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(54) Title: PROCESSES FOR PURIFYING A CELLULOSIC MATERIAL

(57) Abstract: A process for treating a cellulosic material comprising extracting the cellulosic material with an extractant to selectively extract hemicellulose therefrom and separating the extracted hemicellulose to form a cellulosic product comprising less hemicellulose than the cellulosic material. The extractant comprises a cellulose solvent and a co-solvent. The cellulosic product advantageously retains its cellulosic fiber morphology. The processes involve separating and recovering the hemicellulose and separating and recycling various process streams employed in the process.



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PROCESSES FOR PURIFYING A CELLULOSIC MATERIAL

PRIORITY CLAIM

[0001] This application claims priority to U.S. App. No. 61/819,150, filed May 3, 2013, and to U.S. App. No. 61/862,917, filed August 6, 2013, the entire contents and disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for purifying a cellulosic material. In particular, the present invention relates to processes for extracting and recovering hemicellulose from pulp and producing a purified pulp comprising cellulose and having reduced hemicellulose content.

BACKGROUND OF THE INVENTION

[0003] Cellulose is typically obtained from wood pulp and cotton and may be further modified to create derivatives including regenerated cellulose, cellulose ethers, cellulose esters and cellulose nitrate, among others. Cellulose derivatives have a variety of commercial uses. For example, cellulose acetate is the acetate ester of cellulose and is used for a variety of products, including textiles (e.g., linings, blouses, dresses, wedding and party attire, home furnishings, draperies, upholstery and slip covers), industrial uses (e.g., cigarette and other filters for tobacco products, and ink reservoirs for fiber tip pens, decking lumber), high absorbency products (e.g., diapers, sanitary napkins, and surgical products), thermoplastic products (e.g., film applications, plastic instruments, and tape), cosmetic and pharmaceutical (extended capsule/tablet release agents and encapsulating agent), medicinal (hypoallergenic surgical products) and others.

[0004] High purity α -cellulose is commonly required as a starting material to make cellulose derivatives, such as cellulose acetate. Acetate-grade pulps are specialty raw materials produced in commercial pulp processes, but the cost for such pulps is high. Commercial paper grade pulps contain less than 90% α -cellulose and are potential crude cellulosic sources for making cellulose derivatives. Paper grade pulp contains a high amount of impurities, such as hemicellulose, rendering it incompatible with certain industrial uses, such as making cellulose acetate flake or tow.

[0005] Zhou et al. discusses the use of dimethyldioxirane (DMDO), a pulp bleaching agent, to treat birch pulp and obtain acetate-grade pulp. However, currently, DMDO is not commercially available due to its instability. Therefore, it is not an ideal solvent for producing large quantities of

high α -cellulose content pulp. Zhou et al. "Acetate-grade pulp from birch," BioResources, (2010), 5(3), 1779-1778.

[0006] Studies have been done regarding the treatment of biomass to form biofuels. Specifically, it is known that various ionic liquids can be used to dissolve cellulosic material. S. Zhu et al. in Green Chem. 2006, 8, pp. 325-327, describe the possibility of dissolving cellulose in ionic liquids and recovering it by addition of suitable precipitating agents such as water, ethanol, or acetone.

[0007] Others have used ionic liquids to break down the cellulosic materials to make biofuels by way of glucose. For example, U.S. Pub. No. 2010/0112646 discloses a process for preparing glucose from a cellulose material, in which a cellulose-comprising starting material is provided and treated with a liquid treatment medium comprising an ionic liquid and an enzyme. Similarly, U.S. Pub. No. 2010/0081798 discloses a process for preparing glucose from a material containing ligno-cellulose, in which the material is first treated with an ionic liquid and then subjected to enzymatic hydrolysis. U.S. Pub. No. 2010/0081798 describes obtaining glucose by treating a material containing ligno-cellulose with an ionic liquid and subjecting same to an enzymatic hydrolysis and fermentation. However, in order to turn cellulose containing materials into glucose, the methods disclosed in these references result in breaking down the cellulose molecules, making them unsuitable for use as starting materials to make cellulose derivatives.

[0008] U.S. Pat. 7,828,936 describes a method for dissolving cellulose in which the cellulose based raw material is admixed with a mixture of a dipolar aprotic intercrystalline swelling agent and an ionic liquid. This method results in the complete dissolution of the cellulose and destruction of the fiber morphology of the cellulose. Although the cellulose may be regenerated using a non-solvent, the crystallinity of the regenerated cellulose is lower than the original cellulose sample.

[0009] The need exists for processes for producing high purity cellulose from lower grade starting materials without destroying the fiber morphology and other characteristics of the cellulose structure. In particular, the need exists for cost effective processes for removing and recovering hemicellulose from cellulosic materials to yield high purity cellulose that can be converted to other cellulose derivatives.

SUMMARY OF THE INVENTION

[0010] The present invention is directed to processes for purifying a cellulosic material, e.g., wood pulp or paper grade wood pulp, and preferably for recovering hemicellulose therefrom. In one embodiment, for example, the invention is to a process for purifying a cellulosic material,

comprising extracting hemicellulose from the cellulosic material with an extractant to form an intermediate cellulosic material having a reduced hemicellulose content; concentrating the intermediate cellulosic material to form a concentrated cellulosic material having an increased solids content; and recovering the separated hemicellulose. The concentrated cellulosic material preferably is dried to recover a finished cellulosic product. The extracting hemicellulose step preferably comprises directing the cellulosic material and the extractant to an extractor; extracting hemicellulose from the cellulosic material in the extractor to form an extraction mixture; and filtering and washing the extraction mixture with an extractant wash to form the intermediate cellulosic material and an extraction filtrate.

[0011] In another embodiment, the invention is to a process for purifying a cellulosic material, comprising extracting hemicellulose from the cellulosic material in an extractor with an extractant to form an intermediate cellulosic material having a reduced hemicellulose content; filtering and washing the intermediate cellulosic material to form a washed intermediate cellulosic material and an extraction filtrate; recovering recovered extractant from the extraction filtrate; and directing the recovered extractant to the extractor.

[0012] In another embodiment, the invention is to a process for purifying a cellulosic material, comprising extracting hemicellulose from the cellulosic material in an extractor with an extractant to form an intermediate cellulosic material having reduced hemicellulose content; filtering and washing the intermediate cellulosic material to recover an extraction filtrate comprising extractant and separated hemicellulose; precipitating the separated hemicellulose in a precipitator with a precipitation agent; and returning recovered extractant from the precipitator to the extractor.

[0013] It is preferred, in all embodiments of the present invention, that the extractant comprises a cellulose solvent and a co-solvent, and the cellulose solvent is selected from the group consisting of an ionic liquid, an amine oxide and combinations thereof. The co-solvent is preferably selected from the group consisting of dimethyl sulfoxide, tetramethylene sulfone, piperylene sulfone, tetramethylene sulfoxide, N-methyl pyrrolidone, dimethyl formamide, acetonitrile, acetic acid, water, and mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWING

[0014] The present invention will be better understood in view of the appended non-limiting figure, in which:

[0015] FIG. 1 shows an exemplary purification process in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

I. Introduction

[0016] The present invention relates to processes for purifying a cellulosic material, comprising separating, e.g., extracting, hemicellulose and other cellulosic impurities (e.g., dichloromethane (DCM) extractables and degraded cellulose) from the cellulosic material with an extractant to form an intermediate cellulosic material having a reduced hemicellulose content; concentrating the intermediate cellulosic material to form a concentrated cellulosic material having an increased solids content; and recovering the separated hemicellulose. The extractant used in the separating step comprises a cellulose solvent and a cellulose co-solvent. The cellulose solvent should be suitable for dissolving hemicellulose, and preferably degraded cellulose and other impurities in the cellulosic material, but should have little solubility for α -cellulose. The cellulose solvent is selected from the group consisting of an ionic liquid, an amine oxide and combinations thereof, and the cellulose co-solvent is preferably selected from the group consisting of dimethyl sulfoxide ("DMSO"), tetramethylene sulfone, tetramethylene sulfoxide, N-methyl pyrrolidone, dimethyl formamide ("DMF"), acetonitrile, acetic acid, water, and mixtures thereof. The concentrated cellulosic material may be dried to form a finished cellulosic product.

[0017] The processes of the invention are particularly suitable for separating and removing impurities, such as hemicellulose and/or degraded cellulose, from a cellulosic material to form a finished cellulosic product, the purity of which may vary widely depending largely on the composition of the starting cellulosic material, the composition of the extractant used, and extraction conditions. In preferred aspects, the finished cellulose product comprises acetate (or higher) grade cellulose.

[0018] During extraction, hemicellulose and preferably degraded cellulose are preferentially separated from the intermediate cellulosic material to form an extraction filtrate comprising extractant, extracted hemicellulose and preferably extracted degraded cellulose. As a result, the intermediate cellulosic material, the concentrated cellulosic material and the ultimately formed cellulosic product comprise less hemicellulose, and preferably less degraded cellulose, than the starting cellulosic material, e.g., at least 10% less, at least 20% less or at least 30% less hemicellulose than the starting cellulosic material and at least 5% less, at least 10% less or at least 20% less degraded cellulose than the starting cellulosic material. During extraction, and throughout the cellulose purification and hemicellulose recovery process, the generation of side products or by-products, e.g., mono-, di-, and oligo-saccharide, may be limited. However, if side products and/or

by-products are generated, they may be removed from the process according to conventional means. This removal may be preferred if the process is continuous, so as to prevent build-up of side products and/or by-products.

[0019] The intermediate cellulosic material formed in the extraction step may initially comprise a minor amount of residual extractant, residual hemicellulose and/or residual degraded cellulose, and may be washed with an extractant wash to remove one or more of these materials. Depending on the extractant wash, the washing may occur at a temperature from its melting point to its boiling point, conveniently, from 0 to 95°C, e.g., from 30 to 95°C or from 75 to 95°C. In some embodiments, the extractant wash may be selected from the group consisting of an alcohol, a ketone, a nitrile, an ether, an ester, a carboxylic acid, a halide, a hydrocarbon compound, an amine, a heterocyclic compound, water, and combinations thereof. In other embodiments, the extractant wash may be selected from the group consisting of acetonitrile, acetone, methanol, ethanol, isopropanol, methyl acetate, ethyl acetate, vinyl acetate, propionitrile, dichloromethane, chloroform, butyronitrile, chloroacetonitrile, water, and combinations thereof. In yet other embodiments, the extractant wash may be selected from the group consisting of water, ethylene glycol, glycerin, formamide, N,N-dimethylformamide, N-methylpyrrolidinone, N,N-dimethylacetamide, DMSO, a mixture of water and alcohol, and combinations thereof. Extractant wash can also be the extractant which comprises cellulose solvent and co-solvent. After washing, the intermediate cellulosic material preferably comprises less than 5 wt.% extractant, e.g., less than 1 wt.%, or less than 0.1 wt.% extractant, based on the total weight of the intermediate cellulosic material (including any residual extractant). The washing step may be repeated, as necessary, to remove residual extractant to a desired level.

[0020] The processes of the invention also involve the separation and recycle of various process streams, e.g., extractant, extractant wash, precipitation agent, and precipitant wash streams, used in the cellulose and hemicellulose purification processes. For example, after the washing step, the resulting extractant wash filtrate may be subjected to a separation step, e.g., in one or more distillation columns, to separate extractant wash from the extractant. The recovered extractant may be recycled to the extraction step, and the recovered extractant wash may be recycled to the washing step. As described above, any side products and/or by-products that are generated in the extraction process may be removed from the system using appropriate separating technology, e.g., membrane, ion exchange or similar separation technologies.

[0021] In this invention, various separation processes describe separating and recovering hemicellulose from the starting cellulosic material. In this process, it is implicit that separation of

hemicellulose may include separation of other undesirable components such as degraded cellulose and other extractables, the content of which may need to be reduced to reach desired treated cellulose quality.

[0022] The process may also comprise recovering hemicellulose from the extraction filtrate. Hemicellulose recovery may be achieved by concentrating the extraction filtrate, optionally in an ultrafiltration unit or in an evaporator, to form a hemicellulose concentrate and recovered extractant. The recovered extractant, which may be enriched in co-solvent, may be advantageously recycled to the extractor or be employed as a washing agent, e.g., extractant wash, for the cellulosic product, while the hemicellulose concentrate may be directed to a precipitator, to which a precipitation agent is added to form a precipitation slurry. The precipitation agent is selected from the group consisting of alcohol, a ketone, a nitrile, an ether, an ester, a carboxylic acid, a halide, a hydrocarbon compound, an amine, a heterocyclic compound, water, and combinations thereof. The precipitation agent is selected from the group consisting of methanol, ethanol, isopropanol, butanol, acetone, 2-butanone, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, tetrahydrofuran, diethyl ether, dibutyl ether, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, propylene carbonate, acetic acid, formic acid, formamide, dichloromethane, chloroform, 1-chlorobutane, 1,2-dichloroethane, hexane, 2,2,4-trimethylpentane, benzene, toluene, ethylamine, butylamine, ethyldiamine, pyridine, pyrrole, pyrrolidine, piperidine, water, and combinations thereof. The precipitation slurry may then be filtered and optionally washed with a precipitant wash, e.g., water, to form a precipitation agent filtrate and recovered solid hemicellulose. The precipitation agent filtrate may be separated, e.g., in a distillation column, to form a second recovered extractant, recovered precipitation agent and optionally recovered precipitant wash. The recovered precipitation agent may be recycled to the precipitator, optionally after being combined with additional precipitation agent. The second recovered extractant may be recycled to the extractor, optionally after being combined with additional extractant. The optional recovered precipitant wash may be recycled to the precipitant wash step, optionally after being combined with additional precipitant wash. The recovered solid hemicellulose may then be dried, optionally with either or both heat and/or mechanical means, e.g., squeeze rolls, to form a finished hemicellulose product.

II. Cellulosic Material

[0023] The present invention is broadly applicable to the treatment of natural cellulosic materials, including plant and plant-derived materials. As used herein, the term “cellulosic material” refers to any material comprising cellulose, such as a pulp, and which may contain, for example, α -

cellulose, hemicellulose and degraded cellulose. In preferred embodiments, the cellulosic material comprises wood pulp, e.g., paper grade wood pulp. When the cellulosic material is paper grade wood pulp, the processes described herein may be advantageously used to produce acetate grade wood pulp from the paper grade wood pulp, although the processes of the invention are not limited to the use of paper grade wood pulp as the starting cellulosic material.

[0024] In some embodiments, the cellulosic material may comprise a cellulosic raw material, which may include, without limitation, plant derived biomass, corn stover, sugar cane stalk, bagasse and cane residues, rice and wheat straw, agricultural grasses, hard wood, hardwood pulp, soft wood, softwood pulp, herbs, recycled paper, waste paper, wood chips, pulp and paper wastes, waste wood, thinned wood, cornstalk, chaff, and other forms of wood, bamboo, soyhull, bast fibers, such as kenaf, hemp, jute and flax, agricultural residual products, agricultural wastes, excretions of livestock, microbial, algal cellulose, and all other materials proximately or ultimately derived from plants. Such cellulosic raw materials are preferably processed in pellet, chip, clip, sheet, attritioned fiber, powder form, or other form rendering them suitable for extraction with the extractant.

[0025] Generally, cellulosic material may be derived from lignin-containing materials, where lignin has been removed therefrom. In cellulosic materials, hemicellulose is linked to cellulose by hydrogen bonds. Overall, the cellulose material has a linear shape of fiber morphology, which is surrounded by hemicellulose via hydrogen bonds. These bonds between cellulose and hemicellulose may become weakened by treating the cellulosic material with an extractant to selectively dissolve the hemicellulose while maintaining the fiber morphology of the cellulose material, e.g., leaving the fiber morphology unchanged.

[0026] In one embodiment of the invention, the cellulosic material is a paper grade pulp provided in forms such as, but not limited to, rolls, sheets, or bales. Preferably, the paper grade pulp comprises at least 70 wt.% α -cellulose, e.g., at least 80 wt.% α -cellulose or at least 85 wt.% α -cellulose. Paper grade pulp typically also comprises at least 5 wt.% hemicellulose, at least 10 wt.% hemicellulose or at least 15 wt.% hemicellulose. In another embodiment, the cellulosic material may be another α -cellulose containing pulp, such as viscose grade pulp, rayon grade pulp, semi-bleached pulp, unbleached pulp, bleach pulp, Kraft pulp, absorbent pulp, dissolving pulp, or fluff. While these cellulosic materials comprise various concentrations of α -cellulose, the inventive processes may advantageously treat them, based on optimized process design, to produce higher purity α -cellulose products.

[0027] Cellulose is a straight chain polymer and is derived from D-glucose units, which condense through β -1,4-glycosidic bonds. This linkage motif contrasts with that for α -1,4-glycosidic bonds present in starch, glycogen, and other carbohydrates. Unlike starch, there is no coiling or branching in cellulose and cellulose adopts an extended and rather stiff rod-like confirmation, which is aided by the equatorial confirmation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighboring chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength, which then overlay to form the macrostructure of a cellulose fiber. In preferred embodiments of the invention, the finished cellulosic product retains its fiber structure throughout and after the extraction step.

[0028] As used herein, the term "hemicellulose" refers to any of several heteropolymers, e.g., polysaccharides, present in plant cell walls. Hemicellulose can include any one of xylan, glucuronoxylan, arabinoxylan, glucomannan, galactomannan, and xyloglucan. These polysaccharides contain many different sugar monomers and can be hydrolyzed to invert sugars, such as xylose, mannose, galactose, rhamnose and arabinose. Xylose is typically the primary sugar present in hard woods and mannose is the primary sugar present in softwoods.

[0029] The processes of the present invention are particularly beneficial in that they are effective for use with paper grade wood pulp that is derived from softwoods and hardwoods. The processes of the present invention provide a technique for upgrading paper grade pulp produced from softwood species, which are generally more abundant, and faster growing, than most hardwood species.

[0030] Softwood is a generic term typically used in reference to wood from conifers (i.e., needle-bearing trees from the order Pinales). Softwood-producing trees include pine, spruce, cedar, fir, larch, douglas-fir, hemlock, cypress, redwood and yew. Conversely, the term hardwood is typically used in reference to wood from broad-leaved or angiosperm trees. The terms "softwood" and "hardwood" do not necessarily describe the actual hardness of the wood. While, on average, hardwood is of higher density and hardness than softwood, there is considerable variation in actual wood hardness in both groups, and some softwood trees can actually produce wood that is harder than wood from hardwood trees. One feature separating hardwoods from softwoods is the presence of pores, or vessels, in hardwood trees, which are absent in softwood trees. On a microscopic level, softwood contains two types of cells, longitudinal wood fibers (or tracheids) and transverse ray cells. In softwood, water transport within the tree is via the tracheids rather than the pores of hardwoods.

III. Extractant

[0031] As described above, hemicellulose and optionally degraded cellulose is extracted from the cellulosic material using an extractant. The extractant comprises a cellulose solvent and a co-solvent. The cellulose solvent is selected from the group consisting of an ionic liquid, an amine oxide and mixtures thereof, examples of which are described below. The cellulose solvent may or (more preferably) may not fully dissolve α -cellulose, but preferably dissolves at least hemicellulose and degraded cellulose. α -cellulose preferably is less soluble in the co-solvent than in the cellulose solvent.

a. Ionic Liquid

[0032] Ionic liquids are organic salts with low melting points, preferably less than 200°C, less than 150°C, or less than 100°C, many of which are consequently liquid at room temperature. Specific features that make ionic liquids suitable for use in the present invention are their general lack of vapor pressure, their ability to dissolve a wide range of organic compounds and the versatility of their chemical and physical properties. In addition, ionic liquids are non-flammable making them particularly suitable for use in industrial applications. In some embodiments, the cellulose solvent comprises one or more ionic liquids.

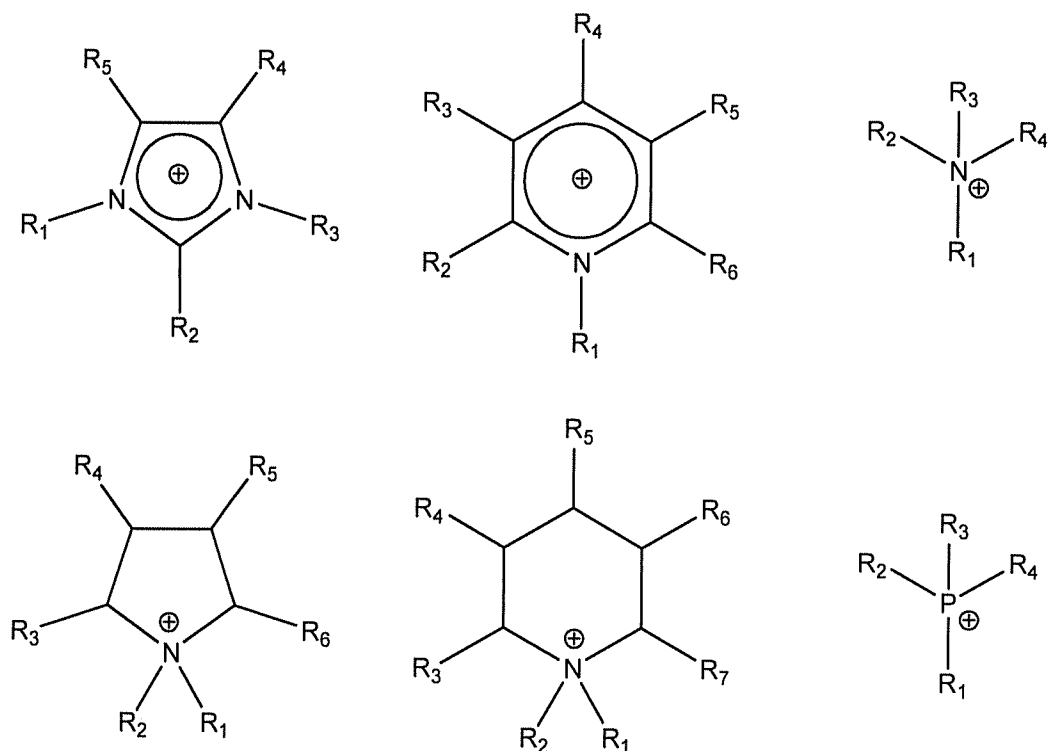
[0033] It has been found that, in addition to these beneficial properties, when contacted with cellulosic materials, including plant matter and plant matter derivatives, the ionic liquids are capable of acting as a cellulose solvent, dissolving the hemicellulose and cellulose contained therein. In addition, with the appropriate choice of treatment conditions (for example, duration of contact, temperature, and co-solvent composition), ionic liquids penetrate the structure of the cellulose-containing material to break down the material and extract organic species therein. In particular when used in combination with one or more co-solvents, α -cellulosic components remaining in the cellulosic material are preserved and the fiber morphology is advantageously retained.

[0034] Ionic liquids, in pure form, generally are comprised of ions and do not necessitate a separate solvent for ion formation. Ionic liquids existing in a liquid phase at room temperature are called room temperature ionic liquids. Generally, ionic liquids are formed of large-sized cations and a smaller-sized anion. Cations of ionic liquids may comprise nitrogen, phosphorous, sulfur, or carbon. Because of the disparity in size between the cation and anion, the lattice energy of the compound is decreased resulting in a less crystalline structure with a low melting point.

[0035] Exemplary ionic liquids include the compounds expressed by the following Formula (1):



[0036] In one embodiment, the ionic liquid is selected from the group consisting of substituted or unsubstituted imidazolium salts, pyridinium salts, ammonium salts, triazolium salts, pyrazolium salt, pyrrolidinium salt, piperidinium salt, and phosphonium salts. In preferred embodiments, $[A]^+$ is selected from the group consisting of:



[0037] wherein, $R_1, R_2, R_3, R_4, R_5, R_6$ and R_7 are each independently selected from the group consisting of hydrogen, C_1 - C_{15} alkyls, C_2 - C_{15} aryls, and C_2 - C_{20} alkenes, and the alkyl, aryl or alkene may be substituted by a substituent selected from the group consisting of sulfone, sulfoxide, thioester, ether, amide, hydroxyl and amine. $[B]^-$ is preferably selected from the group consisting of Cl^- , Br^- , I^- , OH^- , NO_3^- , SO_4^{2-} , $CF_3CO_2^-$, $CF_3SO_3^-$, BF_4^- , PF_6^- , CH_3COO^- , $(CF_3SO_2)_2N^-$, $AlCl_4^-$, $HCOO^-$, $CH_3SO_4^-$, $(CH_3)_2PO_4^-$, $(C_2H_5)_2PO_4^-$ and $CH_3HPO_4^-$.

[0038] Examples of ionic liquids include tetrabutylammonium hydroxide 30 hydrate ($TBAOH \cdot 30H_2O$), benzyltriethylammonium acetate ($BnTEAAc$), tetraethylammonium acetate tetrahydrate ($TEAAc \cdot 4H_2O$), benzyltrimethylammonium hydroxide ($BnTMAOH$), tetramethylammonium hydroxide ($TMAOH$), ammonium acetate, hydroxyethylammonium acetate, hydroxyethylammonium formate, tetramethylammonium acetate, tetraethylammonium acetate, tetrabutylammonium acetate, tetrabutylammonium hydroxide, 1-butyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl

imidazolium hydrogensulfate, 1-butyl-3-methyl imidazolium hydrogensulfate, methylimidazolium chloride, 1-ethyl-3-methyl imidazolium acetate, 1-butyl-3-methyl imidazolium acetate, tris-2(hydroxyl ethyl)methylammonium methylsulfate, 1-ethyl-3-methyl imidazolium ethylsulfate, 1-ethyl-3-methyl imidazolium methanesulfonate, methyl-tri-n-butylammonium methylsulfate, 1-butyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium thiocyanate, 1-butyl-3-methyl imidazolium thiocyanate, 1-aryl-3-methyl imidazolium chloride, and mixtures or complexes thereof, but the disclosed concept of utilizing ionic liquids is not limited to the disclosed species.

[0039] In some embodiments, the ionic liquid is selected from the group consisting of ammonium-based ionic substances, imidazolium-based ionic substances, phosphonium-based ionic substances, and mixtures thereof. The ammonium-based ionic liquid may be selected from the group consisting of ammonium acetate, hydroxyethylammonium acetate, hydroxyethylammonium formate, tetramethylammonium acetate, tetrabutylammonium acetate, tetraethylammonium acetate, benzyltriethylammonium acetate, benzyltributyl ammonium acetate and combinations thereof. The imidazolium-based ionic liquid may be selected from the group consisting of 1-butyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium hydrogensulfate, 1-butyl-3-methyl imidazolium hydrogensulfate, methylimidazolium chloride, 1-ethyl-3-methyl imidazolium acetate, 1-butyl-3-methyl imidazolium acetate, tris-2(hydroxyl ethyl)methylammonium methylsulfate, 1-ethyl-3-methyl imidazolium ethylsulfate, 1-ethyl-3-methyl imidazolium methanesulfonate, methyl-tri-n-butylammonium methylsulfate, 1-butyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium thiocyanate, 1-butyl-3-methyl imidazolium thiocyanate, 1-aryl-3-methyl imidazolium chloride, 1-ethyl-3-methylimidazolium dimethyl phosphate, 1-ethyl-3-methyl diethyl phosphate (EMIMDEP), 1,3-dimethylimidazolium dimethyl phosphate (DMIMDMP) and mixtures or complexes thereof. The ionic liquid may also be selected from the group consisting of N,N-dimethylpyrrolidinium acetate, N,N-dimethylpiperidinium acetate, N,N-dimethylpyrrolidinium dimethyl phosphate, N,N-dimethylpiperidinium dimethyl phosphate, N,N-dimethylpyrrolidinium chloride, N,N-dimethylpiperidinium chloride, and combinations thereof.

[0040] In still other embodiments, the ionic liquid may be selected from the group consisting of 1-butyl-3-methylimidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium hydrogensulfate, 1-butyl-3-methyl imidazolium hydrogensulfate, methylimidazolium chloride, 1,3-diethylimidazolium acetate (EEIM Ac), 1-ethyl-

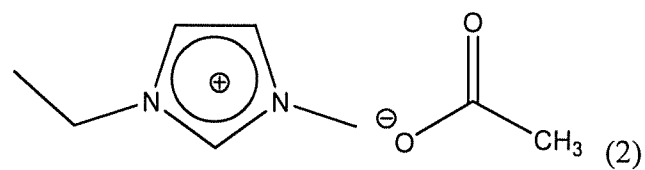
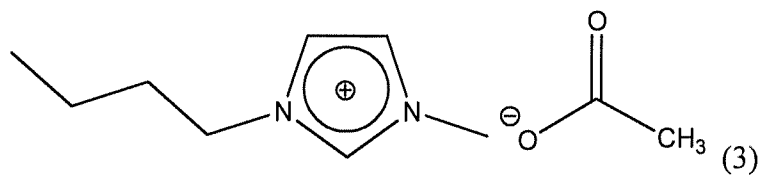
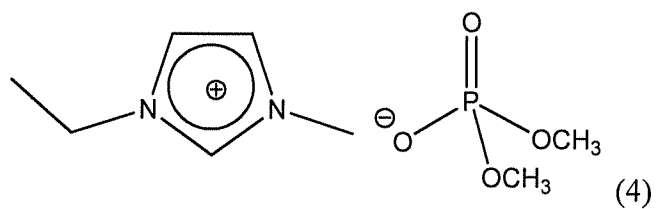
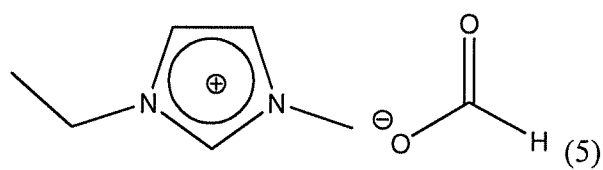
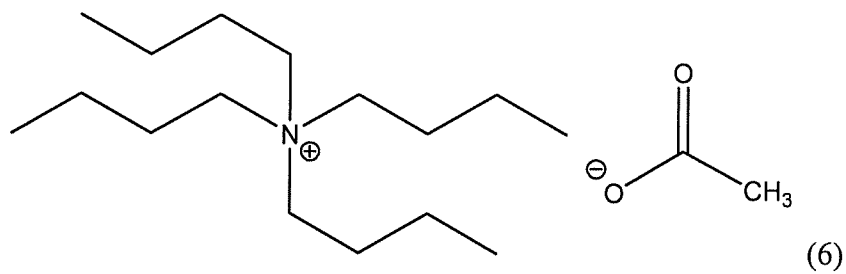
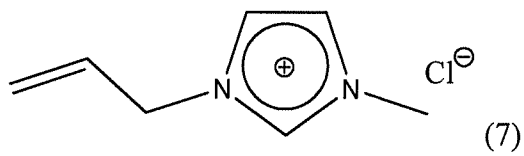
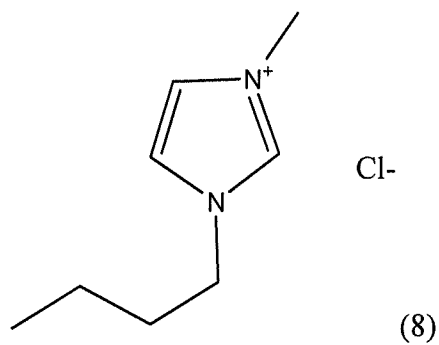
3-methyl imidazolium acetate, 1-butyl-3-methyl imidazolium acetate, tris-2(hydroxyl ethyl)methylammonium methylsulfate, 1-ethyl-3-methyl imidazolium ethylsulfate, 1-ethyl-3-methyl imidazolium methanesulfonate, methyl-tri-n-butylammonium methylsulfate, 1-butyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium thiocyanate, 1-butyl-3-methyl imidazolium thiocyanate, 1-aryl-3-methyl imidazolium chloride, 1-ethyl-3-methylimidazolium dimethyl phosphate, 1-ethyl-3-methyl diethyl phosphate, 1,3-dimethylimidazolium dimethyl phosphate and combinations and complexes thereof.

[0041] In further embodiments, the ionic liquid may be selected from the group consisting of ethyltributylphosphonium diethylphosphate, methyltributylphosphonium dimethylphosphate, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, tributylmethylphosphonium methylsulfate, trihexyltetradecylphosphonium decanoate, trihexyltetradecylphosphonium dicyanamide, ethyltriphenylphosphonium acetate, ethyltributylphosphonium acetate, benzyltriethylphosphonium acetate, benzyltributylphosphonium acetate, tetrabutylphosphonium acetate, tetraethylphosphonium acetate, tetramethylphosphonium acetate, and combinations thereof.

[0042] The ionic liquid may be commercially available, and may include Basonic™ AC 01, Basonic™ AC 09, Basonic™ AC 25, Basonic™ AC 28, Basonic™ AC 75, Basonic™ BC 01, Basonic™ BC 02, Basonic™ FS 01, Basonic™ LQ 01, Basonic™ ST 35, Basonic™ ST 62, Basonic™ ST 70, Basonic™ ST 80, Basonic™ VS 01, and Basonic™ VS 02, but the invention is not limited to use of these species.

[0043] In preferred embodiments, the ionic liquid compound, as shown below, may be 1-ethyl-3-methyl imidazolium acetate (EMIMAc) of the structural formula (2), 1-butyl-3-methyl imidazolium acetate (BMIMAc) of the structural formula (3), 1-ethyl-3-methyl imidazolium dimethylphosphate of structural formula (4), 1-ethyl-3-methyl imidazolium formate of the structural formula (5), tetrabutylammonium acetate (TBAAc) of the structural formula (6), 1-allyl-3-methyl imidazolium

chloride of the structural formula (7), or 1-n-butyl-3-methyl imidazolium chloride of the structural formula (8):



b. Amine Oxide

[0044] Amine oxides are chemical compounds that contain the functional group $R_3N^+-O^-$, which represents an N-O bond with three additional hydrogen and/or hydrocarbon side chains. Amine oxides are also known as tertiary amines, N-oxides, amine-N-oxide and tertiary amine N-oxides. In one embodiment, amine oxides that are stable in water may be used.

[0045] In some embodiments, the amine oxide may be selected from the group consisting of compounds with chemical structure of acyclic $R_3N^+-O^-$, compounds with chemical structure of *N*-heterocyclic compound *N*-oxide, and combinations thereof. In further embodiments, the amine oxide may be an acyclic amine oxide compound with structure of $R_1R_2R_3N^+-O^-$, wherein R_1 , R_2 and R_3 are alkyl or aryl chains, the same or different, with chain length from 1 to 18, e.g. trimethylamine N-oxide, triethylamine N-oxide, tripropylamine N-oxide, tributylamine N-oxide, methyldiethylamine N-oxide, dimethylethylamine N-oxide, methyldipropylamine N-oxide, tribenzylamine N-Oxide, benzyldimethylamine N-oxide, benzyldiethylamine N-oxide, dibenzylmethylamine N-oxide, monomethyldiethylamine, dimethylmonoethylamine, monomethyldipropylamine, N-dimethyl-, N-diethyl- or N-dipropylcyclohexylamine, N-dimethylmethylcyclohexylamine, pyridine, and pyridine N-oxide.

[0046] In some embodiments, the amine oxide may be a cyclic amine oxide compound including the structures such as pyridine, pyrrole, piperidine, pyrrolidine and other N-heterocyclic compounds, e.g. N-methylmorpholine N-oxide (NMMO), pyridine N-oxide, 2-, 3-, or 4-picoline N-oxide, N-methylpiperidine N-oxide, N-ethylpiperidine N-oxide N-propylpiperidine N-oxide, N-isopropylpiperidine N-oxide. N-butylpiperidine N-oxide, N-hexylpiperidine N-oxide. N-methylpyrrolidine N-oxide, N-ethylpyrrolidine N-oxide N-propylpyrrolidine N-oxide, N-isopropylpyrrolidine N-oxide. N-butylpyrrolidine N-oxide, N-hexylpyrrolidine N-oxide. In some embodiments, the amine oxide may be the combination of the above mentioned acyclic and/or cyclic amine oxides.

[0047] In specific embodiments, the amine oxide may be selected from the group consisting of trimethylamine *N*-oxide, triethylamine *N*-oxide, tripropylamine *N*-oxide, tributylamine *N*-oxide, methyldiethylamine *N*-oxide, dimethylethylamine *N*-oxide, methyldipropylamine *N*-oxide, tribenzylamine *N*-Oxide, benzyldimethylamine *N*-oxide, benzyldiethylamine *N*-oxide, dibenzylmethylamine *N*-oxide, *N*-methylmorpholine *N*-oxide (NMMO), pyridine *N*-oxide, 2-, 3-, or 4-picoline *N*-oxide, *N*-methylpiperidine *N*-oxide, *N*-ethylpiperidine *N*-oxide *N*-propylpiperidine *N*-oxide, *N*-isopropylpiperidine *N*-oxide. *N*-butylpiperidine *N*-oxide, *N*-hexylpiperidine *N*-oxide. *N*-

methypyrrolidine *N*-oxide, *N*-ethylpyrrolidine *N*-oxide *N*-propylpyrrolidine *N*-oxide, *N*-isopropylpyrrolidine *N*-oxide. *N*-butylpyrrolidine *N*-oxide, *N*-hexylpyrrolidine *N*-oxide, and combinations thereof.

[0048] Cellulose is insoluble in most solvents because of its strong and highly structured intermolecular hydrogen bonding network. Without being bound by theory, NMMO is able to break the hydrogen bonding network that keeps cellulose insoluble in most solvents. Therefore, the use of NMMO alone would destroy the fiber morphology of cellulose. It has now been discovered that by using the proper ratio of an amine oxide, such as NMMO, with a co-solvent, α -cellulosic components in the cellulosic material may be beneficially preserved and the fiber morphology retained. NMMO is typically stored in 50 to 70 vol.%, e.g., 60 vol. %, aqueous solution as pure NMMO tends toward oxygen separation. See, e.g., US Patent 4,748,241, the entirety of which is incorporated herein by reference. Further contaminants in commercial NMMO product, e.g., *N*-methylmorpholine, peroxides, and acid components, tend to degrade the storage stability. In other words, further application of NMMO needs to address all stability concerns. For example, developed stabilizers like propyl gallate may be added.

c. Co-solvent

[0049] As stated above, the extractant also comprises a co-solvent. Co-solvents in the context of this invention include solvents that do not have the ability to readily dissolve α -cellulose. In exemplary embodiments, the co-solvent is selected from the group consisting of water, acetic acid, alcohols such as methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, *tert*-butanol, diols and polyols such as ethanediol and propanediol, amino alcohols such as ethanolamine, diethanolamine and triethanolamine, aromatic solvents, e.g., benzene, toluene, ethylbenzene or xylenes, halogenated solvents, e.g. dichloromethane, chloroform, carbon tetrachloride, dichloroethane or chlorobenzene, aliphatic solvents, e.g. pentane, hexane, heptane, octane, ligroin, petroleum ether, cyclohexane and decalin, ethers, e.g. tetrahydrofuran, diethyl ether, methyl *tert*-butyl ether and diethylene glycol monomethyl ether, ketones such as acetone and methyl ethyl ketone, esters, e.g. ethyl acetate, dimethyl carbonate, dipropyl carbonate, propylene carbonate, amides, e.g., formamide, dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAC), DMSO, acetonitrile and mixtures thereof. Since the boiling points of co-solvents vary significantly, the efficient purification processes associated with each co-solvent may not be exactly the same.

[0050] In one embodiment, a second co-solvent may be used in conjunction with the first co-solvent and the cellulose solvent, e.g., amine oxide or ionic liquid, as described above. In one

embodiment, the second co-solvent decreases the viscosity of the extractant. The second co-solvent may have a viscosity, for example, of less than 2.0 mPa•s, e.g., less than 1.8 mPa•s or less than 1.5 mPa•s at 25°C. In some embodiments, the second co-solvent is selected from the group consisting of formamide, DMF, dimethylacetamide, DMSO, N-methylpyrrolidone, propylene carbonate, acetonitrile and mixtures thereof. It is postulated that using a low viscosity second co-solvent in the extractant, the extraction rate is enhanced and a smaller amount of ionic liquid is needed to extract the hemicellulose in the cellulosic material.

[0051] Without being bound by theory, the insolubility of the α -cellulose in the co-solvent and the resulting extractant maintains the cellulose fiber morphology, e.g., leaving the fiber morphology unchanged, while the extractant penetrates the cellulosic material, dissolves and extracts the hemicellulose and preferably degraded cellulose from the cellulosic material. Depending on the specific co-solvent used in the extractant, the weight percentage of the cellulose solvent and the co-solvent in the extractant may vary widely.

d. Extractant Compositions

[0052] The specific formulation of the extractant employed may vary widely, depending, for example, on the hemicellulose and degraded cellulose content of the starting cellulosic material, and the processing scheme employed. In one embodiment, the extractant optionally comprises at least 0.1 wt.% amine oxide, e.g., at least 2 wt.% or at least 4 wt.%. In terms of upper limits, the extractant optionally comprises at most 85 wt.% amine oxide, e.g., at most 75 wt.%, or at most 70 wt.% amine oxide. In terms of ranges, the extractant optionally comprises from 0.1 wt.% to 85 wt.% amine oxide, e.g., from 2 wt.% to 75 wt.%, or from 4 wt.% to 70 wt.%. The extractant optionally comprises at least 0.1 wt.% co-solvent, e.g., at least 1 wt.%, or at least 3 wt.% co-solvent. In terms of upper limits, the extractant optionally comprises at most 99.9 wt.%, at most 98 wt.%, or at most 97 wt.% co-solvent. In terms of ranges, the extractant optionally comprises from 0.1 wt.% to 99.9 wt.% co-solvent, e.g., from 1 wt.% to 98 wt.%, or from 3 wt.% to 97 wt.% co-solvent.

[0053] In one embodiment, the extractant comprises an aqueous co-solvent, e.g., water, and an amine oxide. For example, the extractant optionally comprises at least 40 wt.% amine oxide, e.g., at least 50 wt.% or at least 60 wt.%. In terms of upper limits, the extractant optionally comprises at most 90 wt.% amine oxide, e.g., at most 85 wt.%, or at most 80 wt.% amine oxide. In terms of ranges, the extractant optionally comprises from 40 wt.% to 90 wt.% amine oxide, e.g., from 50 wt.% to 85 wt.%, or from 60 wt.% to 80 wt.% amine oxide. The extractant optionally comprises at least 1 wt.% aqueous co-solvent, e.g., at least 5 wt.%, or at least 10 wt.% aqueous co-solvent. In

terms of upper limits, the extractant optionally comprises at most 50 wt.% aqueous co-solvent, at most 40 wt.%, or at most 30wt.%. In terms of ranges, the extractant optionally comprises from 1 wt.% to 50 wt.% aqueous co-solvent, e.g., from 5 wt.% to 40 wt.%, or from 10 wt.% to 30 wt.%.

[0054] In one embodiment, the extractant comprises an organic co-solvent and an amine oxide. In this aspect, the extractant optionally comprises at least 0.1 wt.% amine oxide, e.g., at least 1 wt.% or at least 2 wt.% amine oxide. In terms of upper limits, the extractant optionally comprises at most 85 wt.% amine oxide, e.g., at most 80 wt.%, or at most 70 wt.%. In terms of ranges, the extractant optionally comprises from 0.1 wt.% to 85 wt.% amine oxide, e.g., from 1 wt.% to 80 wt.%, or from 2 wt.% to 70 wt.%. In this aspect, the extractant optionally comprises at least 15 wt.% organic co-solvent, e.g., at least 20 wt.%, or at least 30 wt.%. In terms of upper limits, the extractant optionally comprises at most 99.9 wt.% organic co-solvent, at most 98 wt.%, or at most 97 wt.%. In terms of ranges, the extractant optionally comprises from 15 wt.% to 99.9 wt.% organic co-solvent, e.g., from 20 wt.% to 98 wt.%, or from 30 wt.% to 97 wt.%. In one embodiment, the organic co-solvent is DMSO.

[0055] In one embodiment, the extractant includes an amine oxide, a first co-solvent and a second co-solvent. In one embodiment, the extractant includes an amine oxide, an aqueous co-solvent, e.g., water, and an organic co-solvent, e.g., DMSO. In this aspect, the amine oxide concentration may range, for example, from 1 wt.% to 85 wt.%, the water concentration may range from 1 wt.% to 35 wt.%, and the organic co-solvent, e.g., DMSO, concentration may range from 1 wt.% to 98 wt.%.

[0056] In other embodiments, the cellulose solvent used in the extractant comprises one or more ionic liquids. For example, the extractant optionally comprises at least 0.1 wt.% ionic liquid, e.g., at least 1 wt.% or at least 2 wt.%. In terms of upper limits, the extractant optionally comprises at most 95 wt.% ionic liquid, e.g., at most 90 wt.%, or at most 85 wt.%. In terms of ranges, the extractant optionally comprises from 0.1 wt.% to 95 wt.% ionic liquid, e.g., from 1 wt.% to 90 wt.%, or from 2 wt.% to 85 wt.%. The extractant optionally comprises at least 5 wt.% co-solvent, e.g., at least 10 wt.%, at least 15 wt.%, or at least 20 wt.%. In terms of upper limits, the extractant optionally comprises at most 99.9 wt.% co-solvent, at most 99 wt.%, or at most 98 wt.%. In terms of ranges, the extractant optionally comprises from 5 wt.% to 99.9 wt.% co-solvent, e.g., from 10 wt.% to 99 wt.%, or from 20 wt.% to 98 wt.%.

[0057] In one embodiment, the cellulose solvent comprises one or more ionic liquids and the co-solvent comprises an aqueous co-solvent, e.g., water. In this aspect, the extractant preferably

comprises at least 50 wt.% ionic liquid, e.g., at least 65 wt.% or at least 80 wt.%. In terms of upper limits, the extractant optionally comprises at most 95 wt.% ionic liquid, e.g., at most 90 wt.%, or at most 85 wt.%. In terms of ranges, the extractant optionally comprises from 50 wt.% to 95 wt.% ionic liquid, e.g., from 65 wt.% to 90 wt.%, or from 70 wt.% to 85 wt.%. The extractant optionally comprises at least 5 wt.% aqueous co-solvent, e.g., at least 10 wt.%, at least 15 wt.%, or at least 20 wt.%. In terms of upper limits, the extractant optionally comprises at most 50 wt.% aqueous co-solvent, e.g., at most 35 wt.%, or at most 20 wt.% aqueous co-solvent. In terms of ranges, the extractant may comprise from 5 wt.% to 50 wt.% aqueous co-solvent, e.g., from 10 wt.% to 35 wt.%, or from 15 wt.% to 20 wt.%.

[0058] In one embodiment, when the extractant comprises one or more ionic liquids as cellulose solvent and an organic co-solvent, the extractant preferably comprises at least 0.1 wt.% ionic liquid, e.g., at least 1 wt.% or at least 2 wt.%. In terms of upper limits, the extractant optionally comprises at most 20 wt.% ionic liquid, e.g., at most 15 wt.%, or at most 10 wt.%. In terms of ranges, the extractant may comprise from 0.1 wt.% to 20 wt.% ionic liquid, e.g., from 1 wt.% to 15 wt.%, or from 2 wt.% to 10 wt.%. The extractant optionally comprises at least 80 wt.% organic co-solvent, e.g., at least 85 wt.%, or at least 90 wt.%. In terms of upper limits, the extractant may comprise at most 99.9 wt.% organic co-solvent, e.g., at most 98 wt.%, or at most 97 wt.%. In terms of ranges, the extractant optionally comprises from 80 wt.% to 99.9 wt.% organic co-solvent, e.g., from 85 wt.% to 98 wt.%, or from 90 wt.% to 97 wt.%. In one embodiment, the organic co-solvent is DMSO.

[0059] In one embodiment, when the extractant comprises one or more ionic liquids as cellulose solvent and an organic co-solvent, the extractant preferably comprises at least 0.1 wt.% ionic liquid, e.g., at least 1 wt.% or at least 2 wt.%. In terms of upper limits, the extractant optionally comprises at most 40 wt.% ionic liquid, e.g., at most 30 wt.%, or at most 20 wt.%. In terms of ranges, the extractant may comprise from 0.1 wt.% to 40 wt.% ionic liquid, e.g., from 1 wt.% to 30 wt.%, or from 2 wt.% to 20 wt.%. The extractant optionally comprises at least 60 wt.% organic co-solvent, e.g., at least 70 wt.%, or at least 80 wt.%. In terms of upper limits, the extractant may comprise at most 99.9 wt.% organic co-solvent, e.g., at most 98 wt.%, or at most 97 wt.%. In terms of ranges, the extractant optionally comprises from 60 wt.% to 99.9 wt.% organic co-solvent, e.g., from 70 wt.% to 98 wt.%, or from 80 wt.% to 97 wt.%. In one embodiment, the organic co-solvent is DMSO.

[0060] In one embodiment, the extractant includes a cellulose solvent, e.g., amine oxide or ionic liquid, a first co-solvent and a second co-solvent. In this aspect, the weight ratio of first co-solvent to second co-solvent is preferably from 20:1 to 1:20, e.g. from 15:1 to 1:15 or from 10:1 to 1:10. Since the production costs of ionic liquids are generally higher than those of co-solvents, the use of a large amount of the second co-solvent beneficially reduces the cost of purifying the cellulosic material.

[0061] In one embodiment, the extractant includes an ionic liquid, a first co-solvent and a second co-solvent. In one embodiment, the extractant includes an ionic liquid, an aqueous co-solvent, e.g., water, and an organic co-solvent, e.g., DMSO. In the tertiary extractant system, the extractant may include at most 50 wt.% ionic liquid, e.g., at most 40 wt.%, or at most 30 wt.%. In terms of lower limit, the extractant may include at least 0.1 wt.% ionic liquid, e.g., at least 5 wt.% or at least 10 wt.%. In terms of ranges, the extractant may include from 0.1 wt.% to 50 wt.% ionic liquid, e.g., from 5 wt.% to 40 wt.%, or from 10 wt.% to 30 wt.%. In some embodiments, the extractant may include at most 20 wt.% the first co-solvent, i.e., at most 16 wt.%, or 10 wt.%. In terms of ranges the extractant may include from 0.5 wt.% to 20 wt.% the first co-solvent, e.g., from 3 wt.% to 16 wt.% or from 5 wt.% to 10 wt.%. In one embodiment, water is the first co-solvent. In one embodiment, DMSO is the second co-solvent. Without being bound by theory, it is postulated that the decrease in viscosity in the extractant by using the second co-solvent beneficially enhances the extraction rate and increases the amount of hemicellulose extracted from the cellulosic material.

[0062] In one embodiment, the extractant comprises an aqueous co-solvent, an ionic liquid and an amine oxide. In this aspect, the co-solvent concentration may range, for example, from 5 wt.% to 50 wt.%, the ionic liquid concentration may range from 0.1 wt.% to 50 wt.%, and the amine oxide concentration may range from 0.1 wt.% to 85 wt.%.

[0063] In one embodiment, the extractant comprises an organic co-solvent, an ionic liquid and an amine oxide. In this aspect, the co-solvent concentration may, for example, range from 5 wt.% to 99 wt.%, the ionic liquid concentration may range from 0.1 wt.% to 50 wt.%, and the amine oxide concentration may range from 0.1 wt.% to 50 wt.%.

IV. Cellulosic Material Purification

[0064] As described herein, cellulosic material may be purified through an inventive extraction process that removes hemicellulose and preferably degraded cellulose. FIG. 1 illustrates one non-limiting exemplary system for purifying a cellulosic material, and recovering a hemicellulose byproduct. As shown in FIG. 1, the cellulosic material may be purified in purification process 100,

which comprises a cellulosic material purification zone 101 and a hemicellulose recovery zone 102. As shown, the cellulosic material is fed via line 103 to extractor 105. Line 103 may represent, for example, a pneumatic lock hopper, a screw feeder, a belt feeder, a rotary valve feeder, or another type of solid transport equipment. Extractant, comprising a cellulose solvent and co-solvent, as described above, is fed to extractor 105 via line 104. Although cellulosic material 103 and extractant 104 are shown as fed separately to extractor 105, it is contemplated that they may be completely or partially mixed prior to being fed to extractor 105. As shown in FIG. 1, cellulosic material 103 and extractant 104 may be combined in extractor 105 to form an extraction mixture. The extraction mixture within extractor 105 may comprise, for example, from 0.1 to 20 wt.% solids, e.g., from 0.5 to 15 wt.% or from 1.25 to 10 wt.% solids.

[0065] Extractant 104 for extracting cellulosic material 103 may be any extractant capable of dissolving preferably at least 50% of the hemicellulose, more preferably at least 75% or at least 90% of the hemicellulose, in cellulosic material 103, as determined by UV absorbance analysis of hemicellulose concentration and mass measurements of the feed, cellulosic product, and hemicellulose product. Extractant 104 comprises a cellulose solvent and co-solvent in relative amounts that do not overly degrade the cellulose. For example, in one embodiment, the extractant dissolves less than 15% of the α -cellulose in cellulosic material 103, e.g., less than 10%, or less than 5%, as determined similarly by UV absorbance analysis and mass measurements.

[0066] As described above, amine oxides and ionic liquids may tend to dissolve α -cellulose. The extractant preferably comprises sufficient co-solvent to reduce α -cellulose solubility in the overall extractant to a point that the α -cellulose does not readily dissolve therein. Preferably, the α -cellulose is substantially insoluble in the co-solvent. Extractant 104 in accordance with the present invention, therefore, has the property of selectively dissolving the hemicellulose and preferably degraded cellulose that is in cellulosic material 103.

[0067] Exemplary compositions for the cellulosic material and extractant fed to the extractor, and for the resulting extraction mixture are provided in Table 1.

TABLE 1
EXTRACTOR 105

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Cellulosic Material 103</u>			
"Cellulose"*	50 to 90	55 to 85	60 to 80
"Hemicellulose"***	1 to 40	5 to 30	10 to 25
Water	0.1 to 20	1 to 20	1 to 10
<u>Extractant 104</u>			
Solvent	0.1 to 99.9	2 to 90	3 to 80
Co-solvent	0.1 to 99.9	10 to 98	20 to 97
<u>Extraction Mixture in</u> <u>Extractor 105</u>			
Cellulose	0.3 to 14	0.3 to 13	0.3 to 12
Hemicellulose***	0.005 to 6	0.03 to 5	0.05 to 4
Water	0.001 to 3	0.005 to 3	0.005 to 2
Solvent	0.09 to 99.4	1.7 to 90	2.6 to 80
Co-solvent	0.09 to 99.4	8.5 to 98	17 to 97

*"Cellulose" refers to cellulose of all forms including degraded cellulose

** "Hemicellulose" in cellulosic material 103 refers to hemicellulose alone excluding non-hemicellulose impurities

*** "Hemicellulose" after being dissolved in extractant 104 refers to hemicellulose, degraded cellulose, and other impurities

[0068] The treatment of cellulosic material 103 with extractant 104 may be conducted at an elevated temperature, and preferably occurs at atmospheric pressure or slightly above atmospheric pressure. Preferably, the contacting is conducted at a temperature from 30°C to 300°C, e.g., from 40°C to 200°C, or from 50°C to 150°C. In terms of upper limits, the treatment of cellulosic material 103 may be conducted at a temperature of less than 300°C, e.g., less than 200°C, or less than 150°C. In terms of lower limit, the treatment of cellulosic material 103 may be conducted at a temperature of greater than 30°C, e.g., greater than 40°C, or greater than 50°C. The pressure (absolute, unless otherwise indicated) is in the range from 100 kPa to 10 MPa, preferably from 100 kPa to 5000 kPa, more preferably from 100 kPa to 1100 kPa. In some embodiments, the pressure may be reduced below 100 kPa, e.g., from 1 to 99 kPa.

[0069] Cellulosic material 103 may contact extractant 104 (or have a residence time in extractor 105 for continuous processes) between 5 minutes to 1000 minutes, e.g., between 20 minutes to 500 minutes, or from 40 minutes to 200 minutes. In terms of lower limits, the treatment of cellulosic material 103 may be for at least 5 minutes, e.g., at least 20 minutes or at least 40 minutes. In terms

of upper limits, the treatment of cellulosic material 103 may be for at most 1000 minutes, e.g., at most 500 minutes, or at most 200 minutes.

[0070] The extraction process may be conducted in a batch, a semi-batch or a continuous process with material flowing either co-current or counter-current in relation to one another. In a continuous process, cellulosic material 103 contacts extractant 104 in one or more extraction vessels. In one embodiment, extractant 104 may be heated to the desired temperature before contacting cellulosic material 103. In one embodiment, the extraction vessel(s) may be heated by any suitable means to the desired temperature. Additionally, an inert gas (not shown), e.g., nitrogen or CO₂, may be supplied to the extractor to improve turbulence in the extractor and thus improving heat and mass transfers. The flow rate of inert gas will be controlled not to cause hydrodynamic problem, e.g. flooding. When the size and concentration of solid materials along with the flow rate of inert gas are well controlled, the addition of an inert gas may cause the solids in extractor 105 to float on the surface of the extraction mixture allowing for the solids to be skimmed off the surface of the liquid phase contained in extractor 105.

[0071] In the extraction step, the mass ratio of extractant to cellulosic material may range from 5:1 to 500:1, e.g., from 7:1 to 300:1, or from 10:1 to 100:1. The solid:liquid volume ratio may range from 0.005:1 to 0.17:1, e.g., from 0.01:1 to 0.15:1 or from 0.02:1 to 0.1:1, depending on the extraction apparatus and set-up. In one embodiment, a solid:liquid ratio of from 0.01:1 to 0.02:1 or about 0.0125:1 may be used to facilitate the filtration operation in a batch process. In another embodiment, a solid:liquid ratio of 0.1:1 to 0.17:1 can be used, in particular for extractors employing countercurrent extraction. The amount of extractant employed has a significant impact on process economics. Counter-current extraction may achieve greater extraction efficiency while maintaining reasonable extractant usage. Counter-current extraction of solubles from pulp can be accomplished in a variety of commercial equipment such as, but not limited to, a series of agitated tanks, hydropulpers, continuous belt extractors, and screw extractors. Twin-screw extractors are generally more efficient than single-screw extractors. After extraction, the separation of solid and liquid phases can be completed in suitable commercial equipment, which includes filters, centrifuges, and the like.

[0072] In one embodiment, the cellulosic material is subjected to repeated extraction steps. For example, the cellulosic material may be treated with the extractant in an initial extraction step followed by one or more additional extraction steps, in the same or multiple extractors, to further extract residual hemicellulose and/or degraded cellulose. In one embodiment, the cellulosic product

may be subjected to an initial extraction step, followed by an extractant wash step (discussed below), followed by a second extraction step. In some embodiments, the cellulosic product may be subjected to a third or fourth extraction step. When multiple extraction steps are employed, the extractant in each extraction step may be the same or varied to account for the different concentrations of hemicellulose and degraded cellulose in intermediate cellulosic materials between extraction steps. For example, a first extraction may use an extractant comprising an ionic liquid and a co-solvent and a second extraction may use an extractant comprising an amine oxide and a co-solvent, or vice versa, optionally with one or more extractant wash steps between and/or after the second extraction step. Similar configurations can be designed and optimized based upon the general chemical engineering principles and process design theory.

[0073] In another embodiment (not shown), the process may further include enzymatic digestion of hemicellulose, extraction and/or isolation of digested hemicellulose and recovery of a cellulosic product with reduced hemicellulose content. Without being bound by theory, by treating the cellulosic material first with the extractant, enzymes may be better able to penetrate the cellulosic material to hydrolyze residual hemicellulose and/or degraded cellulose contained therein. On the contrary, experimental data has shown that less hemicellulose may be removed from the cellulosic material if it is first treated with an enzyme cocktail under optimum enzyme hydrolysis conditions, followed by an extraction step. For enzymes to be effective in hydrolyzing hemicellulose, a pretreatment step (e.g., prehydrolysis) is preferred in order to make the cellulosic materials amenable to enzymatic hydrolysis. The pretreatment step preferably comprises treating the cellulosic material with high pressure steam, optionally at low or high acid concentrations, or ammonia treatment. Some modification to the process flow scheme may be desired since the enzyme treatment would likely necessitate increased residence time to complete enzymatic hydrolysis. In addition, acidity (pH), temperature and ionic strength would likely need to be adjusted for effective enzymatic treatment.

[0074] In this embodiment, after the extraction step, the cellulosic material may be treated with an enzyme, preferably a hemicellulase, to break down residual hemicellulose contained in the cellulosic material. The hemicellulase includes one or more enzymes that hydrolyze hemicellulose to form simpler sugars, ultimately yielding monosaccharides, such as glucose, hexoses and pentoses. Suitable hemicellulase include one or more of xyloglucanase, β -xylosidase, endoxylanase, α -L-arabinofuranosidase, α -glucuronidase, mannanase, and acetyl xylan esterase. Preferably, the enzymes include a combination of both endo-enzymes (i.e., enzymes hydrolyzing internal

polysaccharide bonds to form smaller poly- and oligosaccharides) and exo-enzymes (i.e., enzymes hydrolyzing terminal and/or near-terminal polysaccharide bonds) to facilitate the rapid hydrolysis of large polysaccharide molecules. Suitable commercial hemicellulase include SHEARZYME (available from Novozymes A/S, Bagsvaerd, Denmark), PULPZYME (available from Novozymes A/S, Bagsvaerd, Denmark), FRIMASE B210 (available from Puratos, Groot-Bijgaarden, Belgium), FRIMASE B218 (available from Puratos, Groot-Bijgaarden, Belgium), GRINDAMYL (available from Danisco, Copenhagen, Denmark), ECOPULP TX200A (available from AB Enzymes, Darmstadt, Germany), MULTIFECT Xylanase (available from Genencor/Danisco, Palo Alto, USA), PENTOPAN Mono BG (available from Novozymes, Bagsvaerd, Denmark), and PENTOPAN 500 BG (available from Novozymes, Bagsvaerd, Denmark).

[0075] The enzymes generally can be used in amounts that are not particularly limited. For example, hemicellulase can be used in amounts ranging from about 0.001 mg/g to about 500 mg/g (e.g., about 0.05 mg/g to about 200 mg/g, about 0.1 mg/g to about 100 mg/g, about 0.2 mg/g to about 50 mg/g, or about 0.3 mg/g to about 40 mg/g). The concentration units are milligrams of enzyme per gram of cellulosic material to be treated.

[0076] After the desired contacting time, an extraction mixture is removed from extractor 105 via line 106. The extraction mixture 106 comprises extractant, dissolved hemicellulose, dissolved degraded cellulose, side products, e.g., mono-, di-, and oligo-saccharide, and an intermediate cellulosic material having reduced hemicellulose content and preferably reduced degraded cellulose content. As shown, extraction mixture 106 is fed to filter/washer 110 to remove extractant, dissolved hemicellulose, and dissolved degraded cellulose. Removal of the extractant in the filtering step reduces the amount of residual hemicellulose that must be further processed with the intermediate cellulosic material. It also reduces the amount of extractant that must be separated from the intermediate cellulose in subsequent steps. Filter/washer 110 may comprise solid-liquid separation equipment, including but not limited to, for example, rotary vacuum drums, belt filters and screw presses. Filter/washer 110 forms a filtered intermediate cellulosic material and an extraction filtrate 111.

[0077] Prior to exiting filter/washer 110, optionally while on a vacuum belt filter, the intermediate cellulosic material may be washed with extractant wash 107 to further reduce the amount of extractant remaining in the filtered extraction mixture. The washing may be conducted in a batch, a semi-batch or a continuous process with material flowing either co-current or counter-current in relation to one another. In some embodiments, the intermediate cellulosic material may be

washed more than once in separate washing units from filter/washer 110. When more than one washing step is used, the composition of the extractant wash may vary in the different washing steps. For example, a first washing step may use DMSO as an extractant wash to remove residual hemicellulose and a second washing step may use water as an extractant wash to remove residual DMSO. A similar configuration can be designed and optimized based upon the general chemical engineering principles and process design theory.

[0078] Extractant wash 107 preferably comprises a co-solvent, which dissolves residual hemicellulose and/or degraded cellulose from the cellulosic material, but may also include some low level of extractant resulting from the sequence of washing steps. In one embodiment, the extractant wash is selected from the group consisting of water, acetonitrile, DMF, DMAC, ketones (e.g. acetone), aldehydes, esters (e.g. methyl acetate, ethyl acetate), ethers (e.g., MTBE), lactones, carboxylic acids (e.g., acetic acid), alcohols, polyols, amino alcohols, DMSO, formamide, propylene carbonate, aromatic solvents, halogenated solvents, aliphatic solvents, vinyl acetate, nitriles (propionitrile, chloroacetonitrile, butyronitrile), chloroform, dichloromethane, and mixtures thereof. In another embodiment, extractant wash 107 is selected from the group consisting of DMSO, DMF, N-methyl pyrrolidone, methanol, ethanol, isopropanol, dimethyl carbonate, propylene carbonate, acetone, water, and mixtures thereof. In some embodiments, at least two extractant washes are used in series, such as DMSO and water. It should be understood that, depending on the amount of residual hemicellulose contained in the cellulosic material, the amount of extractant wash may be minimized to reduce capital cost and energy requirements for subsequent separation and recycle, described below. Additionally, it should be understood that the one or more extractant washes may also be used to remove side products, e.g., mono-, di-, and oligo-saccharides from the extraction mixture.

[0079] The extractant wash may further comprise one or more washing aids that improve the removal of extractant from the cellulosic material, improve operability, or otherwise improve the physical properties of the intermediate cellulose material. The washing aids may include, for example, defoamers, surfactants, and mixtures therefore. The amount of washing agent can vary widely based upon the amount of residual extractant, quality requirement for cellulosic product, and process operability.

[0080] The extractant wash may then be removed via line 112, e.g., as used extractant wash filtrate. The washed intermediate cellulosic material exits filter/washer 110 as an intermediate cellulosic material 113 having reduced hemicellulose content and preferably reduced degraded

cellulose content. Intermediate cellulosic material 113 may comprise less than 6 wt.% extractant, e.g., less than 5 wt.% or less than 4 wt.% extractant. In some embodiments, the intermediate cellulosic material 113 may comprise less than 0.5 wt.% cellulose solvent (ionic liquid and/or amine oxide), e.g., less than 0.05 wt.%, less than 0.005 wt.%, or less than 0.001 wt%. Intermediate cellulosic material 113 may comprise from 9.9 to 99% solids, e.g., from 19 to 90% or from 28 to 85%.

[0081] Exemplary compositions using DMSO as the co-solvent and water as the extractant wash for the intermediate cellulosic material are provided in Table 2. When DMSO is used as the co-solvent and water is used as the extractant wash, at least 90% of the cellulose in cellulosic material 103 is maintained in cellulose product 123, as described herein.

TABLE 2
FILTER/WASHER 110

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>Extraction Mixture 106</u>			
Cellulose	0.24 to 14	0.26 to 13	0.29 to 12
Hemicellulose*	0.008 to 7	0.03 to 5	0.05 to 5
Solvent (e.g., Ionic Liquid)	0.09 to 99.4	1.7 to 90	2.6 to 80
Co-solvent (e.g., DMSO)	0.09 to 99.4	8.5 to 98	17 to 97
<u>Washed Intermediate Cellulosic Material 113</u>			
Cellulose	9.9 to 99	19 to 90	28 to 85
Hemicellulose*	0.003 to 12	0.02 to 9	0.06 to 7
Extractant wash (e.g., water)	1 to 90	10 to 80	15 to 70
<u>Extraction Filtrate 111</u>			
Cellulose	0.002 to 1.4	0.003 to 1.3	0.003 to 1.2
Hemicellulose*	0.008 to 6.7	0.03 to 5.2	0.05 to 4.4
Solvent (e.g., Ionic Liquid)	0.09 to 99.9	1.7 to 90	2.6 to 80
Co-solvent (e.g., DMSO)	0.09 to 99.9	8.5 to 99.6	17.0 to 99.3
<u>Used Extractant wash (Filtrate) 112</u>			
Water	91 to 99.8	93 to 99.7	94 to 99.7
Solvent (e.g., Ionic Liquid)	0.004 to 2.7	0.004 to 2.0	0.004 to 1.5
Co-solvent (e.g., DMSO)	0.01 to 2.7	0.02 to 2.2	0.03 to 1.9

*“Hemicellulose” in these streams includes hemicellulose, degraded cellulose and other impurities

[0082] Intermediate cellulosic material 113 may then be further de-liquored, e.g., mechanically concentrated in a concentrator 115 to form a concentrated cellulosic material 117 having an

increased solids content and a residual extractant wash 116, which may be recycled to and combined with either extractant wash 107 or stream 112. The solids content in concentrated cellulosic material 117 may range from 10 to 99 wt%, e.g., from 20 to 90 wt% or from 30 to 85 wt%. The concentrator may include squeeze rolls, rotating rolls, and/or ringer rolls as well as optional heat exchangers to vaporize the liquids. Additional water removal methods may be used to concentrate the cellulosic material, depending on the desired solids content and available energy supply. The concentrated cellulosic material may comprise from 2 to 99 wt.% cellulose (e.g., from 3 to 95 wt.% cellulose), from 1 to 60 wt.% water (e.g., from 1 to 50 wt.% water), and from 0.01 to 20 wt.% hemicellulose (e.g., from 0.5 to 10 wt.% hemicellulose).

[0083] In some embodiments, when the process comprises more than one washing step, a concentrator may be utilized between washing steps or after all washing steps in order to maximize the washing separation of hemicellulose, as well as improve washing efficiency for the solvent and co-solvent thereby reducing total washing agent quantity required and associated energy and disposal costs.

[0084] Concentrated cellulosic material 117 or 113 may then be further dried in dryer 120. Hot gas may be fed to dryer 120 via line 121 and may exit dryer 120 via line 122. A finished cellulose product may then exit dryer 120 via line 123. The dryer may function to remove residual extractant wash. The finished cellulose product may comprise from 80 to 99.9 wt.% cellulose (e.g., from 90 to 95 wt.% cellulose), from 0.01 to 25 wt.% hemicellulose (e.g., from 0.1 to 15 wt.% hemicellulose) and from 0.1 to 20 wt.% water (e.g., from 3 to 15 wt.% water). Exemplary dryers include disintegrator dryers, flash dryers, apron dryers, rotary dryers, heated rolls, infrared dryers, ovens and vacuums. Without being bound by theory, the disintegrator dryer may be used to further open the cellulosic material, which may be advantageous for subsequent processing, e.g., in the formation of cellulose acetate, and derivatives thereof. In another embodiment, dryer 120 comprises heated rolls which may be used to form baled sheets or product rolls of cellulosic material. Finished cellulose product 123 may comprise less than 20 wt.% water, e.g., less than 15 wt.%, less than 10 wt.% or less than 5 wt.% water.

[0085] Depending on the purity of the starting cellulosic material, in accordance to preferred embodiments of the present invention, high purity α -cellulose product may be produced. In preferred embodiments, the finished cellulose product comprises high purity α -cellulose products such as high purity dissolving grade pulps with less than 5 wt.% hemicellulose, e.g., less than 2 wt.% hemicellulose or less than 1 wt.% hemicellulose. In one embodiment, the cellulosic product has an

UV absorbance of less than 2.0 at 277 nm, e.g., less than 1.6 at 277 nm, or less than 1.2 at 277 nm. Paper grade pulp typically has an UV absorbance of greater than 4.7 at 277 nm, as determined by standard UV absorbance measurements. Conveniently and accurately, purity of the α -cellulose product may be indicated by a lower absorbance at a certain wavelength.

[0086] In addition to retaining the fiber morphology of the cellulosic product, the high purity α -cellulose grade pulp product also may advantageously retain other beneficial characteristics such as intrinsic viscosity and brightness. The high purity α -cellulose grade pulp product may be further processed to make cellulose derivatives, such as cellulose ether, cellulose esters, cellulose nitrate, other derivatives of cellulose, or regenerated cellulose fiber, such as viscose, lyocell, rayon, etc. Preferably, the high purity α -cellulose grade pulp may be used to make cellulose acetate.

[0087] Returning to extractant filtrate 111, in one embodiment, the stream may be sent to a hemicellulose concentrator 130 to form a (first) recovered extractant 131 and hemicellulose concentrate 132. The recovered extractant 131 will likely be enriched in co-solvent and lean in ionic liquid relative to extractant 104. The hemicellulose concentrator 130 may comprise a filtration unit or an evaporator. The filtration unit may be an ultrafiltration unit or a nanofiltration unit, or membrane separation unit, and may comprise a membrane. The filtration unit may be operated at a pressure from 1 kPa to 5,000 kPa and a temperature from 0°C to 200°C and appropriate flow rates. If an evaporator is used, the conditions employed preferably include a pressure from 1 kPa to 1,000 kPa and temperature from 30°C to 200°C.

[0088] Exemplary compositions for the recovered extractant and the hemicellulose concentrate are provided in Table 3.

TABLE 3
Hemicellulose Concentrator 130

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
<u>(First) Recovered Extractant 131</u>			
Solvent (e.g., Ionic Liquid)	0 to 5	0 to 3	0 to 1
Co-solvent (e.g., DMSO)	95 to 100	97 to 100	99 to 100
<u>Hemicellulose Concentrate 132</u>			
Cellulose	0.003 to 13.4	0.003 to 12.6	0.003 to 11.9
Hemicellulose*	0.008 to 67	0.03 to 51	0.06 to 44
Solvent (e.g., Ionic Liquid)	0.09 to 99.9	1.8 to 99	2.7 to 98
Co-solvent (e.g., DMSO)	0.009 to 99.3	0.17 to 96	0.26 to 93
Water	0.0005 to 3.0	0.005 to 2.5	0.005 to 1.8

*“Hemicellulose” in stream 132 includes hemicellulose, degraded cellulose and other impurities

[0089] The recovered extractant 131 may be recycled to the extractor. In some embodiments, recovered extractant 131 may be combined with extractant 104, as shown. In other embodiments, when recovered extractant 131 consists essentially of co-solvent, recovered extractant 131 may be directly fed to filter/washer 110, or optionally used as a first stage washing agent or combined with extractant wash 107 in washing the intermediate cellulose material.

[0090] Hemicellulose concentrate 132 may then be fed to precipitator 135 to precipitate hemicellulose therefrom. Precipitation agent may be fed to precipitator 135 via line 133 and combined with hemicellulose concentrate 132 to form a precipitation slurry 136. Precipitator 135 may comprise one or more stirred tanks or other agitation equipment, and may be either batch or continuous. It may utilize electrostatic charge to facilitate precipitation. Precipitation agent 133 may be selected from the group consisting of isopropanol, and butanol; ketone, e.g., acetone, 2-butanone; nitrile, e.g., acetonitrile, propionitrile, butyronitrile, chloroacetonitrile; ether, e.g., tetrahydrofuran, diethyl ether, dibutyl ether; ester, e.g., methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, propylene carbonate; carboxylic acid, e.g., acetic acid, formic acid; amide, e.g., formamide; halide, e.g., dichloromethane, chloroform, 1-chlorobutane, 1,2-dichloroethane; hydrocarbon compound; e.g., hexane, 2,2,4-trimethylpentane, benzene, toluene; amine, e.g., ethylamine, butylamine, ethyldiamine; heterocyclic compound, e.g., pyridine, pyrrole, pyrrolidine, piperidine; water, and combinations thereof. Precipitation agent 133 may also comprise a mixture of an alcohol and water, optionally at an alcohol:water mass ratio from 0.9:1 to 20:1 from 1:1 to 20:1 or from 2:1 to 15:1. Precipitation slurry 136 may comprise, for example, from 0.001 to 7 wt.% cellulose, from 0.003 to 34 wt.% hemicellulose, from 0.0003 to 7 wt.% water, from 0.05 to 50 wt.% solvent, and from 50 to 99 wt.% precipitation agent.

[0091] In another embodiment, a gas, optionally an inert gas, e.g., nitrogen, may be fed to precipitator 135. In some embodiments, the inert gas is carbon dioxide, optionally supercritical carbon dioxide. In this embodiment, the supercritical carbon dioxide may lead to the formation of a carbon dioxide phase, a solvent phase and a hemicellulose phase. In this aspect, hemicellulose is automatically separated out as a solids rich stream. The carbon dioxide may be flashed under low pressure, recovered using a compressor, and returned to precipitator 135. Some or all of the co-solvent may be flashed at reduced pressure and recycled (not shown). This type of concentrating process for hemicellulose may advantageously reduce the downstream washing requirements and associated energy costs (described below).

[0092] As shown, precipitation slurry 136 may then be sent to filter/washer 137 which separates a precipitation agent filtrate 139 from recovered solid hemicellulose. Filter/washer 137 may comprise solid-liquid separation equipment, including but not limited to rotary vacuum drums, belt filters and screw presses. Prior to exiting filter/washer 137, the recovered solid hemicellulose may be washed with precipitant wash 134 to form washed recovered solid hemicellulose 138. The washing step may serve to further reduce the amount of extractant and/or precipitation agent remaining in the recovered solid hemicellulose. The washing may be conducted in a batch, a semi-batch or a continuous process with material flowing either co-current or counter-current in relation to one another.

[0093] In another embodiment, the precipitator may comprise a crystallizer as long as the hemicellulose solubility is sensitive to solvent temperature. In this aspect, the reduced temperature may cause the hemicellulose to precipitate as solids from the solution.

[0094] Precipitant wash 134 preferably comprises a co-solvent, which dissolves the impurities inside the hemicellulose, but may also include some low level of cellulose solvent, e.g., ionic liquid or amine oxide, resulting from the sequence of washing steps. In one embodiment, the precipitant wash is selected from the group consisting of the group of alcohol, e.g., methanol, ethanol, isopropanol, and butanol; ketone, e.g. acetone, 2-butanone; nitrile, e.g., acetonitrile, propionitrile, butyronitrile, chloroacetonitrile; ether, e.g., tetrahydrofuran, diethyl ether, dibutyl ether; ester, e.g., methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, propylene carbonate; carboxylic acid, e.g., acetic acid, formic acid; amide, e.g., formamide; halide, e.g., dichloromethane, chloroform, 1-chlorobutane, 1,2-dichloroethane; hydrocarbon compound; e.g., hexane, 2,2,4-trimethylpentane, benzene, toluene; amine, e.g. ethylamine, butylamine, ethyldiamine; heterocyclic compound, e.g., pyridine, pyrrole, pyrrolidine, piperidine; water, and combinations thereof.. In another embodiment, precipitant wash 134 is selected from the group consisting of DMSO, DMF, N-methyl pyrrolidone, methanol, ethanol, isopropanol, dimethyl carbonate, propylene carbonate, acetone, water, and mixtures thereof. The precipitant wash may then be removed either via line 139 with the precipitation agent filtrate or via line 112 with the extractant wash.

[0095] Precipitation agent filtrate 139 may be fed to separation equipment, e.g., a membrane or a distillation column 150, to form recovered precipitant wash 151, recovered precipitation agent 152 and second recovered extractant 153. Recovered precipitant wash 151 preferably comprises high concentration, e.g., at least 95 wt.% precipitant wash, e.g., water, and may be recycled and become a first stage precipitant wash stream or part of stream 134. Recovered precipitation agent 152

preferably comprises high concentration, e.g. at least 80 wt.% precipitation agent, optionally greater than 85 wt.% precipitation agent, e.g., an alcohol such as ethanol, and optionally at most 20 wt.% precipitant wash, optionally at most 10 wt.% precipitant wash, e.g., water, and may be recycled and combined with precipitation agent in line 133. Second recovered extractant 153 preferably comprises high concentration, e.g. at least 80 wt.% co-solvent, e.g., at least 85 wt.% co-solvent (e.g., DMSO), and at most 20 wt.% cellulose solvent, e.g., at most 15wt.% cellulose solvent (e.g., ionic liquid or amine oxide). The second recovered extractant may be recycled and combined with extractant 104. When distillation is employed, column 150 may be operated at a temperature from 0°C to 300°C, e.g., from 10°C to 200°C or from 25°C to 150°C and at a pressure (absolute) from 1 to 2,000 kPa, e.g., from 2 to 1,000 kPa, from 5 to 800 kPa or from 10 to 600 kPa. At least a portion of the overhead stream 152 may be returned as reflux to improve separation (not shown). In some embodiments, a second distillation column (not shown) may be used to separate residual cellulose solvent and/or co-solvent from the recovered precipitant wash 151.

[0096] Returning to the used extractant wash removed via line 112, this stream may be treated in separation equipment, e.g., a membrane or a distillation column 140, to form recovered extractant wash 142 and a third recovered extractant 141. Distillation column 140 may be operated at a temperature from 0°C to 300°C, e.g., from 10°C to 200°C or from 25°C to 150°C and at a pressure (absolute) from 1 to 2,000 kPa, e.g., from 2 to 1,000 kPa, from 5 to 800 kPa or from 10 to 600 kPa. At least a portion of the recovered extractant wash may be refluxed to distillation column 140, as shown. The remainder of the stream may be recycled and combined with extractant wash 107. As shown in FIG. 1, one or more of the third recovered extractant 141, second recovered extractant 153 and (first) recovered extractant 131 may be combined and recycled to extractant 104.

[0097] In another embodiment, the used extractant wash removed via line 112 may be directed to the separation equipment 150 when the extractant wash and precipitation wash are the same material. In this embodiment, the function of distillation column 140 has been addressed by separation equipment 150 and distillation column 140 can be advantageously eliminated from the process.

[0098] Returning to washed hemicellulose 138, the stream may then be mechanically deliquored, e.g., concentrated in a concentrator 144 to form concentrated hemicellulose material 143 and a second residual precipitant wash 145 that may be combined with precipitant wash 134. The solids content in concentrated hemicellulose material 143 may be from 10 to 99 wt.%, e.g., from 20 to 90 wt.% or from 30 to 85 wt.%. Concentrated hemicellulose material 143 may comprise from 0.1

to 20 wt.% cellulose (e.g., from 1 to 15 wt.% cellulose), from 20 to 99 wt.% hemicellulose (e.g., from 30 to 90 wt.% hemicellulose), and from 1 to 75 wt.% water (e.g., from 10 to 70 wt.% water). The concentrator may include squeeze rolls, rotating rolls, and/or wringer rolls. It should be understood that additional water removal methods may be used to concentrate the hemicellulose, depending on the desired solids content and available energy supply.

[0099] Concentrated hemicellulose material 143 or 138 may then be further dried in dryer 146. Hot gas may be fed to dryer 146 via line 148 and may exit dryer 146 via line 149. A finished hemicellulose product may then exit dryer 146 via line 147. The dryer may function to remove residual precipitant wash, e.g., water. Exemplary dryers may include disintegrator dryers, flash dryers, apron dryers, rotary dryers, heated rolls, infrared dryers, ovens and vacuums. The finished hemicellulose product 147 may comprise from 1 to 25 wt.% cellulose (e.g., from 5 to 20 wt.% cellulose), from 60 to 99 wt.% hemicellulose (e.g., from 70 to 95 wt.% hemicellulose), and from 1 to 30 wt.% water (e.g., from 3 to 20 wt.% water).

[0100] The finished hemicellulose product has a broad application to generate high value chemicals. Some, but not all, examples are described briefly here. Firstly, it may be advantageously used as an intermediate in furfural, methyl furfural, or valerolactone production. Secondly, the finished hemicellulose product may also be used as a feedstock to produce ethanol and/or as a fuel to a recovery boiler. Thirdly, hemicellulose can be used as a starting material to produce functional chemicals, such as adhesives and sweeteners. Fourthly, it can be recycled back to paper mill to make papers with special features.

[0101] While the above invention is applicable to processes in which mono-, di-, and oligo-saccharide and/or other side products may be generated in the extraction process, flashing process, and/or other operating steps, several other technologies can also be chosen to remove them from the system in order to maintain continuous operation. In one embodiment, the process may comprise a first washing step with an alcohol, followed by a washing step with a co-solvent. The alcohol may dissolve cellulose solvent but has limited solubility to mono-, di-, and oligo-saccharides. The co-solvent wash may dissolve mono-, di-, and oligo-saccharides from hemicellulose. In some embodiments, evaporation, membrane, ion exchange, activated carbon bed, simulated moving bed chromatographic separation, flocculant, e.g., polydiallyldimethylammonium chloride (polyDADMAC), and/or their combinations may be employed to separate mono-, di-, and oligo-saccharide from the liquid stream. In other embodiments, polymer-bound boronic acid has been demonstrated to be able to form complex with sugars so that the sugars are separated from the liquid

stream. In yet other embodiments, the small sugars may be converted by either enzymatic treatment or acid-catalytic process into furfural, ethanol, acetic acid, and/or other products which can be further separated out from the system. In still other embodiments, mono-, di-, and oligo-saccharide and other side products can be removed in one or more operations, which are located before the separation of the extraction filtrate, after precipitation step, in the hemicellulose wash steps, and/or in other steps. The operating conditions are also determined by the stability of the extractant. Without being bound by theory, it is believed that this allows for the minimization of degradation products of the extractant. For a continuous operation, degradation products may be removed by directly purging a degradation products stream. Additionally, distillation may be used to purge degradation products from a column as a distillate or a residue, depending on the boiling point(s) of the degradation product(s). In some embodiments, combinations of these degradation product removal strategies may be employed.

[0102] The present invention will be better understood in view of the following non-limiting examples. Examples 1-6 are based on experimental results and Example 7 is based on Aspen™ simulation modeling.

V. Examples

Example 1

[0103] A cellulosic material comprising 74.8 wt.% cellulose, 18.7 wt.% hemicellulose and 6.5 wt.% water was fed to an extraction unit. Separately, an extractant comprising 3.5 wt.% EMIM Ac and 96.5 wt.% DMSO was fed to the extraction unit. The extraction was conducted at a temperature of 90-110°C and a pressure of 90-110 kPa. An extraction mixture comprising 3.6 wt.% cellulose, 0.89 wt.% hemicellulose, 0.31 wt.% water, 3.3 wt.% ionic liquid and 91.9 wt.% DMSO was removed from the extractor and sent through a vacuum filter and washed with an extractant wash to remove an extraction filtrate comprising extractant and hemicellulose. The extractant wash was water and was fed at a 10:1 mass ratio of water to pulp. The washed cellulosic material, e.g., the intermediate cellulosic material, comprised 24.5 wt.% cellulose, 0.5 wt.% hemicellulose and 75 wt.% water. The intermediate cellulosic product was then de-liquored to concentrate the intermediate cellulosic product. The resulting concentrated cellulosic product comprised 49 wt.% cellulose, 1 wt.% hemicellulose, and 50 wt.% water. The concentrated cellulosic product was then further dried in a disintegrator drier to produce a finished cellulosic product comprising 92 wt.% cellulose, 1.9 wt.% hemicellulose and 6.5 wt.% water.

[0104] The extractant wash filtrate comprising 72 wt.% water, 1 wt.% ionic liquid and 27 wt.% DMSO was also removed from the vacuum filter. Then ionic liquid and DMSO was separated from water using evaporator at 10 kPa and 115°C. The water was recycled to be used as extractant wash and the ionic liquid and DMSO were recycled to the extractor.

[0105] The extraction filtrate comprised 0.4 wt.% cellulose, 1 wt.% hemicellulose, 0.1 wt.% water, 3.5 wt.% ionic liquid and 95 wt.% DMSO. This stream was sent through an evaporator to separate the ionic liquid and DMSO from the hemicellulose. This recovered extractant was recycled to the extractor. The recovered hemicellulose, e.g., hemicellulose concentrate, comprised 2.7 wt.% cellulose, 6.1 wt.% hemicellulose, 0.6 wt.% water, 22 wt.% ionic liquid, and 68 wt.% DMSO, and was sent to a precipitator. A precipitation agent comprising ethanol was also sent to the precipitator to form a precipitation slurry which comprised 1.3 wt.% cellulose, 3.1 wt.% hemicellulose, 0.3 wt.% water, 11 wt.% ionic liquid, 34 wt.% DMSO and 50 wt.% ethanol. In order to completely precipitate the hemicellulose, the volume ratio of ethanol to liquid filtrate is at least 0.95, e.g. at least 1.5, e.g. at least 2.0. The precipitation slurry was then vacuum filtered, washed with a precipitant wash comprising water, de-liquored, and further dried with hot air to produce a finished hemicellulose product comprising 28 wt.% cellulose, 65 wt.% hemicellulose and 7 wt.% water. As indicated above, the weight percentage of degraded cellulose is included in that of hemicellulose.

Example 2

[0106] The finished cellulosic product and the finished hemicellulose product were prepared as in Example 1, except that the extraction process was completed in a 2-stage counter-current operation. The extraction time was dropped to 60 minutes at temperature of 90°C for dissolving the same amount of hemicellulose, which was indicated by the UV absorbance value of 1.2 at 277 nm wavelength, or equivalently 2.8 wt.% hemicellulose.

Example 3

[0107] The finished cellulosic product and the finished hemicellulose product were prepared as in Example 1, except that the extractant wash comprised 90 wt.% acetic acid and 10 wt.% water. The value of UV absorbance at 277 nm for the final pulp is 0.98, or equivalently 1.9 wt% hemicellulose.

Example 4

[0108] The finished cellulosic product and the finished hemicellulose product were prepared as in Example 1, except that the extractant wash comprised acetic acid. The value of UV absorbance at 277 nm for the final pulp is 1.03, or equivalently 2.1 wt% hemicellulose.

Example 5

[0109] The finished cellulosic product and the finished hemicellulose product were prepared as in Example 1, except that the extractant comprised 75 wt.% ionic liquid and 25 wt.% water. The value of UV absorbance at 277 nm for the final pulp was 1.01, or equivalently 2.0 wt% hemicellulose. The cost of this process was higher than the costs of the process of Examples 1-4 due to the higher amount of ionic liquid used and not recovered.

Example 6

[0110] The finished cellulosic product and the finished hemicellulose product were prepared as in Example 5, except that the extractant wash comprised acetic acid. The value of UV absorbance at 277 nm for the final pulp was 1.1, or equivalently 2.4 wt% hemicellulose

Example 7

[0111] The separation of extractant from extractant wash in distillation column 140 was simulated using Aspen Software, as shown below with varied solvent to co-solvent ratios. In the simulation, EMIM Ac and DMSO were include as one component EMIM Ac/DMSO since their boiling points, i.e., greater than 185°C at normal pressure, are significantly greater than those of water and ethanol. In Example A, the extractant comprised a combination of EMIM Ac/DMSO and water. The feed to column 140 comprised 44.6 wt.% water and 55.4 wt.% EMIM Ac/DMSO. The distillation column was operated at a temperature of 87.8°C and a pressure of 4.4 kPa. In Example B, the extractant comprised a combination of water, EMIM Ac/DMSO, and ethanol at 35.9 wt.%, 29.8 wt.%, and 34.3 wt.%, respectively. The distillation column further comprised a side stream (not shown). The distillation column was operated at a temperature of 65°C and a pressure of 2.13 kPa. In Example C, the extractant comprised a combination of water, EMIM Ac/DMSO, and ethanol at 17.7 wt.%, 38.3 wt.%, and 44 wt.%, respectively. The distillation column further comprised a side stream (not shown). The distillation column was operated at a temperature of 65°C and a pressure of 2.13 kPa. The results of the separation in distillation column 140 are shown below in Table 4.

TABLE 4
DISTILLATION COLUMN 140

	Feed (112)	Distillate (wt.%) (142)	Residue (wt.%) (141)	Side Stream (wt.%)
Example A				
Water	44.6	99.99	0.01	---
EMIM Ac/ DMSO	55.4	0.01	99.99	---
Example B				
Water	35.9	11	0.05	98.90
EMIM Ac/ DMSO	29.8	0.01	99.5	0.07
Ethanol	34.3	88.99	<0.001	0.03
Example C				
Water	17.7	11	0.005	98.7
EMIM Ac/ DMSO	38.3	<0.001	99.5	1.2
Ethanol	44	88.99	<0.001	0.1

[0112] While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. It should be understood that aspects of the invention and portions of various embodiments and various features recited above and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of ordinary skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

We claim:

1. A process for purifying a cellulosic material, comprising:
extracting hemicellulose from the cellulosic material with an extractant to form an intermediate cellulosic material having a reduced hemicellulose content;
concentrating the intermediate cellulosic material to form a concentrated cellulosic material having an increased solids content; and
recovering the separated hemicellulose;
wherein the extractant comprises a cellulose solvent and a co-solvent, and the cellulose solvent is selected from the group consisting of an ionic liquid, an amine oxide and combinations thereof.
2. The process of claim 1, wherein the extracting forms an extraction mixture and wherein the extraction mixture is separated in a filter to form the intermediate cellulosic material and an extraction filtrate comprising the hemicellulose, the cellulose solvent and the co-solvent.
3. The process of claim 2, further comprising:
directing the extraction filtrate to a membrane to remove at least a portion of the cellulose solvent and the co-solvent from the extraction filtrate; and
precipitating the extraction filtrate with a precipitation agent in a precipitator to form a precipitation slurry,
wherein the precipitation agent is selected from the group consisting of alcohol, a ketone, a nitrile, an ether, an ester, a carboxylic acid, a halide, a hydrocarbon compound, an amine, a heterocyclic compound, water, and combinations thereof, preferably wherein the precipitation agent is selected from the group consisting of methanol, ethanol, isopropanol, butanol, acetone, 2-butanone, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, tetrahydrofuran, diethyl ether, dibutyl ether, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, propylene carbonate, acetic acid, formic acid, formamide, dichloromethane, chloroform, 1-chlorobutane, 1,2-dichloroethane, hexane, 2,2,4-trimethylpentane, benzene, toluene, ethylamine, butylamine, ethyldiamine, pyridine, pyrrole, pyrrolidine, piperidine, water, and combinations thereof.

4. The process of claim 2, further comprising:
directing the extraction filtrate directly to a precipitator to precipitate the extraction filtrate with a precipitation agent to form a precipitation slurry.
5. The process of any of the preceding claims, wherein mono-, di-, and oligo-saccharide and other side products formed in the process are removed from the process.
6. The process of any of the preceding claims, wherein the concentrated cellulosic material is dried to recover a finished cellulosic product.
7. The process of any of the preceding claims, wherein the intermediate cellulosic material comprises at least 10 wt.% less hemicellulose than the cellulosic material.
8. The process of any of the preceding claims, wherein the ionic liquid is selected from the group consisting of 1-butyl-3-methylimidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium hydrogensulfate, 1-butyl-3-methyl imidazolium hydrogensulfate, methylimidazolium chloride, 1-ethyl-3-methyl imidazolium acetate, 1,3-diethyl imidazolium acetate, 1-butyl-3-methyl imidazolium acetate, tris-2(hydroxyethyl)methylammonium methylsulfate, 1-ethyl-3-methyl imidazolium ethylsulfate, 1-ethyl-3-methyl imidazolium methanesulfonate, methyl-tri-n-butylammonium methylsulfate, 1-butyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, 1-ethyl-3-methyl imidazolium thiocyanate, 1-butyl-3-methyl imidazolium thiocyanate, 1-aryl-3-methyl imidazolium chloride, 1-ethyl-3-methylimidazolium dimethyl phosphate, 1-ethyl-3-methyl diethyl phosphate, 1,3-dimethylimidazolium dimethyl phosphate and combinations and complexes thereof.
9. The process of any of the preceding claims, wherein the amine oxide is selected from the group consisting of trimethylamine N-oxide, triethylamine N-oxide, tripropylamine N-oxide, tributylamine N-oxide, methyldiethylamine N-oxide, dimethylethylamine N-oxide, methyldipropylamine N-oxide, tribenzylamine N-Oxide, benzyldimethylamine N-oxide, benzyldiethylamine N-oxide, dibenzylmethylamine N-oxide, N-methylmorpholine N-oxide (NMMO), pyridine N-oxide, 2-, 3-, or 4-picoline N-oxide, N-methylpiperidine N-oxide, N-ethylpiperidine N-oxide N-propylpiperidine N-oxide, N-isopropylpiperidine N-oxide. N-

butylpiperidine N-oxide, N-hexylpiperidine N-oxide. N-methylpyrrolidine N-oxide, N-ethylpyrrolidine N-oxide N-propylpyrrolidine N-oxide, N-isopropylpyrrolidine N-oxide. N-butylpyrrolidine N-oxide, N-hexylpyrrolidine N-oxide, and combinations thereof.

10. The process of any of the preceding claims, wherein the co-solvent is selected from the group consisting of dimethyl sulfoxide, tetramethylene sulfone, tetramethylene sulfoxide, N,N-dimethylacetamide, N-methyl pyrrolidone, dimethyl formamide, piperylene sulfone, acetic acid, water, and mixtures thereof.
11. The process of any of the preceding claims, wherein the extracting hemicellulose comprises:
directing the cellulosic material and the extractant to an extractor;
extracting hemicellulose from the cellulosic material in the extractor to form an extraction mixture; and
filtering and washing the extraction mixture with an extractant wash to form the intermediate cellulosic material and an extraction filtrate.
12. The process of claim 11, wherein the extractant wash is selected from the group consisting of an alcohol, a ketone, a nitrile, an ether, an ester, a carboxylic acid, a halide, a hydrocarbon compound, an amine, a heterocyclic compound, water, and combinations thereof, preferably wherein the extractant wash is selected from the group of methanol, ethanol, isopropanol, acetone, methyl isobutyl ketone, propionitrile, butyronitrile, chloroacetonitrile, ether, tetrahydrofuran, acetone, acetic acid, formic acid water, ethylene glycol, glycerin, formamide, N,N-dimethylformamide, N-methylpyrrolidinone, N,N-dimethylacetamide, DMSO, a mixture of water and alcohol, and combinations thereof.
13. The process of any of claims 11-12, further comprising:
concentrating hemicellulose from the extraction filtrate in a hemicellulose concentrator to form a recovered extractant and a hemicellulose concentrate; and
recycling the recovered extractant to the extractor or using it as an extractant wash.
14. The process of claim 13, further comprising:

precipitating the hemicellulose concentrate with a precipitation agent in a precipitator to form a precipitation slurry;

filtering the precipitation slurry to form a precipitation agent filtrate and filtered hemicellulose;

washing the filtered hemicellulose with a precipitant wash to form washed hemicellulose; and

drying the washed hemicellulose to form a finished hemicellulose product.

15. The process of claim 14, further comprising:

separating the precipitation agent filtrate in a distillation column to form a recovered precipitant wash, a recovered precipitation agent, and a second recovered extractant.

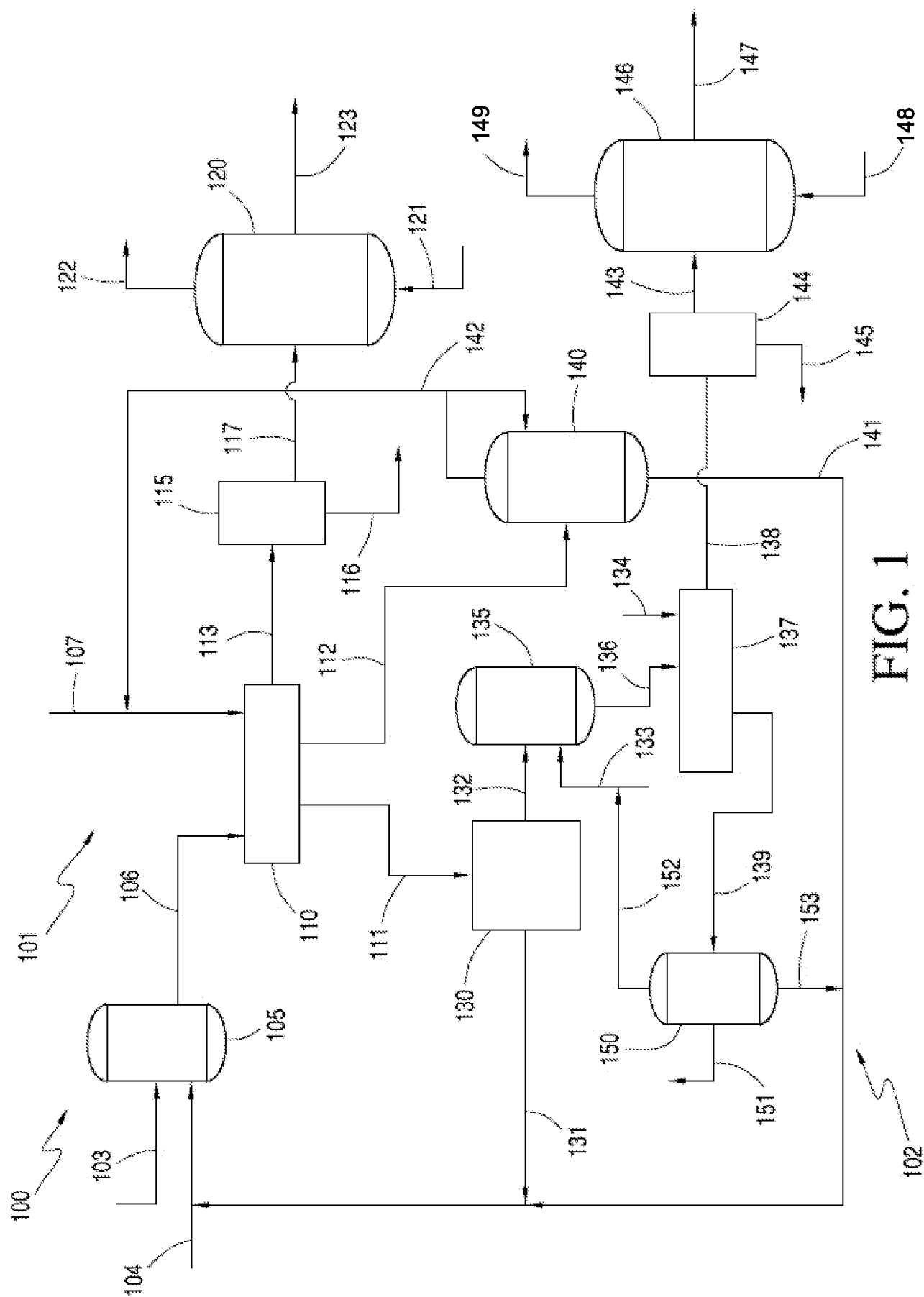


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/036550

A. CLASSIFICATION OF SUBJECT MATTER INV. D21C3/20 D21C9/00 D21C9/02 D21C11/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D21C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<div style="display: flex; justify-content: space-between;"> ☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">1 September 2014</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">05/09/2014</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Karlsson, Lennart</div>

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International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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