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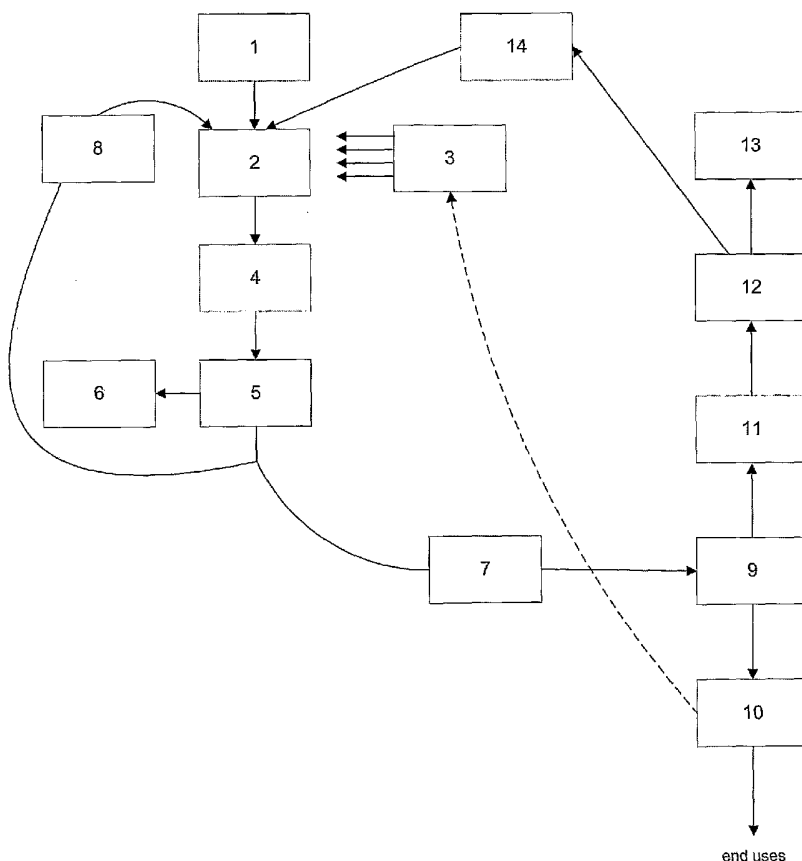
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(54) Title: SOLVENTS FOR USE IN THE TREATMENT OF LIGNIN-CONTAINING MATERIALS



(57) Abstract: A method for the treatment of a lignin-containing material such as wood pulp, bagasse and other plant-derived materials, comprising contacting the lignin-containing material with an ionic liquid to extract the lignin therefrom. The ionic liquid is suitably a substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, phosphonium or sulfonium salt of a substituted or unsubstituted aryl sulfonate, such as an ionic liquid salt of a xylene sulfonate.



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SOLVENTS FOR USE IN THE TREATMENT OF
LIGNIN-CONTAINING MATERIALS

Field of Invention

5 The present invention relates to solvents for use in the treatment of lignin-containing materials, including lignocellulosic materials. Such materials include plant matter and plant matter derivatives. The present
10 invention further relates to methods for extracting useful products from lignin-containing materials, including lignin and optionally other products, and the products obtained by such methods. The present invention additionally relates to new chemical species found to be
15 suitable for use in these processes.

Background of Invention

20 Plant products, which are ligno- and lignocellulosic materials, are used by man in the production of a number of different valuable commodities.

However, the lignocellulosic residues that are produced in large volumes from agricultural cropping of sugar, wheat, rice and corn, for example, are largely considered
25 of little value and, if not collected, are often plowed-in, burnt or otherwise discarded. Some efforts have been made to extract useful materials from such waste lignocellulosic material (biomass). Examples of these
30 processes utilize pretreatment with heat and chemicals followed by enzymatic digestion, or the application of concentrated mineral acids, to extract fermentable sugars and lignin. The derived sugars are intended to provide a feedstock for conversion into a renewable source of
35 greenhouse gas neutral liquid fuels such as ethanol, or other valuable industrial and fine chemicals. Processes contemplated to achieve this have a number of similarities to wood pulping processes, as they may involve

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fractionation and separation of the lignin content from the cellulose, although in the case of the biomass the digestion conditions are more extreme so as to also cause the ultimate breakdown of the cellulose content into smaller chemical products.

There is room for improvement on the known processes for the treatment of lignin-containing material, including the wood pulping methods (the kraft pulping method being most common) and the lignocellulosic biomass treatments.

Novel pulping processes should:

- Manage suitably prepared hardwood, softwood and herbaceous raw materials
- Not degrade cellulose and hemicelluloses
- Preferably require lower temperatures, pressures and pulping times than are usual in conventional pulping
- Utilize known and tested engineering methods and equipment already perfected for conventional pulping, wherever possible
- Have an optimal size smaller than that of a typical pulp mill.

In addition, the resulting pulp should:

- Be directly substitutable by current end-users for conventional pulps with equivalent properties
- Be readily bleachable
- Offer high yield
- Allow valuable by-products to be recovered.

Finally, the process should:

- Have efficient and simple chemical recycling systems
- Close the chemical cycle of the process, with little or no make-up chemical consumption
- Have low specific energy consumption
- Avoid malodorous emissions by being totally sulphur free

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- Permit complete recovery of process water with minimal discharge
- For occupational health and safety, product residue, environmental, and other regulatory and public policy requirements, employ known chemicals that have negligible or low human and environmental toxicity, be non-flammable and non-explosive
- Facilitate economic, environmental and other efficiencies in existing conventional pulping mills, if possible

Various "organosolv" processes have been contemplated as alternatives for the kraft process for the treatment of lignin-containing materials. Few, if any, of these have satisfied enough of the criteria outlined above to be commercially feasible.

The proposed processes for extracting lignin from waste lignocellulosic biomass have also suffered from disadvantages that have prevented any significant commercial adoption of the processes to date.

In the late 1950s McKee (CA 631,051) developed an "organosolv" alternative to kraft pulping which involved pulping under elevated temperature and pressure with a hydrotropic mixture of water and the crystalline salt sodium xylenesulphonate.

While this process appeared to offer some advantages over conventional pulping methods, it still suffered from a number of drawbacks. Under this process, a maximum of 40% of the salt is used in the solvent mixture, and with this hydrotropic system, the maximum temperature that can be attained under atmospheric pressure conditions is not much higher than the boiling point of water. As a consequence of this, to obtain sufficiently extreme conditions to break down the woody material into lignin and other

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byproducts including furfural and acetic acid, it is necessary to conduct the process at elevated pressure. The equipment required to achieve this introduces higher costs and design complications into the process, and makes
5 it difficult to conduct the process continuously.

Consequently, there is room for improvement on the various processes known in the art for the treatment of lignin-containing materials.

10

Brief Summary

The present invention relates to the application of ionic
15 liquids (preferably salts of acids with aryl functionality) as solvents or additives for treating (for example, dissolving, digesting, extracting and/or isolating materials from) natural sources or materials such as lignin-containing materials, including biomass.

20

Thus, according to a first aspect of the present invention, there is provided a method for the treatment of a lignin-containing material comprising the step of contacting the lignin-containing material with an ionic
25 liquid.

Preferably, the method further comprises the step of extracting lignin from the lignin-containing material into the ionic liquid, and recovering the lignin from the ionic
30 liquid. The material remaining after the lignin has been extracted is either cellulosic fibre that can be further processed into pulp for conversion to paper, or fully degraded to fermentable sugar monomers, or may be referred to as a waste material. According to one embodiment, the
35 cellulosic fibre or waste material is separated from the ionic liquid following extraction of the lignin into the ionic liquid.

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According to a second aspect of the present invention, there is provided the use of an ionic liquid in the treatment of a lignin-containing material.

5

According to a third aspect of the present invention, there is provided a product produced by the process described above.

10 Certain ionic liquids contemplated for use in the process of the present invention are novel per se, and therefore according to a fourth aspect of the present invention there is provided an ionic liquid comprising:

- 15 - an substituted or unsubstituted aryl organic acid anion; and
- an ionic liquid-forming inorganic cation or an organic cation.

20 Thus, the present invention also provides the use of the novel ionic liquids in the treatment of natural materials, such as plant materials and plant-derived materials.

Brief Description of the Figures

25 Figure 1 is a schematic illustration of a process according to one embodiment of the invention.

Detailed Description

30 *Ionic Liquid*

Ionic liquids are organic salts with low melting points (up to 100°C), many of which are consequently liquid at room temperature. Specific features that make ionic
35 liquids suitable for use in the present invention are their 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,

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ionic liquids are non-flammable, which makes them suitable for use in the industrial applications contemplated by the present application.

5 It has been found that, in addition to these beneficial properties, when contacted with lignin-containing materials such as lignocellulosic materials, including plant matter and plant matter derivatives, the ionic liquids are capable of penetrating these materials, and
10 removing the lignin therefrom. In addition, with the appropriate choice of treatment conditions (for example, time of contact and temperature), ionic liquids penetrate the structure of the lignin-containing material to break the material down to extract further organic species
15 making up the lignin-containing material. Any cellulosic component remaining in the lignocellulosic material is preserved. Once separated from the ionic liquid liquor, the cellulosic component may then be optionally broken down into smaller organic compounds such as hexose and
20 pentose sugars, which can be converted into fuel sources such as ethanol.

Although not wishing to be bound by theory, it is also believed that the ionic liquids contemplated for use in
25 these applications have surfactant behaviour and/or catalytic ability that make them particularly useful in various embodiments.

Further, ionic liquids remain liquid at high temperatures
30 without evaporating, when used alone or in high concentrations with a cosolvent. Thus, the ionic liquids can be used in the treatment of lignin-containing materials at high temperature, without the necessary application of pressure. Additional advantages of certain
35 preferred ionic liquids are their ease of handling and low toxicity.

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The ionic liquid may be a single species, or may be a mixture of different ionic liquid species. The ionic liquid may be used alone, or in combination of a cosolvent. Suitable cosolvents include water and organic solvents such as alcohols, ethers, acids and so forth. Water is particularly suitable.

According to one embodiment, the ionic liquid comprises:

- an substituted or unsubstituted aryl organic acid anion; and
- an ionic liquid-forming inorganic cation or an organic cation.

Anion

Regarding the anion component, the term aryl denotes single, polynuclear, conjugated and/or fused residues of aromatic hydrocarbon or aromatic heterocyclic ring system. Examples of aryl include phenyl, biphenyl, terphenyl, quaterphenyl, phenoxyphenyl, naphthyl, tetrahydronaphthyl, anthracenyl, dihydroanthracenyl, benzanthracenyl, dibenzanthracenyl, phenanthrenyl, fluorenyl, pyrenyl, indenyl, azulenyl, chrysenyl, pyridyl, 4-phenylpyridyl, 3-phenylpyridyl, thienyl, furyl, pyrrol, pyrrolyl, furanyl, imadazolyl, pyrrolydiny, pyridinyl, piperidinyl, indolyl, pyridazinyl, pyrazolyl, pyrazinyl, thiazolyl, pyrimidinyl, quinolinyl, isoquinolinyl, benzofuranyl, benzothienyl, purinyl, quinazolinyl, phenazinyl, acridinyl, benzoxazolyl, benzothiazolyl and the like. If the aryl in the case of the anion is an aromatic heterocyclic ring system, this suitably contains 1 to 4 heteratoms independently selected from N, O and S and up to 9 carbon atoms in the ring. The aromatic functionality of the aryl organic acid anion may include any hetero-atoms, branched and/or ring fragments with the substituent promoting the solvent properties and/or physical properties of the corresponding ionic liquid.

According to one embodiment, the aryl is a hydrocarbon (ie non-heterocyclic) aryl group, typically phenyl or naphthyl.

5 The aryl may be unsubstituted or substituted by one or more substituents. Suitably substituents may be selected from one or a combination of alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, 10 haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitrile, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, imino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, 15 alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio, organic acid or 20 ester such as sulfonate, and the like.

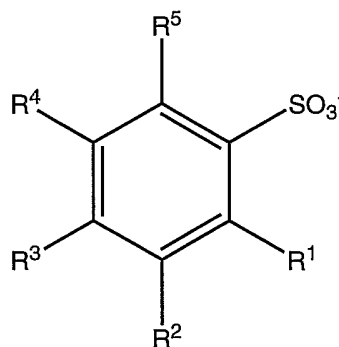
When a substituted aryl is used (preferably phenyl, naphthyl or pyridyl), there are suitably between 1 and 4 substituents, and these are preferably independently 25 selected from the group consisting of alkyl, hydroxy, amino and halo. More preferably the substituents are alkyl. According to one particular embodiment, the substituents are methyl.

30 The term "alkyl" denotes straight chain, branched or mono- or poly- cyclic alkyl, preferably C1-30 alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, hexyl, octyl, dodecyl, 1-methylundecyl and the 35 like. The term halo encompasses chloro, iodo, fluoro and bromo.

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The term "organic acid" in the context of the anion component of the ionic liquid refers the organic acids of sulfur, carbon and phosphorous, and therefore the anion species of these acids (i.e. in which the proton of the acid is removed) encompasses the sulfonates, sulfates, carboxylates, phosphinates, phosphates and so forth. The sulfonates (the anion of the organic acid sulfonic acid) is the subject of a number of embodiments of the present invention. It is noted that the anion may contain more than one organic acid group - such as the aryl disulfonate anions.

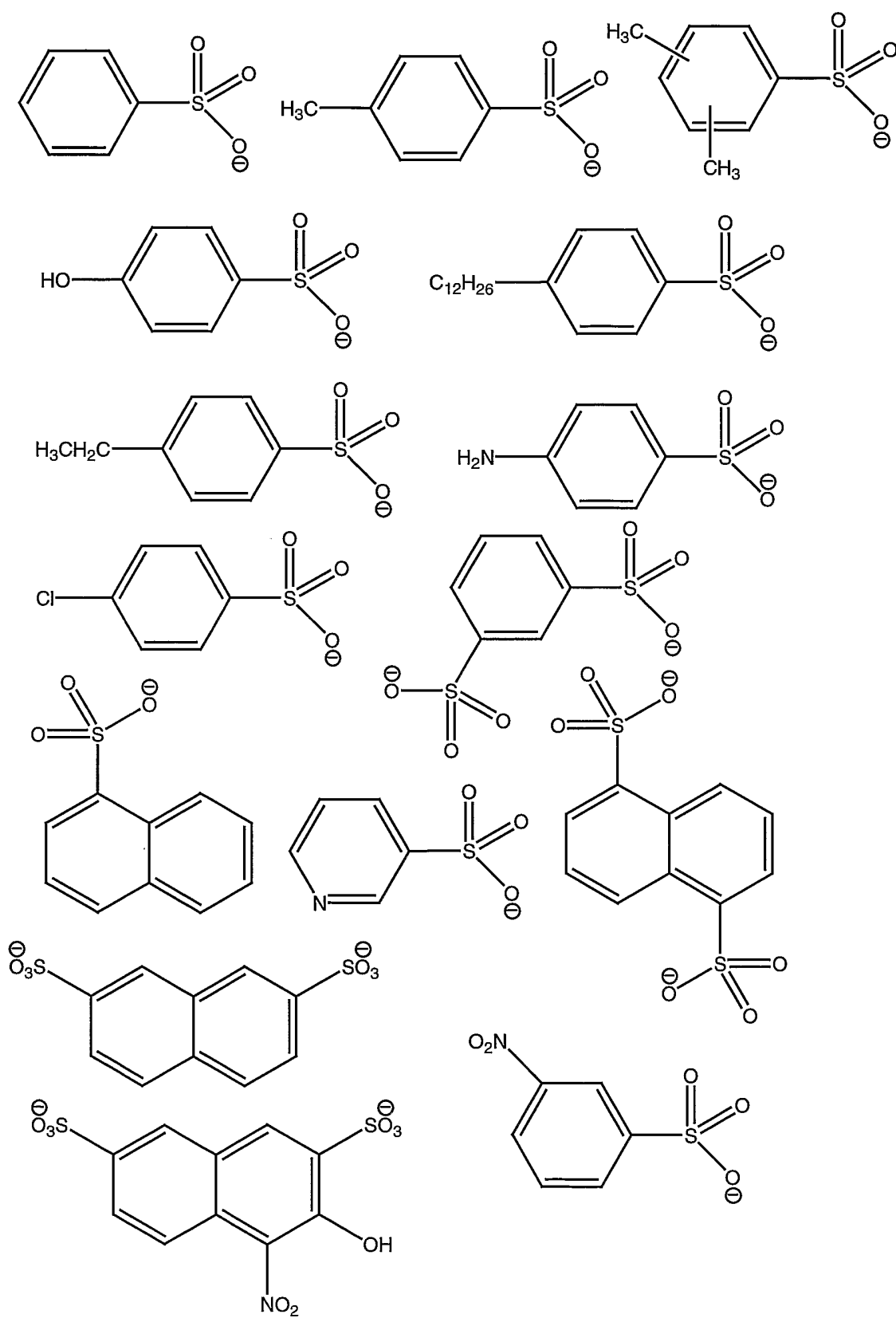
The ionic liquid of one embodiment is thus a salt of arylsulfonic acids. The anions of Formula 1 are examples of this class.



Formula 1

In this structure R¹, R², R³, R⁴, R⁵ are each independently selected from the group consisting of hydrogen, alkyl (including but not limited to methyl, ethyl, dodecyl), alicyclyl, aryl (including but not limited to benzyl and naphthyl), aralkyl, alkylaryl, heteroaryl, halogeno, haloaryl and sulfonate. In the case of sulfonate, the dianion may be partially or fully neutralised.

Other examples of anions that may be used are represented below.



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The sulfonates are a particularly useful class of the substituted or unsubstituted aryl organic acid anions. The results set out in the Examples below show that ionic liquids containing anions based on aryl sulfonate group (substituted or unsubstituted) are particularly effective in extracting lignin from the lignin-containing materials.

Cation

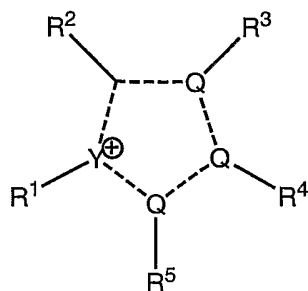
The cation component is either an ionic liquid-forming inorganic cation or an organic cation.

Regarding inorganic cations, it will be understood that simple alkali metals or alkaline earth metal cations that form crystalline salts with the anion component are not within the scope of the present invention, and therefore Na salts are excluded. Suitable inorganic cations include the rare earth metals.

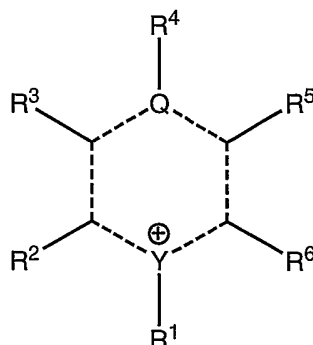
Amongst the organic cations, the present invention encompasses substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium equivalents of the above-mentioned groups, ammonium, phosphonium and sulfonium cations. In the case of substituted cations, the substituents are preferably selected from one or more of the optional substituents referred to above in the context of the anions, but they are preferably selected from hydrogen, aliphatic (i.e. optionally substituted alkyl, alkenyl, alkynyl), alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, haloaryl.

Some representative examples of the cations encompassed are the cations of Formulae 2 (2a, 2b and 2c) and 3:

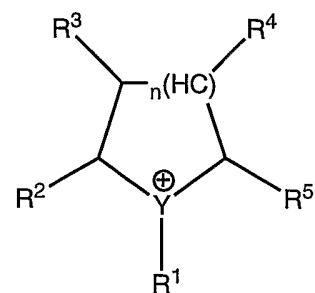
- 12 -



Formula 2a



Formula 2b



Formula 2c

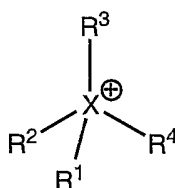
in which:

the dotted lines represent single or double bonds;

Q represents N, CH, O or S, and wherein when X represents
 5 O or S, the group R is absent and the adjoining bonds are
 single bonds;

Y represents N or P; and

n is 1 or 2



Formula 3

10

wherein:

X represents N, P or S;

R¹ to R⁴, are each independently selected from aliphatic
 (i.e. optionally substituted alkyl, alkenyl, alkynyl),
 15 alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl and
 haloaryl.

Choline and derivatives thereof are other examples of
 suitable cations.

20

*Further components which may be included in mixture with
 ionic liquid contacted with lignin-containing material*

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The salts which are the subject of this invention, are generally liquids at some temperature below 250°C either in their pure state or when mixed with one or more other salts. The salts that may be mixed with the ionic liquid
5 may be a second ionic liquid as described above, or any other known ionic liquid.

The ionic liquids may be used as solvents or additives. When used as a solvent, the solvent may also include a
10 further component which is a molecular solvent such as water, ethanol, toluene and other solvents well known in the field of chemistry. In some embodiments of the invention, the ionic liquid may constitute between 50 and 100% of the solvent composition, for instance between 70%
15 and 100% of the solvent composition.

When used as a solvent, the solvent composition may be used in any suitable solvating amount with respect to the lignin-containing material. It may for instance be used
20 in an amount of between 2 and 50 times the amount of lignin-containing material, based on weight.

Commonly used acids and bases may also be added to this solvent composition for simple pH management of optimal
25 conditions or other advantageous effect. Such acids or bases may be present at weight percentages from 0.01% - 90%. The pH may be controlled within the range 3.0 to 14.0, suitably 5.0 to 12.0, as required by the process. The more vigorous the conditions, in terms of pH, time and
30 temperature, the greater the expected penetration of the lignin-containing material for the extraction of lignin and other extractable chemicals.

Any other components may be used in the solvent
35 composition, including Na and/or Li salts, transition metal or other oxidation catalysts, air or molecular oxygen. Such components (including sodium xylene

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sulfonate) may be used for catalytic effect or otherwise. Such additives may be present at weight percentages from 0.01% - 90%, suitably 0.01 - 10% by weight.

5 In an alternative application, the ionic liquids that are the subject of this invention may be used as additives, and therefore they may be added to the composition of conventional kraft alkali liquors to facilitate and accelerate removal of lignin. The new ionic liquids may
10 be used in the treatment of any natural products to extract extractable chemicals therefrom.

Natural sources and lignin containing materials

15 The present invention is broadly applicable to the treatment of natural sources, including plant and plant-derived materials. This therefore encompasses lignin-containing materials. The term lignin-containing material encompasses, without limitation, plant derived biomass,
20 corn stover, sugar cane bagasse and cane residues, rice and wheat straw, agricultural grasses, woodchips, bamboo, and all other materials proximately or ultimately derived from plants.

25 Lignin is a complex polymeric material (mostly comprised of phenolic groups, anisole, primary, secondary alcoholic groups and aldehydes) located in the woody cell wall that confer strength and rigidity to the woody cell. In the preparation of paper, the lignin is removed to leave the
30 cellulosic material for formation into paper.

Processing steps

The ionic liquid is used in the treatment of materials. Treatment encompasses dissolving, digesting, extracting
35 and/or isolation of components therefrom.

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One suitable treatment comprises contacting a lignin-containing material with the ionic liquid to extract lignin and optionally other chemicals into the liquid phase, and thereafter separating the liquid phase from
5 remaining solids. In the case where the lignin-containing material is a lignocellulosic material, the remaining solids comprise cellulosic fibre.

The contacting stage is suitably conducted at an elevated
10 temperature, and preferably at atmospheric pressure. Preferably the this stage is conducted at a temperature between 50 and 200°C, more preferably between 100 - 180°C, most preferably between 120 - 160°C. Preferably the time of contact is between 1 and 8 hours.

15 The lignin-containing material is contacted with the ionic liquid in a vessel, and the contents heated to the desired temperature by any suitable means. One suitable heater is a boiler, which may be powered by any fuel, such as the
20 lignin recovered during downstream processing of the ionic liquid.

After separation of the liquid phase from the remaining solids, the process suitably comprises the step of
25 precipitating lignin from the liquid phase. This maybe achieved by any of a number of ways, for example precipitation may be induced by adding water and/or varying temperature or pH. Alternatively, the liquid phase may be contacted with an immiscible organic solvent
30 into which the lignin products report, or with a polyethylene glycol (PEG) solution to form an aqueous biphasic system within which the lignin products will preferably move to the organic PEG phase. Thereafter the precipitated lignin is recovered from the liquid phase,
35 for example by filtration, or from the immiscible organic solvent by distillation, or from the PEG phase of the biphasic system by pH adjustment followed by filtration.

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The recovered lignin may be used as a fuel or feedstock for this or any other process.

5 Once the extractable chemicals such as lignin have been extracted into the ionic liquid, and thereafter removed, the ionic liquid can be recovered by any suitable means from the process liquor (i.e. re-concentrated and separated from contaminants), or alternatively reused directly. Recovery can be achieved by a number of
10 methods, including, without limitation, salting out with an appropriate inorganic salt (e.g. Potassium phosphate salt), reverse osmosis, or solidification by temperature reduction. The last of these examples is of particular interest for ionic liquids with higher melting points. By
15 reducing the extracted liquid phase temperature to a sufficiently low level, the ionic liquid is solidified in a non-crystalline form.

According to one embodiment of the invention, a separate
20 stream of the liquid phase, from which the solids have been separated, is directly recycled to an upstream stage of the process for contacting with further lignin-containing material without any removal of lignin.

25 The diluted stream of ionic liquid, from which the precipitated lignin has been removed, may be dewatered to remove excess water (added during dilution) therefrom. Thereafter, the dewatered ionic liquid may be subjected to distillation to remove other chemicals extracted from the
30 lignin-containing materials therefrom. These other chemicals may include acetic acid and/or furfural. Thereafter, the ionic liquid is recycled for contacting with further lignin-containing material.

Other features of the ionic liquids

The new ionic liquids identified in the present application also display high electrochemical stability compared to conventional electrolytes. Typically large electrochemical windows are observed using cyclic voltammetry. Ionic liquids of this type are therefore also suitable for use as electrolytes, or ionic additives, for electrochemical applications such as electrowinning technologies. Any metal salt, including; copper, titanium, and aluminium, that can be dissolved in the ionic liquid and electrochemically reduced is potentially recoverable in the metallic form.

Examples

The present invention will now be described in further detail with reference to the following non-limiting examples.

Synthesis of novel materials

Ionic liquids were generally prepared by heating constituent salts in toluene to allow a metathesis reaction to proceed to yield the target ionic liquid.

Example 1

1-ethyl-3-methylimidazolium xylenesulfonate (EmImXS) was prepared by metathesis of sodium xylenesulfonate and 1-ethyl-3-methylimidazolium bromide.

EmImXS is a useful liquid salt for the extraction of lignin from pulp at temperatures around 150°C in a solvent mixture which contains water and some residual sodium xylenesulfonate.

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The procedure for the production of EmImXS was the same as that used for the production of tetrabutylammonium xylenesulphonate (TBABXS) from tetrabutylammonium bromide and sodium xylenesulphonate, and tetrabutylammonium benzoate (TBABBz) from tetrabutylammonium bromide and sodium benzoate.

This procedure involved the following steps. Approximately equimolar amounts of 1-ethyl-3-methylimidazolium bromide or tetrabutylammonium bromide and sodium xylenesulphonate were added to a 2-litre round bottom flask. Toluene (600 ml, 5-6 times the mass of salts) and boiling chips were added to the flask. The flask was fitted with a condenser and the slurry was heated at reflux overnight. Upon cooling, the slurry was filtered to remove the sodium bromide metathesis product. The filtrate was evaporated to dryness on a rotary evaporator to give a thick viscous liquid. Acetone was added to the flask and the ionic liquid was dispersed with vigorous mixing. The solution was filtered and the filtrate was evaporated to dryness once more. The resultant ionic liquid was left to rotate on the rotary evaporator at a very low speed and at high temperature (~90°C) to remove as much residual toluene as possible. The residual oil was then used as neat ionic liquid.

Example 2

Trihexyltetradecylphosphonium xylenesulfonate (P66614XS) was prepared using two different methods.

In a first method, an ion-exchange column was loaded with xylenesulfonate anions and a solution of trihexyltetradecylphosphonium chloride was passed through several times until complete exchange was indicated by the lack of chloride ions in the eluent. ¹Hnmr (CDCl₃) δ 0.85-0.95 (m, 12H, CH₃), 1.20-1.35 (m, 48H, CH₂), 1.40-1.60 (m,

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14H, P-CH₂ & Ar-CH₃), 6.90-7.30 & 7.60-7.90 (m, 3H, CH).
Electrospray Mass Spec: ES+ 483 [P66614+] m/z. ES- 185
[XS-] m/z.

5 According to the second method,
trihexyltetradecylphosphonium chloride (P66614 chloride;
1.1 mole) was refluxed with 1 mole of sodium
xylenesulfonate (NaXS) in toluene overnight. The product
was filtered and toluene removed by rotary evaporation
10 under vacuum to recover the ionic liquid. The ionic liquid
was characterized by NMR/ES MS.

This phosphonium cation based hydrophobic ionic liquid was
synthesised because it precludes water which may
15 facilitate removal of inorganics such as silica into the
water phase during extraction of lignocellulose materials
and also would make it suitable for use in some noble
metal electrochemical extraction applications. In
addition, the asymmetric nature of cation produces a
20 liquid substance at room temperature.

P66614XS was tested and found to display excellent thermal
stability at 150 °C. Thermogravimetric analysis indicates
the loss of less than 0.2% volatile material during 4
25 hours at this temperature. Thermal decomposition
temperature was calculated using the step-tangent method
and found to be 310°C.

Example 3

30 Tetrabutylammonium dodecylbenzenesulfonate N4444DDBS is
prepared by neutralising an aqueous solution of
dodecylbenzenesulfonic acid with tetrabutylammonium
hydroxide and removing water by evaporation.

Example 4

35 N-butyl-N-methylpyrrolidinium 4-hydroxybenzenesulfonate is
prepared directly in one-pot by alkylating N-

- 20 -

butylpyrrolidine with the methyl ester of 4-hydroxybenzenesulfonic acid.

Example 5

5 Tetrabutyl ammonium xylenesulfonate (N4444 XS) was prepared by a reflux reaction between tetrabutyl ammonium bromide (N4444 Br) and sodium xylenesulfonate (solid) in toluene for 10-12 hours. The product was filtered and the toluene evaporated from the reaction mixture, followed by
10 washing with acetone to yield the pure ionic liquid. ¹H NMR (300 MHz, D₂O): ppm 0.9 (t, *J* = 7.5 Hz, 12H, (CH₃CH₂CH₂CH₂)₄N), 1.12-1.26 (m, 8H, (CH₃CH₂CH₂CH₂)₄N), 1.4-1.54 (m, 8H, (CH₃CH₂CH₂CH₂)₄N), 2.18 (s, 3H, Xy-CH₃), 3.00 (s, 3H, Xy-CH₃), 3.01 (t, 8H, *J* = 8.4 Hz (CH₃CH₂CH₂CH₂)₄N),
15 6.99-7.3 (m, 2H, Xy-H), 7.51-7.59 (m, 1H, Xy-H).

N4444 XS is a hydrophilic ionic liquid. Being hydrophilic, this ionic liquid can penetrate the wood chips and extract lignin effectively.

20

Example 6

Phenyltrimethylammonium xylenesulfonate (Ph(Me)₃N XS) ionic liquid was prepared in a reflux reaction between phenyltrimethylammonium chloride (Ph(Me)₃N Cl) and sodium
25 xylenesulfonate (NaXS; solid) in toluene for 10-12 hours. The product was filtered and evaporated toluene from the reaction mixture to yield a crude solid product. The crude ionic liquid was washed with DCM to remove impurities.

30 *Testing and Use of novel materials*

Example 7

An extraction process was carried out as follows:
A reaction vessel is charged with a solution of ionic
35 liquid based solvent. Biomass such as wood chips or herbaceous material are added to the vessel. The mixture is heated and stirred for several hours. Solid cellulosic

- 21 -

material is filtered and prepared for pulping to paper. Dilution of the filtrate after repeated digestion cycles with water precipitates lignin, which is collected. Distillation of the filtrate affords various volatile
5 chemicals. The ionic liquid based solvent is recycled to the beginning of the process.

In the above process, the following specific conditions and materials were used.

10

Bagasse was used as a prototype biomass. Bagasse has the following average composition on a dry weight basis: Cellulose 41%; Hemicellulose 23.2%; Lignin 21.2%; Ash 10.9%; Extractives 4.5%

15

2.58 grams of sifted (2-3 mm mesh) bagasse was combined with 22.62grams of tetrabutylammonium xylene sulphonate, 2.5 grams of water and sufficient acetic acid to bring the pH to 4.0 in a 100ml round bottom flask. This mixture was
20 subjected to an impregnation step, 90 minutes refluxing at 130°C. The temperature of the mixture was then increased to 160°C by removing the reflux condenser to allow excess water to evaporate. The reflux condenser was replaced and the mixture subjected to digestion at 160°C for 2 hours.
25 Upon reaction termination the solid bagasse pulp was removed by filtration, the filter cake being subjected to washing with water (x2 100ml) and acetone (x1 50ml). All filtrates were then combined and 600ml of warm water added to precipitate the extracted lignin and cellulose
30 materials. This reaction produced 1.24g of digested bagasse and 1.2g of lignin/cellulose extract (95% mass retention).

35

Example 8 - Extraction trials

General procedure.

- 22 -

The following procedure was used in the extraction trials, with the exception of P66614XS where the mass was reduced.

Ionic liquid was warmed to assist in its transfer to the
5 reaction flask. The IL (~90 g) was added to a 250-ml two-necked round bottom flask and the IL mass was recorded. Water (~10 g) was added and the flask was swirled to mix the contents evenly. Acid or base was added to the flask as required and the amount of acid or base was recorded.
10 Bagasse (~10 g) was added and the flask was warmed to help ensure that the bagasse was thoroughly wetted by the IL solution. The flask was fitted with a reflux condenser (and a stopper in the second neck) and heated in an oil bath at reflux for 1 hour. The condenser was then
15 replaced with a stillhead, to which the condenser was reattached. The temperature of the oil bath was then increased to drive the distillation of water and residual toluene from the reaction flask. The distillate was recovered in a tared collection flask. The temperature
20 within the reaction flask rose to 150°C and it was maintained in the range of 150°-160°C for 2 hours. The distillation apparatus was then dismantled and the masses of the distillate and residue were recorded. The residue was diluted with acetone (200 ml) and filtered (Whatman
25 no. 1) while still hot. The residual pulp was washed with further acetone until the filtrate appeared near colourless. The pulp was washed with water and more acetone and was then oven-dried. The combined filtrates were then evaporated to remove water and acetone, and the
30 black oily residue that remained was weighed. It was assumed that this residue contained the recovered IL and the extracted lignin.

Results

The results for the cooking experiments are shown in
5 Tables 1 and 2. Table 1 shows a general mass balance for
each experiment, while Table 2 more specifically shows the
performance in extracting lignin from bagasse and the
recovery of the ionic liquid.

10 Notes

- It is apparent from mass balance results obtained
following digestion of the bagasse that the cellulose
and hemicellulose in the pulp generally suffered little
15 degradation, which indicates that ionic liquid pulping
is highly selective for lignin extraction.
- Lignin was not separated from the ionic liquid after
separation from the pulp. The degree of lignin removal
was calculated based on the Kappa number of the
20 resultant pulp.
- The high recovery of EMIMXS was related to the low
toluene content in the ionic liquid before the cooking
trial. Toluene was not collected in the distillate for
the EMIMXS trials. In contrast, several grams of
25 toluene was collected in the distillate for the trials
using TBAXS and TBABz. This probably explains the yield
of recovered IL for the TBAXS trials.
- The results with TBABz were not as good as for the other
ionic liquids. The smaller quantities of TBABz used in
30 these trials also contributed to experimental inaccuracy
for this ionic liquid. Furthermore, on completion of
the trials with TBABz, a strong ester-like odour was
evident, suggesting that some chemical transformation
had occurred.
- 35 • Acidic trials appeared to be more efficient as judged by
eye and from the Kappa number results.

Table 1. Overall mass balance for ionic liquid extractions of bagasse

Ionic liquid	Bagasse in (wet) ^a	Dry bagasse	IL	Added water	Acid/base	pH	Total in	Residue	Pulp	IL + lignin	Distillate	Total out	Overall loss (%)
EMIMXS	10.03	6.50	90.04	10.17	0	6	110.24	98.69	5.61	92.62	7.28	105.51	4.29
EMIMXS	10.38	6.73	90.11	10.35	0.37	4	111.21	99.2	5.53	91.52	8.06	105.11	5.49
TBAXS	10.06	6.52	87.85	10	0.43	4.5	108.34	85.52	4.87	80.1	15.89	100.86	6.90
TBAXS	10.05	6.51	90.45	10	0	9	110.5	88.05	5.25	76.86	15.35	97.46	11.80
TBABz	3.94	2.55	35.03	3.94	0	7	42.91	31.22	1.97	17.29	5.72	24.98	41.79
TBABz	4.03	2.61	34.96	3.94	0.2	4.5	43.13	31.24	1.8	19.87	7.64	29.31	32.04
P66614XS	0.724	0.47	6.29	0.715	0		7.729	6.705	0.22	6.46	1	7.68	0.63%

EMIMXS, ethylmethyimidazolium xylenesulphonate; TBAXS, tetrabutylammonium xylenesulphonate; TBABz, tetrabutylammonium benzoate; P66614XS, trihexyltetradecylphosphonium xylene sulphonate

^a Bagasse moisture: 35.2%

Table 2. Efficiency in removal of lignin from bagasse and recovery of ionic liquids

Ionic liquid	Bagasse in (wet)	Dry bagasse	pH	IL	IL + lignin	Pulp	Pulp kappa	% Lignin in pulp ^a	Lignin in pulp	Total available lignin ^b	% Lignin removed	Recovery d IL (%) ^c
EMIMXS	10.03	6.50	6	90.04	92.62	5.61	48.05	7.21	0.40	1.38	0.97	102%
EMIMXS	10.38	6.73	4	90.11	91.52	5.53	61.1	9.17	0.51	1.43	0.92	101%
TBAXS	10.06	6.52	4.5	87.85	80.1	4.87	55.6	8.34	0.41	1.38	0.98	90%
TBAXS	10.05	6.51	9	90.45	76.86	5.25	60.9	9.14	0.48	1.38	0.90	84%
TBABz	3.94	2.55	7	35.03	17.29	1.97	57.9	8.69	0.17	0.54	0.37	48%
TBABz	4.03	2.61	4.5	34.96	19.87	1.8	53	7.95	0.14	0.55	0.41	56%
P66614XS	0.724	0.47	7	6.29	6.46	0.22	41.4	6.21	0.01	0.10	0.09	101%

^a Based on formula (% lignin = $0.15 \times \text{Kappa no.}$)

^b Assumed lignin content in bagasse ~21.2% on dry weight

^c Based on lignin recovery as calculated by Kappa number determination

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Example 9 - Continuous Process

Figure 1 illustrates a continuous process for conducting the process of one embodiment of the invention.

5

Biomass is prepared 1 and fed into a digester 2 together with ionic liquid from two different sources, as will be described in further detail below.

10

The digester 2 is heated by a boiler 3. The lignin is extracted from the biomass into the ionic liquid in the boiler. Thereafter, the material from the digester is washed/refined 4, and subjected to solid/liquid separation 5. The solid cellulosic fibre is recovered 6 and used for

15

paper production or similar. The ionic liquid is separated into two streams - a first stream (2/3 of the ionic liquid) being recycled 7 to the digester 2, and the second (1/3 of the ionic liquid) being sent to lignin

20

precipitation process step 8. The precipitated lignin is separated from the ionic liquid by liquid/solid separation 9, and the lignin recovered 10 for various end uses. One possible use represented by the dashed line is as fuel for the boiler 3. The ionic liquid is then dewatered 11, prior to distillation/concentration 12 to recover organic byproducts 13 such as furfural and acetic acid. Water removed during dewatering 11 is recycled to the washing/refining stage 4. The ionic liquid from the distillation/concentration stage is regenerated 14 for recycling to the digester 2.

25

30

It will be understood to persons skilled in the art that many modifications may be made to the embodiments and Examples described above without departing from the spirit and scope of the invention.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for the treatment of a lignin-containing material comprising contacting the lignin-containing material with an ionic liquid.
5
2. The method of claim 1, wherein lignin from the lignin-containing material is extracted into the ionic liquid, and the lignin is recovered from the ionic liquid.
10
3. The method of claim 2, wherein solids remaining after the lignin has been extracted into the ionic liquid are separated from the ionic liquid.
- 15 4. The method of any one of claims 1 to 3, wherein the lignin-containing material is contacted with a single species of ionic liquid.
- 20 5. The method of any one of claims 1 to 3, wherein the lignin-containing material is contacted with a mixture of different ionic liquid species.
- 25 6. The method of any one of claims 1 to 5, wherein the lignin-containing material is contacted with a combination of the ionic liquid and a cosolvent.
- 30 7. The method of claim 6, wherein the lignin-containing material is contacted with a combination of the ionic liquid and water.
- 35 8. The method of any one of claims 1 to 7, wherein the lignin-containing material is contacted with a solvent composition comprising between 50 and 100% of the ionic liquid.

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9. The method of any one of claims 1 to 8, wherein the lignin-containing material is contacted with ionic liquid which comprises:

- an substituted or unsubstituted aryl organic acid anion;
- 5 and
- an ionic liquid-forming inorganic cation or an organic cation.

10. The method of claim 9, wherein the anion component of the ionic liquid is a substituted or unsubstituted phenyl, naphthyl or pyridyl organic acid anion.

11. The method of claim 10, wherein the aryl is substituted by between 1 and 4 substituents independently selected from the group consisting of alkyl, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, halogeno, hydroxy, nitro, haloaryl and sulfonate.

12. The method of any one of claims 9 to 11, wherein the organic acid anion is a sulfonate, sulfate, carboxylates, phosphinate or a phosphate.

13. The method of any one of claims 9 to 12, wherein the organic acid anion is a sulfonate.

14. The method of any one of claims 9 to 13, wherein the anion is a substituted or unsubstituted aryl disulfonate anion.

15. The method of any one of claims 9 to 14, wherein the cation of the ionic liquid is a substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium equivalents of one of the preceding groups, an ammonium, phosphonium or sulfonium cation.

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16. The method of claim 15, wherein the cation is substituted by one or more selected from the group consisting of aliphatic, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, hydroxy, nitro and haloaryl.

5

17. The method of any one of claims 1 to 7, wherein the ionic liquid is a substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, phosphonium or sulfonium salt of a substituted or unsubstituted aryl sulfonate.

10

18. The method of claim 1, wherein the lignin-containing material is contacted with a kraft alkali liquor in the presence with an ionic liquid additive.

15

19. The method of any one of claims 1 to 18, wherein the lignin-containing material is a ligno-cellulosic material.

20. The method of claim 19, wherein the lignin is selectively extracted into the ionic liquid, without significant degradation of the cellulose and hemicellulose of the ligno-cellulosic material.

20

21. The method of any one of claims 1 to 18, wherein the lignin-containing material is a plant or plant derivative material.

25

22. The method of any one of claims 1 to 21, wherein the lignin-containing material is selected from one or more of lignocellulostic residues of sugar, wheat, rice and corn or other biomass, agricultural grasses, woodchips, bamboo, as well as any materials proximately or ultimately derived from plants.

30

35

23. The method of any one of claims 1 to 22, comprising contacting the lignin-containing material with the ionic

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liquid to extract lignin and optionally other chemicals into the liquid phase, and separating the liquid phase from remaining solids.

5 24. The method of claim 23, wherein the lignin-containing material is a lignocellulosic material, the remaining solids comprise cellulosic fibre.

10 25. The method of claim 23 or claim 24, wherein the lignin-containing material is contacted with the ionic liquid at an elevated temperature.

26. The method of claim 25, wherein the temperatures is between 50 and 200°C.

15 27. The method of claim 26, wherein the lignin-containing material is contacted with the ionic liquid at atmospheric pressure.

20 28. The method of any one of claims 23 to 27, wherein the time of contact is between 1 and 8 hours.

25 29. The method of any one of claims 23 to 28, comprising precipitation of lignin from the liquid phase after separation of the liquid phase from the remaining solids.

30. The method of claim 29, comprising recovering the precipitated lignin from the liquid phase.

30 31. The method of claim 30, comprising dewatering the diluted stream of ionic liquid, from which the precipitated lignin has been removed, to remove excess water therefrom.

35 32. The method of claim 31, comprising distilling the dewatered ionic liquid to remove other chemicals extracted from the lignin-containing materials therefrom.

33. The method of claim 32, comprising recycling the ionic liquid recovered following distillation for contacting with further lignin-containing material.
- 5 34. A product produced by the method of any one of claims 1 to 33.
- 10 35. Use of an ionic liquid in the treatment of a lignin-containing material.
36. Use of claim 35, wherein the ionic liquid comprises:
- an substituted or unsubstituted aryl organic acid anion; and
 - 15 - an ionic liquid-forming inorganic cation or an organic cation.
37. Use of claim 36, wherein the anion component of the ionic liquid is a substituted or unsubstituted phenyl, naphthyl or pyridyl organic acid anion.
- 20 38. Use of claim 36, wherein the aryl is substituted by between 1 and 4 substituents independently selected from the group consisting of alkyl, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, halogeno, hydroxy, nitro, haloaryl and sulfonate.
39. Use of any one of claims 35 to 38, wherein the organic acid anion is a sulfonate, sulfate, carboxylates, phosphinate or a phosphate.
- 30 40. Use of any one of claims 35 to 39, wherein the organic acid anion is a sulfonate.
- 35 41. Use of any one of claims 35 to 40, wherein the anion is a substituted or unsubstituted aryl disulfonate anion.

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42. Use of any one of claims 35 to 41, wherein the cation of the ionic liquid is a substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium equivalents of one of the preceding groups, an ammonium, phosphonium or sulfonium cation.

43. Use of claim 42, wherein the cation is substituted by one or more selected from the group consisting of aliphatic, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, hydroxy, nitro and haloaryl.

44. Use of claim 43, wherein the ionic liquid is a substituted or unsubstituted imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, phosphonium or sulfonium salt of a substituted or unsubstituted aryl sulfonate.

45. An ionic liquid comprising

- an substituted or unsubstituted aryl organic acid anion; and
- an ionic liquid-forming inorganic cation or an organic cation.

46. The ionic liquid of claim 45, wherein the anion component of the ionic liquid is a substituted or unsubstituted phenyl, naphthyl or pyridyl organic acid anion.

47. The ionic liquid of claim 45, wherein the aryl is substituted by between 1 and 4 substituents independently selected from the group consisting of alkyl, alicyclyl, aryl, aralkyl, alkylaryl, heteroaryl, halogeno, hydroxy, nitro, haloaryl and sulfonate.

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48. The ionic liquid of any one of claims 45 to 47,
wherein the organic acid anion is a sulfonate, sulfate,
carboxylates, phosphinate or a phosphate.
- 5 49. The ionic liquid of any one of claims 45 to 48,
wherein the organic acid anion is a sulfonate.
50. The ionic liquid of any one of claims 45 to 49,
wherein the anion is a substituted or unsubstituted aryl
10 disulfonate anion.
51. The ionic liquid of any one of claims 45 to 50,
wherein the cation is a substituted or unsubstituted
imidazolium, triazolium, pyrazolium, pyridinium,
15 pyrrolidinium, piperidinium, phosphonium equivalents of
one of the preceding groups, an ammonium, phosphonium or
sulfonium cation.
52. The ionic liquid of claim 51, wherein the cation is
20 substituted by one or more selected from the group
consisting of aliphatic, alicyclyl, aryl, aralkyl,
alkylaryl, heteroaryl, hydroxy, nitro and haloaryl.
53. An ionic liquid comprising a substituted or
25 unsubstituted imidazolium, triazolium, pyrazolium,
pyridinium, pyrrolidinium, piperidinium, ammonium,
phosphonium or sulfonium salt of a substituted or
unsubstituted aryl sulfonate.
- 30 54. The ionic liquid of claim 53, wherein the substituted
or unsubstituted aryl sulfonate is a substituted or
unsubstituted phenyl, naphthyl or pyridyl sulfonate.
55. The ionic liquid of claim 53 or claim 54, wherein the
35 substituents of the aryl sulfonate component are selected
from the group consisting of aliphatic, alicyclyl, aryl,

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aralkyl, alkylaryl, heteroaryl, hydroxy, nitro and haloaryl.

56. Use of the ionic liquid of any one of claims 45 to 55
5 in the treatment of a natural material.

57. Use of claim 56, wherein the natural material is a plant materials and plant-derived materials.

1/1

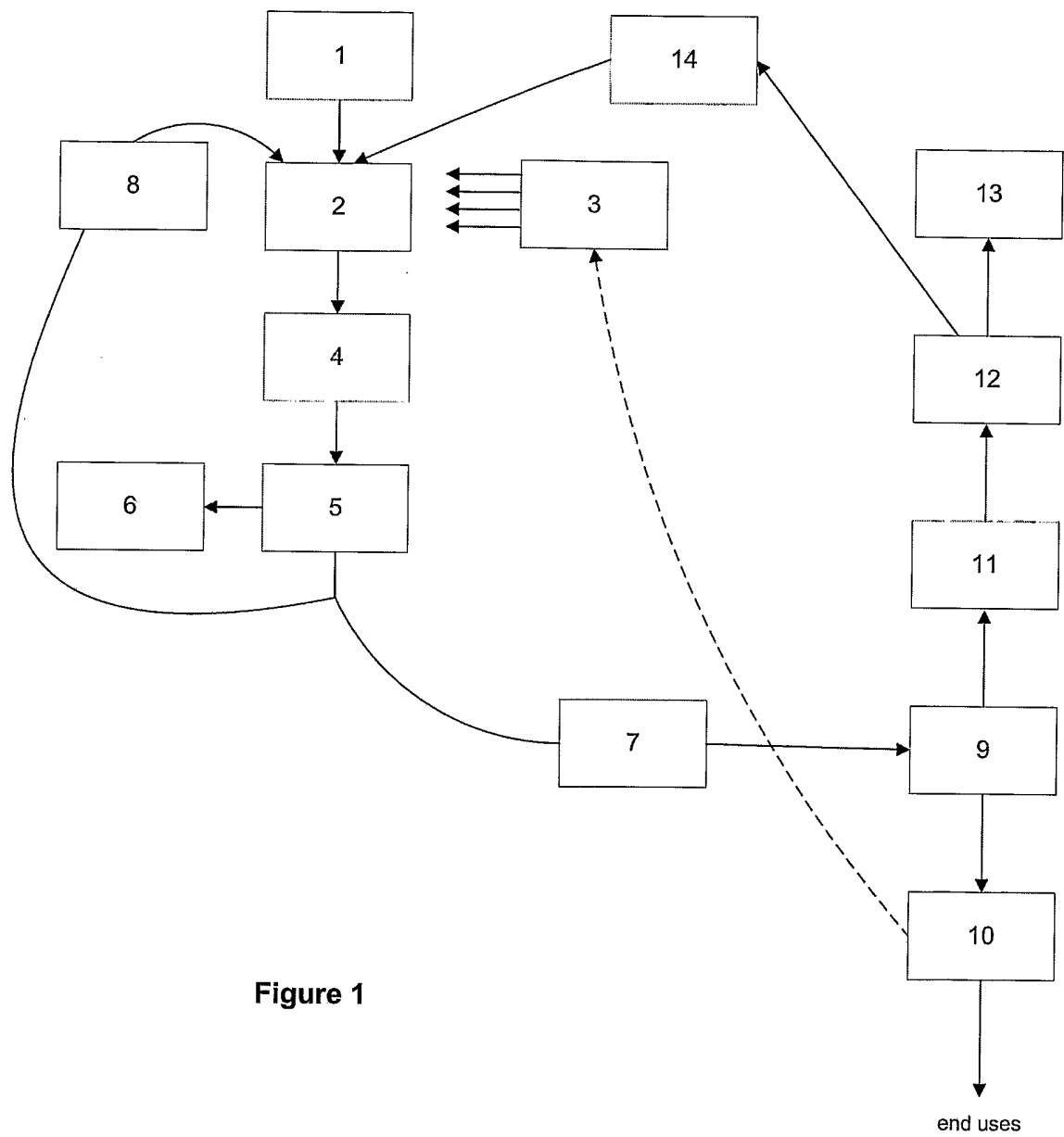


Figure 1

INTERNATIONAL SEARCH REPORT

International application No,
PCT/AU2004/001093

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : D21C 3/04		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: D21C 3/- & Keywords: imidazolium, triazolium, pyrazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, ammonium, sulphonium		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 957198 A (DOW CORNING CORPORATION) 17 November 1999 Whole document	1-44
X	US 2003/0041982 A (PRIOR) 6 March 2003 Whole document	1-8, 17-35
X	US 5385641 A (BERG ET AL) 31 January 1995 Whole document	1-8, 19, 21,- 26, 28-35
X	US 4652341 A (PRIOR) 24 March 1987 Whole document	1-7, 18-35
☒ Further documents are listed in the continuation of Box C ☒ See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 September 2004		Date of mailing of the international search report 7 NOV 2004
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer GEORGE CARTER Telephone No : (02) 6283 2154

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2004/001093

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 1990/011401 A (EXXON CHEMICAL PATENTS, INC) 4 October 1990 Whole document	1, 9-15, 17-44
X	GB 2076034 A (NATURAL FIBRES (UK) LIMITED) 25 November 1981 Whole document	1-7, 15, 18-35
X	US 6139683 A (NIMZ ET AL) 31 October 2000 Whole document	1-8, 19-35

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2004/001093

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 45, 53
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
It is not economically feasible to search these 2 independent claims given their breadth of scope.
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

1. Claims 1-44. The first invention is directed to a method of treatment of a lignin-containing material with an ionic liquid, and this comprises a first "special technical feature".
2. Claims 45-57. Claim 45 is a composition claim directed to an ionic liquid comprising a substituted or unsubstituted aryl organic acid anion and an organic or inorganic cation. While claim 53 is directed to an ionic liquids comprising certain cations. Therefore the second "special technical feature" comprises the organic or inorganic cation

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-44

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/AU2004/001093

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member				
EP	0957198	AU	28035/99	CA	2271900	ID	23328
		JP	11335989	NO	992021		
US	2003041982	NONE					
US	5385641	CA	2062474	EP	0508064	FI	920830
		NO	920828				
US	4652341	NONE					
WO	9011401	AU	54041/90	BR	9007254	CA	2049360
		EP	0465579	NO	913780	US	5032224
GB	2076034	NONE					
US	6139683	CA	2104765	DE	4228171	EP	0584675
		FI	933729	JP	6322682		
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
END OF ANNEX							