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(54) **PROCESS FOR FIBRILLATING LIGNOCELLULOSIC MATERIAL, FIBRES AND THEIR USE**

VERFAHREN ZUM FIBRILLIEREN VON LIGNOZELLULOSEMATERIAL, FASERN UND IHRE VERWENDUNG

PROCEDE DE FIBRILLATION DE MATIERE LIGNOCELLULOSIQUE, FIBRES ET LEUR UTILISATION

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## Description

### FIELD OF THE INVENTION

**[0001]** The invention relates to a process for fibrillating lignocellulosic material wherein the process comprises treating lignocellulosic material with ionic liquid and recovering basically intact fibres of said lignocellulosic material. Typically the process comprises increasing the surface area of said lignocellulosic material. Another object of the invention is to provide an activated and/or basically intact fibre wherein the lignocellulosic material is treated with ionic liquid and a basically intact fibre of said lignocellulosic material is recovered.

**[0002]** The invention further relates to the use of the basically intact fibre of the invention in the production of bio-based materials, preferably bio-plastics, more preferably conductive polymers, stimuli-responsive polymers, bio-based polymer composites, ceramics, fabrics, or elastomers. A process for producing paper, board, pulp or the like from fibers of lignocellulosic material which have been treated with ionic liquid and recovered as basically intact fibres is also enclosed.

### BACKGROUND OF THE INVENTION

**[0003]** The treating of lignocellulosic material has become even more important due to growing energy demands and environmental concerns. Traditional methods of chemical modification employed for treating lignocellulosic materials are fibre modification, pulping, fractionation and depolymerisation.

**[0004]** The fibre modification method involves enhancement of the fibre properties by additive functionalization, which means adding functionalities that demonstrate enhanced properties of the product. A typical example would be fatty acid (hydrophobic functionality) functionalization of wood fibre hydroxyl groups in the production of hydrophobic materials (plastics, hydrophobic coatings, etc).

**[0005]** Traditional chemical pulping involves fibrillation of woody material and selective degradation of the lignin contained within it. The fibrous quality of the enriched polysaccharide fraction, which consist mainly of cellulose, is maintained and is essential for performance in its present applications (mainly paper making). Typically the depolymerised lignin is collected as a solid material and burnt to recover raw materials and to produce energy to fuel the whole process. Apart from chemical pulp, other common forms of pulp are thermo mechanical pulp (TMP) and chemothermo mechanical pulp (CTMP). These involve thermo mechanical separation of wood into fibrous material, with an optional chemical pre-treatment. The quality of these fibres, as pulp, is generally low, due to their high lignin content. This material is further upgraded by vigorous chemical bleaching to afford different grades of pulp.

**[0006]** Fractionation involves separation of the lignocellulosic components. This should be distinct from pulping, as pulping involves depolymerisation of lignin, whereas fractionation should maintain the molecular weight of the lignin. Methods exist for the commercial production of high molecular weight lignins and other components, but these involve depolymerisation of the polysaccharide components (e.g. organosolv lignin).

**[0007]** Depolymerisation of lignocellulosic material, or fractionated/enriched materials, is a method whereby the polymeric structures are degraded to low molecular weight species. This may be selective degradation of certain components or structures for the production of commodity chemicals (bioethanol, monosaccharide, disaccharides, oligosaccharides, phenols, catechols, LGO, furanoids, hydroxyalcohols, etc) or indiscriminate degradation of components for the production of mixtures of chemicals, tars and oils, liquid biofuel or wood gas (syngas). This may involve the catalysed degradation of components in solution (e.g. aqueous-acid catalysis), anaerobic thermal degradation of material in solution or solid state (pyrolysis) or aerobic thermal degradation of material (gasification). All these methods have in common the degradation of the fibrous properties of the material. This degradation may allow for more efficient fractionation, however, the nature of the resulting polysaccharide materials is changed so drastically that it is rendered useless for traditional pulping applications.

**[0008]** The present invention surprisingly shows that ionic liquids can be used for fibrillating lignocellulosic materials under mild conditions, compared to the conditions used in traditional methods for treating lignocellulosic materials, in order to receive a novel type of fibres.

**[0009]** Ionic liquids are ambient temperature molten salts. They usually have melting points below 100 °C and are seemingly composed of ions, with no additional molecular solvent present to render the mixture liquid (i.e. as opposed to aqueous salt solutions). Ionic liquids have been described, for example, in US patent application US 20080190321 A1, which discloses the preparation of ionic liquids and a method for dissolving cellulose into a solution comprising an ionic liquid. German patent application DE 102005062608 A1 also discloses the preparation of ionic liquids and their use as dissolution systems for celluloses.

**[0010]** JP 2009 179913 A discloses a process wherein a cellulosic material is treated with an ionic liquid and then cellulose fibres are recovered.

**[0011]** Further uses of ionic liquids for different purposes are known from US patent application US 20070215300 A1, which relates to a method for the treatment of a lignin-containing material with an ionic liquid to extract lignin there from.

The lignin is recovered from the ionic liquid. US patent application US 20080185112 A1 relates to thermolysis of lignocellulosic materials where ionic liquids are used for pre-treatment of lignocelluloses and US patent application US 20080190013 A1 describes a method for converting lignocellulosic material into biofuel. Ionic liquids are used for pre-treatment by dissolution of the lignocellulosic materials in the ionic liquid. WO 2008119770 A1 relates to a method for modifying the structure of a cellulose material and dissolution of lignocellulosic material is described in WO 2005017001 A1.

## SUMMARY OF THE INVENTION

**[0012]** The invention relates to a process for fibrillating lignocellulosic material, such as wood chips, wherein the process comprises treating lignocellulosic material with ionic liquid to produce basically intact fibres of the lignocellulosic material, with minimal degradation. The fibrillation may also be combined with mechanical treatment, such as a thermomechanical or chemithermomechanical treatment. Typically the process of the invention comprises increasing the surface area of said lignocellulosic material by the fibrillation.

**[0013]** Another object of the invention is to provide a basically intact fibre which is obtained by treating lignocellulosic material with ionic liquid and by recovering the basically intact fibre. The present invention further relates to a process for producing paper, board, pulp and the like from the basically intact fibres of the invention.

**[0014]** A further object of the present invention is application of the fibrillated material of the invention in the production of bio-based materials such as conductive polymers, stimuli-responsive polymers, bio-based polymer composites, ceramics, fabrics, elastomers and bio-plastics in general from the fibres.

**[0015]** Another embodiment of the invention provides a refined and efficient lignocellulose functionalization, for the production of novel materials. This feature of the treatment, in combination with the wide range of chemical or physical modification, allows for tuning of the physiochemical properties to produce high value materials for a given application with increased yields. The modification is used to effect changes in hydrophobicity, electrical conductivity/resistance, stimuli response, rheological properties, visual properties, solvent (e.g. water) absorbtivity/barrier properties, swelling properties, elasticity, tensile properties or thermal resistance of the fibres. One preferred application is inclusion of hydrophobic functionalities, such as fatty acid esters derived from rosin acids, tall oil fatty acids (TOFA) or alkyl ketene dimer (AKD) sizing reagents. This can help to "compatibilize" the material for the formation of composite materials with traditional hydrophobic polymers.

**[0016]** The invention is based on the finding that ionic liquids can be used for fibrillating lignocellulosic materials under mild conditions, compared to the conditions of the traditional methods for treating lignocellulosic materials, in order to receive a novel type of fibers. The present invention can further be used as an ionic liquid-mediated fibrillation pre-treatment from where components of the remaining fibrous material are more easily degradated.

**[0017]** One advantage of the invention is that ionic liquids affords a media which do not contribute to environmentally polluting volatile organic compound (VOC) emissions. This is in part due to the extremely low volatility of most ionic liquid media. The ionic liquid technology research is a rapidly expanding area of materials science. Ionic liquids seem to offer potential sustainable technology platforms for some environmentally benign new and alternative processes.

**[0018]** A further advantage of the invention is that the basically intact fibres are closer to their native structure and molecular weight, than those obtained from traditional pulping, fractionation or extraction processes. During the ionic liquid treatment, the treated fibres maintain their advantageous fibrous properties and yet retain a practically similar mass compared to the mass of the starting lignocellulosic material.

**[0019]** Several advantages are further achieved when the present invention is used for pre-treatment of wood, for example before chemical pulping, such as Kraft pulping. The ionic liquid treatment allows for milder cooking, for example influences the cooking temperature and time and therefore reduces the energy consumption. The process according to the invention also increases the surface area of the lignocellulosic material for the delignification process. Further mild delignification under aqueous basic conditions is achieved, even in the absence of sulphur, yielding a sulphur-free lignin. This is an advantage compared to traditional pulping due to reduced catalyst poisoning during cracking, lower sulphur emissions during combustion or easier reagent recovery.

**[0020]** Furthermore, according to one embodiment of the invention, small portions of wood components, such as polymeric and oligomeric polysaccharides (pectins or hemicelluloses) in particular, are regenerated from the ionic liquid, for example by precipitation with a co-solvent. Typically these components are extracted into the ionic liquid mixture during the fibrillation process. Therefore, one benefit of the invention is the increased efficiency of extraction of extractives or particular polysaccharide components, such as pectins or hemicelluloses, from the lignocellulosic material. Pectins and hemicelluloses are particularly useful as food additives and their scope is expanding. Extractives may have wide ranging applications as commodity chemicals or as intermediates or drug candidates for agrochemical or pharmaceutical applications.

**[0021]** In research related to wood, the use of ionic liquids for fibrillation opens up new possibilities also for studies of wood components and structures with the aim of increased utilization of natural renewable wood reserves. One advantage

of the invention is the mild deconstruction and optionally reconstruction of the native lignocellulosic material with other bio-based materials. Due to more detailed knowledge of wood structure and the physical and chemical properties of ionic liquids, increased efficiency of the process and an increased quality of product are achieved.

**[0022]** The objectives of the invention are accomplished with a process and product having the characteristics as mentioned in the independent claims. The preferred embodiments of the invention are presented in the independent claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0023]**

**Fig. 1,** A schematic view of one embodiment of the process of the invention.

**Fig. 2,** $^{31}P$ NMR analysis of the [mmim]$Me_2PO_4$ residue from pine fibrillation according to Example 4.

## DETAILED DESCRIPTION OF THE INVENTION

**[0024]** The present invention relates to a process for fibrillating lignocellulosic material wherein the process comprises treating lignocellulosic material with ionic liquid and recovering basically intact fibres of said lignocellulosic material.

**[0025]** In the present specification and claims, the following terms have the meanings defined below.

**[0026]** The term "fibrillation" refers to changes in the fibre structure of the lignocellulosic material, i.e. the fibre walls, whereby a number of fibrils or tracheids are completely or partially separated and the binding between the remaining fibrils or tracheids is weakened, to the state of being reduced to fibres with high aspect ratio. The removal of pectins from the lumen by ionic liquid significantly contributes to the fibrillation process, but the fibre structure and aspect ratio are maintained.

**[0027]** The term "basically intact fibre" refers to the fibres of lignocellulosic material having a basically intact cell structure. Typically the average 2D aspect ratio of the fibres is >5, more preferably >20 and most preferably >50. Dissolution on the other hand generally results in recovery of non-fibrous material, which should be regarded as no longer "basically intact".

**[0028]** The term "activated" as used in the present specification and claims refers to fibres of lignocellulosic material which have been activated in the sense that the surface area for reaction is increased, due to fibrillation or swelling of the fibre surface. This affords a material that is more easily subjected to further treatments, such as different kinds of modification, for example chemical functionalization.

**[0029]** The term "modification" in the present specification and claims refers to chemical or physical modification of the fibre material. For example chemical functionalization, involving breakage or formation of chemical bonds, comprises adding functionalities which afford enhanced properties of the fibrous material, for example physiochemical properties such as hydrophobicity, electrical conductivity/resistance, rheological properties, visual properties, solvent (e.g. water) adsorbtivity/absorbtivity, swelling properties, elasticity, tensile properties or thermal resistance. For example increasing the resistance to oxidation of the remaining lignin diminishes the requirement for bleaching or ageing of the material and results in a high yield of a product. Further examples of modification comprise increasing the molecular weight and fragmentation or depolymerization of the lignocellulosic material. Fragmentation and/or depolymerization is useful in the production of enriched biopolymer preparations, such as lignin, or monomeric and low molecular weight materials to be used as bulk chemicals, commodity chemicals or bio-based fuels. Physical modification may involve physical formation or defomation of the material. For example a process of grinding, as is used in the production of TMP, or shearing, as is used for the production of microfibrillar cellulose (MFC), may be used. The modification can take place in the presence of another solid, liquid or gaseous material to affect some chemical, morphological or physical transformation in general.

**[0030]** The term "wood chips" refers to pieces of wood most of which are bigger than 1 cm x 0.5 cm x 0.1 mm, preferably at least 50 % of the wood chips are bigger than 1 cm x 0.5 cm x 0.1 mm, more preferably at least 80 %, most preferably at least 95 %.

**[0031]** The term "lignocellulosic material" in the present specification and claims refers to a natural material comprising cellulose, hemicellulose and lignin that has not been subjected to previous pulping or fibrillation processes. The lignocellulosic material may be close to its native (unprocessed) form, or it can be partially processed using typical harvesting and pre-treatment techniques. The material may also contain "extractives" which are a range of different low molecular weight compounds and are of value in the forestry product chain. For example carbohydrate polymers (pectins, cellulose and hemicelluloses) are tightly bound to the lignin, by hydrogen and covalent bonds. Hemicelluloses are embedded in the cell walls of plants - they bind with pectin and lignin to cellulose to form a network of cross-linked fibres. The lignocellulosic material also refers to biomass of different types, such as wood residues (including sawmill and paper mill discards), agricultural residues (including corn stover and sugarcane bagasse), dedicated energy crops (which are

mostly composed of fast growing tall, woody grasses), and trees (felled for pulp, construction, materials, chemicals or energy). According to the present invention lignocellulosic materials can for example be obtained from vascular plants such as hardwood, softwood, straws, grasses (e.g., rice, esparto, wheat and sabai), canes, reeds (e.g., bagasses or sugar cane), bamboo, bast fibres (e.g., jute, flax, kenaf, linen, ramie, cannabis) and/or leaf fibres (e.g., agaba, minila hemp, sisal). Preferably the lignocellulosic material is wood, such as softwood or hardwood, for example in the form of wood chips.

**[0032]** The term "treatment" in the present specification and claims refers to treatment of lignocellulosic material with ionic liquid and may involve one or more common treatments such as heating, vacuum, pressure, stirring, vibration, microwave, ultrasound, or other common methods of agitation of mixtures.

**[0033]** The term "ionic liquid", is commonly defined as molten salts, which are comprised of ions and are liquids at certain temperatures. In the present specification and claims, the term "ionic liquid" refers to molten salts with melting point ranges between -100 °C to 200 °C or even up to 300 °C. The ionic liquids comprise one or more anions and one or more cations. In a further extension of the definition according to the present invention, ionic liquids should be regarded as molten salts at any suitable process conditions. The present definition of ionic liquids includes "room temperature ionic liquids" which are molten salts with melting points below room temperature (~17-25 °C in most laboratory settings). Under the present definition of ionic liquids, the fact that the ions may be closely paired or clustered in the solution state (by columbic interaction, hydrogen bonding or weaker interactions), does not exclude them from being classed as ionic liquids.

**[0034]** The terms "phosphate", "phosphonate", "sulfate", "sulfonate" and "carboxylate" in the present specification and claims refer to anions of ionic liquids and can mean any homologues of substituted phosphate, phosphonate, sulfate, sulfonate and carboxylate anions respectively. For example, methylhydrogenphosphonate can be refered to as a phosphonate. Homologues containing alkyl, aryl and partially or perhalogenated substituents are also included under this definition.

**[0035]** The present invention relates to a process for fibrillating lignocellulosic material wherein the process comprises treating lignocellulosic material with ionic liquid and recovering basically intact fibres of said lignocellulosic material. Typically the treatment involves heating (by standard methods), vacuum, pressure, stirring, vibration, microwave, ultrasound, or other common methods of agitation of mixtures to enhance the fibrillation. The heating typically involves using process temperatures between 20 °C and 150 °C, preferably between 50 °C and 120 °C, more preferably between 75 °C and 120 °C. Microwaves and ultrasound have in the prior art been found to aid dissolution of cellulose with ionic liquids. However, the use of microwaves and/or ultrasound to enhance fibrillation according to one embodiment of the present invention requires appropriate control of the fibrillation conditions, not to dissolve material. According to another embodiment, the treatment to facilitate fibrillation involves heating in combination with mechanical treatment. Such a treatment is for example used in the production of thermomechanical pulp or chemothermomechanical pulp.

**[0036]** According to one embodiment of the invention the basically intact fibre fibrillated according to the process of the invention has an average 2D aspect ratio at least 5, more preferably at least 20 and most preferably at least 50. According to other preferred embodiments the average 2D aspect ratio of the basically intact fibre of the invention is at least 10, at least 15, at least 25, at least 30, at least 35, at least 40, at least 45 or at least 55.

**[0037]** According to another embodiment of the invention the basically intact fibre is activated during the treatment of the lignocellulosic material and/or modified after the recovery of the basically intact fibres. Such a modification of the basically intact fibre is preferably made by chemical or physical modification or upgrading of the fibres. Examples of chemical modifications are esterification, redox reactions, etherifications, carbamate formations, carbonate formation, crosslinking and/or other reactions where covalent linkages are formed. Examples of physical modification are grinding, as is used in the production of TMP or CTMP, or shearing, as is used for the production of MFC. According to one aspect of the invention the fibrillated lignocellulosic material can be modified after recovery from the ionic liquid media but according to another aspect of the invention the fibrillated lignocellulosic material is modified in the ionic liquid media before recovery. According to one option of the present invention the fibres, which are present in the ionic liquid or which have been recovered from the ionic liquid, are in an activated state.

**[0038]** According to one embodiment the basically intact fibre of the invention is chemically modified by additive chemical functionalization. Such functionalization involves modification of functional groups on the surface or through the fibre in order to produce a fibrous material with enhanced properties. One example of this embodiment is fatty acid functionalization of the surface hydroxyl groups of the basically intact fibre to form a bio-based plastic material.

**[0039]** The invention also relates to a process for recovery of the fibrillated lignocellulosic material, components dissolved from the lignocellulosic material and purified ionic liquid. Typically separation of the solid material from the liquid material is done at any stage of the process by filtration, centrifugation and other common solid/liquid separation techniques. According to one embodiment small amounts of molecular solvent are added to the reaction mixture to increase the efficiency of separation, yet still avoiding precipitation of the dissolved components. Optionally dissolved compounds, such as pectins, are recovered by addition of a further molecular solvent, allowing for solid/liquid separation, or by membrane filtration. Typically the ionic liquid is recovered after precipitation of dissolved components and/or removal

of solid material by evaporation of the solvent used for precipitating. One or more of the components are optionally recycled. According to a further option a range of molecular solvents is used to remove traces of ionic liquid remaining on the fibre by heating.

**[0040]** Another object of the invention is to provide a basically intact fibre which is obtained by treating lignocellulosic material with ionic liquid and recovering basically intact fibres of said lignocellulosic material. Typically the ionic liquid treatment increases the surface area of the fibres.

**[0041]** The basically intact fibre of the invention typically has an average 2D aspect ratio of at least 5, more preferably at least 20 and most preferably at least 50. According to other preferred embodiments the 2D aspect ratio values of the basically intact fibre of the invention is at least 10, at least 15, at least 25, at least 30, at least 35, at least 40, at least 45 or at least 55.

**[0042]** According to one embodiment of the invention the basically intact fibre is activated during treatment of the lignocellulosic material and/or thereafter modified either in the ionic liquid or after the recovery of the basically intact fibres. Such a modification of the basically intact fibre is preferably made by chemical or physical modification.

**[0043]** According to still another embodiment of the invention the basically intact fibre is dissolved in an ionic liquid after being recovered from the ionic liquid used for treating the lignocellulosic material.

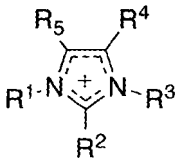
**[0044]** A further object of the invention is the use of the basically intact fibre of the process of the invention in the production of bio-based materials, preferably bio-plastics, more preferably conductive polymers, stimuli-responsive polymers, bio-based polymer composites, ceramics, fabrics, or elastomers.

**[0045]** A still other object of the invention is to provide a process for producing paper, board, pulp or the like from fibers of lignocellulosic material which have been treated in ionic liquid and recovered as basically intact fibres of said lignocellulosic material.

**[0046]** The ionic liquid of the invention typically comprises at least one anionic portion and at least one cationic portion. The choice of one or more cationic portions and anionic portions depends first of all on the lignocellulosic material and thereto on the treatment and the conditions chosen.

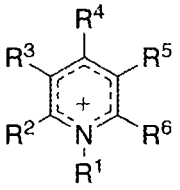
**[0047]** The cationic portion of the ionic liquid according to the invention can depending on the lignocellulosic material and the treatment and conditions chosen comprise one or more organic cations prepared by derivatizing one or more of imidazole, pyrazole, thiazole, isothiazole, azathiazole, oxothiazole, oxazine, oxazoline, oxazaborole, dithiazole, triazole, selenazole, oxaphosphole, pyrrole, borole, furan, thiophene, phosphole, pentazole, indole, induline, oxazole, isoxazole, isotetrazole, tetrazole, benzofuran, dibenzofuran, benzothiophene, dibenzothiophene, thiadiazole, pyridine, pyrimidine, pyrazine, pyridazine, piperazine, piperdine, morpholone, pyran, annoline, phthalazine, quinazoline, guanidinium, quinxaline, choline-based analogues or combinations thereof with variable substituents such as alkyl, alkenyl, alkynyl, alkoxy, alkenoxy, alkynoxy, vinyl, allyl and propargyl groups. The substituents may also be aromatic substituents, such as substituted or unsubstituted phenyl, substituted or unsubstituted benzyl, or a variety of heterocyclc aromatics having one, two or three heteroatoms in the ring portion thereof, said heterocyclics being substituted or unsubstituted. Further the substituents may include additional terminal functionalities such as disubstituted chalcogens (ethers, thioethers etc.), carboxylic acids, carboxylic esters, thioacids, thioesters, carbonates, carbamates, nitriles, imines, amides, aldehydes, ketones or other heteroatom-containing functionalities. The basic cation structure can be singly substituted, multiply substituted, unsubstituted or covalently linked to one or more cations to give dicationic, tricationic or polymeric cationic species.

**[0048]** Preferably the ionic liquid of the invention comprises a cationic portion, which comprises a cation of imidazolium type of Formula I



(I)

wherein $R^1$, $R^2$ and $R^3$ independently of each other are H or $C_1$-$C_6$, preferably H or $C_1$-$C_2$, and $R^4$ and $R^5$ independently of each other are H or $C_1$-$C_8$. Another preferred ionic liquid of the invention comprises a cationic portion, which comprises a cation of pyridinium type of Formula II



(II)

wherein $R^1$, $R^2$, $R^3$ and $R^4$ independently of each other are H or $C_1$-$C_6$, preferably H or $C_1$-$C_2$, and $R^5$ and $R^6$ independently of each other are H or $C_1$-$C_8$. The side chain functionalities of the compounds of Formula I or II are cyclic or acyclic and the imidazolium is preferably di- or trisubstituted. The pyridinium is prefereably mono- or di-substituted. The cation structures are drawn as the canonical resonance hybrid structures and are assumed to encompass the contributing canonical resonance structures.

**[0049]** Imidazole based ionic liquids are one preferred type of ionic liquids that can be used according to the present invention. In another preferred type of ionic liquids the imidazole is replaced with a pyridinium cation, as a low cost heterocycle.

**[0050]** Examples of ionic liquid cations according to the invention, which depending on the lignocellulosic material and the treatment and conditions used are preferred, comprise 1-butyl-3-methylimidazolium ([bmim]$^+$), 1-allyl-3-methylimidazolium ([amim]$^+$), 1-methyl-3-methylimidazolium ([emim]$^+$), 1,3-dimethylimidazolium ([mmim]$^+$), 1-hydrogen-3-methylimidazolium ([hmim]$^+$), 1-benzyl-3-methylimidazolium ([bnmim]$^+$), 1-(2-hydroxyethyl)-3-methylimidazolium ([hemim]$^+$), 1-propyl-3-methylimidazolium ([prmim]$^+$), 1-isopropyl-3-methylimidazolium ([$^i$prmim]$^+$), 1,2,3-trimethylimidazolium ([mmmim]$^+$), 1-ethyl-2,3-dimethylimidazolium ([emmim]$^+$), 2-ethyl-1,3-dimethylimidazolium ([memim]$^+$), 1-allyl-2,3-dimethylimidazolium ([ammim]$^+$), and 1-vinyl-3-methylimidazolium ([vmim]$^+$), 1-methylpyridinium ([mPyr]$^+$), 1-ethylpyridinium ([ePyr]$^+$), 1-propylpyridinium ([prPyr]$^+$), 1-isopropylpyridinium ([$^i$prPyr]$^+$), 1-allylpyridinium ([aPyr]$^+$), 1-butylpyridinium ([bPyr]$^+$), 1-vinylpyridinium ([vPyr]$^+$), 1-benzylpyridinium ([bnPyr]$^+$), 1-hydrogenpyridinium ([HPyr]$^+$), 1-(2-hydroxyethyl)pyridinium ([hePyr]$^+$), 1,3-dimethylpyridinium ([mmPyr]$^+$), 1-methyl-3-methylpyridinium ([emPyr]$^+$) or other homologues or regioisomers of imidazolium or pyridinium cations.

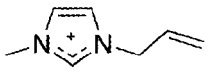
**[0051]** A list of some structures of preferred examples of ionic liquid cations, useful according to the invention is presented below. The structures are shown as their canonical resonance hybrids.



[mmim]$^+$



[emim]$^+$



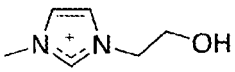
[amim]$^+$



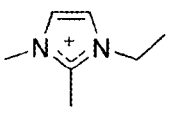
[Hmim]$^+$



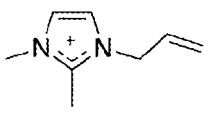
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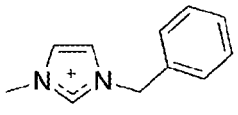
[hemim]$^+$



[emmim]$^+$



[ammim]$^+$



[bnmim]$^+$



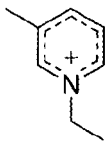
[mPyr]$^+$



[aPyr]$^+$



[hePyr]$^+$



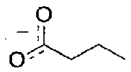
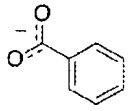
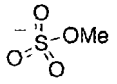
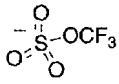
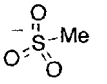
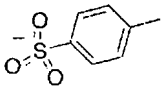
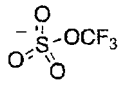
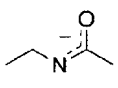
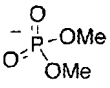
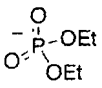
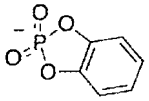
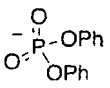
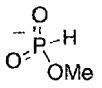
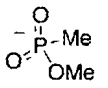
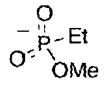
[emPyr]$^+$

**[0052]** The anionic portion of ionic liquids typically comprises one or more inorganic moieties, one or more organic moieties, or combinations thereof. The anionic portion of the ionic liquid according to the invention can depending on the lignocellulosic material and the treatmentand conditions chosen comprise one or more portions selected from halogens, phosphates, alkylphosphates, arylphosphates, alkylphosphonates, arylphosphonates, partially halogenated or perhalogenated alkylphosphates, such as $(CF_3CF_2O)_2PO_2^-$ or $(CF_3CF_2O)(CH_3CH_2O)PO_2^-$, partially halogenated or perhalogenated alkylphosphonates, such as $CF_3CF_2HPO_3^-$ or $CF_3CF_2FPO_3^-$, partially halogenated or perhalogenated alkylsulfates, such as $CF_3CF_2SO_4^-$ or $CF_3SO_4^-$, partially halogenated or perhalogenated alkylsulfonates, such as $CF_3CF_2SO_3^-$ or $CF_3SO_3^-$, bis(trifluoromethylethylsulphonyl)imide, $BF_4^-$, $PF_6^-$, $AsF_6^-$, $NO_3^-$, $N(CN)_2^-$, $N(SO_3CF_3)_2^-$, amino acids, substituted or unsubstituted carboranes, perchlorates, pseudohalogens such as cyanides, thiocyanates, cyanates, fulminates, azides, alkylsulfonates, tosylates, triflates alkylsulfates and perfluorinated alkylsulfates, a combination of anions with metal chloride-based Lewis acids (e.g. zinc dichloride, indium trichloride or aluminium trichloride) or $C_{1-8}$ carboxylatessuch as formate, acetate, propionate, butyrate, valerate, pivalate, hexanoate, heptanoate, octanoate, maleate, fumarate, oxalate, lactate, pyruvate, tartarate and their isomers.

**[0053]** According to a preferred embodiment of the invention the anionic portion of the invention is chosen from a list consisting of phosphate, diphosphate, phosphonate, carboxylate, halides, sulphonate, sulphate or perfluorinated alkylphosphate or combinations thereof.

**[0054]** Examples of ionic liquid anions, which depending on the lignocellulosic material and the treatment and conditions used may be used according to the invention, include chloride ($Cl^-$), bromide ($Br^-$), iodide ($I^-$), formate ($HCOO^-$), acetate ($AcO^-$), propanoate ($C_2H_5COO^-$), butyrate ($C_3H_7COO^-$), pivalate ($Me_3CCOO^-$), valerate ($C_4H_9COO^-$), hexanoate ($C_5H_{11}COO^-$), benzoate ($PhCOO^-$), methylsulfate ($MeSO_4^-$), ethylsulfate ($EtSO_4^-$), propylsulfate ($PrSO_4^-$), isopropylsulfate ($^iPrSO_4^-$), butylsulfate ($BuSO_4^-$), phenyl sulfate ($PhSO_4^-$), *p*-tolylsulfate (*p*-$TolSO_4^-$), xylenesulfate ($MeSO_4^-$), benzylsulfate ($BnSO_4^-$), trifluoromethylsulfate ($CF_3SO_4^-$), methylsulfonate ($MeSO_3^-$), ethylsulfonate ($EtSO_3^-$), propylsulfonate ($PrSO_3^-$), isopropylsulfonate ($^iPrSO_3^-$), butylsulfonate ($BuSO_3^-$), phenylsulfonate ($PhSO_3^-$), *p*-tolylsulfonate ($TsO^-$), xylenesulfonate ($MeSO_4^-$), benzylsulfonate ($BnSO_3^-$), trifluoromethylsulfonate ($CF_3SO_3^-$), methylacetamide ($MeAcN^-$), ethylacetamide (EtAcN), dimethylphosphate ($Me_2PO_4^-$), diethylphosphate ($Et_2PO_4^-$), methylethylphosphate ($EtMePO_4^-$), dipropylphosphate ($Pr_2PO_4^-$), diisopropylphosphate ($Pr^i_2PO_4^-$), catecholmonophosphate ($CatPO_4^-$), diphenylphosphate ($Ph_2PO_4^-$), methylhydrogenphosphonate ($MeHPO_3^-$), ethylhydrogenphosphonate ($EtHPO_3^-$), propylhydrogenphosphonate ($PrHPO_3^-$), isopropylhydrogenphosphonate ($Pr^iHPO_3^-$), dimethylphosphonate ($Me_2PO_3^-$), diethylphosphonate ($Et_2PO_3^-$), dipropylphosphonate ($Pr_2PO_3^-$), diisopropylphosphonate ($Pr^i_2PO3^-$), *O*-ethyl-*P*-methylphosphonate ($MeEtPO_3^-$), *O*-methyl-*P*-ethylphosphonate ($EtMePO_3^-$), or related structures.

**[0055]** A list of some structures of preferred examples of ionic liquid anions, according to the invention is presented below. The structures are shown as their canonical resonance hybrids.

| | | | |
|---|---|---|---|
| $Cl^-$ | $Br^-$ | $I^-$ |  |
| | | | $HCOO^-$ |
|  |  |  |  |
| $AcO^-$ | $C_2H_5COO^-$ | $C_3H_7COO^-$ | $PhCOO^-$ |
|  |  |  |  |
| $MeSO_4^-$ | $MeSO_4^-$ | $MeSO_3^-$ | $TsO^-$ |
|  |  |  |  |
| $MeSO_3^-$ | $MeAcN^-$ | $EtAcN^-$ | $Me_2PO4^-$ |
|  |  |  |  |
| $Et_2PO_4^-$ | $EtMePO_4^-$ | $CatPO_4^-$ | $Ph_2PO_4^-$ |
|  |  |  |  |

(continued)

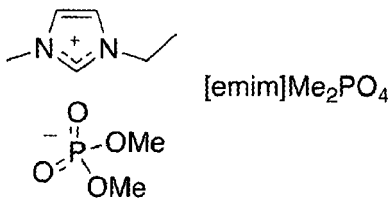
$MeHPO_3^-$ $ETHPO_3^-$ $Me_2PO_3^-$ $MeEtPO_3^-$

**[0056]** The above lists of possible cations and anions according to the invention is not intended to be an exhaustive listing of all possible cationic and anionic portions. A variety of ionic liquids can be prepared and used according to the present invention by combining one or more cations with one or more anions to form ionic liquid.

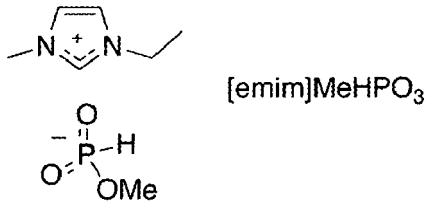
**[0057]** Some preferred ionic liquids, according to the present invention, are for example: 1-allyl-3-methylimidazolium dimethylphosphate 1,3-dimethylimidazolium dimethylphosphate; 1-ethyl-3-methylimidazolium dimethylphosphate, 1-allyl-3-methylimidazolium methylhydrogenphosphonate 1,3-dimethylimidazolium methylhydrogenphosphonate; 1-ethyl-3-methylimidazolium methylhydrogenphosphonate, 1-allyl-3-methylimidazolium formate 1,3-dimethylimidazolium formate; 1-ethyl-3-methylimidazolium formate, 1-allyl-3-methylimidazolium acetate 1,3-dimethylimidazolium acetate; 1-ethyl-3-methylimidazolium acetate, 1-allyl-3-methylimidazolium propionate 1,3-dimethylimidazolium propionate; 1-ethyl-3-methylimidazolium propionate, 1-allylpyridinium dimethylphosphate, 1-ethylpyridinium dimethylphosphate, 1-methylpyridinium dimethylphosphate, 1-allylpyridinium methylhydrogenphosphonate, 1-ethylpyridinium methylhydrogenphosphonate, 1-methylpyridinium methylhydrogenphosphonate, 1-allylpyridinium formate, 1-ethylpyridinium formate, 1-methylpyridinium formate, 1-allylpyridinium acetate, 1-ethylpyridinium acetate, 1-methylpyridinium acetate, 1-allylpyridinium propionate, 1-ethylpyridinium propionate, 1-methylpyridinium propionate

**[0058]** According to preferred embodiments of the present invention the ionic liquid(s) of the invention comprises the use of various ionic liquids incorporating acetates, phosphates and phosphonates as the anionic portion and dialkylimidazoliums as the cationic portion. In other preferred embodiments, the ionic liquids useful according to the invention encompass pyridinium halides, pyridinium carboxylates, pyridinium phosphates or pyridinium phosphonates.

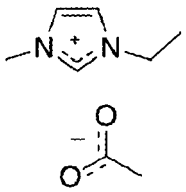
**[0059]** Examples of specific preferred examples of the present invention are 1-ethyl-3-methylimidazolium dimethylphosphate ([emim]$Me_2PO_4$), 1-ethyl-3-methylimidazolium methylphosphonate ([emim]$MeHPO_3$) and 1-ethyl-3-methylimidazolium acetate ([emim]OAc).



[emim]$Me_2PO_4$

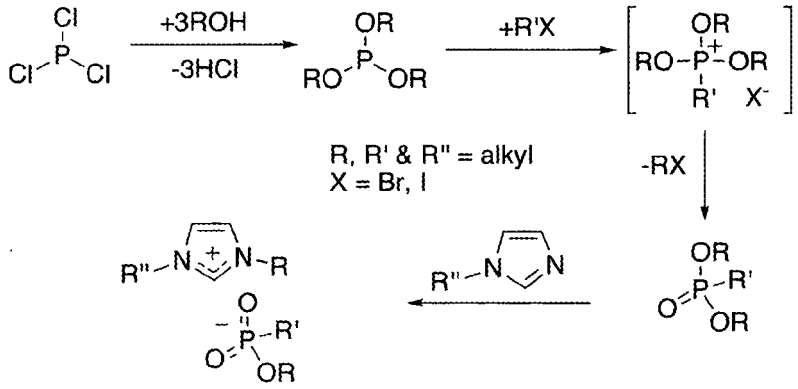


[emim]$MeHPO_3$



[emim]OAc

**[0060]** Based on the description it is clear how to arrive at still further ionic liquids for the ionic liquid treatment according to the invention by combining one or more cations with one or more anions to form a ionic liquid. Multiple heterocyclic or acyclic ionic liquids could be used as well. It is further known that dicationic materials exhibit increased thermal stability and are thus useful in embodiments, where it is desirable to carry out the treatment of the lignocellulosic materials at increased temperatures. Dicationic ionic liquids can be prepared using any combination of cations and anions, such as those described above. For example, imidazoles and pyridines could be used in preparing dicationic ionic liquids in a similar manner as described for ionic liquids having only a single cationic moiety. Ionic liquids are typically relatively easy to prepare by known syntheses. For the synthesis of a ionic liquid based on imidazolium phosphates or phosphonates the Menschutkin reaction (amine quaternization), where a substituted imidazole is reacted with a trialkylphosphate or dialkylhydrogenphosphonate (dialkylphosphite) or trialkylphosphonate, is generally used. Related compounds can be prepared by transesterification of phosphites, phosphates or phosphonates starting with alcohols, such as, partially fluorinated or perfluorinated alcohols, allyl alcohol, propargyl alcohol, phenol or higher chain homologues with differing degrees of unsaturation. In the synthesis of trialkylphosphonates, further variation in substitution may be accessed, by employing the Michaelis-Arbuzov reaction (shown below), by starting from easily accessible trialkylphosphite esters:




**[0061]** Phosphate and phosphonate based ionic liquids typically have lower viscosities compared to halide-based ionic liquids, which makes them particularly easy to use without the need for excessive heating.

**[0062]** Other preferred methods of forming ionic liquids comprises derivatization which involves functionalization of some existing molecular heterocyclic or acyclic compound with a substituent or it involves anion metathesis where an existing anion of an ionic liquid is replaced or reacted with a reagent leaving another anion in its place. This may give a completely new pure ionic liquid, or an ionic liquid, which contains a mixture of anions and cations. A further preferred method of ionic liquid preparation involves direct mixing of two pure salts to give a molten salt or ionic liquid mixture. Yet another method of ionic liquid preparation involves direct mixing of a pure salt with a non-ionic (molecular) compound, to afford an ionic liquid or eutectic mixture with high ionic character. Such compounds are not typically thought of as ionic liquids, but are herein referred to as ionic liquids.

**[0063]** The invention further relates to the use of various mixtures of ionic liquids. In fact, ionic liquid mixtures can be useful for providing mixtures having customized physiochemical properties, such as viscosity or ability to process different materials, according to the present invention. For example, 1-benzyl-3-methylimidazolium dimethylphosphate ([bnmim] $Me_2PO_4$) is a relatively viscous ionic liquid, however, its viscosity can be significantly reduced by mixing it with another ionic liquid such as [emim]$MeHPO_3$. The viscosity of the ionic liquid mixture can thus be adjusted by varying the ratio between the more viscous component and the less viscous component.

**[0064]** According to a further embodiment of the invention various pure ionic liquids or ionic liquid mixtures are mixed with additives, such as molecular solvents, preferably inorganic or organic solvents and/or an organic acid or base. Typical solvents are polar aprotic solvents such as dimethylsulfoxide (DMSO) in small quantities (< 20 %). DMSO is a cheap and non-toxic solvent. It can also be easily produced as a side stream from Kraft chemical pulping of lignocelluloses. Pressurized $CO_2$ and water may also be added to moderate the process.

**[0065]** Figure 1 shows one embodiment of the process according to the invention. The lignocellulosic material is a typical pulpwood feedstock, and the process involves chipping debarked wood (1) to give wood chips (2) of the appropriate size. The chips may also be extracted with a solvent, such as acetone, to further dry the sample or remove extractives. The wood chips (2) are fibrillated in ionic liquid media with heating and mechanical treatment to give the fibres in ionic liquid media (3). This material is diluted with the appropriate amount of solvent, such as methanol, and filtered to give the "wet" fibres (4). The filtrate solution, which can be a mixture of ionic liquid, polysaccharides (pectins and/or hemicelluloses) and extractives (7), is retained. The "wet" fibres may be further treated with a solvent at elevated temperatures to remove any remaining traces of ionic liquid from the fibres. The mixture is again filtered and dried to give dried fibres (5), the yield of which will be typically 90-95 %. The filtrate from the second filtration step is combined with the solution of ionic liquids, polysaccharides (pectins and/or hemicelluloses) and extractives. Any polysaccharides or extractives (9) may be recovered in 5-10 % yield by a suitable method such as filtration and/or membrane filtration. The remaining ionic liquid and solvent (8) is treated by evaporation and/or pervaporation as a final step in recycling the ionic liquid and molecular solvents.

**[0066]** The dried fibre (5) product of Fig. 1 may be treated further (6). The further treatment, involves for example a sequence of chemical modification steps, such as one or more of bleaching, mild pulping, esterification, etherification or further extraction using additional solvents such as supercritical-$CO_2$ extraction (sc-$CO_2$), pressurized hot water extraction (PHWE), traditional molecular solvent extraction or additional ionic liquid extraction. The isolated polysaccharides and extractives (9) are optionally further separated (10) using techniques such as solvent and chemical extraction, membrane filtration (nanofiltration, ultrafiltration) or selective precipitation.

**[0067]** The following examples are given to further illustrate the invention. Based on the above description a person skilled in the art will be able to modify the invention in many ways to provide increased efficiency of fibrillation, pulping, fractionation or novel materials based on chemical functionalization of the novel fibrillated material.

**Example 1, Preparation of 1-methyl-3-methylimidazolium dimethylphosphate ([mmim]$Me_2PO_4$)**

**[0068]** A mixture of 1-methylimidazole (50 ml, 0.519 mol) was added over a space of 4 hrs to trimethylphosphate (60.7 ml, 0.519 mol) at 100 °C, with stirring. The solution was heated at 100 °C for a further 18 hrs. The reaction of the mixture was determined to be complete by analyzing a sample by $^1$H NMR from $CDCl_3$. The mixture was rotary evaporated under high vacuum for 18 hrs to give a pale yellow oily product (110 ml). The purity of the product was determined to be > 99% by $^1$H NMR analysis.

**Example 2, Preparation of 1-ethyl-3-methylimidazolium dimethylphosphate ([emim]Me2$PO_4$)**

**[0069]** A mixture of 1-ethylimidazole (50 ml, 0.519 mol) was added over a space of 4 hrs to trimethylphosphate (60.7 ml, 0.519 mol) at 120 °C with stirring. The solution was heated at 120 °C for a further 18 hrs. The reaction of the mixture was determined to be complete by analyzing a sample by $^1$H NMR from $CDCl_3$. The mixture was rotary evaporated under high vacuum for 18 hrs to give a pale yellow oily product (110 ml). The purity of the product was determined to be > 99% by $^1$H NMR analysis.

**Example 3, Preparation of 1-ethyl-3-methylimidazolium methylhydrogenphosphonate ([emim]$MeHPO_3$)**

**[0070]** A mixture of 1-ethylimidazole (50 ml, 0.519 mol) was added over a space of 4 hrs to diethylphosphite (47.6 ml, 0.519 mol) at 140 °C with stirring. The solution was heated at 140 °C for a further 18 hrs. The reaction of the mixture was determined to be complete by analyzing a sample by $^1$H NMR from $CDCl_3$. The mixture was rotary evaporated under high vacuum for 18 hrs to give a pale yellow oily product (97 ml). The purity of the product was determined to be > 99% by $^1$H NMR analysis.

**Examples 4-39, Fibrillation of soft and hardwood chips in different ionic liquids**

**[0071]** Fibrillation capability was assessed for a series of ionic liquids and wood species. Some specific examples of ionic liquids, capable of efficiently fibrillating lignocellulose, are chosen from a series of ionic liquids that were screened in a methodical manner. Screening involved varying both the cation and anion structures of the ionic liquids. Screening was also assessed against a selection of hardwoods, such as birch, aspen and oak, and softwoods, such as such as pine and spruce. The results are presented in Table 1.

**[0072]** The fibrillation experiments were performed in one of the following ways:

Pine, spruce (softwood) ,birch or aspen (hardwood) chips (ca. 2.5 cm x 1 cm x 0.2 mm) were soaked for 2 days at room temperature in acetone, in order to remove extractives and partially dry the material. The chips were then dried in an oven at 105 °C. Extracted and dried wood chips (2 g) in ionic liquid (20 ml) were heated without agitation between 95 - 110 °C for 18 - 66 hr in ionic liquid. Hardwoods required higher temperatures. Methanol (40 ml) was added to the mixture and the fibres were filtered. The fibres were thoroughly washed with further methanol and dried in an oven at 105 °C for 18 hrs to give pale cream coloured fibres as product (1.9 g). The ability of different ionic liquids to fibrillate different wood samples is presented in Table 1.

**Table 1,** The efficiency of fibrillation for different wood species with different ionic liquid structures, Examples 4-39.

| Example | Ionic Liquid | Preparation | Fibrillation Efficiency[a] |
|---|---|---|---|
| 4 | [mmim]$Me_2PO_4$ | According to Ex. 1 | +++ (Softwood) |
| 5 | [amim]Cl | Synthesized | ++ (gels) (Softwood) |
| 6 | [amim]Br | Synthesized | - (Softwood) |
| 7 | [amim]$Me_2PO_4$ | Synthesized | +++ (Softwood) |
| 8 | [emim]Cl | Merck | - (Softwood) |
| 9 | [emim]$Me_2PO_4$ | According to Ex. 2 | +++++(Softwood) |
| 10 | [emim]$Et_2PO_4$ | Synthesized | ++++ (Softwood) |
| 11 | [emim]SCN | Merck | - (Softwood) |
| 12 | [emim]$MeHPO_3$ | According to Ex. 3 | +++++ (Softwoods) [No darkening of fibres] |
| 13 | [emim]$EtHPO_3$ | Synthesized | +++ (Softwood) |
| 14 | [emim]$HSO_4$ | Merck | - (Softwood) |

(continued)

| Example | Ionic Liquid | Preparation | Fibrillation Efficiency[a] |
|---|---|---|---|
| 15 | $[emim]MeSO_4$ | Iolitec | -(Softwood) [Darkening of solution and fibres] |
| 16 | [emim]OTs | Iolitec | - (Softwood) |
| 17 | [emim]OAc | Iolitec | ++++ (Hard and Softwoods) |
| 18 | $[emim]Me_2PO_3$ | Synthesized | - (Softwood) |
| 19 | $[eeim]Et_2PO_4$ | Synthesized | ++ (Softwood) |
| 20 | $[mmmim]Me_2PO_4$ | Synthesized | ++ (Softwood) |
| 21 | [emmim]Cl | Synthesized | - (Softwood) |
| 22 | $[emmim]Et_2PO_4$ | Synthesized | +++ (Softwood) |
| 23 | $[prmim]Me_2PO_4$ | Synthesized | +++ (Softwood) |
| 24 | $[^{i}prmim]Pr^{i}_2PO_4$ | Synthesized | + (Softwood) |
| 25 | $[bmim]Me_2PO_4$ | Synthesized | ++ (Softwood) |
| 26 | $[bmim]HSO_4$ | Merck | - (Softwood) |
| 27 | $[omim]OctSO_4$ | Merck | - (Softwood) |
| 28 | [hemim]Cl | Iolitec | - (Softwood) |
| 29 | [Hmim]Cl | BASF | - (Softwood) |
| 30 | $P_{4444}Cl$ | Iolitec | - (Softwood) |
| 31 | $P_{14444}Cl$ | Iolitec | - (Softwood) |
| 32 | $P_{14666}Cl$ | Iolitec | - (Softwood) |
| 33 | $P_{4442}Et_2PO_4$ | Iolitec | - (Softwood) |
| 34 | $P4_{441}OTs$ | Iolitec | - (Softwood) |
| 35 | $[HTMG]OCOC_2H_5$ | Synthesized | - (Softwood) |
| 36 | $[PMG]Me_2PO_4$ | Synthesized | -(Softwood) |
| 37 | $[PMG]MeHPO_3$ | Synthesized | - (Softwood) |
| 38 | $[eTMG]EtHPO_3$ | Synthesized | - (Softwood) |
| 39 | $[mPyr]MeHPO_3$ | Synthesized | ++ (Softwood) |

[a] efficiency of fibrillation: +++++ (strong fibrillation), - (no fibrillation)

**[0073]** The chemical names of the ionic liquids of examples 4 to 39:

4. $[mmim]Me_2PO_4$ - 1,3-dimethylimidazolium dimethylphosphate
5. [amim]Cl - 1-allyl-3-methylimidazolium chloride
6. [amim]Br- 1-allyl-3-methylimidazolium bromide
7. $[amim]Me_2PO_4$-1-allyl-3-methylimidazolium dimethylphosphate
8. [emim]Cl - 1-ethyl-3-methylimidazolium chloride
9. $[emim]Me_2PO_4$ - 1-ethyl-3-methylimidazolium dimethylphosphate
10. $[emim]Et_2PO_4$ - 1-ethyl-3-methylimidazolium diethylphosphate
11. [emim]SCN - 1-ethyl-3-methylimidazolium thiocyanate
12. $[emim]MeHPO_3$- 1-ethyl-3-methylimidazolium methylhydrogenphosphonate
13. $[emim]EtHPO_3$ - 1-ethyl-3-methylimidazolium ethylhydrogenphosphonate
14. $[emim]HSO_4$- 1-ethyl-3-methylimidazolium hydrogensulfate
15. $[emim]MeSO_4$ - 1-ethyl-3-methylimidazolium methylsulfate
16. [emim]OTs - 1-ethyl-3-methylimidazolium tosylate
17. [emim]OAc - 1-ethyl-3-methylimidazolium acetate
18. $[eeim]Et_2PO_4$- 1,3-diethylimidazolium diethylphosphate
19. $[mmmim]Me_2PO_4$ -1,2,3-trimethylimidazolium dimethylphosphate
20. [emmim]Cl - 1-ethyl-2,3-dimethylimidazolium diethylphosphate
21. $[emim]Me_2PO_3$ - 1-ethyl-3-methylimidazolium methylmethylphosphonate
22. $[emmim]Et_2PO_4$- 1,2,3-trimethylimidazolium diethylphosphate
23. $[prmim]Me_2PO_4$- 1-propyl-3-methylimidazolium dimethylphosphate
24. $[^{i}prmim]Pr^{i}_2PO_4$ - 1-isopropyl-3-methylimidazolium dimethylphosphate

25. [bmim]$Me_2PO_4$ - 1-butyl-3-methylimidazolium dimethylphosphate
26. [bmim]$HSO_4$ - 1-butyl-3-methylimidazolium hydrogensulfate
27. [omim]$OctSO_4$ - 1-octyl-3-methylimidazolium octylsulfate
28. [hemim]Cl - 1-(2-hydroxyethyl)-3-methylimidazolium chloride
29. [Hmim]Cl - 1-methylimidazoliumhydrogen chloride
30. $P_{4444}Cl$ - tetrabutylphosphonium chloride
31. $P_{14444}Cl$ - tetradecyltributylphosphonium chloride
32. $P_{14666}Cl$ - tetradecyltrihexylphosphonium chloride
33. $P_{4442}Et_2PO_4$ - ethyltributylphosphonium diethylphosphate
34. $P_{4441}OTs$ - methyltriisobutylphosphonium tosylate
35. [HTMG]$OCOC_2H_5$-tetramethylguanidiniumhydrogen propionate
36. [PMG]$Me_2PO_4$ - pentamethylguanidinium dimethylphosphate
37. [PMG]$MeHPO_3$ - pentamethylguanidinium methylhydrogenphosphonate
38. [eTMG]$EtHPO_3$ - ethyltetramethylguanidinium ethylhydrogenphosphonate
39. [mPyr]$MeHPO_3$ - methylpyridinium methylhydrogenphosphonate

**[0074]** It was determined that [emim]$MeHPO_3$ was the most preferred ionic liquid tested for fibrillating softwoods such as pine and spruce, while [emim]OAc was also capable of fibrillating hardwoods such as Birch, Aspen and Oak (at 95 °C over 18 hr). The combination of [emim]$MeHPO_3$ with softwoods under milder conditions (110 °C over 18 hr) was able to produce fibres with no significant darkening, characteristic of dehydration and lignin oxidation, in comparison to the starting wood material. Ionic liquids such as [emim]$Me_2PO_4$ and [mmim]$Me_2PO_4$ fibrillated softwood under harsher conditions (110 °C up to 3 days) and yielded fibres that were more colourized than the [emim]$MeHPO_3$ fibrillated samples. Although all of the above combinations in these particular examples of on one hand lignocellulosic material (the specific softwood or hardwood species) and on the other hand ionic liquid and treatment conditions did not lead to fibrillation, also these ionic liquids are believed to fibrillate other lignocellulosic materials according to the process of the invention.

**Example 40, Total sugar analysis of fibrillated pine wood chips, after treatment with [mmim]$Me_2PO_4$.**

**[0075]** Pine was treated with [mmim]$Me_2PO_4$ (according to Examples 1 and 4) and analysed by total sugar analysis (Table 2).

**Table 2,** Total sugar analysis, according to methods detailed in DOI10.1007/s00226-005-0039-4, of fibrillated pine wood chips, after treatment with [mmim]$Me_2PO_4$. Values are relative against internal standards.

| Monomer | Wood Chips | Fibrillated Sample 1 | Fibrillated Sample 2 | Average Fibrillated Sample | Late Wood |
|---|---|---|---|---|---|
| Arabinose | 11 | 9 | 9 | 9 | 10 |
| Xylose | 51 | 52 | 59 | 56 | 62 |
| Rhamnose | 2.1 | 1.1 | 0.8 | 1.0 | 0.8 |
| Glucuronic Acid | 0.0 | 0.4 | 0.6 | 0.5 | 0.3 |
| Galacturonic Acid | 10.2 | 1.7 | 2.1 | 1.9 | 2.6 |
| Mannose | 106 | 87 | 97 | 92 | 112 |
| Galactose | 15 | 23 | 12 | 17 | 14 |
| Glucose | 37 | 47 | 56 | 52 | 65 |
| 1,4-bis-O-MeGlcA | 3.6 | 2.8 | 2.6 | 2.7 | 2.4 |
| Unknown | 1.4 | 1.1 | 1.0 | 1.1 | 0.9 |
| Unknown | 0.7 | 0.6 | 0.8 | 0.7 | 0.8 |
| **Total** | 239 | 225 | 242 | 234 | 270 |

**[0076]** It was determined that a large portion of galacturonic acid residues were missing, indicating extraction of pectins. This indicates that pectins, which are present in the lumen of woody material, acts as a binder for adjacent tracheids. The ionic liquid residue was evaporated to dryness by rotary evaporation to be submitted for $^{31}P$ NMR analysis. This involved functionalization of the remaining hydroxyl groups as phosphite esters and observing the resulting $^{31}P$ resonances according to Fig. 2, wherein (1) shows the internal standard, (2) the methyl (methanol) phosphite ester resonance, (3) the aliphatic (alcohol) phosphite ester resonance region, (4) the guiacyl (phenol) phosphite ester resonance region and (5) a carboxylate phosphite mixed anhydride (carboxylic acid) resonance region.

**[0077]** Using this technique it was possible to determine that there was a very low lignin content in the material that was extracted. This is evident from the lack of lignin guiacyl phenolic resonances (5) against both internal standard (1) and aliphatic resonances (3). The small (5 %) weight loss of the fibres also indicated that lignin was not being extracted to any significant degree. Moreover, due to the mild nature of the treatment, the extracted pectins are thought not to be covalently linked to lignin. Lignin is also present in its highest concentration in the lumen.

**Example 41, Fatty acid (oleic acid) surface modification of fibrillated pine**

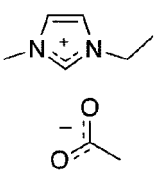
**[0078]** Pyridine (1 ml) and oleoyl chloride (1 ml) were added to a solution of ionic liquid fibrillated pine (360 mg) in dioxane (12 ml). The mixture was heated in an oil bath with stirring at 90 °C for 18 hrs. The resulting fibers were filtered, washed with toluene and hot methanol. The fibres were dried at 105 °C for 18 hrs to obtain pale cream coloured fibres as product (900 mg). The product was hydrophobic to the extent that it floated on water, even after agitation. The ATR-IR spectra showed a high ratio of C=O to OH stretch indicating a high degree of substitution as fatty acid ester.

**[0079]** The present invention has been described herein with reference to specific embodiments. It is however clear to those skilled in the art that the process(es) may be varied within the bounds of the claims.

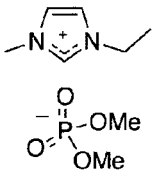
## Claims

1. A process for fibrillating lignocellulosic material, **characterized in that** said process comprises

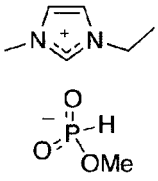
   a) treating lignocellulosic material with ionic liquid selected from a list consisting of



[emim]OAc



[emim]$Me_2PO_4$



[emim]$MeHPO_3$

   and

   b) recovering basically intact fibres of said lignocellulosic material.

2. The process according to claim 1 wherein said treating is performed by heating.

3. The process according to claim 2 wherein said heating is performed at temperatures between 20°C and 150°C.

4. The process according to any of the preceding claims further comprising c) physical or chemical modification of the basically intact fibres.

5. The process according to any one of the preceding claims **characterized in that** the average 2D aspect ratio of said basically intact fibre is at least 5, more preferably at least 20 and most preferably at least 50.

6. A basically intact fibre obtained by the process according to any of claims 1 to 5.

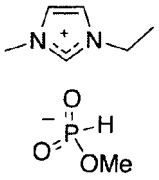
7. The basically intact fibre of claim 6 **characterized in that** the surface area of the fibre is increased.

8. The basically intact fibre of claims 6 or 7 **characterized in that** the average 2D aspect ratio of said basically intact fibre is at least 5, more preferably at least 20 and most preferably at least 50.

9. The basically intact fibre of any of claims 6 to 8 **characterized in that** said lignocellulosic material is activated during the ionic liquid treatment and/or modified after recovery of the fibre from the ionic liquid.

10. Use of the basically intact fibre of claim 6 to 9 in the production of paper, board, pulp or the like or in the production of bio-based materials, preferably bio-plastics, more preferably conductive polymers, stimuli-responsive polymers, bio-based polymer composites, ceramics, fabrics, or elastomers.

11. Use of



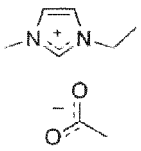
[emim]MeHPO$_3$

for treating lignocellulosic material.

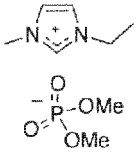
**Patentansprüche**

1. Ein Verfahren zum Fibrillieren von Lignocellulosematerial, **dadurch gekennzeichnet, dass** das Verfahren umfasst

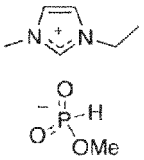
a) Behandeln von Lignocellulosematerial mit ionischer Flüssigkeit, ausgewählt aus einer Liste bestehend aus



[emim]OAc



[emim]Me$_2$PO$_4$



[emim]MeHPO$_3$

oder

und
b) Gewinnen im Wesentlichen intakter Fasern des Lignocellulosematerials.

2. Das Verfahren nach Anspruch 1, wobei das Behandeln durch Erwärmen durchgeführt wird.

3. Das Verfahren nach Anspruch 2, wobei das Erwärmen bei Temperaturen zwischen 20°C und 150°C durchgeführt wird.

4. Das Verfahren nach einem der vorhergehenden Ansprüche, weiter umfassend c) physikalisches oder chemisches Modifizieren der im Wesentlichen intakten Fasern.

5. Das Verfahren nach einem der vorhergehenden. Ansprüche, **dadurch gekennzeichnet**, das das mittlere 2D-Seitenverhältnis der im Wesentlichen intakten Faser mindestens 5, stärker bevorzugt mindestens 20 und am meisten bevorzugt mindestens 50 beträgt.

6. Eine im Wesentlichen intakte Faser, verhalten durch das Verfahren nach einem der Ansprüche 1 bis 5.

7. Die im Wesentlichen intakte Faser nach Anspruch 6, **dadurch gekennzeichnet, dass** der Oberflächenbereich der Faser vergrößert ist.

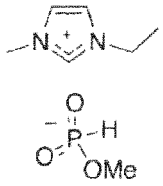
8. Die im Wesentlichen intakte Faser nach den Ansprüchen 6 oder 7, **dadurch gekennzeichnet, dass** das mittlere 2D-Scitenverhältnis der im Wesentlichen intakten Faser mindestens 5, stärker bevorzugt mindestens 20 und am meisten bevorzugt mindestens 50 beträgt.

9. Die im Wesentlichen intakte Faser nach einem der Ansprüche 6 bis 8, **dadurch gekennzeichnet, dass** das Ligi-

tocellulosematerial während der Behandlung mit ionischer Flüssigkeit aktiviert und/oder nach der Gewinnung der Faser aus der ionischen Flüssigkeit modifiziert wird.

**10.** Verwendung der im Wesentlichen intakten Faser nach Anspruch 6 bis 9 bei der Herstellung von Papier, Karton, Zellstoff oder dergleichen oder bei der Herstellung von biobasierten Materialien, vorzugsweise Biokunststoffen, stärker bevorzugt leitfähigen Polymeren, Stimuli-responsiven Polymeren, biobasieilen Polymerverbundstoffen, Keramik, Gewebe oder Elastomeren.

**11.** Verwendung von



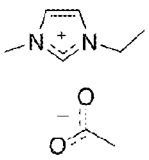
[emim]$MeHPO_3$

zur Behandlung von Lignocellulosematerial.

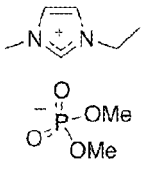
**Revendications**

**1.** Procédé de fibrillation de matière lignocellulosique, **caractérisé en ce que** ledit procédé comprend

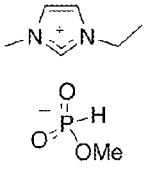
a) le traitement de la matière lignocellulosique avec un liquide ionique choisi dans la liste se composant de



[emim]OAc ,



[emim]$Me_2PO_4$ ou



[emim]$MeHPO_3$

et

b) la récupération de fibres sensiblement intactes de ladite matière lignocellulosique.

**2.** Procédé selon la revendication 1, dans lequel ledit traitement est réalisé par chauffage.

**3.** Procédé selon la revendication 2, dans lequel ledit chauffage est réalisé à des températures comprises entre 20 °C et 150 °C.

**4.** Procédé selon l'une quelconque des revendications précédentes comprenant en outre c) la modification physique ou chimique des fibres sensiblement intactes.

**5.** Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le rapport d'aspect 2D moyen de ladite fibre sensiblement intacte est d'au moins 5, plus préférablement d'au moins 20 et de manière préférée entre toutes d'au moins 50.

**6.** Fibre sensiblement intacte obtenue par le procédé selon l'une quelconque des revendications 1 à 5.

**7.** Fibre sensiblement intacte selon la revendication 6, **caractérisée en ce que** la surface de la fibre est augmentée.

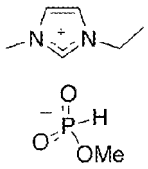
**8.** Fibre sensiblement intacte selon la revendication 6 ou 7, **caractérisée en ce que** le rapport d'aspect 2D moyen de ladite fibre sensiblement intacte est d'au moins 5, plus préférablement d'au moins 20 et de manière préférée entre toutes d'au moins 50.

**9.** Fibre sensiblement intacte selon l'une quelconque des revendications 6 à 8, **caractérisée en ce que** ladite matière

lignocellulosique est activée pendant le traitement avec un liquide ionique et/ou modifiée après la récupération de la fibre du liquide ionique.

**10.** Utilisation de la fibre sensiblement intacte selon l'une quelconque des revendications 6 à 9 pour la production de papier, carton, pâte ou analogue ou pour la production de biomatériaux, de préférence des bioplastiques, plus préférablement des polymères conducteurs, des polymères sensibles à des stimulus, des biocomposites polymères, des céramiques, des tissus ou des élastomères.

**11.** Utilisation de



[emim]$MeHPO_3$

pour le traitement d'une matière lignocellulosique.

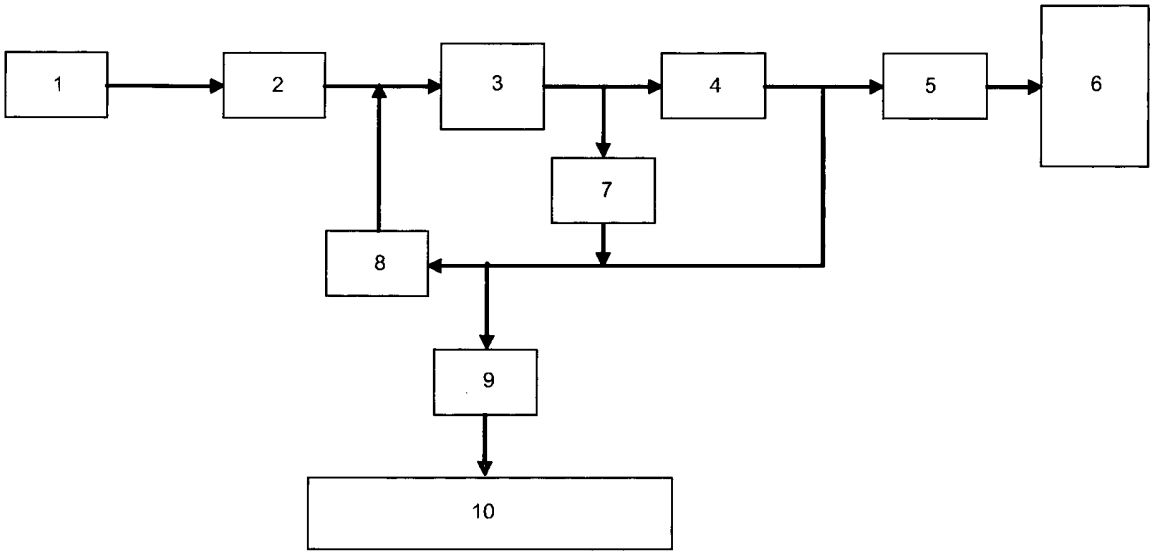



**Figure 1**

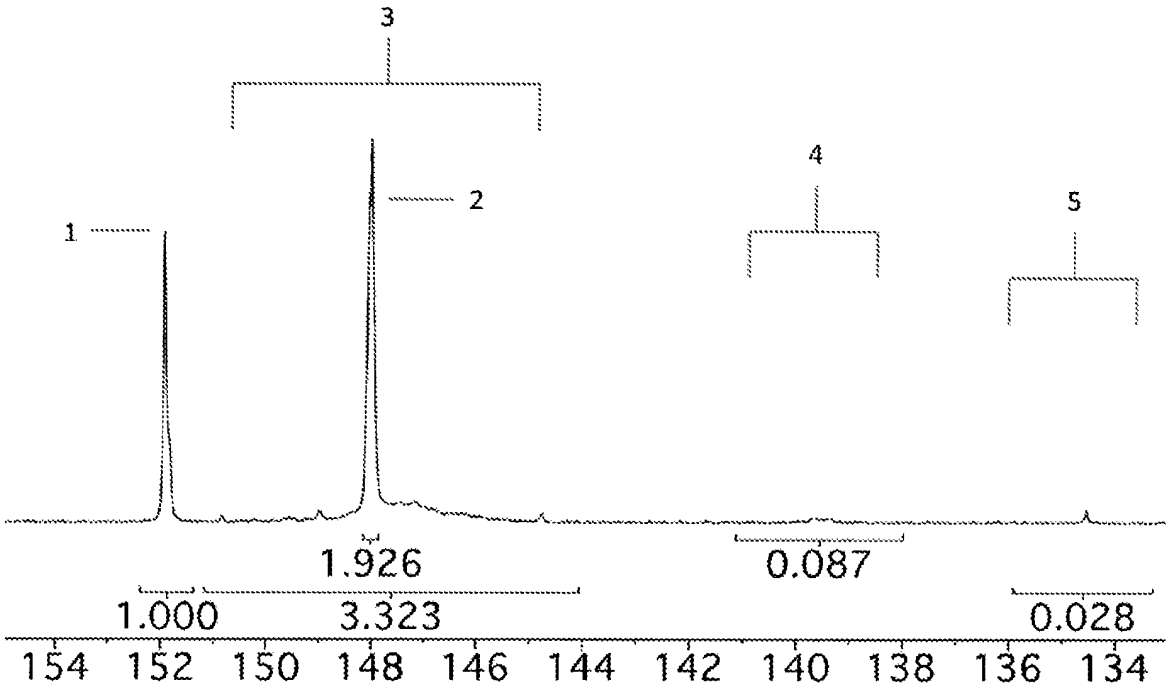

3
4
2
5
1
1.926
0.087
1.000
3.323
0.028
154 152 150 148 146 144 142 140 138 136 134

**Figure 2**

## REFERENCES CITED IN THE DESCRIPTION

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