexanol.

[0065] By carrying out the methods of the invention, there can be provided a suspension including (on a weight basis): (a) two hundred parts S1 solvent carrying a contaminant load; and (b) at least one part lime solids.

[0066] Optionally, the lime solids are present as an aqueous slurry.

[0067] Optionally, the contaminant load includes at least 0.2% furfurals relative to the solvent.

[0068] Optionally, the contaminant load includes at least 0.2% phenolic compound relative to the solvent.

[0069] Optionally, the suspension includes calcium acetate.

[0070] Optionally, the suspension includes calcium formate.

[0071] In some exemplary embodiments of the invention, there is provided a method including: (a) contacting an acid hydrolyzate of a lignocellulosic substrate with a flow of extractant including an S1 solvent to produce an acid-reduced hydrolyzate containing sugars and a first extract containing S1 solvent and a contaminant load;

(b) subjecting the acid-reduced hydrolyzate to a secondary hydrolysis reaction and chromatographic separation to produce a de-acidified hydrolyzate containing sugars;

(c) contacting the de-acidified hydrolyzate with the extractant at an upstream point in the flow; (d) treating the first extract by a method according to the invention to produce a first extract with a reduced contaminant load; and (e) recycling at least a portion of the first extract with a reduced contaminant load.

[0072] In some exemplary embodiments of the invention, there is provided a method including: (a) diverting a portion of an extractant flow including S1 solvent carrying a contaminant load from an industrial process; (b) contacting the portion with lime to form a lime treated portion; (c) separating the lime from the lime treated portion to form extractant including S1 solvent carrying a reduced contaminant load; and (d) re-using the S1 solvent with reduced contaminant load in the industrial process.

[0073] Optionally, the industrial process is acid-catalyzed hydrolysis of lignocellulosic substrate.

[0074] Optionally, the method includes carbonatating any liquid or solid resulting from the separation with CO₂ gas to form a slurry including calcium carbonate.

[0075] Optionally, at least 30% of the extractant from the industrial process is used in (a) through (d).

[0076] In some exemplary embodiments of the invention, there is provided a method of producing a sugar composition from lignocellulosic substrate including:

(a) contacting a lignocellulosic substrate with hydrochloric acid to produce a hydrolyzate and an HCl-including lignin composition; (b) treating at least one of the hydrolyzate and the lignin composition with an extractant including S1 solvent to form an extract including S1 solvent carrying a contaminant load;

(c) de-acidifying the extract to form de-acidified extract; (d) contacting lime with the de-acidified extract to form a lime treated extract; (e) reducing the contaminant load by removing solids to form an extract with reduced contaminant load; (f) using at least a portion of the extract with reduced contaminant load in the treating; (g) processing the hydrolyzate to produce a sugar composition.

[0077] Optionally, the sugar composition contains at least 1ppm of an impurity from the contaminant load.

[0078] In some exemplary embodiments of the invention, there is provided a method of producing a commercial product from lignocellulose including: (a) contacting a lignocellulosic substrate with hydrochloric acid to produce a hydrolyzate; (b) extracting the hydrolyzate with an extractant including S1 solvent to separate hydrochloric acid therefrom and to form an extract including S1 solvent carrying a contaminant load; (c) de-acidifying the extract to form de-acidified extract and recover hydrochloric acid; (d) contacting lime with the de-acidified extract to recover S1 solvent carrying a reduced contaminant load; and (e) processing the hydrolyzate to produce a commercial product.

[0079] Optionally, the commercial product is an acrylic-based or poly-acrylic based product.

[0080] 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 present 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.

[0081] For purposes of this specification and the accompanying claims any feature, process or component depicted or described in the singular shall also represent two or more of the feature, process or component so depicted or described.

[0082] 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.

[0083] The phrase "consisting essentially of" or grammatical variants thereof when used herein are to be taken as specifying the stated features, integers, steps or components but do not preclude the addition of one or more additional features, integers, steps, components or groups thereof but only if the additional features, integers, steps, components or groups thereof do not materially alter the basic and novel characteristics of the claimed composition, device or method.

[0084] 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 architecture and/or computer science.

[0085] Percentages (%) of chemicals typically supplied as powders or crystals (e.g. lime) are W/W (weight per weight) unless otherwise indicated. Percentages (%) of chemicals typically supplied as liquids (e.g. HCl) are also W/W (weight per weight) unless otherwise indicated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0086] 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. The attached figures are:

Fig. 1 is schematic overview of an exemplary system for hydrolysis of lignocellulosic substrate which serves as a context for some exemplary embodiments of the invention;

Fig. 2 is schematic representation of an exemplary contaminant reduction apparatus according to some exemplary embodiments of the invention;

Fig. 3 is schematic overview of a contaminant reduction process according to some exemplary embodiments of the invention;

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

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

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

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

Fig. 6a is a schematic representation of materials flow according to some exemplary embodiments of the invention;

Fig. 6b is a schematic representation of materials flow according to additional exemplary embodiments of the invention; and

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

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

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

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

DETAILED DESCRIPTION OF EMBODIMENTS

[0087] Embodiments of the invention relate to methods and apparatus for solvent purification.

[0088] Specifically, some embodiments of the invention can be used to purify a solvent to a sufficient degree so that it can be recycled in an industrial process. Optionally, the industrial process relates to acid hydrolysis of lignocelluloses to produce sugars and/or lignin.

[0089] The principles and operation of a method and/or apparatus according to exemplary embodiments of the invention may be better understood with reference to the drawings and accompanying descriptions.

[0090] 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.

Overview of exemplary system

[0091] 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" as described hereinbelow can be used as lignocellulosic substrate input 112.

[0092] As used in this specification and the accompanying claims the term "woody material" or "lignocellulosic material" includes, but is not limited to, wood and by-products of wood processing (e.g. chips, sawdust, and shavings) as well as residual plant material from agricultural products and paper and paper industry byproducts (e.g. cellulose containing residues and/or paper pulp)

[0093] Residual plant material from agricultural products includes processing by-products and field remains.

[0094] Processing by-products include, but are not limited to, corn cobs, sugar cane bagasse, sugar beet pulp, empty fruit bunches from palm oil production, straw (e.g. wheat or rice), soy bean hulls, residual meals from the vegetable oil industry (e.g. soybean, peanut, corn or rapeseed), wheat bran and fermentation residue from the beer and wine industries.

[0095] Field remains include, but are not limited to, corn stover, post harvest cotton plants, post harvest soybean bushes and post harvest rapeseed plants.

[0096] Lignocellulosic materials also include "energy crops" such as switch grass and broom grass which grow rapidly and generate low-cost biomass specifically as a source of carbohydrates.

[0097] These lignocellulosic carbohydrate sources contain cellulose, hemicellulose and lignin as their main components and also contain mineral salts (ashes) and lipophilic organic compounds, such as tall oils.

[0098] Cellulose and hemicellulose are polysaccharides which can release sugars suitable for fermentation and/or chemical conversion to products of interest if they are hydrolyzed. Lignin is typically resistant to acid hydrolysis.

[0099] Although conversion of lignocellulosic material to sugars via enzyme-catalyzed and/or acid-catalyzed hydrolysis of polysaccharides and pyrolysis of lignocellulosic material have been previously described, industrial scale application of the proposed technologies has presented technical problems which remain to be overcome.

[0100] Substrate 112 is brought into contact with a concentrated solution of HCl (or another strong acid such as sulfuric acid) in reactor 110 and hemicellulose and/or cellulose in the substrate are hydrolyzed to produce a mixture of soluble sugars (product) and residual lignin (co-product). These materials are collected separately as sugar mixture 130 and lignin stream 120 (which also contains sugars), each of which contains a large amount of acid. In addition, sugar mixture 130 and lignin stream 120 each contains a variety of impurities which may originate in substrate 112 and/or result from degradation of sugars produced by hydrolysis.

[0101] Since the acid acts as a catalyst, it is not consumed in the process. Therefore, downstream use of sugar mixture 130 and/or lignin stream 120 may require that their acid content be reduced. According to various exemplary embodiments of the invention, separation of acid from sugar mixture 130 and/or lignin stream 120 is conducted under conditions minimizing thermal degradation of sugars.

[0102] Details of exemplary hydrolysis methods and systems are described in detail in co-pending US provisional applications 61/483,777 and 61/487,319.

[0103] US 61/358,894 describes processing of sugar mixture 130 including removal of acid and/or adjustment of the mixture in a sugar refining module, designated here generically as 201.

[0104] Optionally, additional sugar mixture is recovered from lignin stream 120 as described in co-pending US provisional application US 61/491,243. In some exemplary embodiments of the invention, this additional sugar mixture is routed to refining module 201.

[0105] Refining module 201 employs a flow of organic solvent 155 (solid arrows) to extract acid 140 (dashed arrows) from sugar mixture 130.

[0106] Although de-acidified sugars 230 are the primary product of refining module 201, the module also produces a stream of acid 140 mixed with solvent 155 (depicted as parallel dashed and solid arrows respectively for clarity) which is routed to a solvent/acid recovery module 150. Recovery module 150 separates acid 140 from solvent 155. In some exemplary embodiments of the invention, separation is by distillation. Acid 140 is recycled to hydrolysis reactor 110 and de-acidified solvent 155 is recycled to refining module 201.

[0107] In some exemplary embodiments of the invention, acid and/or solvent are also recovered from lignin stream 120 and routed to recovery module 150. Briefly this involves separation of acid and sugars from lignin stream and recovery of these materials. This process is analogous to that described here for sugar stream 130 and optionally uses recovery module 150 or a parallel module with similar function.

[0108] According to various exemplary embodiments of the invention, recovery module 150 includes, or is in communication with, a contaminant reduction module 200. In other exemplary embodiments of the invention contaminant reduction module 200 is included in, or in communication with, refining module 201.

[0109] Contaminant reduction module 200 processes at least a portion of solvent 155 to reduce a contaminant burden therein. In some exemplary embodiments of the invention, the portion of solvent 155 processed by contaminant reduction module 200 is mixed with unprocessed solvent 155.

[0110] Although recovery module 150 is depicted and described here as operating on sugar mixture 130 via refining module 201, similar procedures can be applied to lignin stream 120 to produce additional exemplary embodiments of the invention.

Exemplary contaminant reduction equipment

[0111] Fig. 2 is a schematic representation of an exemplary contaminant reduction apparatus indicated generally as 200. Depicted exemplary apparatus 200 includes a decontamination module 210 adapted to contact lime with an extract, namely a de-acidified extract comprising an S 1 solvent carrying a contaminant load to produce limed extract.

[0112] In the depicted exemplary embodiment of the invention, there is an adaptation to contact lime with a de-acidified extract which includes a connection to recovery module 150 so that de-acidified extract (represented for simplicity as S1 solvent 155) is delivered to module 210 as indicated by rightward pointing solid arrow. Recovery module 150 can be described as a de-acidification module adapted to separate acid from an extract comprising acid and S 1 solvent carrying

a contaminant load and output the de-acidified extract.

[0113] In some exemplary embodiments of the invention, adaptation to contact lime with a de-acidified extract includes a connection to a lime source 212 which can deliver an appropriate amount of lime to module 210 as indicated by a leftward pointing hollow arrow.

[0114] Optionally, source 212 is adapted to deliver 1 unit of 10% lime slurry for every 20 units of S1 solvent introduced into module 210. Alternatively or additionally, source 212 is adapted to deliver 1 unit of lime solids for every 200 units of S1 solvent introduced into module 210.

[0115] Alternatively or additionally, in some exemplary embodiments of the invention, adaptation to contact lime with a de-acidified extract includes provision of a mixing mechanism in module 210. In the depicted embodiment, the mixing mechanism includes a mechanical stirrer 214 in module 210. In some exemplary embodiments of the invention, the mixing mechanism can include, for example, a shaker or rocker which moves all of module 210 so that liquid contained therein is agitated. In some exemplary embodiments of the invention, the mixing mechanism can include a re-circulation pump that creates a flow of liquid in module 210 so that the liquid contained therein is agitated.

[0116] Depicted exemplary apparatus 200 also includes a solids removal mechanism adapted to remove solids from limed extract resulting from contact between lime supplied by lime source 212 with de-acidified extract arriving from recovery module 150. According to various exemplary embodiments of the invention solids removal may include settling and/or decantation and/or centrifugation and/or filtration. In the depicted embodiment the solids removal mechanism includes a filter 222. In some exemplary embodiments of the invention, filter 222 is a gravimetric filter. In the depicted exemplary embodiment, filter 222 is connected to a vacuum source 224. Optionally, use of vacuum increase filtration rates. In some exemplary embodiments of the invention, decreasing a pore size in filter 222 contributes to an increase in efficiency of solids removal.

[0117] Depicted exemplary apparatus 200 includes an optional carbonatation mechanism 230 adapted to bubble a stream of gas 238 comprising CO₂ through limed extract present in module 210. In the depicted embodiment, carbonatation mechanism 230 includes a CO₂ source 232 depicted as a pressurized cylinder equipped with a regulator 236. CO₂ source 232 is connected to module 210 by a hose 234 (depicted as a rightward pointing arrow) which delivers a stream of gas 238 bubbles through limed extract present in module 210. According to various exemplary embodiments of the invention CO₂ source 232 can be provided as dry ice or as exhaust gas from a fermentor. In other exemplary embodiments of the invention, the apparatus is configured so that the carbonatation mechanism bubbles a stream of gas comprising CO₂ through removed solids, optionally provided as a slurry.

[0118] In the depicted embodiment, module 210 is equipped with a heat source 216 so that contacting between lime and the de-acidified extract can be conducted at a desired temperature.

[0119] In the depicted exemplary embodiment, apparatus 200 includes a controller 250 designed and configured to coordinate activity of module 210 with lime source 212 and/or de-acidification module 150. Alternatively or additionally, controller 250 can be designed and configured to operate components of module 210 such as heater 216 and/or the mixing mechanism (e.g. stirrer 214). Alternatively or additionally, controller 250 can be designed and configured to operate the solids removal mechanism (e.g. filter 222) in coordination with a schedule. Alternatively or additionally, controller 250 can be designed and configured to operate carbonatation mechanism 230, optionally in coordination with a schedule.

[0120] According to various exemplary embodiments of the invention design and configuration of controller 250 is performed so that a contaminant load in the limed extract after solids removal (255) is less than 80%; 70%; 60%; 50%; 40%; 30%; 20%; 10% of a contaminant load in extract 155 introduced into de-acidification module 150.

[0121] In some exemplary embodiments of the invention, design and configuration of controller 250 is performed so that that a contaminant load in said first portion is maintained in a desired range.

Exemplary process overview

[0122] Fig. 3 is schematic overview of a contaminant reduction process according to some exemplary embodiments of the invention indicated generally as 300. According to exemplary process 300, a hydrolyzate 130 as described above in the context of Fig. 1 is contacted with an S1 extractant 310. Since S1 is only slightly soluble in water, this contacting produces an unstable mixture which is easily separated into an aqueous sugar solution 312 and an extract 320. Extract 320 contains significant amounts of acid (typically HCl) as well as S1 solvent and a contaminant load. Because the acid and S1 extractant 310 have separate roles in the scheme described above in the context of Fig. 1, it is desirable to attempt to separate them so that each can be re-cycled independently.

[0123] In the depicted embodiment, this separation is achieved (at least in part) by de-acidification 330 to produce a de-acidified extract 340 (still containing S1 solvent and the contaminant load). De-acidification 330 also produces acid 332 (typically HCl) containing hydrophilic impurities. In some exemplary embodiments of the invention, de-acidification 330 relies, at least in part, on distillation.

[0124] The remainder of depicted exemplary process 300 deals with reduction of the contaminant load present in

extract 320 and carried through to de-acidified extract 340. In the depicted exemplary embodiment, de-acidified extract 340 is contacted with lime 350 to produce a limed extract 360. Optionally, solids 352 are removed at this stage. Removal can be, for example, by filtration and/or centrifugation and/or settling and/or decanting.

[0125] In the depicted exemplary embodiment limed extract 360 is carbonated by bubbling a stream of CO₂ containing gas 370 through it. Carbonation causes formation of calcium carbonate which is insoluble in the extract so that a slurry of calcium carbonate forms. Solids 372 are removed at this stage. Optionally, additional lime 371 is added prior to, or concurrent with removal of solids 372. Again, removal can be, for example, by filtration and/or centrifugation and/or settling and/or decanting.

[0126] Optionally, the extract is washed 375 with water to remove dissolved salts at this stage. The final product is a refined extract 380.

First exemplary method

[0127] Fig. 4a is a simplified flow diagram depicting a method to reduce a contaminant load in a solvent indicated generally as 400. Depicted exemplary method 400 includes contacting 410 lime with an extract comprising an S1 solvent and a contaminant load to form a lime treated extract 420 and reducing 430 the contaminant load by removing solids. In some exemplary embodiments of the invention, the lime employed at contacting 410 includes 25; 30; 35; 40; 45; 50; 55; 60; 65; 70 or 75% or intermediate or greater percentages of lime recycled from a previous round of contacting. Optionally, this recycling is repeated. In some exemplary embodiments of the invention, the repetition is with a constant percentage and/or a varying percentage of lime. Optionally, contacting 410 reduces the contaminant load in ways not directly related to solids removal, as described below in the section entitled "exemplary hydrolysis considerations".

[0128] In some exemplary embodiments of the invention, method 400 includes carbonating 440 lime treated extract 420 with CO₂ gas to form a slurry comprising calcium carbonate. Optionally, this occurs before reducing 430 the contaminant load by removing solids. Removal of solids at this stage is indicated as 372 in Fig. 3.

[0129] In other exemplary embodiments of the invention, carbonating 440 is performed on removed solids 352 (Fig. 3) from extract 420 to form a slurry comprising calcium carbonate.

[0130] Optionally, method 400 includes contacting the slurry with additional lime 450 before and/or during reducing 430 the contaminant load by removing solids. Optionally, the removed solids are recovered as described below in the context of item 680 (Figs. 6a and/or 6b). In some exemplary embodiments of the invention, a portion of the removed solids are salts of esters derived from the solvent. Optionally, removal of these esteric salts contributes to reduction of the contaminant load and/or regenerates solvent. In some exemplary embodiments of the invention, method 400 includes washing 460 with water. Optionally, wash 460 removes residual salts, such as calcium salts.

[0131] In some exemplary embodiments of the invention, contacting 410 has a duration of at least 1 minute and/or occurs at a temperature of at least 50°C. Optionally, the contacting temperature is 60, 70, 80, 90, 100 or 110 degrees centigrade or intermediate or higher temperatures. Alternatively or additionally, the contact time is optionally at least 5, 10, 20, 40, 80 or 160 minutes or intermediate or longer times. Alternatively or additionally, the contact time is less than 10, 9, 8, 7, 6, 5, 4, 3, 2 or 1 hours. In some exemplary embodiments of the invention, the contact time is in the range of 5 minutes to 120 hours, optionally 10 minutes to 8 hours, optionally 1 hour to 5 hours.

[0132] In some exemplary embodiments of the invention, S1 includes, consists of, or consists essentially of, an alcohol, and the contaminant load includes an alkyl chloride corresponding to said alcohol. Alternatively or additionally, in some exemplary embodiments of the invention S1 includes, consists of, or consists essentially of, an alcohol, and the contaminant load includes an alcohol-carboxylic acid ester. Exemplary alcohol-carboxylic acid esters include, but are not limited to formates, acetates, and levulinates.

[0133] Alternatively or additionally, the contaminant load may optionally include one or more of phenols, aldehydes, furfurals (e.g. furfural and hydroxymethylfurfural), chloride complexes of transition metals, tall oils, wood extractives and products of their reaction with acid and/or the S1 extractant.

[0134] According to various exemplary embodiments of the invention, the contaminant load is reduced by at least 20, optionally at least 30, optionally at least 40, optionally at least 50, optionally at least 60, optionally at least 70, optionally at least 80, optionally at least 90% or intermediate or greater percentages.

[0135] In some exemplary embodiments of the invention, method 400 includes preparing 470 the extract by contacting the S 1 solvent with an acid hydrolyzate of a lignocellulosic substrate to produce an acidic extract and de-acidifying the acidic extract to produce the extract employed at 410 as shown in Fig. 4a.

[0136] Alternatively or additionally, method 400 includes preparing 470 the extract by contacting the extractant comprising said S1 solvent with an acid comprising lignin composition to produce the extract employed at 410 as shown in Fig. 4a.

[0137] In some exemplary embodiments of the invention, the apparent pH of lime treated extract 420 is at least 6.5. In some exemplary embodiments of the invention, the apparent pH of lime treated extract 420 is not more than 8.5. Optionally, the apparent pH of lime treated extract 420 is between 6.5 and 8.5, optionally between 7 and 8, optionally

between 7.3 and 7.6.

[0138] As used in this specification and the accompanying claims the term "apparent pH" of an organic solution indicates the pH in an aqueous solution in equilibrium with the organic solution.

[0139] Alternatively or additionally, in some exemplary embodiments of the invention, the pH of the slurry produced at 440 is at least 6.5. In some exemplary embodiments of the invention, the pH of the slurry produced at 440 is not more than 8.5. Optionally, the pH of the slurry produced at 440 is between 6.5 and 8.5, optionally between 7 and 8, optionally between 7.3 and 7.6.

Second exemplary method

[0140] Fig. 4b is a simplified flow diagram of a solvent recycling method according to some exemplary embodiments of the invention depicted generally as method 401. Depicted exemplary method 401 includes contacting 411 an acid hydrolyzate (e.g. 130 in Fig. 1) of a lignocellulosic substrate with a first extractant comprising an S1 solvent to produce an acid-reduced hydrolyzate 421 containing sugars and a first extract 431 containing S1 solvent carrying a contaminant load. The contaminant load includes contaminants extracted from the hydrolyzate by contacting 411 and optionally contaminants which were present prior to contacting 411.

[0141] In depicted exemplary embodiment 401, acid-reduced hydrolyzate 421 is contacted 441 with a second extractant comprising an S1 solvent and an S2 solvent to produce a de-acidified hydrolyzate 461 containing sugars and a second extract 451 comprising S1 solvent, S2 solvent, acid and water.

[0142] In other exemplary embodiments of the invention, transformation of acid-reduced hydrolyzate 421 to de-acidified hydrolyzate 461 is carried out by other methods. Optionally, two, three, four or five or more rounds of contacting 411 are conducted. Optionally, a second hydrolysis reaction is performed between a pair of these rounds of contacting 411. Alternatively or additionally, chromatographic separation, such as ion exchange chromatography, may be employed (see description of Fig. 7 below).

[0143] In some exemplary embodiments of the invention, first extract 431 is treated by method 400 (Fig. 4a; beginning from contacting 410) to produce a first extract with a reduced contaminant load 481. According to method 401, at least a portion of extract 481 with a reduced contaminant load is recycled 490.

[0144] Optionally, recycling 490 includes use 492 of at least a portion of extract 481 with a reduced contaminant load as part of the first extractant at 411. Alternatively or additionally, recycling 490 optionally includes use 494 of at least a portion of extract 481 with a reduced contaminant load as part of the second extractant at 441. Alternatively or additionally, recycling 490 optionally includes use 496 of at least a portion of extract 481 with a reduced contaminant load to de-acidify a lignin stream.

Third Exemplary Method

[0145] Fig. 4c is a simplified flow diagram of a solvent recycling method according to some exemplary embodiments of the invention depicted generally as method 402. Depicted exemplary method relates to de-acidification 496 (Fig. 4b) of a lignin stream (e.g. 120 in Fig. 1). Depicted exemplary method 402 includes de-acidifying 496 the lignin stream to produce an acid-depleted lignin stream 412 and an acidic extract 422 of lignin comprising S1. The remainder of method 402 relates to treatment of extract 422.

[0146] Depicted method 402 includes separating acid 432 from acidic extract 422 to form separated acid 442 and S1 452 recovered from lignin carrying a contaminant load.

[0147] In some exemplary embodiments of the invention, S1 452 recovered from lignin carrying a contaminant load is treated by method 400 (Fig. 4a; beginning from contacting 410) to produce S1 462 recovered from lignin carrying a reduced contaminant load.

[0148] Depicted exemplary method 402 includes recycling 472 at least a portion of S1 462 recovered from lignin carrying a reduced contaminant load.

[0149] Optionally, recycling 472 includes using 493 at least a portion of S1 462 recovered from lignin carrying a reduced contaminant load as part of the first extractant at 411 (Fig. 4b).

[0150] Alternatively or additionally, recycling 472 includes using 495 at least a portion of S1 462 recovered from lignin carrying a reduced contaminant load as part of the second extractant at 441 (Fig. 4b).

[0151] Alternatively or additionally, recycling 472 includes using 497 at least a portion of S1 462 recovered from lignin carrying a reduced contaminant load to de-acidify 496 a lignin stream.

Fourth Exemplary Method

[0152] Fig. 5 is a simplified flow diagram of a solvent recycling method according to some exemplary embodiments of the invention depicted generally as method 500. Depicted exemplary method 500 manages flow of an S1-extractant

circulation system 501.

[0153] In some exemplary embodiments of the invention, S1 extractant circulation system 501 is installed in the context of system 100 as depicted in Fig. 1. In some exemplary embodiments of the invention, S1 extractant circulation system 501 is designed and configured to bring an extractant containing S1 into contact with acid hydrolyzate 130 and/or lignin stream 120. Various exemplary uses of S1 solvent circulating in the system are described hereinabove in the context of Figs. 4b (e.g. 490; 492; 494; 496) and 4c (e.g. 472; 493; 495 and 497).

[0154] As will become clear from the following explanation, S1 extractant circulation system 501 contains a mixture of de-acidified extract 340 and refined extract 380 (Fig. 3).

[0155] Depicted exemplary method 500 includes cyclically contacting 510 a first portion of S1 extractant in system 501 with an acid hydrolyzate of a lignocellulosic substrate to produce an acid reduced hydrolyzate 520 and an extract 530 comprising acid and S1 solvent carrying a contaminant load. Since contacting 510 is cyclic, the contaminant load would tend to increase in proportion to the number of cycles if no action to reduce the contaminant load is implemented.

[0156] Depicted exemplary method 500 also includes de-acidifying 540 extract 530 and removing acid 541 from system 501. Optionally, acid 541 is recycled to the hydrolysis reaction in 110 (Fig. 1). De-acidifying 540 produces a de-acidified extract comprising S1 542 carrying a contaminant load which is returned to system 501. S1 542 carrying the contaminant load is analogous to de-acidified extract 340 of Fig. 3.

[0157] System 501 also carries water. Due to the properties of S1 solvents described above, this water tends to migrate to the acid phase, however some water will be present in S1 542 carrying a contaminant load and this water will return to system 501.

[0158] Depicted exemplary method 501 also includes cyclically routing 550 a second portion of S1 extractant carrying a contaminant load to a decontamination module which applies a contaminant reduction process 560 to the S1 solvent to produce S1 solvent 570 with a reduced contaminant load which is returned to system 501. S1 solvent 570 with a reduced contaminant load is analogous to refined extract 380 of Fig. 3.

[0159] In the depicted embodiment, the process which is depicted as a linear progression in Fig. 3 is implemented as two separate processing loops which intersect at system 501. Division of the linear progression into separate processing loops allows separate regulation of the relative amount of S1 in system 501 which is subject to the two halves of the total process (i.e. the relative sizes of the first portion at 510 and the second portion at 550).

[0160] Optionally, method 500 includes cyclically contacting a third portion of an extractant comprising S1 solvent in system 501 with an acid comprising lignin stream from hydrolysis of a lignocellulosic substrate to produce an acid reduced lignin stream and an extract comprising S1 solvent and a contaminant load. This extract is depicted as "distillation purge" 611 in Fig. 6b hereinbelow. The third portion can optionally be diverted from the first portion, the second portion, or from system 501. In some exemplary embodiments of the invention, a size of the third portion is larger than a size of the second portion.

Fifth exemplary method

[0161] Fig. 7 is a simplified flow diagram of a solvent recycling method according to some exemplary embodiments of the invention depicted generally as method 700. Depicted exemplary method 700 includes contacting 711 an acid hydrolyzate of a lignocellulosic substrate with a flow of extractant comprising an S1 solvent to produce an acid-reduced hydrolyzate 721 containing sugars and a first extract 731 containing S1 solvent and a contaminant load.

[0162] Depicted exemplary method 700 includes subjecting acid-reduced hydrolyzate 721 to secondary hydrolysis reaction and chromatographic separation 741 to produce a de-acidified hydrolyzate 761 containing sugars. In the depicted embodiment, de-acidified hydrolyzate 761 is contacted 731 with the extractant at an upstream point in the flow. Since the extractant flows in a countercurrent direction to the hydrolyzate, contacting 731 is a "first contact" from the standpoint of the extractant and a "second" contact from the standpoint of the hydrolyzate. Conversely, contacting 711 is a "first contact" from the standpoint of the hydrolyzate and a "second" contact from the standpoint of the extractant.

[0163] In the depicted embodiment, first extract 731 is treated by a method according to as described above (Fig. 4a; 410) to produce a first extract 781 with a reduced contaminant load. Method 700 includes recycling 790 at least a portion of extract 781 with a reduced contaminant load. According to various exemplary embodiments of the invention recycling 790 includes use 792 as first extractant at 711 and/or use 796 to deacidify a lignin stream.

Sixth exemplary method

[0164] Fig. 8a is a simplified flow diagram of a method for recycling extractant in an industrial process according to some exemplary embodiments of the invention depicted generally as method 801.

[0165] Depicted exemplary method 801 includes diverting 803 a portion of an extractant flow comprising S1 solvent carrying a contaminant load from an industrial process 899 and contacting 805 the portion with lime to form a lime treated portion 807.

[0166] Depicted exemplary method 801 also includes separating 809 the lime 811 from lime treated portion 807 to form extractant 813 comprising S1 solvent carrying a reduced contaminant load re-using extractant 813 in the industrial process 899.

[0167] Optionally, industrial process 899 is acid-catalyzed hydrolysis of a lignocellulosic substrate.

[0168] In some exemplary embodiments of the invention, method 801 includes carbonatating a liquid and/or solid resulting from lime treated portion 807 before and/or after separation 809 with CO₂ gas to form a slurry comprising calcium carbonate.

[0169] Optionally, the diverted portion of the extractant is at least 30% of the extractant in process 899.

Seventh exemplary method

[0170] Fig. 8b is a simplified flow diagram of sugar production method according to some exemplary embodiments of the invention depicted generally as method 802.

[0171] Depicted exemplary method 802 includes contacting 810 a lignocellulosic substrate with hydrochloric acid to produce a hydrolyzate 812 and an HCl-comprising lignin composition 820.

[0172] Exemplary method 802 includes treating at least one of hydrolyzate 812 and lignin composition 820 with an extractant 830 comprising S1 solvent to form an extract 840 comprising S1 solvent carrying a contaminant load. Exemplary method 802 includes de-acidifying 850 extract 840 to form de-acidified extract 851 and contacting lime 860 with de-acidified extract 851 to form a lime treated extract.

[0173] Method 802 includes reducing the contaminant load by removing solids 860 to form an extract 861 with reduced contaminant load. In some exemplary embodiments of the invention, at least a portion of extract 861 is used in treating at 830. Alternatively or additionally, at least a portion of HCL 852 can be used in the hydrolysis at 810.

[0174] Depicted exemplary method 802 also includes processing 8790 hydrolyzate 812 to produce a sugar composition 880.

[0175] Optionally, sugar composition 880 contains at least 1ppm of an impurity from the contaminant load. Sugar composition 880 is an additional exemplary embodiment of the invention.

Eighth exemplary method

[0176] Fig. 8c is a simplified flow diagram of a production method for commercial products according to some exemplary embodiments of the invention depicted generally as method 804.

[0177] Depicted exemplary method 804 includes contacting 810 a lignocellulosic substrate with hydrochloric acid to produce a hydrolyzate 812 and extracting hydrolyzate 812 with an extractant 830 comprising S 1 solvent to form an extract comprising S 1 solvent 840 carrying a contaminant load. In the depicted embodiment, extract 840 is de-acidified 850 to form de-acidified extract 851 and recover hydrochloric acid 852.

[0178] In the depicted exemplary embodiment, de-acidified extract 851 is contacted with lime 860 to recover S1 solvent 861 carrying a reduced contaminant load. In the depicted exemplary embodiment, processing 872 of hydrolyzate 812 produces a commercial product 882.

[0179] In some exemplary embodiments of the invention, commercial product 882 is an acrylic-based or poly-acrylic based product. Such products include, but are not limited to plastics, floor polishes, carpets, paints, coatings, adhesives, dispersions, flocculants, elastomers, acrylic glass, absorbent articles, incontinence pads, sanitary napkins, feminine hygiene products, and diapers.

[0180] Products 882 produced according to method 804 are additional exemplary embodiments of the invention.

Exemplary contaminant load regulation considerations

[0181] Since S1 solvent in system 501 re-circulates, addition to the contaminant load at 510 creates a need for a compensatory removal from the contaminant load at 560. If this need is not met, the contaminant load in system 501 will increase and will eventually reach a point where it interferes with the extraction at 510. According to various exemplary embodiments of the invention different ways to achieve this compensation are implemented.

[0182] Some of the ways to achieve this compensation rely on volume regulation.

[0183] In some exemplary embodiments of the invention, a size of the first portion at 510 is larger than a size of the second portion at 550. Optionally, this strategy may be advantageous if contaminant reduction process 560 is efficient. In this context "efficient" means that a total amount of contaminants removed from the second portion by contaminant reduction process 560 is at least equal to a total amount of contaminants added to the first portion, despite the fact that the first portion is larger.

[0184] In other exemplary embodiments of the invention, a size of the first portion at 510 is smaller than a size of the second portion at 550. Optionally, this strategy may be advantageous if contaminant reduction process 560 is inefficient.

In this context "inefficient" means that a total amount of contaminants removed from the second portion by contaminant reduction process 560 will only be at least equal to a total amount of contaminants added to the first portion if the second portion is larger.

[0185] Alternatively or additionally, some of the ways to achieve this compensation consider and/or rely on frequency regulation.

[0186] In some exemplary embodiments of the invention, a frequency of cyclically contacting 510 is higher than a frequency of cyclically routing 550. In some exemplary embodiments of the invention, the extraction which occurs at 510 to produce extract 530 is a counter current extraction. Optionally, counter current extraction takes a relatively short time (e.g. seconds to minutes). In some exemplary embodiments of the invention, hydrolyzate 130 is withdrawn from reactor 110 on an ongoing basis and the extraction at 510 is likewise on-going. In this situation, the rate of addition to the contaminant load is high, at least partly because the frequency of addition to the contaminant load approaches infinity. In contrast, contaminant reduction process 560 may take a longer time to implement (e.g. tens of minutes to hours). In some exemplary embodiments of the invention, the second portion at 550 can be made sufficiently larger than the first portion at 510 to insure that the total contaminant load in system 501 does not increase due to the frequency difference. These considerations are in addition to the "efficiency" considerations discussed above.

[0187] In other exemplary embodiments of the invention, a frequency of cyclically contacting 510 is lower than a frequency of said cyclically routing 550. This may occur if removal of hydrolyzate 130 from reactor 110 is batch-wise (i.e. a fixed volume at defined intervals). If the intervals are long (e.g. once in 8 hours), two or more rounds of contaminant reduction process 560 may be conducted in this time). Again, these considerations are in addition to the "efficiency" considerations discussed above.

[0188] In some exemplary embodiments of the invention, cyclically contacting 510 and cyclically routing 550 are coordinated so that a contaminant load in the first portion at 510 is maintained in a desired range.

[0189] In some exemplary embodiments of the invention, contaminant reduction process 560 includes carbonatation, in addition to treatment with lime and solids removal as described above.

First exemplary contaminant reduction process

[0190] Fig. 6a is a schematic representation of materials flow consistent with some exemplary embodiments of method 500 indicated generally as 600. Depicted exemplary materials flow 600 corresponds to the left side of method 500 from cyclically routing 550 to the return of S1 solvent 570 with reduced contaminant load 570 to system 501. Materials flow 600 is presented to illustrate in greater detail one exemplary way to carry out contaminant reduction process 560.

[0191] In depicted exemplary materials flow 600, carbonatation is conducted without removal of S1 solvent.

[0192] Referring now to Fig. 6a as well as Fig. 5:

In Fig. 6a, system 501 is represented schematically as a horizontal solid arrow at the top of the page. Solid arrows are used throughout the figure to indicate a flow of S1 solvent. Dashed arrows are used throughout the figure to indicate a flow of lime suspension. Dotted arrows are used throughout the figure to indicate a flow of aqueous waste.

[0193] In depicted materials flow 600, a flow splitter 610 cyclically routes 550 S1 solvent from system 501 to a lime contact chamber 620 where a lime suspension is added as indicated by the dashed arrow. Alternatively or additionally, a distillation purge 611 is added at this stage (hollow arrow). Optionally, only distillation purge 611 is added.

[0194] In some exemplary embodiments of the invention, distillation purge 611 includes a stream of solvent originating from flash distillation used to separate HCl from solvent in purification of lignin stream 120. Details of this flash distillation process are provided in co-pending application US 61/491,243 which is fully incorporated herein by reference. Optionally, use of distillation purge 611 reduces a chance that portions of the contaminant load related to lignin purification will cross over to sugar purification procedures. In some cases, this may contribute to increased purity of the final sugar product.

[0195] Contact of lime and S1 containing extractant in chamber 620 marks the beginning of contaminant reduction process 560 (Fig. 5) according to the depicted embodiment. According to various exemplary embodiments of the invention splitter 610 diverts 10, 20, 30, 40, 50, 50, 70, 80, or 90% or intermediate or greater percentages of the flow in system 501 to lime contact chamber 620. Optionally, the percentage varies in accord with frequency and/or efficiency considerations as discussed above.

[0196] In depicted exemplary materials flow 600, the S1 solvent mixed with lime suspension then flows to a second lime contact chamber 621 where it is carbonatated with a stream of CO₂ bubbles 630 to produce a calcium carbonate slurry. The carbonatated mixture is then transferred to lime contact chamber 622. Optionally, additional lime is added at this stage as indicated by the dashed arrow.

[0197] Although the flow of materials from contact chamber 620 to 621 and then to 622 is indicated by a solid arrow, the flow at this stage is a mixture of S1 and lime suspension, optionally with calcium carbonate (after carbonatation).

[0198] Optionally, each of contact chambers 620, 621 and 622 includes a mixer and/or heater (not depicted). According

to various exemplary embodiments of the invention the mixture of S1 and lime suspension is incubated in each of chambers 620, 621 and 622 for a desired time under desired conditions.

[0199] The mixture exiting chamber 622 is now depicted as two separate arrows for clarity (dashed indicating lime; solid indicating S1). Again, each of these streams carries water, which is not separately depicted at this stage.

[0200] In this exemplary embodiment, contaminant reduction process 560 (Fig. 5) continues with cyclonic separation of S1 from lime. In the depicted embodiment two cyclonic separators 640 and 642 are provided in series.

[0201] In the depicted embodiment S1 solvent exiting the top of each of cyclonic separators 640 and 642 is routed to a wash unit 650. In wash unit 650 the S1 solvent stream is mixed thoroughly with water (hollow arrow). This washing can remove salts, such as calcium salts as well as other water soluble contaminants which may be present at this stage. The upward pointing arrow indicated return of S1 to system 501 and the conclusion of contaminant reduction process 560 from the standpoint of the solvent.

[0202] Residual wash water from wash unit 650 is optionally routed back to cyclonic separator 640 as indicated by the dotted line. In some exemplary embodiments of the invention, a portion of this water is diverted by a flow splitter 660 to lime suspension generator 660, where it is mixed with solid lime (grey arrow) and optionally additional water (white arrow) to generate lime suspension (rightward dashed arrow). The lime suspension may be used, for example, in lime contact chamber 620 and/or 622.

[0203] Returning now to cyclonic separators 640 and 642, lime suspension exiting separator 642 can be filtered in a filter unit 670. The resultant aqueous solution (dotted lines) can optionally be recycled to cyclonic separator 640 as indicated.

[0204] Solids accumulating in filter 670 can periodically be removed as a solids cake 680.

[0205] Although not explicitly depicted in Fig. 6a, a controller of the same type as controller 250 (Fig. 2) can be installed to control a flow of one or more streams in materials flow 600 in some exemplary embodiments of the invention.

Second exemplary contaminant reduction process

[0206] Referring now to Fig. 6b as well as Fig. 5:

Fig 6b is a schematic representation of materials flow consistent with some exemplary embodiments of method 500 indicated generally as 601. Depicted exemplary materials flow 601 corresponds to the left side of method 500 (Fig. 5) from cyclically routing 550 to the return of S1 solvent 570 with reduced contaminant load to system 501. Materials flow 601 is presented to illustrate in greater detail another exemplary way to carry out contaminant reduction process 560.

[0207] In depicted exemplary materials flow 601, carbonatation is conducted following removal of S1 solvent.

[0208] In Fig.6b, system 501 is represented schematically as a horizontal solid arrow at the top of the page. Solid arrows, dashed arrows and dotted arrows are used throughout the figure to indicate flows as in Fig. 6a.

[0209] Conceptually, it may be convenient to think of system 501 as pointing to a lignin purification/HCL recovery loop on the left and a sugar purification/HCL recovery loop on the right. According to various exemplary embodiments of the invention different amounts of total S 1 extractant in system 501 may be routed to the two loops. Optionally, the split is about half and half. In some exemplary embodiments of the invention, about 5/8 of the S1 extractant is routed to the lignin purification loop.

[0210] In depicted materials flow 601, flow splitter 610 cyclically routes 550 S1 solvent from system 501 to a lime contact chamber 620 where a lime suspension is added as indicated by the dashed arrow. Optionally, a distillation purge is also added at this stage (not depicted). This marks the beginning of contaminant reduction process 560 (Fig. 5) according to the depicted embodiment. According to various exemplary embodiments of the invention splitter 610 diverts different percentages of the flow in system 501 to lime contact chamber 620 as described above in the context of Fig. 6a.

[0211] Optionally, contact chamber 620 includes a mixer and/or heater (not depicted). According to various exemplary embodiments of the invention the mixture of S1 and lime suspension is incubated in chamber 620 for a desired time under desired conditions.

[0212] In depicted exemplary materials flow 601, the S1 solvent mixed with lime suspension then flows to cyclonic separation of S1 from lime. In the depicted embodiment two cyclonic separators 640 and 642 are provided in series. Solvent exiting the top of separators 640 and 642 is returned to system 501, optionally after washing in washing unit 650 as described above in the context of Fig. 6a.

[0213] In the depicted embodiment, water exiting washing unit 650 goes to lime suspension generator 660 which functions as described above in the context of Fig. 6a.

[0214] Treatment of lime suspension exiting separator 642 is different than in materials flow 600.

[0215] In depicted exemplary materials flow 601, lime suspension exiting separator 642 is split into two streams by flow splitter 643.

[0216] A first stream goes to carbonatation chamber 644 where it is exposed to a stream of CO₂ bubbles 630. This carbonatation produces a slurry of calcium carbonate. This carbonatation reaction is conducted on a lime suspension with substantially no S1 solvent present. Lime suspension carrying calcium carbonate slurry exits chamber 644 and can be filtered in filter unit 670. The resultant aqueous solution (dotted lines) can optionally be concentrated by evaporator 672 and/or sent to a waste water treatment plant (WWTP) as indicated. Solids accumulating in filter 670 can periodically be removed as a solids cake 680, optionally provided as a slurry or filtrate including a relatively large amount of water or other liquids.

[0217] A second stream from flow splitter 643 goes to lime contact chamber 620 where it is joined with lime suspension being introduced into the chamber.

[0218] According to various exemplary embodiments of the invention the relative sizes of the first and second streams from flow splitter 643 can vary widely. Optionally, either of the two streams can include as little as 10% or as much as 90% of the total flow or any intermediate percentage. It was surprisingly discovered that lime recycled to contact chamber 620 retains significant activity in terms of its ability to adsorb impurities and/or hydrolyze esters. According to various exemplary embodiments of the invention routing of a significant portion (e.g. 50, 55, 60, 65, 70, 75 or 80% or intermediate or greater percentages) of the lime to this recycling pathway contributes to a reduction in the cost of reagents and/or reduces waste flow.

[0219] In some exemplary embodiments of the invention, the first stream flowing to carbonatation chamber 644 is 20, 25, 30, 35, 40, 45 or 50% or intermediate or smaller percentages of the total flow.

[0220] Although not explicitly depicted in Fig. 6b, a controller of the same type as controller 250 (Fig. 2) can be installed to control a flow of one or more streams in materials flow 601 in some exemplary embodiments of the invention.

Exemplary S 1 solvents

[0221] Optionally, S1 includes, or consists primarily of, or consists substantially solely of, or is n-hexanol. Optionally, S1 includes, or consists primarily of, or consists substantially solely of, or is 2-ethyl-1-hexanol.

Exemplary ratios

[0222] Referring again to Fig. 3, in some exemplary embodiments of the invention, lime 350 is added to de-acidified extract 340 as a 10% slurry of CaO and/or Ca(OH)₂ in water. Optionally, a ratio of S1 solvent to 10% lime slurry 30:1; 25:1; 20:1; 15:1 or 10:1 or intermediate or lesser ratios.

[0223] Alternatively or additionally, a ratio of S1 solvent to lime on a weight basis is 300:1; 250:1; 200:1; 150:1 or 100:1 or intermediate or lesser ratios.

[0224] According to various exemplary embodiments of the invention, the greater the amount of lime applied to each unit of solvent, the greater the percentage of lime that can be recycled for additional rounds of contaminant load reduction.

Exemplary impurities concentrations

[0225] Referring again to Fig. 6b, exemplary concentrations of specific impurities in the contaminant load of the S1 solvent are described as the solvent exits washing unit 650 and returns to system 501.

[0226] In some exemplary embodiments of the invention, the contaminant load includes furfurals. Optionally, the furfurals are present in an amount not exceeding 0.25% on a weight basis. Alternatively or additionally, a concentration of the furfurals is at least 0.02 % by weight.

[0227] In some exemplary embodiments of the invention, the contaminant load includes phenolic compounds at a concentration of at least 0.1 % by weight.

[0228] Alternatively or additionally, in some exemplary embodiments of the invention, the contaminant load includes an acetate ester of the solvent. Alternatively or additionally, the contaminant load includes less than 0.01% of a formate ester of said solvent.

[0229] In some exemplary embodiments of the invention, the S1 solvent is hexanol. In some exemplary embodiments of the invention, the S1 solvent is 2-ethyl-hexanol.

Exemplary calcium cake compositions

[0230] Referring again to Fig. 6b, exemplary compositions of calcium cake 680 are discussed. All percentages of cake ingredients are expressed on a dry weight basis.

[0231] In some exemplary embodiments of the invention, cake 680 includes at least 1; optionally 5; optionally 10; optionally 15; optionally 20; optionally 30; optionally 35% calcium carbonate (or intermediate or greater percentages) and at least 1% furfurals. Optionally, the percentage of calcium carbonate is 21, 25, 27 or 30% or intermediate or greater

percentages. Optionally, the percentage of furfurals is at least 5 %; 10%; 15% or 20% or intermediate or greater percentages.

[0232] In some exemplary embodiments of the invention, cake 680 includes phenolic compounds. Optionally, the percentage of phenolic compounds is at least 1; 2; 5; 10; 20; 25 or 30% or intermediate or greater percentages.

[0233] In some exemplary embodiments of the invention, cake 680 includes calcium acetate. Optionally, the amount of calcium acetate is at least 0.1; 0.2; 0.3; 0.5 or 0.5% or intermediate or greater percentages.

[0234] In some exemplary embodiments of the invention, cake 680 includes calcium formate. Optionally, the amount of calcium formate is at least 0.5; 0.6; 0.7; 0.7; 0.8; 0.9 or 1.0%.

[0235] Optionally, the cake includes hexanol. Optionally, the cake includes 2-ethyl hexanol.

Exemplary solvent/lime suspensions

[0236] Some exemplary embodiments of the invention, relate to a suspension of at least one part lime solids to two hundred parts S1 solvent carrying a contaminant load (on a weight basis). Optionally, the lime is provided as an aqueous slurry so that the suspension includes water. For example, 1 part 10% lime slurry and 20 parts S1. Optionally, two, three, four, five or intermediate or greater numbers of parts of lime slurry are employed.

[0237] In some exemplary embodiments of the invention, the contaminant load in the solvent includes at least 0.2% furfurals relative to said solvent.

[0238] Alternatively or additionally, in some exemplary embodiments of the invention, contaminant load includes at least 0.2% phenolic compound relative to said solvent.

[0239] Alternatively or additionally, according to various exemplary embodiments of the invention the suspension includes calcium acetate and/or the contaminant load includes hexyl acetate.

[0240] Alternatively or additionally, according to various exemplary embodiments of the invention the suspension includes calcium formate and/or the contaminant load includes hexyl formate.

[0241] Optionally, the S1 solvent is hexanol. Optionally, S1 solvent is 2-ethyl hexanol.

Exemplary hydrolysis considerations

[0242] Referring again to Fig. 3, in some exemplary embodiments of the invention, de-acidified extract 340 contains one or more esters. Optionally, the esters are derived from S1 solvent. These esters may include, but are not limited to acetates, formates, lactates, levulinates, and galactouronates.

[0243] In some exemplary embodiments of the invention, lime 350 added to extract 340 causes hydrolysis of these esters to regenerate the S1 solvent and produce calcium salts. Optionally, lime 350 and extract 340 are contacted under temperature conditions which favor hydrolysis. Optionally, temperatures of 160, 140, 120, 100, 80 or 60 degrees centigrade or intermediate or lower temperatures can favor hydrolysis. In some exemplary embodiments of the invention, S1 solvent at about 160 degrees centigrade is contacted with lime slurry and cooled to about 80 degrees centigrade.

[0244] In some exemplary embodiments of the invention, calcium salts produced by hydrolysis of esters with $\text{Ca}(\text{OH})_2$ and/or CaO are insoluble. Optionally, removal of these insoluble calcium salts contributes to reducing the contaminant load as it is the result of reducing the load of esters which are impurities in the S 1 solvent.

Exemplary equipment

[0245] In some exemplary embodiments of the invention, contact between an S1 extractant and a hydrolyzate (e.g. from lignin stream 120 and/or from acid hydrolyzate 130) is implement via countercurrent extraction. Optionally, this countercurrent extraction can be implemented using at least one pulsed column. Optionally, the pulsed column is a Bateman pulsed column (Bateman Litwin, Netherlands).

[0246] In some exemplary embodiments of the invention, solvent and lime wetted with water are separated by a cyclonic separator or "hydroclone" as depicted in Figs. 6a and 6b (640 and/or 642). Cyclonic separators are commercially available and may be purchased, for example, from Odis Filtering Ltd (Petach Tikva; Israel) or from GN Solids Cintrol-Tangshan Guanneng Machinery Equipment Co. Ltd. (Tangshan;China).

Exemplary flow control considerations

[0247] According to various exemplary embodiments of the invention, flows of liquids may be aided by pumps installed at various points in the described/depicted systems and/or modules. Alternatively or additionally, solid or semisolid materials can optionally be moved by solid transport mechanisms. According to various exemplary embodiments of the invention solid transport mechanisms include, but are not limited to, conveyor belts and augers.

[0248] Alternatively or additionally, the pumps and/or solid transport mechanisms may be connected to, and under

the control of, controller 250. According to various exemplary embodiments of the invention control of pumps and/or solid transport mechanisms by controller 250 can be implemented using an appropriate control interface. Such control interfaces can include mechanical and/or electric and/or electronic components and/or combinations thereof.

5 Additional exemplary considerations

[0249] During operation of hydrolysis reactor 110 (Fig. 1), "black specs" of undefined composition may appear in hydrolyzate 130 in some cases. It is believed that these specs result from degradation of sugars following prolonged exposure to concentrated acid. In some exemplary embodiments of the invention, ultra-filtration (e.g. 300 kDa filter) of the hydrolyzate is implemented to remove these specs. The filtrate proceeds to, or is returned to, refining module 201.

[0250] The retentate containing a high concentration of black specs is washed with water to recover sugars and/or HCL and re-filtered. Optionally, this washing and re-filtering is repeated until a desired degree of HCl and/or sugar recovery is achieved and a washed retentate including black specs and water remains. In some exemplary embodiments of the invention, this washed retentate is added to prior to or after carbonation (e.g. to filter 670 or a flow of material entering this unit) so that the black specs are incorporated into cake 680. Optionally, incorporation into cake 680 neutralizes acid remaining on the specs and/or other wise inactivates them.

[0251] It is expected that during the life of this patent many new types of pumps, countercurrent extraction apparatus and cyclonic separators will be developed and the scope of the invention is intended to include all such new technologies *a priori*.

[0252] As used herein the term "about" refers to $\pm 10\%$.

[0253] 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.

[0254] 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 embodiments of 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.

[0255] 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.

[0256] It should be further understood that the individual features described hereinabove can be combined in all possible combinations and sub-combinations to produce additional embodiments of the invention. The examples given above and/or below 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 recycling and/or purification of solvents used to extract an acid hydrolyzate of a lignocellulosic substrate but might also be used in any industrial process involving purification and/or recycling of a solvent.

[0257] Citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art with regard to the instant specification.

[0258] The terms "include", and "have" and their conjugates as used herein mean "including but not necessarily limited to".

[0259] 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 examples, which are illustrative, rather than limiting. Additionally, various embodiments, features and aspects of the invention as delineated hereinabove and as claimed in the claims section below find experimental support in the following examples.

EXAMPLES

[0260] Reference is now made to the following examples, which together with the above descriptions, illustrate the invention in a non limiting fashion.

Example 1:

Relative contaminant loads of de-acidified extract,

limed extract and refined extract

[0261] An acid hydrolyzate was prepared by hydrolyzing sugarcane bagasse in a 42% HCl solution. The concentrations of the HCl and of the carbohydrates in the formed hydrolyzate were 31.7%wt and 12.8%wt, respectively. The acid hydrolyzate was equilibrated with hexanol. HCl was selectively extracted to the solvent and an organic extract containing 14.9%wt HCl was formed.

[0262] HCl was distilled out of the extract at a pressure of 50mm mercury to produce a de-acidified extract. HCl concentration in the de-acidified extract was 0.1%wt. In order to quantify the contaminant load in abstract terms, a sample of the de-acidified extract was taken and checked for absorption at several wavelengths between 310nm and 600nm. The results are presented in Table 1 (first line "de-acidified extract"). The high absorption levels at the various wavelengths are indicative of a large contaminant load containing a variety of different impurities.

[0263] In order to demonstrate the capacity of liming for reducing the contaminant load, a limed extract was prepared as follows:

7.86gr of the de-acidified extract were mixed in a vial with 2.2gr of a 2%wt $\text{Ca}(\text{OH})_2$ slurry for three hours at 85°C. The resultant mixture contained limed extract (organic phase) and an aqueous slurry of lime.

[0264] A sample of the mixture was separated. Filtering away the lime from the organic phase was difficult. Absorption at wavelengths between 310nm and 600nm was measured as for the de-acidified extract above. The results are presented in Table 1 (second line, limed extract). A marked reduction in absorption was observed, especially at wavelengths of 450 nm or below. This decrease in absorption indicates a reduction in contaminant load.

[0265] In order to demonstrate the capacity of carbonatation for further reducing the contaminant load, a limed extract was carbonatated as follows:

While mixing, CO_2 was bubbled through de-acidified extract as described above. Bubbling was continued until the pH of the aqueous solution reached 7.0. Then, 0.46gr of 2%wt $\text{Ca}(\text{OH})_2$ slurry was added and mixing was continued at 85°C for another hour. The organic phase was separated. Filtering away the lime from the organic phase was much easier than for non-carbonatated limed extract as described above.

[0266] The filtered organic phase was washed three times with 1gr water to remove any calcium hydroxide and then analyzed. Its calcium content was 76 ppm.

[0267] Absorption of the washed organic phase, refined extract, was measured at wavelengths between 310nm and 600nm as for the de-acidified extract and limed extract above. The results are presented in Table 1 (third line, refined extract). A marked reduction in absorption was observed at wavelengths of 400 nm to 600nm. This decrease in absorption indicates a reduction in contaminant load. This is consistent with visual evaluation which indicated a reduction in intensity of the yellow color. At 310 and 350 nm, absorbance was higher than for the limed extract. This suggests an increase in contaminant load for some types of impurities as a result of carbonatation.

Table 1: Absorption of different extract types at various wavelengths in the UV-Vis range *,

Wavelength (nm)	A310	A350	A400	A450	A500	A600
De-acidified extract	28.2	19.5	9.0	5.0	3.1	1.4
Limed extract	10.3	7.3	4.5	3.47	2.93	2.37
Refined extract**	14.1	9.0	3.7	1.90	1.14	0.54
* For absorption measurements, the solutions were diluted. The figures in the table were calculated by multiplying the measured absorption by the degree of dilution.						
**Refining of the de-acidified extract with CO_2 gas and 2% $\text{Ca}(\text{OH})_2$						

Example 2:*Relative contaminant loads**limed extract and refined extract**additional experiment with 3% Ca(OH)₂*

[0268] In order to assess the impact of the Ca(OH)₂ concentration employed in refining, an additional experiment was conducted:

2.32gr Ca(OH)₂ 3% solution was applied to 7.87gr of de-acidified extract as in example 1 and mixed for 3 hours at 85°C to produce limed extract. Absorption data as in Example 1 are summarized in Table 2 (first line ; limed extract).

[0269] In order to produce refined extract, CO₂ was bubbled through the limed extract to reach pH=6.7, followed by addition of 0.43gr Ca(OH)₂ 3% solution. The mixture was mixed for another hour at 85°C and the phases were treated as described above. Results are summarized in Table 2 (second line; refined extract).

Table 2: Absorption at various wavelengths in the UV-Vis range*,

Wavelength	A310	A350	A400	A450	A500	A600
Limed extract	15.4	8.0	2.1	0.76	0.31	0.02
Refined extract **	16.0	8.3	2.2	0.75	0.28	0.01
* For absorption measurements, the solutions were diluted. The figures in the table were calculated by multiplying the measured absorption by the degree of dilution. ** Refining of the limed extract was with CO ₂ and 3% Ca(OH) ₂						

[0270] Results presented in Table 2 indicate that Ca(OH)₂ 3% solution reduced the contaminant load in both limed extract and refined extract for impurities with absorption in the range of 400 to 600 nm. These results confirm those of Example 1 and suggest that increasing the concentration of Ca(OH)₂ can contribute to a reduction in contaminant load, especially for certain types of impurities.

Example 3:*Relative contaminant loads**limed extract and refined extract**additional experiment with 10% Ca(OH)₂*

[0271] In order to assess the impact of the Ca(OH)₂ concentration employed in refining further, an additional experiment was conducted:

5gr Ca(OH)₂ 10% solution were applied to 18gr of de-acidified extract as in example 1 and mixed for 3 hours at 85°C. Absorption data as in Example 1 are summarized in Table 3 (line 1; limed extract).

[0272] In order to produce refined extract, CO₂ was bubbled through the limed extract to reach pH=6.9, followed by addition of 1gr Ca(OH)₂ 10% solution and mixing for another hour at 85°C and the phases were treated as described above. Results are summarized in Table 3 (line 2; refined extract).

Table 3: Absorption at various wavelengths in the UV-Vis range*,

Wavelength	A310	A350	A400	A450	A500	A600
Limed extract	10.1	6.5	2.1	0.79	0.35	0.08

(continued)

Wavelength	A310	A350	A400	A450	A500	A600
Refined extract **	10.1	6.3	2.0	0.75	0.34	0.11
* For absorption measurements, the solutions were diluted. The figures in the table were calculated by multiplying the measured absorption by the degree of dilution. ** Refining of the recycle extractant with 10% Ca(OH) ₂						

[0273] Results presented in Table 3 indicate that Ca(OH)₂ 10% solution reduced the contaminant load in both limed extract and refined extract for impurities with absorption in the range of 310 to 350 nm relative to results of Example 1. Table 3 also shows that both limed extract and refined extract had absorption in the range of 400 to 600 nm comparable to the results of Example 2. These results confirm the validity of liming followed by carbonatation as a means for reduction in contaminant load across a wide range of impurities.

Example 4:

Carbonatation in the presence and absence of lime

[0274] In order to examine the influence of residual lime on efficacy of subsequent carbonatation with respect to contaminant load reduction in a de-acidified extract, two experiments were performed. In the first experiment the solvent was separated by decantation and filtration from the lime sludge and CO₂ was added to the clear filtrate solution (procedure a). In the second experiment CO₂ was added without separation of the lime sludge (procedure b).

[0275] In order to prepare a de-acidified extract 273gr lignin (15% dissolved sugars (DS)) was mixed with 100gr water and 200gr hexanol. The mixture was evaporated at azeotropic condition. Water was added back 100gr and Hexanol was added back 100 gr Hexanol and the resultant azeotrope was evaporated off. The resultant solution was filtered through a 1 micron filter paper to produce a de-acidified extract including dry hexanol with an acid content of 0.03%.

(procedure a) carbonatation in the absence of lime

[0276] 18gr of the de-acidified extract, pH 1.6 %HCl 0.03, was mixed with 5 gr of 10% lime solution (Ca(OH)₂). The solution, pH11.4, was mixed at 80°C for 3 hours and left to stand overnight for approximately 12 hours. The lime sludge settled out as a wet cake with a weight of about 8 gr. The dark liquid supernatant was decanted and filtered through a 0.45 micron filter to produce 8 gr of a clear filtrate with a slight yellow color. The filtrate was carbonatated with CO₂ from pH 9.9 to pH7.4. After carbonatation 0.5 gr of water was added to the clear solution to wash out salts. The washed organic phase (refined extract) was checked for absorption at several wavelengths between 400nm and 650nm. Absorption results at various wavelengths are summarized in Table 4.

(procedure b) carbonatation in the presence of lime

[0277] 18gr of the de-acidified extract produce above, pH 1.6 %HCl 0.03, was mixed with 4 gr of 10% lime solution. The solution, pH11.4, was mixed at 80°C for 3 hours. The solution was carbonatated with 10% CO₂ solution, to pH 7.5 then 1 gr of additional lime (as powdered solid) was added, mixed and the solution was stirred for 15 hrs and filtered with 0.45 micron filter to give a clear filtrate with a slight yellow color in both the aqueous phase and the hexanol phase. The hexanol phase was washed with 1 gr aliquots of water 3 times to remove any calcium hydroxide. Concentration of calcium in the hexanol was 76 ppm and the pH was 8.3. Absorption results at various wavelengths are summarized in Table 4.

Table 4: Absorption at various wavelengths in the UV-Vis range

	A400	A420	A450	A500	A600	A650
Pure Hexanol	0.065	0.064	0.06	0.058	0.057	0.054
Procedure a: filtered then carbonatated	0.138	0.121	0.101	0.084	0.07	0.065
Procedure b: carbonatated without filtration	0.19	0.16	0.15	0.15	0.153	0.151

[0278] Results presented in Table 4 indicate that decantation and filtration prior to carbonatation (procedure a) reduce

the contaminant load in an extract prepared from lignin more efficiently.

Example 5:

Acid catalyzed hydrolysis of hexyl

acetate in the presence of hexanol

[0279] Hexyl acetate, can be formed during hydrolyzate extraction with S1 solvent (e.g Hexanol) as a result of esterification driven by acid or base. The influence of pH conditions on hydrolysis of hexyl acetate was assayed in a series of experiments. The hydrolysis of hexyl acetate is catalyzed by acid or base, and both types of catalysts were assayed in different conditions. This example relates specifically to acid catalyzed hydrolysis. In general hydrolysis of hexyl acetate produces hexanol (regenerated S1 solvent) and an acetate moiety. In some exemplary embodiments of the invention, hydrolysis of hexyl acetate serves to regenerate S1 solvent. Optionally, the acetate moiety produced by the hydrolysis is, or can be converted to calcium acetate. In some exemplary embodiments of the invention, calcium carbonate is generated by contacting acetic acid in a lime solution with CO₂ gas.

[0280] In order to evaluate hydrolysis:

A mixture of 92.2gr hexanol, 1.03gr hexyl acetate, 7.03gr H₂O and 1.05gr HCl was stirred in a 250 ml round-bottom flask under reflux at 80°C. Samples were taken from the organic phase every hour for six hours and another example after 18 hours. The ratio between the area % of hexanol and hexyl acetate was monitored by gas chromatography (GC) analysis, to get an indication of degree of hydrolysis.

[0281] Briefly, GC conditions were as follows:

An HP 5890 (Hewlett Packard, Palo Alto CA; USA) using an HP-5 30mx0.32mmx0.25um coupled to a flame ionization detector (FID) was employed. The program was 50°C-5°C/min-90°C-30°C/min-250°C (5min); Det, Inj 250°C with a 1ul injection volume using nitrogen as a carrier gas.

[0282] Results are summarized in Table 5.

Table 5: Acid hydrolysis of hexyl acetate in 13.0% HCl/(HCl+water) w/w.

Time (hours)	Hexyl acetate/ hexanol area ratio (GC)
0	1.07%
1	0.90%
2	0.85%
3	0.85%
4	0.85%
5	0.87%
6	0.87%
18	0.87%

[0283] Results presented in Table 5 suggest that partial hydrolysis occurred under these experimental conditions during the first 2 hours, but no additional hydrolysis occurred subsequently.

[0284] In order to assess the impact of the acidic catalysis even further, three additional experiments using systems A,B and C as described below were performed:

System A: A mixture of 684gr hexanol, 36gr hexyl acetate, 25gr H₂O and 4gr HCl was reflux at 82°C. HCl/(HCl+H₂O)=13.79%

System B: A mixture of 6842gr hexanol, 36gr hexyl acetate, 5gr H₂O and 0.035gr HCl was reflux at 131°C. HCl/(HCl+H₂O)=0.70%

System C: A mixture of 223.25gr hexanol, 11.75gr hexyl acetate, 0.3gr H₂O and 0.0003gr HCl was reflux at 150°C. HCl/(HCl+H₂O)=0.10%

[0285] In each experiment, 100 gr of each system was prepared according to the above ratios. In each case, a single clear and colorless phase was obtained. Part of the mixture was transferred to a 50 ml round-bottom flask, dipped in hot oil bath and equipped with a mini scale distillation kit. The mixture was constantly stirred with a magnetic stirrer for 30-90 minutes.

[0286] There was no apparent distillation in any of the systems even after more than 30 minutes. In system C, strong boiling was observed after about 10 minutes.

[0287] Samples were analyzed by GC analysis at times 0, 30, 360 and 90 minutes. Results are summarized in Table 6.

Table 6: Acidic hydrolysis of hexyl acetate in various HCl/(HCl+water) ratio.

Time (min.)	Hexyl acetate/hexanol area ration (GC)		
	System A	System B	System C
0	4.45%	4.41%	4.40%
30	4.21%	4.32%	4.32%
60	4.24%		
90			4.50%
As in the previous experiment, results presented in Table 6 suggest that no hydrolysis occurred under the conditions of systems A, B and C.			

Example 6:

NaOH catalyzed hydrolysis of hexyl

acetate in the presence of hexanol

[0288] Basic hydrolysis using NaOH as a catalyst was assayed by applying a chosen basic catalyst mixture (A or B; see table 7) to a "hydrolysis substrate" including 92gr hexanol, 1.0gr hexyl acetate, 7.0gr H₂O and 0.03gr HCl. HCl(HCl+H₂O) of this substrate is 0.4% on a weight basis.

[0289] The substrate was refluxed at 80°C in the presence of catalyst for 6 hours. Samples were taken from the organic phase over time and the ratio between the area % of hexanol and hexyl acetate was monitored by GC analysis to indicate hydrolysis progress as in the previous experiments.

[0290] Basic catalyst mixtures A and B with NaOH were prepared. The Basic catalyst mixture and the w/w ratio of NaOH to basic mixture and the w/w ratio of NaOAc to basic mixture are presented in table 7.

Table 7: basic catalyst mixtures with NaOH.

	NaOH (gr)	NaOAc (gr)	H ₂ O (gr)	% NaOH out of basic mixture	% NaOAc out of basic mixture
A	2.50	0.83	24.4	9	3
B	2.50	2.78	22.5	9	10

[0291] The weight ratio of the hydrolysis substrate to the catalyst mixture was 3.6. About 1-2 ml were sampled from upper phase, then centrifuged and filtered through 0.45µm syringe filter for GC analysis at each time point. Results are summarized in Table 8.

Table 8: Basic hydrolysis of hexyl acetate with NaOH

Time (hours)	Hexyl acetate/ hexanol area ration (GC)	
	Catalyst mixture A	Catalyst mixture B
0	0.85%	0.91%
1	0.00%	0.91%
2	0.00%	0.91%
3	0.00%	0.91%

(continued)

	Hexyl acetate/ hexanol area ration (GC)	
Time (hours)	Catalyst mixture A	Catalyst mixture B
4	0.00%	0.91%
5	0.00%	0.91%
6	0.00%	0.91%

[0292] Results presented in Table 8 indicate that at 3% NaOAc full hydrolysis occurred after one hour. However at 10% NaOAc no hydrolysis occurred. These results indicate that adding sodium acetate can shift the hydrolysis equilibrium so that no hydrolysis occurs.

[0293] An additional experiment was performed on the same hydrolysis substrate as that used above using a basic catalyst mixture containing 2.78gr NaOH, and 25gr H₂O. The basic catalyst mixture was added to the substrate and mixed for 6 hours at room temperature (~24°C). About 1-2 ml were sampled from the upper phase, then centrifuged and filtered through a 0.45µm syringe filter for GC analysis. The w/w ratio of NaOH to total basic catalyst mixture is 10%. The weight ratio of the hydrolysis substrate to the catalyst mixture is 3.6. Results are summarized in Table 9.

Table 9: Basic hydrolysis of hexyl acetate (The w/w ratio of NaOH to total basic mixture is 10%).

Time (hours)	Hexyl acetate/ hexanol area ration (GC)
0	0.92%
1	0.85%
2	0.79%
3	0.72%
4	0.71%
6	0.63%

[0294] Results presented in Table 9 indicate that at room temperature partial hydrolysis occurs and that the degree of hydrolysis increases as a function of time.

Example 7:

Ca(OH)₂ catalyzed hydrolysis of hexyl

acetate in the presence of hexanol

[0295] In order to ascertain the influence of different bases on hydrolysis, an additional experiment using Ca(OH)₂ instead of NaOH was performed using the same hydrolysis substrate as in Example 6.

[0296] Three experiments were performed with the w/w ratio of Ca(OH)₂ to total mixture 10% and the w/w ratio of Ca(OAc)₂ to total mixture 1.5%. The basic catalyst mixture and the weight ratio between the hydrolyzed mixture to the catalyst mixture are presented in table 10a.

Table 10a: basic catalyst mixtures.

system	Ca(OH) ₂ (gr)	Ca(OAc) ₂ (gr)	H ₂ O (gr)	Hydrolysis substrate/ catalyst mixture
A	2.78	0.42	24.6	3.6
B	5.56	0.83	49.2	1.8
C	1.39	0.21	12.3	7.2

[0297] The basic catalyst mixture was added to the hydrolysis substrate and mixed at 80°C, examples were taken for GC analysis at different time points. Results are summarized in Table 10b.

Table 10b: Basic hydrolysis of hexyl acetate with $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OAc})_2$

Time (hrs)	Hexyl acetate/ hexanol area ration (GC)		
	System A	System B	System C
0	0.92%	0.92%	0.92%
1	0.83%	0.85%	0.87%
2	0.77%		0.85%
3	0.67%		0.82%
4	0.64%	0.74%	0.92%
5			0.79%
6	0.60%	0.64%	
21	0.33%		

[0298] Results presented in Table 10b indicate that partial hydrolysis occurs in all three systems and that the degree of hydrolysis increases with time. The best results after 6 hours were achieved with a hydrolyzed mixture/catalyst mixture ratio of 3.6 (system A).

Example 8:

Influence of temperature on $\text{Ca}(\text{OH})_2$ catalyzed

hydrolysis of hexyl acetate in the presence of hexanol

[0299] In order to evaluate the effect of reaction temperature on hydrolysis an additional experiment with $\text{Ca}(\text{OH})_2$ was conducted.

[0300] A hydrolysis substrate was prepared by mixing 96gr hexanol, 4gr hexyl acetate and 6.72gr water. A basic catalyst was prepared by mixing 2.96gr $\text{Ca}(\text{OH})_2$ and 26.7gr water. The basic catalyst was added to the hydrolysis substrate so that the w/w ratio of $\text{Ca}(\text{OH})_2$ to total mixture was 10% and the substrate/catalyst ratio was 3.6 w/w. The reaction was carried out at 82°C and at 110°C. Samples were taken hourly and analyzed by GC as in previous examples until the hexyl acetate area percentage was reduced to 50% of its initial value. Results are summarized in Table 11.

Table 11: Effect of temperature on basic hydrolysis of hexyl acetate with $\text{Ca}(\text{OH})_2$ at 82°C and 110°C

Time (hrs)	temperature	
	82°C	110°C
Time (hrs)	Hexyl acetate % area (GC)	
0	3.08%	2.93%
1	2.96%	2.87%
2	2.89%	2.72%
3	2.80%	2.53%
4	2.73%	2.30%
5	2.62%	2.16%
6	2.52%	2.03%
7	2.44%	1.85%
8	2.25%	1.63%
9	2.19%	1.44%
10	2.08%	

(continued)

	temperature	
	82°C	110°C
Time (hrs)	Hexyl acetate % area (GC)	
11	1.95%	
12	1.91%	
13	1.75%	
14	1.64%	
15	1.53%	

[0301] Results presented in table 11 indicate that sufficient hydrolysis to reduce the area of hexyl acetate to 50% of its original value occurred earlier at 110°C than at 82°C (9 hours and 15 hours respectively). These results suggest that although a higher temperature contributes to faster hydrolysis it is possible to use a lower temperature applied for a longer time. Optionally, this strategy can contribute to reduced energy consumption.

[0302] Results from examples 5 to 8 indicate that basic catalysts are more efficient for the hydrolysis of hexyl acetate. Hydrolysis with sodium hydroxide and 3% sodium acetate seems to be more efficient than hydrolysis with calcium hydroxide. After one hour with sodium hydroxide, complete hydrolysis was achieved, whereas hydrolysis in all three calcium hydroxide systems, though observed, occurred at a more gradual rate and was not observed to reach completion.

[0303] However, calcium hydroxide is far less soluble than sodium hydroxide, and this may be advantageous under certain circumstances.

Example 9:

Ca(OH)₂ catalyzed hydrolysis of esters in the presence of hexanol

followed by carbonatation

[0304] An additional series of four experiments was conducted in order to examine the feasibility of using liming solution (10% Ca(OH)₂) in the purification of loaded extractant (hexanol). As demonstrated by the previous examples, calcium hydroxide (lime) can hydrolyze esters such as hexyl acetate and hexyl formate formed during extraction of HCl. In addition, it was hypothesized that lime may adsorb other impurities such as furfural and its derivatives. The lack of specificity of adsorption seemed potentially useful in treating a solvent extract with a wide variety of impurities.

[0305] Experiments a through d were conducted as follows:

- a. A liming substrate was prepared by addition of 0.030g hexyl acetate to 15.001g distilled hexanol to produce 0.277% weight/weight out of hexanol. A limed substrate was prepared by addition of 5.55g of 9.99% lime solution to the substrate in a 50 ml pressure vessel. At this stage, pH was 11.4. The limed substrate was mixed at 85°C (oil bath) for 6 hrs, until the concentration of hexyl acetate was decreased to 0.134% (as measured by GC) and left to cool to room temperature. The limed substrate was carbonatated by bubbling CO₂ into the cooled substrate while stirring slowly until pH reached 7. After carbonatation, 1.237g lime 10% solution was added in order to reach pH 10.63 and the mixture was gravity filtered. The amount of hexyl acetate was 0.116% in the resulting filtered hexanol.
- b. A liming substrate was prepared by addition of 0.0332g hexyl acetate to 15.006g distilled hexanol to produce 0.267% w/w out of hexanol. A limed substrate was prepared by addition of 6.79g of 9.78% lime solution to the substrate in a 50 ml pressure vessel. The pH was 12.17 at this stage. The limed substrate was mixed at 85°C (oil bath) for 6 hrs, until hexyl acetate concentration decreased to 0.15% (as measured by GC) and cooled to room temperature. The limed substrate was carbonatated by bubbling CO₂ into the cooled substrate while stirring slowly until pH reached 7.23. After carbonatation, 0.332g lime 10% solution was added in order to reach pH 10.91 and the mixture was filtered under vacuum. The amount of hexyl acetate was 0.126% in the resulting filtered hexanol.
- c. A liming substrate was prepared by addition of 0.029g hexyl acetate to 15.005g distilled hexanol to produce 0.273% w/w out of hexanol. A limed substrate was prepared by addition of 8.344g of 9.95% lime solution to the substrate in a 50 ml pressure vessel. The pH was 12.2 at this stage. The limed substrate was mixed at 85°C (oil bath) for 4 hrs, until hexyl acetate concentration decreased to 0.158% (as measured by GC) and left to cool to room temperature. The limed substrate was carbonatated by bubbling CO₂ into the cooled substrate while stirring slowly

until pH reached 7.69. After carbonatation, 1.564g lime 10% solution was added in order to reach pH 10.25 and the mixture was filtered under vacuum. The amount of hexyl acetate was 0.116% in the resulting filtered hexanol.

d. A liming substrate was prepared by addition of 0.030g hexyl acetate to 15.006g distilled hexanol to produce 0.247% w/w out of hexanol. A limed substrate was prepared by addition of 11.067g of 10% lime solution to the substrate in a 50 ml pressure vessel. At this stage, pH was 12.58. The limed substrate was mixed at 85°C (oil bath) for 4 hrs, until hexyl acetate concentration decreased to 0.13% (as measured by GC) and left to cool to room temperature. The limed substrate was carbonatated by bubbling CO₂ into the cooled substrate while stirring slowly until pH reached 7.4. After carbonatation, 0.728g lime 10% solution was added in order to reach pH 11.6 and the mixture was filtered under vacuum. The amount of hexyl acetate was 0.090% in the resulting filtered hexanol.

[0306] Results of experiments a-d indicate that addition of an additional portion of 10% Ca(OH)₂ consistently causes hydrolysis of more than 50% of hexyl acetate present in hexanol. Alternatively or additionally, these results confirm that carbonatation to produce calcium carbonate simplifies removal of calcium salts. The results also show that hexyl formate is rapidly hydrolyzed to calcium formate and hexanol. Adsorption of furfural and other compounds was not assayed here.

Example 10:

Partial recycling of Ca(OH)₂

[0307] In order to examine liming solution (10% Ca(OH)₂) efficiency in the purification process of the loaded solvent (hexanol), 35% w/w out of the 10% Ca(OH)₂ solution was removed and solvent was treated with 65% recycled 10% w/w Ca(OH)₂ solution supplemented with 35% "fresh" 10% w/w Ca(OH)₂ solution. This experiment corresponds to Fig 6b when 65% of the lime at flow splitter 643 is routed back to lime contact chamber 620 and 35% is routed to carbonatation chamber 634.

[0308] The amount of impurities' built-up within the 10% Ca(OH)₂ solution after recycling six times 65%wt of the lime solution was measured.

[0309] Loaded solvent with the following ingredients- 8.67% HCl, 2.71% hexyl acetate, 0.9% hexyl formate, weight/weight ratio out of hexanol, and hexyl chloride to hexanol ratio of 0.31%:99.6%, was used to represent recycled extractant.

[0310] The experimental procedure was as described at example 9d above conducted in a 100ml round bottom flask with a magnetic stirrer at 82-83°C for 4 hours. At the end of the reaction, while still warm, the contents were transferred to 15ml polypropylene tubes and put into a centrifuge at 5000RPM (3354xg) for 10min.

[0311] After centrifugation two phases were observed, i.e. organic and aqueous.

[0312] The organic phase was separated from the aqueous phase, and the aqueous phase was returned to the round bottom flask. At this stage, 35%wt of the aqueous phase was removed, and 35%wt of "fresh" 10%Ca(OH)₂ was added to the flask.

[0313] This lime mixture (65% recycled/35% fresh) was used in an additional round of liming with fresh batch of loaded solvent, under the same conditions described above.

[0314] This process of recycling 65% of the lime and discarding 35% was repeated 6 times so that a total of 7 liming cycles were conducted (the first cycle uses 100% "fresh" lime).

[0315] Results of analyses are summarized in Table 12. Results for Furfurals were calculated according to calibration at 280nm (spectrophotometric measurements). Results for all other components below are based upon GC calibrated results.

Table: 12: influence of repeated liming on contaminant load in hexanol solvent

	hexyl chloride : hexanol (Area ratio)	Hexyl formate	Hexyl acetate	% Hexyl acetate that was hydrolyzed	Hexyl ether	Furfurals	% Furfurals that were reduced
Loaded solvent	0.37%:99.63%	0.903%	2.714%	-----	0.019%	0.099%	-----
Liming No.1	0.41%:99.59%	n.d.*	1.491%	45%	0.017%	n.d.*	
Liming No.2	0.39%:99.61%	n.d.*	1.450%	46%	0.018%	0.012%	88%

(continued)

	hexyl chloride : hexanol (Area ratio)	Hexyl formate	Hexyl acetate	% Hexyl acetate that was hydrolyzed	Hexyl ether	Furfurals	% Furfurals that were reduced
Liming No.3	0.40%:99.60%	n.d.*	1.512%	44%	0.016%	0.009%	91%
Liming No.4	0.44%:99.56%	n.d.*	1.777%	34%	n.d.*	0.012%	88%
Liming No.5	0.41%:99.59%	n.d.*	1.492%	45%	0.018%	0.013%	87%
Liming No.6	0.40%:99.60%	n.d.*	0.887%	67%	0.010%	0.010%	90%
Liming No.7	0.38%:99.62%	n.d.*	0.806%	70%	0.009%	0.012%	88%
*n.d. indicates none detected.							

[0316] Results presented in table 12 indicate that lime recycled as described above retained significant capacity to reduce the contaminant load in the loaded solvent. Specifically:

hydrolysis of hexyl formate was complete in each cycle;
hydrolysis of hexyl acetate varied in the range of 30 to 65% with an average of about 50%;
furfurals were consistently reduced by 88% or more;
hexyl chloride and hexyl ether were apparently not affected by the liming in this experiment.

[0317] Results presented in this example indicate that liming is sufficient to reduce or eliminate some impurity types. For those impurity types which are not reduced by liming (e.g. hexyl chloride and hexyl ether), a portion needs to be subjected to additional treatments and/or periodically replaced.

[0318] In summary, liming optionally in combination with carbonatation provides a viable strategy for limiting accumulation of a contaminant load in an S 1 solvent such as hexanol.

Example 11:

Predicted influence of liming on specific impurities

in the contaminant load

[0319] This Example projects how the amount of specific impurities in the contaminant load might be reduced using treatments according to exemplary embodiments of the invention as described and/or exemplified above.

[0320] Hypothetical results presented in table 13 show how a contaminant load including 4 impurities at measured concentrations from actual untreated solvent would be expected to behave if it were subjected to liming with a 10% Ca(OH)₂ slurry at a ratio of solvent/slurry of 20:1.

[0321] The presented results presume: hexyl formate is fully hydrolyzed; hexyl acetate is 50% hydrolyzed and furfurals are reduced by 88% as demonstrated in Example 10. The presented results also presume phenols are 80% adsorbed to lime.

[0322] Formate and acetate esters are converted to regenerated solvent and corresponding calcium salts by hydrolysis as indicated.

[0323] As indicated in Figs. 6a and 6b, the calcium cake (680) is removed after carbonatation in many exemplary embodiments of the invention. Carbonatation transforms calcium hydroxide to calcium carbonate. Results presented in table 13 for calcium cake presume that this transformation proceeds to completion and that substantially all of the calcium originally introduced as calcium hydroxide is present as calcium carbonate. The molecular weight of calcium carbonate is 100 while the molecular weight of calcium hydroxide is 74.1. This means that as the degree that the carbonatation transformation is incomplete increases, the percentage of lime in the calcium cake (on a weight basis) would decrease and the percentages of each specific impurity in the cake would increase proportionately to the difference in molecular weights.

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[0324] Alternatively or additionally, soluble calcium salts which do not find their way into the calcium cake have been ignored for purposes of calculation.

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Table: 13: influence of liming on specific impurities in solvent

impurity	SOLVENT							
	Hexanol				2-ethyl-hexanol			
Hexyl formate	untreated 0.06%	Solvent after liming 0%	Removed lime slurry* Not applicable	Calcium cake Not applicable	untreated 0.02%, Not applicable	Solvent after liming 0%	Removed lime slurry* Not applicable	Calcium cake Not applicable
Ca formate	Not applicable	Not applicable	1.2%	3.8%	Not applicable	Not applicable	0.4%	1.1%
Hexyl acetate	0.02%	0.01%	Not applicable	Not applicable	0.05%	0.025%	Not applicable	Not applicable
Ca acetate	Not applicable	Not applicable	0.2%	0.6%	Not applicable	Not applicable	0.5%	1.4%
Furfurals	0.4%	.048%	7%	22.3%	0.5%	0.06%	8.8%	24.4%
Phenolic compounds	0.6%	0.12%	9.6%	30.43%	0.8%	0.16%	12.4%	35.6%
lime	Not applicable	Not applicable	~10%	42.8%**	Not applicable	Not applicable	~10%	37.5%**

*presumes that the solvent was provided with no water content. If the solvent carries water, values may be lower.

** assumes complete conversion of calcium hydroxide to calcium carbonate by carbonatation.

[0325] The hypothetical results presented in this example are purely illustrative and do not suggest that the contaminant load would include only, or even primarily, the four specific impurities listed. Alternatively or additionally, the term "specific impurity" does not necessarily refer to a single chemical entity. For example "furfurals" may include derivatives of furfural including, but not limited to hydroxymethylfurfural. Alternatively or additionally, "phenolic compounds" may include a large number of different chemical entities. According to various exemplary embodiments of the invention the profile of specific impurities which make up the contaminant load may vary depending on the specific substrate 112 (Fig. 1) hydrolyzed in reactor 110. For example, hydrolysis of pine wood chips may produce a different impurities profile than hydrolysis of sugar cane bagasse. Alternatively or additionally, the profile of specific impurities which make up the contaminant load may vary among different batches of a same substrate type. For example, the composition of pine wood may vary according to geographic region and/or altitude and/or post harvest storage conditions and/or age at harvest.

Example 12

Hydrolysis of hexyl chloride under various conditions

[0326] Results presented in Example 10 suggested that hexyl chloride was not removed under the liming conditions employed in that experiment. In order to improve the ability to remove hexyl chloride from solvent, an additional series of experiments using 10% Ca(OH)₂; 10% NaOH and 10% KOH at a 6:1 molar excess (relative to hexyl chloride) were conducted at various temperatures. Hydrolysis of hexyl chloride produces HexOH dihexyl ether as well as hexane. Hexene was not measured in these experiments. Results are summarized in Tables 14 to 19 below.

[0327] Tables 18 and 19 show that the most efficient hydrolysis conditions among those assayed were 10% KOH at a temperature of 129 degrees C or more, KOH/HexCl molar ratio 6:1 and HexCl:HexOH 50:50 %wt.

[0328] These conditions produced 14% HexCl, 84% HexOH and 1.3% dihexyl ether 5hrs after 5 hours (Table 19) and 11.74% HexCl, 86.13% HexOH and 2.13% dihexyl ether after 24 hours (table 18). Presence of large amounts of hydrolysis product (50% HexOH) did not seem to interfere with reaction progress.

Abbreviations

[0329]

HexCl = Hexyl chloride; HexOH = Hexanol; Hex₂O = Dihexyl ether

Table 14: Hydrolysis with 10% Ca(OH)₂ at 125 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexO	Ca(OH) ₂ /HexCl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
50%	0%	6:1	125-135°C	3hrs	51.27%	48.53%	0.20%	n.a.
50%	0%	6:1	125-135°C	24hrs	34.19%	64.18%	1.63%	n.a.
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. n.a. = not analyzed								

Table 15: Hydrolysis with 10% Ca(OH)₂ at 98 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexC	HexOH	Ca(OH) ₂ /HexCl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
50%	50%	6:1	98-105°C	3hrs	46.15%	53.79%	0.06%	n.a.
50%	50%	6:1	98-105°C	24hrs	48.13%	51.62%	0.25%	n.a.
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. n.a. = not analyzed								

Table 16:Hydrolysis with 10% NaOH at 126 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	NaOH/HexCl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
50%	50%	6:1	126-137°C	3hrs	38.60%	60.77%	0.63%	<i>n.a</i>
50%	50%	6:1	126-137°C	24hrs	20.66%	77.15%	2.19%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Di hexyl ether% is an area ratio between HexCl to HexOH and Di hexyl ether. <i>n.a. = not analyzed</i>								

Table 17:Hydrolysis with 10% NaOH at 95 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	NaOH/Hex Cl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
50%	0%	6:1	95-103°C	3hrs	45.76%	54.15%	0.09%	<i>n.a</i>
50%	0%	6:1	95-103°C	24hrs	45.97%	53.69%	0.34%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. <i>n.a. = not analyzed</i>								

Table 18:Hydrolysis with 10% KOH at 129 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	KOH/HexC 1 molar ratio	Temp. in Bath	Tim	HexCl	HexOH	Hex ₂ O	Hexene
50%	50%	6:1	129-133°C	2hrs	39.29%	60.35%	0.36%	<i>n.a</i>
50%	50%	6:1	129-133°C	3hrs	38.01%	61.58%	0.41%	<i>n.a</i>
50%	50%	6:1	129-133°C	24hr	11.74%	86.13%	2.13%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. <i>n.a. = not analyzed</i>								

Table 19:Hydrolysis with 10% KOH at 130 degrees C

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	KOH/HexCl	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
50%	50%	6:1	130-135°C	1.5hrs	35.04%	64.71%	0.25%	<i>n.a</i>
50%	50%	6:1	130-135°C	4hrs	19.50%	79.59%	0.91%	<i>n.a</i>
50%	50%	6:1	130-135°C	5hrs	14.45%	84.30%	1.25%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. <i>n.a. = not analyzed</i>								

Example 13

Influence of ethanol on hydrolysis of

hexyl chloride under various conditions

[0330] In order to examine the possibility that presence of ethanol might improve hydrolysis kinetics at lower temperatures, two additional hydrolysis experiments were conducted using KOH in Example 12 in which a portion (10% or

50%) of the hexanol was substituted by ethanol and the temperature was lowered. Results presented in Tables 20 and 21 show that addition of ethanol had no significant impact on hydrolysis at temperatures lower than 100°C (compare to tables 15 and 17).

Table 20: Hydrolysis with 10% KOH at 88 degrees C with 10% Ethanol out of Hexanol

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	KOH/HexCl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
52.50%	47.50%	6:1	88-95°C	2hrs	51.00%	48.95%	0.05%	<i>n.a</i>
52.49%	47.51%	6:1	88-95°C	4hrs	49.56%	50.38%	0.07%	<i>n.a</i>
52.50%	47.50%	6:1	88-95°C	24hrs	46.46%	53.39%	0.16%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. <i>n.a.</i> = not analyzed								

Table 21: Hydrolysis with 10% KOH at 91 degrees C with 50% Ethanol out of Hexanol

Initial Composition			Reaction Conditions		Final Composition			
HexCl	HexOH	KOH/HexCl molar ratio	Temp. in Bath	Time	HexCl	HexOH	Hex ₂ O	Hexene
65.44%	34.56%	6:1	91-93°C	3hrs	64.47%	35.48%	0.05%	<i>n.a</i>
66.34%	33.66%	6:1	91-93°C	6hrs	61.69%	38.23%	0.08%	<i>n.a</i>
66.00%	34.00%	6:1	91-93°C	24hrs	57.96%	41.92%	0.12%	<i>n.a</i>
*The hexyl chloride %, hexanol% and Dihexyl ether% is an area ratio between HexCl to HexOH and Dihexyl ether. <i>n. a.</i> = not analyzed								

[0331] Results presented in Examples 12 and 13 show that it is possible to hydrolyze hexyl chloride under sufficiently strong conditions of temperature and alkalinity.

Claims

1. A method comprising:

- (a) contacting lime with an extract comprising an S1 solvent carrying a contaminant load to form a lime treated extract; and
- (b) reducing said contaminant load by removing solids;

wherein said S1 solvent is an organic solvent selected from the group consisting of alcohols, ketones, and aldehydes having at least 5 carbon atoms, and further wherein said contaminant load comprises one or more impurities selected from the group consisting of mineral acids, organic acids, anionic chloride complexes of heavy metals, alkyl chlorides, alkyl acetates, phenolic compounds, aldehydes, furfural, hydroxymethylfurfural, tall oils, wood extractives and products of their reaction.

2. The method of claim 1, comprising washing said lime treated extract with water.

3. The method according to claim 1, wherein said S1 solvent is n-hexanol.

4. The method according to any one of the preceding claims, wherein said contaminant load is reduced by more than 20%.

5. The method according to claim 1, wherein the apparent pH of the lime treated extract is at least 6.5.

6. An apparatus comprising:

- (a) a decontamination module adapted to contact lime with an extract comprising an S1 solvent carrying a contaminant load to produce limed extract;
- (b) a solids removal mechanism adapted to remove solids from said limed extract;
- (c) an acidulating mechanism adapted to acidify said limed extract; and
- (d) a washing mechanism adapted to wash said acidulated extract;

wherein said S1 solvent is an organic solvent selected from the group consisting of alcohols, ketones, and aldehydes having at least 5 carbon atoms, and further wherein said contaminant load comprises one or more impurities selected from the group consisting of mineral acids, organic acids, anionic chloride complexes of heavy metals, alkyl chlorides, alkyl acetates, phenolic compounds, aldehydes, furfural, hydroxymethylfurfural, tall oils, wood extractives and products of their reaction.

Patentansprüche

1. Verfahren, das Folgendes umfasst:

- (a) In-Kontakt-Bringen von Kalk mit einem Extrakt, der ein S1-Lösungsmittel umfasst, das schadstoffbelastet ist, um einen mit Kalk behandelten Extrakt zu bilden; und
- (b) Verringern der Schadstoffbelastung durch Entfernen der Feststoffe;

wobei das S1-Lösungsmittel ein organisches Lösungsmittel ist, das aus der Gruppe ausgewählt wird, die aus Folgendem besteht: Alkoholen, Ketonen und Aldehyden mit mindestens 5 Kohlenstoffatomen und ferner wobei die Schadstoffbelastung eine oder mehrere Verunreinigungen umfasst, die aus der Gruppe ausgewählt werden, die aus Folgendem besteht: Mineralsäuren, organischen Säuren, anionischen Chlorid-Komplexen von Schwermetallen, Alkylchloriden, Alkylacetaten, phenolischen Verbindungen, Aldehyden, Furfural, Hydroxymethylfurfural, Tallölen, Holzextrakten und Produkten ihrer Reaktion.

2. Verfahren nach Anspruch 1, das das Waschen des mit Kalk behandelten Extrakts mit Wasser umfasst.

3. Verfahren nach Anspruch 1, wobei das S1-Lösungsmittel n-Hexanol ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Schadstoffbelastung um mehr als 20 % verringert wird.

5. Verfahren nach Anspruch 1, wobei der scheinbare pH-Wert des mit Kalk behandelten Extrakts mindestens 6, 5 beträgt.

6. Vorrichtung, die Folgendes umfasst:

- (a) ein Dekontaminationsmodul, das dafür ausgelegt ist, Kalk mit einem Extrakt zu kontaktieren, der ein S1-Lösungsmittel umfasst, das eine Schadstoffbelastung trägt, um einen Kalkextrakt herzustellen;
- (b) einen Feststoffentfernungsmechanismus, der dafür ausgelegt ist, Feststoffe aus dem Kalkextrakt zu entfernen;
- (c) einen Ansäuerungsmechanismus, der dafür ausgelegt ist, den Kalkextrakt anzusäuern; und
- (d) einen Waschmechanismus, der dafür ausgelegt ist, den angesäuerten Extrakt zu waschen;

wobei das S1-Lösungsmittel ein organisches Lösungsmittel ist, das aus der Gruppe ausgewählt wird, die aus Folgendem besteht: Alkoholen, Ketonen und Aldehyden mit mindestens 5 Kohlenstoffatomen und ferner wobei die Schadstoffbelastung eine oder mehrere Verunreinigungen umfasst, die aus der Gruppe ausgewählt werden, die aus Folgendem besteht: Mineralsäuren, organischen Säuren, anionischen Chlorid-Komplexen von Schwermetallen, Alkylchloriden, Alkylacetaten, phenolischen Verbindungen, Aldehyden, Furfural, Hydroxymethylfurfural, Tallölen, Holzextrakten und Produkten ihrer Reaktion.

Revendications

1. Procédé comprenant :

- (a) la mise en contact de chaux avec un extrait comprenant un solvant S1 porteur d'une charge contaminante pour former un extrait traité à la chaux ; et
- (b) la réduction de ladite charge contaminante par l'élimination de la matière solide ;

5 ledit solvant S1 étant un solvant organique choisi dans le groupe constitué par les alcools, les cétones et les aldéhydes ayant au moins 5 atomes de carbone, et ladite contaminante comprenant au moins une impureté choisie dans le groupe constitué par les acides minéraux, les acides organiques, des complexes chlorure anionique de métaux lourds, les chlorures d'alkyle, les acétates d'alkyle, les composés phénoliques, les aldéhydes, le furfural, l'hydroxyméthylfurfural, le tallöl, les produits d'extraction du bois et les produits de leur réaction.

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- 2. Procédé de la revendication 1, comprenant le lavage dudit extrait traité à la chaux avec de l'eau.
 - 3. Procédé de la revendication 1, dans lequel ledit solvant S1 est le n-hexanol.
 - 15 4. Procédé de l'une quelconque des revendications précédentes, dans lequel ladite charge contaminante est réduite de plus de 20 %.

- 5. Procédé de la revendication 1, dans lequel le pH apparent de l'extrait traité à la chaux est d'au moins 6,5.

- 20 6. Appareil comprenant :

- (a) un module de décontamination adapté pour mettre en contact de la chaux avec un extrait comprenant un solvant S1 porteur d'une charge contaminante pour produire un extrait traité à la chaux
- 25 (b) un mécanisme d'élimination de matière solide adapté pour éliminer la matière solide dudit extrait traité à la chaux
- (c) un mécanisme d'acidulation adapté pour acidifier ledit extrait traité à la chaux ; et
- (d) un mécanisme de lavage adapté pour lavé ledit extrait acidulé ;

30 ledit solvant S1 étant un solvant organique choisi dans le groupe constitué par les alcools, les cétones et les aldéhydes ayant au moins 5 atomes de carbones, et ladite charge contaminante comprenant en outre au moins une impureté choisie dans le groupe constitué par les acides minéraux, les acides organiques, des complexes chlorure anionique de métaux lourds, les chlorures d'alkyle, les acétates d'alkyle, les composés phénoliques, les aldéhydes, le furfural, l'hydroxyméthylfurfural, le tallöl, les produits d'extraction du bois et les produits de leur réaction.

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Fig. 1

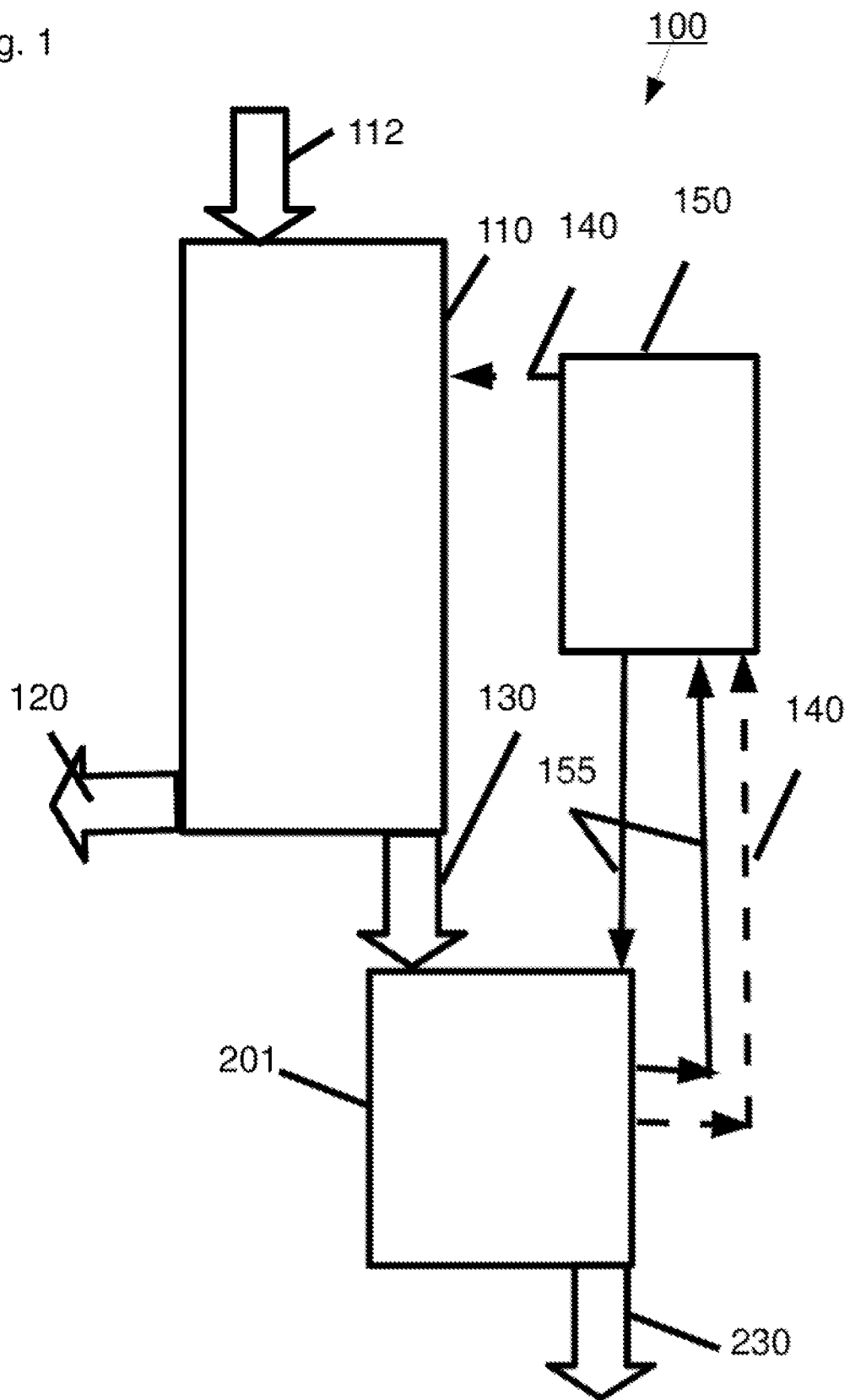


Fig. 2

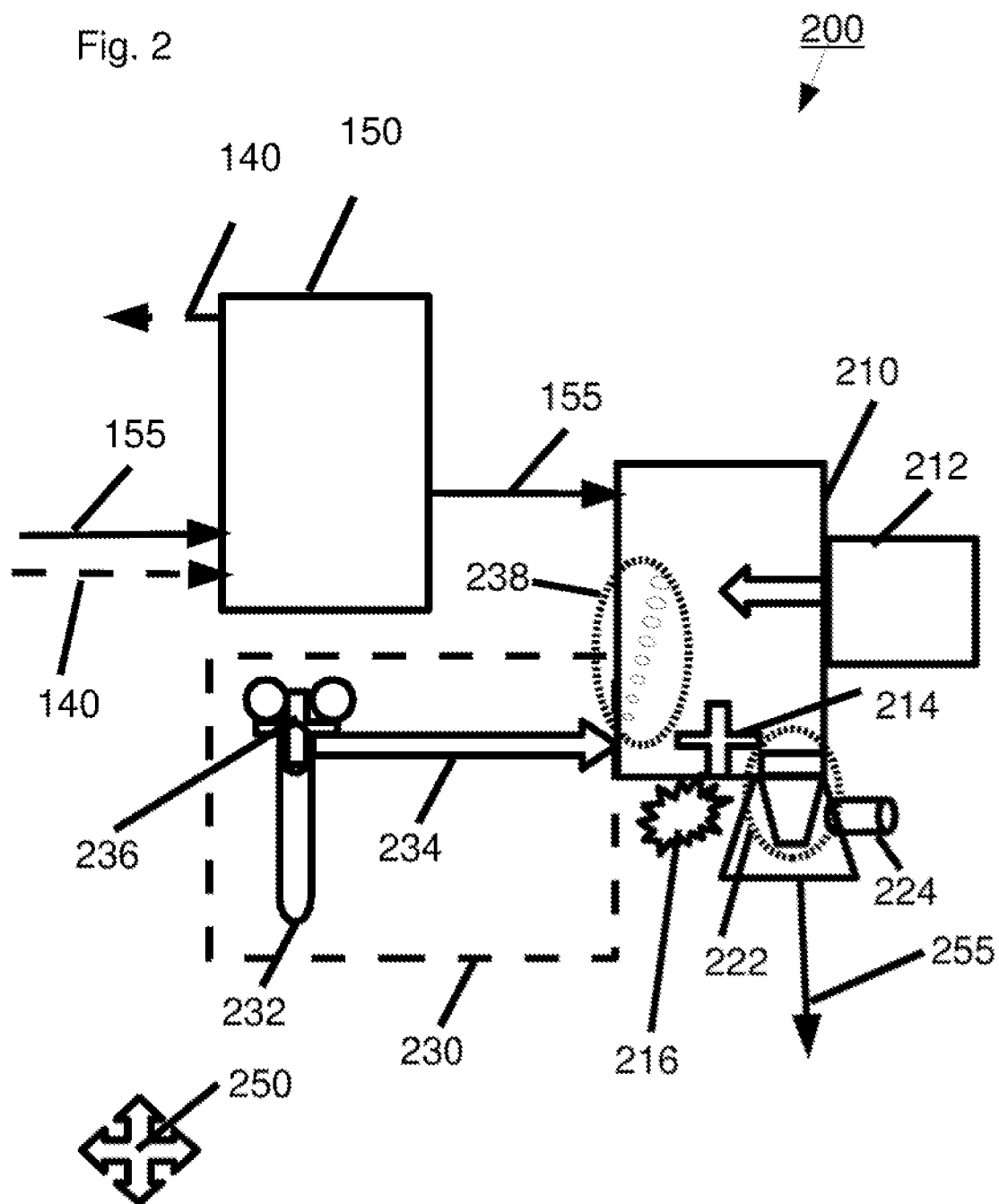


Fig. 3

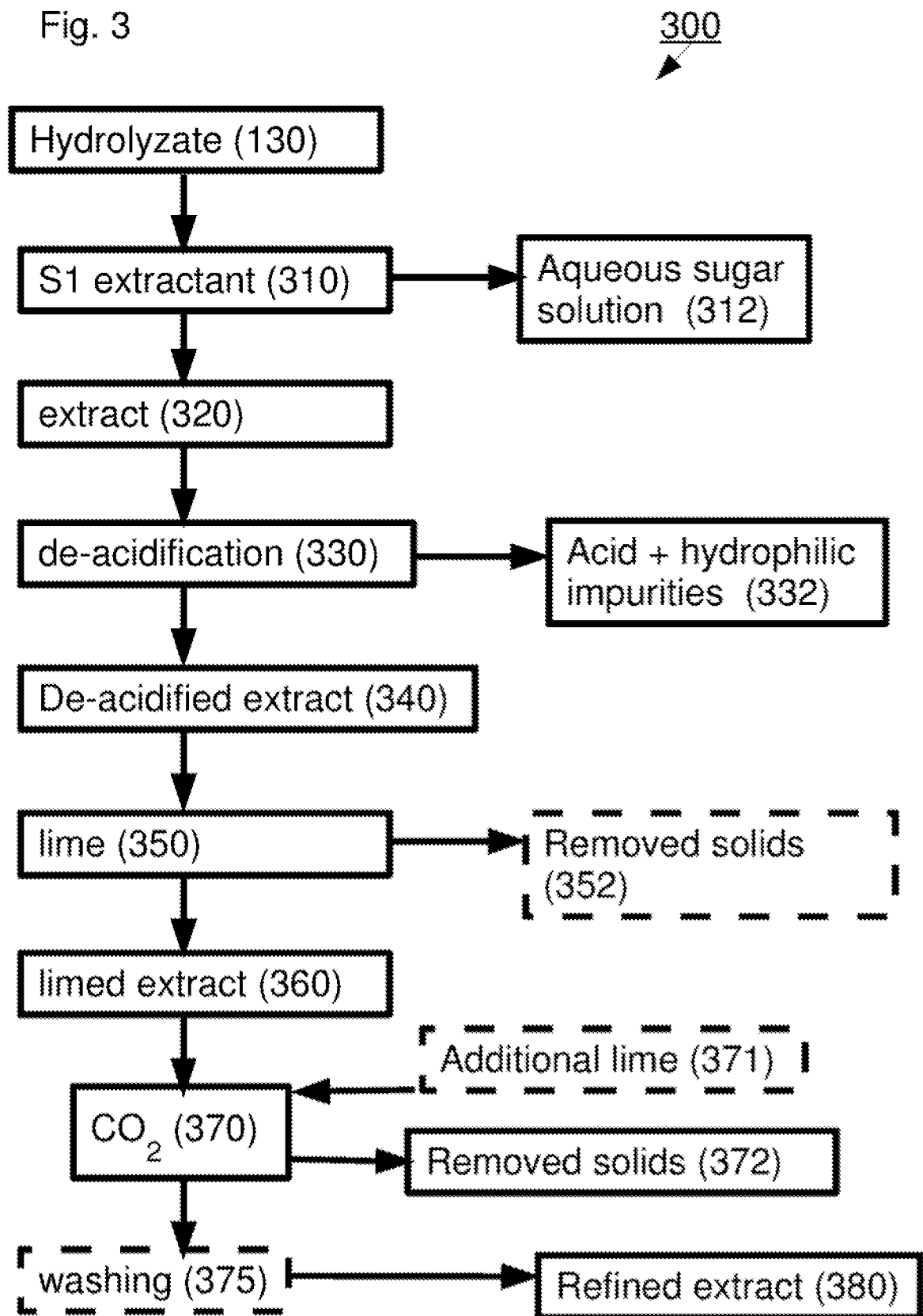


Fig. 4a

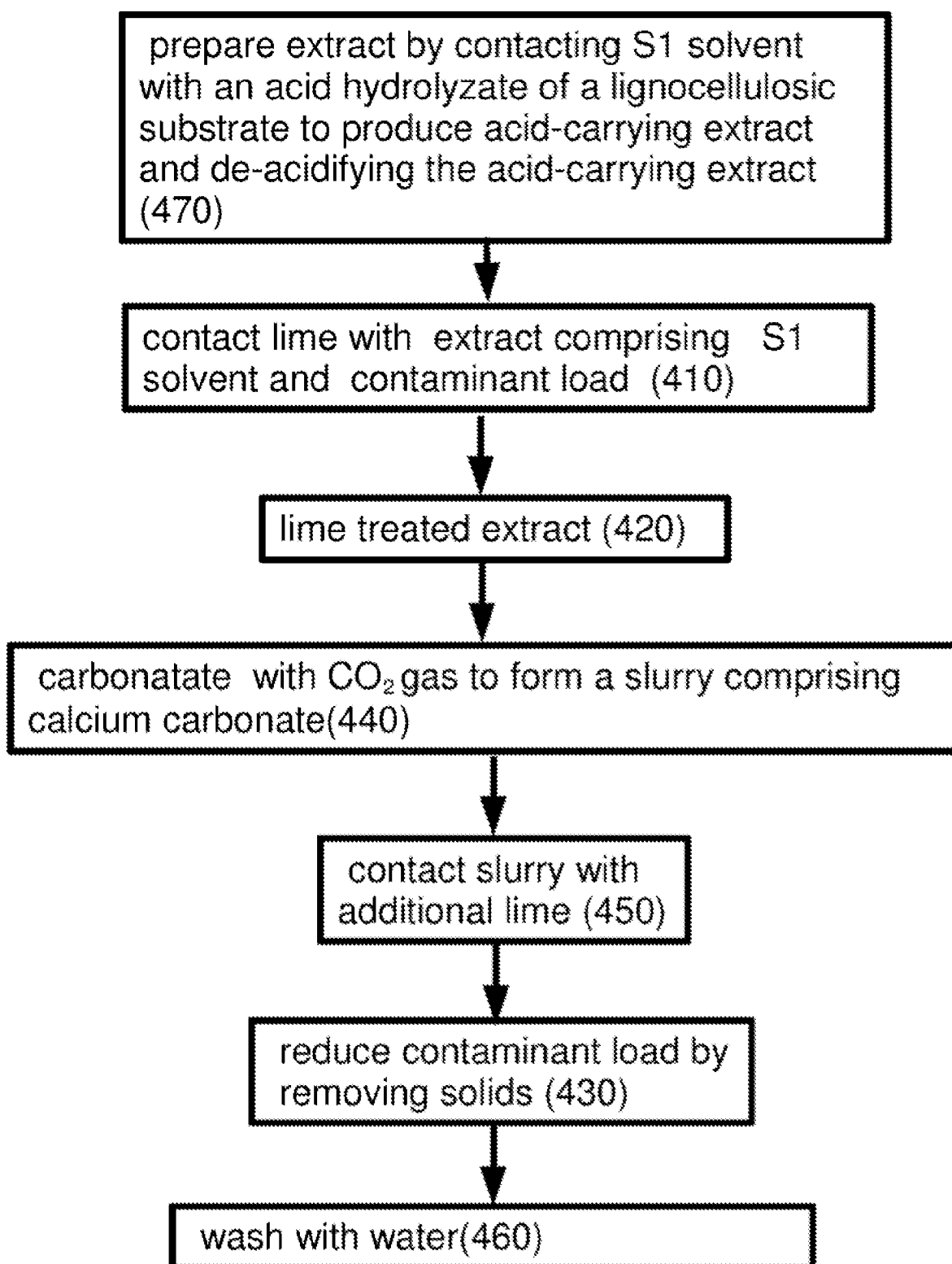
400
▲

Fig. 4b

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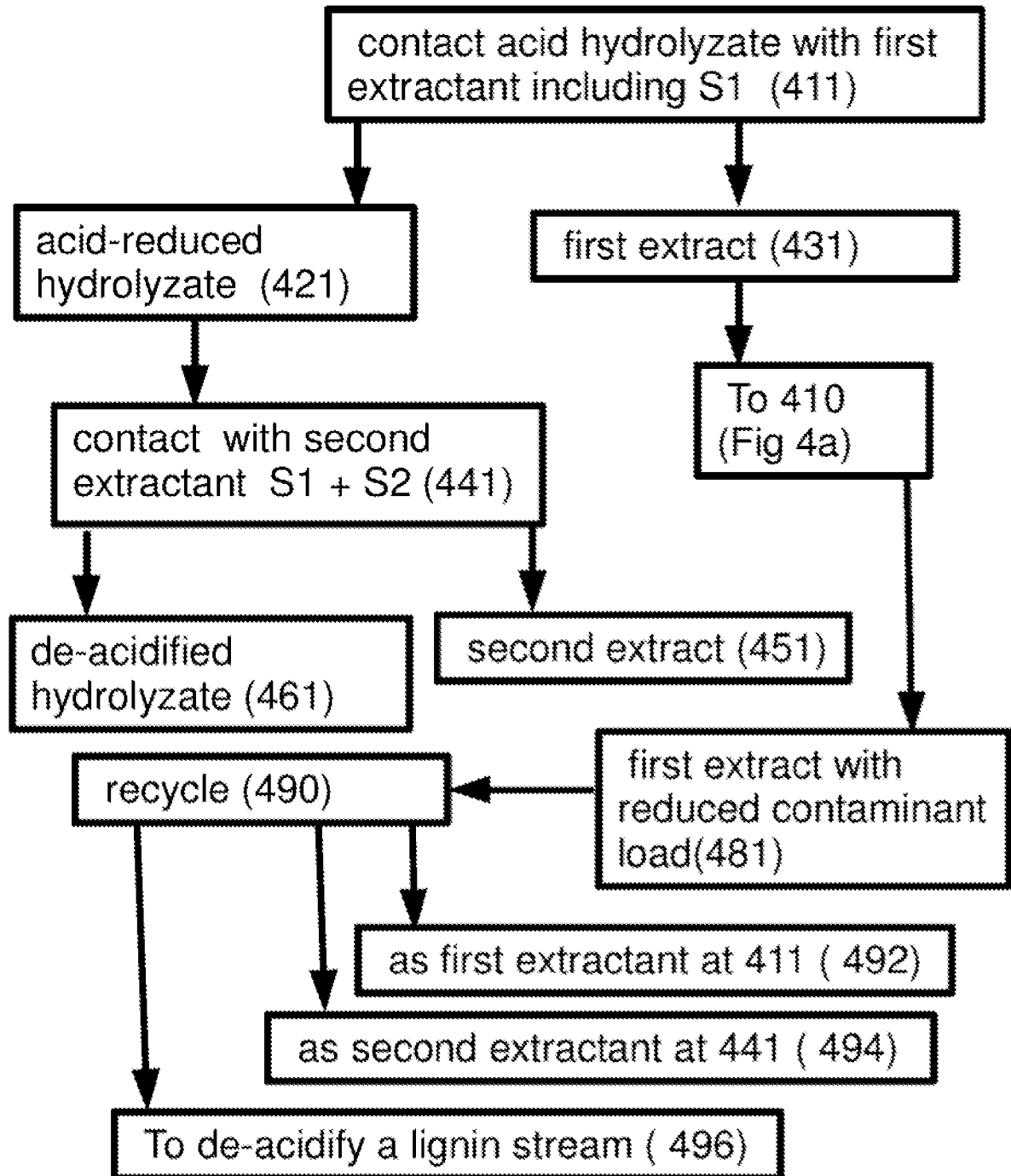


Fig. 4c

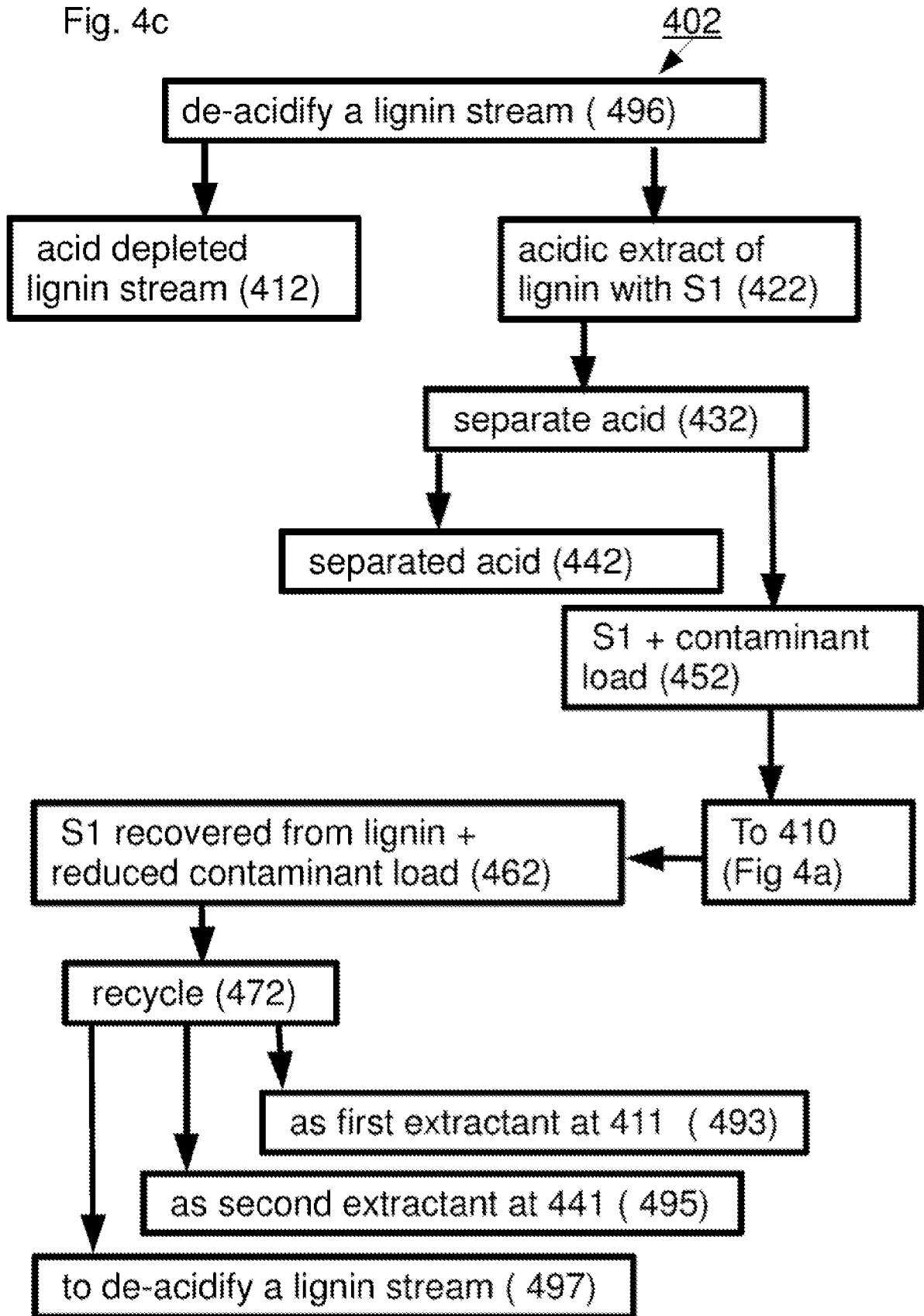
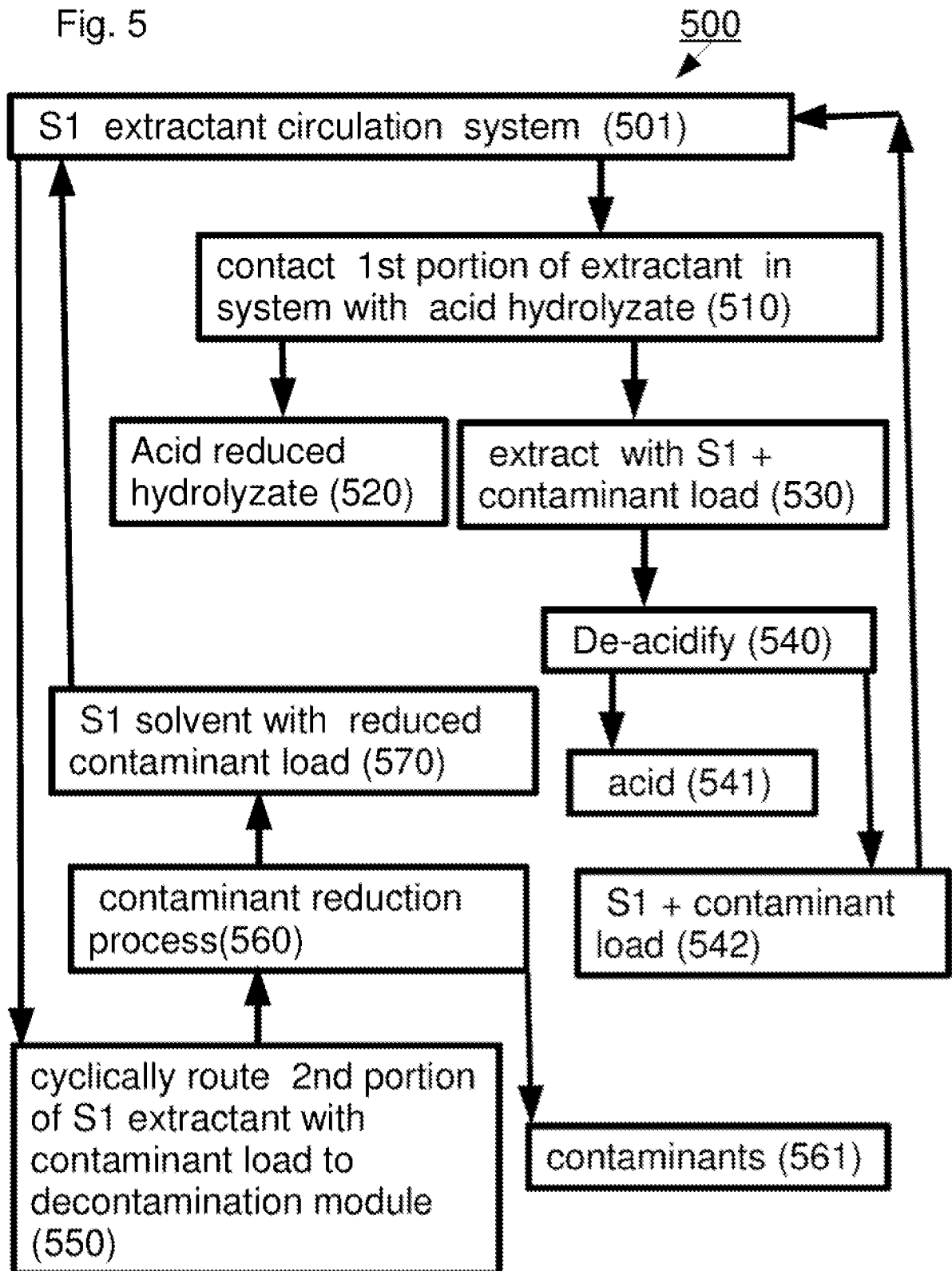
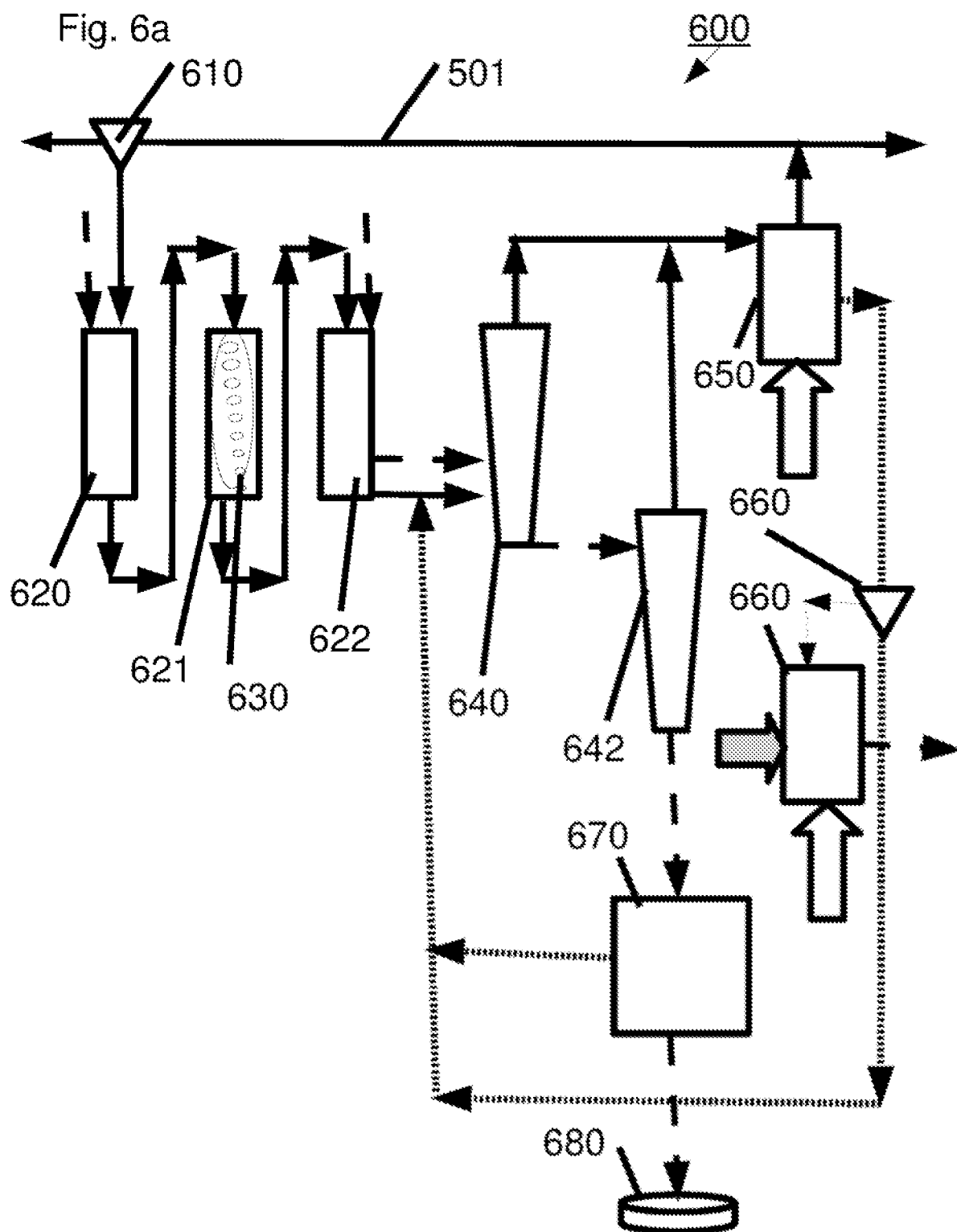


Fig. 5





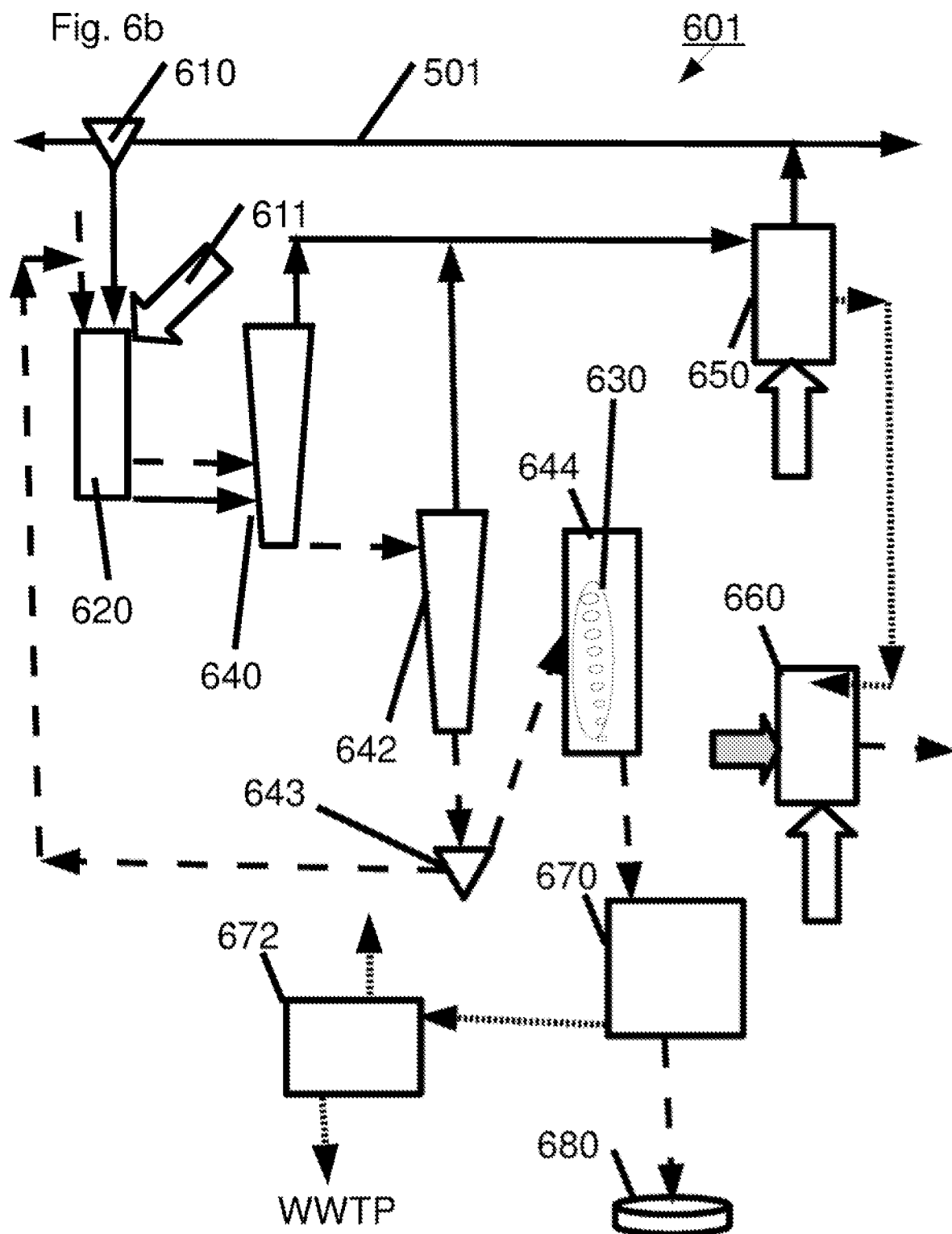


Fig. 7

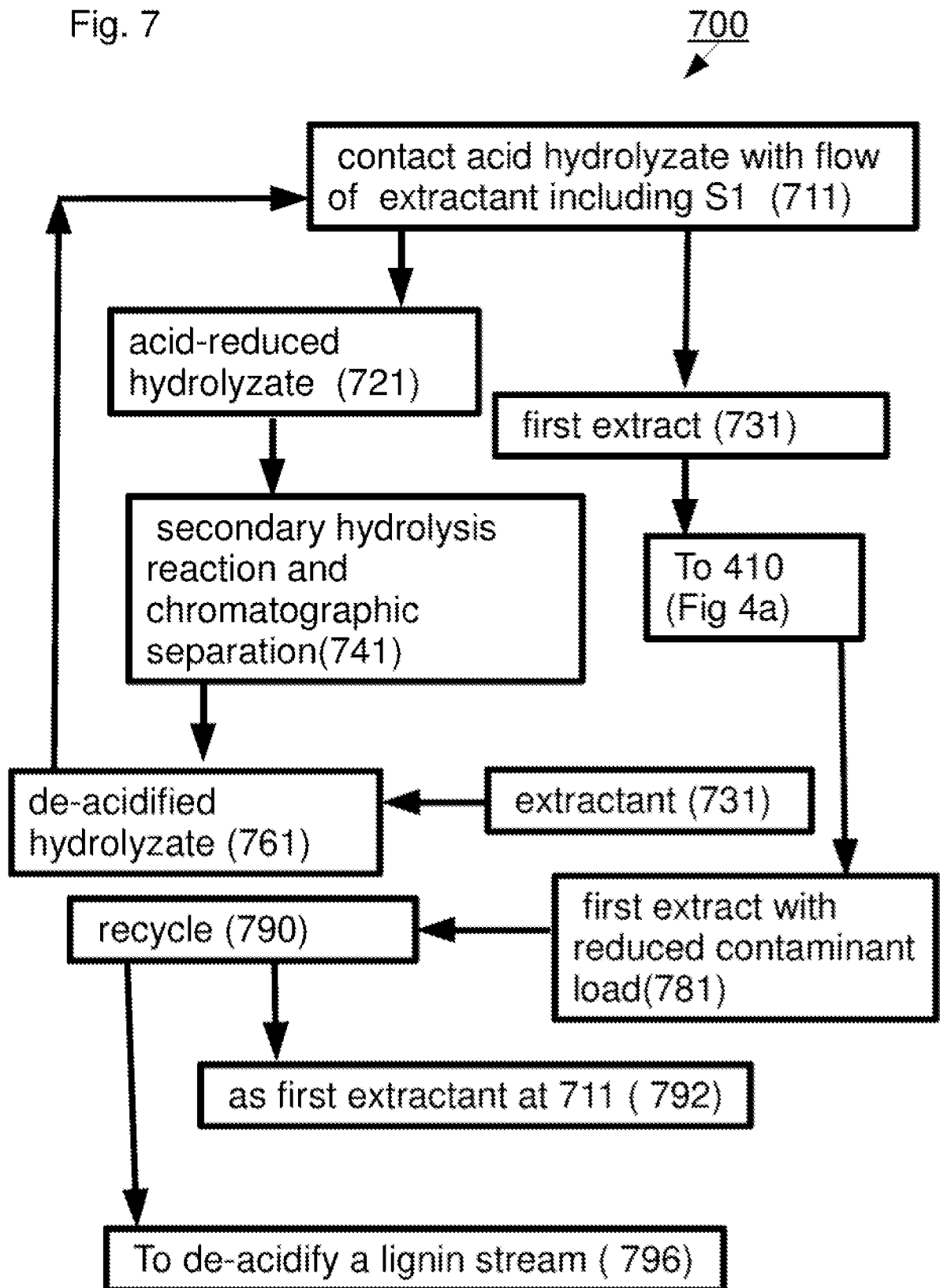


Fig. 8a

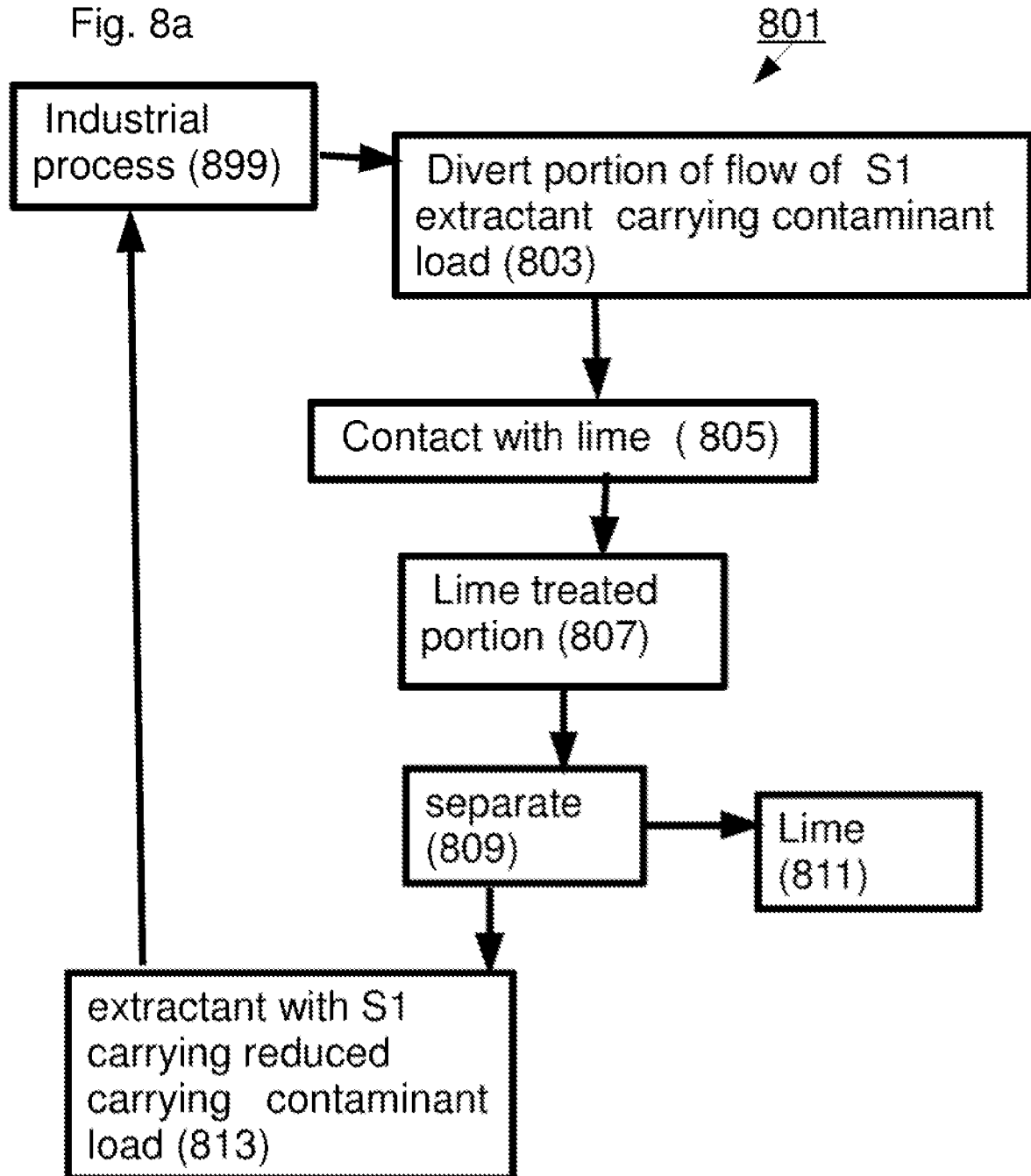


Fig. 8b

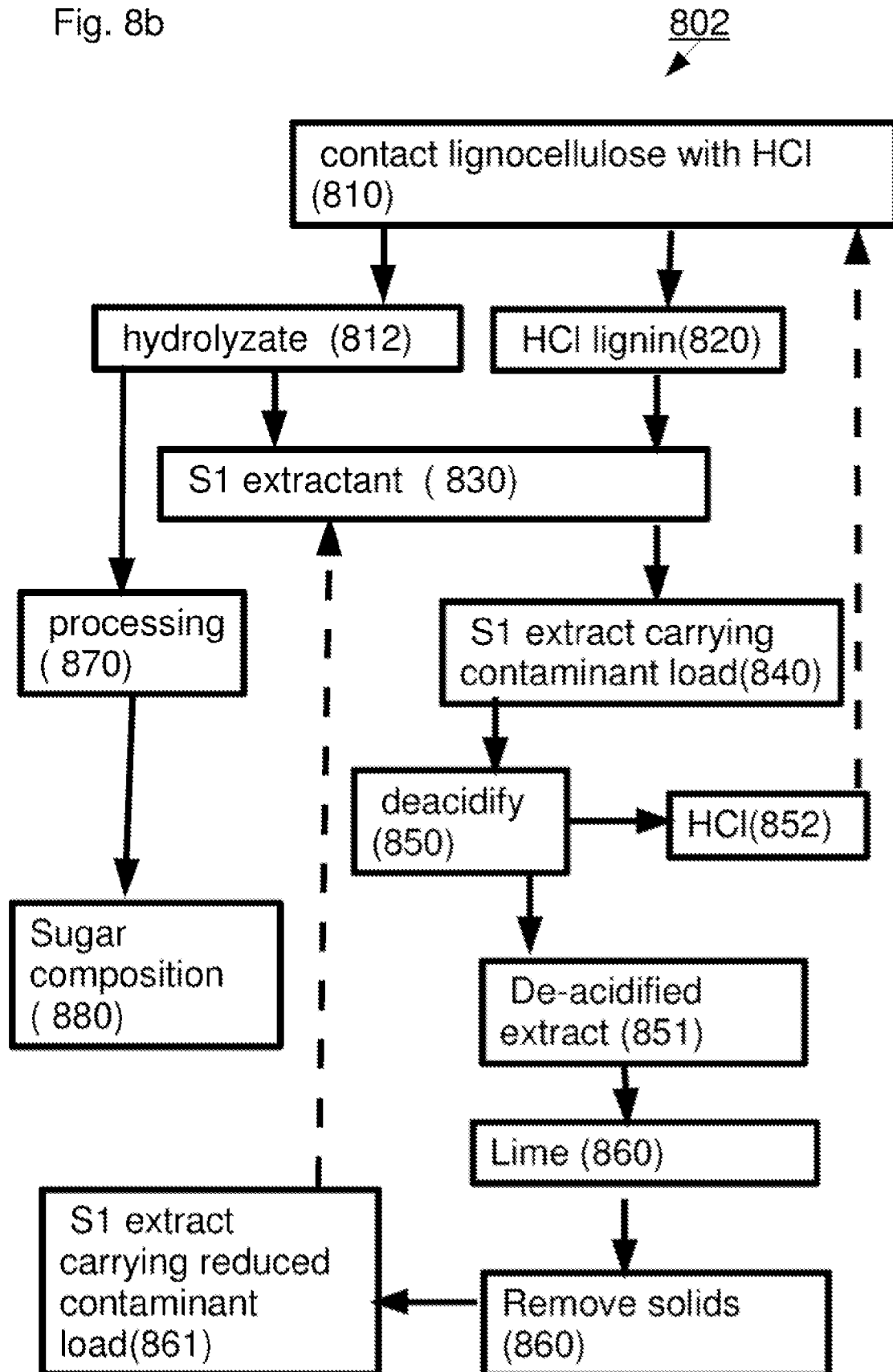
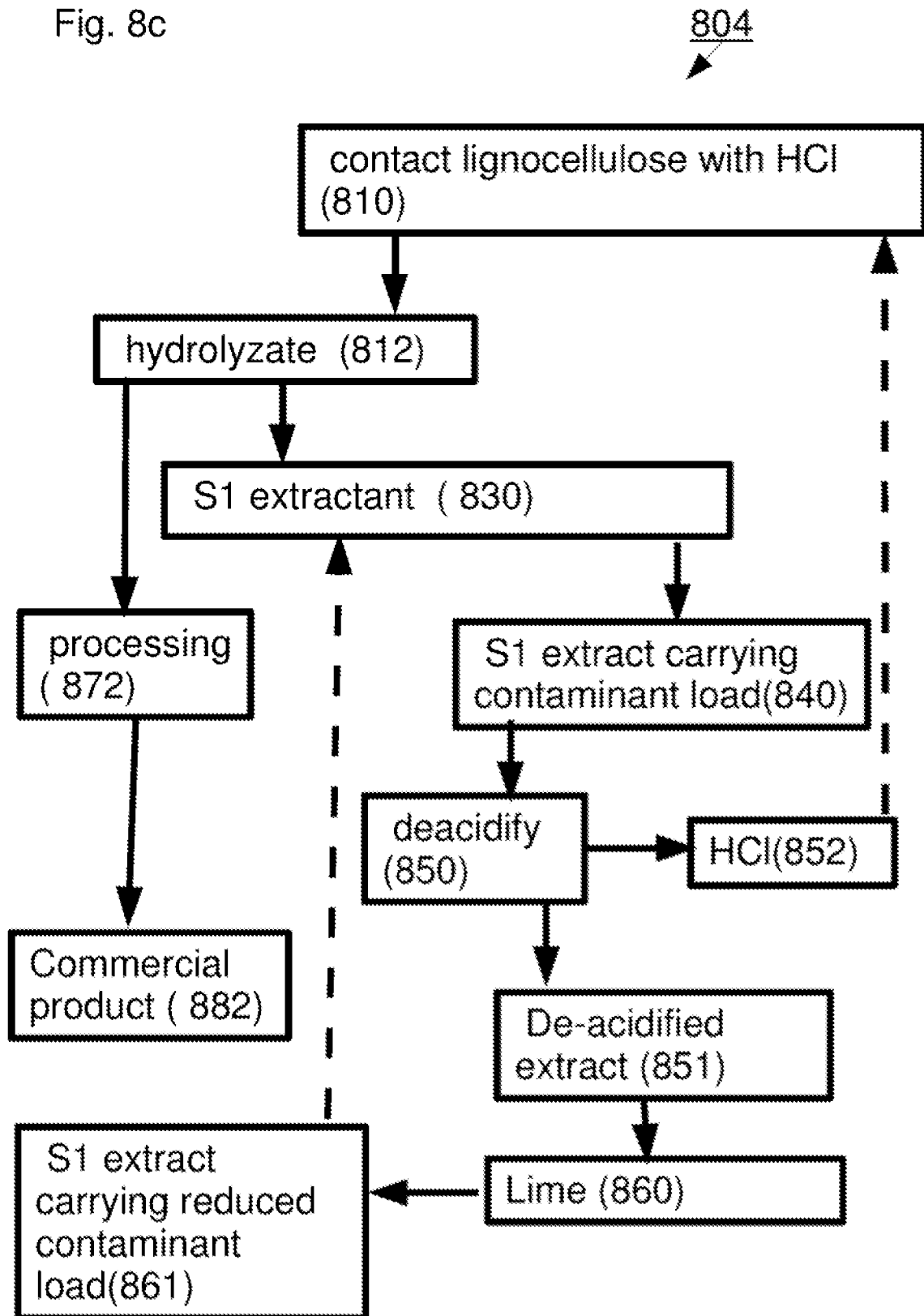


Fig. 8c



REFERENCES CITED IN THE DESCRIPTION

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Eljárás és rendszerek oldószeres tisztításra

Szabadalmi igénypontok

1. Eljárás, melynek során:

- (a) meszet érintkeztetünk egy szennyező anyagot hordozó S1 oldószert tartalmazó extraktummal, egy mésszel kezelt extraktum képzésére; és
- (b) a szennyező anyag mennyiségét a szilárd anyag eltávolításával csökkentjük; ahol az S1 oldószer egy legalább 5 szénatomot tartalmazó alkoholok, ketonok és aldehidek közül választott szerves oldószer, és továbbá, ahol a szennyező anyag ásványi anyagok, nehézfémek anionos klorid komplexei, alkilkloridok, fenolos vegyületek, aldehidek, furfural, hidroximetil-furfural, tallolaj, fa extraktumok és ezek reakciótermékei közül választott egy vagy több szennyezés.

2. Az 1. igénypont szerinti eljárás, melynek során a mésszel kezelt extraktumot vízzel mossuk.

3. Az 1. igénypont szerinti eljárás, ahol az S1 oldószer n-hexanol.

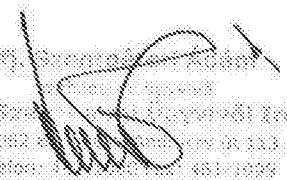
4. Az előző igénypontok bármelyike szerinti eljárás, ahol a szennyező anyag tartalmát 20%-nál nagyobb mértékben csökkentjük.

5. Az 1. igénypont szerinti eljárás, ahol a mésszel kezelt extraktum látszólagos pH-értéke legalább 6.5.

6. Berendezés, mely az alábbiakat tartalmazza:

- (a) egy szennyezés-eltávolító egység, a méssznek egy szennyező anyagot hordozó S1 oldószert tartalmazó extraktummal történő érintkezésére, egy mésszel kezelt extraktum képzésére;
- (b) szilárdanyag eltávolító szerkezet, mely a mésszel kezelt extraktumból a szilárd anyag eltávolítására kialakított;
- (c) savasító szerkezet, mely a mésszel kezelt extraktum savasítására kialakított; és

(d) mosó szerkezet, mely a savasított extraktum mosására kialakított;
ahol az S1 oldószer egy legalább 5 szénatomot tartalmazó alkoholok, ketonok és aldehidek közül választott szerves oldószer, és továbbá, ahol a szennyező anyag ásványi anyagok, nehézfémek anionos klorid komplexei, alkilkloridok, fenolos vegyületek, aldehidek, furfural, hidroximetil-furfural, tallolaj, fa extraktumok és ezek reakciótermékei közül választott egy vagy szennyezés.


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