Methods are disclosed for bleaching medium consistency cellulose pulp including generating a stream of ozone-containing gas having an ozone concentration of at least 10% by weight and radially injecting the stream of ozone-containing gas into a stream of cellulose pulp flowing through a reactor so as to provide a stream of bleached cellulose pulp. A low to medium intensity mixer operating at no more than 800 rpm may be used, downstream from the injection site.
Conversion of ozone

FIG. 1
Bleaching of Medium Consistency Pulp with Ozone without High Shear Mixing

Cross-reference to related applications

[0001] The present application is a continuation-in-part of U.S. patent application Ser. No. 09/763,221, filed May 15, 2001, the disclosure of which is incorporated herein by reference.

Field of the invention

[0002] The present invention relates to a method of bleaching medium consistency pulp with an ozone-containing gas. More particularly, the present invention relates to the proper utilization of the very fast reaction of ozone, by providing efficient but pulp-preserving mixing immediately on introducing a substantial amount of ozone into the pulp.

Background of the invention

[0003] A number of methods for the bleaching of pulp with ozone are known in the art. These methods have developed with the goal of carrying out the bleaching stage with medium consistency pulp, i.e., having a consistency of about 7 to 16 percent.

[0004] Generally, ozone bleaching of medium consistency (MC) pulp according to current practice can be described as ozone generation followed by compression before introducing the ozone containing gas into the MC pulp flow. The gas-liquid-fiber suspension is thus vigorously treated in one or several high shear mixers before the suspension is led into a bleaching tower. The ozone may be introduced at several points along the pulp stream. Vent gases must be treated because of excess ozone which is carried over.

[0005] The principle thus described may well be a result of the application of oxygen bleaching methods. Oxygen, however, operates at much slower rate, and the temperatures which are used are significantly higher than those employed in ozone bleaching.

[0006] Typical and frequent problems arise from the difficulty in keeping the suspension uniform. Segregation into two-phase flow readily occurs, and the ozonization rate drops significantly (to less than 1% of its optimum rate). This is a dominant problem, which may be reduced by using a mixture of ozone. This results in less gas void and consequently less need for vigorous mixing. A typical solution in the present state of the art is the use of more than one mixer. This does not, however, eliminate the problem, and by applying more shear forces to the pulp, the strength properties of the resulting product are severely affected.

[0007] A basic problem with such mixers is the short residence time, and if mixing time is increased, undesired backmixing may occur.

[0008] After leaving the mixers, the gas-pulp suspension rapidly segregates into two-phase flow having a relatively small gas-liquid interface per unit volume. The chemical consequences of this are low capacity and a non-uniform bleaching result. Obvious evidence of this phenomenon is the significant ozone surplus often remaining after the bleaching stage, representing both a hazard and an economical loss.

[0009] A pulp bleaching method comprising introduction of high pressure ozone in a carrier gas into a pulp stream with vigorous mixing and subsequent removal of carrier gas is disclosed in, e.g., European Patent No. 511 433. The major issue in this patent is the removal of gas from the pulp after injection into the mixer and the reaction is said to take place essentially within ten seconds in a vertical reaction vessel situated immediately following the fluidizing mixer. Gas at about 10 to 13 bar, containing about 3 to 10% ozone by weight (6.8% vol %) is used. Preferably, the gas-pulp mixture is carried in a horizontal path following the vertical reaction step to effect separation of the large amount of carrier gas involved.

[0010] Austrian patent application no. 2203/92 describes a method wherein medium consistency pulp is treated with an ozone-containing gas comprising more than 120 g O₃/normol m³ gas (5.6 vol %) whereby the gas is introduced as fine bubbles with a low differential pressure (preferably less than 1 bar). It is considered that using gas with a high ozone content, a sufficient amount of ozone can be suspended into the gas to achieve the desired bleaching. Further, Austrian patent application no. 2203/92 discloses the use of mixers with or without fluidization effects, and of an ozone reaction stage subsequent to the mixing stage, as well as additional ozone addition stages, with degassing stages in between. Characteristically, the highly concentrated ozone is introduced in static mixers at several points, possibly removing the inert carrier gas (normally oxygen) between stages, and the final reaction between ozone and fiber takes place in a bleaching reactor, typically of the traditional upflow type.

[0011] A common feature of several other publications disclosing ozone bleach processes for medium consistency pulp is the use of fluidizing mixers in connection with the injection of ozone-carrying gas, and the use of subsequent, relatively extended reaction stages and gas separation.

[0012] In chemical process terms, MC ozonization can be described as ozone molecules in a gas phase that must be transported to the vicinity of the fiber and react with the fiber or other substrates. The ozone must diffuse through the gas-liquid interface, through the liquid to the fiber. The applied mixing affects the size and the relative velocity of the gas bubbles, as well as the amount of fiber-liquid interface. The rate limiting step completely dominating the interaction of ozone with the fiber material is the transport of ozone through the gas-liquid interface. The liquid-gas transfer rate in a given volume is heavily dependant on the bubble size, i.e., gas-liquid surface area m² gas/m³ suspension, and on the partial pressure of ozone. Other rate limiting steps, like diffusion in the fiber material itself, are determined by the nature and the consistency of the pulp, which is primarily affected by the temperature.

[0013] Due to its dependency on mass transfer, the reaction rate of ozone is, theoretically and empirically, first order.

[0014] The high gas void, i.e. the low concentration of ozone generated by most present ozone generators, limits the possibilities to improve the situation. Reduced gas void in subsequent generations of ozone generators will reduce the need for mixing and reduce energy requirements, as well as the volume of the equipment. Higher ozone concentrations will also increase the ozonization rate.
Consequently, the following are characteristics of efficient process solutions:

- The residence time distribution (RTD) must follow a plug-flow pattern (in contrast, backmixing commonly occurs in dynamic mixers), which requires a special reactor geometry to avoid backmixing e.g. appropriate turbine and baffles. High intensity, high shear mixing is detrimental;

- Mean residence time in transfer/mixer/reactor must match transport and reaction times for complete conversion of ozone; consequently reactor diameter, shape and rotation rate of a possible turbine must match flow rate; and

- All ozone should be introduced in one step.

A low intensity mixer is sufficient for bleaching using moderate ozone concentrations, as long as the other criteria for ozone use are fulfilled. As the ozone concentration increases, the need for mixing decreases, and a static mixer is sufficient for distributing the ozone in the pulp. At sufficiently high ozone concentrations, a mixer is not necessary.

SUMMARY OF THE INVENTION

In accordance with the present invention, these and other objects have now been realized by the invention of a method for bleaching medium consistency cellulose pulp comprising providing a stream of ozone-containing gas and radially injecting the stream of ozone-containing gas representing a single ozone addition into a stream of cellulose pulp flowing through a reactor, so as to provide a stream of bleached cellulose pulp, the reactor being operated in plug flow mode at a pressure of at least 3 bar and at a temperature of 50°C or lower. Downstream from the ozone injection site, a low to medium intensity dynamic mixer operating at no more than 500 rpm may be used. The method according to the invention may include the use of static mixers, e.g. baffles. These may preferably be used at higher ozone concentrations. Preferably, the ozone concentration is at least 10 percent by weight; more preferably at least 15 percent by weight; and most preferably about 20 percent by weight. The expression “percent by weight” refers to the weight of ozone in the feed gas mixture.

In a preferred embodiment the method includes generating the stream of ozone-containing gas from a mixture of pressurized oxygen and at least one other gas or liquid.

In accordance with one embodiment of the method of the present invention, the method includes radially injecting the stream of ozone-containing gas at a pressure of at least 7 bar into the stream of cellulose pulp.

In accordance with another embodiment of the method of the present invention, the method includes radially injecting the stream of ozone-containing gas into the stream of cellulose pulp from a plurality of nozzles adapted to direct the ozone.

High-concentration, high pressure ozone is introduced into the pulp line, whereby conditions approaching plug flow are achieved, a high concentration of ozone is reached with a mass transfer area in the suspension which is sufficient for effective delignification.

According to one aspect of the present invention, the ozone is introduced using effective injection nozzles providing for the efficient dispersion necessary for obtaining a uniform distribution as well as sufficient mass transfer area to overcome the rate-limiting mass transfer threshold present in methods according to the prior art. Thus, the need for fiber-destroying high shear fluidizing mixers is removed.

According to a further aspect of the invention, a reactor for bleaching medium consistency pulp according to the above defined method is provided. The reactor comprises a vessel and means, for radically injecting ozone into a pulp stream flowing through the vessel, e.g. nozzles.

According to another aspect of the present invention, a dynamic low to medium intensity mixer is provided in the pulp stream downstream of the ozone injection site. Such a mixer delivers to the pulp stream amounts of energy which are well below fluidization energies, and does not mechanically affect the fiber.

Preferably, the low to medium intensity mixer is of the helix screw type with high pitch in the center, preferably 20 to 45 degrees, and lower peripheral pitch, preferably 5-30 degrees.

Baffles can be either of the helix-type on the vessel inside with a negative pitch, preferably 5-45 degrees with respect to the mixer, or flat discs dividing the reactor volume, preferably in at least 5 segments (compartments); or both baffle types at the same time. If flat disc baffles are used, a double helix-mixer with opposite signs on the pitch may be used.

According to another aspect of the present invention, a static mixer is provided in the pulp stream immediately downstream of the ozone injection site.

Preferably, the process is operated at temperatures below 25°C to reduce the decomposition of ozone to negligible values. At temperatures above 40°C, the self-decomposition of ozone increases significantly, and the process according to the invention should be operated at a temperature not higher than 50°C.

Higher temperatures will lead to higher requirements of ozone charge, but also to shorter residence times and smaller bleaching reactors.

The mean residence time of the pulp in the reactor may vary between about 10 to about 150 s, and longer time is required for higher ozone charges and for lower ozone pressure and concentration. Preferably, the mean residence time is between about 15 and about 40 s.

The mixing efficiency is not sensitive to the gas void level and the reactor can handle gas voids from 10 to 50 vol %.

With the aid of recent technology, as disclosed, e.g., in Swedish Patent Application No. 9502339-6, ozone with a concentration of up to 18 to 20% by volume may be generated. References to concentrations as high as 300 g O3/Nm3 have been made in prior art publications (e.g. European Application No. 426,652, with a priority date of Oct. 30, 1989), but such concentrations have not been technically feasible until recently. Using a high ozone concentration (300 g/m³ and higher) and at high pressure (10 bars and higher) together with a proper injection technique,
the reaction between ozone and fiber can now take place at a rate such that the subsequent use of an upflow bleach tower is not necessary. The gas pressure is obtained by using precompressed oxygen, optionally mixed with other gases or liquids (e.g. argon) to maintain a suitable conductivity for ozone generation.

[0036] Oxygen is the most common carrier gas used for ozone. Highly concentrated ozone is usually considered to be an explosion hazard. As the ozone generating technology has developed, the accepted limit for stable oxygen-ozone mixtures has been repeatedly pushed upwards, and it appears that no absolute concentration limit for the safe handling of ozone has yet been established. Thus, use of very high ozone concentrations may yet be possible, which further facilitates use of methods according to the present invention. According to the present invention, the concentration of ozonating gas introduced into the pulp stream is sufficient for achieving bleaching without any fiber-destroying mechanical impact.

[0037] The initial distribution of highly concentrated ozone into the pulp is of importance, for selectivity, as the carbohydrate component itself may be attacked by ozone if exposed for an extended time. The absence of backmixing, as may occur in high shear mixers, and the presence of plug flow conditions counteract this phenomenon.

BRIEF DESCRIPTION OF THE DRAWING

[0038] The present invention will be more fully appreciated with reference to the following detailed description, which in turn refers to the drawing, in which:

[0039] FIG. 1 is a graphical comparison between the changes in reaction rates against time in a prior art ozone pulp bleaching process using a medium consistency mixer, and a process according to the present invention.

DETAILED DESCRIPTION

[0040] The present invention may be appreciated with reference to the following specific examples;

EXAMPLE 1

[0041] Ozone-carrying gas having a pressure of about 15 bar and an ozone concentration of 14% by volume is introduced into a medium consistency pulp line carrying 1000 tons/day by means of a collar of radially arranged nozzles. Preferably, the nozzles are arranged to direct the gas radially into the pulp flow, essentially in a direction perpendicular to the pulp flow. A number of nozzles sufficient for evenly distributing the gas must be used. On this basis, 186 nozzles with an inlet diameter of a maximum of 1 mm may be used.

[0042] A sufficient mean residence time (10 to 40 seconds) must be allowed before any other disturbing action to the pulp.

EXAMPLE 2

[0043] A medium intensity (low-shear) mixer is adapted into the pulp stream of the previous example, preferably immediately following the gas injection site. The mixer turbine is preferably a double or multiple screw with blade angles and rotation rate balanced to maintain the plug flow residence time distribution (RTD) and giving good radial mixing efficiency. The center blade has a steeper angle than the outer screw blade. Alternatively, porous metal injector devices for introduction of ozone can be arranged peripherally or on the turbine.

[0044] FIG. 1 shows a comparison between a system employing a traditional medium consistency mixer with a very high capacity for a short interval dropping rapidly to zero, compared to a system according to the present invention, with a moderately high capacity kept constant for a long period. The dotted line represents state-of-the-art traditional medium consistency mixer technology. The first, steep section shows the effect of the mixer with high reaction and uniform distribution. The low rate section shows the effect of the corrosion of the gas-suspension interface. The reaction takes place with a nonuniform distribution and the pulp is mechanically stressed by high shear mixing.

[0045] The solid line represents a system according to the present invention. Throughout the process, a moderately fast reaction is taking place in a mildly stressed pulp with a uniform distribution of ozone.

| Table 1 |
|---|---|---|---|
| Calculus Base | Units | Conventional | Modern | Present invention |
| Consistency | % | 70 | 70 | 70 |
| Ozone pressure | bar | 9 | 9 | 9 |
| Ozone concentration | w % | 20 | 20 | 20 |
| Ozone charge | kg/h | 0.0146 | 0.0146 | 0.0146 |
| (3–5) | | 0.0001 | 0.0001 | 0.0001 |
| Ozone generator | kg/h | 208 | 208 | 208 |
| Ozone volume flow | m³/s | 0.0146 | 0.0146 | 0.0146 |
| Nozzle diameter | m | 186 | 186 | 186 |
| Number of nozzles | Process | | | |
| Process temperature | °C | 40 | 40 | 40 |
| Process pressure | bar | 7 | 7 | 7 |
| Pulp Flow | % | 42 | 42 | 42 |
| Volume Flow | m³/h | 375 | 375 | 375 |
| MC pulp | % | 234 | 165 | 53 |
| Ozone gas charge | at actual press. | | | |
| Gas void* Equipment | 1–3 mixers | 31 | | |
| Ozone compressor | Bleach tower | | | |
| No ozone compressor | No mixer | | | |
| Small bleach reactor | | | | |

*Note: Gas void is proportional to process problems

[0046] Table 1 shows a comparison in numbers between a typical conventional MC bleaching system, a state-of-the-art system and a system according to the present invention.

1. A method for bleaching medium consistency cellulose pulp comprising providing a stream of ozone-containing gas and radially injecting the stream of ozone-containing gas in a single ozone addition step into a stream of cellulose pulp flowing through a reactor so as to provide a stream of
bleached cellulose pulp, wherein said reactor operates in plug flow mode at a pressure of at least 3 bar and at a temperature of 50°C or less and said reactor does not include a high shear mixer.

2. The method of claim 1 wherein said ozone-containing gas has an ozone concentration of at least 10 percent by weight.

3. The method of claim 1 wherein said ozone-containing gas has an ozone concentration of at least 15 percent by weight.

4. The method of claim 1 wherein said ozone-containing gas has an ozone concentration of at least 20 percent by weight.

5. The method of claim 1 including radially injecting said stream of ozone-containing gas into said stream of cellulose pulp by means of a plurality of porous metal injectors.

6. The method of claim 1 wherein the mean residence time of said pulp in said reactor is between about 10 and about 150 s.

7. The method of claim 6 wherein the mean residence time of said pulp in said reactor is between about 15 and about 40 s.

8. The method of claim 1 wherein the stream of ozone-containing gas is generated from a mixture of pressurized oxygen and at least one other gas or liquid.

9. A reactor for bleaching medium consistency pulp wherein said reactor comprises a vessel, means for radially injecting an ozone-containing gas into a stream of cellulose pulp flowing through said vessel, and said reactor further comprising a mixer of the rotatable helix screw type having a first pitch in the center and a second pitch at the periphery, the second pitch being lower than the first pitch, downstream from said injecting means.

10. The reactor of claim 9 wherein the first pitch is in the range of 20 to 45 degrees and the second pitch is in the range of 5 to 30 degrees.

11. The reactor of claim 9 including baffles on the vessel inner wall.

12. The reactor of claim 11 wherein said baffles are of the helix type, having a negative pitch in respect to the mixer.

13. The reactor of claim 12 wherein said baffles have a pitch in the range of 5 to 45 degrees.

14. The reactor of claim 11 wherein said baffles comprise flat disc baffles dividing the reactor volume.

15. A method for bleaching medium consistency cellulose pulp comprising providing a stream of ozone-containing gas and radially injecting the stream of ozone-containing gas in a single ozone addition step into a stream of cellulose pulp flowing through a reactor so as to provide a stream of bleached cellulose pulp, wherein said reactor operates in plug flow mode at a pressure of at least 3 bar and at a temperature of 50°C or less and said reactor includes a mixer operating at not more than 800 rpm downstream from the injection site.

16. The method of claim 15 wherein said ozone-containing gas has an ozone concentration of at least 10 percent by weight.

17. The method of claim 15 wherein said ozone-containing gas has an ozone concentration of at least 15 percent by weight.

18. The method of claim 15 wherein said ozone-containing gas has an ozone concentration of at least 20 percent by weight.

19. The method of claim 15 wherein said mixer includes a static mixer.

20. The method of claim 15 wherein said mixer includes a dynamic mixer.

21. The method of claim 15 wherein said mixer includes a rotatable helical screw mixer.

22. The method of claim 15, including radially injecting said stream of ozone-containing gas into said stream of cellulose pulp by means of a plurality of porous metal injectors.

23. The method of claim 15 wherein the mean residence time of said pulp in said reactor is between about 10 and about 150 s.

24. The method of claim 23 wherein the mean residence time of said pulp in said reactor is between about 15 and about 40 s.

25. The method of claim 15 wherein the stream of ozone-containing gas is generated from a mixture of pressurized oxygen and at least one other gas or liquid.

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