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(54) Title: A METHOD OF FRACTIONATING A LIGNOCELLULOSIC MATERIAL AND PRODUCTS OBTAINED BY SAID METHOD

(57) Abstract: The present invention relates to the fields of treating lignocellulosic material. Specifically, the invention relates to a method of fractionating a lignocellulosic material, wherein said method comprises contacting a lignocellulosic material with a specific composition to obtain a liquid fraction comprising said specific composition and dissolved compounds from the lignocellulosic material, and a solid fraction, and bleaching the solid fraction. Also, the invention concerns a hemicellulose, cellulose or lignin product, or any combination thereof, obtained by the method of the present invention.

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A method of fractionating a lignocellulosic material and products obtained by said method

FIELD OF THE INVENTION

The present invention relates to the fields of treating lignocellulosic material. Specifically, the invention relates to a method of fractionating a lignocellulosic material, wherein said method comprises contacting a lignocellulosic material with a specific composition to obtain a liquid fraction comprising said specific composition and dissolved compounds from the lignocellulosic material, and a solid fraction, and bleaching the solid fraction. Also, the invention concerns a hemicellulose, cellulose or lignin product, or any combination thereof, obtained by the method of the present invention.

BACKGROUND OF THE INVENTION

Lignocellulosic material comprises carbohydrate polymers (cellulose, hemicellulose), and an aromatic polymer (lignin). Purified cellulose has a well-known use in textile industry or as a raw material for production of cellulose derivatives. Purified sulphur free lignin and hemicelluloses can be used as polymers or feedstock in bioconversion or chemical conversion methods. Purified sulphur free lignin and hemicelluloses cannot currently be produced in large amounts.

Lignocellulosic raw material can be converted into many chemicals and materials. Solvents are required for fractionations of lignocellulosic material and treatments of said material with e.g. deep eutectic solvents (DES), Low transition temperature mixture (LTTM) are intensively studied in the literature. DESs/LTTMs are widely used in processes of dissolution and fractionation and may also be used in post-delignification processes of modified lignocellulosic materials. DESs are able to dissolve e.g. a significant amount of lignin and also carbohydrates (hemicellulose) from the lignocellulosic material.

Despite of extensive studies and world-wide interest, the field of lignocellulosic materials still lacks efficient and simple methods of fractionating lignocellulosic materials for production of large amounts of substantially pure cellulose, hemicellulose and sulphur free lignin.

BRIEF DESCRIPTION OF THE INVENTION

It is an aim of the invention to provide a method of fractionating lignocellulosic materials for obtaining cellulose, hemicellulose and/or lignin, and/or other components, from a lignocellulosic material. In this way fractions containing an increased amount of components of interest are obtained.

A fractionation method of the present invention enables purification and recovery of e.g. polymeric compounds of wood as relatively pure fractions. The method is based on at least two steps which together create said method for obtaining high purity fractions of wood polymers such as cellulose, hemicellulose and/or lignin. In said method deep eutectic solvents (DES) (A in figure 1) are utilized with bleaching technologies (B in figure 1) and optionally with different extraction (C in figure 1) and separation technologies to produce purified fractions from lignocellulosic material (see figure 1). The present invention thus provides a single method by combining DES treatment with bleaching in an inventive way, thus enabling synergistic effects. And indeed, said single method enables production of large amounts of substantially pure cellulose, (sulphur free) lignin and/or hemicellulose.

In addition to other advantages the method of the present invention is very simple, efficient and cost-effective. Due to the effectiveness, less chemicals and fewer bleaching stages are needed in the fractionation method of the present invention compared to the fractionation methods of the prior art. Indeed, the present invention enables easier bleaching of the lignocellulosic material compared to the prior art methods.

The invention is defined by the features of the independent claims. Specific embodiments are defined in the dependent claims.

The present invention relates to a method of fractionating a lignocellulosic material, wherein said method comprises contacting a lignocellulosic material with a composition comprising a deep eutectic solvent (DES) to obtain a liquid fraction comprising DES and dissolved compounds from the lignocellulosic material, and a solid fraction, and bleaching the solid fraction.

Also, the present invention relates to a carbohydrate, hemicellulose, cellulose or lignin product or fraction obtained by the method of the present invention.

Also, the present invention relates to a combination of hemicellulose, cellulose and lignin products or fractions obtained by the method of the present invention.

And still, the present invention relates to use of the hemicellulose, lignin or cellulose product, or any combination thereof, obtained by the method of the present invention e.g. in industry.

And still, the present invention relates to use of the cellulose (or cellulose product) obtained by the method of the present invention in textile industry or in production of cellulose derivatives.

And still further, the present invention relates to use of the hemicellulose and/or small molar mass cellulose (or hemicellulose and/or small molar mass cellulose product) obtained by the method of the present invention in industry, e.g. as a substrate in the production of specialty chemicals, such as sugars and alcohols, or packing and packaging material.

Further features and advantages of specific embodiments will be discussed in more detail in the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a fractionation method for lignocellulosic material according to the present invention. Products obtainable by said method are also shown in figure 1. In one step of the process (e.g. the first step) a lignocellulosic material is treated with DES or a composition comprising DES (A). Significant amount of lignin and carbohydrates (e.g. hemicellulose) and/or other components are dissolved in said DES or composition (L1), i.e. a liquid fraction of the method of the present invention is obtained. Dissolved compounds in said liquid fraction are optionally recovered (e.g. separated by membrane filtration and/or precipitation processes) from the liquid fraction (D). The fractions of lignin (P1) and/or hemicellulose (P2) and/or other components are obtained. Residual DES may be purified for reuse (E). The solid fraction from DES treatment (S1) comprises cellulose and hemicellulose and some lignin. The residual lignin of the solid fraction is removed surprisingly efficient by

bleaching (B) and after bleaching the solid fraction comprises cellulose and hemicellulose (S2). Hemicellulose may optionally be extracted from the solid fraction e.g. by alkaline extraction or with hot water (C, L2) and the obtained residual solid material comprises mainly cellulose (P4). The lignin (P1), hemicellulose (carbohydrates) (P2, P3) and cellulose (P4) fractions obtained by the present invention may optionally be further purified.

DETAILED DESCRIPTION OF THE INVENTION

In the present context, the term "lignocellulosic material" comprises plant dry matter comprising carbohydrate polymers including cellulose and hemicellulose, and lignin. "Lignocellulosic material" includes virgin lignocellulosic material such as wood chips or saw dust from, for example, softwood, for example spruce, pine or larch, or from hardwood, such as birch, poplar, aspen, alder, eucalyptus or mixed tropical hardwood, or mixtures thereof. "Lignocellulosic material" also includes recycled lignocellulosic materials as well as waste lignocellulosic material, such as by-products from industry and agriculture such as corn stover, sugarcane, bagasse, cotton, straw *etc.* and saw mill, pulp mill and paper mill discards.

"Chips" includes wood chips, bark chips and nutshells. In particular, "chips" refers to slate-like or plate-like particles.

The term "aqueous liquids" means liquids in which there is at least some water present including for example, industrial effluents such as hot water extraction liquors, extraction liquors from wood pulping mills, waste waters from pharmaceutical plants, waste waters from oil refineries, as well as agricultural run-offs and waterways such as canals and rivers, other bodies of water such as reservoirs, and natural or man-made ponds or lakes.

"Liquids" may be e.g. aqueous or non-aqueous liquids or anhydrous liquids. Thus, the "liquid" can be for example be formed by an organic liquid, such as a polar or non-polar organic liquid. Such liquids are typically selected from the group of aliphatic and aromatic alcohols ketones, aldehydes, ethers, esters as well as various hydrocarbon liquids, which may be halogenated. In one embodiment the liquid may comprise "a solvent" (i.e. a substance that dissolves a solute resulting in a solution). A solvent is usually a liquid but can also be a solid, a gas, or a supercritical fluid.

"Extraction Liquor" or "extraction liquid" is a solution into which organic substances have been extracted from lignocellulosic material.

As used herein "precipitation" refers to a creation of a solid from a solution. Precipitation utilized in the present invention may be carried out by a decreased temperature either alone or in combination with other methods such as lowering the pH or by adding antisolvents.

The present invention is based on a single method, wherein DES treatment of lignocellulosic material is followed by bleaching, thus enabling simple and cost effective production of large amounts of cellulose (e.g. substantially pure cellulose), (sulphur free) lignin and/or hemicellulose.

In a very specific embodiment the methods and techniques provided by this invention enable lignocellulosic material e.g. wood or herbaceous biomass to be fractionated very efficiently in a single method, wherein the lignocellulosic material is contacted with a composition comprising a solvent in order to obtain i) a liquid fraction comprising said solvent, lignin, hemicellulose and optionally other components, and ii) a solid fraction (comprising e.g. cellulose, hemicellulose and/or lignin).

In one embodiment the lignocellulosic material comprises wood, such as softwood, for example spruce, pine or larch, hardwood, such as birch, poplar, aspen, alder, eucalyptus or mixed tropical hardwood, or mixtures thereof. In one embodiment of the invention the lignocellulosic material comprises or is in the form of wood chips or saw dust. In one embodiment the lignocellulosic material has a d_{50} particle size of 0.05 mm – 10.0 cm, e.g. 0.05 – 5 mm, 0.1 – 3 mm, 1 - 2 mm, 0.5 cm to 10.0 cm, specifically 2.0 to 7.0 cm, or suitably 4.0 to 6.0 cm. Any moisture content of the lignocellulosic material is suitable for the present invention. Specifically, the moisture content of the lignocellulosic material may be e.g. from 0.5% to 70%, such as 0.5 to 5% (such as about 1%), 5 to 30%, 30 to 50% or 50 to 60%.

Liquid fraction obtained by contacting a lignocellulosic material with a composition comprising DES

In the present invention a lignocellulosic material is contacted with a composition comprising a solvent and thus a liquid fraction is obtained (see (A) and L1 in figure

1). In an embodiment of the invention the liquid fraction comprises dissolved hemicellulose, lignin, lipophilic extractives, phenolic extractives, oligosaccharides and/or monosaccharides, other compounds or any combination thereof. In a specific embodiment of the invention the liquid fraction comprises at least dissolved hemicelluloses and/or lignin. In the present invention the lignocellulosic material is treated with a composition comprising DES to remove at least a portion of the hemicelluloses and/or lignins and/or other components contained therein.

In a specific embodiment the liquid fraction obtained by the DES treatment comprises at least about 30%, 60% or 80% (by mass) or more of the lignin of the lignocellulosic material to be treated. In a specific embodiment the liquid fraction obtained by the DES treatment comprises about 70% or less, about 50% or less, about 40% or less, about 30% or less, about 20% or less, about 10% or less, or about 5% or less (by mass) of the hemicellulose of the lignocellulosic material to be treated. In a very specific embodiment the liquid fraction obtained by the DES treatment comprises at least about 30%, 60% or 80% (by mass) or more of the lignin of the lignocellulosic material to be treated and about 70% or less, about 50% or less, about 40% or less, about 30% or less, about 20% or less, about 10% or less, or about 5% or less (by mass) of the hemicellulose of the lignocellulosic material to be treated. The principal hemicellulose in softwood is galactoglucomannan, which accounts for approx. 20% of the dry material. Xylan is the main hemicellulose in hardwood and varies in content within the limits of 15-30% of the dry wood.

In a very specific embodiment of the invention the treatment of the lignocellulosic material with a composition comprising DES is the first stage of the fractionation method.

In one embodiment at least 30%, e.g. about 35% or about 40% or more, of the dry solids by weight are dissolved in the DES treatment (i.e. when the lignocellulosic material is contacted with a composition comprising DES). In one embodiment of the invention the liquid fraction obtained after contacting the lignocellulosic material with a composition comprising DES comprises about 40-60% by mass of the dry matter of the lignocellulosic material to be contacted with DES.

The composition of the present invention used for treating the lignocellulosic material comprises DES and optionally any other agent such as any other solvent, e.g. water or alcohol (such as ethanol, methanol, glycerol, carboxylic acids, guaindine

hydrochloride). In one embodiment the composition comprising DES is a liquid composition. In a specific embodiment the composition consists of DES only.

As used herein DES refers to a deep eutectic solvent. DESs are a type of ionic liquid analogues formed from a eutectic mixture of Lewis or Brønsted acids and bases, i.e. a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD). Compared to traditional ionic liquids DESs offer several advantages including their low toxicity, low price, and biodegradability. The physicochemical properties of DESs are similar to those of traditional ionic liquids. In general, the term DES is used to refer to a mixture of compounds at a ratio that is close to their eutectic point, i.e. where they form a mixture with lowest freezing (or melting) point. Typically, a DES is made up of two compounds, an HBA and an HBD, but in some cases a complexing agent may be required. In summary, the term “deep eutectic solvent” or acronym “DES” is used to describe a solvent which comprises two or more separate chemical compounds at a ratio that has the lowest melting point.

Deep eutectic solvents are usually formed by mixing a hydrogen bond acceptor (HBA) such as an ammonium, phosphonium, or sulfonium cation, and a hydrogen bond donor (HBD) such as a carboxylic acid, a urea, or a glycerol. Exemplary cations used include, but are not limited to, choline chloride, betaine, *N*-ethyl-2-hydroxy-*N,N*-dimethylethanaminium chloride, 2-(chlorocarbonyloxy)-*N,N,N*-trimethylethanaminium chloride, and *N*-benzyl-2-hydroxy-*N,N*.dimethylethanaminium. Exemplary hydrogen bond donors include, but are not limited to, urea, acetamide, methylated ureas, glycerol, ethylene glycol, malonic acid, acetic acid, formic acid, lactic acid, adipic acid, oxalic acid, and citric acid. Examples of deep eutectic solvents include but are not limited to lactic acid : choline chloride (e.g. in the molar ratio 12:1 – 2:1, such as 9:1), acetic acid : choline chloride (e.g. in the molar ratio 18:1 – 2:1, such as 9:1), sorbitol : choline chloride (e.g. in the molar ratio 5:1 – 1:1, such as 5:1, 2:1 or 1:1), glycerol : choline chloride (e.g. in the molar ratio 5:1 – 1:1, such as 2:1), boric acid : choline chloride (e.g. in the molar ratio 3:1 – 1:1, such as 2:1), formic acid : choline chloride (e.g. in the molar ratio 1:1 – 3:1, such as 2:1), carboxylic acids : choline chloride (e.g. in the molar ratio 3:1 – 1:1, such as 2:1), guaindine hydrochloride : lactic acid (e.g. in the molar ratio 1:2 – 1:10, such as 1:9). In a specific embodiment DES is selected from the group consisting of choline chloride/lactic acid, choline chloride/acetic acid, choline chloride/sorbitol:glycerol, choline chloride/boric acid, choline chloride/formic acid, and choline chloride/guanidine hydrochloride, and any combination thereof. In a very specific embodiment DES choline

chloride/lactic acid has a ratio between choline chloride and lactic acid from 1:100 to 1:4 by molar mass, specifically at least 1:20 by molar mass, suitably about 1:9 by molar mass.

In one embodiment of the invention, a composition comprising DES is contacted with the lignocellulosic material at a ratio between DES and the lignocellulosic material from 100:1 to 4:1 by mass, specifically at least 20:1 by mass, suitably about 10:1 by mass.

In a specific embodiment the lignocellulosic material is allowed to contact with a composition comprising DES for at least 2 hours, at least 5 hours, e.g. 2-25 hours, 5-25 hours, or 10-25 hours, such as 18 hours. In another specific embodiment the lignocellulosic material is allowed to contact with a composition comprising DES at a temperature of at least 60 °C or at least 80 °C, e.g. about 90 to 200 °C or about 90 to 150 °C. Optionally, physical treatment, such as increased pressure, microwave irradiation or ultra-sonication, of the lignocellulosic material may be carried out when contacting the lignocellulosic material with a composition comprising DES. These treatments typically decrease the treatment time needed in DES. In very specific embodiments when the physical treatment and DES treatment are combined, the lignocellulosic material is allowed to contact with a composition comprising DES e.g. less than 2 hours.

Contacting a lignocellulosic material with a composition comprising DES may be carried out e.g. by adding a DES composition to the lignocellulosic material by one, two, three or several times or contacting the lignocellulosic material with a DES composition one, two, three or several times.

In one embodiment of the invention the liquid fraction comprising the composition comprising DES and dissolved compounds is separated from the solid fraction.

In a further embodiment one or more dissolved compounds present in the liquid fraction, e.g. at least lignin, hemicelluloses, and/or wood extractives (e.g. fatty and resin acids, sterols and phenolic compounds), are separated from said liquid fraction by a filtration (e.g. molecular or membrane filtration), extraction and/or precipitation (see (D) and P1 and P2 in figure 1). As used herein “membrane filtration” refers to a technique which is used to separate particles from a liquid for the purpose of pu-

rifying it, in other words a solvent and impurities are passed through a semi-permeable membrane. Membrane filtration techniques include nanofiltration, ultrafiltration, microfiltration and reverse osmosis. E.g. high molar mass hemicelluloses are easier to separate from a liquid fraction by ultrafiltration than hemicelluloses of lower molar mass. In one embodiment the precipitation is carried out by adding aqueous liquid such as water to the liquid fraction. Thereby fractions of lignin and/or hemicellulose may be produced.

In one embodiment of the present invention after separating the dissolved compounds from the liquid fraction by a filtration and/or precipitation the method further comprises purification of lignin from the obtained precipitate or filtrate, e.g. comprising cutting and/or dissolving hemicellulose of the obtained precipitate or filtrate with an acid hydrolysis and thereafter optionally filtrating the hydrolyzed precipitate or filtrate to obtain purified lignin. In a very specific embodiment the purity of lignin precipitated by water from DES solution is about 99% based on the pyrolysis analysis.

In one embodiment the lignin or hemicellulose fraction obtained e.g. after filtration or precipitation is optionally washed and/or dried.

In one embodiment of the invention the DES contacted with the lignocellulosic material and wherein at least lignins and/or hemicelluloses have been removed, is further purified for reuse by removing at least part of the carbohydrates, extractives and/or phenols (see (E) in figure 1).

Solid fraction obtained by contacting a lignocellulosic material with a composition comprising DES

Removal of at least a portion of the hemicelluloses and/or lignins and/or other components contained in the lignocellulosic material by a composition comprising DES provides a solid fraction (see S1 in figure 1). In one embodiment of the invention the solid fraction comprises at least cellulose, hemicellulose and/or lignin. In one embodiment the solid fraction from DES treatment comprises mostly cellulose and hemicellulose and a minor amount of lignin.

In one embodiment of the invention the solid fraction obtained after contacting a lignocellulosic material with a composition comprising DES has a hemicellulose content which is at least 10%, 20%, 30% or 40% smaller than that of the lignocellulosic material before contacting with the composition comprising DES. In one embodiment of the invention the hemicellulose content of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is about 90% or less, about 80% or less, or about 70% or less of the hemicellulose content of the lignocellulosic material to be fractionated.

In one embodiment the cellulose content of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is about 60 wt % or more, about 70 wt % or more, about 75 wt % or more, about 80% or more, or about 85 wt % or more.

In a further embodiment the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES has a lignin and/or other component content which is about 70 % or less, about 60 % or less, about 50 % or less, about 40 % or less, or about 30 % or less, about 20 % or less, about 10 % or less, about 5 % or less or about 3 % or less of the lignin content and/or other component content of the lignocellulosic material, respectively, before contacting the lignocellulosic material with a composition comprising DES.

In one embodiment of the invention the purity of the carbohydrate of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is about 80% or more or about 85% or more. In one embodiment of the invention the purity of the cellulose of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is about 55% or more or about 60% or more, e.g. 63%.

The residual lignin present in the solid fraction after DES treatment is removed by bleaching (see (B) in figure 1). Indeed, in the present invention bleaching of the lignocellulosic material is carried out after contacting the lignocellulosic material with a composition comprising DES, more specifically after separating the liquid fraction comprising DES and the solid fraction. In one embodiment of the present invention either one or more (e.g. two, three or four) bleaching stages of the solid fraction are carried out. One bleaching step is enough for excellent fractionation results of the

present disclosure. Indeed, a DES treatment prior to bleaching significantly improves the bleaching efficiency, makes bleaching easier and simplifies the bleaching process. Without DES treatment many (even 4 or 5 or more) bleaching stages are needed to achieve the very low residual lignin content of the solid fraction obtained by the method of the present invention.

Bleaching is a very common method and any bleaching agents and conditions known to a skilled person may be utilized in the method of the present invention. As used herein "a bleaching agent" is an agent that lightens or whitens a substrate through a chemical or biochemical reaction. These reactions may involve the destruction or modification of chromophoric groups in the substrate as well as the degradation of color bodies into smaller, more soluble units that are more easily removed in the bleaching process. In one embodiment of the present invention the bleaching is carried out with an agent selected from the group consisting of oxidizing agents (such as chlorine or its derivatives (such as sodium chlorite) or peroxygen or its derivatives (such as hydrogen peroxide, sodium perborate)), reducing agents (such as hydrosulfite (dithionites e.g. sodium dithionite), sodium borohydride, sulfur dioxide, sulfurous acid, bisulfites, sulfites, sodium sulfoxylate formaldehyde); and enzymes; and any combination thereof.

Chlorine-containing bleaching agents may be divided into four classes: chlorine (e.g. solid chlorine bleaching agents such as chlorinated isocyanurates, e.g. sodium dichloroisocyanurate dihydrate), hypochlorites (e.g. sodium hypochlorite, calcium hypochlorite, bleach liquor, bleaching powder or tropical bleach), *N*-chloro compounds (e.g. halogenated hydantoins, sodium *N*-chlorobenzenesulfonamide (chloramine B)), and chlorine dioxide.

Enzymes, e.g. in free and/or immobilized form, can be used for example for generation of the oxidizing agent necessary for bleaching as well as for direct bleaching of the textile substrate. Suitable enzymes include but are not limited to the glucose oxidases, chloroperoxidases, laccases, and catalases.

Suitable bleaching conditions include but are not limited to a temperature (e.g. a liquor temperature) from a room temperature (25°C) to 90°C (e.g. 30°C, 40°C, 50°C, 60°C, 70°C, 80°C), and even above 90°C, e.g. for 5 - 90 minutes (e.g. 10, 15, 20, 30, 40, 50, 60, 70, or 80 minutes). As is understood by a skilled person very different

bleaching conditions may be chosen e.g. for chemical agents compared to enzymes. Optionally, commonly known bleaching activators or enhancers, bleach catalysts and/or any other suitable agents known to a person skilled in the art may be used in the bleaching of the present invention.

In one embodiment of the invention there are one or several washing steps after bleaching the solid fraction but before optional extraction step. Washing temperatures include any temperature common to a person skilled in the art, for example below 100°C, below 40°C or even a room temperature (25°C).

After DES treatment and bleaching the solid fraction comprises or mainly consists of cellulose and hemicellulose (see S2 in Table 1 and Figure 1). In one embodiment of the invention at least a part or at least a majority of the lignin compounds or fragments have been removed from the lignocellulosic material by contacting said material with a composition comprising DES and bleaching. In one embodiment the lignin content of the bleached solid fraction is about 6 wt % or less, about 5 wt % or less, about 4 wt % or less, about 3 wt % or less, or about 2 wt %. In one embodiment the hemicellulose content of the bleached solid fraction is about 50% or less, 30% or less, 20% or less or 15% or less of the hemicellulose content of the lignocellulosic material to be fractionated. In one embodiment the cellulose content of the bleached solid fraction is about 65 wt % or more, about 75 % or more, about 80 wt % or more, or about 90 wt %. In a very specific embodiment the lignin content of the bleached solid fraction is about 3 wt % or less, about 2 wt % or less, or about 1 wt % or less, and the hemicellulose content is about 20 wt % or less, about 10 wt % or less, or about 5 wt % or less of the mass of the bleached solid fraction, and the cellulose content is about 75 wt % or more, or about 80 wt % or more.

In one embodiment of the invention the purity of the carbohydrate in the DES treated and bleached solid fraction is about 95% or more, or about 98% or more (of the organic material). In one embodiment the purity of the cellulose in the DES treated and bleached solid fraction is about 70% or more, or about 80% or more (of the organic material).

In a very specific embodiment of the invention an extraction of the solid fraction is carried out after bleaching the solid fraction to separate hemicellulose from cellulose (see (C) in figure 1). Any suitable extraction method known to a person skilled in the

art may be utilized in the present method. In one embodiment the extraction is carried with an aqueous solution, optionally containing an alkaline, acidic or buffering component, to remove a significant portion of the hemicelluloses and/or other compounds contained in the bleached solid fraction. In one embodiment the extraction is a hot (pressurized) water extraction, said hot water extraction specifically being carried out at a temperature in excess of 100 °C and e.g. up to 250 °C, for example about 110 to 250 °C, in particular 110 to 200 °C, such as 145 to 200 °C, specifically for a time period of 5 min to 1 day. The treatment time depends on the temperature. Typically the duration is 5 min to 1 day, for example 10 min to 1 day for example 15 min to 720 min. Higher temperatures and longer extraction times lead to higher extraction yields, i.e. a greater amount of the hemicelluloses is extracted as the temperature and time of extraction increase. Alternatively to the extraction with pressurized water at a high temperature (e.g. PWHE (pressurized hot water extraction)) the extraction can be made using e.g. alkaline compounds, e.g. sodium hydroxide or other chemical, to enhance the dissolution of hemicelluloses.

In one embodiment of the invention the hemicellulose content of a liquid fraction obtained after extraction is about 5 % or more, about 10 % or more, about 20 % or more of the hemicelluloses in the lignocellulosic material to be fractionated (see (C), L2 and P3 in figure 1 and table 1). The hemicellulose content of a liquid fraction obtained after extraction may depend on the extraction reagent (e.g. water extraction vs. alkali extraction). In one embodiment of the invention the hemicellulose content of the lignocellulosic material to be extracted is about 16 - 17 % of the hemicelluloses in the lignocellulosic material to be fractionated (i.e. before the DES treatment. In one embodiment the cellulose content of the extracted solid fraction is about 60 wt % or more, about 80 wt % or more, or about 85 wt % or more, or about 90 wt % or more (see (C) and P4 in figure 1 and table 1). In a specific embodiment of the invention, the cellulose content of a solid fraction obtained after PHWE extraction is about 70 wt % or more, about 80 wt % or more, or about 85 wt % or more, or about 90 wt % or more. In another specific embodiment, the cellulose content of a solid fraction obtained after alkaline extraction is about 45% or more, about 55% or more, about 60 % or more, about 65% or more, about 80% or more, or about 90% or more of the cellulose content of the lignocellulosic material to be fractionated.

Still, in one embodiment of the invention the purity of the cellulose obtained from the optional extraction is about 80 wt% or more, about 90 wt% or more, or even about

95 wt% or 99 wt% or more. In one embodiment of the invention wherein the extraction is made with hot water (e.g. with PHWE extraction) the purity of the cellulose obtained from the optional extraction is about 80 wt% or more. In one embodiment of the invention wherein the extraction is made with an alkaline agent (e.g. with sodium hydroxide such as with 17.5% sodium hydroxide) the purity of the cellulose obtained from the optional alkaline extraction is about 90 wt% or more.

In one embodiment the solid fraction and extraction liquid are separated. In a further embodiment the solid fraction comprising cellulose, hemicellulose and lignin (after hot water extraction) or comprising mostly cellulose (after alkaline extraction) is optionally washed and/or dried. In a further embodiment very pure carbohydrate solution is recovered from the extraction liquid.

Indeed, a hemicellulose, cellulose or lignin product or fraction, or any combination thereof, is obtained by the effective method of the present invention. Lignin, hemicellulose and cellulose fractions obtained by the present invention are very desirable and useful as raw materials. In an embodiment at least a portion of the recovered hemicelluloses, lignin or cellulose is directed to further processing e.g. for use in industry. In one embodiment at least a portion of the recovered cellulose is directed to further processing e.g. for use in textile industry or in production of cellulose derivatives. In one embodiment at least a portion of the recovered hemicelluloses and/or dissolved small molar mass cellulose are directed to further processing for use in industry, e.g. as a substrate in the production of specialty chemicals such as sugars and alcohols, or at least a portion of the recovered hemicelluloses and/or dissolved small molar mass cellulose are refined for use e.g. as packing and packaging material. Lignin obtained by the present invention may for example be burned as fuel, thus producing energy. As used herein “energy production” refers to e.g. production of heat by burning the recovered lignin. Furthermore, high quality lignin may be used as a renewable source of aromatic compounds for the chemical industry. Thus, in one embodiment of the invention at least a portion of the recovered lignin is directed to further processing for use in industry e.g. for producing energy or as a source of aromatic compounds.

In a specific embodiment the hemicellulose (or carbohydrate), cellulose or lignin product obtained by the effective method of the present invention has the following characteristics, respectively. In a very specific embodiment the purity of carbohydrate (P3) is about 85 % or more, 90 % or more, or 95 % or more, and optionally the

yield from original wood is about 5% or 10% or more. In a very specific embodiment the purity of cellulose (P4) is about 80-99 wt% or more depending on the optional extraction process (PHWE or alkaline extraction), and optionally the yield from original wood is about 40%, 50%, 60% or more. In a very specific embodiment the lignin purity (P1) is about 90 wt% or more and yield 40 % or 45 % or more. In a specific embodiment average molar mass of lignin (P1) is 5000 g/mol and polydispersity about 2.7. Lignin obtained by the present invention is sulphur free in contrast to lignin available today e.g. from kraft pulping process.

In one embodiment of the invention in the hemicellulose, cellulose or lignin product or the combination thereof
the purity of carbohydrate product (P4) is about 95 wt% or more, about 97 wt% or more, 98 wt% or more, or 99 wt% or more,
the purity of cellulose product is about 80-99 wt% or more, and/or
one or more characteristics of the lignin product are selected from the group consisting of the lignin product purity about 70 wt% or 80 wt% or 90 wt% or 99 wt% or more, average molar mass of lignin 5000 g/mol, polydispersity about 2.7., and sulphur free.

In a specific embodiment any combination of the hemicellulose, cellulose or lignin product (see e.g. P1 and P3, P1 and P4, P3 and P4, P1, P3 and P4) obtained by the method of the present invention has specific characteristics. In one embodiment of the invention, in a combination of lignin and hemicellulose products, the lignin purity (P1) is about 70 wt% or 80 wt% or 90 wt% or 99 wt% or more (and optionally yield 40 % or 45 % or more of the lignocellulosic material to be fractionated, and/or optionally said lignin product is sulphur free), and the purity of hemicellulose (P3) is about 80 % or more, 85 % or more, or 90 % or more. In one embodiment of the invention, in a combination of lignin and cellulose products, the lignin purity (P1) is about 70 % or 80 % or 90% or 99% or more (and optionally yield 40 %, 41 %, 42 %, 43 %, 44 %, 45 %, 46 % or more of the lignocellulosic material to be fractionated, and/or optionally said lignin product is sulphur free), and the purity of cellulose (P4) is about 80-99% or more. In one embodiment of the invention, in a combination of hemicellulose and cellulose products, the purity of hemicellulose (P3) is about 80 % or more, 85 % or more, or 90 % or more, and the purity of cellulose (P4) is about 80-99 wt% or more. In one embodiment of the invention, in a combination of lignin, hemicellulose and cellulose products, the lignin purity (P1) is about 70 wt% or 80 wt% or 90 wt% or 99 wt% or more (and optionally yield 40 % or 45 % or more of the

lignocellulosic material to be fractionated, and/or optionally said lignin product is sulphur free), the purity of hemicellulose (P3) is about 80 % or more, 85 % or more, or 90 % or more, and the purity of cellulose (P4) is about 80-99 wt% or more.

The combination of hemicellulose, cellulose and/or lignin products may refer to a combination of e.g. separate products or mixed products.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described below but may vary within the scope of the claims.

EXAMPLES

In this example 100 g of wood chips were fractionated by the developed process (Fig. 1). At first the DES treatment (105 °C, 18 h, DES: 1:9 ratio choline chloride and lactic acid, DES/wood mass ratio 10:1) was made for birch chips (average size 3*3*0.5 cm, moisture content 1%) (see A of figure 1). After the treatment the DES solution was separated from the solid fraction (L1 of figure 1). The liquid fraction from the DES treatment contained about 43.5% by weight of the dry matter of the wood. By adding water to the liquid fraction (DES-solution) about 23% of the dry solids by weight in the DES-solution was precipitated (P1 of figure 1). The precipitate contained 46% of the lignin of the birch chips. After solid-liquid separation the residual solid material consisted mostly of lignin (purity of lignin was 99%%) (see P1 in figure 1). The residual DES may be purified for reuse (E of figure 1). Optionally, further purification of lignin in the precipitate was done e.g. by acid hydrolyses, which depolymerize hemicelluloses. By acid hydrolysis hemicelluloses are dissolved in an acid solution.

The solid fraction after DES treatment still contained about 35% of the original lignin in birch chips (S1 of figure 1). This was easily removed by sodium chlorite solution (0.5 mmol/g). Indeed the DES-treatment had a very positive effect on the bleaching efficiency. One stage bleaching of DES-treated wood with $NaClO_2$ solution (1 g $NaClO_2$/ 2.5 g solid matter, 80 ml water, 0.5 ml acetic acid, 75 °C one hour) removed approximately 94% of residual Klason lignin (B of figure 1). As a result the residual amount of lignin in the DES treated and once bleached lignocellulosic material was only 2% of the original amount of Klason lignin in wood chips. The carbohydrate

purity in the solid fraction after DES treatment and bleaching (once) was almost 95.5% and cellulose purity 78% (figure 1 and S2 of table 1). Optionally to remove hemicelluloses from cellulose by extraction (C of figure 1) e.g. hot water extraction or alkaline extraction can be applied. Non-optimized extraction with 17.5% NaOH solution removed about over 50% of hemicellulose and about 8% of cellulose also dissolved (L2 of figure 1). Pressurized hot water extraction dissolved mainly hemicelluloses. The purity of hemicellulose (carbohydrates about 86%) in this fraction (see P3 of figure 1) is significantly better than what can be achieved with pressurized hot water extraction (PHWE) of virgin wood. Due to the DES treatment and bleaching the amount of lignin in the extract is negligible and therefore, membrane-based fractionation and concentration of hemicellulose can be efficiently carried out.

The residual solid fraction after extraction (P4) contained mainly cellulose, actually about 70% of the original cellulose after PHWE and 60% after alkaline extraction. The residual solid fraction or cellulose can be used in the applications where dissolving pulp are used today e.g. in textile industry or to produce cellulose derivatives. Purity of carbohydrates in the P4 fraction is 98% (Table 2).

Table 1. Composition and cellulose purity after different treatment stages (see also fig. 1) (Purity refers to wt%, if there is a solid fraction in question.)

	Code in Fig. 1	**Cellulose**	**Hemicellulose**	**Polymeric carbohydrate**	**Lignin (Klason)**	**Lignin (Acid soluble)**	**Extractives**	**Ash**
Original wood, g/100 g		49.3	27.2	76.5	17	4.7	1.6	0.2
DES treatment (56.5 g), g	S1	35.4	8.8	46.1	6.2	1.5	2.7	0.04
Purity		62.7%	15.6%	81.6%	11.0%	2.7%		
Yield		71.8%	32.4%	60.3%	36.5%	31.9%		
Bleaching (41.8. g), g	S2	32.4	4.5	39.9	0.4	0.8	0.4	0.3
Purity		77.5%	10.8%	95.5%	1.0%	1.9%		
Yield		65.7%	16.5%	52.2%	2.4%	17.0%		

After 17.5% NaOH extraction (33.4 g), g	P4	29.8	2.1	32.7	0	0.4	0.2	0.11
Purity		89.2%	6.3%	97.9%	0.0%	1.2%		
Yield		60.4%	7.7%	42.7%	0.0%	8.5%		

Table 2. Purity of products and yield from original wood. (Purity refers to wt%, if there is a solid fraction in question.)

	Product	**Purity**	**Yield from original wood**
P1	Lignin	99%	46%
P3	Hemicelluloses	85%	10%
P4	Cellulose + other carbohydrates	98%	43%
	- Cellulose	89%	60%

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Claims

1. A method of fractionating a lignocellulosic material, wherein said method comprises

contacting a lignocellulosic material with a composition comprising a deep eutectic solvent (DES) to obtain a liquid fraction comprising DES and dissolved compounds from the lignocellulosic material, and a solid fraction, and

bleaching the solid fraction in one or two bleaching stages, wherein the bleaching is carried out with an agent selected from the group consisting of oxidizing agents, reducing agents and any combination thereof.

2. The method according to any of the preceding claims, wherein the oxidizing agent is selected from chlorine or its derivatives (such as sodium chlorite) and peroxygen or its derivatives (such as hydrogen peroxide, sodium perborate)), and/or the reducing agent is selected from the group consisting of sodium dithionite, sodium borohydride).

3. The method according to any of the preceding claims, wherein the lignocellulosic material is allowed to contact with said composition comprising DES for at least 2 hours, e.g. 2-25 hours.

4. The method according to any of the preceding claims, wherein the lignocellulosic material is allowed to contact with said composition comprising DES at a temperature of at least 60 °C, e.g. 90 to 200 °C.

5. The method according to any of the preceding claims, wherein the composition comprising DES is contacted with the lignocellulosic material at a ratio between DES and the lignocellulosic material from 100:1 to 4:1 by mass, specifically at least 20:1 by mass, suitably 10:1 by mass.

6. The method according to any of the preceding claims, wherein DES is selected from the group consisting of choline chloride/lactic acid, choline chloride/acetic acid, choline chloride/sorbitol/glycerol, choline chloride/boric acid, choline chloride/formic acid, and choline chloride/guanidine hydrochloride.

7. The method according to claim 6, wherein DES choline chloride/lactic acid has a ratio between choline chloride and lactic acid from 1:100 to 1:4 by mass, specifically at least 1:20 by mass, suitably 1:9 by mass.

8. The method according to any of the preceding claims, wherein the liquid fraction comprises 20-70% by mass or 40-60% by mass of the dry matter of the lignocellulosic material.

9. The method according to any of the preceding claims, wherein the liquid fraction comprising the composition comprising DES and dissolved compounds is separated from the solid fraction.

10. The method according to any of the preceding claims, wherein one or more dissolved compounds of the liquid fraction are selected from the group consisting of lignin, carbohydrates e.g. hemicellulose and wood extractives (e.g. fatty and resin acids, sterols and phenolic compounds).

11. The method according to any of the preceding claims, wherein one or more dissolved compounds present in the liquid fraction are separated from said liquid fraction by a filtration, extraction and/or precipitation.

12. The method according to claim 11, wherein the precipitation is carried out by adding aqueous liquid such as water to the liquid fraction.

13. The method according to claim 11 or 12, wherein the filtration is a molecular or membrane filtration.

14. The method according to any of claims 11-13, wherein after the precipitation or filtration the method further comprises purification of lignin from the obtained precipitate or filtrate, e.g. comprising cutting and/or dissolving hemicellulose of the obtained precipitate or filtrate with an acid hydrolysis and thereafter optionally filtrating the hydrolyzed precipitate or filtrate to obtain purified lignin.

15. The method according to claim 14, wherein the purity of lignin obtained from the purification is at least 70%.

16. The method according to any of the preceding claims, wherein the DES is purified for reuse by removing at least part of the carbohydrates, extractives and/or phenols.

17. The method according to any of the preceding claims, wherein the lignocellulosic material comprises wood, such as softwood, for example spruce, pine or larch, hardwood, such as birch, poplar, aspen, alder, eucalyptus or mixed tropical hardwood, or mixtures thereof.

18. The method according to any of the preceding claims, wherein the lignocellulosic material has a d_{50} particle size of 0.05 mm – 10.0 cm, e.g. 0.05 – 5 mm, 0.1 – 3 mm, 1 - 2 mm, 0.5 cm to 10.0 cm, specifically 2.0 to 7.0 cm, or suitably 4.0 to 6.0 cm.

19. The method according to any of the preceding claims, wherein the moisture content of the lignocellulosic material is from 0.5% to 70%, such as 0.5 to 5%, 5 to 30%, 30 to 50% or 50 to 60%.

20. The method according to any of the preceding claims, wherein the solid fraction comprises cellulose, hemicellulose and/or lignin.

21. The method according to any of the preceding claims, wherein at least a part or at least a majority of the lignin compounds or fragments have been removed from the lignocellulosic material by contacting said material with a composition comprising DES and bleaching.

22. The method according to any of the preceding claims, wherein the lignin content of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is 50 % or less, 40 % or less, or 30 % or less of the lignin content of the lignocellulosic material to be fractionated.

23. The method according to any of the preceding claims, wherein the lignin content of the bleached solid fraction is 4 wt % or less, 3 wt % or less, 2 wt % or less, or wt 1 % or less.

24. The method according to any of the preceding claims, wherein the hemicellulose content of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is 50 % or less or 30 % or less of the hemicellulose content of the lignocellulosic material to be fractionated.

25. The method according to any of the preceding claims, wherein the hemicelluloses content of the bleached solid fraction is 50% or less, or 30% or less or 15 %

or less of the hemicelluloses content of the lignocellulosic material to be fractionated.

26. The method according to any of the preceding claims, wherein the cellulose content of the solid fraction obtained after contacting the lignocellulosic material with a composition comprising DES is 70 % or more, or 80 % or more of the cellulose content of the lignocellulosic material to be fractionated.

27. The method according to any of the preceding claims, wherein the cellulose content of the bleached solid fraction is 65 % or more, or 75 % or more of the cellulose content of the lignocellulosic material to be fractionated.

28. The method according to any of the preceding claims, wherein the purity of the carbohydrate in the bleached solid fraction is 95 wt % or more, or 98 wt % or more.

29. The method according to any of the preceding claims, wherein the purity of the cellulose in the bleached solid fraction is 70 wt % or more, or 80 wt % or more.

30. The method according to any of the preceding claims, wherein an extraction of the solid fraction is carried out after bleaching the solid fraction.

31. The method according to claim 30, wherein the extraction is carried with an aqueous solution, optionally containing an alkaline, acidic or buffering component, to remove a significant portion of the hemicelluloses and/or other compounds contained in the bleached solid fraction.

32. The method according to claim 30 or 31, wherein the extraction is a hot water extraction, said hot water extraction specifically being carried out at a temperature in excess of 100 °C and up to 250 °C, in particular at 110 to 200 °C, specifically for a time period of 5 min to 1 day.

33. The method according to any of claims 30-32, wherein the hemicellulose content of a liquid fraction obtained after extraction is 5 % or more, or 10 % or more of the hemicellulose content of the lignocellulosic material to be fractionated.

34. The method according to any of claims 30-33, wherein the cellulose content of a solid fraction obtained after PHWE extraction is 50 % or more, 60% or more, or

70 % or more of the cellulose content of the lignocellulosic material to be fractionated.

35. The method according to any of claims 30-34, wherein the purity of the cellulose obtained from the extraction is 80 % or more.

36. The method according to any of claims 30-33, wherein the cellulose content of a solid fraction obtained after alkaline extraction is 45 % or more, or 55% or more, or 65% or more of the cellulose content of the lignocellulosic material to be fractionated.

37. The method according to claim 36, wherein the purity of the cellulose obtained from the alkaline extraction is 89 % or more.

38. The method according to any of the preceding claims, wherein at least a portion of the recovered hemicelluloses, lignin or cellulose is directed to further processing e.g. for use in industry.

39. The method according to any of the preceding claims, wherein at least a portion of the recovered cellulose is directed to further processing e.g. for use in textile industry or in production of cellulose derivatives.

40. The method according to any of the preceding claims, wherein at least a portion of the recovered hemicelluloses and/or dissolved small molar mass cellulose are directed to further processing for use in industry, e.g. as a substrate in the production of speciality chemicals such as sugars and alcohols, or at least a portion of the recovered hemicelluloses and/or dissolved small molar mass cellulose are refined for use e.g. as packing and packaging material.

41. The method according to any of the preceding claims, wherein at least a portion of the recovered lignin is directed to further processing for use in industry e.g. for producing energy or as a source of aromatic compounds.

42. A carbohydrate, hemicellulose, cellulose or lignin product obtained by the method of anyone of claims 1-41.

43. A combination of hemicellulose, cellulose and lignin products obtained by the method of anyone of claims 1-41.

44. The hemicellulose, cellulose or lignin product according to claim 42 or the combination thereof according to claim 43, wherein
the purity of total carbohydrate (hemicellulose+cellulose) product is 95 wt % or more, 98 wt % or more, or 99 wt % or more,
the purity of cellulose product is 80-99 wt % or more, and/or
one or more characteristics of the lignin product are selected from the group consisting of the lignin product purity 80 wt% or 90 wt% or more or 99 wt % or more, yield 40 % or 45 % or more, average molar mass of lignin 5000 g/mol, polydispersity 2.7., and sulphur free.

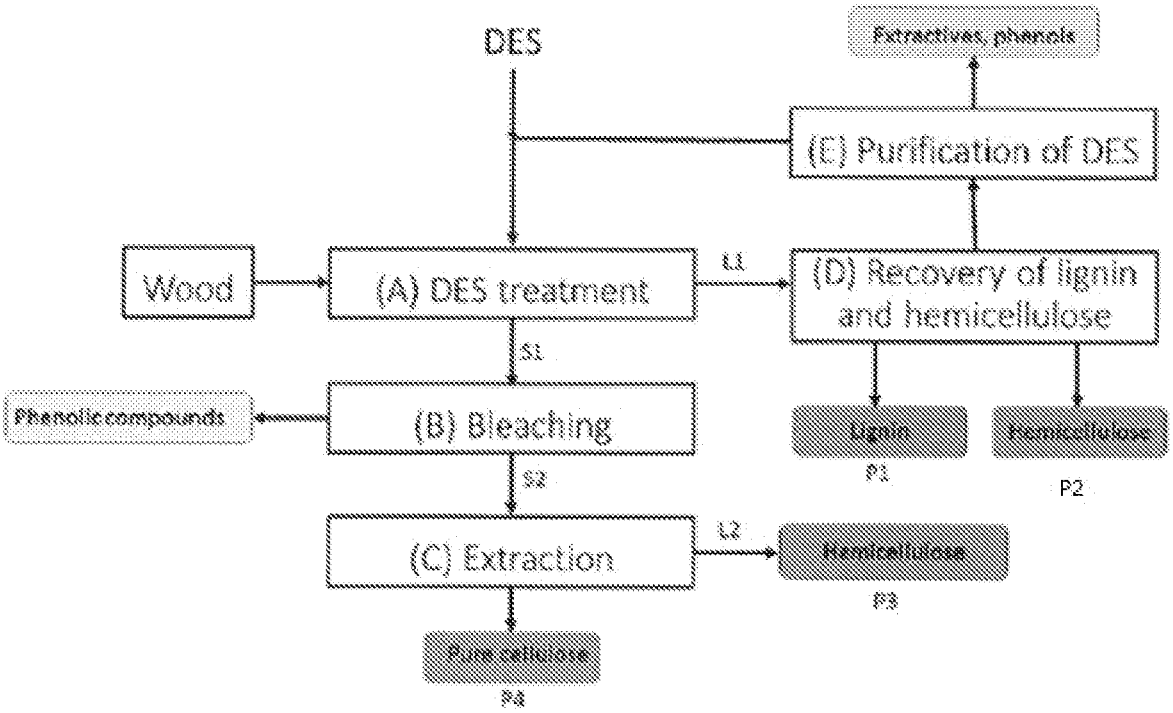
DES
Extractives, phenols
(E) Purification of DES
Wood
(A) DES treatment
L1
(D) Recovery of lignin and hemicellulose
S1
Phenolic compounds
(B) Bleaching
Lignin
Hemicellulose
P1
P2
S2
(C) Extraction
L2
Hemicellulose
P3
Pure cellulose
P4

Figure 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2020/050321

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21C3/20 D21C9/10 D21C9/14 D21C9/16 D21H17/25
D21H27/10 C08H8/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21C D21H C09J C08H

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"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	Date of mailing of the international search report
13 August 2020	21/08/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Karlsson, Lennart

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2020/050321

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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