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(54) Title: METHOD FOR LIGNIN PURIFICATION

(57) Abstract: The invention is directed to a method for producing a purified lignin salt from alkaline spent liquor from the chemical cooking of lignocellulosic raw materials. The method comprises the steps of decreasing the spent liquor pH to form a lignin precipitate suspension; filtering the lignin precipitate to form a lignin filter cake and a filtrate; mixing the lignin filter cake into a dilution liquid to form an alkalilignin agglomerate colloid; subjecting the alkalilignin agglomerate colloid to large-pore membrane filtration; and recovering a purified lignin salt concentrate.

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Method for Lignin Purification

FIELD

[0001] The present invention relates to lignin separation and purification. In particular, the present invention concerns a two-stage method of producing purified lignin salt from black liquor.

BACKGROUND

[0002] Lignin is a promising raw-material for bio-based products. Significant quantities of lignin are available in the spent liquors from industrial Kraft pulping, i.e. in black liquor. Lignin concentration in black liquor is typically only 20-40 %-w on dry basis, with the rest of the dry matter comprising spent pulping chemicals and dissolved non-lignin wood components. High purity is important in lignin products. Hence, cost efficient separation and purification operations are needed to make Kraft lignin utilization feasible in industrial scale.

[0003] A well-known method for purification of lignin is ultrafiltration as described i.a. by Luque et al, TAPPI Pulping Conference 1994, 7. Ultrafiltration is a fractionation process to produce from liquor, in high alkalinity (pH >12) where lignin is in dissolved form, a concentrate which is enriched in high molecular mass lignin (e.g. 29 % over 15.000 Dalton, Luque et al.) and a permeate which contains more of the low molecular mass lignin and other low molecular mass black liquor components, inorganic salts and organic acids.

[0004] Evidently, ultrafiltration increases the share of high molecular mass lignin in the concentrate, but only modestly, from 15 to 29 % lignin over 15.000 Dalton (Luque et al). In addition to the rather modest fractionation result, the ultrafiltration technical operation using Kraft black liquor is difficult due to concentration polarization and membrane fouling. A continuous decline of flux rate takes place, and ultrafiltration is not a very good fractioning method to produce a product of specific molar mass, since the fouling of membranes leads to a situation where the molecular mass distribution of the concentrated material changes all the time.

[0005] A further example of conventional ultrafiltration is given in Rojas et al., "LIGNIN SEPARATION FROM KRAFT BLACK LIQUORS BY TANGENTIAL

ULTRAFILTRATION", Science and Technology, La Chimica e l'Industria - Gennaio-Febbraio '06 n. 1 - ANNO 88. (2006). This article provides an example of the problems faced in this approach. It is described how typical Kraft black liquor was ultra-filtrated using typical membranes. The average molecular weight for the examined industrial black liquor ranged from ca. 1700 to 20000 Da. The Mw of the concentrates and filtrates correlated with the membrane molecular weight cut-off (MWCO). However, Rojas et al. found that the effective molecular size of filtered particles was smaller than the membrane nominal molecular weight cut-off. This difference may be due to the typical clogging of membranes that is an inherent problem in this type of application, as well as reduction in filtration flux due to membrane plugging and/or fouling.

[0006] Black liquor contains a lot of inorganic salts and organic aliphatic and phenolic compounds which compromise the membrane performance thus making the molecular weight fractioning process very challenging, as described by Aminzadeh et al., MEMBRANE FILTRATION OF KRAFT LIGNIN: STRUCTURAL CHARACTRISTICS AND ANTIOXIDANT ACTIVITY OF THE LOW-MOLECULAR-WEIGHT FRACTION, Industrial Crops & Products 112 (2018) 200–209.

[0007] Producing purified lignin from black liquor with ultrafiltration is thus not very useful. It is very likely that the purification performance stays low, and constant material flow is very limited even if the UF membranes are washed periodically (Aminzadeh et al).

[0008] Another method to purify Kraft lignin is represented by the commercial and patented Lignoboost process (WO 2006/038863 and WO 2013/002687). Using the Lignoboost process, Kraft lignin is separated in a two-stage process. The first stage comprises lignin precipitation, e.g. by CO2 addition, followed by filtration. In the second stage, the filtered precipitate is re-slurried usually into H2SO4-water solution, followed by an acidic washing in a second filtration. The drawback of the process is the demand for significant expenditure in process equipment and addition of sulphuric acid and thereby introduction of excess sulphur into the closed Kraft pulping recovery cycle, which distorts the pulp mill's Na/S balance.

DEFINITIONS

[0009] In the present context, the term "large-pore membrane filtration" refers to cross-flow filtration of particles formed of agglomerated lignin macromolecules. The cutoff point is at least 40 000 Dalton. Advantageously, the cutoff point in a large-pore membrane filtration according to the present invention is in the range of 40 000-500 000 Da, preferably 50 000-200 000 Da.

[0010] In the present context, a "dilution liquid" is an aqueous liquid having no significant ionic strength or significant amount of dissolved organic material. In addition to plain water, examples of dilution liquids commonly occurring in pulp mills are condensate from an evaporation plant, filtrate from a bleach plant, or mill hot water.

[0011] In the present context, a lignin salt is a chemical form of lignin, in which part of the acid groups in lignin are dissociated and the negative charge of the dissociated acid groups is counterbalanced by cations. The lignin salt may involve various cations, but typically there is one principal cation, which is the same as the cation of that alkaline pulping process, where the lignin salt originates from. In case of Kraft lignin salt, the primary cation is sodium (Na^+).

[0012] In the present context, a lignin precipitate suspension is formed when the original pulp mill black liquor pH is lowered to 9-10.5 using an acidic substance.

[0013] In the present context, a lignin filter cake is formed from the lignin precipitate suspension by filtering on a filtering media.

[0014] In the present context, a lignin agglomerate is a union aggregate of lignin macromolecules in a colloidal state, whereby the particle size of the aggregate is large enough (> 50 kDalton) to be filtered out (to remain on the membrane) in a large-pore membrane filtration. It is important to note that these agglomerate lignin particles are at least ten times the size of the lignin macromolecules in the original black liquor (typically 5 kDalton) which flow through a large-pore membrane.

SUMMARY OF THE INVENTION

[0015] The invention is defined by the features of the independent claim. Some specific embodiments are defined in the dependent claims.

[0016] It is the aim of the invention to overcome at least some of the drawbacks relating to the known state-of-the-art technical solutions described in the background section.

[0017] According to a first aspect of the present invention, there is provided a method for producing a purified lignin salt from alkaline spent liquor from the chemical cooking of lignocellulosic raw materials. The method comprises the steps of:

- decreasing the spent liquor pH to form a lignin precipitate suspension
- filtering the lignin precipitate to form a lignin filter cake and a filtrate
- mixing the lignin filter cake into a dilution liquid to form an alkalilignin agglomerate colloid
- subjecting the alkalilignin agglomerate colloid to large-pore membrane filtration
- recovering a purified lignin salt concentrate.

The purified lignin concentrate constitutes the product. Small-molecular organic and inorganic components are removed in a flown-through liquid.

[0018] It is to be noted the new unexpected finding: Mixing the lignin precipitation filter cake into an aqueous solution under certain controlled conditions described below results in large lignin agglomerates which can be separated and enriched using large-pore membrane filtering. Considerable advantages are obtained by this invention which enables a method that:

- avoids using the small-pore conventional ultrafiltration membranes and all their associated difficulties
- separates a relatively pure lignin product by retaining the lignin agglomerates on the large-pore membrane and permitting small molecular organic and inorganic components to flow through and be removed thereby
- avoids acid wash and use of sulphuric acid that would distort the chemical balance of the pulp mill supplying the spent liquor

[0019] Advantageously, the decrease in pH in the spent liquor is carried out by the addition of H_2SO_4, HCl, SO_2 or CO_2. Preferably, the decrease in pH is carried out by addition of CO_2.

[0020] Advantageously, the decrease in pH in the spent liquor is carried out at a temperature in the range 40 – 85 °C.

[0021] Advantageously, the pH in the spent liquor is decreased to below 11. Preferably, the spent liquor pH is decreased to 9 – 10.5.

[0022] Advantageously, the large-pore-membrane filtration is carried out at a temperature in the range 20 – 85 °C.

[0023] Advantageously, the large-pore-membrane filtration is carried out at a pH in the range 7 – 11.

[0024] Next, the embodiments will be examined in more detail with reference to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIGURE 1 is a general schematic diagram of the lignin purification process according to the invention,

DETAILED DESCRIPTION

[0026] As briefly discussed above, presented is a method for producing purified alkalilignin salt. The method is a two-stage process as generally described in Figure 1.

[0027] In the first stage of the present invention, an alkalilignin precipitate suspension is formed from the alkaline pulping spent liquor, i.e. black liquor (1), (dry solids content typically 25-45 weight-%) by decreasing pH to 9 – 10.5 (3), at a temperature between 40 – 85 °C. The formed alkalilignin suspension is filtered (5) making a filter lignin cake (7) and a permeate liquid (6) containing black liquor soluble components which are taken back to the pulp mill chemical cycle process.

[0028] In the second stage the above mentioned filter lignin cake (7) is mixed with dilution liquid (8) using certain controlled mixing and temperature (9) and forming an alkalilignin agglomerate colloid (10) at typically 10 weight-% dry solids content. This is the new, unexpected finding, the existence of alkalilignin as large colloidal agglomerate particles in diluted aqueous solution, which particles have an average particle-mass over 50 kilodaltons and which enable the technically and industrially useful production of purified alkalilignin salt.

[0029] The alkalilignin agglomerate colloid (10) is fed on a large-pore membrane (11) having cut-off pore size of 50 – 200 kilodalton typically in the temperature range of 20 – 85 °C. The alkalilignin remains in the concentrate (12), whereas most of the smaller particle and small molecular soluble components transfer through the large-pore membrane into the permeate (13). The difference and the technical advantage are significant compared to conventional ultrafiltration of lignin from black liquor using typically 5 kilodalton pore-size special technology membranes.

[0030] A significant advantage of the present invention compared to the prior art lignin membrane separation (ultrafiltration) is that alkalilignin can be enriched as large, colloidal particles, here called alkalilignin agglomerates. This is evident as an enriched concentrate can be made on a large-pore membrane characterized by ”molecular mass” cut-off of 50 – 200 kilodalton. Here this is called large-pore membrane filtration. The ”large-pore” in practical terms means typically a membrane pore size ten times the pore size used in conventional ultrafiltration.

[0031] Large-pore membrane filtration according to the present invention is distinguished from ultrafiltration by several improvements and advantages. First of all, tight and technically very demanding macromolecule separation membranes, for which the molecular weight cut-off is typically 5 kilodalton, are not needed at all. The 50-200 kilodalton large-pore membranes are much easier to operate and maintain. Secondly, the starting material, alkalilignin filter cake, has already undergone a purification: A lot of the soluble small molecular components, especially inorganic salts, have been removed from the cake as a filtrate. Therefore, the re-diluted membrane filtering process in the second stage is fundamentally in a cleaner environment, and thus, membrane polarization and fouling is considerably less prominent. Thirdly, the product, alkalilignin salt concentrate, is the final product. There is no need for

acid wash or other secondary cleaning stages, which require the use of extra chemicals distorting the re-cycle and re-use of the removed components in the permeate.

[0032] Commercially available conventional membranes types can be used in the large-pore membrane filtration step. The membranes may be constructed from organic materials such as PP, PE, PTFE, polyacrylic, cellulose acetate, polyacrylonitrile, polysulfone, etc. High durability inorganic membrane materials, such as aluminum oxide or zirconium oxide, can also be used, but such materials are not needed.

[0033] Advantageously, the large-pore membrane filtration is carried out at a pH in the range of 7 to 11 and at a temperature in the range 20 – 85 °C.

[0034] The concentrate may be used as such, or undergo further treatment such as evaporation, freeze-drying or spray drying. A possible further treatment is to further purify the product by diluting the concentrate and repeating the large-pore-membrane-filtration once or several times.

[0035] Various embodiments of the present invention have been described above but a person skilled in the art realizes also further minor alterations, which would fall into the scope of the present invention. The breadth and scope of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the claims and their equivalents.

EXAMPLE 1. Production of a purified Kraft lignin salt by large-pore membrane filtration

[0036] The pH of softwood kraft black liquor was decreased to 10.0 using CO_2 at 60°C. The lignin precipitate suspension was filtered to obtain a kraft lignin filter cake with 57% dry matter content. The lignin filter cake was mixed with deionized water to form a lignin agglomerate colloid at 10% dry solids content. The lignin agglomerate colloid volume was pre-filtered and subjected to large-pore membrane filtration using Alfa Laval-GR51PP 50 kDa cut-off membrane. The large-pore membrane filtration test was carried out at 50°C to reach volume reduction Vr = 0.7 (Vr = Vpermeate/Vinitial). The resulting oven dry solids concentrations in the concentrate and permeate volumes were 19% and 2.7%, respectively.

[0037] 81% of the lignin in the feed was recovered in the concentrate volume, while 63% of the main inorganic anions (carbonate, sulphate) and 41% of the sodium were

transferred into the permeate. Lignin concentration in the concentrate was 82% of total dry matter content, compared to 67% in the feed. The concentration of the main inorganic anions (carbonate and sulphate) in the permeate was more or less half of that in the feed. The results indicate considerable enrichment of lignin in the concentrate and inorganics in the permeate. More detailed results are shown in Table 1 below.

Table 1. The concentration and yield of selected components in the feed, concentrate, and permeate volumes of large-pore membrane filtration test in Example 1.

	FEED #1	CONCENTRATE #1		PERMEATE #1	
	Concentration, % of dry matter	Concentration, % of dry matter	Yield, % of feed	Concentration, % of dry matter	Yield, % of feed
Lignin	67	82	81	11	3
Sodium (Na+)	7.6	5.4	47	17	41
Carbonate	4.5	2.0	30	15	63
Sulfate	1.2	0.6	37	4.0	63

EXAMPLE 2. Further purification of the lignin salt via repeated large-pore membrane filtration.

[0038] The concentrate volume from Example 1 was mixed with deionized water to achieve 10% dry solids content and subjected to another large-pore membrane filtration test using Alfa Laval-GR51PP 50 kDa cut-off membrane. The test was carried out at 50°C and continued until volume reduction Vr = 0.7 was reached (Vr = Vpermeate/Vinitial). The resulting oven dry solids concentrations in the concentrate and permeate volumes were 21% and 1.3%, respectively.

[0039] 95% of the lignin in feed #2 was recovered in the concentrate, while more than half of the carbonate was transferred thru the membrane into the permeate. Lignin concentration in the concentrate was 90% of total dry matter content, compared to 82% in the feed. The results of example 2 indicate that considerable further purification of lignin was achieved by re-diluting the concentrate and repeating the large-pore membrane filtration. More detailed results are shown in Table 2 below.

[0040]

Table 2. The concentration and yield of selected components in the feed, concentrate, and permeate volumes of the second large-pore membrane filtration test in Example 2.

	FEED #2 (CONCENTRATE #1)	CONCENTRATE #2		PERMEATE #2	
	Concentration, % of dry matter	Concentration, % of dry matter	Yield, % of feed #2	Concentration, % of dry matter	Yield, % of feed #2
Lignin	82	90	95	15	2
Sodium (Na+)	5.4	4.9	78	17	29
Carbonate	2.0	0.8	33	13	53

[0041] EXAMPLE 1 and EXAMPLE 2 demonstrate that large-pore membrane filtration efficiently enriches and purifies the lignin agglomerates in the concentrate. High retention of lignin is achieved using 50 kDa membrane. This aspect is exceptional compared to for instance separation and purification of lignin macromolecules by ultrafiltration of black liquor, which, while using a smaller pore 15 kDa membrane, only results in small lignin enrichment in the concentrate (20-30% of the lignin in feed, Vr = 0.9). [Wallberg et al (2003), Holmqvist et al. (2005)]

[0042] It is to be understood that the embodiments of the invention disclosed are not limited to the particular structures, process steps, or materials disclosed herein, but are extended to equivalents thereof as would be recognized by those ordinarily skilled in the relevant arts. It should also be understood that terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting.

[0043] Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment.

[0044] As used herein, a plurality of items, structural elements, compositional

elements, and/or materials may be presented in a common list for convenience. However, these lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary. In addition, various embodiments and example of the present invention may be referred to herein along with alternatives for the various components thereof. It is understood that such embodiments, examples, and alternatives are not to be construed as de facto equivalents of one another, but are to be considered as separate and autonomous representations of the present invention.

[0045] Furthermore, the described features, structures, or characteristics may be combined in any suitable manner in one or more embodiments. In the following description, numerous specific details are provided, such as examples of lengths, widths, shapes, etc., to provide a thorough understanding of embodiments of the invention. One skilled in the relevant art will recognize, however, that the invention can be practiced without one or more of the specific details, or with other methods, components, materials, etc. In other instances, well-known structures, materials, or operations are not shown or described in detail to avoid obscuring aspects of the invention.

[0046] While the foregoing examples are illustrative of the principles of the present invention in one or more particular applications, it will be apparent to those of ordinary skill in the art that numerous modifications in form, usage and details of implementation can be made without the exercise of inventive faculty, and without departing from the principles and concepts of the invention. Accordingly, it is not intended that the invention be limited, except as by the claims set forth below.

[0047] The verbs “to comprise” and “to include” are used in this document as open limitations that neither exclude nor require the existence of also un-recited features. The features recited in depending claims are mutually freely combinable unless otherwise explicitly stated. Furthermore, it is to be understood that the use of "a" or "an", i.e. a singular form, throughout this document does not exclude a plurality.

CITATION LIST

Patent literature

WO 2006/038863

WO 2013/002687

Non-patent literature

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3. Orlando J. Rojas, John Song, Dimitris S. Argyropoulos Forest Biomaterials Laboratory, College of Natural Resources, North Carolina State University, Raleigh, NC 27695-8005, USA, Juan Bullón Department of Chemical Engineering, Universidad de Los Andes, Mérida (Venezuela), "LIGNIN SEPARATION FROM KRAFT BLACK LIQUORS BY TANGENTIAL ULTRAFILTRATION", Science and Technology, La Chimica e l'Industria - Gennaio-Febbraio '06 n. 1 - ANNO 88. (Year 2006)
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5. Wallberg, O.; Jönsson, A.-S.;Wimmerstedt, R., Ultrafiltration of kraft black liquor with a ceramic membrane., Desalination 2003, 156, 145–153.
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CLAIMS:

1. A method for producing purified lignin salt from alkaline spent liquor from chemical cooking of lignocellulosic raw materials, comprising the steps of

- decreasing the spent liquor pH to form a lignin precipitation suspension,
- filtering the lignin precipitate to form a filter cake, comprising lignin, and a filtrate,
- mixing the filter cake into a dilution liquid to form an alkalilignin agglomerate colloid,
- subjecting the alkalilignin agglomerate colloid to a large-pore membrane filtration, and
- recovering a purified lignin salt concentrate.

2. The method according to claim 1, wherein the spent liquor pH is lowered below 11.

3. The method according to claim 2, wherein the spent liquor pH is lowered to 9 – 10.5.

4. The method according to any claim 1-3, wherein the pH is lowered by addition of H_2SO_4, SO_2, HCl or CO_2.

5. The method according to any claim 1-3, wherein the pH is lowered by addition of CO_2.

6. The method according to claim 1, wherein the dilution liquid is water.

7. The method according to claim 1, wherein the formed alkalilignin agglomerate colloid is subjected to large-pore-membrane filtration with nominal cut-off values in the range 40 – 400 kDa.

8. The method according to claim 7, wherein the cut-off value is in the range 50 – 200 kDa.

9. The method according to claim 1, wherein the pH decrease is carried out at a temperature in the range 40 – 85 °C.

10. The method according to claim 1, wherein the large-pore-membrane filtration is performed at a temperature in the range 20 – 85 °C.

11. The method according to claim 1, wherein the large-pore-membrane filtration is performed at a pH in the range 7 – 11.

12. A method according to claim 1, additionally comprising at least one step of rediluting the purified lignin salt and subjecting it to large-pore-membrane filtration.

13. A method according to claim 1, further comprising treatment of the concentrate.

14. A method according to claim 13, wherein the treatment is evaporation, freeze-drying or spray drying.

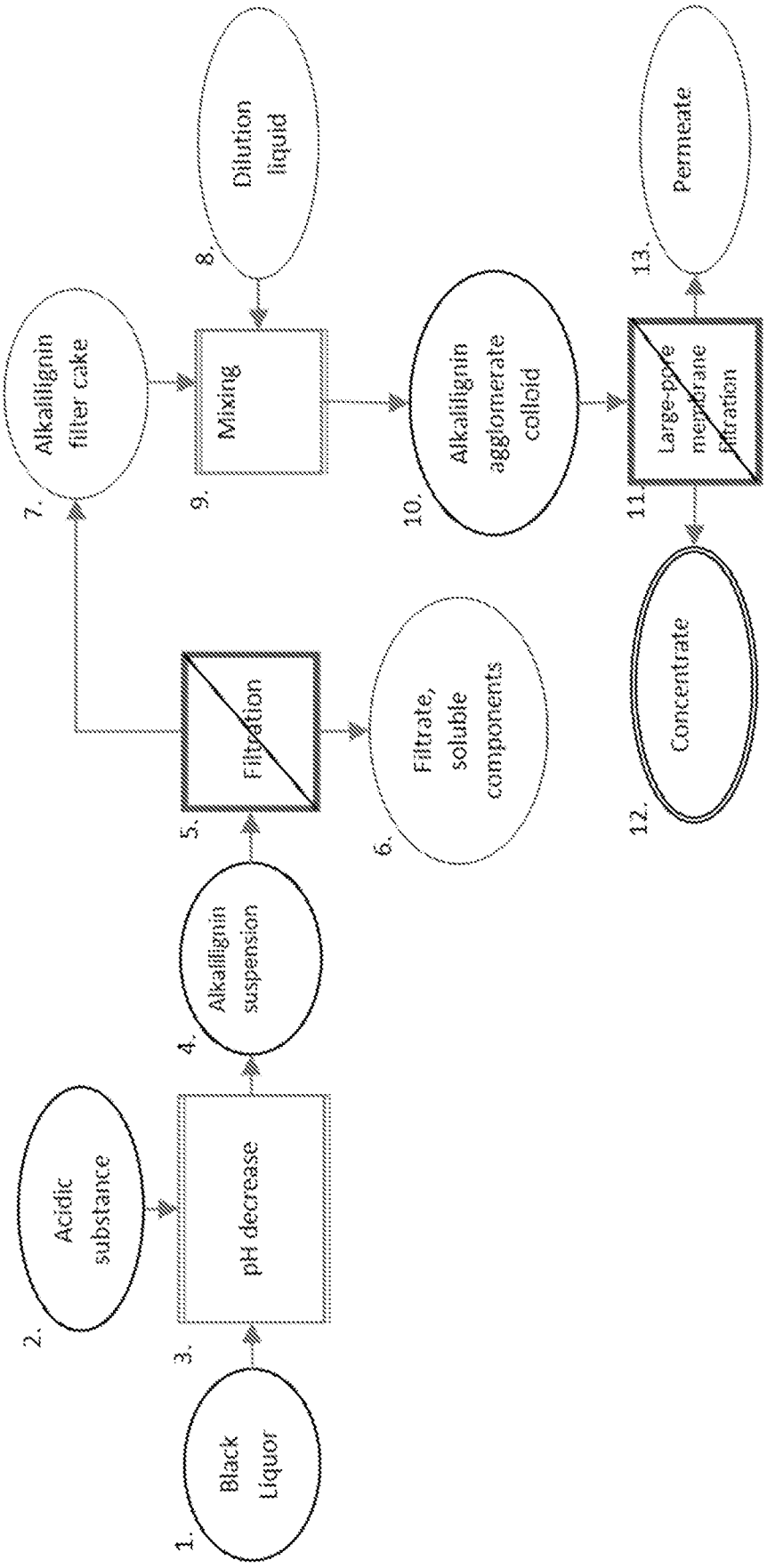

1. Black Liquor
2. Acidic substance
3. pH decrease
4. Alkalilignin suspension
5. Filtration
6. Filtrate, soluble components
7. Alkalilignin filter cake
8. Dilution liquid
9. Mixing
10. Alkalilignin agglomerate colloid
11. Large-pore membrane filtration
12. Concentrate
13. Permeate

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2020/050079

A. **CLASSIFICATION OF SUBJECT MATTER**

See extra sheet

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)

IPC: D21C, C07G, C08H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base, and, where practicable, search terms used)

EPODOC, EPO-Internal full-text databases, Full-text translation databases from Asian languages, WPIAP, PRH-Internal, XPESP, COMPDX, INSPEC, Paperbase,Google.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101476257 B (BEIJING GHEMU TECH CO LTD [CN]) 26 January 2011 (26.01.2011) & abstract [online] EPOQUENET EPODOC & WPI & machine translation into English by EPO and Google [online] [retrieved 04.05.2020 from https://fi.espacenet.com] page 3, lines 29-30; page 4,lines 26-27; page 5, lines 6-9 and 17-33; page 6, lines 1-16	1-14
Y	US 2406867 A (TOMLINSON GEORGE H et al.) 03 September 1946 (03.09.1946) column 2, line 18-column 3, line 68	1-14
Y	LIU G. ET AL. Treatability of kraft spent liquor by microfiltration and ultrafiltration. In: Desalination Elsevier, 2004-01-15, Vol. 160, No. 2, pages 131-141, ISSN 0011-9164, <DOI:10.1016/S0011-9164(04)90003-3> the whole document, especially table 3; paragraph 3.1 "Molecular size fractionation"	1-14

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"D"	document cited by the applicant in the international application	"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
"E"	earlier application or patent but published on or after the international filing date	"&"	document member of the same patent family
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
06 May 2020 (06.05.2020)	08 May 2020 (08.05.2020)

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2020/050079

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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