(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
19 December 2013 (19.12.2013)

(10) **International Publication Number**
WO 2013/188401 A1

(51) **International Patent Classification**:
D21H 11/04 (2006.01) ***D21C 3/00*** (2006.01)

(21) **International Application Number**:
PCT/US2013/045177

(22) **International Filing Date**:
11 June 2013 (11.06.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/659,032 13 June 2012 (13.06.2012) US

(71) **Applicant**: **LIQUID LIGNIN COMPANY** [US/US]; A South Carolina Corporation, 109 Smith Street, Charleston, SC 29403 (US).

(72) **Inventors**: **LAKE, Michael, A.**; 708 Seratina Point, Mt. Pleasant, SC 29464 (US). **BLACKBURN, John, C.**; 109 Smith Street, Charleston, SC 29403 (US).

(74) **Agent**: **LIPSCOMB III, Ernest, B.**; Barnwell Whaley Patterson & Helms, LLC, P.O. Box Drawer H, Charleston, SC 29402 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) **Title**: PROCESS FOR PRODUCING ENERGY FROM LIGNIN

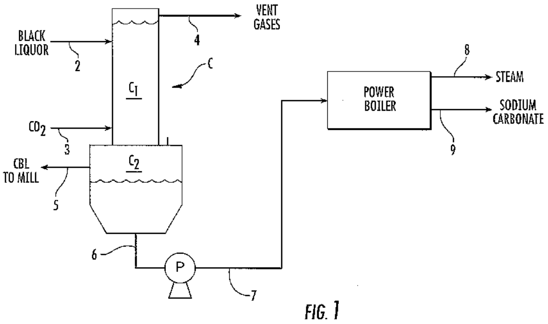

FIG. 1

(57) **Abstract**: A process for producing energy from lignin. Black liquor from a pulp mill is introduced into an absorption column at an elevated pH and carbonated at elevated temperature and pressure with C02 to neutralize NaSH and/or NaOH. The black liquor and lignin is allowed to undergo a phase separation creating a carbonated liquid-lignin phase and a lignin-depleted carbonated black liquor phase. The lignin-depleted carbonated black liquor phase is returned to the recovery plant. The carbonated liquid- lignin is fed directly to a power boiler and burned to produce energy. Alternatively, the carbonated liquid-lignin phase is separated and passed to a flash tank to remove the water; then the friable mostly solid lignin is pulverized and sent to the power boiler. In another embodiment, a slip stream of the carbonated liquid-lignin may be passed to a pure lignin recovery system.

WO 2013/188401 A1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PROCESS FOR PRODUCING ENERGY FROM LIGNIN

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The contents of Provisional application U.S. Ser. No. 61/659,032 filed June 13, 2012, on which the present application is based and benefit claimed under 35 U.S.C. §119(e), is herein incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] (1) Field of the Invention

[0003] The present invention relates to a process for producing energy from lignin. More particularly, the present invention relates to a process for carbonating black liquor from a pulp mill to recover carbonated liquid-lignin and burning the lignin to create energy.

[0004] (2) The Prior Art

[0005] Lignin, a component of wood, is the second most abundant biopolymer in the world behind cellulose. Lignin is primarily recovered from the black liquor stream produced in a kraft pulp mill. Black liquor is removed from the pulp mill's recovery system downstream of an efficiently performing soap separator, since tall oil impurities in the black liquor are deleterious to the operation of the unit operations of the process and the downstream applications. Alternatively, lignin can be recovered from enzymatic conversions of biomass cellulose, where lignin remains in a byproduct or waste stream. Although there are a number of uses for lignin, their high ash content - mainly Na^+, K^+, and other active cations associated either with anions or carboxylic or phenolic groups on the lignin itself - limits lignin's usefulness.

[0006] With its high energy density and variety of functional groups and structure, lignin holds promise to be an efficient biofuel source or green chemical precursor. Thus, one use for lignin is to recover lignin as a solid and burn the solid lignin as a fuel or to use the lignin as a binder for energy producing fuel pellets.

[0007] By way of background, several methods are presently used for recovering lignin from the black liquor produced in the kraft pulp mill. Issues with these methods include the potential for diluting the black liquor with water, controlling temperature of the process, and the residual inorganic ash in the final product. Lignin containing a high salt content creates issues with applications sensitive to high ash. Also, there is the problem of cooling and diluting the black liquor that is returned to the host mill, which creates a high energy penalty in the black liquor recovery operation. The filtrates from these methods have to be returned to the host papermaker to recover the sodium, but the black liquor is cooled significantly (from >200°F to ≈140°F) and includes wash water, which is added.

[0008] Removing a fraction of the lignin from black liquor allows pulp and paper mills that have reached the maximum throughput of their extremely expensive recovery boilers to increase production proportional to the fraction of lignin removed. For example, a large paper mill recovering 30% of their lignin from black liquor allows the mill to increase the overall production rate approaching that same percentage.

[0009] Most kraft pulp and paper mills have the infrastructure to gather residual wood within an economically effective radius of the mill. Many of these mills have reached the limit of their recovery furnaces because of heat-transfer limitations within the furnace. The multiple tubes within the furnace that generate steam on the inside with heat transferred from the burning concentrated black liquor on the outside risks catastrophic consequences (recovery furnace explosions); thus pulp mills don’t exceed that limit. Removing a fraction (≤ 30%) of the lignin allows the mills to increase their overall production rate of paper by that same fraction.

[0010] Many states are implementing renewable energy thresholds on electricity generating power furnaces, many of which burn coal. However, burning significant fractions of residual wood, as the paper industry does, requires a different design of the furnace, which would have a larger footprint and requires more capital than a coal burning furnace.. A major factor is the low energy content of residual wood containing significant levels of water. Wet residual wood has as low as 25% the energy density (Btu/lb) as coal. Also, residual wood contains significant levels of inorganics, which result in must higher levels of ash within the fuel, which requires either specialized equipment to continuously remove the ash or periodic shut down to remove the ash. The paper industry historically has built power furnaces capable of burning large fractions of residual wood; the power companies have not.

SUMMARY OF THE INVENTION

[0011] In accordance with the present invention there is provided a process for recovering lignin from black liquor produced during the kraft pulping process and producing energy from the recovered lignin. More specifically, the present invention is a process comprising introducing a black liquor stream from a pulp mill into an absorption column at an elevated pH; carbonating the black liquor, at elevated temperature and pressure, with CO_2 to neutralize NaSH and/or NaOH; and allowing the carbonated black liquor and carbonated lignin to undergo a phase separation creating a carbonated liquid-lignin phase and a lignin-depleted carbonated black liquor phase. The lignin-depleted carbonated black liquor phase, being mostly black liquor, is returned to the pulp mill recovery boiler at a temperature higher than the temperature of the black liquor received, thus, removing a major impediment for commercial implementation by a pulp and paper mill.

[0012] The carbonated liquid-lignin phase is a homogeneous stream exiting the carbonating column at an operating temperature >200°F. The pressure is maintained at about 50 psi to prevent boiling. The carbonated liquid-lignin may be fed directly to a power boiler with enthalpy loss less than 10% from the water vaporization where the carbonated liquid-lignin is burned to produce energy. Alternatively, the carbonated liquid-lignin is separated; passed to a flash tank to remove the water; then the friable mostly solid lignin is pulverized; and sent to the power boiler and burned to form energy.

[0013] In another embodiment, a slip stream of carbonated liquid-lignin is passed to a lignin recovery system where the slip stream of carbonated liquid-lignin is acidified to form a dense lignin phase and further treated to recover a purified lignin. The amount of carbonated liquid-lignin in the slip stream will be determined by the capacity of the pulp mill recovery boiler. The remainder of the carbonated liquid-lignin is sent to the power boiler and burned.

[0014] It is therefore the general object of the present invention to provide a process for treating black liquor to produce a lignin suitable for burning to produce energy.

[0015] Another object of the present invention is to provide both relief of a constricted pulp mill recovery boiler and an efficient platform for lignin recovery processes.

[0016] Other features and advantages of the invention will be apparent to those skilled in the art from the following detailed description taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Having described the invention in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale, and wherein:

[0018] FIG. 1 is a schematic flow diagram illustrating an embodiment of the process of the present invention showing the black liquor carbonating step, the liquid-lignin separation step and the energy producing step; and

[0019] FIG. 2 is a schematic flow diagram illustrating an embodiment of the process of the present invention showing the black liquor carbonating step, the liquid-lignin separation step, the lignin purification step and the energy producing step.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0020] The present invention now will be described more fully hereinafter. This invention may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art.

[0021] Black liquor is removed from the pulp mill's recovery plant downstream of an efficiently performing soap separator because tall oil impurities are deleterious to the operation of the unit operations of the process. The use of lignin for fuel in the present process involves two major unit operations: a black liquor carbonation system for producing liquid-lignin and a powe boiler for burning the lignin.

[0022] Referring now to FIG. 1, pressurized black liquor at a high pH (*e.g.*, above pH 13) is introduced through line **2** to a CO_2 absorption column $\mathbf{C_1}$. Black liquor, leaving the soap separator in the pulp mill, is pumped at a pressure of about 50 psig. Typically black liquor, removed midway in the evaporator train, is 25-45% solids and has a temperature of about 180°F to about 250°F. Keeping the heat of reaction in the system raises the temperature significantly. The heat of reaction of black liquor with CO_2 typically raises the temperature 25°F.

[0023] The black liquor is introduced into the top $\mathbf{C_1}$ of a two part CO_2 absorption column **C**. The size of the column will depend upon the volume of black liquor being treated. For example, in a column designed to process 50,000 tons of lignin per year the upper portion of the column may be approximately 5' diameter, 20' tall. The black liquor, with a high NaOH content and a pH above pH 13, more normally about pH 14, reacts with the CO_2 injected through line **3** to form $NaHCO_3$. The column operates at a nominal pressure of about 50 psig and a temperature betwee4n about 180°F and about 350°F, preferably about 200°F to about 300°F, most preferably about 200°F to 250°F. In the column, the NaOH is neutralized, lowering the pH to 8-11, preferably about pH 8 to 10. This reaction causes the release of a substantial exotherm, increasing the temperature of the stream about 25°F, depending on the NaOH content and the solids level of the stream. The viscosity of the lignin in the black liquor decreases as the temperature rises above the melt point. The melt point of lignin depends strongly on the level of Na^+ ions, the source of the lignin, and water within the liquid-lignin phase, so the viscosity is difficult to predict.

[0024] The vent gases leave the top of column $\mathbf{C_1}$ through line **4** and contain essentially H_2S and CO_2 with no air and are scrubbed completely by bubbling through as little as two feet of 10% caustic solution (not shown). The bubbles collapse completely as the H_2S and CO_2 react rapidly with NaOH near ambient temperature. Vent gases from the CO_2 absorption column can be scrubbed with a white liquor solution from the paper mill forming NaSH from the absorbed H_2S, creating value as a pulping agent in the papermaker's host system. Other non-condensable sulfur gases that escape a NaOH scrubber can be treated with thermal oxidation efficiently with the absence of air.

[0025] The carbonated black liquor and carbonated liquid-lignin flow into the bottom portion of the column $\mathbf{C_2}$, where the two phases undergo complete separation. The high temperature and pressure separation preserve heat from the heats of reaction of the reaction with CO_2 that enables sending that heat back to the recovery plant in the lignin-depleted black liquor and improves the phase separation. The lower portion $\mathbf{C_2}$ of the

CO_2 column provides a large, quiet zone for phase separation. For example, $\mathbf{C_2}$ may be approximately 5,000 gal vessel for a 50,000 ton lignin per year column.

[0026] The lignin-depleted carbonated black liquor separates as the light (top) phase and is returned to the recovery plant of the pulp mill through line **5**. The lignin-depleted carbonated black liquor is returned to the host mill at a higher temperature than the black liquor withdrawn, due to the heat of reaction with CO_2 with black liquor components.

[0027] The carbonated liquid-lignin stream **6** leaving the bottom of the carbonation column $\mathbf{C_2}$ contains approximately 40% moisture. The carbonated liquid-lignin stream is homogeneous at operating temperatures of >250°F. The pressure is maintained at about 50 psig to prevent boiling. The carbonated liquid-lignin stream is fed through pump **P** and line **7** directly to a power boiler at an elevated temperature (>250°F) so that sensible heat needed to raise the carbonated liquid-lignin to burning temperature is minimized. The enthalpy loss is less than 10% from the water vaporization. The steam produced from the burning lignin exits through line **8**, while the sodium carbonate exits through line **9** and is recycled to the host mill.

[0028] Alternatively, if the carbonated liquid-lignin goes through a pressure-reducing valve water is flashed from the carbonated liquid-lignin. The resulting material is a solid but porous lignin structure having lava-like appearance. This porous carbonated liquid-lignin solid is friable, *e.g.*, easily crushed by hand. This friable solid easily dewaters. So as an alternative, the power boiler is fed with solidified carbonated liquid-lignin that has been dewatered. The moisture content of the solid carbonated liquid-lignin is less than 20%, and the water that drains away has high levels of sodium bicarbonate that may be mixed with lignin-depleted carbonated black liquor at the same pH (about 8) and returned to the host mill. In this alternative, the ash loading of the power boiler would be reduced but the capital would be increased from the flashing and dewatering equipment.

[0029] All the sodium in the original black liquor is retained by the liquid-lignin in the energy producing step. From a material balance calculation, about 80% of the sodium in the black liquor is returned to the host mill in the lignin-depleted carbonated black liquor stream from the carbonation system, and about 20% is returned via the ash from the power boiler. The ash is primarily sodium carbonate with other inorganic components (such as sodium sulfate) being determined by the inorganics in the black liquor.

[0030] The process of this invention concentrates the lignin in black liquor relative to both water and ash, as shown in the table below. Both the lignin:water and lignin:ash ratios are increased by a factor of three, making burning much more efficient.

Ratio of Lignin	In Black Liquor at 40% Solids	In CLL at 60% Solids
to ash	1:1	3:1
to water	1:3	1:1

[0031] The carbonation system can be designed flexibly to allow scale-up by oversizing the carbonation column diameter and pump; the height of the column remains the same. The equipment used in the process of the present invention can be sized to fit the need of increasing throughput to the recovery furnace in the short term. The power boiler is designed to meet this demand. As the market development of kraft lignin expands, a lignin recovery system may be added as part of the process. The power boiler size would be unchanged as lignin production is ramped upward.

[0032] An embodiment of the lignin recovery system that may be used with the process for producing energy is shown in FIG. 2 wherein the carbonating step is the same as for the process shown in FIG. 1. In the embodiment of FIG. 2 a slip steam of carbonated liquid-lignin is continuously passed through line **10** to an acidifier where the carbonated liquid-lignin stream is acidified to neutralize residual NaOH and other basic components, thereby generating an acidified dense lignin phase. In a preferred embodiment, the acidifying step is accomplished with an acid, such as a strong acid, like sulfuric acid in an amount sufficient to reduce the pH to less than 4, preferably a pH between 1.5 and 3.5. The acidifying step is carried out at a temperature up to 390°F, preferably at a temperature between about 180°F to about 300°F to form a dense liquid-lignin. Sodium sulfate is removed through line **11**. The dense phase lignin is removed from the acidifier through line **12** and washed to remove residual acid and ash content, thereby generating purified lignin. One such acidification process is known as the Sequential Liquid-Lignin Recovery and Purification (SLRP) process which is the subject of Ser. No. 13/147,785 filed August 3, 2011.

[0032] A wide variety of biomass-burning power boilers are under development. The list of companies offering biomass power boilers includes major manufacturers such as Alstom Power, Andritz Oy, Babcock & Wilcox, and ThyssenKrupp VDM, as well as smaller manufacturers such as Heuristic Engineering, Keystone, and Nebraska Boilers. In a commercial process burning 50,000 ton/yr of lignin, about 100,000 lb/hr of steam and about 20 tons/day of sodium as ash will be generated. The carbonated liquid-lignin, either as a true liquid or as the lava-like solid, requires evaluation by the boiler manufacturer. If the carbonated liquid-lignin is burned as a true liquid, the 40% water in the phase actually can assist combustion by creating small particles as the pressure is reduced within the burner by the rapid expansion of the water.

[0034] The ash content of the carbonated liquid-lignin is relatively high compared to most biofuels. Carbonated liquid-lignin has an ash content of 25% based on solids, whereas typical biofuels have ash contents less than 10%. However, the inorganics contributing to the ash in carbonated liquid-lignin are constrained to relatively few components; whereas the variety of ash components in waste biofuels is relatively broad. The carbonated liquid-lignin ash is primarily sodium bicarbonate ($NaHCO_3$) at pH 8 which converts readily at combustion temperatures to Na_2CO_3 and/or Na_2O, depending on the temperature and residence time in the boiler. Some sulfur is present in the carbonated liquid-lignin as sodium sulfate and organically-bound sulfur, but this latter component is readily converted to Na_2SO_4 in an oxygen-rich combustion zone.

[0035] The formation of liquid phases within biomass power boilers pose special challenges which are being addressed by the industry. The presence of silicates in typical biomass boilers risk formation of glass phases when combined with high levels of sodium, but in the typical carbonated liquid-lignin, the silicate levels are low, so this risk is mitigated. Boiler experts will be able to assess the characteristics of carbonated liquid-lignin and recommend biomass boiler designs which fit the characteristics of the liquid-lignin for fuel process of the present invention.

[0036] Many modifications and other embodiments of the inventions set forth herein will come to mind to one skilled in the art to which these inventions pertain having the benefit of the teachings presented in the foregoing descriptions. Therefore, it is to be understood that the inventions are not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

What is claimed is:

1. A process for producing energy for the recovery boiler of a paper mill comprising:

(a) introducing a black liquor stream containing lignin from a paper mill into an absorption column at elevated pH by and carbonating said black liquor at an elevated temperature and pressure to neutralize NaSH and/or NaOH in said black liquor and precipitate said lignin;

(b) allowing said black liquor and precipitated lignin to undergo a phase separation creating a carbonated liquid-lignin phase and a lignin-depleted black liquor phase;

(c) returning said lignin-depleted black liquor phase to a pulp mill recovery plant at a temperature higher than the temperature of the black liquor received from the pulp mill; and

(d) burning said carbonated liquid-lignin phase to produce energy.

2. The process according to Claim 1 wherein said carbonation is carried out by contacting said black liquor with carbon dioxide countercurrently in an amount sufficient to reduce the pH of the black liquor to a pH between 8.0 and 11.

3. The process according to Claim 1 wherein carbonating step is carried out at a temperature between about 180°F and about 350°F.

4. The process according to Claim 1 wherein said burning produces steam and sodium-rich ash that is mainly sodium carbonate, which are returned to the pulp mill.

5. The process according to Claim 1 wherein said carbonated liquid-lignin phase is flashed to remove steam from the carbonated liquid-lignin to form a porous solid lignin, and pulverizing said porous solid lignin.

6. The process according to Claim 1 further comprising:

passing a slip steam of carbonated liquid-lignin continuously to an acidifier where the carbonated liquid-lignin stream is acidified to neutralize residual NaOH and other basic components, thereby generating an acidified dense lignin phase;

removing said dense phase lignin from said acidifier; and

washing said dense phase lignin to remove residual acid and ash content, thereby generating purified lignin.

7. The process according to Claim 1 wherein said acidifying is accomplished with an acid in an amount sufficient to reduce the pH to less than 4.

8. The process according to Claim 7 wherein said acid is sulfuric acid in an amount sufficient to reduce the pH between 1.5 and 3.5.

9. The process according to Claim 1 wherein said acidifying step is carried out at a temperature up to 390°F to form a dense liquid-lignin.

10 A process for producing energy for the recovery boiler of a paper mill comprising:

(a) introducing a black liquor stream containing lignin from a paper mill into an absorption column at a pH above 13 by and carbonating said black liquor at a temperature between about 200°F and about 300°F at an elevated pressure to neutralize NaSH and/or NaOH in said black liquor and precipitate said lignin;

(b) allowing said black liquor and precipitated lignin to undergo a phase separation creating a carbonated liquid-lignin phase and a lignin-depleted black liquor phase;

(c) returning said lignin-depleted black liquor phase to a pulp mill recovery plant at a temperature higher than the temperature of the black liquor received, thus, removing a major impediment for commercial implementation by paper mills; and

(d) burning said carbonated liquid-lignin phase to produce energy.

11. The process according to Claim 10 wherein said carbonation is carried out by contacting said black liquor with carbon dioxide countercurrently in an amount sufficient to reduce the pH of the black liquor to a pH between 8.0 and 10.

12. The process according to Claim 10 further comprising:

passing a slip steam of carbonated liquid-lignin is continuously to an acidifier where the carbonated liquid-lignin stream is acidified to neutralize residual NaOH and other basic components, thereby generating an acidified dense lignin phase;

removing said dense phase lignin from said acidifier; and

washing said dense phase lignin to remove residual acid and ash content, thereby generating purified lignin.

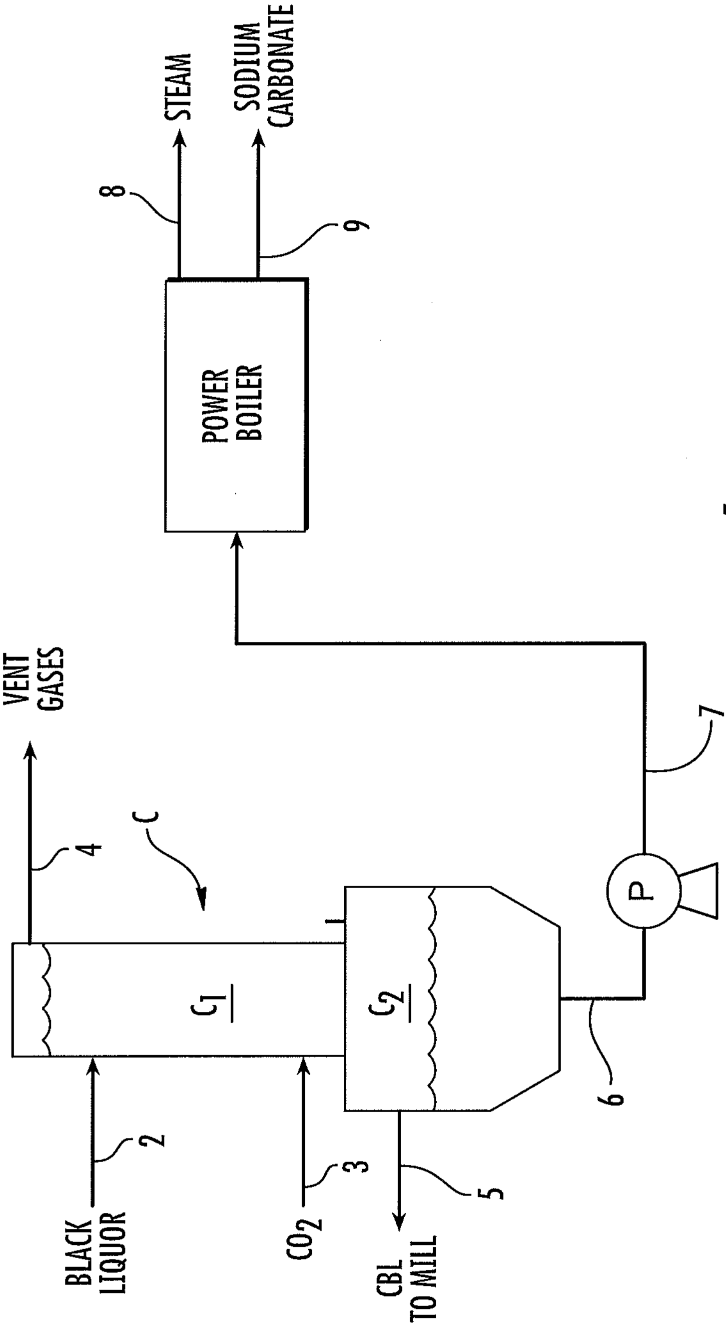
BLACK LIQUOR
2
CO_2
3
CBL TO MILL
5
C_1
C_2
C
4
VENT GASES
6
P
7
POWER BOILER
8
STEAM
9
SODIUM CARBONATE

FIG. 1

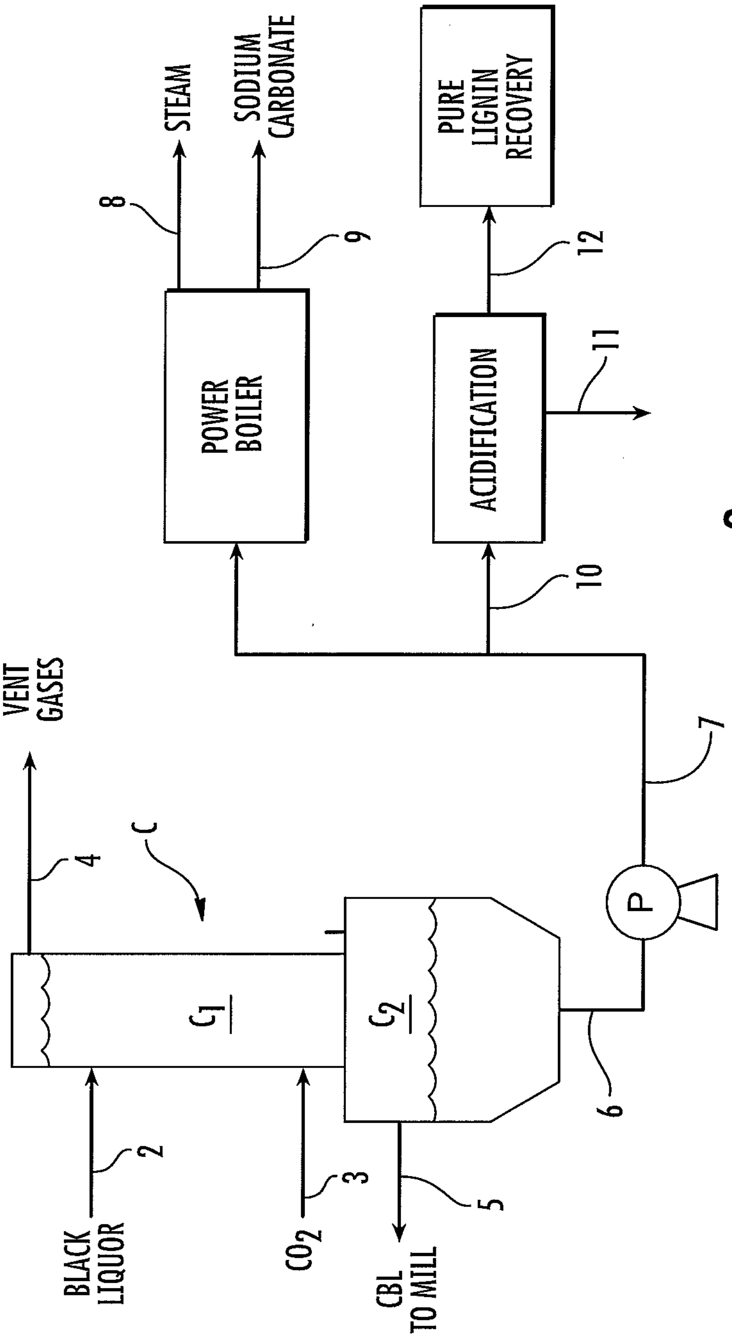
BLACK LIQUOR
2
CO_2
3
CBL TO MILL
5
C
C_1
C_2
1
4
VENT GASES
6
P
7
10
POWER BOILER
8
STEAM
9
SODIUM CARBONATE
ACIDIFICATION
11
12
PURE LIGNIN RECOVERY

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/045177

A. CLASSIFICATION OF SUBJECT MATTER

D21H 11/04(2006.01)i, D21C 3/00(2006.01)i

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)
D21H 11/04; D21C 11/04; D21C 11/12; D21C 11/00; C08H 7/00; C08H 5/02; C07G 1/00; D21C 3/20; D21C 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: black liquor, lignin, paper mill, recovery, carbonating, burning

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011-0294991 A1 (LAKE, MICHAEL A. et al.) 01 December 2011 See abstract; pages 1-5; claims 1-4 and 6-8.	1-12
A	WO 2009-104995 A1 (LIGNOBOOST AB) 27 August 2009 See abstract; claims 1 and 4-6.	1-12
A	US 4764596 A (LORA, JAIRO H. et al.) 16 August 1988 See abstract; claims 1-5 and 12.	1-12
A	WO 2008-156397 A1 (METSO POWER AB) 24 December 2008 See abstract; page 196; figure 1.	1-12
A	SUN, RUNCANG et al., `Effects of precipitation pH on the physico-chemical properties of the lignins isolated from the black liquor of oil palm empty fruit bunch fibre pulping`, Polymer Degradation and Stability, 28 February 1999, Vol.63, No.2, pp.195-200. See abstract; page 196; figure 1.	1-12

☐ 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 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
"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 23 September 2013 (23.09.2013)	Date of mailing of the international search report **24 September 2013 (24.09.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. +82-42-472-7140	Authorized officer HEO Joo Hyung Telephone No. +82-42-481-8150

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2013/045177

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011-0294991 A1	01/12/2011	WO 2011-037967 A2	31/03/2011
		WO 2011-037967 A3	13/10/2011
WO 2009-104995 A1	27/08/2009	CN 101952504 A	19/01/2011
		EP 2247785 A1	10/11/2010
		EP 2247785 A4	12/09/2012
		US 2010-0325947 A1	30/12/2010
US 04764596 A	16/08/1988	EP 0224721 A1	10/06/1987
		EP 0224721 B1	05/06/1991
		EP 0569526 A1	12/01/2000
		JP 08-500854 A	30/01/1996
		JP 62-110994 A	22/05/1987
		US 05788812 A	04/08/1998
		WO 92-13849 A1	20/08/1992
		WO 93-15261 A1	05/08/1993
WO 2008-156397 A1	24/12/2008	None	