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(54) Title: FRACTIONATION OF TECHNICAL LIGNIN

(57) Abstract: Disclosed are methods to obtain useful lignin fractions by fractionation of technical lignins. In some methods, suc-  
cessively solvents of increasing polarity are applied and/or an extraction column is used which provided with a packed stationary  
phase comprising technical lignin mixed with inert particles having a particle size in the range of from 1 to 1000 micrometers. Dis-  
closed is also an extraction column provided with a packed stationary phase, wherein the packed stationary phase comprises technic-  
al lignin mixed with inert particles having a particle size in the range of from to 000 micrometers.



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Title: FRACTIONATION OF TECHNICAL LIGNIN

## 5           **Field of the Invention**

The invention is in the field of fractionation of technical lignin. Particularly, some embodiments of the invention provide an environmentally sound method of obtaining valuable and useful fractions  
10   from technical lignin.

## **Background of the invention**

Lignin is the second most abundant natural substance in the world  
15   after cellulose. Currently, a major part of industrial lignin is used as low value solid fuel. This, however, does not do full justice to its potential, where a much higher economic value would result for the use of lignin as a raw material for chemical conversion. In this respect, however, lignin is underutilized by industry (Vishtal et al., 2011, BioResources 6(3), 3547-  
20   3568).

The invention specifically relates to technical lignins. Technical lignins are isolated as by-streams of the current pulp and paper industry and lignocellulosic bio refineries, including e.g. kraft, soda, organosolv, hydrolysis lignins, and lignosulfonates. They have a modified structure  
25   compared to native lignin and contain impurities that are dependent on the extraction process. Unlike native lignins, technical lignins are not contained in a biomass matrix, but are isolated therefrom. Hence, technical lignins, although isolated, can still be present in a composition remaining from biomass but are at least not chemically bound thereto.

30           In order for technical lignins to become suitable as raw materials for chemical conversion, a challenge is to recover and purify them. S available

methods are precipitation, filtration, and ultrafiltration. These methods either do not produce sufficiently purified fractions of technical lignin, or are not economically feasible, or both.

In the field of lignins, it has been known to carry out solvent  
5 extraction of non-isolated lignins, in steam exploded lignocellulose. A reference in this respect is EP 446 556. Herein a steam exploded lignocellulosic material is subjected to fractionation. Steam explosion is known as a pre-treatment process for biomass, but it does not result in an isolated technical lignin. Rather, the substrate in EP 446 566 still is a  
10 lignocellulosic material, i.e. having lignin contained in a biomass matrix, from which it is desired to obtain lignin fractions. In the reference, the lignin as fractionated from said steam-exploded lignocellulosic material is obtained mainly as a thermosetting fraction and as a thermoplastic fraction.

The invention is directed to a much more advanced problem, viz. the  
15 fractionation of technical lignin itself. This requires a separation between different lignin molecules, rather than of lignin from other lignocellulosic constituents. Also, a more precise separation into fractions is desired than the relatively rough separation as disclosed in EP 446 566.

Gouveia et al., *Bioresource Technology* 121 (2012) 131-138 point out  
20 that the main drawbacks of lignin utilization are its heterogeneity and wide molar mass distribution. This influences its reactivity and leads to unpredictable and uncontrollable reactions. In the art, various attempts have been made to fractionate technical lignins.

E.g., Likon et al., *Acta Chim. Slov.* 1999, 46(1), pp 87-97 concerns the  
25 fractionation of isolated lignin obtained by the delignification of spruce wood with trichloro acetic acid. The fractionation is conducted by extraction in a Soxhlet apparatus with several sequential solvents, including pentane and dichloromethane. Both the type of extraction method and the choice of solvents is less-desired from an environmental viewpoint. Soxhlet extraction  
30 consumes heat of evaporation, and is less suitable for use on an industrial

scale. Pentane and, particularly, dichloromethane, are not considered to be environment-friendly. The environment-friendliness is important in the development of a sustainable technical lignin fractionation process, since one of the reasons for increased interest in technical lignins, is the fact that they originate from a natural source. The valorization of biomass being an environment-friendly method of obtaining useful functional biochemicals, the methods chosen for such valorization should preferably not, or at least as low as possible, involve technical measures that would be perceived as harmful to the environment.

Also Gosselink et al., 2010, *Holzforschung* 64, 193-200, suggest overcoming the above problems of utilization of technical lignins by solvent extraction. The resulting fractions contain an increasing molar mass, a decreasing polydispersity and an increased level of impurities like ash and residual carbohydrates and proteins. Here too, the method disclosed, and the solvents of choice (again including dichloromethane) are interesting from a scientific point of view, but undesirable in practice.

Cui et al., *ACS Sustainable Chemistry and Engineering*, 2014, 959-968, disclose a fractional precipitation of lignin, wherein use is made of hexane and acetone.

Thring et al., *The Canadian Journal of Chemical engineering* 71(1) 116-123 (1993)) relates to processing sawdust involving thermomechanosolvolytic treatment of medium consistency suspension. Quantities of lignin were fractionated into three fractions by sequential extraction with organic solvents of increasing hydrogen-bonding capacity, such as ethyl acetate followed by methanol.

The invention seeks to provide methods by which technical lignins can be fractionated by a less tedious procedure, preferably using environmentally sound, preferably biobased solvents, which can be easily scaled up, and which would be open to being performed continuously.

## Summary of the Invention

In order to better address one or more of the foregoing desires, the invention concerns, in one aspect, a method for the fractionation of technical  
5 lignin wherein the technical lignin to be fractionated is provided as a stationary phase in an extraction column, and a plurality of solvents is allowed to sequentially flush through the column, wherein the solvents are selected from the group consisting of alcohols, ethers, ketones, esters, mixtures thereof, and mixtures of one or more of said solvents and water,  
10 and are applied in an order of increasing polarity.

In another aspect, the invention provides an extraction column provided with a packed stationary phase, wherein the packed stationary phase comprises technical lignin mixed with inert particles having a particle size in the range of from 1 to 1000 micrometers, preferably 5 to 500  
15 micrometers, more preferably 10-200 micrometers, dispersed through the technical lignin.

The invention is further directed to a method for the fractionation of technical lignin wherein the technical lignin to be fractionated is provided as a stationary phase in such an extraction column. In such a method the  
20 technical lignin to be fractionated is provided as a stationary phase in the extraction column, and a solvent is allowed to flush through the column or a plurality of solvents is allowed to sequentially flush through the column.

The invention is further directed to a method for the fractionation of technical lignin, comprising contacting said lignin successively with solvents  
25 selected from the group consisting of alcohols, ethers, ketones, esters, mixtures thereof, and mixtures of one or more of said solvents and water, in order of increasing polarity; preferably selected from the group consisting of ethylacetate, methyl ethyl ketone, methanol, acetone, and mixtures of any of these with water; most preferably with the following solvents: ethylacetate,  
30 methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of methyl ethyl

ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water. For example, the lignin can be sequentially flushed with said solvents. Preferably, for these solvents, the technical lignin is provided as fixed bed or moving bed, or as a suspension or slurry.

- 5 Optionally, the technical lignin to be fractionated is provided as a stationary phase in an extraction column, and the plurality of solvents is allowed to sequentially flush through the column. The method may be carried out for instance as a batch process or as a continuous process. Sequentially flushing within a continuous process includes flushing various zones of a reactor  
10 and/or stages of the process.

### **Brief description of the drawings**

Fig. 1 depicts a model formula for the structure of lignin.

15

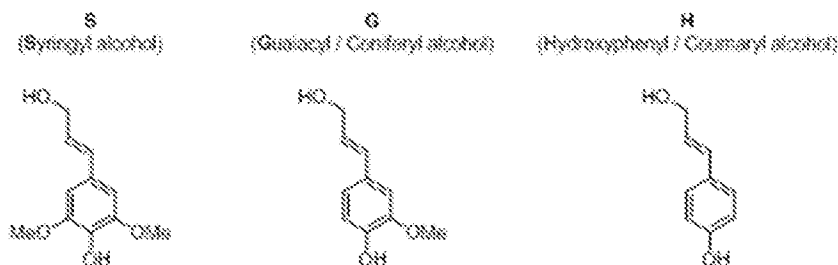
### **Detailed Description of the Invention**

In a general sense, the invention is based on the judicious insight to preferably combine two technical measures that, surprisingly,  
20 turn out to work in concert in preferred embodiments. One is that the use of environmentally non-friendly solvents in the fractionation of technical lignins can be avoided by choosing solvents of the various groups having in common the presence of a carbon to oxygen bond, viz. ethers, alcohols, ketones, and esters. The other is to increase the extraction efficiency by  
25 providing the technical lignins to be fractionated as a packed stationary phase in an extraction column. The invention includes methods applying either or preferably both of these two measures.

The method of the invention using a column with technical lignin as stationary phase is fundamentally different from the methods known in the  
30 art, wherein studies are performed on different technical lignins by using

successive solvent extraction, rather than column fractionation. Also in these studies non-environmentally sound solvents such as dichloromethane and resulting mixtures were used. Embodiments of the methods of the invention are more environment-friendly and/or more efficient as to time and/or costs.

The technical lignins to be fractionated can be of any source available in the field. As mentioned above, technical lignins are isolated from lignocellulosic biomass, typically by-streams of lignocellulosic biorefineries, including e.g. kraft, soda, organosolv, hydrolysis lignins, and lignosulfonates. Technical lignins have a modified structure, including more condensed structures, less ether linkages, and more resistant carbon-carbon linkages, compared to native lignin and contain impurities that are dependent on the extraction process. Lignin consists of three different aromatic building blocks as given in the formulae hereafter, with reference to the structures of Syringyl (S), Guaiacyl (G), and 4-Hydroxyphenyl (H):



As an example, a model structure for a softwood lignin is given in Fig.1 (Softwood lignin structure as proposed by Brunow (2001) in: Biopolymers. Volume 1. Lignin, Humic Substances and Coal, (Eds.) M. Hofrichter, A. Steinbüchel, Vol. 1, Wiley-VCH Verlag GmbH. (2001) pp. 106).

Particularly, the technical lignins are selected from the group consisting of organosolv lignin, soda lignin, and kraft lignin, but are not limited to these. Typical sources for the lignins include, but are not limited

to, softwood (e.g. pine), hardwood, herbaceous plants, e.g. corn stover, bagasse, grass and straw lignin.

In a preferred embodiment, the technical lignin is selected from the group consisting of organosolv straw lignin, soda straw lignin, kraft pine  
5 lignin, organosolv hardwood lignin, kraft softwood lignin, sarkanda grass soda lignin, hardwood soda lignin, milled wood lignin, and mixtures thereof.

Native lignins are present in biomass, and chemically bound thereto in an amount of 20-25 wt.%. Technical lignins, although isolated, can still be present in a composition remaining from biomass (but are no longer  
10 chemically bound thereto). In such a composition, the lignins are generally present in an amount of at least 40 wt.%, preferably at least 50 wt.%, and more preferably the method starts with technical lignins of at least 90 wt.% purity. Preferably, the technical lignin to be fractionated comprises at least 40 wt.%, or at least 50 wt.%, or at least 90 wt.% lignins.

15 In some embodiments, the lignins are packed in an extraction column. The column hardware can be of any type considered suitable by the skilled person. Typically, the column can be made of, e.g., metal, particularly aluminum, glass, or suitable plastics such as polyolefins, polycarbonate. Methods of loading of the lignin as stationary phase in the  
20 column hardware are well-known to the skilled person. It will be understood that optionally only the column hardware is provided, as end users may pack the column with the technical lignins to be fractionated.

For further improving the fractionation method, the inventors encountered a particular challenge when using technical lignins as the  
25 packing material in an extraction column. Technical lignins turn out to be fundamentally different from native or pretreated non-isolated lignins, in their ability to be well-packed in a column, and still be well-extractable. Solvents were found to pass through a well-packed bed of technical lignins only to a limited extent, especially when the bed was placed on an inert

filter bed consisting of inert materials such as glass wool, glass pearls, and inert particles.

It was found that this can be addressed to some extent by a preferred method using a loosely packed bed of the technical lignins. For a loosely  
5 packed bed, extraction by flushing the lignins with the desired sequence of solvents was more successful, and the process had the advantages of avoiding a tedious operation, of allowing to be turned into a continuous operation, of avoiding environmentally non-friendly solvents, and of being easy to scale up. Hence, optionally, the technical lignin to be fractionated is  
10 provided as a loosely packed stationary phase in an extraction column

However, with loosely packed technical lignins the method is not optimal as to efficiency, and additional measures (e.g., shaking) are desired to prevent the loosely packed technical lignins from setting, as a result of which solvents may become blocked from flushing through it, or at  
15 least from flushing through it as efficiently as desired.

Therefore, more preferably, the extraction column is provided with a packed stationary phase, wherein the packed stationary phase comprises technical lignin mixed with inert particles having a particle size in the range of from 1 to 1000 micrometers, preferably 5 to 500 micrometers,  
20 more preferably 10-200 micrometers, dispersed through the technical lignin.

This preferred embodiment allows to just normally pack the technical lignins (not requiring a specific packing density), and still allow extraction fluids to more efficiently flush through the packed bed of technical lignins. Hence, looseness of packing is not critical in this preferred method. This  
25 preferred method involves mixing the technical lignins with inert particles, preferably having particles sizes in the range of 1 to 1000 micrometers, preferably 5 to 500 micrometers, more preferably 10-200 micrometers. Without wishing to be bound by theory, the inventors believe that dispersing these particles through the technical lignins creates room for

liquids to flow through the packed bed, for example in the form of interstitial channels such as randomly divided channels.

Generally, technical lignin is preferably provided as particulate material, preferably having a particle size in the range of from 1 to 1000  
5 micrometers, or 5 to 500 micrometers, more preferably 10-200 micrometers.

For completeness' sake, it is added that the stationary phase of lignin is preferably placed on top of a bed of inert material such as glass wool, glass pearls, and inert particles. The aforementioned mixing of the lignin with inert particles comes in addition thereto.

10 In view of the foregoing, the invention, in another aspect, also relates to an extraction column provided with a packed stationary phase, wherein the packed stationary phase comprises technical lignin mixed with inert particles having a particle size in the range of from 1 to 1000 micrometers, preferably 5 to 500 micrometers, more preferably 10-200, or  
15 25-180 micrometers, dispersed through the technical lignin. For example, the particles may be essentially spherical or have other shapes. For example, the particles may have a D90 (by mass) particle size within these ranges, or at least 90% by mass of the particles may fall within these ranges for example as measured by sieve analysis.

20 The particles are inert in the sense that they preferably do not contain matter that would dissolve in the extraction solvents, and/or react with these solvents. Suitable inert materials include, but are not limited to inorganic particles such as (calcinated) diatomaceous earth or silica containing particles. Diatomaceous earth generally has a particle size of 3  
25 micrometers to 1 millimeter, and more typically 10 to 200 micrometers. Other suitable inert materials are, e.g., glass pearls, silica containing particles, inert polymer beads. Inert particles can be mixed with technical lignin in an amount of for example at least 1.0 wt.%, at least 5 wt.%, at least 10 wt.%, for instance less than 50 wt.%, such as in the range of 10 to  
30 30 wt.%, based on weight of technical lignin.

The extraction column can be used in any kind of method for the fractionation of technical lignin wherein lignin is provided as stationary phase, in principle with any kind of solvent.

Such inert particles can also be useful for fractionation of other  
5 materials than technical lignin. More generally, also provided are methods for the fractionation of solid materials, preferably particulate materials, which material to be fractionated is provided as a stationary phase in an extraction column provided with a packed stationary phase, wherein the packed stationary phase comprises said material mixed with inert particles  
10 of a different material having a particle size in the range of from 1 to 1000 micrometers, wherein the method comprises flushing one or more solvents for fractions of said material through the column. Preferably the particles are dispersed throughout the material to be fractionated. The material can for instance be biomass derived.

15 The method may for example comprise a step of providing technical lignin in an extraction column. The method may for example comprise a step of contacting technical lignin with a solvent or sequentially contacting lignin with a plurality of solvents. For example, the method may comprise a step of flushing a solvent through the column or flushing a plurality of  
20 solvents sequentially through the column.

The invention includes as an aspect a method wherein the solvents used for extracting different fractions from technical lignin, are selected from the group of solvents that have a molecular structure comprising at least one carbon to oxygen bond, viz. alcohols, ethers, ketones, and esters.  
25 The solvents used as extraction liquids in this method can also be used as mixtures. Also, mixtures of one or more of said solvents and water can be used. The solvents are applied in order of increasing polarity. I.e., the first solvent used for flushing the lignin-packed column is the least polar solvent, and the last one is the most polar solvent. At least two and preferably 3, 4 or

5 or more solvents from said group are applied in order of increasing polarity.

The combinations of solvents can be applied in any kind of fractionation, leaching or solid/liquid extraction process for technical lignin, using for instance a moving bed, a slurry or a fixed bed of technical lignin.

For instance, lignin may be moved through a reactor with various zones, for example with twin screws, the zones each provided with for example counter current flow of the solvents. Another example is using a plurality of tanks or vessels in series each containing said solvent and moving a slurry of lignin through said tanks or vessels.

The polarity of a solvent is known to the skilled person. The polarity of mixtures of solvent, or of mixtures of a solvent and water, can be easily calculated or determined by the skilled person. In case one of the solvents is a mixture with water, sequence is determined by the polarity of the mixture.

The solvents thus selected avoid the use of hydrocarbon solvents, and particularly chlorinated solvents (such as dichloromethane), which are not environment-friendly.

Alcohols used as an extraction solvent in this method of the invention will generally have one to six carbon atoms, and may be straight-chain or branched, linear or cyclic. Preferred alcohols are methanol, ethanol, propanol, and butanol. The most preferred alcohol is methanol.

Ketones used as an extraction solvent in this method of the invention can be symmetrical or asymmetrical. The groups bonded to the ketone carbonyl will generally be aliphatic groups having one to six carbon atoms. These chains may be straight-chain or branched, linear or cyclic, or together may form a ring. Preferred ketones are: methyl ethyl ketone (MEK), acetone, methyl propyl ketone (MPK).

Ethers used as an extraction solvent in this method of the invention can be symmetrical or asymmetrical. The groups bonded to the ether oxygen

will generally be aliphatic groups having one to six carbon atoms. These groups may, together with the ether oxygen, form a ring (such as a tetrahydrofuran). Preferred ethers include diethylether and 2-methyltetrahydrofuran.

5                   Esters used as an extraction solvent in this method of the invention can originate from alcohols and acids (or other carboxylic ester-forming compounds) having generally one to six carbon atoms. The chains in the ester, originating from both the alcohol and the acid will generally have one to six carbon atoms, and may be straight-chain or branched, linear or  
10                   cyclic. Preferred esters are methylacetate, ethylacetate, propylacetate. The most preferred ester is ethylacetate.

                  The most preferred set of solvents comprises: ethylacetate (ester), methyl ethyl ketone (ketone), methanol (alcohol), acetone (ketone), and mixtures of any of these solvents with water, in particular mixtures of  
15                   methyl ethyl ketone with water and acetone with water. The volume ratios of ketone to water in these mixtures preferably range from 5:95 to 95:5, particularly from 10:90 to 90:10, more particularly from 75:25 to 25:75. An interesting mixture is that of methyl ethyl ketone and water, in a volume ratio preferably ranging from 10-30 vol.% of methyl ethyl ketone and 70-90  
20                   vol.% of water. Another interesting mixture is that of acetone and water, in a ratio preferably ranging from 70-90 vol.% of acetone and 30-10 vol.% of water. Typical examples are a mixture of 20 vol.% of methyl ethyl ketone and 80 vol. % water, and a mixture of 80 vol. % of acetone and 20 vol. % water.

25                   The polarity of solvents, mixtures thereof, and mixtures of solvents and water, can be generally determined on the basis of the dielectric constant of the solvent or solvent mixture. Water, which is highly polar, is indicated, at 0°C, by a dielectric constant of 88. Solvents with a dielectric constant of less than 15 are generally considered to be nonpolar.  
30                   The polarity of the solvent or solvent mixtures used as extraction fluids in

some methods of the present invention is determined as the Hildebrand solubility parameter ( $\delta$ ). The polarity is further indicated by the molecule's dipole moment (in Debye). Solvents with an increase of the hydrogen bonding capacity and polarity, as expressed by an increase of the solubility parameter of Hildebrand  $\delta$  ( $\text{cal}^{1/2} \text{cm}^{-3/2}$ ). (Hildebrand & Scott, 1950).

The Hildebrand solubility parameter of technical lignins was calculated from the energy of vaporization (E) and the molar volume (V) of the phenylpropane repeating units of the polymer.

By way of guidance, a list of solvents with their polarity is given in Table 1 below.

Table 1

| Solvent                   | Solubility ( $\delta$ ) | Dipole moment |
|---------------------------|-------------------------|---------------|
| Pentane                   | 7.0                     | 0.00 D        |
| Cyclopentane              | 1.97                    | 0.00 D        |
| Hexane                    | 7.24                    | 0.00 D        |
| Cyclohexane               | 2.02                    | 0.00 D        |
| Benzene                   | 2.3                     | 0.00 D        |
| Toluene                   | 2.38                    | 0.36 D        |
| 1,4-Dioxane               | 2.3                     | 0.45 D        |
| Chloroform                | 9.2                     | 1.04 D        |
| Diethyl ether             | 7.62                    | 1.15 D        |
| Dichloromethane (DCM)     | 9.93                    | 1.60 D        |
| Tetrahydrofuran (THF)     | 7.5                     | 1.75 D        |
| Ethyl acetate             | 9.1                     | 1.78 D        |
| Acetone                   | 10                      | 2.88 D        |
| Dimethylformamide (DMF)   | 38                      | 3.82 D        |
| Acetonitrile (MeCN)       | 37.5                    | 3.92 D        |
| Dimethyl sulfoxide (DMSO) | 46.7                    | 3.96 D        |

|                                          |       |        |
|------------------------------------------|-------|--------|
| Propylene carbonate                      | 64.0  | 4.9 D  |
| Formic acid                              | 58    | 1.41 D |
| n-Butanol                                | 18    | 1.63 D |
| Isopropanol (IPA)                        | 18    | 1.66 D |
| 2-propanol                               | 11.6  | 1.68 D |
| Ethanol                                  | 12.92 | 1.69 D |
| Methanol                                 | 14.3  | 1.70 D |
| Acetic acid                              | 6.2   | 1.74 D |
| Nitromethane                             | 35.87 | 3.56 D |
| Water                                    | 23.4  | 1.85 D |
| Methyl ethyl ketone                      | 9.3   |        |
| Methyl ethyl ketone/water<br>(20/80 v/v) | 20.6  |        |
| Acetone/water (80/20 v/v)                | 12.7  |        |

In this method, the solvents or mixtures of solvents are applied successively, in an order of increasing polarity. As such, this refers to a fractionation process that a skilled person will be able to conduct without further guidance. The successive application of the solvents is done  
5 preferably sequentially, i.e., one after the other, if desired with an intermission between solvents. However, it is also possible to gradually apply a next solvent, whilst the former solvent is still flushing the column.

This method, by virtue of providing a technical lignin-packed  
10 column, can be conducted in a continuous manner, if desired. This merely requires a continuous harvesting of solvent fractions at the outlet of the column (when operated by gravity flow: down) and a continuous supply of solvents, in the desired order, at the inlet of the column (when operated by gravity flow: top) or in the reverse mode. Additionally, the extraction can  
15 also be operated using pumps to drive the extraction liquid. In that case

columns other than vertical can also be used. Preferably, though, the extraction column is positioned substantially vertically. A single column can be used, or a plurality of columns in parallel.

The method, preferably in combination with using the packed column  
5 comprising inert particles, leads to an increased speed of extraction, particularly of the most desired lower molar mass fractions from technical lignins. Particularly, the method allows producing higher quality lignin fractions than available by pre-existing methods. This provides a more time and costs effective process compared to traditional liquid-solid extraction.

10 As a result of the method, and of the packed column preferably used therein, fractionated lignins can be obtained that exhibit different and higher quality properties towards applications as wood adhesives, polyol substitution in polyurethane foams and coatings, and other chemical applications where low molecular weight lignins are desired.

15 The fractionated lignins exhibit a lower to higher average molar mass, i.e. a more distinguished mass fraction. A higher homogeneity is obtained expressed as lower polydispersity in the lower to medium molecular mass fractions. A higher concentration of functional groups in the lower molecular mass fractions is obtained. The method leads to lower  
20 viscosity profiles for the lower molecular mass fractions and a higher purity in the lower molecular mass fractions. Moreover the fractionated lignins obtained according to the present methods exhibit a higher reactivity towards chemicals, e.g. isocyanates, due to a higher homogeneity, lower viscosity, and higher amount of reactive hydroxyl groups.

25 By "lower molecular mass" reference is generally made to fractions having a weight average molecular mass in a range of from 500 to 1500, 1500 – 2500, 2500 – 4500, 4500 – 6000, 6000 – 9000 Dalton (g/mol).

By contrast, the aforementioned EP 446 556 results in fractions of number average molecular mass up to 600 Daltons, 800-1000 Daltons, 1500-  
30 2000 Daltons, in low yields.

An embodiment of the invention relates to a method for the fractionation of technical lignin wherein the technical lignin to be fractionated is provided as a stationary phase in an extraction column, and a plurality of solvents is allowed to sequentially flush through the column, wherein the solvents are selected from the group consisting of alcohols, ethers, ketones, esters, mixtures thereof, and mixtures of one or more of said solvents and water, and are applied in an order of increasing polarity; wherein preferably successively the following solvents are applied: ethylacetate, methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of methyl ethyl ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water.

The invention will be illustrated hereinafter with reference to the following, non-limiting examples.

### Example 1

Organosolv straw lignin (supplied by CIMV, France) is applied as the stationary phase in a packed column. Thereby a lignin packed bed is formed after making a layer of glass wool and pearls and inert earth particles on the bottom of the column and mixing lignin with earth particles (ratio 10/2). The different technical lignins are fractionated by successively flushing the column with the following solvents of increasing polarity (the order of flushing is as indicated by numbering, starting with F1): 1. Ethylacetate (F1); 2. Methyl ethyl ketone (F2); 3. Methanol (F3); 4. Methyl ethyl ketone / water 20/80 (F4); and 5. Acetone/water 80/20 (F5).

For each solvent the extraction fluid is collected, the extraction fluid is removed under reduced pressure, and its contents determined.

The results are given in Table 2. Therein F0 is the unfractionated technical lignin. The fractions obtained are analyzed in respect of their

number average molecular weight (Mn) and their weight-average molecular weight (Mw), in Daltons (g/mol). Also, the resulting polydispersity (Mw/Mn) is given. The lignin fractions exhibit a higher homogeneity as displayed by a lower polydispersity compared to the original nonfractionated technical lignin.

Table 2

| 1. Organosolv straw lignin |           |      |       |            |
|----------------------------|-----------|------|-------|------------|
|                            | Yield (%) | Mn   | Mw    | PD (Mw/Mn) |
| F0                         | --        | 1051 | 11143 | 10.6       |
| F1                         | 10.1      | 242  | 1479  | 6.1        |
| F2                         | 8.4       | 356  | 2561  | 7.2        |
| F3                         | 12.7      | 685  | 4491  | 6.6        |
| F4                         | 1.9       | 774  | 4132  | 5.3        |
| F5                         |           |      |       |            |
| Residue                    | 67.0      | 2180 | 22243 | 10.2       |

By way of comparison Example 1B, below (Table 3) the fraction yields are given for Organosolv Straw lignin subjected to solid/liquid extraction with subsequent solvents as given in Table 3, including dichloromethane.

Table 3

| Solvent (solid/liquid extraction) | Organosolv Straw lignin fractions (%) |
|-----------------------------------|---------------------------------------|
| F1 (dichloromethane)              | 13.5                                  |
| F2 (methanol)                     | 7.7                                   |
| F3 (methanol/dichloromethane 7/3) | 22.6                                  |
| F4 (acetone)                      | 2.5                                   |
| F5 (acetone/water 8/2)            | 19.4                                  |
| F6 (residue)                      | 34.2                                  |
| total                             | 99.87                                 |

Further, an analysis is given of the functional groups present in the various fractions (#) of comparative conventional solid/liquid extraction of Organosolv straw lignin (Table 4). A similar analysis is given for Organosolv straw lignin with inventive column fractionation (Table 5). The functional groups analyzed are aliphatic hydroxyl (Aliph.OH), condensed aromatic

hydroxyl (Cond.OH), syringyl alcohol (S-OH), guaiacyl alcohol (G-OH), 4-Hydroxyphenyl alcohol (H-OH), and carboxyl (COOH). It should hereby be noted that aliphatic OH generally is indicative of carbohydrate impurities, and particularly G-OH and COOH represent desired functionalities for resin and polymer application.

Table 4

(comparative fractionation: functional groups in mmol/g)

| #  | Aliph.OH | Cond.OH | S-OH  | G-OH  | H-OH  | COOH  | Total |
|----|----------|---------|-------|-------|-------|-------|-------|
| F0 | 1.509    | 0.502   | 0.309 | 0.542 | 0.223 | 0.688 | 3.77  |
| F1 | 0.941    | 0.402   | 0.453 | 0.706 | 0.123 | 0.666 | 3.29  |
| F2 | 2.512    | 0.433   | 0.331 | 0.666 | 0.308 | 0.809 | 5.06  |
| F3 | 1.682    | 0.536   | 0.360 | 0.633 | 0.267 | 0.481 | 3.96  |
| F4 | na       | na      | na    | na    | na    | na    | na    |

na = not applied.

Table 5

(inventive fractionation: functional groups in mmol/g)

| #  | Aliph. OH | Cond.OH | S-OH | G-OH | H-OH | COOH | Total OH |
|----|-----------|---------|------|------|------|------|----------|
| F0 | 1.43      | 0.57    | 0.34 | 0.63 | 0.30 | 0.68 | 3.96     |
| F1 | 1.20      | 0.55    | 0.62 | 1.20 | 0.37 | 1.22 | 5.17     |
| F2 | 1.70      | 0.65    | 0.54 | 0.94 | 0.40 | 0.54 | 4.76     |
| F3 | 1.77      | 0.61    | 0.41 | 0.74 | 0.35 | 0.51 | 4.40     |

It can be seen that the fractions obtained with an inventive example method (Table 5) have a higher degree of functionality than the fractions obtained in a conventional manner (Table 4). Also, it can be seen that key indicators for functionality, such as the concentration of G-OH and COOH groups, are consistently better for the fractions obtained in accordance with the invention. Further, the aliphatic OH, indicative of impurities, is clearly lower in the event of the fractions of the invention than in the event of the more conventional solid/liquid extraction.

### Example 2

In the same manner as in Example 1, Soda mixed straw and grass lignin (supplied by Greenvalue, Switzerland) is fractionated. The results are given in Tables 6 and 7. The same column as in Example 1 was used.

5

Table 6

|         | 2. Soda lignin |      |       |     |
|---------|----------------|------|-------|-----|
|         | Yield (%)      | Mn   | Mw    | PD  |
| F0      | --             | 743  | 5239  | 7.1 |
| F1      | 27.0           | 376  | 1583  | 4.2 |
| F2      | 9.3            | 654  | 2688  | 4.1 |
| F3      | 40.6           | 1263 | 6241  | 4.9 |
| F4      |                |      |       |     |
| F5      | 9.3            | 1800 | 12614 | 7.0 |
| Residue | 13.8           | 2029 | 18782 | 9.3 |

Table 7

Functional groups in fractionated soda lignin (mmol/g)

|    | Aliph OH | Cond OH | S-OH | G-OH | H-OH | COOH | Total OH |
|----|----------|---------|------|------|------|------|----------|
| F0 | 1.81     | 0.80    | 0.61 | 0.77 | 0.50 | 1.11 | 5.59     |
| F1 | 1.05     | 0.90    | 0.82 | 1.14 | 0.78 | 1.50 | 6.19     |
| F2 | 1.57     | 0.93    | 0.82 | 0.92 | 0.53 | 1.19 | 5.96     |
| F3 | 1.96     | 0.83    | 0.61 | 0.71 | 0.43 | 1.03 | 5.57     |
| F4 |          |         |      |      |      |      |          |
| F5 | 1.91     | 0.65    | 0.40 | 0.48 | 0.33 | 0.79 | 4.55     |

10

### Example 3

In the same manner as in Example 1, Kraft pine lignin (Meadwestvaco, US) is fractionated. The results are given in Tables 8 and 9.

Table 8

|         | 3. Kraft softwood lignin by column |      |       |      |
|---------|------------------------------------|------|-------|------|
|         | Yield (%)                          | Mn   | Mw    | PD   |
| F0      | --                                 | 635  | 6105  | 9.6  |
| F1      | 1.2                                | 305  | 1528  | 5.0  |
| F2      | 25.9                               | 344  | 1836  | 5.3  |
| F3      | 28.8                               | 767  | 4425  | 5.8  |
| F4      |                                    |      |       |      |
| F5      | 24.4                               | 1413 | 15735 | 11.1 |
| Residue | 19.7                               | 1488 | 15942 | 10.7 |

Table 9

Functional groups in fractionated kraft lignin (mmol/g)

|    | Aliph OH | Cond OH | S-OH | G-OH | H-OH | COOH | Total OH |
|----|----------|---------|------|------|------|------|----------|
| F0 | 2.32     | 1.17    | 0.39 | 1.83 | 0.31 | 0.48 | 6.49     |
| F1 | 1.26     | 1.03    | 0.39 | 3.05 | 0.33 | 0.61 | 6.67     |
| F2 | 1.34     | 1.20    | 0.39 | 2.89 | 0.35 | 0.47 | 6.63     |
| F3 | 2.22     | 1.12    | 0.33 | 1.54 | 0.27 | 0.42 | 5.90     |
| F4 |          |         |      |      |      |      |          |
| F5 | 2.60     | 1.10    | 0.32 | 1.27 | 0.29 | 0.36 | 5.94     |

5

**Example 4**

In the same manner as in Example 1, Organosolv mixed hardwood lignin (Alcell®, Repap, Canada) is fractionated. The results are given in Tables 10 and 11.

10

Table 10

|         | 4. Organosolv hardwood lignin by column |      |       |     |
|---------|-----------------------------------------|------|-------|-----|
|         | Yield (%)                               | Mn   | Mw    | PD  |
| F0      | --                                      | 760  | 4536  | 6.0 |
| F1      | 24.8                                    | 556  | 2224  | 4.0 |
| F2      | 21.5                                    | 739  | 3652  | 4.9 |
| F3      | 44.3                                    | 876  | 5784  | 6.6 |
| F4      |                                         |      |       |     |
| F5      | 0.3                                     | 1802 | 12709 | 7.1 |
| Residue | 0.4                                     | 1573 | 12537 | 8.0 |

Table 11

Functional groups in fractionated organosolv hardwood lignin (mmol/g)

| #  | Aliph.OH | Cond.OH | S-OH | G-OH | H-OH | COOH | Free COOH | Total OH |
|----|----------|---------|------|------|------|------|-----------|----------|
| F0 | 1.17     | 0.88    | 1.12 | 0.77 | 0.20 | 0.36 | 0.04      | 4.14     |
| F1 | 0.91     | 0.85    | 1.26 | 0.85 | 0.23 | 0.46 | 0.03      | 4.11     |
| F2 | 1.09     | 0.87    | 1.13 | 0.77 | 0.20 | 0.35 | 0.04      | 4.06     |
| F3 | 1.28     | 0.90    | 1.08 | 0.76 | 0.21 | 0.33 | 0.04      | 4.23     |
| F4 |          |         |      |      |      |      |           |          |
| F5 | 1.39     | 0.86    | 0.69 | 0.60 | 0.20 | 0.25 | 0.05      | 3.73     |

Claims

1. A method for the fractionation of technical lignin wherein the technical lignin to be fractionated is provided as a stationary phase in an extraction column, and a solvent is allowed to flush through the column or a plurality of solvents is allowed to sequentially flush through the column,  
5 wherein the extraction column is provided with a packed stationary phase, wherein the packed stationary phase comprises technical lignin mixed with inert particles having a particle size in the range of from 1 to 1000 micrometers.
- 10 2. A method according to claim 1, wherein a plurality of solvents is allowed to sequentially flush through the column, wherein the solvents are selected from the group consisting of alcohols, ethers, ketones, esters, mixtures thereof, and mixtures of one or more of said solvents and water, and are applied in an order of increasing polarity.
- 15 3. A method according to claim 2, wherein solvents are selected from the group consisting of: ethylacetate, methyl ethyl ketone, methanol, acetone, and mixtures of any of these with water.
- 20 4. A method according to claim 3, wherein successively the following solvents are applied: ethylacetate, methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of methyl ethyl ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water.
- 25 5. A method according to any of claims 1-4, wherein the inert particles have a particle size of from 5 to 500 micrometers, preferably 10-200 micrometers.

6. A method according to any of claims 1-5, wherein the inert particles are diatomaceous earth particles.

7. A method according to any of claims 1-6, wherein the technical lignin  
5 is selected from the group consisting of organosolv lignin, soda lignin, kraft lignin, and mixtures thereof.

8. A method according to any of claims 1-7, wherein the technical lignin is selected from the group consisting of softwood lignin, hardwood lignin,  
10 grass lignin, straw lignin, and mixtures thereof.

9. A method according to any of claims 1-8, wherein the technical lignin is selected from the group consisting of organosolv straw lignin, soda straw lignin, kraft pine lignin, organosolv hardwood lignin, softwood kraft lignin,  
15 sarkanda grass soda lignin, hardwood soda lignin, milled wood lignin, and mixtures thereof.

10. A method for the fractionation of technical lignin wherein the technical lignin to be fractionated is provided as a stationary phase in an  
20 extraction column, and a plurality of solvents is allowed to sequentially flush through the column, wherein the solvents are selected from the group consisting of alcohols, ethers, ketones, esters, mixtures thereof, and mixtures of one or more of said solvents and water, and are applied in order of increasing polarity.

25

11. A method for the fractionation of technical lignin, comprising contacting said lignin successively with the following solvents in order of increasing polarity:  
ethylacetate, methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of

methyl ethyl ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water.

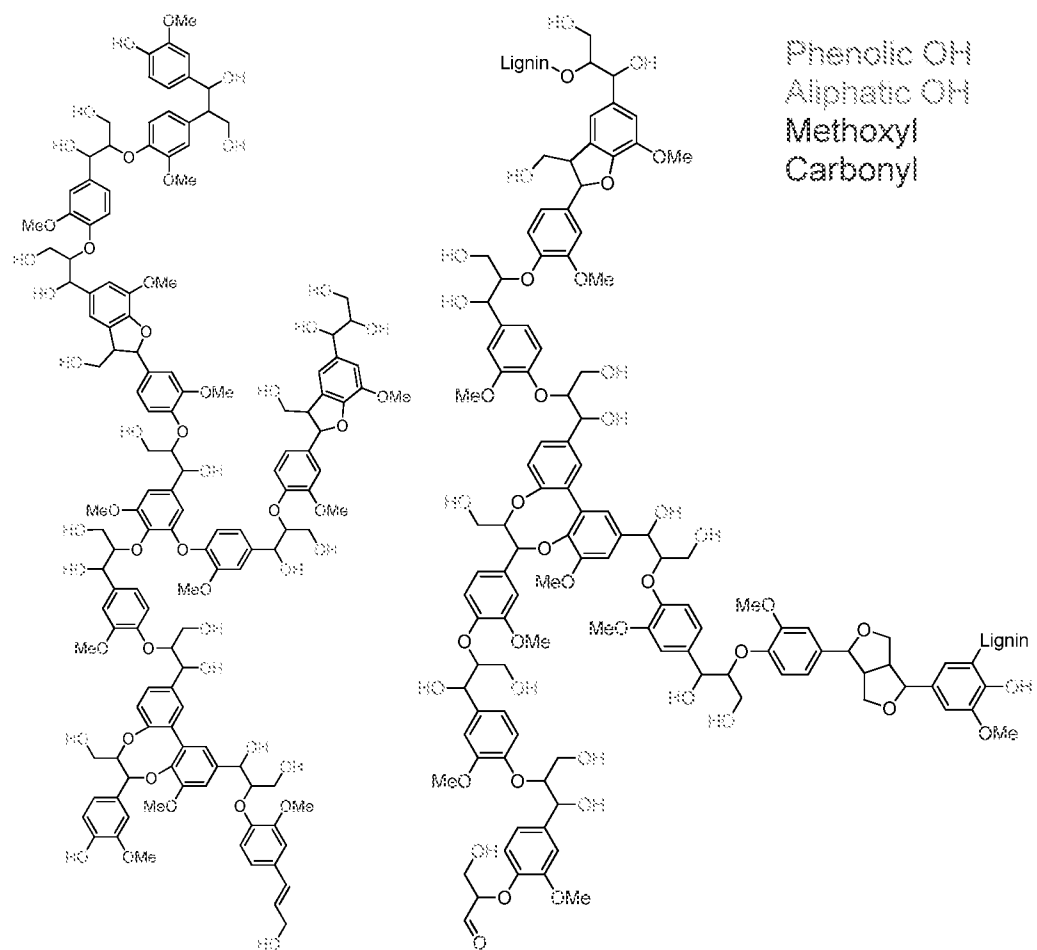
12. A method according to claim 10, wherein successively the following  
5 solvents are applied: ethylacetate, methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of methyl ethyl ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water.

13. A method according to claim 10 or 11 or 12, carried out in an extraction  
10 column as defined in claim 1, preferably wherein the inert particles and/or technical lignin are as defined in any of claims 5-9.

14. An extraction column comprising a packed stationary phase  
comprising technical lignin mixed with inert particles having a particle size  
15 in the range of from 1 to 1000 micrometers.

15. An extraction column according to claim 14, wherein the inert particles and/or technical lignin are as defined in any of claims 5-9.

Fig. 1



# INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2015/050361

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D11/02 C08L97/00  
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)

B01D C08L

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

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                                                        | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | <p>RONALD W. THRING ET AL: "Fractionation of woodmeal by prehydrolysis and thermal organosolv. Process strategy, recovery of constituents, and solvent fractionation of lignins so produced",<br/>THE CANADIAN JOURNAL OF CHEMICAL ENGINEERING,<br/>vol. 71, no. 1,<br/>27 February 1993 (1993-02-27), pages 116-123, XP055156475,<br/>ISSN: 0008-4034, DOI:<br/>10.1002/cjce.5450710116<br/>the whole document</p> <p>-----<br/>-/--</p> | <p>1-9,<br/>13-15</p> |



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)

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"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

11 August 2015

Date of mailing of the international search report

10/11/2015

Name and mailing address of the ISA/

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Arrojo, Sergio

## INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2015/050361

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                 |                       |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                              | Relevant to claim No. |
| A                                                    | <p>RONALD W. THRING ET AL: "Evidence for the heterogeneity of glycol lignin", INDUSTRIAL &amp; ENGINEERING CHEMISTRY RESEARCH, vol. 30, no. 1, 1 January 1991 (1991-01-01), pages 232-240, XP055156477, ISSN: 0888-5885, DOI: 10.1021/ie00049a036 Experimental section</p> <p>-----</p>                                         | 1-9,<br>13-15         |
| A                                                    | <p>CONRAD SCHUERCH:<br/>JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 74, no. 20, 20 October 1952 (1952-10-20), pages 5061-5067, XP055071230, ISSN: 0002-7863, DOI: 10.1021/ja01140a020 the whole document</p> <p>-----</p>                                                                                                    | 1-9,<br>13-15         |
| A                                                    | <p>WO 86/07070 A1 (SVENSKA TRAEFORSKNINGSINST [SE]) 4 December 1986 (1986-12-04) page 4, line 18 - page 6, line 21; table 1</p> <p>-----</p>                                                                                                                                                                                    | 1-9,<br>13-15         |
| A                                                    | <p>THRING R W ET AL: "Fractionation Of Alcell Lignin By Sequential Solvent Extraction", JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, MARCEL DEKKER, NEW YORK, NY, US, vol. 16, no. 2, 1 January 1996 (1996-01-01), pages 139-154, XP009181545, ISSN: 0277-3813, DOI: 10.1080/02773819608545815 page 121; figure 4</p> <p>-----</p> | 1-9,<br>13-15         |

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/NL2015/050361

### 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.:  
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:
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:

see additional sheet

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 fees, this Authority did not invite payment of additional fees.
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.:

1-9, 13-15

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-9, 13-15

Method and device for extracting technical lignin in a column with the technical lignin being the stationary phase, wherein the packed column comprises a mixture of technical lignin and inert particles having a particle size in the range of from 1 to 1000 micrometers.

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2. claims: 10, 12

Method for extracting technical lignin in a column with the technical lignin being the stationary phase, wherein the lignin is extracted with a sequential set of solvents selected from alcohols, ketones, ethers, esters, mixtures thereof or mixtures with water, the solvents being introduced in a sequence of increasing polarity.

---

3. claim: 11

Method for extracting technical lignin, wherein the lignin is extracted with the following sequential order of solvents of increasing polarity: ethylacetate, methyl ethyl ketone, methanol, a mixture of 10-30 vol. % of methyl ethyl ketone and 70-90 vol. % water, and a mixture of 70-90 vol. % of acetone and 30-10 vol. % of water.

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## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/NL2015/050361

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| W0 8607070                                | A1                  | 04-12-1986                 | NONE                |
| -----                                     |                     |                            |                     |