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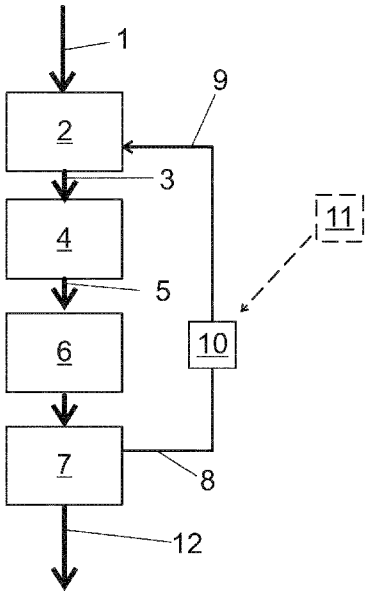

Fig. 1

(57) Abstract: A method and a system for separating lignin from a lignin containing liquid medium. Lignin is precipitated from a lignin containing liquid medium, the method comprising: - adding a pH lowering agent to said lignin containing liquid medium for precipitating lignin, - separating the precipitating lignin as from remaining liquid phase, - suspending the precipitated and separated lignin for obtaining a lignin containing suspension, - carbonizing the lignin containing suspension in a hydro thermal (HT) process for obtaining carbon product having increased carbon content and as a secondary product, off-gas comprising carbon dioxide (CO2), - wherein said pH lowering agent comprises carbon dioxide (CO2) produced in said hydrothermal (HT) process.

[Continued on next page]

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Method and System

Background

The invention relates to a method for separating lignin from a lignin containing liquid medium.

The invention further relates to a system for separating lignin from a lignin containing liquid medium.

It is commonly known methods and systems to separate lignin from a lignin containing alkaline liquid medium, such as pulp mill black liquor, by lowering pH of the liquid medium.

A problem with these is that the known methods are fairly expensive to use because of high costs of pH lowering agent, such as carbon dioxide (CO_2).

Brief description

Viewed from a first aspect, there can be provided a method for separating lignin from a lignin containing liquid medium, wherein lignin is precipitated from a lignin containing liquid medium, the method comprising:

- adding a pH lowering agent to said lignin containing liquid medium for precipitating lignin,
- separating the precipitating lignin as from remaining liquid phase,
- suspending the precipitated and separated lignin for obtaining a lignin containing suspension,
- carbonizing the lignin containing suspension in a hydro thermal (HT) process for obtaining carbon product having increased carbon content and as a secondary product, off-gas comprising carbon dioxide (CO_2),
- wherein said pH lowering agent comprises carbon dioxide (CO_2) produced in said hydrothermal (HT) process.

Thereby a method for separate lignin from a lignin containing alkaline liquid medium having lower expenses may be achieved.

Viewed from a further aspect, there can be provided a system for separating lignin from a lignin containing liquid medium, the system comprising a precipitating reactor for precipitation of lignin from a lignin containing liquid medium, comprising feeding arrangement for adding a pH lowering agent to said lignin containing liquid medium and for separating the precipitating lignin as from remaining liquid phase, a suspending reactor for suspending a lignin suspension from the precipitated and separated lignin, a hydrothermal (HT)

process reactor for producing carbon product having increased carbon content from said lignin suspension, and as a secondary product, off-gas comprising carbon dioxide (CO_2), the hydrothermal process unit comprising a off-gas channel for discharging off-gas comprising carbon dioxide, the discharge channel being arranged to feed said off-gas in the precipitating reactor for being used as said pH lowering agent.

Thereby a system that is able to be run with low costs may be achieved.

The method and the system are characterised by what is stated in the independent claims. Some other embodiments are characterised by what is stated in the other claims. Inventive embodiments are also disclosed in the specification and drawings of this patent application. The inventive content of the patent application may also be defined in other ways than defined in the following claims. The inventive content may also be formed of several separate inventions, especially if the invention is examined in the light of expressed or implicit sub-tasks or in view of obtained benefits or benefit groups. Some of the definitions contained in the following claims may then be unnecessary in view of the separate inventive ideas. Features of the different embodiments of the invention may, within the scope of the basic inventive idea, be applied to other embodiments.

In one embodiment, CO_2 is obtained by hydro thermal carbonization (HTC) process. An advantage is that the costs of lignin separating process may be lowered and also it is possible to reduce CO_2 emissions in the atmosphere.

In one embodiment, CO_2 is obtained by hydro thermal liquefaction (HTL) process. An advantage is that the costs of lignin separating process may be lowered and also it is possible to reduce CO_2 emissions in the atmosphere.

In one embodiment, CO_2 is obtained by hydro thermal gasification (HTG) process. An advantage is that the costs of lignin separating process may be lowered and also it is possible to reduce CO_2 emissions in the atmosphere.

In one embodiment, CO_2 is obtained by super critical (SC) process. An advantage is that the costs of lignin separating process may be lowered and also it is possible to reduce CO_2 emissions in the atmosphere.

Brief description of figures

Some embodiments illustrating the present disclosure are described in more detail in the attached drawings, in which

Figure 1 is a process flow chart of a method for separating lignin from a lignin containing liquid medium, and

Figure 2 is a schematic side view of a system for separating lignin from a lignin containing liquid medium.

In the figures, some embodiments are shown simplified for the sake of clarity. Similar parts are marked with the same reference numbers in the figures.

Detailed description

Figure 1 is a process flow chart of a method for separating lignin from a lignin containing liquid medium.

According to an aspect the method may be based on a process known as LignoBoost™. According to another aspect, the method may be based on a process known as Lignoforse™. According to still another aspect, the method may be based on a process known as Liquid Lignin SLRP™.

A lignin containing liquid medium 1 is fed to a precipitation process 2. Basically, the lignin containing liquid medium 1 is a result of a process where lignin is separated or fractionated from biomass, e.g. cellulose, by an alkaline process, such as sulphite, soda or sulphate process.

The origin of lignin may be in other biomass fractionation processes as well. One possible source is the biomass fractionation process where bio-ethanol is made from lignocellulosic biomass through hydrolysis of cellulose to sugars and subsequent fermentation and distillation. This biomass fractionation process leaves a lignin-rich residue which can be used as a starting material for the present method. Thus, all fractionation processes of lignocellulosic biomass where a lignin-rich fraction is produced can serve as the source of the lignin containing liquid medium 1.

It is intended throughout the present description that the expression “lignin containing liquid medium” is any liquid, which contains lignin in dissolved or dispersed form, especially any spent liquor from a biomass fractionating process, especially biomass fractionation in a chemical pulp mill.

In an embodiment, the lignin containing liquid medium 1 comprises black liquor.

In the precipitation process 2, at least one pH lowering agent is added to said lignin containing liquid medium. The pH lowering agent lowers pH of highly alkaline lignin containing liquid medium and, as a result, lignin precipitates from remaining liquid phase. According to an aspect, the precipitation process 2 comprises at least two stages. In a first stage of the precipitation process 2, there is used carbon dioxide (CO_2) for lowering pH value to about pH 9 – 11.

In a second stage of the precipitation process 2, there is used a second pH lowering agent for further lowering pH value, e.g. to about pH 2.5 to pH 4. The second pH lowering agent may comprise e.g. sulphuric acid (H_2SO_4). It is to be noted, however, that the second stage of the precipitation process 2 is not always necessary. For instance, if lignin is to be fed in HTC, HTL, HTG or SC process, the second stage may be omitted.

The precipitated lignin 3 is separated from remaining liquid phase and fed in a suspending process 4.

In the suspending process 4 the precipitated and separated lignin is suspended or dissolved in water or mixture of water and certain chemicals, such as acids, alkalis and/or alcohols, whereupon a lignin containing suspension is obtained.

Lignin containing suspension 5 may then be fed in a suspension handling process 6. This may comprise e.g. dewatering or controlling of water content of the suspension 5. However, the suspension handling process 6 is optional stage of the method.

Lignin containing suspension 5, handled or not, is then fed in a hydro thermal process (HT) 7, whereby the lignin containing suspension is carbonized and it is obtained carbon product having increased carbon content and as a secondary product, off-gas comprising carbon dioxide (CO_2).

The term “increased carbon content” means that the carbon product has higher carbon content than the carbon-containing raw material. In an embodiment, the carbon content of the carbon product is at least 2 – 15 wt% higher than the carbon content of the carbon-containing raw material. The carbon product 12 is removed from the hydro thermal process 7.

The hydro thermal (HT) process 7 may be e.g. hydro thermal carbonization (HTC) process, hydro thermal liquefaction (HTL) process, hydro thermal gasification (HTG) process, or super critical (SC) process.

The hydro thermal carbonization (HTC) process is based on the carbonization of organic matter at an elevated temperature and at a high pressure in an aqueous phase.

The hydro thermal liquefaction (HTL) process is a thermal depolymerization process used to convert wet biomass into crude-like oil -sometimes referred to as bio-oil or biocrude- under moderate temperature and high pressure. The reaction usually involves homogeneous and/or heterogeneous catalysts to improve the quality of products and yields. In the hydro thermal gasification (HTG) process, wet biomass and organic wastes are gasified under hydrothermal conditions.

The super critical (SC) process utilizes supercritical water, i.e. water at conditions where the temperature is above 374°C and the pressure is at least 221 bar, in gasifying organic matter. The reaction usually involves catalysts to improve the quality of products and yields.

As a secondary product of the hydro thermal process 7, there is developed off-gas that comprises inter alia carbon dioxide (CO_2) and/or steam (H_20). The off-gas 8 is removed from the hydro thermal process 7.

At least part of the off-gas 8 is fed as a pH lowering agent 9 in the precipitation process 2.

In an embodiment, prior to feeding to the precipitation process 2, the off-gas 8 may be submitted to a handling process 10 for optimizing its properties as a pH lowering agent 9, and the handled off-gas is fed to the precipitation process 2. The handling process 10 may comprise one or more of the following processes: cleaning, such as filtering, temperature controlling, pressure controlling, adding additional activation medium, etc.

In an embodiment, all of the CO_2 consumed as pH lowering agent 9 in the precipitation process 2 is created in the hydro thermal process 7. It is to be noted that the pH lowering agent 9 may be pure CO_2, or alternatively, gas mixture comprising CO_2.

In another embodiment, the CO_2 needed in the precipitation process 2 comprises CO_2 produced in and originating from the hydro thermal process 7 and additional CO_2 originating from an external source 11. The portion of CO_2 produced in the hydro thermal process 7 may be e.g. 30 wt% - 100 wt%, for instance 30 wt% - 40 wt% of the total consumption of CO_2 in the precipitation process 2.

Figure 2 is a schematic side view of a system for separating lignin from a lignin containing liquid medium. The system 100 may be used for carrying out e.g. the method shown in Figure 1.

A lignin containing liquid medium 1 is fed by a feeding channel 20 to a precipitation reactor 21. The reactor 21 may comprise one or more reactor apparatuses and the process may be carried out in one or more steps.

The lignin containing liquid medium 1 is precipitated by adding one or more pH lowering agent 9 thereto.

The precipitated lignin 3 is removed from the precipitation reactor 21 via a precipitated lignin channel 22.

The precipitated lignin channel 22 is arranged to convey the precipitated lignin 3 in a suspending reactor 23, wherein the precipitated lignin is suspended or dissolved in water. Thus a lignin containing suspension is obtained in the suspending reactor 23.

The lignin containing suspension is fed through a suspension channel 24 to suspension handling arrangement 25. The arrangement 25 may comprise e.g. dewatering systems, an additive feeding means for adding auxiliary compound(s) or substance(s), and/or means for feeding reactant(s) into the suspension, etc. However, it is to be noted that the suspension handling arrangement 25 is an optional means of the system.

The lignin containing suspension 5, handled in the arrangement 25 or not, is forwarded to a hydro thermal process reactor 27, where it is subjected to the hydro thermal process described earlier in this description.

Carbon containing product 12 obtained in the thermal process reactor 27 is removed by a carbon product removal channel 28 for use or further processing.

As a secondary product of the hydro thermal process taking place in the hydro thermal process reactor 27, there is developed off-gas 8 that comprises inter alia carbon dioxide (CO_2). The off-gas 8 is removed from the hydro thermal process reactor 27 by an off-gas channel 28.

At least part of the off-gas 8 is conducted to a pH lowering agent feeding channel and fed therefrom as a pH lowering agent 9 in the precipitation reactor 21.

In an embodiment, prior to feeding in the precipitation reactor 21, the off-gas 8 may be submitted to an off-gas handling means 30 for optimizing its properties as a pH lowering agent 9.

In an embodiment, all of the CO_2 consumed as pH lowering agent 9 in the precipitation process 2 is created in the hydro thermal process 27.

In another embodiment, CO_2 from an external source 11 is added to the CO_2 created in the hydro thermal process 27 in order to provide enough pH lowering agent 9 for the precipitation process 2.

The disclosed method and system may have several advantages. Firstly, expenses for separating lignin from a lignin containing liquid medium, such as black liquor, may be lowered because the need for CO_2 produced by an external supplier can be limited or totally avoided.

Secondly, off-gas inevitably produced in the HT –process needs not to be sent in waste, but it can be utilized in the process for separating lignin from a lignin containing liquid medium process.

The invention is not limited solely to the embodiments described above, but instead many variations are possible within the scope of the inventive concept defined by the claims below. Within the scope of the inventive concept the attributes of different embodiments and applications can be used in conjunction with or replace the attributes of another embodiment or application.

The drawings and the related description are only intended to illustrate the idea of the invention. The invention may vary in detail within the scope of the inventive idea defined in the following claims.

Reference symbols

1	lignin containing liquid medium
2	precipitation process
3	precipitated lignin
4	suspending process
5	lignin containing suspension
6	suspension handling
7	hydro thermal process
8	off-gas
9	pH lowering agent
10	off-gas handling
11	external source
12	carbon containing product
20	lignin containing liquid medium feeding channel
21	precipitation reactor
22	precipitated lignin channel
23	suspending reactor
24	suspension channel
25	suspension handling arrangement
26	feed channel
27	hydro thermal process reactor
28	carbon product removal channel
29	off-gas channel
30	off-gas handling means
31	pH lowering agent feeding channel
100	system

Claims

1. A method for separating lignin from a lignin containing liquid medium, wherein lignin is precipitated from a lignin containing liquid medium, the method comprising:

- adding a pH lowering agent to said lignin containing liquid medium for precipitating lignin,

- separating the precipitating lignin as from remaining liquid phase,

- suspending the precipitated and separated lignin for obtaining a lignin containing suspension,

- carbonizing the lignin containing suspension in a hydro thermal (HT) process for obtaining carbon product having increased carbon content and as a secondary product, off-gas comprising carbon dioxide (CO_2),characterized in that

said pH lowering agent comprises carbon dioxide (CO_2) produced in said hydrothermal (HT) process.

2. The method as claimed in claim 1, wherein the hydro thermal (HT) process is a hydro thermal carbonization (HTC) process.

3. The method as claimed in claim 1, wherein the hydro thermal (HT) process is a hydro thermal liquefaction (HTL) process.

4. The method as claimed in claim 1, wherein the hydro thermal (HT) process is a hydro thermal gasification (HTG) process.

5. The method as claimed in claim 1, wherein the hydro thermal (HT) process is a super critical (SC) process.

6. The method as claimed in any of the preceding claims, wherein the lignin containing liquid medium comprises black liquor.

7. A system for separating lignin from a lignin containing liquid medium, the system comprising:

- a precipitating reactor (21) for precipitation of lignin from a lignin containing liquid medium, comprising feeding arrangement for adding a pH

lowering agent to said lignin containing liquid medium and for separating the precipitating lignin as from remaining liquid phase,

- a suspending reactor (23) for suspending a lignin suspension from the precipitated and separated lignin,

- a hydrothermal (HT) process reactor (27) for producing carbon product having increased carbon content from said lignin suspension, and as a secondary product, off-gas comprising carbon dioxide (CO_2),

c h a r a c t e r i s e d in that

- the hydrothermal (HT) process reactor (27) comprises an off-gas channel (29) for discharging off-gas comprising carbon dioxide (CO_2), and that

- the off-gas channel (29) is arranged to feed said off-gas in the precipitating reactor (21) for being used as said pH lowering agent.

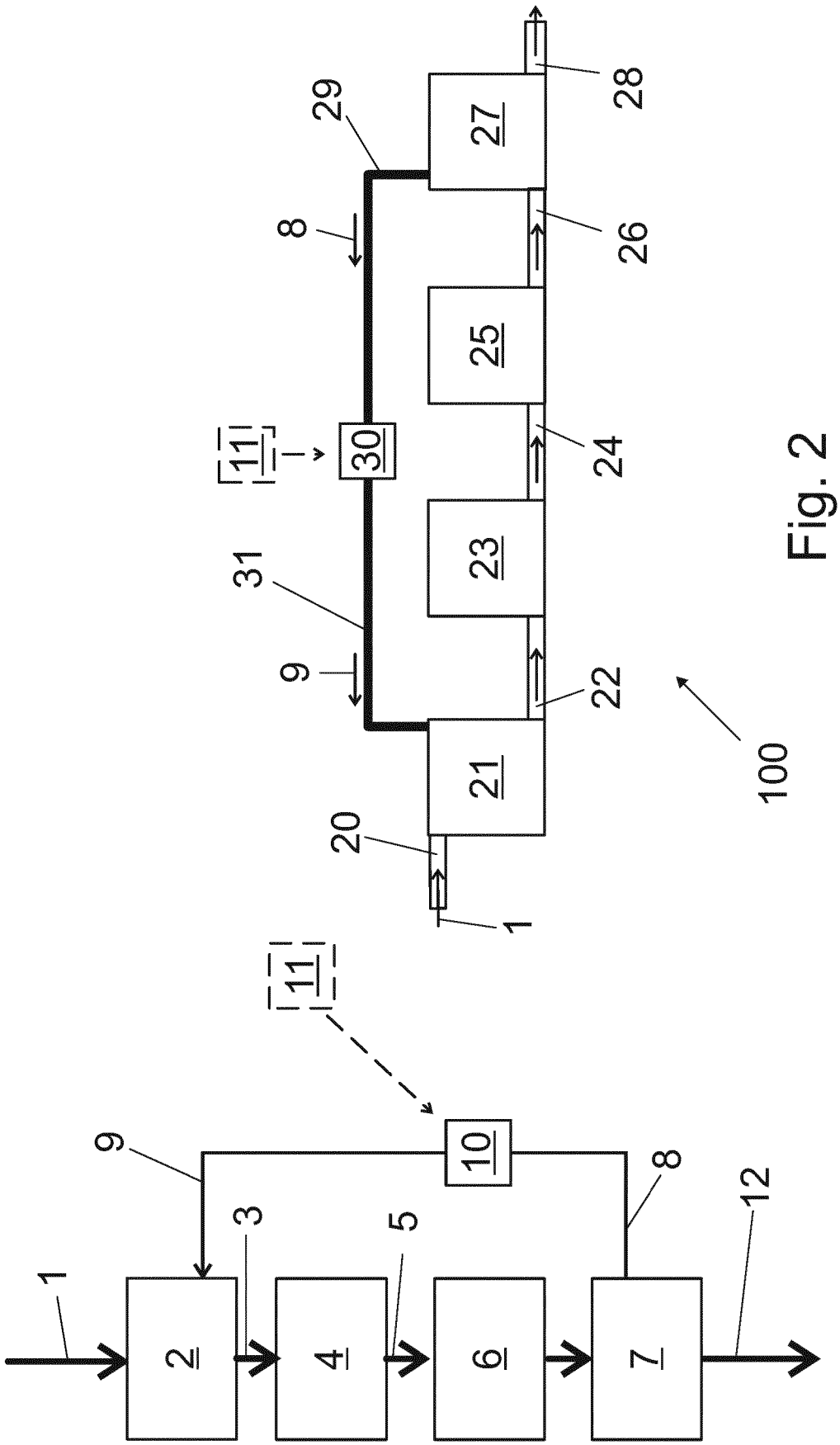

Fig. 1

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2017/050333

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07G1/00 D21C11/00 C08H7/00 C10L9/08 C08L97/00
C10G1/06 C10G3/00 C10L5/44 D21C11/14
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)
C01B C07G D21C C10G C08H C10L C08L C10J

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.
Y	WO 2015/025076 A1 (VALMET TECHNOLOGIES OY [FI]) 26 February 2015 (2015-02-26) claims 1, 4, 12, 13 page 6, lines 10-11 page 8, lines 1, 2 page 12, line 16 figures 1, 2	1-7

Y	CA 2 920 702 A1 (SUNCOAL IND GMBH [DE]) 12 February 2015 (2015-02-12) claim 1 page 6, lines 25-28 page 27, lines 5-18 figure 5	1-7

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

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2017/050333

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SHIMIN KANG ET AL: "Solid fuel production by hydrothermal carbonization of black liquor", BIORESOURCE TECHNOLOGY, vol. 110, 1 April 2012 (2012-04-01), pages 715-718, XP055160041, ISSN: 0960-8524, DOI: 10.1016/j.biortech.2012.01.093 column 1, lines 9-12	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2017/050333

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