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(54) **Titre : PROCEDE AMELIORE POUR LE TRAITEMENT DE LA LIGNINE**
(54) **Title: IMPROVED PROCESS FOR TREATING LIGNIN**

(57) **Abrégé/Abstract:**

This invention provides improvements to processes for making granular lignin from black liquor. One of the improvements is that the use of a pre-carbonation column reduces the CO_2 flow into the sparger of a carbonation column. The pre-carbonation column is used to reduce the pH of the black liquor to about 12. Another improvement is that it has been found that coalescing droplets into a bulk liquid-lignin phase can be enhanced by placing the exit of the carbonation column at or slightly beneath carbonated black liquor/liquid-lignin interface. It has also been found that operating the carbonation settler at a low pressure and pumping the liquid-lignin from the carbonation settler to the acidification reactor operating at a higher pressure allows recycling the vent gas from the acidification reactor to the pre-carbonation column. The invention also provides for a vent gas absorber.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IMPROVED PROCESS FOR TREATING LIGNIN

CROSS REFERENCE TO RELATED APPLICATION

[0001] The contents of Provisional Application U.S. Ser. No. 63/051,609 filed July 14, 2020, 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 INVENTON

(1) Field of the Invention

[0002] The present invention relates to improvements in manufacturing lignin from black liquor from a papermaking operation or a crude lignin waste stream from a biomass enzymatic conversion process.

(2) The Prior Art

[0003] Processes for recovering lignin from black liquor have been developed through the years. One such process is described in United States Patent No. 9,260,464 ("the '464 patent"), which is incorporated herein by reference, in which black liquor is carbonated, allowed to settle into a dense liquid-lignin phase and a carbonated lignin-depleted phase. The dense liquid phase is then acidified to produce a solid lignin. The improvements described herein while broadly applicable to lignin producing processes are especially useful for improving the process described in the '464 patent.

[0004] In the process of the '464 patent, the pH of kraft black liquor from a pulp mill having a pH of about 14 is reduced to a pH between about 9 and 11.5. One known method of reducing the pH of black liquor is by carbonating the black liquor with carbon dioxide (CO_2) in a carbonation column. Above the sparger CO_2 bubbles rising react with the falling black liquor, forming liquid-lignin droplets that coalesce into larger globules of liquid-lignin that sink within the continuous phase of the carbonated black liquor. The larger the globule, the higher is the rate of settling. These globules are fragile and can be cleaved by excessively agitating the carbonated black liquor. The globules that form in the upper part of the carbonation column must pass directly by the sparger, going through the highest zone of agitation created by the CO_2 gas exiting the orifices of the sparger. These globules can be sheared to form a stable liquid-in-liquid emulsion of small liquid-lignin droplets.

[0005] The small liquid-lignin droplets fall into a carbonation settler below the carbonation column. A heavy layer of the emulsion accumulates in the bottom of the carbonation settler and has higher concentrations of carbonated black liquor that the normal bulk liquid-lignin and is undesirably transferred into the acidification reactor. This condition causes several problems, including creation of a stable dispersion of lignin in acid brine which is difficult to filter, resulting in higher amounts of sulfuric acid being consumed by the interstitial carbonated black liquor of the heavy layer, and higher rates of sulfurous vent-gas created in the acidification reactor. It is desirable –but difficult to achieve- that large globules of liquid-lignin remain intact and coalesce into a bulk liquid-lignin phase within the carbonation settler that - when transferred to the acidification reactor - creates easily filtered, irregularly shaped, solid lignin particles using minimal amounts of sulfuric acid (H_2SO_4) and generating minimal levels of sulfur gases.

[0006] A major negative for presently used lignin recovery technologies is the high level of water returned to the mill. Present lignin producing processes indicate returns of two (2) mass units of water to the host mill for each mass unit of lignin recovered. This water is needed: (i) to wash sulfate salts from the lignin to achieve relatively low levels of inorganic ash; (ii) to slurry the carbonated lignin filter cake so that a fluid slurry is formed before the addition of sulfuric acid; and (iii) to keep the normality of the sulfuric acid relatively low to prevent charring the lignin because of localized over-heating. The acidification reactor of the lignin producing process described in the '474 patent is highly agitated, and the temperature is elevated (for example, from 80°C-110°C). The normality of the sulfuric acid added to the dense liquid-lignin can be relatively high without charring the lignin.

SUMMARY OF THE INVENTION

[0007] The present invention provides improvements to processes for making granular lignin. One of the improvements is that it has been found that the use of a pre-carbonation column reduces the CO_2 flow into the sparger of a carbonation column. The pre-carbonation column is used to reduce the pH of the black liquor to about 12 by primarily neutralizing the highly basic inorganic components such as NaOH and NaSH that are present in the black liquor. At pH 12 and higher, very little lignin precipitates.

[0008] Another improvement is that it has been found that coalescing droplets into a bulk liquid-lignin phase can be enhanced by placing the exit of the carbonation column at or slightly beneath carbonated black liquor/liquid-lignin interface. Another feature is that the yield of liquid-lignin and the resulting acidified lignin is improved when structured packaging is placed in the bottom of the carbonation column below the CO_2 sparger and around the upper section of the annulus of the carbonation settler.

[0009] It has also been found that operating the carbonation settler at a low pressure and pumping the liquid-lignin from the carbonation settler to the acidification reactor operating at a higher pressure allows recycling the vent gas from the acidification reactor to the pre-carbonation column.

[0010] The invention also provides for a vent gas absorber. Since there is no air in the pre-carbonation column, carbonation column or the acidification reactor, the vapor spaces are devoid of air and contain only H_2S, CO_2, and water vapor with trace amounts of other sulfur gases. The reaction of these concentrated acid gases in the vent gas absorber with NaOH is rapid and quantitative since mass transfer is not impeded by air.

[0011] It is the general object of the present invention is to provide improvements in processes for producing granular lignin.

[0012] Other objects, 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

[0013] 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:

[0014] FIG. 1 is a schematic flow diagram illustrating an embodiment of a portion of the process of the present invention showing the pre-carbonation column connected to the carbonation absorption column, followed by the acidification stage;

[0015] FIG. 2 is an enlarged schematic flow diagram illustrating the pre-carbonation column of the present invention connected to a carbonation absorption column;

[0016] FIG. 3 illustrates an enlarged portion of the carbonation column of the present invention showing a sparger near the bottom of the column above the carbonation settler;

[0017] FIG. 4 is an enlarged view of carbonation column and settler illustrating the structural packing within the carbonation column;

[0018] FIG. 5 is a schematic diagram which illustrates two options for controlling the liquid-lignin level in a carbonation settler and recycling vent-gas from the acidification reactor;

[0019] FIG. 6 illustrates the acidification reactor for use in the process of this invention; and

[0020] FIG. 7 shows a vent gas absorber for use in the process of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

[0021] The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many difference 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.

[0022] In the production of granular lignin, it has been found that pre-carbonating black liquor in a pre-carbonation column reduces the carbon dioxide (CO_2) flow into the sparger of the carbonation column by one-third or more, splitting the CO_2 load between the pre-carbonation column and the carbonation column. This significantly reduces the turbulence in the zone just above the sparger of the carbonation column and increases the likelihood of large globules of liquid-lignin surviving to enter the quiet zones of the carbonation settler to coalesce further into a bulk phase.

[0023] Referring to FIG. 1, there is shown a schematic flow diagram of an embodiment of a process of the present invention showing the steps of pre-carbonating a stream of black liquor, carbonating to form a liquid-lignin, subjecting the carbonated black liquor to a phase separation wherein a dense liquid-lignin phase is formed, a lignin-depleted phase is formed and NaOH and other basic components are neutralized. Black liquor, leaving the soap separator in a pulp and paper plant, is introduced through line **1** to pre-carbonation column **A**, typically under pressure between about 50 psig and about 200 psig, most preferably about 60 psig. The black liquor has a solids content of between 10% and 70%, but typically a solids content between about 30% to 45%, and has a temperature of about 80°C to about 120°C.

[0024] As shown in FIG. 1 and FIG. 2, the pre-carbonation column **A** has two inlet gas streams near the bottom of the column, one (inlet **2**) for carbon dioxide, preferable pure CO_2, and the other (inlet **3**) for recycled acidic and sulfurous vent-gas from the acidification reactor **D**. The pre-carbonation column **A** is sized so that the pH of the black liquor is the pH of the black liquor can be reduced from 14 to between about 12.5 and 11.5 which is before liquid-lignin starts precipitating. A pH probe **4**, placed at the top of the pre-carbonation column **A** just before the partially carbonated black liquor enters the carbonation column **C**, allows the operator to control this pH by adjusting the flow of the CO_2. The reaction of NaOH and NaSH with CO_2 causes a substantial exotherm, increasing the temperature of the stream depending on the NaOH and NaSH content and the solids level of the stream.

[0025] Since there are no liquid-lignin droplets formed in the pre-carbonation column **A**, agitation from high gas flow through the sparger orifices **9**, shown more clearly in FIG. 2, facilitate contact of the acidic gases with the incoming black liquor **1**. A larger-diameter pipe can enclose the sparger with a small diameter pipe rising vertically to the top of the pre-carbonation column **A**. This assures that any liquid-lignin droplets formed will be carried by the partially carbonated black liquor into the carbonation column **C** and not accumulate in the pre-carbonation column.

[0026] Partially carbonated black liquor from the pre-carbonation column **A** is introduced via line **5** into the top of a two part CO_2 absorption column **C**. The size of the column will depend upon the volume of black liquor to be treated. For example, in a column designed to process 50,000 tons of lignin per year, the upper portion of the column **C$_1$** may be approximately 6 feet in diameter and 40 feet tall. The carbonation column is constructed of a metal that assures that liquid-lignin wets the surface and that the metal will not be corroded by the carbonated black liquor at elevated temperature (100°C-150°C). One such preferred metal is 316 stainless steel which causes liquid-lignin droplets to "wet" and spread forming a bulk liquid-lignin film. The pre-carbonated black liquor has a pH of between 11.5 and 12.5 and a high NaOH content. The upper portion of absorption column **C**, column **C$_1$** operates at a nominal pressure of 150 psig and a temperature between about 80°C and 200°C, preferably about 100°C to 150°C. Carbon dioxide is introduced counter-currently into column **C$_1$** through line **2** and passes through the orifices of sparger **10**. The CO_2 rises and reacts with the multiple phenoxy groups within the lignin polymer, displacing sodium (Na^+) cations with hydrogen (H^+) and making lignin insoluble in the carbonated black liquor. At elevated temperature, the lignin precipitates as a lignin in the form of droplets. When these droplets collide, they coalesce and form larger globule, as shown in FIG. 3. In column **C_1**, due to the reaction of CO_2 with the phenoxy functional groups, the NaOH is neutralized, lowering the pH to less than pH 11, preferably a pH from 9 to 10. Malodorous gases containing high levels of H_2S leave the top of column **C_1** via line **6** and are vented to the vent gas absorber where the H_2S is absorbed, or to a suitable scrubbing device.

[0027] Droplets of liquid-lignin are formed and coalesce in the globules over the entire length of column C_1. The carbonated black liquor and liquid-lignin droplets and globules pass the sparger **10** into the carbonation settler **C_2** where droplets and globules coalesce further, forming a dense liquid-lignin phase. The lower portion of **C_2** of the carbonation column is larger in diameter than the upper portion. For example, the lower portion may be approximately 10 feet in diameter and 15 feet tall for a 50,000 ton per year column. Within the carbonation settler C_2, the lignin-depleted carbonated black liquor separates as a light (top) phase and is returned to the recovery operation of the host paper mill via line **7**. The dense liquid-lignin phase leaves the bottom of the carbonation settler **C_2** via line **8**.

[0028] It is preferred that the carbon dioxide velocity of about 0.6 m/s exiting the sparger **10** in carbon absorption column **C_1** is 0.6 m/s or lower so the liquid-lignin droplets and globules are not sheared excessively as they enter the carbonation settler **C_2**, as can be seen in FIG. 3. Velocities 3.0 m/s or faster exiting the orifices of sparger **10** create excessive shear and can form stable emulsions. In pre-carbonation column **A**, CO_2 (from line **2**) and/or recycled vent-gas (from line **3**) velocities have no such limit in that sparger **9** since there are no liquid-lignin droplets formed in the pre-carbonation column **A**.

[0029] Increasing the downflow velocity allows a smaller diameter carbonation column, thereby decreasing the capital expenditures for the column. However, smaller diameter columns also create more of a pinch-point for the liquid-lignin droplets passing the turbulent zone around the carbonation column sparger. Decreasing the height of the carbonation column decreases the capital expenditures. However, unlike the reaction of CO_2 in the pre-carbonation column with the pH 14 black liquor, which is extremely fast, the reaction of CO_2 in the carbonation column with incoming pre-carbonated black liquor at pH 12 is much slower. In the carbonation column **C_1**, the reaction occurs during the rise of CO_2 bubbles or at the interface at the top of the column.

The carbonation column **C_1** can be as high as economically feasible since higher columns facilitate the reaction and formation of liquid-lignin droplets.

[0030] As carbonated black liquor and liquid-lignin droplets and globules exit the bottom of column **C_2** sparger **10**, the mixture enters a quiet zone within internal sleeve **19**. Coalescing droplets and globules into a bulk liquid-lignin phase, an important aspect of this invention, can be enhanced by placing the exit of internal sleeve **19** at or slightly beneath the carbonated black liquor/liquid-lignin interface **17** as shown in FIG. 4. Even very small droplets will coalesce into the bulk liquid-phase if they impinge the interface. The downward velocity of carbonated black liquor exiting internal sleeve **19**, ideally about 20 cm/min, is so low that the liquid-lignin phase is not significantly perturbed. The lignin-depleted carbonated black liquor rises through the annulus between the internal sleeve and the internal wall of the carbonation settler **C_2** exits though line **7**, and then is neutralized and returned to the mill. As the liquid-lignin droplets and globules exit the bottom of the internal sleeve **19**, they impinge the bulk liquid-lignin phase accumulated in the bottom of the carbonation settler and coalesce naturally into bulk liquid-lignin phase which exits through line **8** to the acidification reactor **D**.

[0031] The coalescence of the liquid lignin droplets and globules is increased and the resulting yield of liquid-lignin in the dense phase is improved when structured packing **16**, such as Koch Flexipac®, is placed in the internal sleeve **19** and the upper annulus of the carbonation settler, as shown in FIG. 4. While structured packing is preferred, dumped packing is an alternative together with a heavy-duty screen at the bottom to retain the packing. The structured packing **16** serves to impede the turbulence in the carbonation column **C_1** created by the sparger and rising CO_2 bubbles from the entering the quiet settling zone within the carbonation settler **C_2**. Also the structural packing **16** provides a tortuous path so that liquid-lignin droplets are likely to impinge on the metal surfaces of the packing and coalesce into a layer of liquid-lignin that drips into the bulk liquid-lignin accumulated in the bottom of the carbonation settler **C_2**. As shown in FIG. 4, a structured packing element is placed in the upper section of the annulus of the carbonation settler and provides "one last chance" to capture liquid-lignin droplets before the droplets leave the process in the carbonated black liquor stream returned to the host mill to be burned.

[0032] As shown in FIG. 4, to properly position the carbonated black liquor/liquid-lignin interface **17**, the plant operator must be able to "see" the interface using an instrument such as a viscosity probe, which is effective for this purpose, since the viscosity of the liquid-lignin phase in the lower portion of the absorption column **C₂** is significantly greater than the viscosity of the carbonated black liquor phase above. Dynatrol® viscosity probes may be used for this purpose. For commercial scale plants a minimum of three probes are recommended: one level with the bottom exit of the carbonation column, one about 5 cm above the exit and the other about 5 cm below. This allows the operator – or an automated control scheme - to adjust the liquid-lignin flow to the acidification reactor **D** to keep the interface properly placed near the bottom of the carbonation settler **C₂**.

[0033] An attractive attribute of the improvements described herein is that the lignin process described in the '464 patent and others, can be placed "on idle" for extended periods of time, keeping the system at operating temperature so the restart is much faster than a cold start. The liquid-lignin phase should not be left stagnant in the bottom of the carbonation settler where it could solidify in localized cold spots on metal surfaces or increases in molecular weight. Thus, a pump-around loop is provided so when the system is placed on idle the loop is activated so the liquid-lignin phase is constantly moving.

[0034] The more time the liquid-lignin phase is retained at the higher temperature within the carbonation settler **C₂**, the higher the molecular weight (MW) of the resulting lignin following treatment in the acidification reactor **D**. Time at elevated temperature at pH 9-10 increases molecular weight of the resulting lignin, the longer the residence time in the carbonation settler, the higher the molecular weight of the lignin.

[0035] As shown in FIG. 4, steep angles of the cone **18** at the bottom of the carbonation settler **C₂** facilitate the viscous liquid-lignin flowing downward to exit the carbonation settler. These steep angles inhibit "dead zones" where the liquid-lignin phase can reside for extended periods of time, causing a high molecular weight "tail" in the distribution. It has been found that a 30° angle of the cone in the bottom of the carbonation settler **C₂** is sufficient to: (a) provide sufficient slope so that the liquid-lignin phase flows to the center of the outlet port; and (b) inhibit "funneling" of the carbonated black liquor into the center of the cone so that carbonated black liquor leaves the bottom of the carbonation settler in two-phase flow with the liquid-lignin as shown in FIG. 4. A 30°-45° slope for the cone **18** and having the exit of the internal sleeve level with the top of the cone **18** provides a good trade-off where liquid-lignin flows freely to the center exit port at the bottom of the cone **18** and into line **8**, making the residence time more uniform eliminating any high-molecular weight tail in the distribution.

[0036] Referring again to FIG. 1, the dense liquid-lignin solution leaving the bottom of **C_2** via line **8** contains approximately 30-40% aqueous phase is pumped **11** via line **13** to acidification reactor **D** where the lignin is contacted with an acid (line **16**), such as acetic or sulfuric acid, to neutralize the residual NaOH. During this step the pH is reduced to a pH less than 4, preferably from about 2 to about 3. The acidification step is carried out at a temperature from about 80°C up to about 120°C, preferably 95°C to 105°C. The acidified lignin from line **15** is then filtered and washed creating a low ash lignin.

[0037] There are two other options for transferring the liquid-lignin from the carbonation settler **C_2** to the acidification reactor **D** coupled with recycling the vent gas (see line **3**) from the acidification reactor **D** to the pre-carbonation column **A** are shown in FIG. 5.

[0038] In the first option, the liquid-lignin is pumped through pump **20** via line **8** from the carbonation settler **C_2** to the acidification reactor **D** and a control valve **21** is used for gas recycle. Operating the carbonation settler at a low pressure, *i.e*, a pressure lower than that of the carbonation column, and pumping the liquid-lignin from the carbonation settler to the acidification reactor operating at a higher pressure allows recycling the vent gas **3** from the acidification reactor **D** to the pre-carbonation column **A** through control valve **21**, shown as "option A" in FIG 5. The advantages of option A are: (a) recycle of the acidic vent gas from the acidification reactor is simple, letting down the pressure through a control valve; and (b) the pump-around loop is possible, which simplifies the start-up and idling of the carbonation column and carbonation settler.

[0039] When using "option B" the carbonation column **C** is operated at high pressure, pushing liquid-lignin into the acidification reactor **D** under pressure using a control valve **22** to maintain the target flow rate of liquid-lignin. This is coupled with a gas jet compressor **23**. The distinctive feature of option B uses a gas-jet compressor powered by CO_2 as the motive gas to push the acidic vent gas from the acidification reactor **D** via line **3** into the pre-carbonation column **A** as shown in FIG. 5. The motive CO_2 replaces or supplements the CO_2 used to reduce the black liquor pH from 14 to 12 in the pre-carbonation column **A**. In the absence of air, the acidic vent gas and motive CO_2 react continuously, quantitatively, and rapidly with the incoming black liquor. The advantages of option B include: (a) the acidification reactor **D** can be operated at a low pressure, near atmospheric, reducing the capital expenditure for the reactor; (b) eliminating the pump for liquid-lignin, using a control valve to regulate the flow from the carbonation settler into the acidification reactor; and (c) the carbonation column can be operated at a higher pressure that accelerates the reaction of CO_2. If the CO_2 is too high causing the pH at the top of the pre-carbonation column **A** to be so low the liquid-lignin droplets are formed, steam can be used as the motive gas.

[0040] Without the possibility of using a pump-around loop for the liquid-lignin, the procedures for start-up and placing the carbonation settler on idle for extended (several hours or even days) are more difficult. Also, the control valves **21**, **22** should to be either a ball valve or a v-port valve, so that if the valve starts to plug, the valve can open fully to free itself.

[0041] Inside the acidification reactor **D** shown in FIG. 6, incoming dense liquid-lignin droplets from the carbonation settler $\mathbf{C_2}$ introduced to the reactor **D** through line **13** react rapidly with the acidic aqueous phase introduced through line **16** to form irregularly shaped lignin particles **13a**, removed through line **15**. Droplets of liquid-lignin virtually explode from the evolution of CO_2, creating solid, porous, irregularly shaped lignin particles. This controlled explosion of the liquid-lignin droplets enhances the mass transfer and removal of sodium sulfate (Na_2SO_4) and other inorganic salts that contributed to the ash content of the final lignin product. The controlled explosion of the liquid-lignin droplets can be explained by the composition of the bulk liquid-lignin phase. Liquid-lignin at pH 9-10 has three major components: lignin (≈50%), inorganic ash (≈20%), and water (≈30%). The water contains dissolved sodium bicarbonate which reacts extremely rapidly with the aqueous sulfuric acid within the acidification reactor as shown in Equation (1):

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2CO_2\ (gas) + 2H_2O \qquad \text{(Equation 1)}$$

The amount of CO_2 emitted by the liquid-lignin droplets is significant. Sodium bicarbonate ($NaHCO_3$) is very soluble in water, about 31 grams per 100 grams of water at 100°C. From stoichiometric calculations, the amount of CO_2 evolved from the liquid-lignin is about 0.10 grams CO_2 per gram lignin, roughly one-half the total CO_2 required by the lignin producing process of the '474 patent (0.20-0.25 grams of CO_2 per gram of lignin).

[0042] Referring to Equation 1 and FIG. 6, as liquid-lignin the droplets enter the acidification reactor **D** through line **13** underneath the liquid surface near the agitator **25**, the $NaHCO_3$ is converted to CO_2 gas that is formed rapidly escapes through acid vent gas line **3**, virtually blowing the small liquid-lignin droplet apart. Also occurring simultaneously, the sodium cations associated with the lignin phenolic and carboxylic groups in the liquid-lignin at pH 9-10 are replaced by hydrogen cations at pH 2-3. The sodium becomes sodium sulfate (Na_2SO_4). Because of the porous nature of the solid particles, Na_2SO_4 is flushed from the lignin during filtration using a wash cycle.

[0043] It is desirable to remove sulfur-containing compounds for the system. Since there is no air in the pre-carbonation column **A**, the carbonation column **C**, or the acidification reactor **D**, the vapor spaces are devoid of air and contain only H_2S, CO_2, and water vapor with trace amounts of other sulfur gases, such as methyl mercaptan (MeSH), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). The reaction of these concentrated acid gases with NaOH solutions is extremely rapid since mass transfer is not impeded by air.

[0044] To remove the sulfur-containing gases from the system, vent gas absorber **F** is provided as best shown in FIG. 7 and includes an absorption section wash **30** and stripping section **31** containing packing. The vent gas absorber **F** is located to conveniently receive vent gas from the carbonation column $\mathbf{C_1}$ through line **6** which is near the bottom of absorption section **30** of vent gas absorber **F**. The other vessels that emit sulfur gases, notably from the neutralization tank for the carbonated black liquor and from the lignin slurry tank receiving slurry prior to filtration (not shown) have their individual vent lines bubbling their air-free off gases into the vent gas absorber **F** through line **26**. The vapor space of the of the stripping section **30** of vent gas absorber **F** is purged with low **27** air flows drawn through the vapor spaces of the wash brine tank and acid brine neutralization tank (not shown). This small air stream carries the DMS and DMDS which are not absorbed into the packed column **31** which is irrigated with fresh 10% NaOH solution through line **28**. Purged air is removed from the top of the packed column **31** and returned to the pulp mill for processing in the non-condensable gas system. The inorganic salt solution which contains NaOH, NaSH and Na_2CO_3 is removed from the bottom of the gas absorber **30** through line **33**.

[0045] The spent scrubbing fluid contains significant quantity of NaSH formed by Reaction 2:

$$H_2S\text{ (gas)} + NaOH \rightarrow NaSH + H_2O \qquad \text{(Reaction 2)}$$

However, there will also be carbonate salts formed from the excess CO_2 in the vent from the carbonation column **C**. Because of the presence of these carbonate salts, the "spent" sodium hydroxide may be combined with the carbonated black liquor and returned to the host mill.

[0046] 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 present 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 invention. 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 recovering purified, solid lignin from black liquor comprising:

(a) in a first carbonating step, pre-carbonating black liquor with CO_2 to reduce the pH to about 11.5 to about 12.5 to form a partially carbonated black liquor;

(b) in a carbonation column, further carbonating said partially carbonated black liquor in a second carbonation step with CO_2 sufficient to reduce the pH to between about 9.0 and about 10.5;

(c) subjecting said carbonated black liquor from said further carbonating step to a phase separation in a carbonation settler wherein a dense liquid-lignin phase is formed, a lignin-depleted liquid phase is formed, and Na OH and other basic components are neutralized;

(d) removing said dense liquid-lignin phase and neutralizing NaOH and other basic components from said phase separation with sufficient acid to reduce the pH below 4 to neutralize residual NaOH and other basic components, thereby generating a granular lignin; and

(e) washing said granular lignin to remove residual acid and ash content.

2. The process according to Claim 1 wherein said black liquor is at a 10% to 70% solids content when entering the pre-carbonating step.

3. The process according to Claim 1 wherein said second step is carried out at a temperature between about 80°C. and 200°C. and a pressure between about 50 psig and about 200 psig in a carbonation column.

4. The process according to Claim 1 wherein the second of said carbonating steps is carried out by contacting said pre-carbonated black liquor with CO_2 counter-currently.

5. The process according to Claim 1 wherein said dense liquid-lignin acid is treated with sulfuric acid.

6. The process according to Claim 1 wherein the aqueous phase of the dense liquid-lignin exiting from the carbonating column is about 30% to about 40%.

7. The process according to Claim 1 wherein said pre-carbonation column includes a sparger to facilitate contact of the CO_2 with the incoming black liquor.

8. The process according to Claim 1 wherein said carbonation column includes a sparger to facilitate contact of the acidic gases with the incoming partially carbonated black liquor.

9 The process according to Claim 1 wherein the vent gas from the acidification step is recycled to said pre-carbonation column.

10. The process according to Claim 1 wherein structural packing in positioned in said carbonation column such that carbonated black liquor may pass there through and serves to impede turbulence in said carbonation column.

11. The process according to Claim 1 wherein said carbonation settler is operated at a pressure lower than the pressure of the carbonation column used in the further carbonating step.

12. The process according to Claim 1 wherein said carbonation column has carbonation settler cone having slope angle of 30°-45°.

13. The process according to Claim 1 wherein the pH of said dense liquid-lignin is reduced to a pH of from about 1.5 to about 3.5.

14. The process according to Claim 1 wherein said carbonation settler is operated at a low pressure and said dense liquid-lignin phase is transferred to said acidification step which is operated at a high pressure allowing recycling of the vent gases to the pre-carbonation step.

15. The process according to Claim 1 wherein said further carbonation step is operated at a high pressure and said dense liquid-lignin phase is transferred to said acidification step and using CO_2 to recycle the vent gas to the pre-carbonation column

16. The process according to Claim 1 wherein the sulfur-containing vent gas from the system are treated with a wash brine portion and an acid brine portion while purged air is removed and NaOH, NaSH and Na_2CO_2 are separately removed.

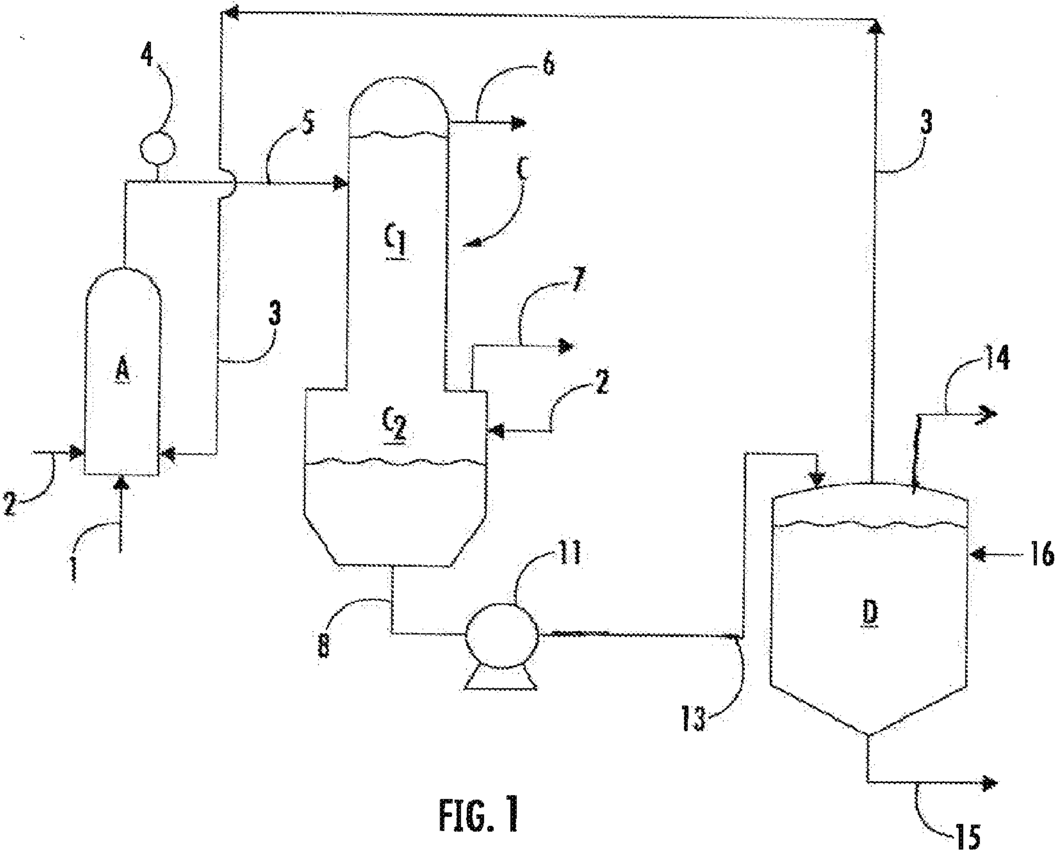


FIG. 1

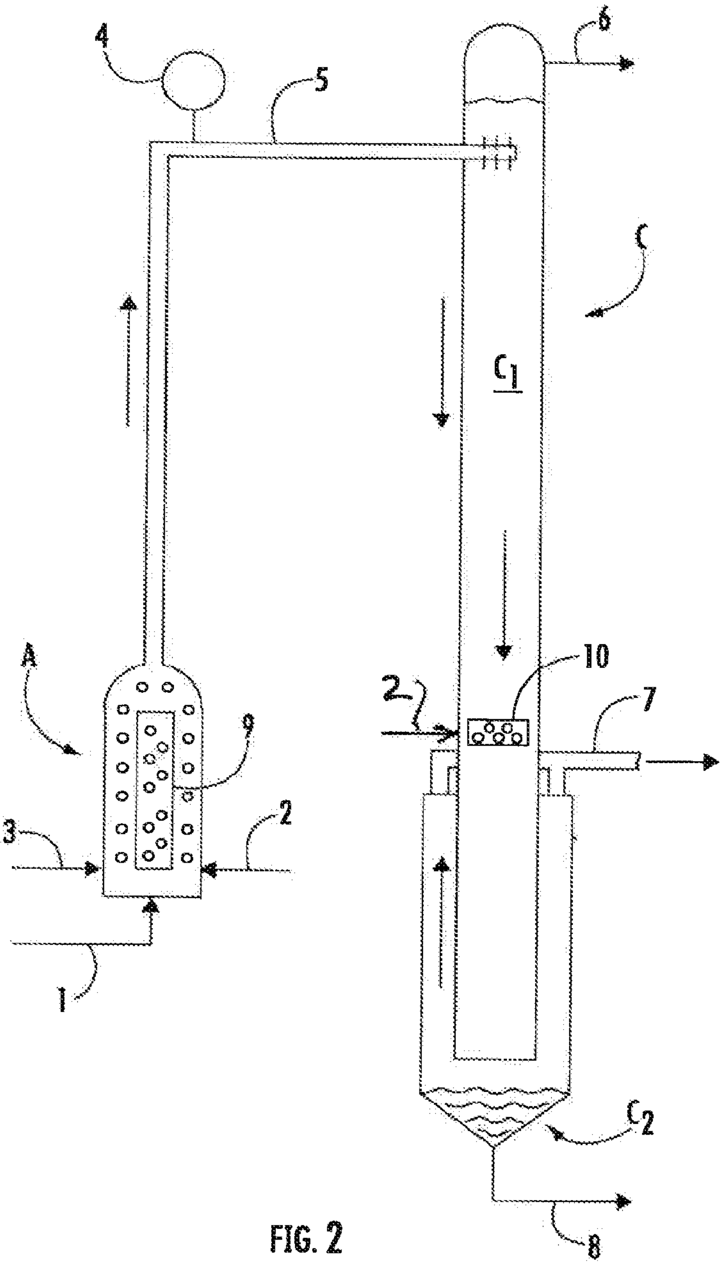


FIG. 2

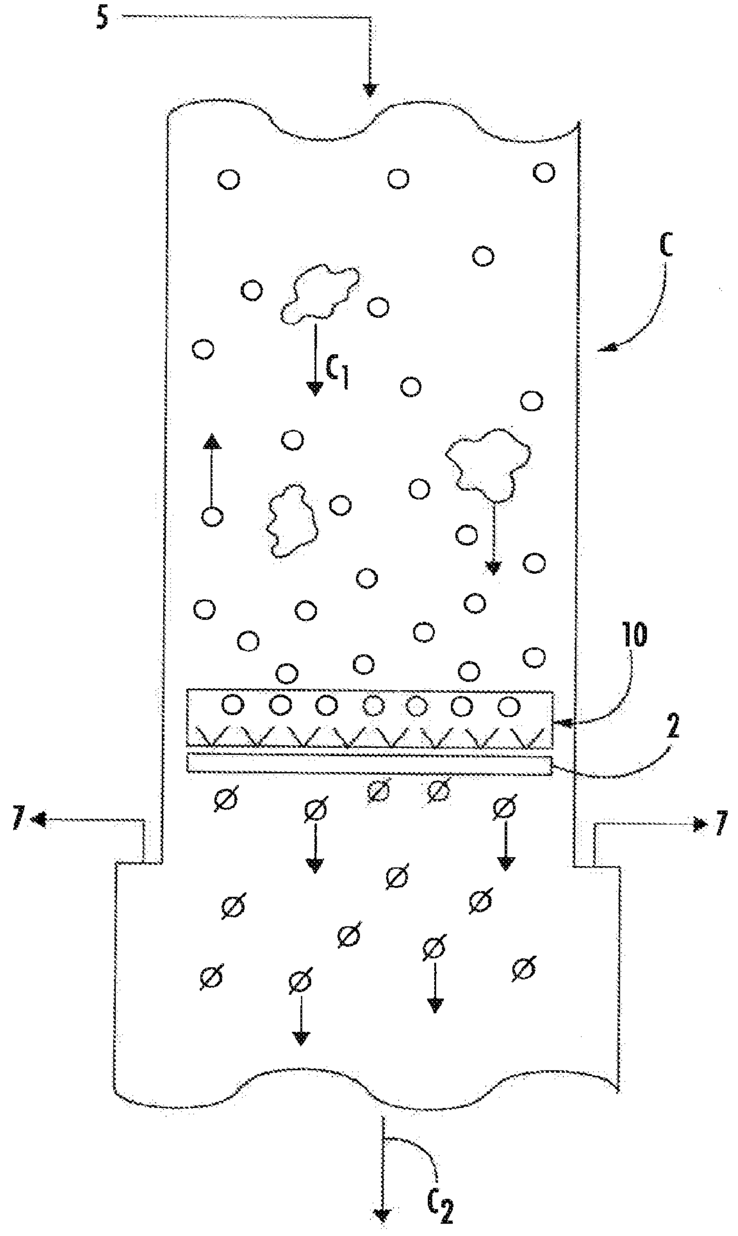


FIG. 3

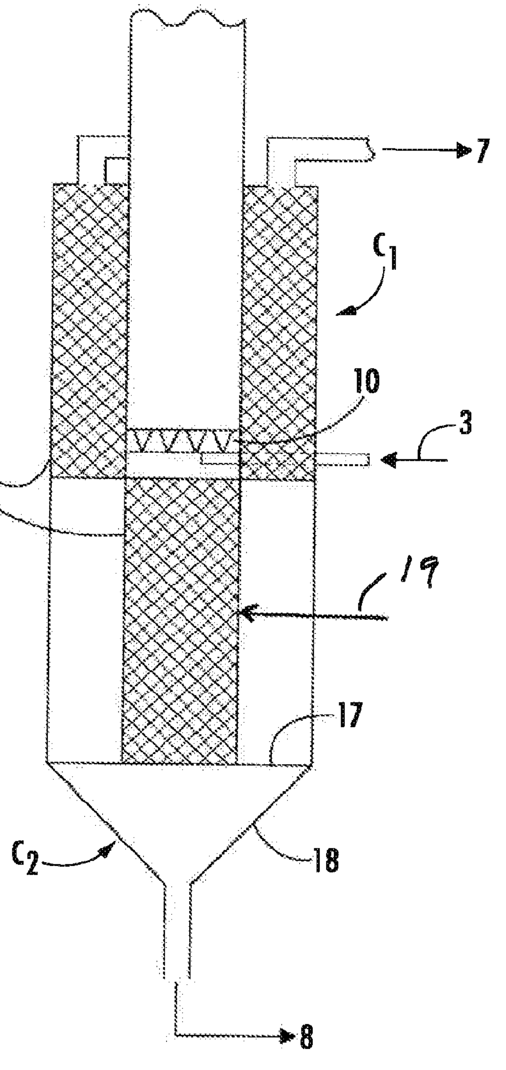
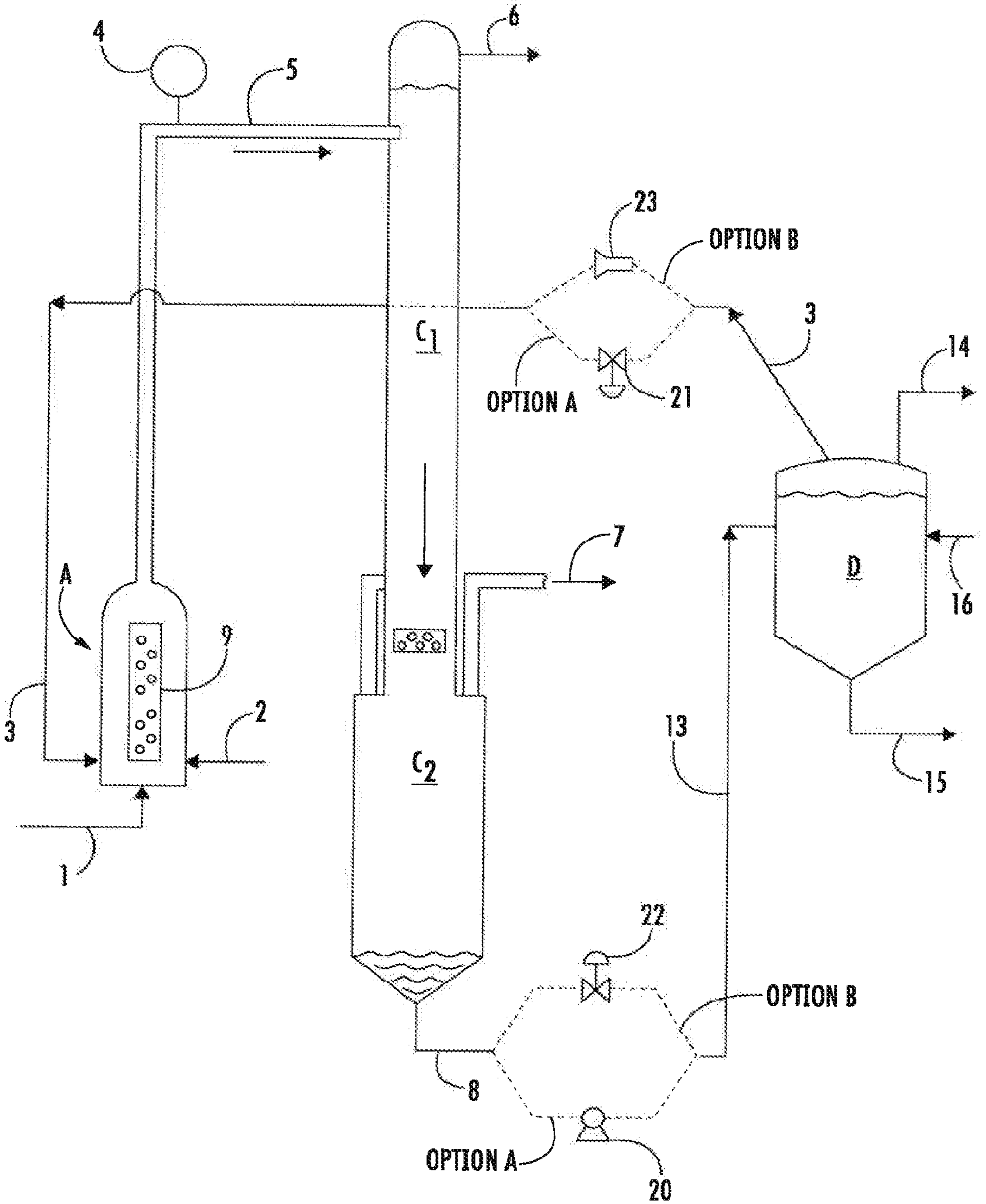


FIG. 4


4
5
6
23
OPTION B
3
C1
OPTION A
21
14
7
A
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D
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3
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C2
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15
1
22
OPTION B
8
OPTION A
20

FIG. 5

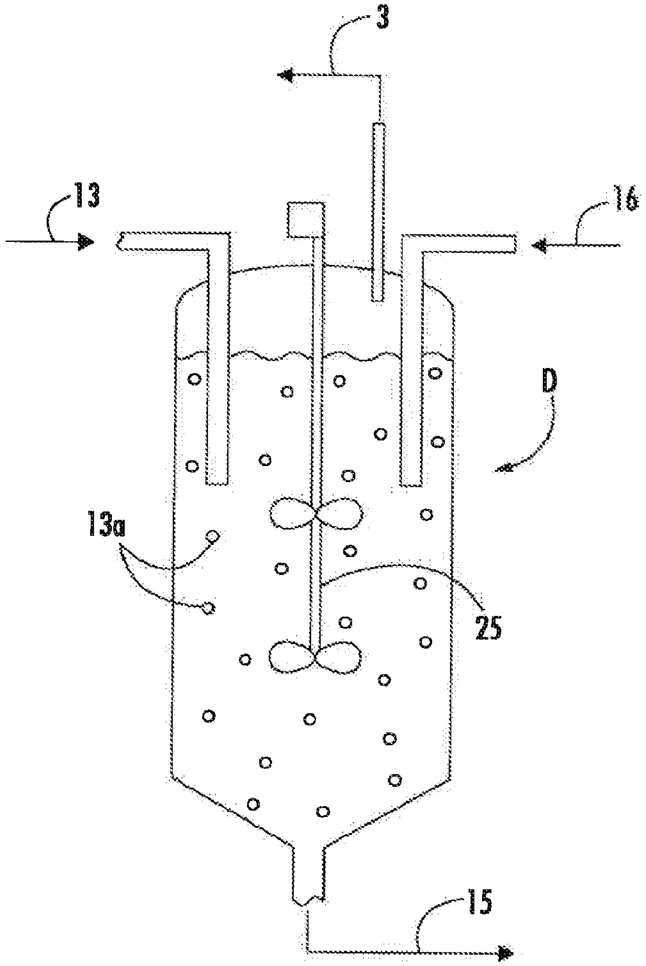

FIG. 6

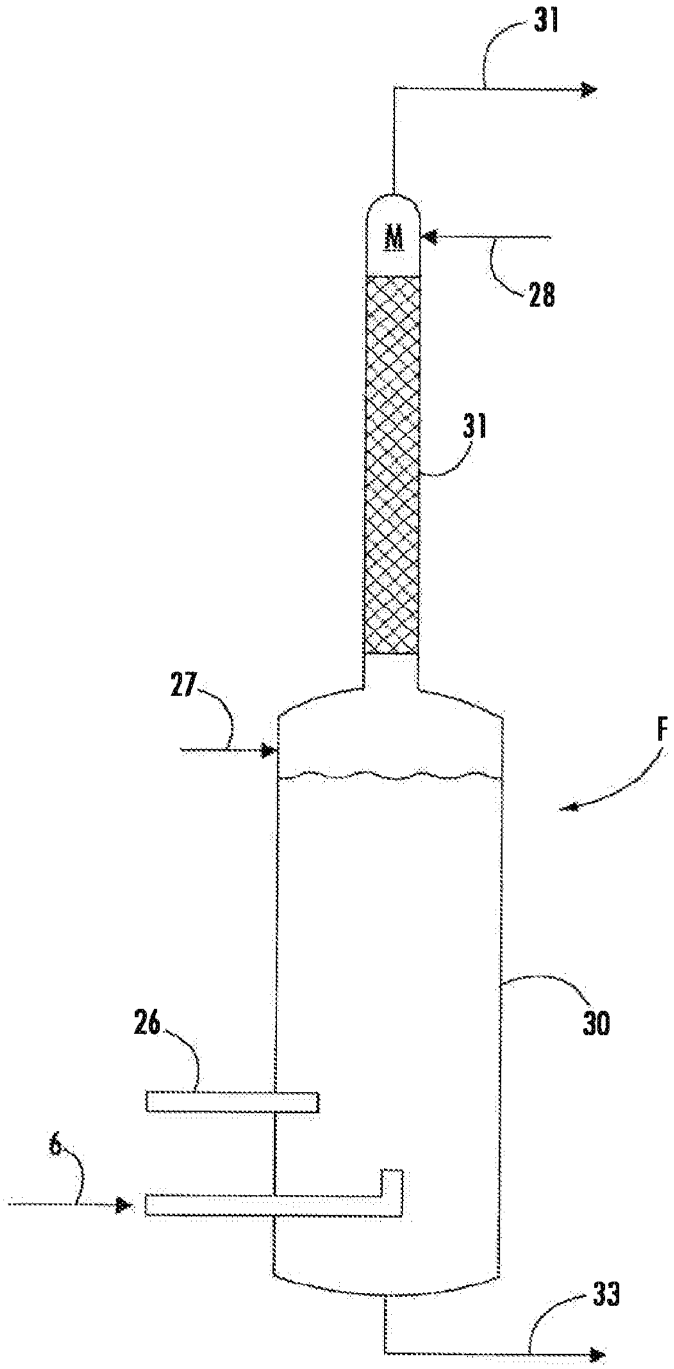

FIG. 7