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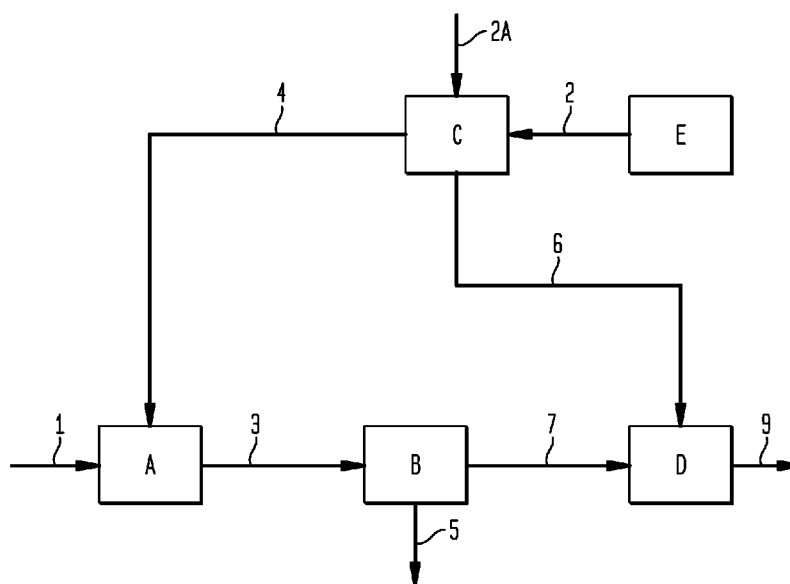
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(54) Title: METHODS FOR OXYGEN DELIGNIFICATION AND OZONE BLEACHING OF PULP



(57) Abstract: A method for treating pulp through oxygen delignification and ozone bleaching is disclosed. The method uses a modified oxygen recovery unit which separates a mixture of oxygen and ozone thereby generating a stream of ozone and a stream of oxygen; feeding the stream of oxygen to an oxygen delignification unit; feeding a pulp to the oxygen delignification unit; feeding the stream of ozone to an ozone bleaching unit; feeding the delignified pulp to the ozone bleaching unit; and recovering the delignified and bleached pulp.



METHODS FOR OXYGEN DELIGNIFICATION AND OZONE BLEACHING OF PULP

CROSS REFERENCE TO RELATED APPLICATIONS

- [0001] The present application claims priority from US Provisional Application Serial No. 62/268,641 filed on December 17, 2015.

BACKGROUND OF THE INVENTION

- [0002] The present invention relates to methods for delignification of pulp using oxygen combined with ozone bleaching of the pulp.
- [0003] Oxygen delignification is the step between digesting wood chips in pulp making and pulp bleaching operations. Oxygen delignification is designed to dislodge and disintegrate residual lignin left in the pulp after the digestion step using oxygen and alkali. It is the direct extension to delignification that occurs during digestion. Contacting pulp in an aqueous alkaline medium with oxygen causes oxidation of lignin which not only breaks molecules but also makes it water soluble. Oxidation of color imparting groups reduces the Kappa Number. As a result, the consumption of bleach chemicals in the bleach plant is reduced. Delignification with oxygen is a more gentle way of reducing the Kappa Number than by extended digesting and bleaching. In recent decades, new pulp mills have been increasingly adopting oxygen delignification systems as an advantageous step in reducing environmental impact and achieve a better return on economic investment.
- [0004] The most commonly practiced oxygen delignification consists of the following steps. The first step involves adding washed pulp into a mixer, adding caustic, adding oxygen and steam to bring the temperature to a range of 70° to 95°C and introducing this pulp mixture into the bottom of a

vertical tall reactor in a continuous fashion. The pulp will flow upwards while lignin in the reactor gets oxidized in the alkaline medium thereby dissolving and disintegrating the lignin and dislodging it from the pulp fibers. The reactor is maintained at 5 to 12 barg pressure to improve on oxygen uptake. The residence time for pulp flowing through a commercially practiced reactor is in the range of between 20 and 100 minutes.

- [0005] Oxygen delignification can be performed with both medium as well as high consistency pulp. Due to limited effectiveness, difficulty in mixing of oxygen and other operating problems with high consistency pulp, oxygen delignification has not achieved widespread success when compared with medium consistency pulp.
- [0006] Oxygen delignification works with pulps from both types of woods, hardwood and softwood, reducing the Kappa Number up to 35% and 50% respectively. In the case of hardwood, a two stage approach is needed where two reactors are placed in series. The first stage is maintained at a higher pressure and lower temperature with less residence time while the second stage is usually maintained at lower pressure but at higher temperatures and greater residence times.
- [0007] There has been limited success using a single stage high efficiency reactor towards achieving short term delignification at smaller and experimental scales. Consequently, there has not been any commercial apparatus embodying this concept.
- [0008] Bleaching with ozone offers a more aggressive reaction with residual lignin and would be offered as a substitute technology versus bleaching using bleaching chemicals like Chlorine, Chlorine Dioxide, Peroxide and others. Ozone offers a very effective bleaching process which has virtually no residual impact on the environment. Chlorine and Chlorine

Dioxide produce adsorbable organic halides (or AOX) in wastewater; compounds that do not easily break down in nature and pose a risk to aquatic life.

- [0009] The use of ozone for pulp bleaching is limited in the industry due to its relatively higher cost. Ozone is produced by reacting nearly-pure oxygen (or air) in a corona or plasma discharge which provides the energy needed to combine diatomic oxygen (O_2) into the triatomic form (O_3) commonly referred to as ozone. In fact, ozone is never produced in its pure form and is always a minor component in a mixture which includes ozone at concentrations of 3 to 15% with the balance comprising either oxygen or air; depending on the method used to produce the ozone (oxygen or air feed).
- [0010] For oxygen-fed ozone generators, the ozone gas mixture is a combination of ozone, oxygen and a small amount of nitrogen. For ozone bleaching, ozone is the effective compound. Oxygen is not an effective bleaching agent; however it has value in other processes in the pulp mill; for example, oxygen delignification.
- [0011] There exists technology that employs adsorbents to separate ozone from oxygen by adsorbing ozone and allowing the oxygen to pass through the adsorbent bed to be re-used as a feed-gas to the ozone generator. Such technology offers significant cost savings to the operator as they can recover a substantial (up to 75%) portion of oxygen which is a major factor in the cost of ozone production. Such systems might be referred to as oxygen recovery units

SUMMARY OF THE INVENTION

- [0012] Pulp mills represent an industry where the need for ozone and oxygen often co-exist in a local area within the production facility. This invention

provides a means of separating an ozone/oxygen gas stream to an ozone stream and an oxygen stream. Ozone will be adsorbed in an adsorbing bed while oxygen passes through the bed. The oxygen can be used for delignification of pulp in the fiber line following the digester. The oxygen gas stream pressure can be increased using a commercially-available oxygen compressor to raise the pressure to 5 to 12 Barg, depending on the requirements of the oxygen delignification reactor(s).

[0013] The ozone stream can be utilized for pulp bleaching following its desorption of the adsorption bed. Desorption is carried out first by depressurizing the bed, then sweeping the ozone to the end using a carrier gas, typically air.

[0014] In a first embodiment of the invention there is disclosed a method for delignifying and bleaching pulp comprising the steps:

- a) Feeding a mixture of oxygen and ozone to an oxygen recovery unit thereby generating a stream of ozone and a stream of oxygen;
- b) Compressing and feeding the stream of oxygen to an oxygen delignification unit;
- c) Feeding a pulp mixture which comprises a pulp slurry and a liquor to the oxygen delignification unit;
- d) Feeding steam to the pulp mixture thereby raising its temperature;
- e) Mixing the pulp mixture of pulp, liquor, steam and oxygen thereby enabling the oxygen to react with lignin and become mixed with the liquor;
- f) Feeding the mixture to at least one washing step thereby removing dissolved lignin from the pulp mixture;

- g) Feeding the stream of ozone to an ozone bleaching unit;
- h) Feeding the delignified, washed pulp mixture to the ozone bleaching unit;
and
- i) Recovering the delignified and bleached pulp.

[0015] The pressure in step b) can range from 5 to 12 Barg.

[0016] During step c), the temperature of the pulp mixture will increase from about 90° up to 120°C.

[0017] The mixing in step d) can be as long as up to 100 minutes in length.

[0018] The at least one washing step in step f) can be two or more washing steps.

[0019] The pulp can be selected from the group consisting of medium and high consistency pulp. The liquor is selected from the group consisting of white liquor, partially oxidized white liquor and completely oxidized white liquor. Typically this pulp is about 10% consistency.

[0020] The concentration of oxygen in the stream of oxygen is greater than 80%.

[0021] The oxygen delignification unit is typically a reactor.

[0022] Typically, the amount of oxygen present in the pulp between 0.011 to 0.026 tons of oxygen per one ton of pulp.

[0023] The mixture of oxygen and ozone is typically produced by an ozone generation unit. The resulting mixture of oxygen and ozone from the ozone generation unit is about 10% ozone and 90% oxygen.

- [0024] The oxygen recovery unit of step a) is typically a pressure swing adsorption system.
- [0025] The ozone bleaching unit of step g) is typically a reactor.
- [0026] Acid may be added to the pulp before the pulp enters the ozone bleaching unit in step h).
- [0027] The ozone is produced using commercially-available ozone generation equipment; specifically those that use oxygen with purity greater than 90% as a feed gas. For typical ozone generation, oxygen is passed through the water-cooled tubes of the heat exchanger. The resulting dilute ozone containing gas stream can be fed directly to the oxygen recovery unit.
- [0028] The ozone generation unit produces a mixture of ozone and oxygen based upon an oxygen feed. This ozone and oxygen mixture is separated using an oxygen recovery unit-style pressure swing adsorption (PSA) system. A high purity adsorbent material that does not significantly decompose adsorbed ozone such as selected silica gel or high silica zeolite adsorbents will concentrate the ozone allowing most of the unreacted oxygen to be recycled back to the ozone generation unit or used in other applications.
- [0029] The separated oxygen stream will be fed to an oxygen delignification unit. The oxygen delignification unit is typically a reactor for mass transfer.
- [0030] The delignified pulp is then passed through a washing step which will remove dissolved solids from the pulp as well as soluble lignins present in the delignified pulp. The dissolved solids can interfere with a bleaching step.

- [0031] After the washing step, the delignified pulp is fed to an ozone bleaching unit. The ozone bleaching unit uses a reactor to contact the pulp with ozone. The ozone source here will be a mixture of ozone and air derived from the oxygen recovery unit and contacted with the pulp until a satisfactory level of whiteness is achieved.
- [0032] The bleached pulp is then recovered and fed to the next steps of the papermaking process or bundled for storage or transport.
- [0033] The use of the reactors will cause a significant reduction in Kappa number over the oxygen delignification reactor when combining with ozone bleaching in the reactor. The reactors will provide mixing to oxidize the pulp further to achieve the low Kappa numbers. The pulp mill can remove or reduce the amount of chlorine based bleaching it performs.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0034] The figure is a schematic of an oxygen delignification and ozone bleaching process according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

- [0035] Turning to the figure, a schematic of an oxygen delignification and ozone bleaching process in communication with an oxygen recovery unit is described.
- [0036] The pulp which is typically a medium or high consistency pulp is fed through line 1 to an oxygen delignification unit A. The pulp will optimally be about 10% pulp slurry. This pulp feed will typically be at a temperature of about 90° to 120°C and a pressure of 5 to 12 barg. The pulp solution is typically a caustic solution aided by the presence of magnesium sulfate.

A blow tank will usually be present to assist in pressure reduction and separation of the pulp slurry and dissolved gases.

- [0037] The oxygen delignification unit A will receive oxygen through line 4 from the modified oxygen recovery unit C which will separate a mixture of ozone and oxygen. Typically the oxygen is gaseous oxygen and is present between 0.011 to 0.026 tons of oxygen per one ton of pulp. The modified oxygen recovery unit C will typically have an external line 2A which will typically utilize clean dry air to assist in desorbing the beds present in the oxygen recovery unit C.
- [0038] The modified oxygen recovery unit C will receive through line 2 a mixture of ozone and oxygen from an ozone generator E. The mixture of ozone and oxygen is typically about 10% ozone and 90% oxygen.
- [0039] The reactor will thoroughly mix the oxygen and the pulp and the resulting delignified pulp will be fed through line 3 to a series of washers step B where dissolved solids and soluble lignin is removed through line 5. The pulp in line 3 will have the same consistency as when fed through line 1 but be nearer to atmospheric pressure. The Kappa reduction is also greater than 35%. The dissolved solids and soluble lignins removed through line 5 form a weak black liquor. The delignified pulp will then be fed through line 7 to an ozone bleaching unit D. The consistency of the pulp slurry will remain the same at about 10% and the pressure remains at near atmospheric after unit B. Acid is typically added to this stream prior to it reaching the ozone bleaching unit D and this stream is raised in pressure through a pump to a range of 5 to 12 barg.
- [0040] The ozone bleaching unit D will also be a reactor which will thoroughly mix the ozone and delignified pulp. The ozone will be derived from the modified oxygen recovery unit C and will be fed through line 6 to the ozone bleaching unit. The mixture is approximately 10 wt % ozone with

the remaining 90% being clean dry air. The reactor will ensure that the ozone and the delignified pulp are thoroughly mixed to provide the desired level of bleaching. The final bleached pulp may then be recovered through line 9 and sent for further processing in the pulp mill.

- [0041] While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims in this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the invention.

Having thus described the invention, what we claim is:

1. A method for delignifying and bleaching pulp comprising the steps:
 - a) Feeding a mixture of oxygen and ozone to an oxygen recovery unit thereby generating a stream of ozone and air and a stream of oxygen;
 - b) Compressing and feeding the stream of oxygen to an oxygen delignification unit;
 - c) Feeding a pulp mixture which comprises a pulp slurry and a liquor to the oxygen delignification unit;
 - d) Feeding steam to the pulp mixture thereby raising its temperature;
 - e) Mixing the pulp mixture of pulp, liquor, steam and oxygen thereby enabling the oxygen to react with lignin and become water soluble and mixed with the liquor;
 - f) Feeding the pulp mixture to at least one washing step thereby removing dissolved lignin from the pulp mixture;
 - g) Feeding the stream of air and ozone to an ozone bleaching unit;
 - h) Feeding the delignified, washed pulp mixture of step f) to the ozone bleaching unit; and
 - i) Recovering the delignified and bleached pulp.
2. The method as claimed in claim 1 wherein the pressure in step b) ranges from 5 to 12 Barg.

3. The method as claimed in claim 1 wherein during step c), the temperature of the pulp mixture increases from about 90° to 120°C.
4. The method as claimed in claim 1 wherein the mixing is up to 100 minutes in length.
5. The method as claimed in claim 1 wherein the at least one washing step is two or more washing steps.
6. The method as claimed in claim 1 wherein the pulp is selected from the group consisting of medium and high consistency pulp.
7. The method as claimed in claim 1 wherein the liquor is selected from the group consisting of white liquor, partially oxidized white liquor and completely oxidized white liquor.
8. The method as claimed in claim 1 wherein the concentration of oxygen in the stream of oxygen is greater than 80%.
9. The method as claimed in claim 1 wherein the oxygen delignification unit is a reactor.
10. The method as claimed in claim 9 wherein the oxygen is present in the pulp between 0.011 to 0.026 tons of oxygen per one ton of pulp.
11. The method as claimed in claim 1 wherein the mixture of oxygen and ozone is produced by an ozone generation unit.
12. The method as claimed in claim 10 wherein the mixture of oxygen and ozone is about 10% ozone and 90% oxygen.
13. The method as claimed in claim 1 wherein the oxygen recovery unit is a

pressure swing adsorption system.

14. The method as claimed in claim 13 wherein the pressure swing adsorption system contains an adsorbent.

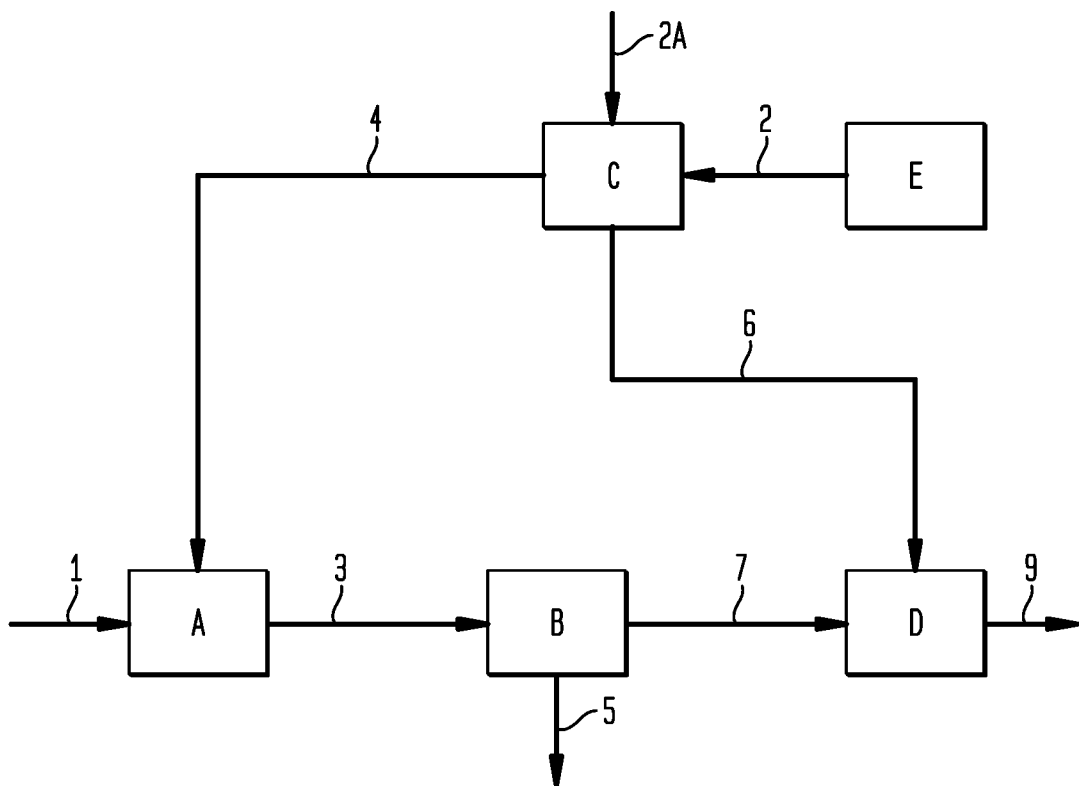
15. The method as claimed in claim 14 wherein the adsorbent is selected from the group consisting of silica gel and high silica zeolite.

16. The method as claimed in claim 1 wherein the ozone bleaching unit is a reactor.

17. The method as claimed in claim 6 wherein the pulp is about 10% consistency.

18. The method as claimed in claim 1 further comprising adding acid to the pulp before the pulp enters the ozone bleaching unit.

The Figure



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/57645

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D21C 7/06, 9/02, 9/10, 9/153 (2016.01)

CPC - D21C 7/06, 9/02, 9/10, 9/153

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)

PC(8) Classifications: D21C 7/06, 9/02, 9/10, 9/153 (2016.01)

CPC Classifications: D21C 7/06, 9/02, 9/10, 9/153

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)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; PubMed; EBSCO Discovery; pulp delignification, bleach, wash ozone, oxygen, air, compress, recycle, separate, pressure swing adsorption, zeolite, silica gel, oxygen generator

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 83/00816 A1 (WEYERHAEUSER COMPANY) 17 March 1983; page 3, lines 10-16, 31-37; page 7, lines 34-36; page 8, lines 1-17; page 11, lines 35-37; page 25, lines 5-14, 22-32; page 28, lines 20-21, 31-34; page 31, lines 39-44; page 32, lines 20-24; page 36, lines 9-11; page 37, lines 13-25; page 45, lines 43-48; claims 102, 115, 198; figures 1-2	1-18
Y	US 2004/0028576 A1 (JAIN, R) 12 February 2004; paragraphs [0013]-[0019], [0029], [0036]	1-18

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

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