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(54) **INTEGRATED PROCESSES FOR PURIFYING  
A CELLULOSIC MATERIAL**

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(57) **ABSTRACT**

A process for converting a starting material to a purified pulp material, comprising removing lignin from a starting material to form a wet pulp comprising at least 5 wt. % water, extracting hemicellulose from the wet pulp with an extractant, and separating the extracted hemicellulose from the extraction mixture to form a cellulosic product comprising less hemicellulose than the wet pulp. The extractant comprises a cellulose solvent and a co-solvent. The cellulosic product advantageously retains its cellulosic fiber morphology. The process involves separating and recovering hemicellulose and separating and recycling various process streams employed in the process.

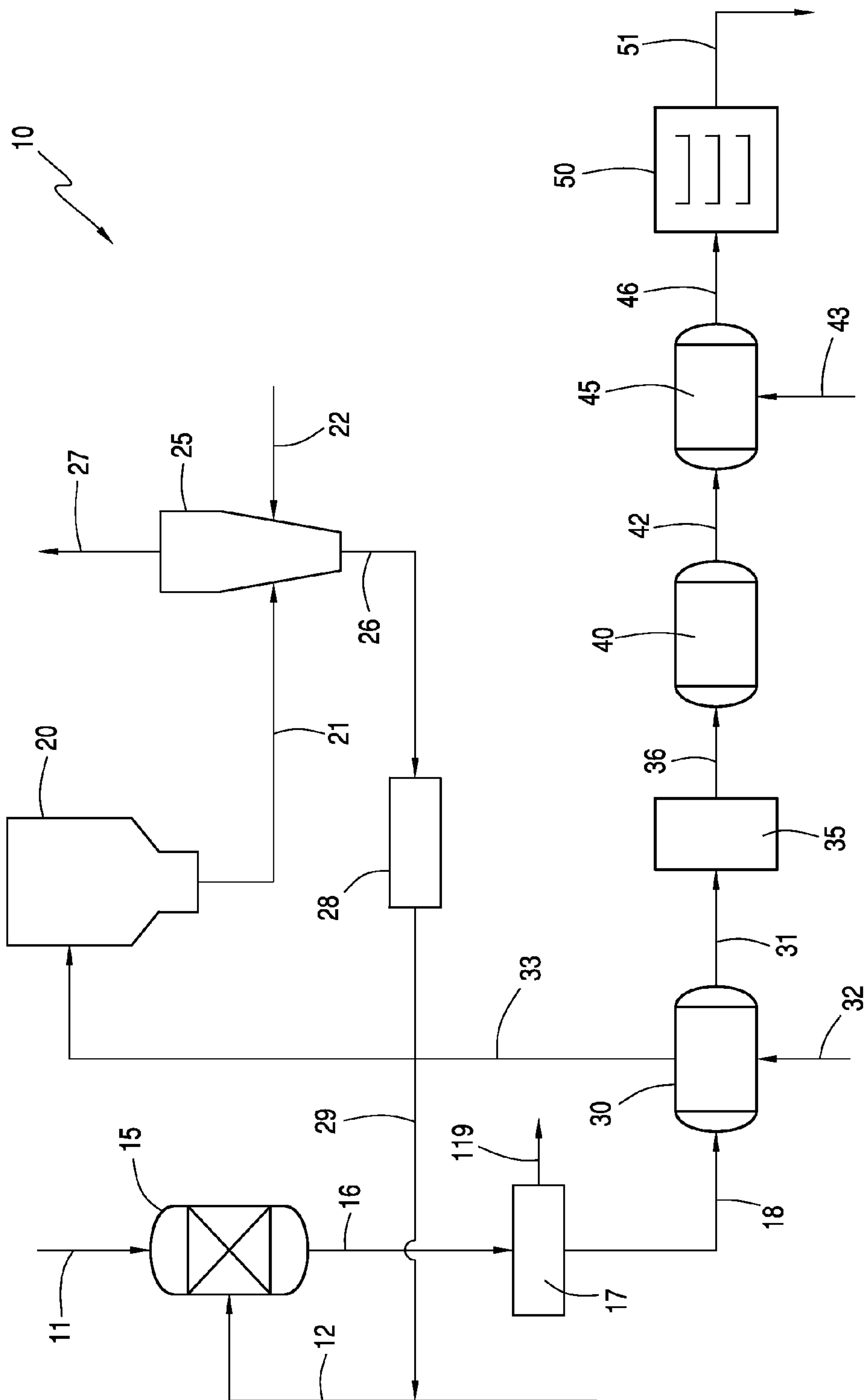


FIG. 1

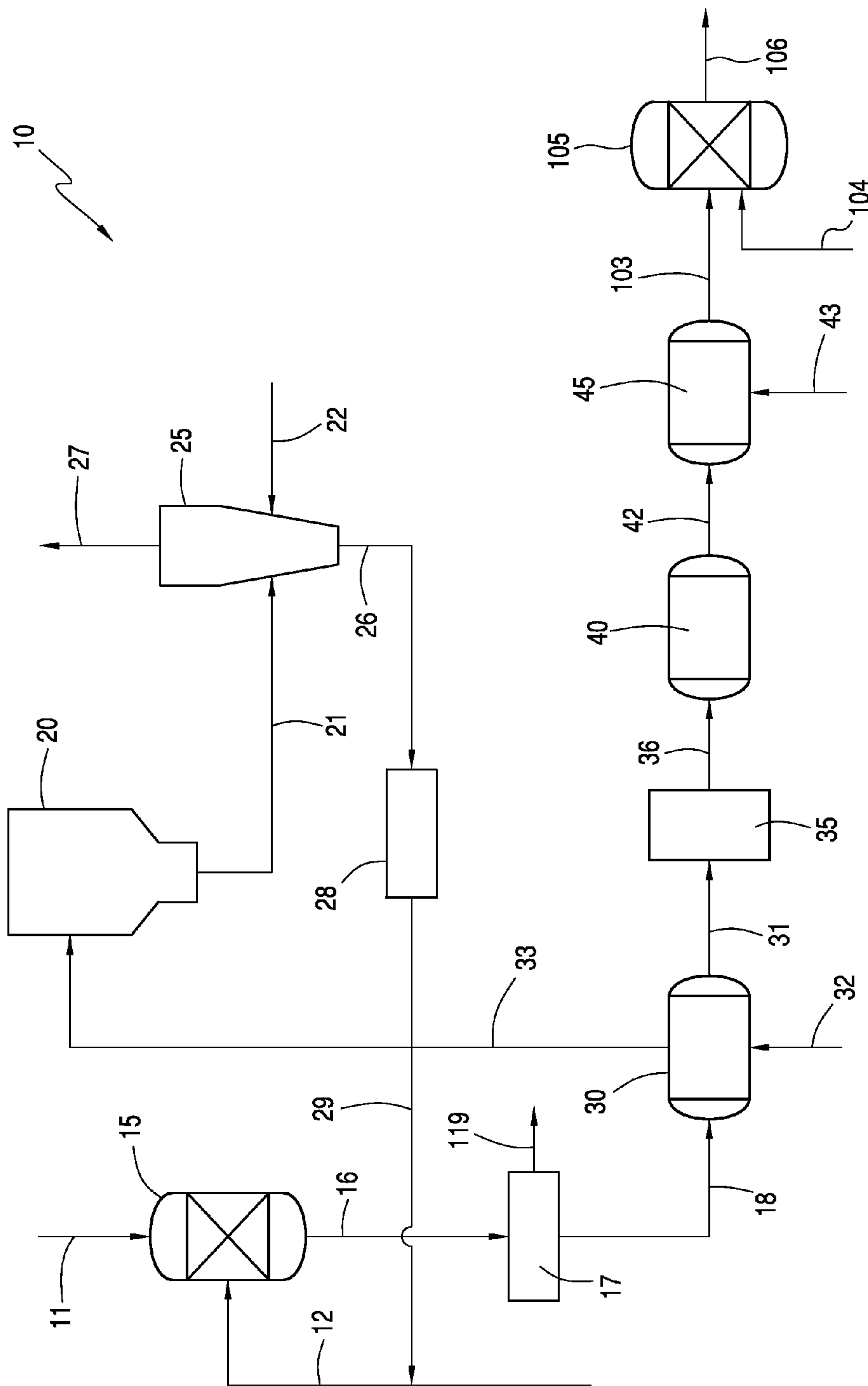


FIG. 2

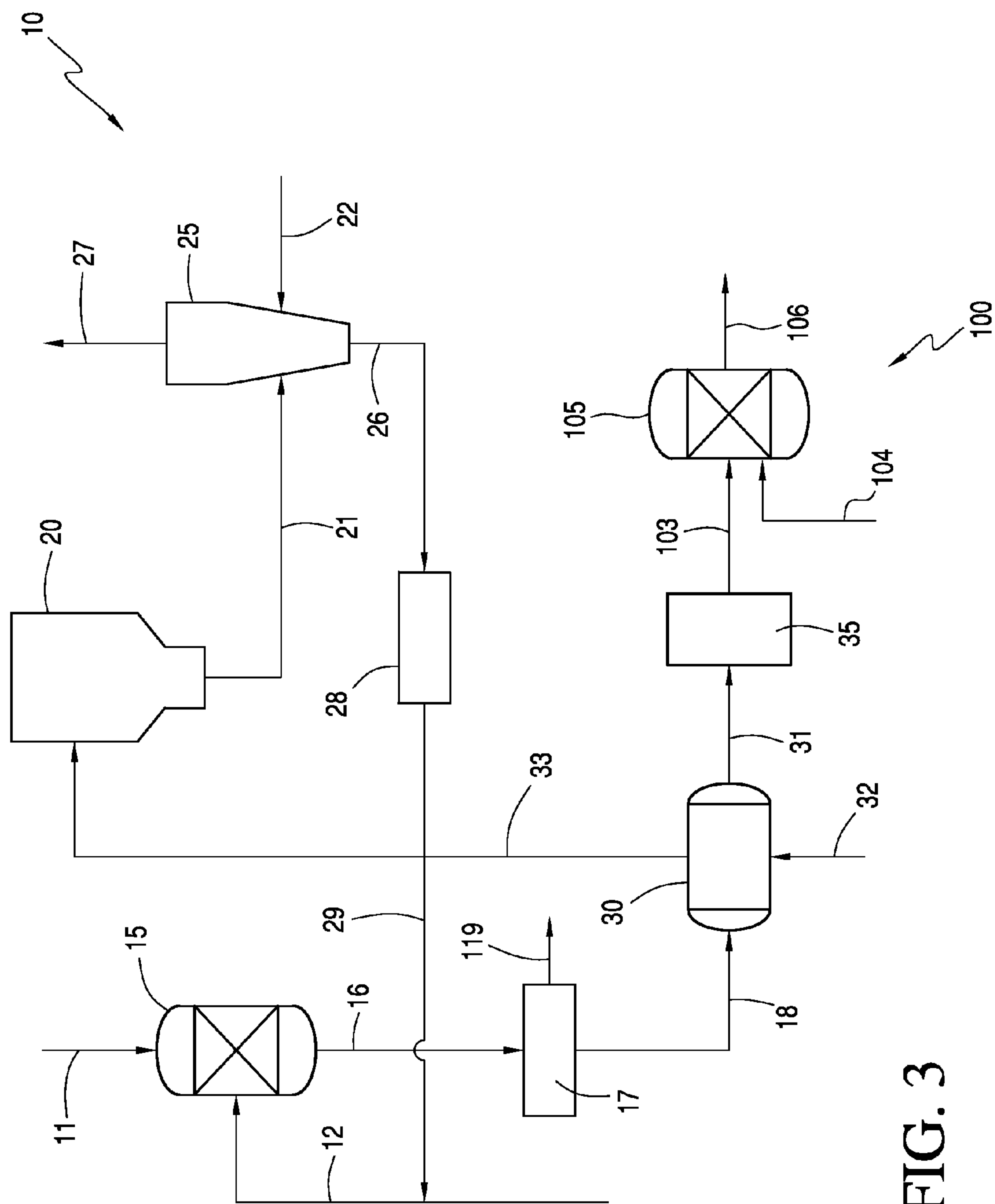


FIG. 3

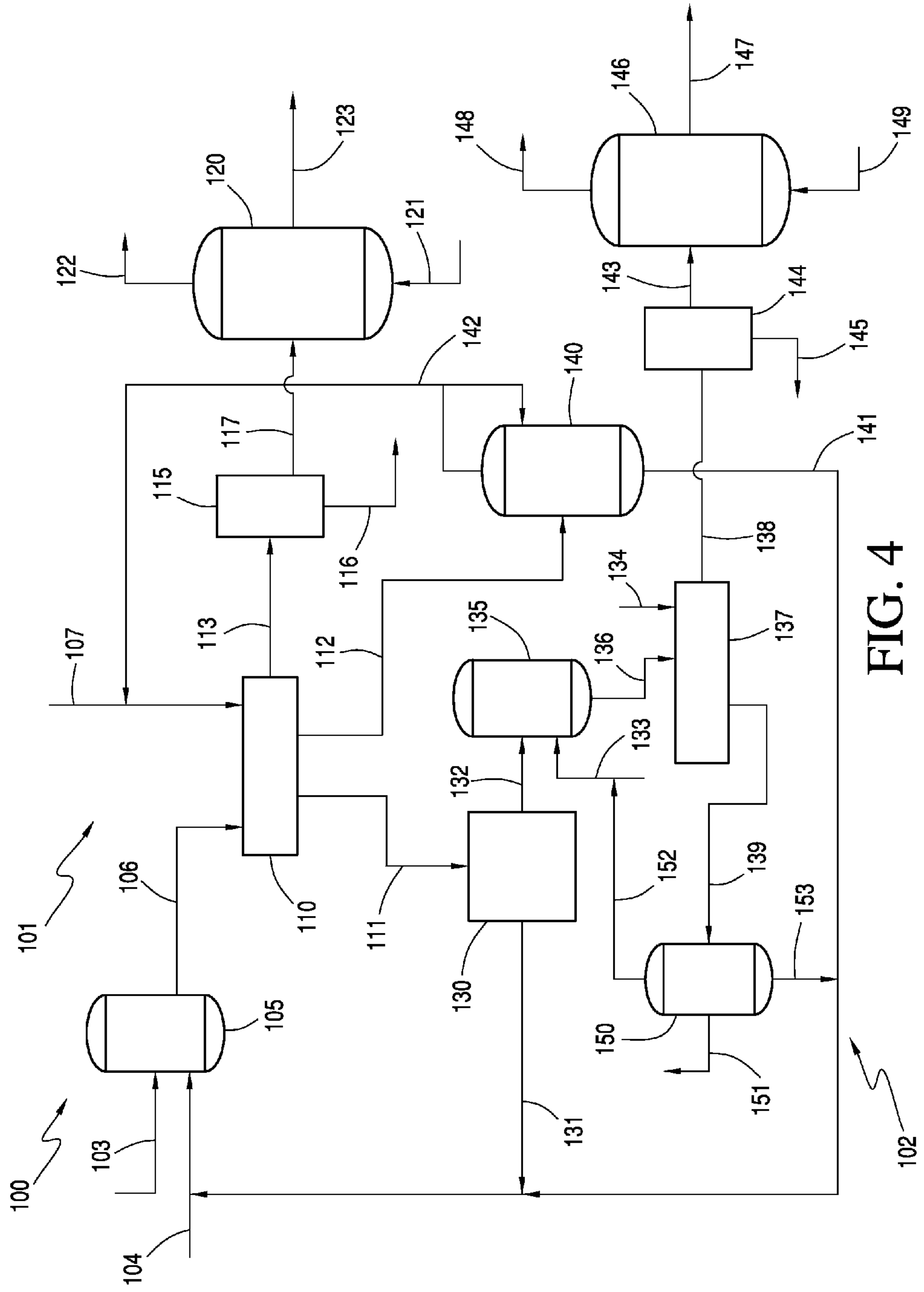


FIG. 4

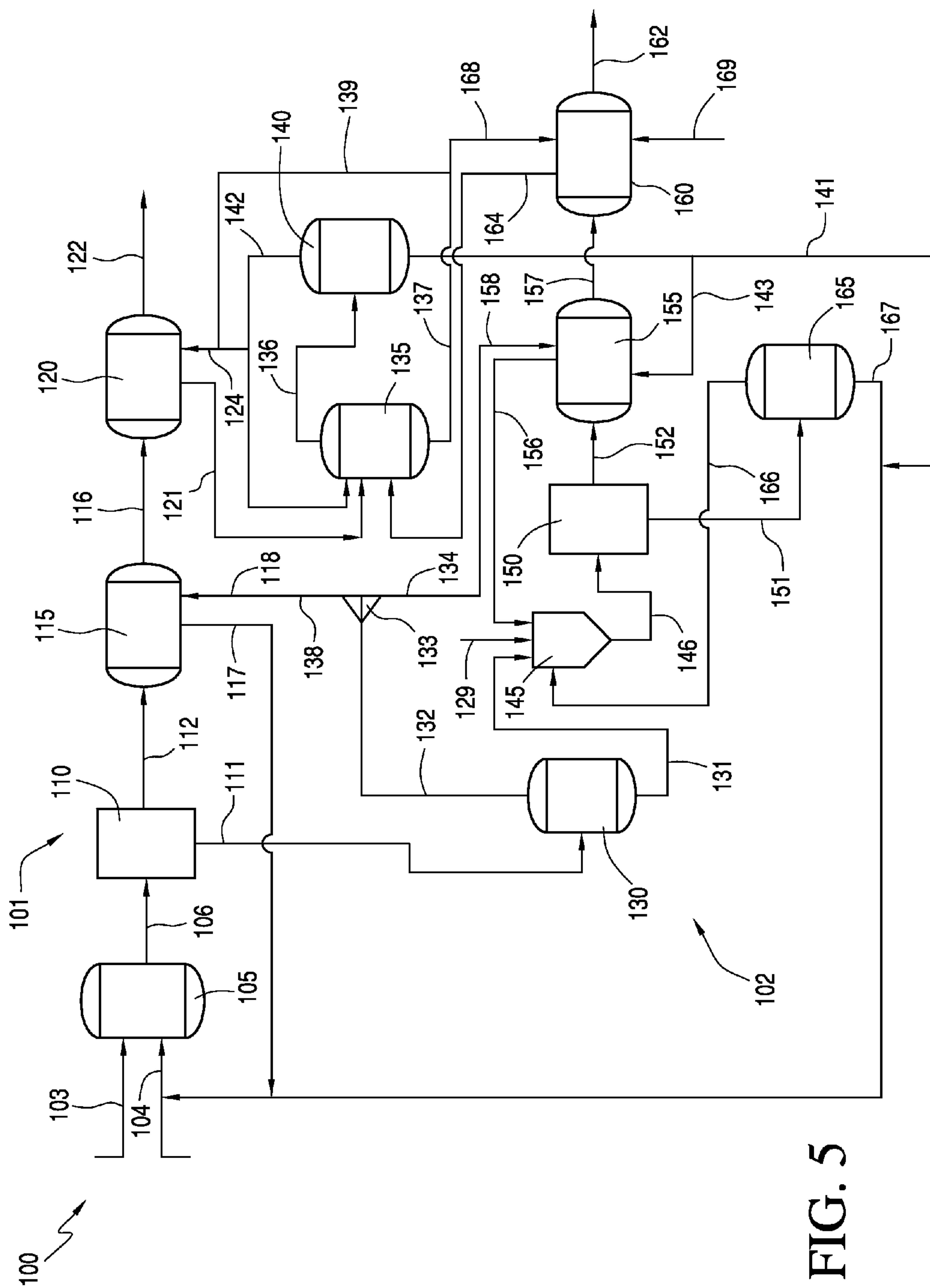


FIG. 5



## INTEGRATED PROCESSES FOR PURIFYING A CELLULOSIC MATERIAL

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This is a non-provisional of U.S. Provisional Appl. Nos. 61/819,150, filed May 3, 2013; 61/862,917, filed Aug. 6, 2013; 61/862,914, filed Aug. 16, 2013; 61/873,764, filed Sep. 4, 2013; and 61/933,203, filed Jan. 29, 2014, the entireties of which are incorporated herein by reference.

### FIELD OF THE INVENTION

[0002] The present invention relates generally to processes for obtaining a cellulosic product from a raw cellulosic material. In particular, the present invention relates to an integrated process for converting a raw cellulosic material into a pulp and then purifying the pulp to produce 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 other uses.

[0004] Known processes for obtaining a wood pulp from a raw cellulosic material include chemical processes, mechanical processes, and semi-chemical processes, as well as organosolv pulping techniques that use an organic solvent to dissolve lignin and hemicellulose. Of the chemical processes, the most commonly used process is the kraft process. The kraft process, described in U.S. Pat. No. 296,935, the entirety of which is incorporated by reference herein, involves the digesting (cooking) of wood chips at elevated temperatures and pressure with an alkaline liquor of sodium hydroxide and sodium sulfide. During the cooking step, most of the lignin and a portion of the hemicellulose from the pulp undergo degradation. The solid pulp from the cooking step is recovered and subjected to multiple washing and bleaching stages. The solid pulp may then be further processed for use in additional processes.

[0005] Another chemical process used to generate pulp from a raw material is the sulfite pulping process, described in U.S. Pat. No. 2,999,045, the entirety of which is incorporated by reference herein. This process, although similar to the kraft process, uses an acidic cooking liquor to extract lignin from wood chips. The cooking liquor may be a salt of sulfurous acid, comprising sulfites or bisulfites, and a counter ion, e.g., sodium, calcium, potassium, magnesium, or ammonium. The sulfite process is generally conducted at a pH from 1.5 to 5, depending on, inter alia, the counter ion and sulfurous acid

salt utilized. Because of the variety in cooking liquors for the sulfite process, there are numerous options for heat and/or chemical recovery.

[0006] Once the wood pulp is obtained, it may be further treated to reach a desired purity. High purity  $\alpha$ -cellulose pulp is commonly required as a starting material to make cellulose derivatives, such as cellulose acetate. The cost of such so-called cellulose produced in commercial pulp processes is high. Commercial paper grade pulps contain less than 90%  $\alpha$ -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. Accordingly, the separation of hemicellulose and/or other impurities from  $\alpha$ -cellulose in paper grade pulp has been investigated using different technical routes.

[0007] Zhou et al. discusses the use of dimethyldioxirane (DMDO), a pulp bleaching agent, to treat birch pulp and obtain acetate-grade pulp. However, DMDO is not currently commercially available due to its instability. Therefore, it is not an ideal solvent for producing large quantities of high  $\alpha$ -cellulose content pulp. Zhou et al. "Acetate-grade pulp from birch," *BioResources*, (2010), 5(3), 1779-1778.

[0008] In other studies regarding the treatment of biomass to form biofuels, various ionic liquids have been 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.

[0009] Others have used ionic liquids to break down the cellulosic materials to make biofuels via an intermediate product 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.

[0010] U.S. Pat. No. 7,828,936 describes a method for dissolving cellulose in which a 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.

[0011] The need exists for processes for efficiently producing high purity cellulose from a cellulosic material without destroying the fiber morphology and other characteristics of the cellulose structure. In particular, the need exists for cost effective integrated processes for processing a raw cellulosic



material to form a wood pulp and to purifying the wood pulp to yield a high purity cellulose product that can be converted to other cellulose derivatives.

#### SUMMARY OF THE INVENTION

**[0012]** The present invention is directed to a process for converting a starting material to a purified pulp material, comprising: removing lignin from a starting material to form a wet pulp comprising at least 5 wt. % water; extracting hemicellulose from the wet pulp with an extractant, wherein the extractant comprises a cellulose solvent and a co-solvent, the cellulose solvent selected from the group consisting of an ionic liquid, an amine oxide, and combinations thereof; and separating the extracted hemicellulose from the wet pulp to form a cellulosic product comprising less hemicellulose than the wet pulp. The removing lignin step may comprise: combining the starting material and a cooking liquor to dissolve lignin and form a cooked pulp comprising cooking liquor, dissolved lignin and pulp; and separating the cooking liquor and lignin from the pulp to form the wet pulp. The separating step may further comprise washing the wet pulp. In some embodiments, the process may further comprise bleaching (completely or partially) the wet pulp prior to the extracting step. In some embodiments, the process may further comprise bleaching (completely or partially) and washing the wet pulp prior to the extracting step. In further embodiments, the process may further comprise bleaching (completely or partially) the cellulosic product. The process may further comprise drying the wet pulp to no less than 1 wt. % water prior to the extracting. In some embodiments, when the wet pulp comprises at least 7 wt. % water, the process further comprises drying the wet pulp to no less than 5 wt. % water prior to the extracting step. In further embodiments, the wet pulp comprises at least 30 wt. % water and may be sent to the extracting step without drying. In some embodiments, the wet pulp may be washed with a pre-extraction wash agent prior to the extracting. The pre-extraction wash agent may be selected from the group consisting of alcohols, esters, ethers, ketones, carboxylic acids, nitriles, amine, amide, halides, hydrocarbon compound or heterocyclic compound and combinations thereof. In some embodiments, the pre-extraction wash agent may be selected from the group consisting of methanol, ethanol, iso-propanol, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, tetrahydrofuran, dimethoxyethane, acetone, acetic acid, formic acid, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, dichloromethane, chloroform, triethylamine, N,N-dimethylformamide, toluene, pyridine, water, and combinations thereof. The pre-extraction wash agent may remove at least 30% of the water from the wet pulp. Prior to the extracting step, the wet pulp may be filtered or deliquored.

**[0013]** In some embodiments, the separating step may comprise: removing an extraction mixture from the extracting step; separating the extraction mixture to form an intermediate cellulosic material and a liquid stream containing hemicellulose; and flashing at least a portion of the liquid stream to form a vapor stream enriched in the co-solvent and a flashed liquid stream comprising the hemicellulose, the cellulose solvent, and the co-solvent. The separating step may further comprise recovering hemicellulose from the flashed liquid stream. In other embodiments, the separating step may comprise: removing an extraction mixture from the extraction step; concentrating the intermediate cellulosic material to form the cellulosic product, wherein the cellulosic product

has an increased solids content; and recovering the separated hemicellulose. Regardless of the separating process used, the process may further comprise drying the cellulosic product to form a sheet product.

**[0014]** In some embodiments, mono-, di-, and oligo-saccharide and other side products are formed in the process and are removed from the process, such as by using evaporation, membrane filtration, ion exchange, activated carbon bed, simulated moving bed chromatographic separation, flocculation, and/or combinations thereof. The mono-, di-, and oligo-saccharide and other side products may be converted into furfural, ethanol, acetic acid, and/or other products by either enzymatic treatment or catalytic process and then separated from the process. In further embodiments, the mono-, di-, and oligo-saccharide and other side products formed in the process may be reacted with polymer-bound boronic acid to form a complex, which is further separated from the liquid stream.

**[0015]** The co-solvent may be 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. In some embodiments, the co-solvent may be selected from the group consisting of alcohols, esters, ethers, ketones, carboxylic acids, nitriles, amines, amides, halides, hydrocarbon compounds, heterocyclic compounds, and combinations thereof. In some embodiments, the co-solvent is selected from the group consisting of methanol, ethanol, iso-propanol, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, tetrahydrofuran, acetone, acetic acid, formic acid, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, dichloromethane, chloroform, triethylamine, N,N-dimethylformamide, toluene, pyridine, water, and combinations thereof. In some embodiments, the co-solvent may comprise DMSO and/or water, acetonitrile and/or water, or acetic acid and/or water. In some embodiments, when the co-solvent is water, the cellulosic solvent may be added directly to the wet pulp prior to the extracting. The extracting step may further comprise extracting impurities from the wet pulp, wherein the impurities include degraded cellulose, resins, rosins, and/or other dichloromethane extractables.

**[0016]** In some embodiments, the cellulose solvent comprises an ionic liquid selected from the group consisting of ammonium-based ionic substances, imidazolium-based ionic substances, pyridinium, pyrrolinium, piperidinium, other nitrogen base ionic liquids, phosphonium-based ionic substances, and combinations thereof.

**[0017]** In some embodiments, the cellulose solvent comprises an ionic liquid selected from the group consisting of ammonium acetate, hydroxyethyl ammonium acetate, hydroxyethyl ammonium formate, tetramethylammonium acetate, tetrabutylammonium acetate, tetraethylammonium acetate, benzyltriethylammonium acetate, benzyltributylammonium acetate, benzyltriethylammonium chloride, benzyltributylammonium chloride, tetramethylammonium hydroxide, tetrabutylammonium hydroxide, benzyltrimethylammonium hydroxide, 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.

**[0018]** In some embodiments, the cellulose solvent comprises an ionic liquid selected from the group consisting of



1-butyl-3-methylimidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium tetrachloroaluminate, 1-ethyl-3-methyl imidazolium hydrogensulfate, 1,3-diethyl imidazolium acetate, 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, 1,3-dimethylimidazolium dimethyl phosphate and combinations and complexes thereof.

[0019] In some embodiments, the cellulose solvent comprises an ionic liquid 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.

[0020] In some embodiments, the cellulose solvent comprises an amine oxide 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 some embodiments, the cellulose solvent comprises an amine oxide 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, benzyl dimethylamine N-oxide, benzyl diethylamine 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.

#### BRIEF DESCRIPTION OF THE DRAWING

[0021] The present invention will be better understood in view of the appended non-limiting figure, in which:

[0022] FIG. 1 shows a pulping process in accordance with conventional pulping processes.

[0023] FIG. 2 shows an exemplary pulping and purification process in accordance with one embodiment of the present invention.

[0024] FIG. 3 shows an exemplary pulping and purification process in accordance with another embodiment of the present invention.

[0025] FIG. 4 shows an exemplary purification process in accordance with another embodiment of the present invention.

[0026] FIG. 5 shows an exemplary purification process in accordance with another embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

##### [0027] I. Introduction

[0028] The present invention relates to processes for converting a starting material to a cellulosic product, comprising removing lignin from the starting material to form a wet pulp comprising at least 1 wt. % water, e.g., at least 5 wt. % water, at least 7 wt. % water, or at least 10 wt. % water, and then separating, e.g., extracting, hemicellulose and other cellulosic impurities (e.g., dichloromethane (DCM) extractables and degraded cellulose) from the wet pulp with an extractant to form the cellulosic product, which comprises less hemicellulose than the starting material and the wet pulp. The cellulosic product may optionally be further processed, depending on the end use. These further processes may include bleaching, washing, refining, wiring, pressing and/or drying. The inventive processes advantageously may result in reduced capital costs, energy consumption, fresh water usage, and/or waste discharge by eliminating one or more operating steps in the pulping process. For example, baling and/or rolling of the pulp for shipment may be advantageously eliminated if the pulping process is co-located with the extraction process. The inventive processes additionally benefit from the use of wet pulp because, without being bound by theory, wet pulp has an open structure that may benefit the extraction.

[0029] 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 wet pulp, but should have little solubility for  $\alpha$ -cellulose. The cellulose solvent is preferably selected from the group consisting of an ionic liquid, an amine oxide and combinations thereof. The cellulose co-solvent preferably is suitable for reducing the solubility of the extractant for  $\alpha$ -cellulose, and may be selected, for example, from the group consisting of alcohols, esters, ethers, ketones, carboxylic acids, nitriles, amines, amides, halides, water, hydrocarbon compounds, heterocyclic compounds, and combinations thereof. The ultimate purity of the cellulosic product formed in the processes of the invention may vary widely depending largely on the composition of the starting material, the composition of the extractant used, and extraction conditions. In preferred aspects, the finished cellulose product comprises acetate (or higher) grade cellulose.

##### [0030] II. Raw Materials

[0031] As described herein, the present invention is applicable to integrated pulping and pulp purification processes for converting a starting material to a cellulosic product via a delignified wet pulp intermediate. It has now been discovered that the integration of a chemical pulping process with a process for purifying pulp via extraction of hemicellulose and other cellulosic impurities allows for significant savings in capital costs, energy, and fresh water usage as well as reduction in waste discharge due, inter alia, to a reduction in one or more pulp processing steps, integration of steam from the pulping process, and/or elimination of pulp shipment for further processing or purification.

[0032] The starting material typically comprises cellulose, lignin and hemicellulose, as well as potentially degraded cellulose and other contaminants. The starting material preferably comprises 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, cotton linters, 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.

**[0033]** Cellulose is a straight chain polymer and is derived from D-glucose units, which condense through  $\beta$ -1,4-glycosidic bonds. This linkage motif contrasts with that for  $\alpha$ -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 conformation, 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 starting material, e.g., cellulosic raw material, as well as wet pulp intermediate and finished cellulosic product, retains the fiber structure throughout the pulping and extraction steps.

**[0034]** In addition to cellulose, the starting material, e.g., cellulosic raw material, typically comprises lignin. Lignin is an abundant, complex phenolic polymer derived from the walls of plant cells such as xylem and sclerenchyma cells. Lignin functionally binds the cells, fibers and vessels in plants. Lignin is a random, three-dimensional network polymer with linked phenylpropane units and comprises from 15 to 25 wt. % of woody plants (dry base). The presence of lignin is generally undesired in many derivative processes that employ  $\alpha$ -cellulose, such as the acetylation of  $\alpha$ -cellulose to form cellulose acetate flake or tow. As a result, the first step of the process is aimed largely at removing lignin as well as some hemicellulose from the starting material to form a wet pulp.

**[0035]** In addition to lignin, the starting material, e.g., cellulosic raw material, also comprises hemicellulose linked to cellulose by hydrogen bonds. 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 wood hemicellulose, while mannose and xylose are the primary sugars present in softwood hemicellulose.

**[0036]** Some hemicellulose typically passes through the pulping step and is present in undesirable quantities in the wet pulp intermediate. Like lignin, the presence of hemicellulose is undesirable in many derivative processes involving  $\alpha$ -cellulose. The second step of the process involves the selective extraction of hemicellulose from the wet pulp formed in the

first step of the process to form a cellulosic product of high  $\alpha$ -cellulose content, which preferably is well-suited for many cellulose derivative processes, such as the formation of cellulose acetate flake or tow.

**[0037]** Overall, the starting material and the wet pulp formed therefrom have a linear shape of fiber morphology, which is surrounded by hemicellulose via hydrogen bonds. These bonds may become weakened by treating the wet pulp with an extractant to selectively dissolve the hemicellulose while maintaining the fiber morphology of the pulp, e.g., leaving the fiber morphology unchanged.

**[0038]** The processes of the present invention are particularly beneficial in that they are effective for use with a starting material that comprises a softwood or a hardwood. These woods may be processed in a first step to form a wet paper grade wood pulp, which is subjected to extraction in a second step to remove hemicellulose and form a cellulosic product. Softwoods, in particular, which are generally more abundant and faster growing than most hardwood species, may be advantageously processed according to the invention into a wet pulp, which may be upgraded via the extraction process to make a higher grade cellulose, such as acetate grade cellulose.

**[0039]** 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 greater 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.

**[0040]** In preferred embodiments, the wet pulp formed in the initial pulping step comprises wood pulp, e.g., paper grade wood pulp. When the wet pulp is paper grade wood pulp, the purification 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 material. In some optional embodiments, the paper grade wood pulp may have an S10 (alkali solubility of cellulose in 10% NaOH) from 8 to 20% and an S18 (alkali solubility of cellulose in 18% NaOH) from 6 to 18% and the acetate grade wood pulp may have an S10 from 2 to 6% and an S18 from 1.5 to 3%.

**[0041]** III. Pulping Processes

**[0042]** Chemical pulping processes for converting a starting material, e.g., cellulosic raw material, into a pulp include the kraft process, the acid-sulfite pulping process, the neutral sulfite semichemical (NSSC) pulping process, the organosolv pulping process and the soda pulping process. Mechanical pulping processes separate fibers from each other by applying mechanical energy to the wood matrix in order to break the bonds between the fibers and to release fiber bundles, single



fibers, and fiber fragments. In general, the pulp made from a chemical pulping process has a lower lignin concentration than that made from a mechanical pulping process. The separation of hemicellulose from  $\alpha$ -cellulose using the extractant process described herein may be applied to the pulps made from either chemical pulping processes, as described herein, or mechanical pulping processes, as long as lignin is dissolved by the extractant. Generally, chemical pulping processes with or without prehydrolysis are used predominantly in paper mills. The chemical pulping processes are similar, mainly differing due to the cooking liquor used to remove lignin from the starting material. As shown in FIG. 1, a pulping process 10 may comprise feeding a raw material 11 and a cooking liquor 12 to a digester 15 to form a cooked pulp 16 comprising cooking liquor and pulp. In some embodiments (not shown), the raw material may be pre-treated or pre-hydrolyzed.

[0043] When pulping process 10 is a kraft process, cooking liquor 12 comprises an aqueous solution of sodium hydroxide and sodium sulfide, also referred to as white liquor. The white liquor functions to dissolve the lignin that binds the cellulose fibers of the wood chips. For this process, digester 15 may be operated at a temperature from 160 to 180° C., e.g., from 170° C. to 176° C., and at pressure of up to 1700 kPa, typically from 300 to 1000 kPa. The residence time of the raw material, e.g., wood chips, and the white liquor in the digester may be adjusted depending on the Kappa number. The Kappa number provides an indication of how well the wood chips have been cooked but varies depending on the composition and moisture content of the wood chips. Generally, the longer the cooking, the higher the yield of pulp. However, if the pulp is overcooked, the strength of the pulp may be degraded.

[0044] When pulping process 10 is a sulfite pulping process, cooking liquor 12 comprises a salt of sulfurous acid, such as a sulfite or a bisulfate with a counter ion such as sodium, calcium, potassium, magnesium, or ammonium. Cooking liquor 12 functions to dissolve the lignin that binds the cellulose fibers of the wood chips, but degrades the lignin to a lesser degree than the kraft process, allowing lignosulfonates from the process to be recovered and used in further processes and/or products. For this process, digester 15 may be operated at a temperature from 120 to 180° C., e.g., from 130° C. to 160° C., for 4 to 14 hours, e.g., from 6 to 12 hours, at a pressure from 300 to 1000 kPa, depending on the cooking liquor used.

[0045] Regardless of whether the kraft process or the sulfite pulping process is used, cooked pulp 16 is sent to blow tank 17 where the pressure is approximately atmospheric, allowing for steam and volatiles to be removed from cooked pulp 16 via line 119. The steam and volatiles may be further separated and treated (not shown). Optionally, the steam may be used in downstream pulp purification processes, specifically to heat one or more of the distillation columns described herein in FIGS. 4 and 5. Besides steam integration, other heat integration with different streams may also provide further reduction in energy consumption. Cooked pulp is removed from blow tank 17 via line 18 and fed to a washer 30 to separate the used cooking liquor from the pulp. The washing liquid fed to washer 30 via line 32 may primarily comprise water to wash away cooking chemicals, e.g. sodium hydroxide and sulfide in the kraft process. Used cooking liquor is removed from the washer via line 33 as black liquor if from the kraft process or as brown or red liquor if from the sulfite process. Black liquor may comprise hemicellulose, sodium

carbonate, sodium hydroxide, sodium sulfate and lignin. Brown liquor may comprise hemicellulose, lignin and other chemicals, depending on the cooking liquor used. Therefore, regardless of the process, used cooking liquor 33 may comprise hemicellulose, lignin, washing liquid 32 and cooking liquor and/or derivatives thereof.

[0046] In the kraft process, used cooking liquor 33 may then be directed to evaporator 20, where it is further concentrated to a solids content of about 55% to about 65%, and then fed via line 21 to recovery furnace 25. It should be understood that although one evaporator is shown, evaporator 20 may comprise a multiple effect system of evaporators, which may have the same or different internal structures and sizes. In recovery furnace 25, lignin is combusted with added air to produce steam via line 27 and smelt comprising sodium carbonate, sodium sulfite, and water via line 26. The generated steam may be used for pulping processes and/or extraction processes. Prior to exiting recovery furnace 25, water via line 22 may be combined with the smelt to form green liquor 26, which comprises sodium carbonate, sodium sulfite, and water. Green liquor 26 is then sent to a causticizing tank 28 where calcium oxide is added to convert the recovered chemicals to white liquor which may be combined with fresh cooking liquor 12 via line 29 or fed directly to digester 15. The sulfite process may include a similar chemical recovery process, which may be modified depending on the composition of the cooking liquor. The concentrated brown liquor may be burned in a recovery boiler to generate steam and to recover the inorganic chemicals for reuse in the pulping process. Additionally or alternatively, the concentrated brown liquor may be neutralized to recover the useful byproducts of pulping.

[0047] Returning to washer 30, washed pulp 31, also referred to as brown stock when formed by the kraft process, may comprise from 30 to 90 wt. % solids, e.g., about 50 wt. % solids, based on the weight of the dry starting material. Washed pulp 31 is sent to pulp screening system 35, which may be used to remove shives, knots, dirt and other debris from the washed pulp. Pulp screening system 35 may comprise a series of different sieves and/or centrifugal cleaning devices. The sieves may be arranged, for example, in a cascading series. The pulp is removed from pulp screening system 35 as screened pulp 36, which may then be fed to bleaching system 40. Screened pulp 36 typically comprises from 1 to 10 wt. % lignin, e.g., less than 5 wt. % lignin, and is preferably suitable for bleaching. The bleaching process may reduce the lignin concentration to less than 3 wt. %, e.g., less than 2 wt. %, or less than 1 wt. %. When the extractant has the capability to remove lignin, the bleaching process may be merged into the extraction process. If the pulp comprises a greater amount of lignin, additional bleaching steps or stronger bleaching agents may be used. The purpose of the optional bleaching step is to remove residual lignin. Bleaching system 40 may comprise, for example, a plurality of bleaching steps, e.g., three, four or more than four bleaching steps with a variety of bleaching agents including chlorine, sodium hypochlorite, chlorine dioxide, oxygen, alkaline hydrogen peroxide, sodium hydroxide, ozone, sodium hydrosulfite, enzymes such as xylanase, and combinations thereof. Additional optional bleaching agents include peroxyacetic acid, peroxyformic acid, dimethyldioxirane, and peroxyphosphoric acid. Preferably, different bleaching agents are used in each bleaching step. One or more bleaching steps may also use chelation to remove metals. Bleaching system 40



may also include washing steps in between one or more or all of the bleaching steps. In some embodiments, the bleaching process is chlorine free. The pH used in each step of bleaching system 40 depends largely on the bleaching agent employed. For example, a bleaching step conducted with chlorine or hypochlorite may be conducted at a pH of less than 1.5, while a bleaching step employing chlorine dioxide may be conducted at a pH from 3.5 to 6. A bleaching step using oxygen may be conducted at a pH of greater than 12. The number of bleaching steps and type of bleaching agent employed determines the brightness of the pulp. Typically, the pulp is bleached to a brightness suitable for the intended use of the pulp.

[0048] After exiting bleaching system 40, which may comprise multiple bleaching and wash steps (not shown), bleached pulp 42 may be directed to washer 45 for removal of the bleaching agent(s). It should be understood that although one washer is shown, washer 45 may comprise multiple washers using the same or different washing agents. The washing agent 43, e.g. water, may be selected depending on the bleaching agents used, and is generally selected from, but not limited to, water and other solvents which may dissolve residual bleaching chemicals from the pulp. Wet pulp 46 may be removed from washer 45 and sent to dryer section 50, which may comprise screening, refining, wiring, pressing, and thermal drying, in order to dry the pulp to the desired water content. In some embodiments, dryer section 50 may include a Fourdrinier machine. When entering dryer 50, wet pulp 46 may comprise from 85 to 99.9 wt. % water, e.g., from 95 to 99 wt. % water. Conventionally, wet pulp is dried to form a dried pulp 51, comprising less than 5 wt. % water, which may be rolled or baled and shipped for further processing and/or purification.

[0049] The inventive processes advantageously reduce or omit some of the steps of chemical pulping processes by integrating the chemical pulping process with a pulp purification (extraction) process. In various embodiments of the invention, depending on the end product requirements and applications as well as the extractant functionality, one or more of washed pulp 31, screened pulp stream 36, bleached pulp stream 42, wet pulp 46 or pulp 51 (e.g., reduced in water content but nevertheless comprising greater than 1 wt. % water, e.g., greater than 5 wt. % water or greater than 10 wt. % water) may be partially and/or completely directed to an extraction unit for hemicellulose removal. It may be preferred to remove the contaminants and impurities that are generated in the digestion and bleaching steps before the pulp goes into the extraction process so that the extractant may maintain its maximum extraction capability.

[0050] In one embodiment, for example, a dryer section 50 is employed to reduce water content as shown in FIG. 1, but the wet pulp is not dried to an extent that it forms dry pulp, as is typically formed for transporting the pulp, i.e., pulp having a water content of less than 5 wt. %. In this manner, the water content of the wet pulp may be reduced to an acceptable level, while advantageously reducing the energy requirements of dryer 50. In this embodiment (not shown), a reduced water content wet pulp, which is subject to a deliquoring operation, may be directed to an extraction unit for further processing to remove hemicellulose. This embodiment may or may not involve a baling step depending primarily on whether it is necessary to transport the wet pulp from the pulping facility to a remotely located extraction facility.

[0051] In another embodiment, the integrated pulping and purification process omits the drying and baling steps used in the kraft and sulfite pulping processes. The pulping process shown in FIG. 2 is substantially similar to the process shown in FIG. 1, until the washed pulp 103 exits washer 45. In some embodiments of the invention, extractant 104 and washed pulp 103, which may be optionally subject to a deliquoring operation, may be fed, separately or as a mixture, to an extractor 105 forming an extraction mixture therein. The extraction mixture may then be removed from extractor 105 as extraction mixture 106 and may then be further purified as shown in FIGS. 4 and 5, described herein. When the purified cellulosic product made from FIGS. 4 and 5 is used directly for downstream applications, e.g., the manufacturing of cellulose acetate, the drying step and baling steps in the typical pulping process may no longer be needed for either the wet pulp or for the cellulosic product. Therefore, by omitting the drying step and baling steps from the pulping process, there are significant capital cost and energy savings due to the reduction in equipment and elimination of shipment of the pulp required when the pulping process is physically separate from the downstream processes.

[0052] In yet another embodiment, depending on the intended end use of the cellulosic product, although the wet pulp is not fed through drying unit 50, the purified cellulosic product may be fed through drying unit 50 and optionally formed into sheets and/or bales. Thus, the integrated process may comprise removing a wet pulp from the pulping process prior to drying unit 50, purifying the wet pulp to form a purified cellulosic product, and introducing the purified cellulosic product into drying unit 50 of the pulping process to dry the purified cellulosic product and to optionally form the dried cellulosic product into sheets and/or bales.

[0053] In another embodiment, the integrated pulping and purification process omits all or a portion of the bleaching, washing, drying and baling steps used in the kraft process or the sulfite pulping process. In these embodiments, the bleaching step may be omitted entirely, if the extractant can separate both hemicellulose and lignin from the pulp, or optionally moved downstream, e.g., after the pulp has been further purified to remove hemicellulose and other contaminants. However, it may be preferable to remove residual chemicals that are generated in the pulping process before the pulp goes into the extraction operation so that the extractant can maintain its maximum extraction capability.

[0054] As shown in FIG. 3, the pulping process is similar to FIG. 1, except that screened pulp 103 exits pulp screening system 35 and is directed to extraction unit 105. In this context, it should be noted that the screened pulp 36, which may be optionally subjected to a washing operation, comprises greater than 1 wt. % water, e.g., greater than 5 wt. % water or greater than 10 wt. % water, thereby constituting wet pulp according to the present invention. Extractant 104 and unbleached wet pulp 103 may then be fed, separately or as a mixture, to extractor 105 to form an extraction mixture 106. The extraction mixture may be further purified as shown in FIGS. 4 and 5, described herein, by removing both hemicellulose and residual lignin from the cellulosic product. When the purified cellulosic product made from FIGS. 4 and 5 is used directly for downstream application, e.g., the manufacturing of cellulose acetate, the drying step and baling steps in the typical pulping process are no longer needed. Therefore, by omitting the bleaching, washing, drying step, sheet making, rolling or baling steps from the pulping process, signifi-



cant capital cost and energy savings due to the reduction in equipment and bleaching agents may be advantageously realized.

**[0055]** In some embodiments, screened pulp **103** comprises at least 5 wt. % water, e.g., at least 7 wt. %, or at least 10 wt. % water, in which case the process may comprise removing water from the wet pulp to no less than 1 wt. %, e.g., no less than 5 wt. % water using filtering, deliquoring, thermal drying, and/or other conventional technologies, before feeding the resulting wet pulp to an extractor for hemicellulose removal. Although the wet pulp is partially dried, the integrated process still reduces capitals cost and is energy efficient because the pulp is not fully dried. Further, the pulp does not need to be baled or shipped if it can be used directly for a downstream treatment process.

**[0056]** In further embodiments, the wet pulp (from whichever stream it may be derived) may be washed with one or more pre-extraction washes to (i) reduce the water content in the pulp that will be fed to the extraction process; and (ii) wash away the residual chemicals that are generated in the pulping process in order to maximize the extraction capability. The washing agent in the pre-extraction wash may be, but is not limited to, the co-solvent in the extractant. The pre-extraction wash agent may be used to remove at least 50% of the water, e.g., at least 75% of the water, from the wet pulp. The resulting mixed stream comprising pre-extraction wash and water may be separated using existing separation equipment already present in the extraction process so that no additional capital cost is required.

**[0057]** In some embodiments, the pre-extraction wash agent may be selected from the group consisting of alcohols, esters, ethers, ketones, carboxylic acids, nitriles, amines, amides, halides, hydrocarbon compounds, heterocyclic compounds, and combinations thereof. In the purification process of FIG. 4, the pre-extraction wash agent may be 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, acetonitrile and mixtures thereof. In the purification process of FIG. 5, the pre-extraction wash agent may be selected from the group consisting of methanol, ethanol, iso-propanol, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, tetrahydrofuran, acetone, acetic acid, formic acid, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, dichloromethane, chloroform, triethylamine, N,N-dimethylformamide, toluene, pyridine, water, and combinations thereof.

**[0058]** As discussed above, regardless of which stream the wet pulp is derived from, the resulting wet pulp comprises at least 1 wt. % water, e.g., at least 5 wt. % water or at least 10 wt. % water. In some embodiments, the wet pulp that is sent to extractor **105** comprises at least 20 wt. % water or at least 30 wt. % water. Preferably, the wet pulp comprises, excluding water, at least 70 wt. %  $\alpha$ -cellulose, e.g., at least 80 wt. %  $\alpha$ -cellulose or at least 85 wt. %  $\alpha$ -cellulose. The wet pulp also typically comprises, excluding water, at least 5 wt. % hemicellulose, at least 10 wt. % hemicellulose or at least 15 wt. % hemicellulose, which is removed along with degraded cellulose and other contaminants in the subsequent extraction step.

**[0059]** Regardless of where the wet pulp is removed from the pulping process, heat from the pulping process may be recovered and integrated with the extraction process. In particular, steam from recovery furnace **25** may be used, for example, in the evaporation and distillation steps of the

extraction process. Additional steam and heat integration opportunities may be explored depending on the steam and heat produced in the pulping process and the steam and heat used in the extraction process. These integration opportunities may be evaluated using established methodologies, e.g., pinch analysis. Similarly, there are opportunities for water integration between the pulping process and the extraction process. Water removed during the de-liquoring step prior to the extraction step, for example, may be used in extracting, washing, and/or forming of a pulp slurry for the drying unit, including the Fourdrinier machine. In addition, the operations can be continuous, batch, and/or semi-batch.

**[0060]** IV. Extractant

**[0061]** As described above, hemicellulose and optionally degraded cellulose is extracted from the wet pulp using an extractant with or without pre-treatment, e.g. pre-hydrolysis, of the pulp. The extractant comprises a cellulose solvent and a co-solvent. The cellulose solvent is preferably 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  $\alpha$ -cellulose, but preferably dissolves at least hemicellulose and preferably degraded cellulose and lignin.  $\alpha$ -cellulose preferably is less soluble in the co-solvent than in the cellulose solvent.

**[0062]** a. Ionic Liquid

**[0063]** 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.

**[0064]** It has been found that, in addition to these beneficial properties, when contacted with cellulosic materials, including plant matter and plant matter derivatives, ionic liquids are capable of acting as a cellulose solvent, dissolving the hemicellulose, degraded cellulose 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,  $\alpha$ -cellulosic components remaining in the wet pulp are preserved and the fiber morphology is advantageously retained.

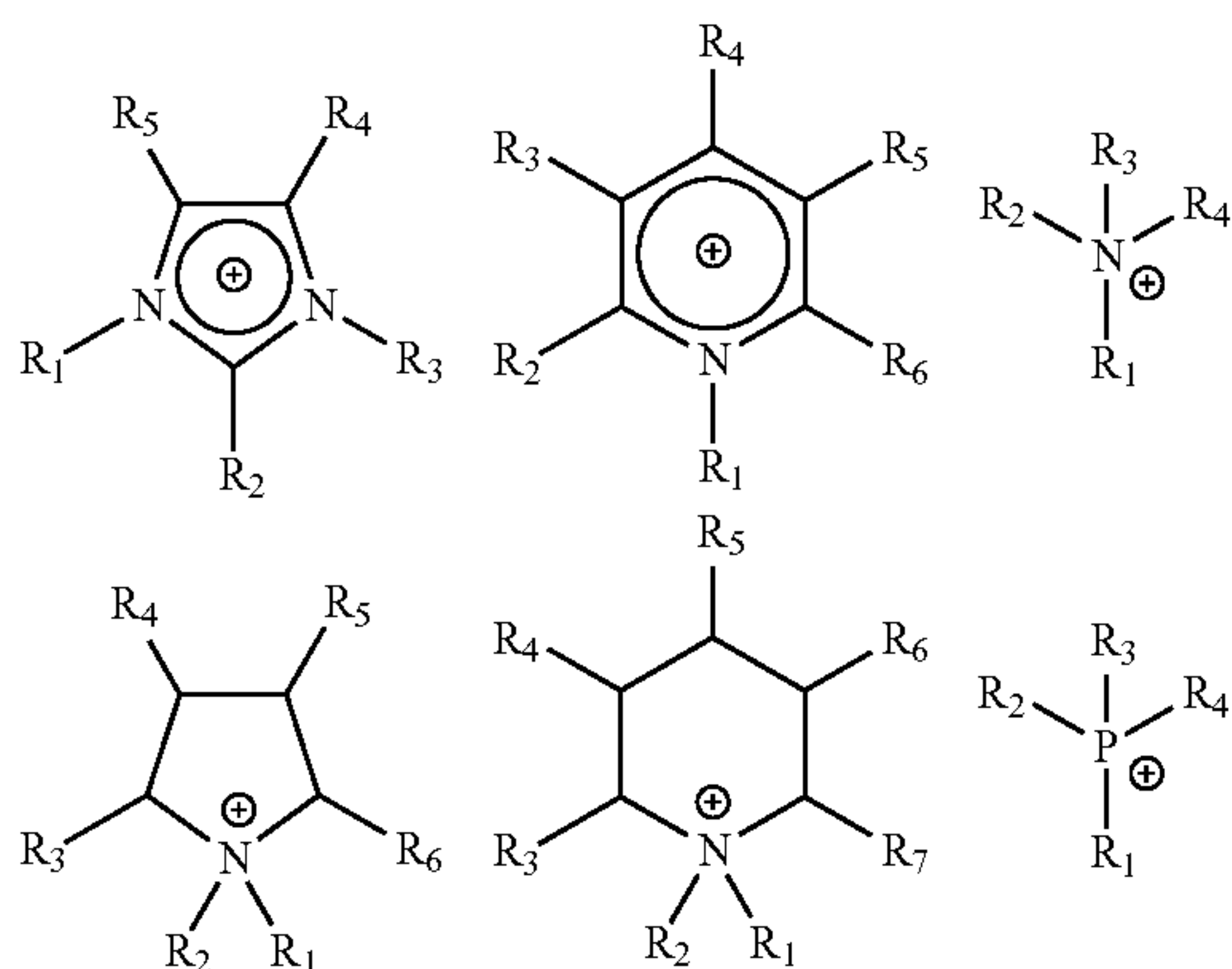
**[0065]** Ionic liquids, in pure form, generally are comprised of ions and do not necessitate a separate solvent for ion formation. Ionic liquids existing in a liquid phase at room temperature are called room temperature ionic liquids. Generally, ionic liquids are formed of large-sized cations and smaller-sized anions. Cations of ionic liquids may comprise nitrogen, phosphorous, sulfur, or carbon. Because of the disparity in size between the cations and anions, the lattice energy of the compound is decreased resulting in a less crystalline structure with a low melting point.

**[0066]** Exemplary ionic liquids include compounds expressed by the following Formula (1):





[0067] 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, piperidium salt, and phosphonium salts. In preferred embodiments,  $[A]^+$  is selected from the group consisting of:



[0068] 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  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $CF_3CO_2^-$ ,  $CF_3SO_3^-$ ,  $PF_6^-$ ,  $CH_3COO^-$ ,  $(CF_3SO_2)_2N^-$ ,  $HCOO^-$ ,  $C_nH_{2n+1}COO^-$  ( $n=2-9$ ),  $C_6H_5COO^-$ ,  $C_6H_5SO_3^-$ ,  $CH_3C_6H_5SO_3^-$ ,  $CH_3SO_4^-$ ,  $C_2H_5SO_4^-$ ,  $CH_3SO_3^-$ ,  $SCN^-$ ,  $N(CN)_2^-$ ,  $CH_3CO_3^-$ ,  $(CH_3)_2PO_4^-$ ,  $(C_2H_5)_2PO_4^-$  and  $CH_3HPO_4^-$ .

[0069] 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, 1,3-diethyl 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.

[0070] 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 ammo-

onium-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, 1,3-diethyl 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.

[0071] 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-ethyl-3-methyl imidazolium acetate, 1,3-diethyl 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.

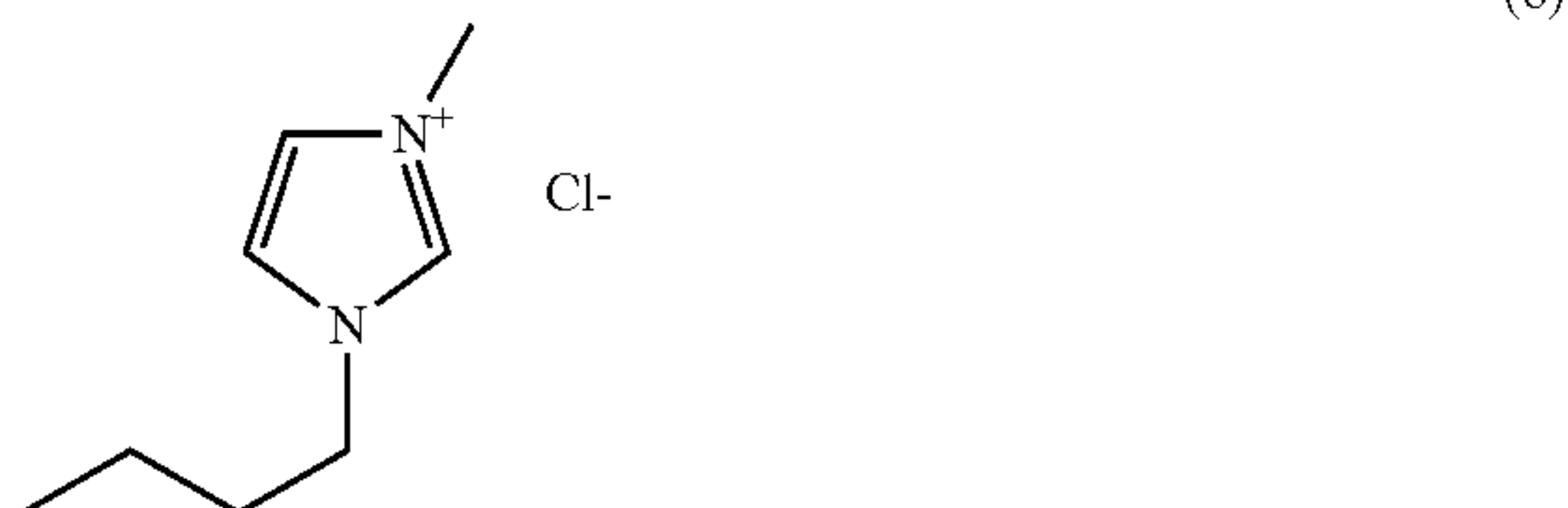
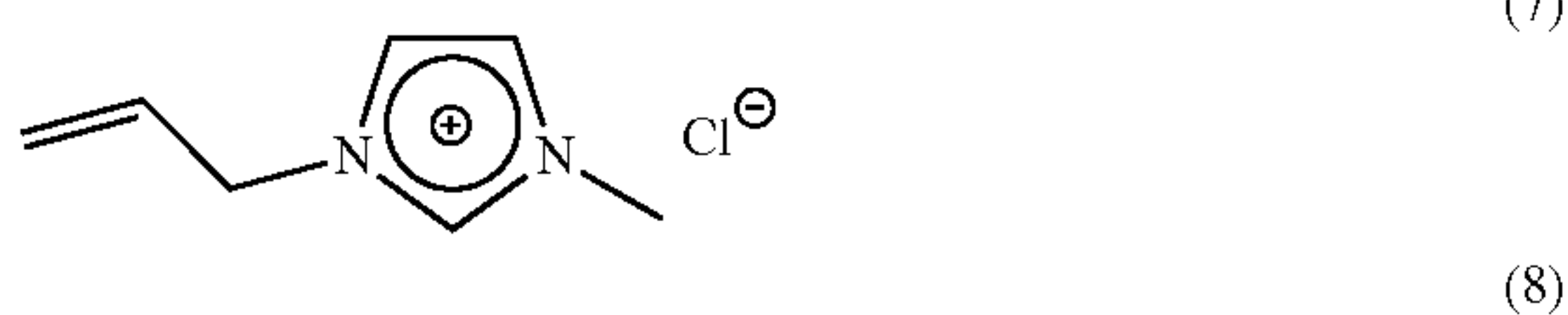
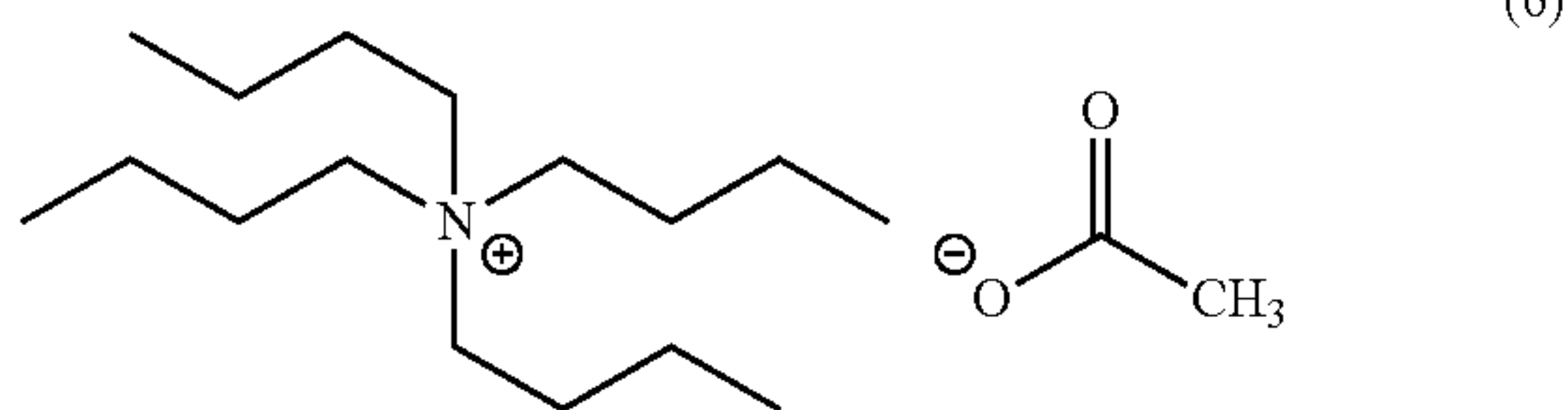
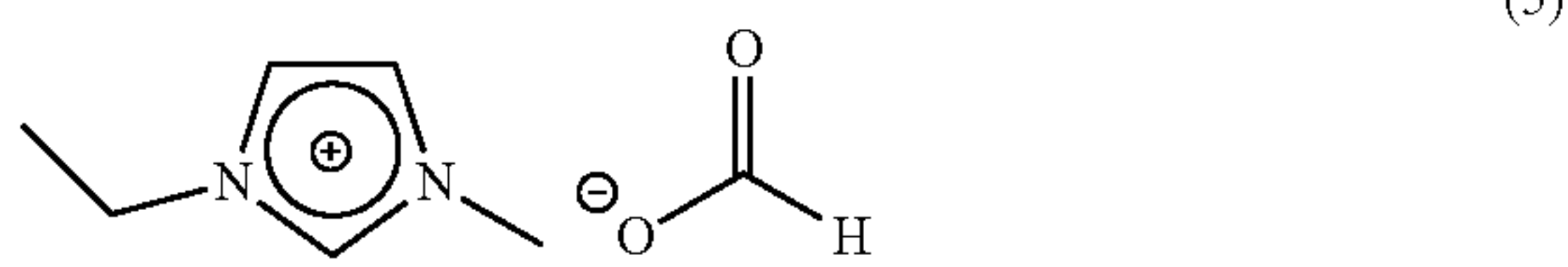
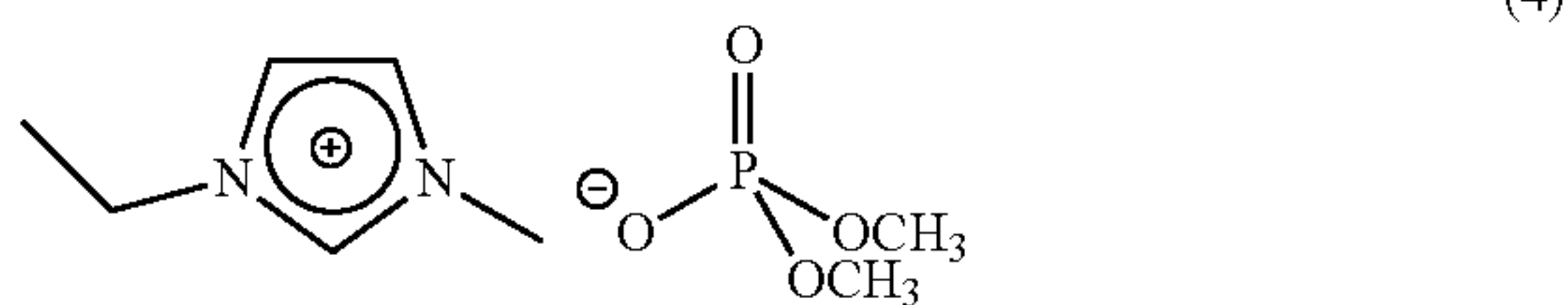
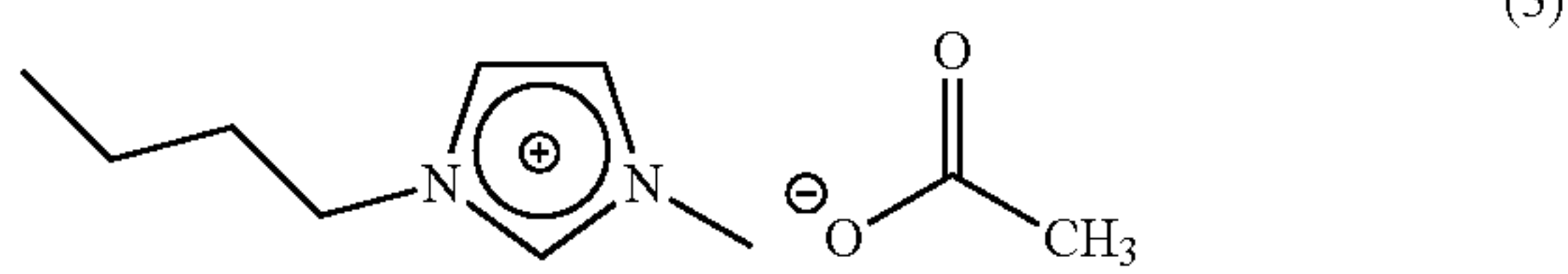
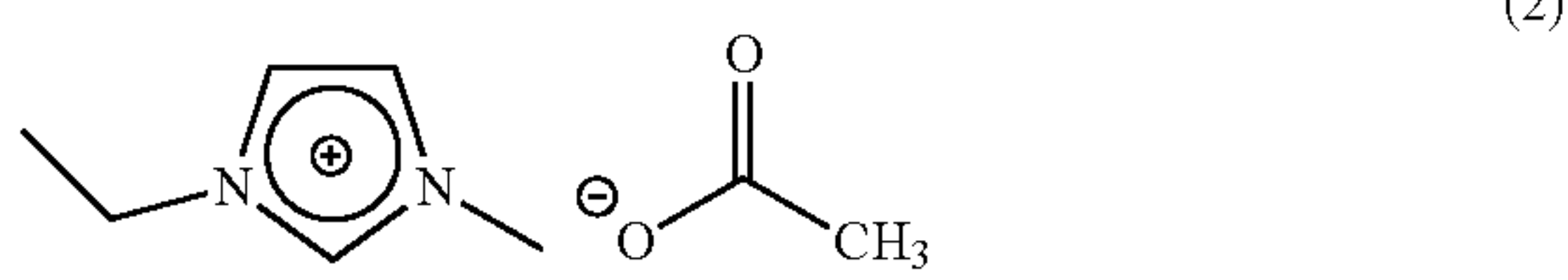
[0072] In further embodiments, the ionic liquid may be selected from the group consisting of ethyltributylphosphonium diethylphosphate, methyltributylphosphonium dimethylphosphate, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, tributylmethylphosphonium methylsulfate, trihexyltetradecylphosphonium decanoate, trihexyltetradecylphosphonium dicyanamide, ethyltriphenylphosphonium acetate, ethyltributylphosphonium acetate, benzyltriethylphosphonium acetate, benzyltributylphosphonium acetate, tetrabutylphosphonium acetate, tetraethylphosphonium acetate, tetramethylphosphonium acetate, and combinations thereof.

[0073] The ionic liquid may be commercially available, and may include Basionic™ AC 01, Basionic™ AC 09, Basionic™ AC 25, Basionic™ AC 28, Basionic™ AC 75, Basionic™ BC 01, Basionic™ BC 02, Basionic™ FS 01,



Basionic™ LQ 01, Basionic™ ST 35, Basionic™ ST 62, Basionic™ ST 70, Basionic™ ST 80, Basionic™ VS 01, and Basionic™ VS 02, but the invention is not limited to use of these species.

[0074] 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):



#### [0075] b. Amine Oxide

[0076] 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. In one embodiment, amine oxides that are stable in water may be used.

[0077] 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.

[0078] 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.

[0079] 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-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.

[0080] 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,  $\alpha$ -cellulosic components in the wet pulp 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., U.S. Pat. No. 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 galate may be added.

#### [0081] c. Co-Solvent

[0082] As indicated 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  $\alpha$ -cellulose. Co-solvents in the context of this invention include solvents that have the ability to readily dissolve hemi-cellulose, lignin, and/or other impurities. The co-solvent may be selected to be miscible with the cellulose solvent and to



reduce the solubility of the resulting extractant for  $\alpha$ -cellulose. In exemplary embodiments, the co-solvent is selected from the group consisting of alcohols, esters, ketones, carboxylic acids, nitriles, amines, halides, hydrocarbon compounds, heterocyclic compounds, and combinations thereof. In other exemplary embodiments, the co-solvent is selected from the group consisting of methanol, ethanol, iso-propanol, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, tetrahydrofuran, acetone, acetic acid, formic acid, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, dichloromethane, chloroform, triethylamine, N,N-dimethylformamide, toluene, pyridine, water, and combinations thereof. In some embodiments, the extractant comprise greater than 15 wt. % co-solvent, e.g., greater than 25 wt. % or greater than 40 wt. %. In one embodiment, the co-solvent may comprise a combination of acetonitrile and water. The acetonitrile and water may be present in a weight ratio from 6:1 to 500:1, e.g., from 10:1 to 200:1 or from 30:1 to 100:1.

**[0083]** In some embodiments, the co-solvent has a boiling point of less than 120° C., or of less than 100° C. Additional co-solvents having a boiling point of less than 120° C. include acetic acid, alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, tert-butanol, halogenated solvents, e.g., carbon tetrachloride, dichloroethane or chlorobenzene, ethers, e.g., tetrahydrofuran, diethyl ether, methyl tert-butyl ether, esters, e.g. dimethyl carbonate, and mixtures thereof.

**[0084]** In still further embodiments, the co-solvent may be 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 may vary, the efficient purification processes associated with each co-solvent may not be exactly the same.

**[0085]** The co-solvent may be chosen in view of its boiling point, to allow for maximized separation of the cellulose solvent from the co-solvent in a flashing step described herein with reference to FIG. 5. For example, in order to maximize flash separation efficiency, the decrease of pressure in the flashing step may vaporize at least 3% of the co-solvent, e.g., at least 10%, or at least 30% of the co-solvent. Additionally, the extractant wash and/or the precipitant wash optionally used in the cellulose and hemicellulose purification process, described below, may be chosen based on the boiling point of the co-solvent chosen. For example, the difference in boiling point between the extractant wash or precipitant wash and the co-solvent may be greater than 10° C., greater than 20° C. or greater than 30° C.

**[0086]** 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 10.0 mPa·s, e.g., less than 5 mPa·s or less than 3 mPa·s at 25° C. In terms of ranges, the viscosity may range from 0.1 to 10 mPa·s, e.g., from 0.15 to 5 mPa·s or from 0.2 to 3 mPa·s. 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. Without being bound by theory, it is postulated that by using a low viscosity second co-solvent in the extractant, the extraction rate may be enhanced and a smaller amount of ionic liquid may be needed to extract the hemicellulose and degraded cellulose from the wet pulp.

**[0087]** Without being bound by theory, the insolubility of the  $\alpha$ -cellulose in the co-solvent and the resulting extractant desirably maintains the cellulose fiber morphology, e.g., leaving the fiber morphology unchanged, while the extractant penetrates the wet pulp, dissolves and extracts the hemicellulose, lignin, and preferably degraded cellulose from the wet pulp. 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.

**[0088]** d. Extractant Compositions

**[0089]** The specific formulation of the extractant employed may vary widely, depending, for example, on the hemicellulose and degraded cellulose content of the wet pulp, 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.

**[0090]** 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 30 wt. %. 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. %.

**[0091]** 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. In another embodiment, the organic co-solvent is acetonitrile.

**[0092]** 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. 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, concentration may range from 1 wt. % to 98 wt. %.

**[0093]** 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. %, at least 20 wt. % or at least 50 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. %.

**[0094]** 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. %, at least 20 wt. % or at least 50 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. %.

**[0095]** 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 50 wt. % ionic liquid, e.g., at most 40 wt. %, or at most 30 wt. %. In terms of ranges, the extractant may comprise from 0.1 wt. % to 50 wt. % ionic liquid, e.g., from 1 wt. % to 40 wt. %, from 2 wt. % to 30 wt. % or from 10 to 30 wt. %. The extractant optionally comprises at least 50 wt. % organic co-solvent,

e.g., at least 60 wt. %, or at least 70 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 50 wt. % to 99.9 wt. % organic co-solvent, e.g., from 60 wt. % to 98 wt. %, or from 70 wt. % to 97 wt. %. In one embodiment, the organic co-solvent is DMSO. In another embodiment, the organic co-solvent is acetonitrile.

**[0096]** 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 10:1 to 500:1, e.g. from 10:1 to 1:15 or from 10:1 to 100:1. Since current production costs of ionic liquids are generally greater than those of co-solvents, the use of a large amount of the second co-solvent beneficially reduces the cost of purifying the wet pulp.

**[0097]** 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. In the tertiary extractant system, the extractant may include at most 85 wt. % ionic liquid, e.g., at most 75 wt. %, or at most 50 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 85 wt. % ionic liquid, e.g., from 5 wt. % to 75 wt. %, from 10 wt. % to 50 wt. % or from 20 to 35 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 0.1 wt. % to 20 wt. % the first co-solvent, e.g., from 0.5 wt. % to 16 wt. % or from 1 wt. % to 10 wt. %. In one embodiment, water is the first co-solvent. In one embodiment, DMSO is the second co-solvent. In another embodiment, acetonitrile 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 wet pulp when operated at the same extraction conditions.

**[0098]** 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 80 wt. %.

**[0099]** 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 80 wt. %.

#### **[0100]** V. Purification Processes

**[0101]** As described herein, the wet pulp from pulping process **10**, whether comprising the washed pulp **31**, screened pulp **36**, bleached pulp **42**, wet pulp **46**, moisture reduced (dried) wet pulp **51**, or a combination thereof, may be purified through an inventive extraction process that removes hemicellulose, lignin, and preferably degraded cellulose. FIG. 4 illustrates one non-limiting exemplary system for purifying wet pulp, and recovering a hemicellulose byproduct. As shown in FIG. 4, the wet pulp may be purified in purification process **100**, which comprises a wet pulp purification zone **101** and a hemicellulose recovery zone **102**. As shown, the



wet pulp is fed via line **103** to extractor **105**. Line **103** may represent, for example, a slurry pump. However, for pulp with reduced water content, other transport apparatus, such as a screw feeder, a belt feeder, a rotary valve feeder, or another type of solid transport equipment, may be applicable. The wet pulp may also be subject to a deliquoring operation and/or a pre-extraction wash in order to optimize the water content in the extraction process. Fresh or recycled extractant, comprising a cellulose solvent and co-solvent, as described above, is fed to extractor **105** via line **104**. Although wet pulp **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. 4, wet pulp **103** and extractant **104** may be combined in extractor **105** to form an extraction mixture. In some embodiments, the mass flow ratio of extractant **104** to wet pulp **103** may range from 5:1 to 20:1. 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. Accordingly, the water content may be up to 99.9 wt %.

**[0102]** Extractant **104** for extracting hemicellulose and degraded cellulose from wet pulp **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 wet pulp **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  $\alpha$ -cellulose in wet pulp **103**, e.g., less than 10%, or less than 5%, as determined similarly by UV absorbance analysis and mass measurements. In some embodiments, the extractant may also dissolve at least 5% lignin, e.g., at least 10%, at least 15%, or at least 20%. As described above, amine oxides and ionic liquids may tend to dissolve  $\alpha$ -cellulose. The extractant preferably comprises sufficient co-solvent to reduce  $\alpha$ -cellulose solubility in the overall extractant to a point that the  $\alpha$ -cellulose does not readily dissolve therein. Preferably, the  $\alpha$ -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, lignin, and preferably degraded cellulose that is in wet pulp **103**.

**[0103]** Exemplary compositions for the wet pulp 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>Wet pulp 103</u>			
Cellulose*	0.1 to 90	5 to 85	10 to 80
Hemicellulose	0.1 to 40	0.1 to 30	1 to 25
Water	1 to 99.9	2.5 to 95	5 to 90
<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

TABLE 1-continued

EXTRACTOR 105			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<u>Extraction Mixture in Extractor 105</u>			
Cellulose	0.2 to 14	0.3 to 13	0.3 to 12
Hemicellulose & Degraded Cellulose	0.008 to 7	0.03 to 5	0.05 to 4
Water	0.001 to 20	0.01 to 16	0.01 to 10
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" in this row refers to cellulose of all forms including degraded cellulose

**[0104]** The treatment of wet pulp **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 20° C. to 300° C., e.g., from 20° C. to 150° C., from 40° C. to 140° C., or from 50° C. to 130° C. In terms of upper limits, the treatment of wet pulp **103** may be conducted at a temperature of less than 300° C., e.g., less than 200° C., less than 150° C., less than 140° C. or less than 130° C. In terms of lower limit, the treatment of wet pulp **103** may be conducted at a temperature of greater than 20° C., e.g., greater than 40° C., or greater than 80° C. The pressure (absolute, unless otherwise indicated) is in the range from 20 kPa to 20 MPa, preferably from 40 kPa to 10 MPa, more preferably from 100 kPa to 5000 kPa. In some embodiments, the pressure may be optimized, e.g., reduced below 20 kPa in order to maintain a liquid phase for the extraction process.

**[0105]** Wet pulp **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 wet pulp **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 wet pulp **103** may be for at most 1000 minutes, e.g., at most 500 minutes, or at most 200 minutes.

**[0106]** 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, wet pulp **103** contacts extractant **104** in one or more extraction vessels. In one embodiment, extractant **104** may be heated to the desired temperature before contacting wet pulp **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 CO<sub>2</sub>, may be supplied to the extractor to improve turbulence in the extractor and improve heat and mass transfer. 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**.

**[0107]** In the extraction step, the mass ratio of extractant to wet pulp 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 mass 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 or columns with or without baffles, 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.

[0108] In one embodiment, the wet pulp is subjected to repeated extraction steps. For example, the wet pulp 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 step may use an extractant comprising an ionic liquid and a co-solvent and a second extraction step 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.

[0109] 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 wet pulp first with the extractant, enzymes may be better able to penetrate the resulting 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 wet pulp 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, the water in the wet pulp may improve the pretreatment (e.g., prehydrolysis) of the pulp, which may be utilized to improve the efficiency of the enzymatic hydrolysis of the pulp. The pretreatment step preferably comprises treating the wet pulp 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.

[0110] In this embodiment, after the extraction step, the resulting 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, endoxylanase,  $\alpha$ -L-arabinofuranosidase,  $\alpha$ -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).

[0111] 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 (e.g., wet pulp) to be treated.

[0112] 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 relative to the wet pulp composition. 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.

[0113] 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.

**[0114]** 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, butyoni-trile), 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 intermediate 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.

**[0115]** 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.

**[0116]** 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%.

**[0117]** 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 wet pulp **103** is maintained in cellulose product **123**, as described herein.

TABLE 2

FILTER/WASHER 110			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<b>Extraction Mixture 106</b>			
Cellulose	0.24 to 14	0.26 to 13	0.29 to 12
Hemicellulose & Degraded Cellulose	0.008 to 7	0.03 to 5	0.05 to 5
Solvent (e.g., Ionic Liquid or Amine Oxide)	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
<b>Washed Intermediate Cellulosic Material 113</b>			
Cellulose	9.9 to 99	19 to 90	28 to 85
Hemicellulose & Degraded Cellulose	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
<b>Extraction Filtrate 111</b>			
Cellulose	0.002 to 1.4	0.003 to 1.3	0.003 to 1.2
Hemicellulose & Degraded Cellulose	0.008 to 6.7	0.03 to 5.2	0.05 to 4.4
Solvent (e.g., Ionic Liquid or Amine Oxide)	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
<b>Used Extractant wash (Filtrate) 112</b>			
Water	91 to 99.8	93 to 99.7	94 to 99.7
Solvent (e.g., Ionic Liquid or Amine Oxide)	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



[0118] 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).

[0119] 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.

[0120] 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. In some embodiments, the drying unit **50** from the pulping process may be used instead of dryer **120**, thus allowing for integration of

pulping process and purification process equipment. 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.

[0121] Depending on the purity of the starting material and of the wet pulp formed in the pulping process, in accordance to preferred embodiments of the present invention, high purity  $\alpha$ -cellulose product may be produced. In preferred embodiments, the finished cellulose product comprises high purity  $\alpha$ -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 a 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 a UV absorbance of greater than 4.7 at 277 nm, as determined by standard UV absorbance measurements. Conveniently and accurately, purity of the  $\alpha$ -cellulose product may be indicated by a lower absorbance at a certain wavelength.

[0122] In addition to retaining the fiber morphology of the cellulosic product, the high purity  $\alpha$ -cellulose pulp product also may advantageously retain other beneficial characteristics such as intrinsic viscosity and brightness. The high purity  $\alpha$ -cellulose 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  $\alpha$ -cellulose pulp may be used to make cellulose acetate, e.g., cellulose acetate flake or tow.

[0123] 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 or amine oxide 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.

[0124] 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. %)
<b>(First) Recovered Extractant 131</b>			
Solvent (e.g., Ionic Liquid or Amine Oxide)	0 to 5	0 to 3	0 to 1
Co-solvent (e.g., DMSO)	95 to 100	97 to 100	99 to 100
<b>Hemicellulose Concentrate 132</b>			
Cellulose	0.003 to 13.4	0.003 to 12.6	0.003 to 11.9
Hemicellulose & Degraded Cellulose	0.008 to 67	0.03 to 51	0.06 to 44
Solvent (e.g., Ionic Liquid or Amine Oxide)	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



[0125] 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.

[0126] 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 an 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; hydrogen-carbon 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.

[0127] 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).

[0128] 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.

[0129] 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.

[0130] 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, iso-propanol, 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; hydrogen-carbon 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.

[0131] 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 a high concentration, e.g., at least 80 wt. % co-solvent optionally at least 85 wt. % co-solvent, and at most 20 wt. % cellulose solvent, optionally at most 15 wt. % 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**.

[0132] 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. 4, 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**.

[0133] 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.

[0134] Returning to washed hemicellulose **138**, the stream may then be mechanically de-liquored, 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.

[0135] 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. In some embodiments, the drying unit **50** from the pulping process may be used instead of dryer **146**, thus allowing for integration of pulping process and purification process equipment. 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).

[0136] 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.

[0137] 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, membranes, ion exchange resins, activated carbon beds, simulated moving bed chromatographic separation, flocculants, 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 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 the 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.

[0138] Another pulp purification process, which is particularly well suited for extractants comprising solvents and co-solvents having disparate boiling points, is shown in FIG. 5. In this process, the extraction mixture is formed as described above for the process of FIG. 4. After the desired contacting time, an extraction mixture is removed from extractor **105** via line **106**. As shown, extraction mixture **106** is fed to filter **110** to remove extractant, dissolved hemicellulose, and dissolved degraded cellulose as well as dissolved side products. 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 **110** may comprise solid-liquid separation equipment, including but not limited to, for example, rotary vacuum drums, belt filters and screw presses. Filter **110** may be operated at a pressure from 20 kPa to 20,000 kPa, from 40 kPa to 10,000 kPa, or from 100 kPa to 5,000 kPa and a temperature from 10° C. to 150° C., from 15° C. to 100° C., or from 20° C. to 80° C. In some embodiments, the pressure on the filtrate side may be reduced to below 100 kPa, e.g., from 1 to 99 kPa for enhanced filtering process rate. Filter **110** forms an intermediate cellulosic material **112** and an extraction filtrate **111**.

[0139] After exiting filter **110**, intermediate cellulosic material **112** may be directed to washer **115** where it is washed with extractant wash **118** to further reduce the amount of extractant remaining in the intermediate cellulosic product. 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, only one washing step is used. In other embodiments, as shown, the intermediate cellulosic material may be washed more than once in separate washers **115** and **120**. 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 co-solvent, e.g., acetonitrile as extractant wash **118** to remove residual cellulose solvent and residual hemicellulose and a second washing step may use water as extractant wash **124** to remove residual acetonitrile. A similar configuration can be designed and optimized based upon the general chemical engineering principles and process design theory and it is understood that multiple washing steps, optionally with drying steps in between, may be used. The washing step may be conducted at a higher temperature in order to enhance mass transfer and to increase solubility. The temperature may be from 10° C. to 100° C., e.g., from 15° C. to 90° C., or from 20° C. to 80° C.

[0140] Extractant wash **118** preferably comprises a co-solvent, which dissolves residual cellulose solvent and residual hemicellulose and/or degraded cellulose from the cellulosic material, but may preferably be substantially free of cellulose solvent. Extractant wash **124** preferably also comprises a co-solvent, which can be used to wash away the residual of the first co-solvent in the cellulose material and can be further separated conventionally from the cellulose material. In one embodiment, the extractant wash is 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 other embodiments, the extractant wash is 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. In some embodiments, first extractant wash **118** may comprise greater than 85 wt. % acetonitrile, e.g., greater than 90 wt. % or greater than 95 wt. %; and second extractant wash **124** may comprise greater than 90 wt.

% washing solvent, preferably water, e.g., greater than 95 wt. % water, greater than 99 wt. % water or greater than 99.5 wt. % 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. The extractant wash may further comprise one or more washing aids described herein.

[0141] The first extractant wash may then be removed via line **117** and the second extractant wash may be removed via line **121**, e.g., as used extractant wash filtrates. In some embodiments, used extractant wash filtrate **117** may be returned to extractor **105**, either directly to extractor **105** or combined with solvent **104**. Used extractant wash filtrate **121** may be used in hemicellulose recovery zone **102**. The intermediate cellulosic material exits filter **110** and washer **115** and washer **120** via line **122**. Washed intermediate cellulosic material **122** has reduced hemicellulose content and preferably reduced degraded cellulose content. Washed intermediate cellulosic material **122** may comprise less than 6 wt. % extractant, e.g., less than 5 wt. % or less than 4 wt. % extractant. In some embodiments, washed intermediate cellulosic material **122** 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. %. Washed intermediate cellulosic material **122** may comprise from 9.9 to 99% solids, e.g., from 19 to 90% or from 28 to 85%.

[0142] Exemplary compositions using acetonitrile as the co-solvent, acetonitrile as the first extractant wash and water as the second extractant wash for the intermediate cellulosic material are provided in Table 4. When acetonitrile is used as the co-solvent and first extractant wash **118**, and water is used as second extractant wash **124**, at least 90% or at least 95% of the cellulose in wet pulp **103** is maintained in washed intermediate cellulosic material **122**, as described herein. If no further processing is required, washed intermediate cellulosic material **122** may be referred to as finished cellulosic material.

TABLE 4

FILTER 110, WASHER 115 and WASHER 120			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<b>Intermediate Cellulosic Material 112</b>			
Cellulose	25 to 80	29 to 79	33 to 78
Hemicellulose & Degraded Cellulose	0.003 to 15	0.02 to 10	0.05 to 8
Solvent (e.g., Ionic Liquid or Amine Oxide)	0.02 to 70	0.34 to 63	0.51 to 56
Co-solvent (Acetonitrile)	0.02 to 70	1.7 to 68	3.4 to 68
Water	0.0003 to 7	0.002 to 6	0.02 to 4
<b>Extraction Filtrate 111</b>			
Cellulose	0.002 to 5.2	0.003 to 3.9	0.004 to 2.9
Hemicellulose & Degraded Cellulose	0.01 to 5.6	0.05 to 5.5	0.07 to 5.4
Solvent (Ionic Liquid or Amine Oxide)	0.08 to 99.3	1.7 to 90	2 to 80
Co-solvent (Acetonitrile)	0.08 to 99.3	8 to 97.4	16 to 96.4
<b>Washed Intermediate Cellulosic Material 116</b>			
Cellulose	25 to 88	29 to 83	33 to 78
Hemicellulose & Degraded Cellulose	0.003 to 15	0.02 to 11	0.05 to 8.1
Extraction Wash (Acetonitrile)	8 to 70	14 to 66	19 to 63
Water	0 to 12	0 to 6.5	0.001 to 2.9



TABLE 4-continued

FILTER 110, WASHER 115 and WASHER 120			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<b>Used Extractant Wash 117</b>			
Water	0 to 16	0 to 8.3	0.001 to 3.9
Solvent (Ionic Liquid or Amine Oxide)	0 to 23	0.02 to 21	0.03 to 19
Co-solvent (Acetonitrile)	61 to 100	71 to 100	78 to 100
<b>Washed Intermediate Cellulosic Material 122</b>			
Cellulose	25 to 88	29 to 83	33 to 78
Hemicellulose & Degraded Cellulose	0.003 to 15	0.02 to 11	0.05 to 8.1
Acetonitrile	0 to 9	0 to 7	0.001 to 6
Water	11 to 70	13 to 67	15 to 63
<b>Used Extractant Wash 121</b>			
Water	69 to 99.6	71 to 99.3	73 to 99.0
Solvent (Ionic Liquid or Amine Oxide)	0 to 7.7	0 to 7.0	0 to 6.5
Co-solvent (Acetonitrile)	0.4 to 24	0.7 to 23	1.0 to 21

[0143] As shown, used extractant wash **121** may be directed to distillation column **135** to form a distillate **136** comprising the first and second extractant washes and a residue **137** comprising the second extractant wash **124**. It is understood that at least a portion of first extractant wash **118** is present in washed intermediate cellulosic material **116**, and is then separated from the cellulosic material and removed with used extractant wash **121**. At least a portion of residue **137** may be directed to washer **120** and at least a portion of residue **137** may be directed to washer **160**, discussed herein. Distillate **136** may be further separated in distillation column **140** to form distillate **142**, also comprising the first and second extractant washes and a residue **141**, comprising all or part of the recovered first extractant wash **118**, e.g., acetonitrile. When the co-solvent and extractant wash are the same, e.g., acetonitrile, residue **141** may be sent directly to extractor **105** or combined with fresh extractant via line **104**. Additionally, at least a portion of residue **141** may be directed to washer **155**, discussed herein, via line **143**. Distillate **142** may be combined with used extractant wash **121** and directed to distillation column **135**. Columns **135** and **140** may each be operated at a temperature from 20° C. to 300° C., e.g., from 30° C. to 250° C. or from 40° C. to 200° C. and at a pressure (absolute) from 1 to 2,000 kPa, e.g., from 2 to 1,500 kPa, from 5 to 1,000 kPa or from 10 to 800 kPa. Generally, the operating pressure of column **140** may be greater than the operating pressure in column **135**. Without being bound by theory, the greater pressure in column **140** may be used to change the concentrations in the acetonitrile/water azeotrope. In some embodiments (not shown), a single distillation column is sufficient for separation of the co-solvent from the washing agent(s).

[0144] In some embodiments (not shown), washed intermediate cellulosic material **122** or **116** may then be further de-liquored, e.g., mechanically concentrated in a concentrator to form a concentrated cellulosic material having an increased solids content, e.g., from 10 to 99 wt %, from 20 to 90 wt % or from 30 to 85 wt %. In some embodiments, the solids content is at least 90 wt. %. The concentrator and concentrated cellulosic material are described herein.

[0145] The concentrated cellulosic material may then be further dried in a dryer (not shown). The dryer may function to remove residual extractant wash. 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, a dryer may be designed to comprise heated rolls which may be used to form baled sheets or product rolls of cellulosic material.

[0146] In some embodiments, as described herein, 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 improve washing efficiency for the cellulose solvent and co-solvent, as well as to maximize separation of any remaining hemicellulose, thereby reducing total washing agent quantity required and associated energy and disposal costs.

[0147] Depending on the purity of the starting material and the wet pulp formed therefrom, in accordance to preferred embodiments of the present invention, high purity  $\alpha$ -cellulose product may be produced as described herein. In a preferred embodiment, extractant filtrate **111** is sent to a flasher **130** to form a vapor stream enriched in co-solvent **132** and a liquid stream enriched in cellulose solvent **131**. The flashing step desirably forms a vapor stream enriched in co-solvent **132** and a liquid stream enriched in cellulose solvent **131** due to the low to negligible vapor pressure of cellulose solvent and the significantly greater vapor pressure of the co-solvent. Vapor stream **132** may be condensed in condenser **133**. At least a portion of the condensed vapor stream may be employed as the first extractant wash **118** via line **138** and at least a portion of the condensed vapor stream may be employed as the hemicellulose precipitant wash **158**, discussed herein, via line **134**. Either a pressure drop from filter **110** to flasher **130** or additional energy supply can drive the separation of the cellulose solvent from the co-solvent in the flasher. Flasher **130** may be operated at a pressure from 1 to 10,000 kPa, e.g., from 10 to 5,000 kPa, or from 100 to 1,000 kPa and at a temperature from 0° C. to 300° C., e.g., from 20° C. to 200° C., or from 80° C. to 160° C. In some embodiments, the extracting step is conducted at a greater pressure than the flashing step, e.g., a pressure at least 3% greater, e.g., at least 10% greater, at least 20% greater, or at least 30% greater. In



other embodiments, the flashing step is conducted at a pressure lower than the extracting step, e.g., a pressure at most 97% of the pressure of the extracting step, e.g., at most 90% or at most 80%. Exemplary compositions for liquid stream **131** and vapor stream **132** are provided in Table 5.

pressure difference between precipitation slurry **146** and filtrate stream **151** may serve as the driving force for filtration. The pressure difference may vary from 1 to 10,000 kPa, e.g., from 10 to 5,000 kPa, or from 100 to 1,000 kPa. Precipitation agent filtrate **151** may be directed to a distillation column **165**

TABLE 5

FLASHER 130			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<b>Liquid Stream 131</b>			
Cellulose	0.002 to 18	0.003 to 13	0.004 to 10
Hemicellulose & Degraded Cellulose	0.01 to 20	0.05 to 19	0.08 to 18
Solvent (e.g., Ionic Liquid or Amine Oxide)	0.09 to 99.5	1 to 90	2 to 81
Co-solvent (Acetonitrile)	0.02 to 99.2	2.5 to 97.1	4.8 to 96.0
Water	0.001 to 9.3	0.01 to 9.2	0.02 to 7.3
<b>Vapor Stream 132</b>			
Cellulose	<0.001	<0.0001	—
Hemicellulose & Degraded Cellulose	<0.001	<0.0001	—
Solvent (e.g., Ionic Liquid or Amine Oxide)	<0.001	<0.0001	—
Co-solvent (e.g., Acetonitrile)	60 to 100	64 to 100	68 to 100
Water	0 to 40	0 to 36	0.003 to 32

[0148] Liquid stream **131** may then be fed to precipitator **145** to precipitate hemicellulose therefrom at a temperature from 0° C. to 100° C. Precipitation agent may be fed to precipitator **145** via line **129** and combined with liquid stream **131** to form a precipitation slurry **146**. Precipitator **145** may comprise one or more stirred tanks or other agitation equipment, and may be either batch or continuous optionally utilizing electrostatic charge to facilitate precipitation. Precipitation agent **129** may be the same as described in FIG. 4. Precipitation agent **129** may also comprise a mixture of an alcohol and water, optionally at an alcohol:water mass ratio from 1:1 to 20:1 or from 2:1 to 15:1. In some embodiments, precipitation agent **129** is the same as the co-solvent, e.g., acetonitrile. When acetonitrile and/or water are used as both the co-solvent and the precipitation agent, the concentration of co-solvent in the precipitation slurry is at least 1% greater than the concentration of co-solvent in the extractant, e.g., at least 2% greater or at least 5% greater. Precipitation slurry **146** may comprise, for example, from 0.001 to 3 wt. % cellulose, from 0.001 to 15 wt. % hemicellulose, from 1 to 10 wt. % water, from 0.05 to 50 wt. % solvent, from 0.05 to 50 wt. % co-solvent, and from 10 to 60 wt. % precipitation agent.

[0149] In another embodiment, the precipitator may comprise a crystallizer and/or precipitation agent **129** may be fed at a lower temperature, e.g., from 10° C. to 60° C. 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.

[0150] In yet another embodiment, a gas, optionally an inert gas, e.g. nitrogen, may be fed to precipitator **145** as described in FIG. 4.

[0151] As shown, precipitation slurry **146** may then be sent to filter **150** which separates a precipitation agent filtrate **151** from filtered intermediate hemicellulose **152**. Filter **150** may comprise solid-liquid separation equipment, including but not limited to rotary vacuum drums, belt filters and screw presses. Without being bound by theory, it is believed that the

to form a distillate **166** comprising precipitation agent and a residue **167** comprising cellulose solvent and co-solvent. In one embodiment, distillate **166** may comprise from 0.1 to 25 wt. % water, from 5 to 40 wt. % co-solvent, from 45 to 90 wt. % precipitation agent and less than 0.0001 cellulose solvent (e.g., substantially free of cellulose solvent). Distillate **166** may be directed to precipitator **145**. Residue **167** may comprise from 20 to 70 wt. % cellulose solvent and from 20 to 80 wt. % co-solvent. Residue **167** may be returned directly to extractor **105** via line **104** or may be combined with fresh extractant and then be directed to extractor **105** via line **104**. Column **165** 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 10,000 kPa, e.g., from 5 to 4,000 kPa, or from 3 to 1,000 kPa.

[0152] After exiting filter **150**, filtered intermediate hemicellulose **152** may be directed to washer **155** where it is washed with precipitant wash **158** to further reduce the amount of precipitation agent remaining in the intermediate cellulosic product as well as cellulose solvent. 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. At least a portion of precipitant wash **158** may be from condensed vapor stream **134**. In some embodiments, only one washing step is used. In other embodiments, as shown, filtered intermediate hemicellulose **152** may be washed more than once in separate washers **155** and **160**. When more than one washing step is used, e.g., two or three washing steps, the composition of the precipitant wash may vary in the different washing steps. For example, a first washing step may use acetonitrile, e.g., comprising at least 90 wt. % acetonitrile, as precipitant wash **158** to remove residual precipitation agent and cellulose solvent and a second washing step may use water as precipitant wash **168**, e.g., comprising at least 90 wt. % water, to remove residual acetonitrile. Depending upon the washing agents, the washing temperature may vary broadly, e.g., from 0° C. to 100° C.



Typically, a greater temperature can help dissolve more residuals and enhance the mass transfer. A similar configuration can be designed and optimized based upon the general chemical engineering principles and process design theory and it is understood that multiple washing steps, optionally with drying steps in between, may be used.

[0153] Precipitant washes **158** and **168** may preferably be substantially free of the cellulose solvent. Further, precipitant wash **158** preferably has high solubility to cellulose solvent but low solubility to mono-, di-, and oligo-saccharide and other side products. In one embodiment, precipitant wash **158** is the same as is described in FIG. 4. The precipitant wash may be enriched in co-solvent and may comprise a condensed portion of the vapor stream of the co-solvent from the flashing step. In another embodiment, the precipitant wash may comprise a stream enriched in precipitation agent. Further, precipitant wash **158** preferably has high solubility to cellulose solvent but low solubility to mono-, di-, and oligo-saccharides and other side products.

[0154] On the other hand, when high purity hemicellulose material **162** is desired, a precipitant wash **168** preferably having a high solubility to side products may be employed. Precipitant wash **168** optionally may be selected from the group consisting of water, ethylene glycol, glycerin, formamide, N,N-dimethylformamide, N-methylpyrrolidinone, N,N-dimethylacetamide, DMSO, mixture of water and alco-

hol, and their combinations. Accordingly, the side products, e.g., mono-, di-, and oligo-saccharide, are dissolved in used precipitant wash **164** and will be removed out using an extra operation (not shown) so that their concentrations in precipitant wash **168** are lower than those in stream **164**. In another embodiment, precipitant wash **158** is the same as extractant wash **118**, and precipitant wash **168** is the same as extractant wash **124**. Precipitant wash **158** may then be removed via line **156** and returned to precipitator **145**. Precipitant wash **168** may then be removed via line **164** and sent to distillation column **135**, discussed herein, to separate co-solvent and/or precipitation agent using distillation and/or evaporation. For the entire process, fresh precipitant wash, e.g., water, may be added to washer **160** via line **169**.

[0155] Exemplary compositions using ethanol as precipitating agent **129**, acetonitrile as precipitant wash **158** and water as precipitant wash **168** are provided in Table 6. When acetonitrile is used as the co-solvent and first extractant wash **118**, and water is used as second extractant wash **124**, at least 90% of the cellulose in wet pulp **103** is maintained in washed intermediate cellulosic material **122**, as described herein. If no further processing is required, washed hemicellulose **162** may be referred to as a finished hemicellulose product in which the ratio of hemicellulose concentration to cellulose concentration is at least 5 times greater than in wet pulp **103**.

TABLE 6

FILTER 150, WASHER 155 and WASHER 160			
	Conc. (wt. %)	Conc. (wt. %)	Conc. (wt. %)
<u>Filtered Hemicellulose 152</u>			
Cellulose	0.01 to 80	0.01 to 79	0.02 to 78
Hemicellulose & Degraded Cellulose	0.07 to 80	0.4 to 80	0.7 to 80
Precipitation Agent (Ethanol)	4.6 to 53	4.9 to 50	5.1 to 48
Solvent (e.g., Ionic Liquid or Amine Oxide)	0.004 to 54	0.09 to 49	0.1 to 44
Co-solvent (Acetonitrile)	0.001 to 54	0.1 to 53	0.2 to 52
Water	0 to 12	0.001 to 12	0.001 to 6
<u>Washed Hemicellulose 157</u>			
Cellulose	0.01 to 80	0.01 to 79	0.02 to 78
Hemicellulose & Degraded Cellulose	0.07 to 80	0.4 to 80	0.7 to 80
Precipitation Agent (Ethanol)	0 to 6.6	0 to 5.9	0 to 5.3
Solvent (e.g., Ionic Liquid or Amine Oxide)	0 to 6.7	0 to 5.8	0 to 4.9
Precipitant Wash/Co-solvent (Acetonitrile)	15 to 67	16 to 64	17 to 60
Water	0 to 4	0 to 3.8	0 to 1.7
<u>Used Precipitant Wash 156</u>			
Water	0 to 16	0 to 15	0 to 6.7
Solvent (Ionic Liquid or Amine Oxide)	0 to 8.9	0 to 7.3	0 to 6.6
Precipitation Agent (Ethanol)	0.2 to 18	0.25 to 16	0.3 to 14
Precipitant Wash/Co-solvent (Acetonitrile)	58 to 100	62 to 100	73 to 100
<u>Washed Hemicellulose 162</u>			
Cellulose	0.01 to 80	0.01 to 79	0.02 to 78.0
Hemicellulose & Degraded Cellulose	0.07 to 80	0.4 to 80	0.7 to 80
Water	20 to 70	21 to 67	22 to 63
<u>Used Precipitant Wash 164</u>			
Water	77 to 99.3	80 to 99.2	82 to 99.1
Co-solvent (Acetonitrile)	0.7 to 22	0.8 to 20	0.9 to 18



**[0156]** Returning to washed hemicellulose **162** or **157**, the stream may then be mechanically de-liquored (not shown), e.g., concentrated in a concentrator to form concentrated hemicellulose material. The solids content in concentrated hemicellulose material may be from 10 to 99 wt. %, e.g., from 20 to 90 wt. % or from 30 to 85 wt. %. In some embodiments, the solids content is greater than 90 wt. %. 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.

**[0157]** In some embodiments, the concentrated hemicellulose material may then be further dried in a dryer and used in further processes, as described herein.

**[0158]** The present invention will be better understood in view of the following non-limiting examples. Examples 1-6 and 8-17 are based on experimental results and Examples 7 and 18 are based on Aspen™ software simulation modeling.

## EXAMPLES

### Example 1

**[0159]** A wet pulp, simulating a wet pulp from a kraft or sulfite pulping process, was pre-extraction washed with DMSO to reduce the water content. Excluding any DMSO from this pre-extraction wash, a pulp 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.

**[0160]** 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

**[0161]** 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 degraded cellulose and 7 wt. % water.

### Example 2

**[0162]** The finished cellulosic product and the finished hemicellulose product were prepared as in Example 1, except that the extraction process was completed in 82-stage counter-current operation. The extraction time was dropped to 60 minutes at a 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

**[0163]** 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

**[0164]** 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

**[0165]** 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 greater than the costs of the process of Examples 1-4 due to the greater amount of ionic liquid used and not recovered.

### Example 6

**[0166]** 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

**[0167]** 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 7. As shown, the separation of EMIM Ac/DMSO from water and ethanol was substantially complete.

TABLE 7

DISTILLATION COLUMN 140				
	Feed (112)	Distillate (wt. %) (142)	Residue (wt. %) (141)	Side Stream (wt. %)
<b>Example A</b>				
Water	44.6	99.99	0.01	—
EMIM Ac/DMSO	55.4	0.01	99.99	—
<b>Example B</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
<b>Example C</b>				
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

## Example 8

[0168] The functionality of ionic liquid and co-solvent, e.g., acetonitrile, was demonstrated by purifying a wet pulp according to the following process and conditions. All the extractions were conducted at no more than 95° C. in a 50 ml glass using a water bath for 1 hr. The solid loading for the experiment was set to 5:100 solid to liquid (S/L) ratio. After the extraction, the pulp was separated from the extraction solution via centrifuge-filtration. The pulp was washed with fresh extractant one or two times. The pulp was then washed with water four times and separated from the wash solution via centrifuge-filtration. The pulp was dispersed in acetone and filtered under vacuum to form a loose mat. The pulp mat was left in a chemical hood for overnight drying at room temperature. The pulp was then subjected to standard UV absorbance measurement for pulp purity characterization. Specifically, the UV absorbance measurement follows the procedure below.

[0169] Pulp (approximately 0.11 g) was dried on a moisture balance twice. The moisture and final weight of pulp were recorded. The dry pulp was placed in a glass tube and hydrolyzed with 72% sulfuric acid (1 ml) at 30° C. for 1 h, then diluted with 5 ml of water. This procedure converted hemicellulose, e.g., xylan, to furfural while cellulose was not affected due to the difference in sugar dehydration rates. UV absorbance from 600 to 210 nm was measured and the peak value at 277 nm was recorded. Qualitatively, for the lower

hemicellulose concentration in the solid, the lower UV intensity was at 277 nm. Quantitatively, for comparison, a high-grade acetylation grade (AG) pulp used as a comparative sample with a lower hemicellulose concentration of 1.5-2.0 wt % was measured for UV absorbance to be from 0.6 to 0.9 at 277 nm.

[0170] The following table shows the UV absorbance of a paper grade hardwood (PGHW) pulp extracted by an EMIM Ac and acetonitrile system (e.g., purified pulp) with different concentration of EMIM Ac in acetonitrile. The greatest extraction of hemicellulose was achieved when EMIM Ac concentration in acetonitrile was from approximately 23 wt. % to approximately 25 wt. %.

TABLE 8

UV ABSORBANCE	
wt. % EMIM Ac	UV @ 277 nm
0%	4.7
5%	4.5
8%	4.6
10%	4.4
15%	2.3
20%	1.1
22%	1.0
23%	0.9
24%	0.9
25%	0.9
30%	1.5
35%	1.2
AG pulp	0.9

## Example 9

[0171] The same procedures as described in Example 8 were followed, except that a paper grade softwood (PGSW) pulp was extracted by an EMIM Ac and acetonitrile extractant system with different concentrations of EMIM Ac in acetonitrile at 95° C. for 1 hr. The extraction of hemicellulose was changed significantly when EMIM Ac was varied from 0 wt. % to 15 wt. %, as shown in the table below.

TABLE 9

UV ABSORBANCE for PGSW Pulp	
wt. % EMIM Ac	UV abs @ 277 nm
0%	2.79
15%	1.26
20%	1.10
22%	0.99
23%	0.96
24%	0.96
25%	0.96

## Example 10

[0172] The same procedures as described in Example 8 were followed, except that the PGSW pulp was extracted by EMIM Ac-acetonitrile-H<sub>2</sub>O extractant system with different concentration of H<sub>2</sub>O in EMIM Ac/Acetonitrile (25/75 w/w) at 95° C. for 1 hr. The extent of hemicellulose extraction changed with the variation of water concentration, as shown in Table 10, along with the UV measurement for standard high-grade AG pulp sample for comparison.



TABLE 10

UV ABSORBANCE		
Sample	% H <sub>2</sub> O in system	UV Abs @ 277 nm
AG Pulp	—	0.66
Sample 1	1.23%	0.92
Sample 2	2.44%	1.02
Sample 3	3.61%	1.17
Sample 4	4.76%	1.34
Sample 5	5.88%	1.51
Sample 6	6.98%	1.63
Sample 7	9.09%	1.81
Sample 8	11.11%	1.65
PGSW Pulp	—	2.88

## Example 11

[0173] The same procedures as described in Example 8 were followed, except that the PGSW pulp and the PGHW pulp were extracted using different ionic liquid under different experimental conditions. The EMIM Ac/acetonitrile system achieved the greatest hemicellulose extraction yield, as shown in Table 11, along with the UV measurement for standard high-grade AG pulp sample for comparison.

TABLE 11

UV ABSORBANCE				
Pulp	Ionic liquid*	Aceto-nitrile content (wt. %)	Extraction Temperature, Time and S/L@ 5:100	UV Abs @ 277 nm
PGSW*	TBAOH•30H <sub>2</sub> O	25%	30° C., 1 h	1.58
PGHW*	TBAOH•30H <sub>2</sub> O	25%	30° C., 1 h	2.36
PGSW	BnTMAOH 40% in water	25%	30° C., 1 h	1.52
PGHW	BnTMAOH 40% in water	25%	30° C., 1 h	1.93
PGSW	TMAOH 25% in water	25%	30° C., 1 h	1.17
PGHW	TMAOH 25% in water	25%	30° C., 1 h	1.69
PGSW	BnTEAAc	25%	95° C., 1 h	1.89
PGHW	BnTEAAc	25%	95° C., 1 h	3.15
PGSW	TEAAc•4H <sub>2</sub> O	25%	95° C., 1 h	2.07
PGHW	TEAAc•4H <sub>2</sub> O	25%	95° C., 1 h	3.59
PGSW	TBAAc	35%	95° C., 1 h	2.16
PGHW	TBAAc	35%	95° C., 1 h	3.31
PGSW	EMIMDMP	60%	95° C., 1 h	0.96
PGHW	EMIMDMP	60%	95° C., 1 h	1.19
PGSW	EMIMDEP	60%	95° C., 1 h	1.24
PGHW	EMIMDEP	60%	95° C., 1 h	1.52
PGSW	DMIMDMP	50%	95° C., 1 h	0.97
PGHW	DMIMDMP	50%	95° C., 1 h	1.27
PGSW	BMIMAc	82%	95° C., 1 h	0.95
PGHW	BMIMAc	82%	95° C., 1 h	1.00
PGSW	EMIMAc	76%	95° C., 1 h	0.96
PGHW	EMIMAc	76%	95° C., 1 h	0.89
PGHW	Control, as received, no treatment			4.70-5.00
PGSW	Control, as received, no treatment			2.80-3.10
AG Pulp	Control, as received, no treatment			0.65-0.85

\*PGSW refers to paper grade softwood

\*\*PGHW refers to paper grade hardwood

## Example 12

[0174] The same procedures as described in Example 8 were followed, except that the PGHW pulp and the PGSW

pulp were extracted by an NMMO.H<sub>2</sub>O/acetonitrile system with different concentrations of NMMO.H<sub>2</sub>O in acetonitrile. The extent of hemicellulose extracted changed when NMMO concentration varied, as shown in the table below along with the UV absorbance measurement of high-grade AG pulp sample for comparison.

TABLE 12

UV ABSORBANCE	
Sample	Abs @ 277 nm
PGHW	5.19
PGHD-15% NMMO	4.38
PGHD-25% NMMO	4.24
PGSW	2.94
PGSW-15% NMMO	2.89
PGSW-25% NMMO	2.35
AG pulp	0.70

## Example 13

[0175] 0.5 gram of paper grade pulp (hardwood pulp (HWPP) or softwood pulp (SWPP)) sample was weighed and put into a 75 ml glass vial with Teflon face lined cap. A pre-calculated amount of ionic liquid (shown in Table 13) and DMSO (total) were added into the glass vial according to the predetermined extractant weight ratio (ionic liquid/DMSO) and mixed well with the pulp samples. The sample thus contained a solid/liquid ratio of 5:100. The glass vials with pulp and extractant solution were placed into a water bath at 95° C. for 1 hr. After the treatment, the glass vial was left to cool to room temperature.

[0176] The content in the glass vial was transferred to a Buchner funnel with 5 µm twilled Dutch wire cloth filter pads and filtered under vacuum until less than one liquid drop came out of the funnel in a minute. The pulp formed a thin sheet of paper on the pads.

[0177] 20 ml fresh DMSO solvent were added to the filter pads and were filtered under vacuum again until less than one liquid drop came out of the funnel in a minute. The color of the pad was checked to ensure that the pulp was white without any color. An additional 20 ml of fresh DMSO was added to wash the sample and the sample was placed under vacuum. The process was repeated until the pulp appeared to be without any color.

[0178] Following the DMSO wash, the pulp sheet from the filter pads was dispersed in 40 to 100 ml of water, and then filtered again. This water wash generally was conducted 4 times. 20 ml of acetone was added to the pulp sheet on the filter pads followed by application of vacuum to dryness. The pulp sheet was left dry in a chemical hood overnight.

[0179] In some experiments, the extracted pulp samples were subjected to another extraction process (as indicated in Table 13) to further improve the pulp purity. In some experiments, instead of the DMSO solvent, the extractant composition (ionic liquid/DMSO) was used to extract the sample for one or more times. Water was used to wash away the extractant composition.

[0180] The results for the amount of hemicellulose in the paper pulp product using the above-described ionic liquid/DMSO binary extractant treatment are shown in Table 13. The absorbance of a commercially available hardwood acetate grade pulp was used as a bench mark. The absorbance of a hardwood paper grade pulp and a softwood paper grade pulp starting material were also measured and used as a comparison.



TABLE 13

IONIC LIQUID AND DMSO EXTRACTION				
Pulp	Ionic liquid	Ionic Liquid Concentration in DMSO	Extraction condition Temp, time, S/L	UV absorbance at 277 nm of the purified pulp
SWPP	TBAOH•30H <sub>2</sub> O	5%	95° C., 1 h, 5%	1.28
HWPP	TBAOH•30H <sub>2</sub> O	5%	95° C., 1 h, 5%	1.91
SWPP	BnTBAAc	20%	95° C., 1 h, 5%	1.77
HWPP	BnTBAAc	20%	95° C., 1 h, 5%	3.32
SWPP	BnTEAAc	25%	95° C., 1 h, 5%	1.58
HWPP	BnTEAAc	25%	95° C., 1 h, 5%	2.71
SWPP	TMAAc	3%	95° C., 1 h, 5%	1.77
HWPP	TMAAc	3%	95° C., 1 h, 5%	2.47
SWPP	TEAAc•4H <sub>2</sub> O	12%	95° C., 1 h, 5%	0.87
HWPP	TEAAc•4H <sub>2</sub> O	12%	95° C., 1 h, 5%	0.96
SWPP	TBAAc (7% H <sub>2</sub> O)	6%	95° C., 1 h, 5%	0.97
HWPP	TBAAc (7% H <sub>2</sub> O)	6%	95° C., 1 h, 5%	1.21
SWPP	HEAAc	10%	95° C., 1 h, 5%	2.29
HWPP	HEAAc	10%	95° C., 1 h, 5%	4.22
SWPP	HEAFo	3.5%	95° C., 1 h, 5%	2.36
HWPP	HEAFo	10%	95° C., 1 h, 5%	4.13
HWPP	NH <sub>4</sub> Ac	5.3%	95° C., 1 h, 5%	3.95
SWPP	BnTBACl	20%	95° C., 1 h, 5%	1.99
HWPP	BnTBACl	20%	95° C., 1 h, 5%	3.46
SWPP	BnTEACl	15%	95° C., 1 h, 5%	1.35
HWPP	BnTEACl	15%	95° C., 1 h, 5%	2.18
SWPP	EMIMAc	3.5%	95° C., 1 h, 5%	1.00
HWPP	EMIMAc	3.5%	95° C., 1 h, 5% (one time extraction with extractant wash)	0.95
HWPP	EMIMAc	3.5%	95° C., 1 h, 5% (one time extraction, no extractant wash)	1.20
HWPP	EMIMAc	3.5%	95° C., 1 h, 5% (two times extraction with extractant wash)	0.80
SWPP	BMIMAc	4.1%	95° C., 1 h, 5%	0.95
HWPP	BMIMAc	4.1%	95° C., 1 h, 5%	1.08
SWPP	EMIMMS	4.2%	95° C., 1 h, 5%	2.49
HWPP	EMIMMS	4.2%	95° C., 1 h, 5%	3.31
SWPP	BMIMMS	4.8%	95° C., 1 h, 5%	2.40
HWPP	BMIMMS	4.8%	95° C., 1 h, 5%	3.60
SWPP	EMIMOf	5.5%	95° C., 1 h, 5%	2.59
HWPP	EMIMOf	5.5%	95° C., 1 h, 5%	4.35
SWPP	EMIMDMP	14%	95° C., 1 h, 5%	0.84
HWPP	EMIMDMP	14%	95° C., 1 h, 5%	1.02
SWPP	EMIMDEP	14%	95° C., 1 h, 5%	0.90
HWPP	EMIMDEP	14%	95° C., 1 h, 5%	1.40
SWPP	DMIMDMP	20%	95° C., 1 h, 5%	0.82
HWPP	DMIMDMP	20%	95° C., 1 h, 5%	0.95
HWPP	Control, as received, no treatment			4.70-5.00
SWPP	Control, as received, no treatment			2.80-3.10
RHJ	Control, as received, no treatment			0.65-0.85

## Example 14

[0181] A dry pulp was mixed with water in the amounts shown in Table 14, to form a pulp/water slurry, simulating wet pulp fed from a pulping process. An ionic liquid was added to the slurry to form a pulp/ionic liquid/water mixture. In one embodiment, EMIM Ac was added into the pulp slurry to form a mixture with a solid to liquid mass ratio of 5:100. The UV results of the extracted pulp are shown in Table 14.

TABLE 14

EMIM Ac/H <sub>2</sub> O EXTRACTION	
EMIM Ac/H <sub>2</sub> O Mixture	UV @ 277 nm
Feed Paper Grade Pulp	4.83
20% water	1.19

TABLE 14-continued

EMIM Ac/H <sub>2</sub> O EXTRACTION	
EMIM Ac/H <sub>2</sub> O Mixture	UV @ 277 nm
30% water	2.19
40% water	3.93
50% water	4.58
60% water	4.69
70% water	4.67
Reference: Acetate grade pulp	0.89

## Example 15

[0182] A dry pulp was mixed with water in the amounts shown in Table 15, to form a pulp/water slurry, simulating wet pulp fed from a pulping process. Amine oxide was added to



the slurry to form a pulp/ionic liquid/water mixture. In one embodiment, NMMO was added into a pulp slurry to form a mixture with a solid to liquid ratio of 5:100. The UV results of the extracted pulp are shown in Table 15.

TABLE 15

NMMO/H <sub>2</sub> O EXTRACTION	
H <sub>2</sub> O % in NMMO/H <sub>2</sub> O Mixture	UV @ 277 nm
Feed: Paper Grade Pulp	4.83
15% water	4.34
20% water	1.57
25% water	2.93
30% water	3.56
35% water	3.74
40% water	4.28
45% water	4.53
250% water	4.61
Reference: Acetate grade pulp	0.89

## Example 16

**[0183]** A pulp was dispersed in water to form a pulp/water slurry, simulating wet pulp fed from a pulping process. The obtained pulp slurry was filtered to remove the water, then washed with DMSO with DMSO/slurry weight ratios as shown in Table 16. The obtained wet cake (pulp/liquids ratio from 1:4 to 1:5) was extracted with 3.5% EMIMAc/DMSO as extractant at 95° C. for 1 h with a dry pulp/extractant (S/L) mass ratio of 1/20. The results for the amount of hemicellulose in the paper pulp product using the above-described ionic liquid/DMSO binary extractant treatment are shown in Table 16. The absorbance of a commercially available hardwood acetate grade pulp was used as a bench mark. The absorbance of a hardwood paper grade pulp and a softwood paper grade pulp starting material were also measured and used as a comparison.

TABLE 16

EMIMAc/DMSO PULP SLURRY EXTRACTION					
Astracel wt. %	Pulp slurry % for filtration	Weight ratio DMSO/slurry	Extractant, wt. %	Extraction condition	UV Abs at 277 nm
0.8	dry	NA	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	0.993
0.8	15%	NA	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	4.408
0.8	10%	5:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	3.396
0.8	15%	5:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	2.906
0.8	20%	5:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	2.668
0.8	25%	5:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	3.281
0.8	15%	10:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	2.751
0.8	15%	2.5:1	EMIMAc/DMSO 3.5%, 16 g	95° C., 1 h, S/L 5%	4.064

## Example 17

**[0184]** A stock solution of 3.5% EMIM in DMSO was prepared by diluting 3.41 mL of EMIM Ac to 100 mL with DMSO. Four samples of lignin [Aldrich, CAS 8072-93-3] (5 mg, 10 mg, 15 mg, and 20 mg) were weighed for initial solubility testing. The samples were transferred to separate vials each containing approximately 10 mL of the 3.5% EMIM/DMSO stock solution. After addition of the lignin, the samples were stirred on a hot plate at approximately 100° C. for 30 minutes. During the 30 minute interval, any solid that remained on the wall of the vial was washed into solution by

manual vigorous shaking to ensure that all of the lignin was introduced into the solution. Upon completing the 30 minute mixing period, the lignin was completely dissolved in solution for samples 1-5. As to sample 6, the maximum solubility point was reached. A fine layer of solid lignin remained on the walls of the vial after the 30 minute mixing period, indicating the maximum solubility point. The following Table 17 shows the total weight of lignin dissolved in 10 mL of stock solution (3.5% EMIMAc in DMSO) while the maximum lignin concentration in 3.5% EMIMAc/DMSO at 100° C. was in the range of 2.5 to 3.1 g/L.

TABLE 17

LIGNIN SOLUBILITY			
Vial #	Volume of stock solution (mL)	Lignin Weight (mg)	Observation
1	10	5	Lignin completely dissolved
2	10	10.1	Lignin completely dissolved
3	10	14.9	Lignin completely dissolved
4	10	19.8	Lignin completely dissolved
5	10	25.2	Lignin completely dissolved
6	10	30.7	Fine lignin particles appears

## Example 18

**[0185]** The process shown in FIG. 5 was designed and modeled using commercial Aspen software, in the simulation model, a wet pulp was pre-extraction washed with acetonitrile to reduce the water content. Excluding acetonitrile, the pulp comprising 74.8 wt. % cellulose, 18.7 wt. % hemicellulose and 6.5 wt. % water was fed to an extraction unit. Separately, a recycled extractant comprising 22.1 wt. % EMIMAc, 72.2 wt. % acetonitrile and 5.6 wt. % water was fed to the extraction unit. The extraction was conducted at a temperature of approximately 120° C. and a pressure of approxi-

mately 1010 kPa, which was greater than the saturated acetonitrile vapor pressure in order to minimize the vaporization of acetonitrile. An extraction mixture comprising 8.0 wt. % cellulose, 2.0 wt. % hemicellulose, 5.7 wt. % water, 19.7 wt. % EMIMAc and 64.4 wt. % acetonitrile was removed from the extractor and sent through a filter at a temperature of approximately 120° C. and a pressure of approximately 1010 kPa to form an intermediate cellulosic material comprising 62.6 wt. % cellulose, 1.6 wt. % hemicellulose, 25.6 wt. % acetonitrile, 7.8 wt. % EMIMAc and 2.3 wt. % water, and an extraction filtrate comprising less than 0.2 wt. % cellulose, 2.1 wt. % hemicellulose, 70.0 wt. % acetonitrile, 21.4 wt. % EMIMAc,



and 6.2 wt. % water at the designed liquid-to-solid ratio of the extracting process. The intermediate cellulosic material was washed with acetonitrile and then with water to form a washed cellulosic material comprising 60.5 wt. % cellulose, 1.5 wt. % hemicellulose and 38.0 wt. % water.

**[0186]** The extraction filtrate was then flashed in a flasher to form a vapor stream comprising 91.2 wt. % acetonitrile, due to the low water concentration in the extraction filtrate. The vapor was condensed and used as the washing agent for the intermediate cellulose material and for the filtered hemicellulose. The liquid stream from the flasher comprised 41.4 wt. % acetonitrile, 50.2 wt. % EMIM Ac and 4.8 wt. % hemicellulose. The liquid stream was sent to a precipitator where it was combined with ethanol to form a precipitation slurry comprising 37.5 wt. % acetonitrile, 18.9 wt. % EMIM Ac, 34.2 wt. % ethanol, 1.7 wt. % hemicellulose and 0.2 wt. % cellulose. The precipitation slurry was filtered to form a filtered intermediate hemicellulose comprising 5.5 wt. % water, 25.6 wt. % hemicellulose, 27.6 wt. % acetonitrile, 25.2 wt. % ethanol and 13.9 wt. % EMIM Ac, and a precipitation filtrate comprising 38.2 wt. %, acetonitrile, 34.9 wt. % ethanol and 19.3 wt. % EMIM Ac. The filtered hemicellulose was washed with acetonitrile and then with water to form a washed hemicellulose comprising 44.5 wt. % hemicellulose, 4.0 wt. % cellulose and 51.6 wt. % water. The precipitation filtrate was separated in a distillation column to return a distillate comprising precipitation agent to the precipitator and a residue comprising solvent and co-solvent to the extractor.

**[0187]** Table 18 shows the information of each stream in FIG. 5, where stream 103 has been subject to a pre-extraction wash with acetonitrile and acetonitrile was excluded from the concentration.

**[0188]** 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 herein 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 converting a starting material to a purified pulp material, comprising:

removing lignin from a starting material to form a wet pulp comprising at least 5 wt. % water;

extracting hemicellulose from the wet pulp with an extractant, wherein the extractant comprises a cellulose solvent and a co-solvent, the cellulose solvent selected from the group consisting of an ionic liquid, an amine oxide, and combinations thereof; and

separating the extracted hemicellulose from the wet pulp to form a cellulosic product comprising less hemicellulose than the wet pulp.

2. The process of claim 1, wherein the removing lignin comprises:

TABLE 18

STREAMS IN FIG. 5								
Stream	Temp (° C.)	Pressure (kPa)	Water (wt %)	Hemicellulose and Degraded Cellulose (wt %)	Cellulose (wt %)	Acetonitrile (wt %)	Ethanol (wt %)	Ionic Liquid (wt %)
103	38	1010	6.5	18.7	74.8	0.0	0.0	0.0
104	125	2061	5.6	0.0	0.0	72.2	0.2	22.1
106	120	1010	5.7	2.0	8.0	64.4	0.1	19.7
111	120	1010	6.2	2.1	0.2	70.0	0.2	21.4
112	120	1010	2.3	1.6	62.6	25.6	0.1	7.8
116	77	101	6.4	2.0	77.9	13.7	0.0	0.0
117	77	101	7.0	0.0	0.0	90.1	0.2	2.7
118	77	101	8.5	0.0	0.0	91.2	0.2	0.0
121	95	101	97.0	0.0	0.0	3.0	0.0	0.0
122	95	101	38.0	1.5	60.5	0.0	0.0	0.0
131	87	101	3.0	4.8	0.4	41.5	0.1	50.2
132	87	101	8.5	0.0	0.0	91.2	0.2	0.0
134	77	101	8.5	0.0	0.0	91.2	0.2	0.0
136	78	1374	17.4	0.0	0.0	82.6	0.0	0.0
137	100	101	100.0	0.0	0.0	0.0	0.0	0.0
139	100	101	100.0	0.0	0.0	0.0	0.0	0.0
141	157	687	0.0	0.0	0.0	100.0	0.0	0.0
142	144	687	23.2	0.0	0.0	76.8	0.0	0.0
143	157	687	0.0	0.0	0.0	100.0	0.0	0.0
146	75	101	7.5	1.7	0.2	37.5	34.2	18.9
151	75	1037	7.6	0.0	0.0	38.2	34.9	19.3
152	75	101	5.5	25.6	2.3	27.6	25.2	13.9
156	76	101	9.2	0.0	0.0	75.5	10.0	5.4
157	76	101	1.2	40.6	3.6	54.6	0.0	0.0
162	79	101	51.6	44.5	4.0	0.0	0.0	0.0
164	79	101	88.6	0.0	0.0	11.4	0.0	0.0
166	75	101	7.6	0.0	0.0	38.2	34.9	19.3
167	155	687	5.0	0.0	0.0	56.3	0.1	38.6
169	100	101	100	0	0	0	0	0



- combining the starting material and a cooking liquor to dissolve lignin to form a cooked pulp comprising cooking liquor, dissolved lignin and pulp; and separating the cooking liquor and lignin from the pulp to form the wet pulp.
- 3.** The process of claim **2**, wherein the separating further comprises washing the wet pulp.
- 4.** The process of claim **1**, wherein the process further comprises partial bleaching of the wet pulp prior to the extracting and partial or complete bleaching of the cellulosic product.
- 5.** The process of claim **1**, wherein the process further comprises pressing the wet pulp prior to the extracting.
- 6.** The process of claim **1**, wherein the process further comprises complete or partial bleaching of the wet pulp and washing of the wet pulp prior to extracting.
- 7.** The process of claim **1**, wherein the wet pulp comprises at least 7 wt. % water and the process further comprises filtering, deliquoring, and/or drying the wet pulp to no less than 5 wt. % water prior to the extracting step.
- 8.** The process of claim **1**, wherein the wet pulp comprises at least 30 wt. % water.
- 9.** The process of claim **1**, wherein the wet pulp is sent to the extracting step without drying.
- 10.** The process of claim **1**, wherein the wet pulp is washed with one or more pre-extraction washes comprising a pre-extraction wash agent prior to the extracting.
- 11.** The process of claim **10**, wherein the pre-extraction wash agent is selected from the group consisting of methanol, ethanol, iso-propanol, methyl acetate, ethyl acetate, propyl acetate, isopropyl acetate, vinyl acetate, tetrahydrofuran, dimethoxyethane, acetone, acetic acid, formic acid, acetonitrile, propionitrile, butyronitrile, chloroacetonitrile, dichloromethane, chloroform, triethylamine, N,N-dimethylformamide, toluene, pyridine, water, and combinations thereof.
- 12.** The process of claim **10**, wherein the pre-extraction wash agent removes at least 30% of the water from the wet pulp.

- 13.** The process of claim **1**, wherein the wet pulp is filtered and/or deliquored prior to the extracting.
- 14.** The process of claim **1**, wherein the co-solvent is water and wherein the cellulosic solvent is added directly to the wet pulp prior to the extracting.
- 15.** The process of claim **1**, wherein the separating comprises:  
removing an extraction mixture from the extracting step;  
separating the extraction mixture to form an intermediate cellulosic material and a liquid stream containing hemicellulose; and  
flashing at least a portion of the liquid stream to form a vapor stream enriched in the co-solvent and a flashed liquid stream comprising the hemicellulose, the cellulose solvent, and the co-solvent.
- 16.** The process of claim **15**, further comprising recovering hemicellulose from the flashed liquid stream.
- 17.** The process of claim **1**, wherein the separating comprises:  
removing an extraction mixture from the extraction step;  
concentrating the intermediate cellulosic material to form the cellulosic product, wherein the cellulosic product has an increased solids content; and  
recovering the separated hemicellulose.
- 18.** The process of claim **1**, wherein the process further comprises drying the cellulosic product to form a sheet product.
- 19.** The process of claim **1**, wherein the co-solvent is selected from the group consisting of alcohols, esters, ethers, ketones, carboxylic acids, nitriles, amine, amide, halides, hydrocarbon compound or heterocyclic compound and combinations thereof.
- 20.** The process of claim **1**, wherein the starting material is pre-treated or pre-hydrolyzed prior to the removing lignin from the starting material.

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