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(54) **Use of deep eutectic solvents in the production of paper**

(57) The present invention relates to the use of a deep eutectic solvent in a process for the production of paper or pulp.

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Description

[0001] The present invention relates to the use of deep eutectic solvents in the production of pulp and/or paper and the treatment of pulp and paper waste and residues.

BACKGROUND OF THE INVENTION

[0002] Imagine one could make pulp with minimal energy, at low temperatures and at atmospheric pressure. Imagine one could make pulp without hazardous chemicals and with hardly any emissions or residues. Use all kinds of biomass - in any quantity, and make a network of local omnivore pulp mills. Make pulp at half the costs of today, in half an hour. Produce strong cellulose fibres that have not been cooked or grinded. And pure sulphur free lignin, as a perfect basis for biobased chemicals.

[0003] The breakthrough in this application is the utilization of deep eutectic solvents (DES). DES solvents are an adaption of a natural phenomenon known from plant metabolism. Science has found plants can build cell walls even under water stress (i.e. during periods of drought or frost). With the help of the organics present in their cells, plants produce so-called deep eutectic solvents. These represent a completely new generation of natural solvents that can dissolve components under mild conditions. DES technology is available at labscale[1].

[0004] DES enables the biobased economy to become reality. This application may allow an economical operation of production facilities as small as 50 ktpa, perfectly meeting the increasing demand for production units based on local or regional resources and serving local and regional markets - drastically reducing transport emissions and costs.

[0005] The first scientific studies on deep eutectic solvents were reported less than 10 years ago although in a totally different field. Since then research activities on their potential grew rapidly; half of the scientific publications on DES were made in 2012[3]. DES (also called Low Transition Temperature Mixtures or LTTM) are designer solvents, typically consisting of mixtures of at least two substances (at least 1 hydrogen donor and at least 1 hydrogen acceptor) that melt at a lower temperature than either of the individual components. This property is a consequence of hydrogen interaction between the components. DES are nonvolatile, biodegradable and do not react with water. In addition to having low vapour pressure and low flammability, DES are composed of non-toxic and relatively inexpensive substances including amides, sugars, and alcohols. Most of these components are natural products or can be made from renewable materials, making DES a sustainable alternative to far more cumbersome solvents used today. They can even be designed (by selecting the most suitable donor-acceptor combinations and ratio's) for specific purposes. They can be easily recovered and recent research gave strong indications that they can as well be combined with enzymes, allowing for bleaching where needed. Lab-scale research has shown that natural DES like the glucose based ones are able to dissolve wood and selectively extract - as a function of the chemical characteristics and the operating conditions - lignin, hemicellulose and most probably cellulose as well[4].

SUMMARY OF THE INVENTION

[0006] The present invention provides in a first aspect a process for producing pulp and/or paper comprising using deep eutectic solvents.

[0007] In a second aspect, it is provided a process for producing pulp and/or paper comprising a dissolving step to dissolve lignin from a lignocellulosic material by using deep eutectic solvents.

[0008] In a third aspect, it is provided a process for processing recycled fibres comprising a contacting step of contacting recycled fibres with deep eutectic solvents.

[0009] In a fourth aspect, it is provided a process for producing paper comprising a dissolving step to dissolve cellulose from a cellulosic material by using deep eutectic solvents and optionally a precipitating step of precipitating the cellulose obtained in the dissolving step in sheet format.

[0010] It is further provided in a fifth aspect a process for recovering cellulose from cellulosic waste material comprising a dissolving step to dissolve cellulose from the waste material by using deep eutectic solvents.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Before the present invention is described in detail below, it is to be understood that this invention is not limited to the particular methodology, protocols and reagents described herein as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art.

[0012] Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

[0013] As used herein "cellulose" is a complex carbohydrate, $(C_6H_{10}O_5)_n$, that is composed of glucose units, forms the main constituent of the cell wall in most plants, and is important in the manufacture of numerous products, such as paper, textiles, pharmaceuticals, and explosives. It is crystalline, strong, and resistant to hydrolysis.

[0014] "DES" refers to deep eutectic solvent. A deep eutectic solvent is a type of ionic liquid (a salt in the liquid state) with special properties composed of a mixture which forms a eutectic with a melting point much lower than either of the individual components. While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs.

[0015] Furfural is an organic compound derived from a variety of agricultural by-products, including corncobs, oat, wheat bran, and sawdust. Furfural is a heterocyclic aldehyde (OC_4H_3CHO).

[0016] As used herein "hemicellulose" is any of several polysaccharides that are more complex than a sugar and less complex than cellulose, present along with cellulose in almost all plant cell walls. While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulose.

[0017] The unit "ktpa" as used herein refers to kiloton per annum.

[0018] "Lignin" is a complex chemical compound most commonly derived from lignocellulosic biomass, and an integral part of the secondary cell walls of plants.

[0019] "Lignocellulose" refers to plant dry matter (biomass), so called lignocellulosic biomass. It is composed of carbohydrate polymers (cellulose, hemicellulose), and an aromatic polymer (lignin).

[0020] "Paper" refers to a thin material currently produced by pressing together moist fibers, typically cellulose pulp derived from wood, rags or grasses, and drying them into sheets. A definition may be found in NACE chapter 17 (Manufacture of paper and paper products, Statistical classification of economic activities in the European Community, chapter 17.12 Manufacture of paper and paperboard and chapter 17.2 Manufacture of articles of paper and paperboard) and PRODCOM 48.

[0021] "Pulping" is a processing of wood, wood chips or other lignocellulosic materials (containing agricultural or agro-industrial side streams) and the like to isolate individual fibres. Pulps produced thereby can often be further subjected to bleaching and purification operations in a bleach plant, including further delignification of the pulp. A definition may be found in NACE, chapter 17 (Manufacture of paper and paper products, Statistical classification of economic activities in the European Community, chapter 17.1 Manufacture of pulp) and PRODCOM 47.

[0022] As used herein, a "lignocellulosic material" is any material that comprises, consists of, includes, contains or encompasses lignocellulose.

[0023] As used herein, a "cellulosic material" is any material that comprises, consists of, includes, contains or encompasses cellulose.

[0024] Some documents are cited throughout the text of this specification. Each of the documents cited herein (including all patents, patent applications, scientific publications, manufacturer's specifications, instructions, DIN norms etc.), whether supra or infra, are hereby incorporated by reference in their entirety. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0025] Generally, the invention provides in a first aspect a process for producing pulp and/or paper comprising using a deep eutectic solvent.

[0026] As mentioned, the invention provides in a second aspect a process for producing pulp and/or paper comprising a dissolving step to dissolve lignin from a lignocellulosic material by using a deep eutectic solvent. Therewith, a lignin containing deep eutectic solvent and a remaining material is obtained. Preferably, the lignocellulosic material is selected from wood, woodchips, fibre crops, paper, board, waste paper or any combination thereof. The dissolving step is typically carried out at a temperature between 40 to 120°C, preferably 40 to 100°C and more preferably between 60 to 80°C. Moreover, the dissolving step is typically carried out for 10 to 120 min, preferably 20 to 60 min and more preferably for 30 to 40 min.

[0027] The process may further comprise a separating step of separating the lignin containing deep eutectic solvent after the dissolving step from the remaining material, which typically contains or consists of cellulose.

[0028] Moreover, the process may further comprise a washing step of washing the remaining material with a washing solvent, wherein the washing solvent preferably comprises or is preferably water, after the separating step. During the washing step the deep eutectic solvent is removed from the remaining material, which typically comprises or consists of cellulose.

[0029] Additionally, the process may further comprise a precipitating step of precipitating the lignin from the lignin containing deep eutectic solvent after the separating step by a solvent; preferably using water, preferably using the water that has been used as a washing solvent in the washing step and is obtained after said washing step. Preferably, the ratio of deep eutectic solvent to water is between 3:1 to 1: 3, more preferably 2:1 to 1: 2, and most preferably 1:1. In general, the separating step may be done in parallel, before or after the washing step.

[0030] After the precipitating step, the process may further comprise a removing step of removing the lignin from the remaining washing solvent/deep eutectic solvent mixture after the precipitating step, preferably by a solid/liquid separation. Typically, 98% of the lignin is recovered.

[0031] The remaining washing solvent/deep eutectic solvent mixture may contain hemicellulose. Therefore, the process may further comprise a converting step of converting the hemicellulose into other chemicals, preferably furfural.

[0032] Additionally, the process may further comprise a recovering step of recovering the used deep eutectic solvent, preferably after the converting step of converting the hemicellulose into other chemicals and optionally removing of said other chemicals. Preferably, the deep eutectic solvent is recovered by nano-filtration.

[0033] As a result, this process may allow recovering lignin, cellulose and hemicellulose at low temperature and atmospheric pressure, from any lignocellulosic resource. It has shown to be possible with wood as well as with straw (where silica is removed with the DES). By adjusting DES properties and the process lay-out, tailor-made fibre qualities can be obtained (e.g. with different lignin-content).

[0034] Further, it is provided in a third aspect a process for processing recycled fibres comprising a contacting step of contacting recycled fibres with a deep eutectic solvent. Preferably, a deep eutectic solvent is used that selectively, or almost selectively, dissolves ink-components and preferably other contaminants from recycled fibres or paper, yielding clean cellulose fibres without fibre losses.

[0035] Additionally, it is provided in a fourth aspect a process for producing paper comprising a dissolving step to dissolve cellulose from a cellulosic material by using a deep eutectic solvent and optionally a precipitating step of precipitating the cellulose obtained in the dissolving step in sheet format. This process may have the advantage that water may be eliminated from the papermaking process.

[0036] Further, it is provided in a fifth aspect a process for recovering cellulose from cellulosic waste material comprising a dissolving step to dissolve cellulose from the cellulosic waste material by using a deep eutectic solvent. The cellulose waste material is preferably selected from papermaking residues, and is in particular selected from papermaking rejects or papermaking sludges. The dissolving step is typically carried out at a temperature of 40 to 120°C, preferably 40 to 100°C and more preferably 60 to 80°C.

[0037] Cellulose solubility in a DES should allow recovering pure cellulose from papermaking residues (rejects, sludges) in the form of clean dissolved pulp or as a basic building block for biochemicals, materials or fuels. This could very well be applied in the treatment of tissue waste after use, closing the loop in this value chain as well.

[0038] The processes as disclosed herein have significant saving potential. Energy consumption in a DES based process will be very different from today's pulping practices, replacing both chemical and (semi) mechanical pulp production by the DES based process, creating a variety of omnivore pulp grades tailor-made for every application. When this new pulping concept is applied throughout the sector, it could reduce fossil CO_2 emissions by 20%, and result in 40% primary energy savings within the current mill boundaries. Savings result from the balance of production of energy from lignin inside the integrated mill boundaries and the lesser energy consumption for pulping in the DES concept.

[0039] Various modifications and variations of the invention will be apparent to those skilled in the art without departing from the scope of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in the relevant fields are intended to be covered by the present invention.

[0040] The following example is merely illustrative of the present invention and should not be construed to limit the scope of the invention as indicated by the appended claims in any way.

EXAMPLES

Example:

[0041]

1. The DES is prepared by mixing the hydrogen donor and acceptor at slightly elevated temperatures.
2. The lignocellulose[1] (woodchips or any other lignocellulosic raw material[2]) is mixed with the DES (choice of DES and process conditions depend on raw material and required product specifications). Lignin and hemicellulose dissolve in the DES, within about 30 minutes at 60-80°C. Ratio DES: lignin to be removed is 1:0,35. The process yields high quality lignin-free cellulose fibres. Resulting fibre is almost white, hardly requiring additional bleaching. Shortening the reaction time results in higher yield fibres (with lignin - resembling current mechanical fibres). Any required additional bleaching or other fibre treatment might be done by enzymes that can also work in the DES.[3]
3. Cellulose and lignin-containing DES are separated by simple solid-liquid separation.
4. DES is washed from the cellulose with water. The resulting water/DES liquid is used for lignin precipitation in step 5 (thus recovering the DES).
5. Lignin is precipitated by adding water (Ratio DES : Water = 1 : 1).
6. Lignin is removed by a simple solid/liquid separation. 98% of lignin is recovered.
7. The hemicellulose remains in the water/DES mixture during lignin recovery. It will be converted into more valuable chemicals like furfural.
8. The furfural will be isolated using CO_2.
9. The DES will be recovered by using nano-filtration.

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[0042]

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Claims

1. A process for producing pulp and/or paper comprising using a deep eutectic solvent.

2. The process according to claim 1 comprising a dissolving step to dissolve lignin from a lignocellulosic material by using a deep eutectic solvent.

3. The process according to claim 2, wherein the lignocellulosic material is selected from wood, woodchips, fibre crops, paper, board, waste paper, other lignocellulosic materials, or any combination thereof.

4. The process according to claim 2 or 3, wherein the dissolving step is carried out at a temperature of 40 to 120°C, preferably 40 to 100°C and more preferably 60 to 80°C.

5. The process according to any of claims 2 to 4, wherein the dissolving step is carried out for 10 to 120 min, preferably 20 to 60 min and more preferably for 30 to 40 min.

6. The process according to any of claims 2 to 5, wherein the process further comprises a separating step of separating a lignin containing deep eutectic solvent, obtained after the dissolving step, from the remaining material after the dissolving step.

7. The process according to claim 6, wherein the process further comprises a washing step of washing the remaining material with a washing solvent, wherein the washing solvent is preferably water, after the separating step.

8. The process according to claim 6 or 7, wherein the process further comprises a precipitating step of precipitating the lignin from the lignin containing deep eutectic solvent after the separating step by using a solvent, preferably water, preferably using water used as a washing solvent in a washing step according to claim 6, preferably by a ratio of deep eutectic solvent to water of 1:1.

9. The process according to any of claims 2 to 8, wherein the process further comprises a recovering step of recovering the used deep eutectic solvent.

10. The process according to claim 1 which is a process for processing recycled fibres comprising a contacting step of contacting recycled fibres with a deep eutectic solvent.

11. The process according to claim 1 comprising

    i. a dissolving step of dissolving cellulose from a cellulosic material by using a deep eutectic solvent and
    ii. optionally a precipitating step of precipitating the cellulose obtained in the dissolving step in sheet format.

12. The process according to claim 1 which is a process for recovering cellulose from cellulose containing waste comprising a dissolving step of dissolving cellulose from the waste material by using a deep eutectic solvent.

13. The process according to claim 12, wherein the cellulose containing waste is selected from papermaking residues, and is in particular selected from papermaking rejects or papermaking sludges.

14. Paper obtained after a process as defined in any of the preceding claims.

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EUROPEAN SEARCH REPORT

Application Number
EP 13 19 4321

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2013/153203 A1 (UNIV EINDHOVEN TECH [NL]) 17 October 2013 (2013-10-17) * page 7, line 4 - line 8 * * page 3, line 6 - line 18 * * claims 1-12 * * page 21, line 19 - page 23, line 5 * -----	1-14	INV. D21C3/20
			TECHNICAL FIELDS SEARCHED (IPC)
			D21C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	28 March 2014	Ponsaud, Philippe

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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28-03-2014

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013153203 A1	17-10-2013	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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