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(54) **METHOD FOR CONTROLLING THE DELIGNFICATION AND BLEACHING OF A PULP SUSPENSION**

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(57) **ABSTRACT**

The invention relates to a process for the bleaching of an aqueous lignocellulosic pulp under acidic conditions in the bleaching plant of a pulp mill. The bleached pulp is used for the production of paper or pulp. The selectivity of the bleaching agent towards primary reactions with lignin is enhanced by the use of a carbon dioxide providing medium in the pulp.

METHOD FOR CONTROLLING THE DELIGNFICATION AND BLEACHING OF A PULP SUSPENSION

[0001] The present invention relates to a process for the delignification and bleaching of an aqueous lignocellulosic pulp under acidic conditions in the bleaching plant of a pulp mill. The invention also includes a process for the production of paper or pulp from said bleached pulp suspension.

[0002] Lignin is an amorphous polymer which, like a glue, keeps the cellulose fibers together in wood. Some lignin also exists in the fiber wall. In its native state in wood lignin is of light color.

[0003] The purpose of chemical pulping, such as kraft pulping, is to dissolve the lignin from the wood matrix with a cooking liquor. During cooking lignin is broken down into smaller units and becomes darker, i.e. increases the light absorption. The dark lignin components, some of which are dissolved and some of which are still in the fiber, give the pulp a dark colour.

[0004] Delignification and bleaching, referred to in the following text and in the appended claims to as "bleaching", are chemical purifications of the fibers in a cooked lignocellulosic pulp. The main aim of acidic bleaching sequences is to remove lignin and other components capable of absorbing visible light and thus influence the brightness of the pulp. The fibers, i.e. the carbohydrate components of the lignocellulose should preferably not be materially affected by the bleaching process.

[0005] The selectivity in the bleaching can be defined as the relative reactivity of the particular reactive species toward lignin and carbohydrate components of the pulp in a competitive situation. The competing initial reactions are believed to consist of the addition of an electrophile to the aromatic ring or the olefin structures in the lignin and the abstraction of a hydrogen atom from the carbohydrates.

[0006] The bleaching stages contemplated within the scope of the present invention comprise acidic bleaching stages such as one or more chlorine dioxide (D) stages, peracetic acid (Paa) stages, ozone (Z) stages, as well as multichemical stages utilizing a combination of bleaching agents.

[0007] Generally the bleaching plant operates with bleaching sequences made up of several bleaching stages, which usually are separated by washing stages, although in some cases the washing may be omitted.

[0008] An example of a modern ECF sequence for production of bleached kraft pulp is D_0(EOP)DED, where D stand for chlorine dioxide bleaching, E stands for extraction and EOP for oxygen and peroxide reinforced extraction. In such a system the unbleached pulp enters the bleach plant with an alkaline pH. The chlorine dioxide bleaching is then carried out under acidic conditions and the subsequent extraction is performed under alkaline conditions.

[0009] Several modern bleaching sequences also include an ozone bleaching stage Z. This stage may, for instance be included in a sequence of ZQ(PO). The ozone may also be combined with chlorine dioxide bleaching in a (ZD) or a (DZ) stage. The pH of the pulp suspension should be decreased to about pH 3 for the ozone in the Z stage to provide an effective bleaching.

[0010] There also exists a bleaching stage using peracetic acid (Paa) wherein bleaching is performed at pH about 4 to 6.

[0011] In addition to various sequences of separate bleaching stages, the pulp may be bleached in a so called multichemical stage where several bleaching processes occur without inter-mediate washing. Examples of such stages are, in addition to the above mentioned (ZD) or (DZ) combination, a (ZPaa) or an (AD) stage, where A stands for acid hydrolysis.

[0012] The acids normally used for acidifying the pulps for the acidic bleaching stage comprises mineral acids such as sulfuric acid. There have been some suggestions for adjusting the pH of acidic bleaching stages with carbon dioxide, which is a gas which in reaction with water provides carbonic acid. However, there is very little actual knowledge of the effect of carbon dioxide on the bleaching.

[0013] Practical experiments have been performed at a mill in Finland with the use of carbon dioxide for adjusting the pH in an enzyme bleaching stage. Further, the use of carbon dioxide in a wash stage at a mill in Sweden has been reported to provide, in addition to the improved washing effect, a decreased consumption of bleaching chemicals (Östberg, G., er al., The World Pulp and Paper Week, Jun. 4-7, 1996, Stockholm, pp. 508-515.)

[0014] Carbon dioxide has also been suggested in GB Patent 815,247 for use in combination with sodium hydroxide to provide a pH buffer in situ for a chlorine dioxide bleach which was to be performed at a pH of 9 to 5. Teder, A., et al., TAPPI 61(1978)12, pp. 59-62 have reported that in a two-step pH adjusted chlorine dioxide bleach the pH may be kept at a high pH for a longer period with the use of $NaHCO_3$ buffer or NaOH.

[0015] The present invention is based on the realization that while carbon dioxide has little or no impact on the final pH of the very acidic bleaching stages such as a D stage, carbon dioxide does affect the bleaching result and can be used for controlling the chemical reactions taking place between the bleaching agent and the various lignin and carbohydrate compounds in the pulp suspension.

[0016] Carbon dioxide is a gas, which dissolves in aqueous media under alkaline conditions, e.g. in water or a pulp suspension. The dissolved gas forms carbonic acid, H_2CO_3, which readily dissociates as shown below:

$$CO_2(g) \xleftrightarrow{H_2O} CO_2(d) + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2H^+ + CO_3^{2-}$$

(g = gas; d = dissolved)

[0017] (g=gas; d=dissolved)

[0018] The carbonic acid produced by the dissolving carbon dioxide is a weak acid which is capable of lowering the pH of an alkaline pulp to neutral and slightly below, down to a pH of about 6. However, in accordance with the present invention it has been found that even though carbon dioxide is capable of lowering the initial pH of an alkaline pulp entering the bleaching stage, its pH lowering effect is lost at the lower pH ranges and, contrary to previous beliefs, carbon dioxide cannot be used to lower the pH of the actual (final) bleaching stage.

[0019] In accordance with the present invention it has been found that carbon dioxide can be used to control the degradation rate and the decomposition of various components of the aqueous lignocellulosic pulp.

[0020] The object of the present invention is thus to provide an acidic bleaching process wherein the degradation of lignin and carbohydrates in a pulp suspension is controlled.

[0021] Another object of the invention is to improve the selectivity of the bleach by directing the attack of the bleaching agent primarily towards a reaction with lignin.

[0022] A further object of the invention is to provide a bleaching process wherein the degradation chain of carbohydrates and/or lignin is influenced so as to suppress the decomposition of said compounds to smaller fragments.

[0023] An object of the invention is to improve the selectivity of the bleach and thus to obtain a higher brightness and/or lower kappa number of the bleached pulp with a given amount of bleaching agent.

[0024] Another object of the invention is to improve the selectivity of the bleach and thus to obtain a the same brightness and/or kappa number with a reduced amount of bleaching agent.

[0025] A further object of the invention is to decrease the chemical oxygen demand (COD) of the bleach filtrate.

[0026] The present invention is defined in the appended claims. Thus, the invention concerns a process for bleaching an aqueous lignocellulosic pulp under acidic conditions in the bleaching plant of a pulp mill, said process comprising the following stages: providing an aqueous lignocellulosic pulp suspension in said bleaching plant; adding bleaching agent to said pulp suspension and providing an acidic pH therein for causing a reaction between lignin and said bleaching agent; prior to or simultaneously therewith adding a carbon dioxide providing medium to said lignocellulosic pulp suspension to provide carbon dioxide in said acidic pulp suspension for controlling the degradation of lignin and its derivatives in their reactions with said bleaching agent; and subsequently subjecting said pulp suspension to an alkaline extraction step to solubilize and remove reacted lignin compounds from said pulp.

[0027] The preferred carbon dioxide providing medium comprises carbon dioxide in gaseous form. The carbon dioxide may, however, also be introduced in liquid or solid form. The carbon dioxide in the acidic aqueous suspension can also be provided by compounds which dissociate and/or decompose at the pH in question and thereby provide carbon dioxide. Such compounds comprise gases or liquids capable of providing carbonate and/or bicarbonate ions in the aqueous suspension under alkaline or neutral conditions. The compounds are exemplified by alkali metal bicarbonates and carbonates which decompose at the lower pH ranges freeing carbon dioxide.

[0028] The carbon dioxide providing medium used according to the present invention is preferably a carbon dioxide containing gas which is fed directly into the aqueous pulp suspension. It may, however, also be a carbon dioxide providing aqueous liquid, such as dilution water, which contains carbon dioxide, bicarbonate or carbonate. For the purpose of the invention it is not critical how the carbon dioxide enters the suspension, it is only required that it will provide carbon dioxide in the aqueous pulp suspension.

[0029] The carbon dioxide should preferably be added directly to the pulp suspension prior to or in immediate connection to the bleaching stage in question, but after any washing stage, that might precede the bleaching stage. If added to the washing stage, most of the carbon dioxide will be removed with the washing water and the effect on the bleach will be inadequate. The carbon dioxide may, however, be added to any dilution water used to dilute the pulp after a preceding washing stage.

[0030] Preferably said the carbon dioxide providing medium comprises gaseous carbon dioxide which is injected into a flowing stream of said pulp suspension just prior to the addition of the bleaching agent of a D, Z, Paa or multichemical stage.

[0031] The use of carbon dioxide for controlling the bleaching reactions in accordance with the present invention has a number of advantages, e.g.:

- [0032] an improved brightness and kappa number of the pulp may be obtained after extraction as the carbon dioxide will channel the attack of the bleaching agent to the initial bleaching reactions with lignin
- [0033] no decrease in viscosity will result from the increased brightness since the attack of the bleaching agent on the carbohydrates will be suppressed by the carbon dioxide
- [0034] an improvement on the COD content of the filtrate can be obtained
- [0035] the improved bleaching action may be used for reducing the consumption of bleaching chemicals
- [0036] there are no environmental hazards associated with carbon dioxide.

[0037] The pulp suspension to be treated according to the present invention is not critical. Almost any kind of lignin containing pulp can be bleached according to the procedures of the present invention. Examples of such pulps are chemical pulps, organosolv pulps, mechanical pulps, chemi-mechanical pulps, semi chemical pulps, pulps containing recycled fibers or broke, or mixtures of any of these in a bleaching plant of a pulp mill.

[0038] The pulp may be introduced into the bleaching plant after cooking or it may be directed to the bleaching plant via an oxygen delignification stage and possibly other treatments.

[0039] The consistency of the pulp may be in the low, medium or high consistency range. For better handling it is generally preferable to use a low or medium consistency pulp. A typical consistency is 1 to 18%, preferably 3 to 15%.

[0040] The present invention also includes the processing of the bleached pulp further in a pulp or paper mill to provide dried pulp and/or paper containing said bleached pulp. The production of dried pulp and paper from the bleached pulp can be performed in the conventional way which is well known to those skilled in the art.

[0041] The pulp suspension entering the bleaching plant is generally alkaline and in the preferred embodiment of the invention the pH is adjusted to an acidic or neutral pH by adding said carbon dioxide providing medium. However, sometimes it may be more economical and also technically adequate to adjust the pH of said pulp by the use of a combination of carbon dioxide and another acid or base.

[0042] Further, it should be noted that carbon dioxide is an environmentally much more acceptable chemical than most other acids. Therefore using carbon dioxide alone is the preferred procedure from an environmental point of view. The final acidic pH adjustment for the actual bleach is preferably performed by the bleaching agent or by adding another and stronger acid to the suspension.

[0043] In the case of an initial D stage, it is technically advantageous to lower the initial pH with carbon dioxide to near neutral and to add the chlorine dioxide so as to obtain the desired pH of about 1.7 to 4.4 taking into account the acidic byproducts of the reactions between lignin and chlorine dioxide. It is to be noted that the carbon dioxide addition does not significantly lower the final pH of the bleach.

[0044] If desired, another acid such as sulfuric acid, sulfurous acid, alum, waste acid from the chlorine dioxide production may be used also for providing the required lower pH.

[0045] The strong acidic conditions of the bleach will liberate carbon dioxide from the carbonates and bicarbonates present in the solution at a higher pH. The freed carbon dioxide effects the bleach to provide a controlled bleaching effect.

[0046] In accordance with the present invention it has surprisingly been found that when an effective amount of carbon dioxide is present in said pulp suspension at the same time as the bleaching agent, the carbon dioxide influences the equilibrium and/or progression of the reactions between lignin (or its derivatives) and the bleaching agent (or its derivatives) to suppress the further reaction chains and the degradation of said lignin derivatives.

[0047] It has also surprisingly been found that an effective amount of carbon dioxide suppresses the degradation of the carbohydrates in the pulp suspension by influencing the equilibrium and/or progression of any carbohydrate degradation reaction chain.

[0048] Both of the above activities increase the selectivity of the bleaching agent towards controlled primary reactions with lignin.

[0049] Since the primary reactions between lignin and bleaching agent generally are sufficient to render the resulting lignin derivative soluble in an aqueous medium under alkaline conditions, any further reactions between lignin derivatives and bleaching agent are superfluous from the bleaching point of view. If the bleaching agent is allowed freely to attack the lignin derivatives, the lignin will react in a chain of reaction steps ultimately leading to decomposition. Among the fragments produced by such a decomposition there is specifically also carbon dioxide.

[0050] Further, if the bleaching agent such as chlorine dioxide or ozone is allowed to freely attack the carbohydrate chains of the cellulosic fibers, the fibers will degrade and finally decompose. The result of such an attack can be seen as a decrease in the viscosity of the bleached pulp.

[0051] The decomposition of lignin and carbohydrates into carbon dioxide can be seen in the bleached pulp as a content of carbon dioxide in the pulp itself as well as in the gas phase in contact with the pulp, even when no carbon dioxide has been introduced into the pulp.

[0052] In accordance with the present invention it has surprisingly been found that the carbon dioxide provided by the carbon dioxide providing medium of the present invention will suppress the secondary reactions degrading the carbohydrate chains and/or the lignin derivatives. Thus, the introduction of an effective amount of carbon dioxide into the pulp pushes the bleaching agent into the preferred primary reactions which cause an active bleaching action.

[0053] In accordance with the present invention it has surprisingly been found that the amount of carbon dioxide in the suspension should be at an effective level and that increasing the amount of carbon dioxide much above an optimum level will counter the beneficial effects of the added carbon dioxide and will lower the brightness and/or increase the kappa number of the bleached and extracted pulp.

[0054] The reason for the counter-effect of a too high level of carbon dioxide in the pulp is not understood at present. However, a person skilled in the art, being taught by the present invention to seek an optimum level of carbon dioxide addition, will readily find an effective amount of carbon dioxide to add to the pulp. This may be done by monitoring the increase of brightness and/or reduction in bleaching chemical consumption caused by the addition of the carbon dioxide providing medium, until the trend changes and the brightness starts to decrease or the chemical consumption starts to increase. A preferred way of monitoring the bleaching selectivity is to measure the COD content of the filtrate of the pulp leaving the bleaching stage. The optimum amount of C_2 at a certain ClO_2 feed will coincide with a minimum in the COD content of the filtrate.

[0055] In a chlorine dioxide bleaching system an effective amount of carbon dioxide has been found to be one that provides a carbon dioxide content in the gas phase of the pulp system which is substantially equal to the carbon dioxide content generated in the gas phase of a similar pulp system bleached under the same conditions but without the addition of a carbon dioxide providing medium.

[0056] It has been found that if a smaller amount of carbon dioxide than the above effective amount is provided in the pulp, the content of carbon dioxide in the gas phase will still be the same, i.e. the reactions during the bleaching stage will generate carbon dioxide due to the decomposition or degradation of the components of the pulp. Without wishing to be bound by any theory, it is believed that when carbon dioxide is actively added to the pulp, the carbon dioxide saturation will be reached without a decomposition of the pulp components. This will suppress the formation of more carbon dioxide and will push the equilibrium of the reactions away from the decomposing and degrading reactions. Thus, the bleaching agent will not be used for causing decomposing reactions which do not provide a bleaching effect.

[0057] It is obvious to those skilled in the art that the present invention forms an improvement in a conventional process in a pulp mill and that the final product of the process is paper or pulp bleached according to the described invention. Consequently, the present invention also concerns a process for producing paper or pulp. In such a process an aqueous unbleached pulp suspension is bleached in one or more acidic bleaching stages with the assistance of a carbon dioxide providing medium, and subsequently extracted in a bleaching plant. The processing of the pulp after said bleaching stage(s) is then performed in a conventional way and the pulp is processed to form a web of paper or pulp.

[0058] The invention will now be described in greater detail with the aid of some examples which are only illustrative and which should not be construed as limiting the invention in any way.

EXAMPLE 1

[0059] Mill Scale Trials With The Addition Of CO_2 In A D Stage

[0060] To estimate the effect of the carbon dioxide addition on the pH of a D stage, trials were run at the fibreline of a paper mill having the sequence D(EO)(EP)D(EP)D. In the trials carbon dioxide was fed after the MC-pumps, but before the chlorine dioxide feed. The used carbon dioxide dosages were 2 and 5 kg/ADt. The first trials lasted for three hours in the $D_0$and D_1 stages. Two more trials were run at the D_1-stage, with the CO_2-dosages of 2 and 5 kg/ADt. Each of these trials lasted for one week.

[0061] The mill was provided with a system which automatically altered the chemical consumption to provide a desired bleaching result.

[0062] The capability of the CO_2 to stabiliZe the pH was measured by titrating the suspension with an alkali. The effect of the carbon dioxide addition on the initial bleaching pH, the final bleaching pH and the pH of the incoming pulp was measured.

[0063] The effect of carbon dioxide on the pH of the incoming pulp was clear. With the 2 kg/ADt carbon dioxide dosage the pH was decreased from 8.9 to 7.4 and with the 5 kg/ADt dosage to 7.0.

[0064] However, neither the initial bleaching pH nor the final pH changed significantly. When the initial pH was measured after the chlorine dioxide feed, the pH remained constant at 3.3. When the final pH was measured at the DO-filter the pH remained constant at 3.0 with the 2.0 kg/ADt carbon dioxide dosage, but increased to 3.1 with the 5 kg/ADt dosage.

[0065] The results clearly showed that even though the pH of the incoming pulp was decreased, the initial pH and the final pH did not decrease.

EXAMPLE 2

[0066] Mill Scale Trials At A D_1 Stage

[0067] Carbon dioxide was fed at the same point as in the trials of Example 1. the bleaching was followed by an EOP extraction stage. Again the chemical consumption was altered according to the automation system. Thus, the chemical consumption had to be calculated through the whole fibreline. Also the sodium hydroxide and hydrogen peroxide consumptions were calculated alongside with the chlorine dioxide consumption. All of these results were compared to the three reference periods before and after these trials, representing a time of totally four weeks.

[0068] All the parameters and the values obtained in the trial are shown in Table 1.

TABLE 1

Chemical consumption in a D_1 trial at a fibreline

CO_2-dosage, kg/ADt	0	2	5
uz,3/8 ClO_2-dosage			
D_0-stage, kg/ADt	31.6	29.2	31.4
D_1-stage, kg/ADt	20.0	18.5	19.3
D_2-stage, kg/ADt	6.9	7.7	7.2
total	58.5	55.4	57.9
NaOH			
EO-stage, kg/ADt	8.4	8.1	7.8
EP-stage, kg/ADt	1.2	1.3	1.3
E_2-stage, kg/ADt	5.4	4.2	6.2
total	15.0	13.6	15.3
H_2O_2			
EP-stage, kg/ADt	4.0	3.8	3.9
E_2-stage, kg/ADt	2.1	2.0	2.2
total	6.1	5.8	6.1
Wash loss			
D_0-stage, kg/ADt	15.4	13.0	14.8

[0069] The results of the trials clearly showed that the chemical consumption was reduced with the use of the carbon dioxide addition. However, the use of the lower carbon dioxide dosage seemed to provide better results. It should be emphasized that neither of these results should be considered as absolute values. The high variation in the chemical consumption in each stage was due to the automatic alteration and the changes of the balance in the delignification and the bleaching loads between each stage.

EXAMPLE 3

[0070] Carbon Dioxide Content Of The Gas Phase Of The Bleached Pulp

[0071] A pulp from the brown stock filters of a mill fibreline was delignified in plastic bags with approximately 30 kg/ADt of chlorine dioxide, as active chlorine, at 60° C. for 60 minutes. Carbon dioxide was added as dry-ice, at approximately 2 and 4 kg/ADt carbon dioxide dosages.

[0072] After the delignification the pulps were cooled in the plastic bags with cold water and transported in a bucket to a gas laboratory. To measure the carbon dioxide content of the gas phases, gas samples (100 ml) were taken from the plastic bags with a syringe and analysed in a gas chromatograph.

[0073] The results showed that carbon dioxide is formed in large amounts when the pulp is delignified at the D_0-stage. The carbon dioxide contents that were found in the gas phases varied between 7.3% and 19.6%. However, there was only a minor difference in the gas content between a zero dosage and a 2 kg/ADt carbon dioxide dosage. The gas contents were 9.5% and 10.7%, respectively.

[0074] When the high carbon dioxide dosage was used, the carbon dioxide content increased significantly. The 4 kg/ADt carbon dioxide dosage provided a carbon dioxide content of the gas phase which was approximately 16.8%.

EXAMPLE 4

[0075] Laboratory Trial Of A Do Stage With Extraction

[0076] A pulp was taken from an MC-pump before a D_0-stage of a fibreline of a pulp mill. The tests were performed in a laboratory with a CRS-reactor capable of controlling the reaction temperature and pressure, the carbon dioxide dosage and the chlorine dioxide dosage, and of measuring the pH of the filtrate.

[0077] The pulp (200 g/air dry) and dilution water were added into the reactor and warmed slightly over the reaction temperature. After the temperature was reached the carbon dioxide was added. Subsequently chlorine dioxide was added and the reaction pressure was reached by moving the piston in the adiabatic cylinder of the apparatus. During the reaction no fluidization was done, only the temperature was controlled.

[0078] At the end of the reaction a gas sample and a filtrate sample were taken and analysed. The pulp was then washed with 15 litres of water and an extraction stage was performed in a plastic bag in a water bath. After the extraction the pulps were again washed with 15 litres of water.

[0079] The consistency of the pulp was measured and the viscosity, the kappa number and the ISO-brightness were measured.

[0080] Totally 12 laboratory tests were run at the D0-stage. To estimate the effects of the different process parameters on the pulp, the filtrate and the gas properties, temperature, pressure and the chlorine dioxide and carbon dioxide dosage were altered. The tests were run at two different temperatures (60 and 70° C.), pressures (4 and 6 bar), chlorine dioxide dosages (26 and 30 kg/ADt) and with three different carbon dioxide dosages (0, 2 and 4 kg/ADt). The results of these tests are shown in Table 2.

TABLE 2

The variables and the results from the laboratory tests

final pH	wash loss, kg/ADt, COD_{cr}	standard distribution	ISO brightness %	standard distribution	kappa number	Standard distribution ml/g	Viscosity ml/g	Generated Co_2, kg/ADt	Total CO_2-content kg/ADt	testpoint
4.5	16.5	0.3	50.1	0.6	6.5	12	1310	4.5	6.5	1
4.5	15.2	0.4	50.8	0.3	6.6	10	1287	4.4	6.4	2
2.9	16.7	0.4	49.3	0.1	6.7	11	1293	5.4	5.4	3
4.8	16.8	0.4	46.7	0.1	8.2	6	1339	0.0	4.0	4
2.5	15.2	0.3	47.2	0.1	7.4	13	1328	1.9	5.9	5
2.7	17.9	0.3	51.1	0.1	6.1	5	1309	6.1	6.1	6
2.9	15.2	0.3	52.3	0.2	5.9	10	1335	4.9	6.9	7
3.4	15.5	0.4	49.7	0.2	6.7	7	1364	3.2	7.2	8
4.0	16.0	0.3	51.5	0.2	6.1	6	1343	2.0	6.0	9
3.4	16.5	0.5	48.3	0.1	7.1	32	1380	3.4	3.4	10
3.1	19.7	0.4	48.6	0.1	6.9	19	1245	5.3	5.3	11
3.1	14.7	0.5	51.6	0.2	5.9	20	1375	3.3	5.3	12

CO_2-content filtrate kg/ADt	CO_2-content gas kg/ADt	CO_2-dosage kg/ADt	Consistency, %	Pressure bar	Temperature, ° C.	Residual Cl, kg/ADt	ClO_2-dosage, kg/ADt	test point
0.9	5.6	2	9	6	60	0.0	29.7	1
0.5	5.8	2	9	6	70	0.0	26.0	2
0.2	5.3	0	9	4	70	0.0	29.4	3
0.9	3.1	4	9	6	60	0.0	29.8	4
0.6	5.3	4	9	6	70	0.0	26.0	5
0.2	5.9	0	9	6	70	0.0	30.0	6
0.6	6.3	2	9	4	70	0.0	30.6	7
0.7	6.5	4	9	4	60	0.0	29.8	8
0.8	5.2	4	9	4	60	0.0	26.0	9
0.1	3.3	0	9	6	60	0.1	26.0	10
0.1	5.2	0	9	4	70	0.0	26.0	11
0.5	4.8	2	9	4	60	0.2	26.0	12

TABLE 2-continued

Kappa number	Carbon dioxide dosage, kg/ADt			Viscosity ml/g	Carbon dioxide dosage, kg/ADt		
Pressure	0	2	4	Pressure	0	2	4
4 bar	6.8	5.9	6.4	4 bar	1270	1350	1350
6 bar	6.6	6.5	7.8	6 bar	1340	1300	1330
Temperature	0	2	4	Temperature	0	2	4
60° C.	7.1	6.2	7.0	60° C.	1380	1340	1350
70° C.	6.6	6.2	7.4	70° C.	1280	1310	1330
ClO_2-dosage	0	2	4	ClO_2-dosage	0	2	4
26 kg/ADt	7.0	6.3	6.8	26 kg/ADt	1310	1330	1340
30 kg/ADt	6.4	6.2	7.4	30 kg/ADt	1300	1320	1350

ISO-brightness, %	Carbon dioxide dosage, kg/ADt			Final pH	Carbon dioxide dosage, kg/ADt		
Pressure	0	2	4	Pressure	0	2	4
4 bar	48.9	52.0	50.6	4 bar	3.0	3.0	3.7
6 bar	49.7	50.4	47.0	6 bar	3.0	4.5	3.6
Temperature	0	2	4	Temperature	0	2	4
60° C.	48.3	50.9	49.3	60° C.	3.4	3.8	4.0
70° C.	49.6	51.5	47.2	70° C.	2.9	3.7	2.5
ClO_2-dosage	0	2	4	ClO_2-dosage	0	2	4
26 kg/ADt	48.4	51.2	49.3	26 kg/ADt	3.2	3.8	3.2
30 kg/ADt	50.2	51.2	48.2	30 kg/ADt	2.8	3.7	4.1

COD content, kg/ADt ,	Carbon dioxide dosage, kg/ADt			Generated CO_2, kg/ADt	Carbon dioxide dosage, kg/ADt		
Pressure	0	2	4	Pressure	0	2	4
4 bar	18.1	14.9	15.	4 bar	5.4	4.1	2.6
6 bar	17.2	15.8	16.0	6 bar	4.7	4.4	1.0
Temperature	0	2	4	Temperature	0	2	4
60° C.	16.5	15.6	16.1	60° C.	3.4	3.9	1.8
70° C.	18.1	15.2	15.2	70° C.	5.6	4.6	1.9
ClO_2-dosage	0	2	4	ClO_2-dosage	0	2	4
26 kg/ADt	18.1	14.9	15.6	26 kg/ADt	4.4	3.8	2.0
30 kg/ADt	17.3	15.8	16.1	30 kg/ADt	5.8	4.7	1.6

[0081] The results show that although are were clear variations depending on chemical additions, temperatures, etc., the bleaching efficiency and selectivity was improved by carbon dioxide. Moreover, the improvement was significantly better with an intermediate addition of carbon dioxide than with a large addition of carbon dioxide. The effect on the pH of the bleach was minimal.

EXAMPLE 5

[0082] Laboratory Trials At A D_1 Stage Without Extraction

[0083] Laboratory tests similar to those of Example 4 were performed for a D_1 stage but without performing an alkaline extraction afterwards. The results showed that without an extraction stage, the same advantages as those gained in Example 4 could not be obtained.

EXAMPLE 6

[0084] Laboratory Trials At A Z Stage

[0085] Two test are run in a laboratory reactor. The consistency of the oxygen delignified pulp is 35% and its pH is 2.5 and temperature 40° C.

[0086] In the first test only ozonising gas is used, in the second test 15% carbon dioxide is thoroughly mixed into the ozonising gas before charging. The gases are charged into the pulp, keeping the total ozone charge at the same level. The reaction is allowed to proceed with fluidizing mixing for 2 minutes.

[0087] After an alkaline extraction of the pulp, the viscosities of the bleached pulps are measured. The viscosity of the pulp treated with ozone has decreased from 22 mPas to 17.5 mPas, while the carbon dioxide treated pulp has a final viscosity of 18.0 mPas.

1. A process for bleaching an aqueous lignocellulosic pulp under acidic conditions in the bleaching plant of a pulp mill, said process comprising the following stages:

providing an aqueous lignocellulosic pulp suspension in said bleaching plant,

adding bleaching agent to said pulp suspension and providing an acidic pH therein for causing a bleaching reaction between lignin and said bleaching agent,

prior to or simultaneously therewith adding a carbon dioxide providing medium to said lignocellulosic pulp suspension to provide carbon dioxide in said acidic pulp suspension for controlling the degradation of lignin or its derivatives in their reactions with said bleaching agent, subsequently subjecting said pulp suspension to an alkaline extraction step to solubilize and remove reacted lignin compounds from said pulp.

2. Process according to claim 1, wherein said carbon dioxide providing medium comprises carbon dioxide in gaseous, liquid or solid form.

3. A process according to claim 2, wherein said medium comprises gaseous carbon dioxide which is injected into a flowing stream of said pulp suspension just prior to the addition of said bleaching agent.

4. A process according to claim 1, wherein said carton dioxide providing medium comprises a gas or a liquid capable of providing carbonate and/or bicarbonate ions in said aqueous suspension under alkaline or neutral conditions.

5. A process according to any one of the preceding claims 1 to 4, wherein said carbon dioxide providing medium provides an effective amount of carbon dioxide in said pulp suspension for influencing the equilibrium and/or progression of the reaction between lignin or its derivatives and said bleaching agent or its derivatives to suppress the degradation of said lignin derivatives.

6. A process according to any one of the preceding claims 1 to 4, wherein said carbon dioxide providing medium provides an effective amount of carbon dioxide to suppress the degradation of the carbohydrates in said pulp suspension by influencing the equilibrium and/or progression of any carbohydrate degradation reaction chain, thus increasing the selectivity of the bleaching agent towards a reaction with lignin.

7. A process according to claims **5** or **6**, wherein said effective amount of carbon dioxide is one that provides a carbon dioxide content in the gas phase of the pulp system which is substantially equal to the carbon dioxide content generated in the gas phase of a similar pulp system bleached under the same conditions but without the addition of a carbon dioxide providing medium.

8. A process according to claims **6** or **7**, wherein a preferred effective amount of carbon dioxide to be added is obtained by monitoring the COD o the filtrate of the bleached and unextracted pulp at varying carbon dioxide addition at amounts and locating the COD minimum for the pulp to be bleached.

9. A process according to claim 1, wherein said aqueous lignocellulosic pulp suspension is at an alkaline pH prior to the addition of said carbon dioxide providing medium.

10. A process according to claim 9, wherein the pH of said pulp suspension is adjusted to pH 6.5 to 7.5 by the addition of gaseous carbon dioxide.

11. A process according to claim 1, wherein said carbon dioxide providing medium is added in and/or after any washing stage preceding said addition of bleaching agent.

12. A process according to claim 1, wherein said bleaching agent is used in a bleaching stage selected from a chlorine dioxide (D) stage, a peracetic acid (Paa) stage, an ozone (Z) stage, and a multichemical stage with a combination of bleaching agents.

13. A process according to claim 12, wherein said bleaching stage comprises a D or Z stage and the final bleaching pH of said pulp suspension is adjusted to pH 1.5 to 4.4.

14. A process according to claim 12, wherein said bleaching stage comprises a Paa ,stage and the final bleaching pH of said pulp suspension is adjust d to pH 4 to 6.

15. A process according to claim any one of the preceding claims 1 to 14, wherein said aqueous cellulosic pulp suspension comprises a chemical pulp, an organosolv pulp, a mechanical pulp, a chemi-mechanical pulp, a semi chemical pulp, a pulp containing recycled fibers or broke, or a mixture of any of these in a bleaching plant of a pulp mill.

16. Process according to claim 1, wherein said aqueous lignocellulosic pulp suspension comprises oxygen delignified pulp.

17. Process according to claim 1, wherein said aqueous lignocellulosic pulp suspension has a consistency of 1 to 18%, preferably 3 to 15%.

18. Process according to any one of the preceding claims 1 to 17, wherein said pulp suspension is subsequently processed into bleached paper or pulp.

19. Use of carbon dioxide for controlling the degradation of ligning in a process for bleaching an aqueous lignocellulosic pulp under acidic Conditions in the bleaching plant of a pulp mill, wherein a carbon dioxide providing medium is added to a lignocellulosic pulp suspension prior to or simultaneously with a bleaching agent to provide carbon dioxide in said pulp suspension at an acidic pH for controlling the degradation of lignin or its derivatives in their reactions with said bleaching agent, reacted lignin compounds subsequently being solubilized and removed by alkaline extraction.

20. A use according to claim 19, wherein said carbon dioxide providing medium is used in an amount effective to suppress the degradation of said lignin derivatives.

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