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(54) Pulping process

(57) The invention refers to a process for the removal of lignin from lignocellulose containing material, whereby the material prior to a pulping process is treated with a delignifying gas comprising gaseous compounds containing oxygen atoms. The delignifying gas can be a gas containing chlorine dioxide, nitrogen oxides, carbon dioxide or sulphur dioxide or mixtures thereof.

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Description

[0001] The present invention relates to a process for removing lignin from lignocellulose containing material wherein the material prior to a pulping process is treated with a delignifying gas comprising gaseous compounds containing oxygen atoms.

Background

[0002] The objective of a pulping process, whether it is a chemical pulping process, a high-yield process or a combination thereof, is to disrupt the structure of the lignocellulose containing material in fragments and/or lay bare individual fibres.

[0003] In chemical pulping processes the objective is to remove the lignin present in lignocellulosic containing material while minimising the damage and loss of the cellulose and hemi-cellulose fibres. In chemical pulping processes, often also referred to as cooking or digestion, the fibre source material is reacted with pulping chemicals at an elevated temperature over a time period to effect a specified degree of delignification. As such, the digestion process is a complex kinetic balance relating delignification to the cooking chemical(s), time and temperature. These variables are balanced to produce a pulp with the highest strength, greatest yield and the lowest lignin content.

[0004] In high-yield or mechanical pulping processes the basic objective is to disrupt the structure of the lignocellulosic containing material in fragments of variable dimensions by the use of mechanical treatment optionally in the presence of chemicals.

[0005] In chemical pulping processes, warm pulping chemicals are introduced into the digester along with the fibre source. The contents are subsequently heated as rapidly as possible to a predetermined digestion temperature, where the contents are held for a predetermined time. As the digestion proceeds the chemical concentration, temperature and time all effect the removal of the lignin from the fibre source.

[0006] However, as the chemical concentration increases there is more of a tendency for chemical attack on the cellulose and hemicellulose fibres. The chemicals react with the carbohydrates and break or cleave the fibre chains resulting in shorter polymer lengths and overall lower fibre strength, i.e. impaired viscosity. This effect is further increased as the temperature increases.

[0007] The solubility of the hemicellulose and cellulose fragments increases as the chemical concentration increases. Consequently, more cellulosic material is present in the pulping liquor. When the spent pulping liquor is removed from the pulp in the post-washing step, these materials are lost resulting in lower pulp yields.

[0008] Side reactions in the cooking process are very temperature dependent. Lignin removal proceeds slowly at first but accelerates markedly as the temperature rises above 160°C. Cellulose removal starts at 120-130°C and levels off when the maximum temperature is reached. Hemicellulose is composed of two main components, glucomannan and xylan. Glucomannan removal is rapid at first and becomes even greater as the temperature increases above 100°C. Xylan on the other hand follows the same pattern as lignin removal starting slowly at first and increasing rapidly as the temperature increases.

[0009] The rate of penetration and diffusion of the pulping chemicals into the fibre source determines the efficiency of the cook. Too little time results in non-uniform cooking and a poor pulp product, while too much time generates overcooked pulps where excessive damage has been done to the fibres via side reactions with the pulping chemicals.

[0010] From the above it can be seen that changes within the cooking process to increase lignin removal usually have a negative impact on the product pulp properties. Higher chemical concentrations and/or temperature result in lower strength and yield. Longer cooking times reduce the throughput through the Digester and lower the pulp production.

[0011] To achieve a given degree of delignification, various combinations of heat-up time, maximum temperature and time at the maximum temperature can be used. To simplify comparisons of different cooking conditions, the pulp and paper industry has developed the H-Factor. This value is the sum of the relative rates of reaction occurring in the cook. For a closer definition of the H-factor we refer to Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 20, 4th Ed., p. 535 which is hereby incorporated by reference. Using the H-Factor and the Kappa Number after the cook, different treatment and cooking processes can be compared on an equivalent basis. For example, reducing the H-Factor for the process would allow for shorter cooking/digesting times and increase pulp production in existing equipment or allow the digestion to be accomplished at a lower temperature resulting in improved yield and strength properties.

[0012] US 5474654 refers to a delignification process where chlorine dioxide gas is used on pulp obtained from pulping processes such as chemical kraft, sulfide or mechanical processes.

[0013] US 3591451 and US 3919041 disclose the use of gaseous chlorine dioxide subsequent a pretreatment step which may be either mechanical, chemical or a combination thereof.

[0014] In accordance with the present invention it has surprisingly been found that the lignin content of lignocellulose containing material can be reduced prior to pulping processes by providing a process according to the claims. More specifically, the invention relates to a process for the removal of lignin from lignocellulose containing material, where the material prior to a pulping process is treated with a delignifying gas comprising gaseous compounds containing oxygen atoms.

[0015] An advantage by treating lignocellulose containing material prior to a pulping process in accordance with the present invention is that the pulp yield and pulp properties such as pulp viscosity subsequent a pulping process are significantly improved at given (corresponding) H-factors.

[0016] Thus, by implementing the present invention in an existing pulping process, improved pulp yield and pulp viscosity is obtained at corresponding Kappa numbers.

[0017] Another advantage is that effluent streams originating from the pulping process are reduced since in-specific properties such as pulp yield and viscosity can be obtained at decreased pulping chemical dosages.

[0018] Another advantage with the present invention when used together with mechanical pulping or high-yield pulping processes is a reduction of energy input to the mechanical pulping process.

[0019] Further advantages of the present invention are apparent from the specification.

Detailed description of the invention

[0020] Suitable lignocellulose containing material used in the present invention can be any lignocellulose containing material derived from natural sources such as softwood, hardwood, gum, straw, bagasse and/or bamboo. The physical state of the lignocellulose containing material is not critical, however, a physical state providing a large surface area is preferred that maximises penetration of the delignifying gas and optionally processing chemicals. Suitably, the lignocellulose containing material is in the form of chips with a size which is governed by the process equipment and process parameters.

[0021] The lignocellulose containing material is suitably treated according to any method known to the skilled artisan which renders the diffusion of the delignifying gas within the fibre source to the lignin more effective such as steaming and/or evacuation.

[0022] According to the present invention the lignocellulosic material is treated with a delignifying gas comprising gaseous compounds containing oxygen atoms. Suitably, the gas contains chlorine dioxide, nitrogen oxides, carbon dioxides or sulphur dioxide or mixtures thereof. Preferably, the gas comprises chlorine dioxide. The chlorine dioxide containing gas preferably contains amounts of inert gases such as nitrogen, oxygen, air or steam or mixtures thereof. The chlorine dioxide containing gas may also contain small amounts of chlorine, however, the gas is suitably substantially free from of chlorine, preferably having less than 10% by volume, more preferably less than 1% by volume of chlorine. The concentration of gaseous compounds containing oxygen atoms, e.g. chlorine dioxide, in the gas is not critical for the invention. Thus, the lignocellulose containing material may be treated with substantially pure chlorine dioxide gas. The upper limit of gaseous compounds containing oxygen atoms comprised in the gas mixture is purely set by safety considerations. Suitable concentrations of gaseous compounds containing oxygen atoms, and specifically chlorine dioxide, comprised in the gas mixture are from about 0.05 up to about 100% by volume, more preferably from about 0.05 up to about 50 % by volume and most preferably from about 1 up to about 20 % by volume.

[0023] The delignifying gas, e.g. a gas containing chlorine dioxide, selectively attacks the lignin leaving the majority of the cellulose and hemicellulose fibres intact. The pre-removal of the lignin allows conditions to be optimised in the cooking process in terms of pulp yield, strength and production rate.

[0024] The use of a delignifying gas overcomes several unsolved problems discovered by earlier researchers using solutions in which a delignifying gas is dissolved. Treatment of the lignocellulosic containing material with solutions containing for example chlorine dioxide is limited by the rate of chlorine dioxide diffusion through the solution to the fibre source followed by the diffusion of the chlorine dioxide within the fibre source to the lignin. The result is a slow delignification process that works primarily on the fibre source surface and an aqueous effluent stream containing chlorine dioxide, dissolved fibre components and chlorides, which is difficult to treat in an environmentally correct manner.

[0025] It has been found that a delignifying gas does not have the diffusion barriers that limit the process when a solution is used. The gas passes rapidly and uniformly into the fibre source resulting in even delignification throughout the material. Furthermore, there are no aqueous effluent streams. The degraded lignin and lignin by-products are carried with the lignocellulose containing material into the cooking process where additional delignification occurs. The total dissolved lignin is then removed in the normal washing step following the cooking process.

[0026] The chlorine dioxide containing gas employed in the present invention is suitably produced using a chlorine dioxide generation process as described in the US patens US 4770868, US 5091166, US 5091197 and US 5380517, which all are incorporated by reference.

[0027] The delignifying gas is generally applied in amounts which provide concentrations suitable for removal of lignin to a desired degree. Usually, increased applied amount of delignifying gas increases the degree of delignification.

The charge of the gaseous compounds containing oxygen atoms is from about 0.5 kg active compound per tonne of oven dry lignocellulosic containing material up to about 300 kg active Cl_2 per tonne of oven dry material and more preferably from about 2 kg active compound per tonne of oven dry material up to about 15 kg active compound per tonne oven dry material. In case of chlorine dioxide containing gas the charge is preferably from about 0.5 kg active Cl_2 per tonne of oven dry lignocellulosic containing material up to about 300 kg active Cl_2 per tonne of oven dry material and more preferably from about 2 kg active Cl_2 per tonne of oven dry material up to about 15 kg active Cl_2 per tonne oven dry material.

[0028] The present invention may be performed at any location prior to chemical or mechanical pulping processes. The lignocellulose containing material is treated with the delignifying gas in any type of equipment. For practical reasons the equipment should be gas tight.

[0029] The delignifying gas is suitably admixed with the lignocellulose containing material in an equipment which is at any suitable pressure including atmospheric, subatmospheric or superatmospheric pressures. Suitably, the treatment is carried out at a pressure ranging from about 13 kPa up to about 300 kPa, preferably from about 53 kPa up to about 200 kPa. The most preferred pressure ranges from about 80 kPa up to about 120 kPa.

[0030] The temperature during the treatment according to the present invention is not critical and can be carried out at surprisingly low temperatures including ambient temperatures. The upper temperature level in the treatment is set by economical and safety considerations. Temperatures may range from about 25 °C up to about 200 °C, suitably from about 50 °C up to about 95 °C and preferably from about 60 °C up to about 90 °C.

[0031] According to one preferred embodiment of the present invention the lignocellulose containing material is pretreated prior to being subjected to the delignifying gas. The pretreatment may be accomplished in the same equipment used for the delignifying gas, yet, the pretreatment can also be performed in any suitable equipment located upstream the treatment with the delignifying gas. Suitably, the pretreatment includes various steaming and/or evacuation processes. The pretreatment is believed to open up the lattice structure of the lignocellulose containing material thereby improving the diffusion of the delignifying gas into the material.

[0032] The removal of lignin from lignocellulose containing material is preferably conducted prior to a chemical pulping process or a high-yield pulping process. Any chemical pulping process known to the skilled artisan can be employed within the scope of the present invention exemplified by the sulphite, bisulphite, kraft (sulphate), soda, soda anthraquinone (soda AQ) or organosolv process or modifications and/or combinations thereof. Suitable chemical pulping processes are further disclosed in Rydholm, Pulping Processes, Interscience Publisher and Ullman's Encyclopedia of Industrial Chemistry, 5th Edition, Vol.A18, 1991, pages 568 and 569, which documents all are incorporated by reference.

[0033] Of particular interest is the soda AQ process in conjunction with the treatment of the lignocellulose containing material with a delignifying gas if minimisation of malodours is an objective. The cooking liquor in a soda AQ chemical pulping process is essentially free from sulphur containing compounds which are the predominant compounds causing malodours. Accordingly, one further objective with the present invention is the minimisation of malodours.

[0034] High-yield or mechanical pulping processes are generally pulping processes where the yield typically is from about 70 up to about nearly 100% by weight. Commonly, high-yield pulping processes are referred to as stone groundwood (SGW), pressurised groundwood (PGW), refiner mechanical pulp (RMP) and modifications thereof, thermomechanical pulp (TMP), chemithermomechanical pulp (CTMP) or chemimechanical pulp (CMP). The basic principle in high-yield pulping processes is to disrupt the wood structure in fragments of variable dimensions by the use of mechanical treatments optionally in conjunction with chemicals such as sulphite. Usually a refiner is used, where wood ships are fed between two metal disks, of which at least one disc is rotating, and the wood fibres are separated by the action of grooves and bars located on the surface of the two disks. Obviously, energy usage is high in high-yield pulping processes, especially in TMP pulping processes.

[0035] Thus, one advantage with the present invention is that by treating lignocellulose containing material prior to high-yield pulping processes the input of energy in said pulping processes can be significantly reduced.

[0036] The process may be operated in either batch or continuous mode.

[0037] Subsequent the process according to the present invention the obtained pulp may be delignified and bleached using any available technique such as totally chlorine free bleaching (TFC), elementary chlorine free bleaching (EFC) or bleaching sequences containing chlorine, although not preferred. The pulp can also be subjected to oxygen delignification subsequent the pulping process.

[0038] To further illustrate the invention the following examples are provided. All parts and percentages are by weight unless otherwise specified. Temperatures are in degrees Celsius.

Example 1

[0039] Southern pine softwood chips obtained from a commercial pulp supplier were used. There was no special handling, separation or classification of the chips prior to the experiment.

[0040] A portion of the wood chips were cooked under Kraft pulping conditions with a fixed H factor to establish the baseline for the process. All the Kraft cooks were done at 170°C with a 22% effective alkali with a liquor to wood ratio of 4.55:1. The Kappa numbers of the untreated wood chips after cooking at various H factors are summarised in Table 1

Table 1:

Untreated Wood Chips			
H Factor	600	800	1200
Kappa No.	72	42	28.2

[0041] Samples of the wood chips were treated in a batch mode using chlorine dioxide containing gas at 2.7 volume % at a temperature of about 50°C and a pressure of about 100 kPa at different time periods. Each batch was then cooked under Kraft pulping conditions at an H factor of 600. The resulting Kappa Numbers after cooking are shown in Table 2.

Table 2 -

Kappa Number Results			
Batch	Treatment time [min]	Kappa After digestion	% Kappa Reduction
reference	0	72	0
1	15	57	27.8
2	30	46	36.1
3	60	38	47.2

Example 2

[0042] The procedure of example 1 was repeated with the difference that each batch was then cooked under Kraft pulping conditions at an H factor of 1200. The resulting Kappa Numbers after cooking are shown in Table 3.

Table 3 -

Kappa Number Results			
Batch	Treatment time [min]	Kappa After Cook	% Kappa Reduction
reference	0	28.2	0
1	15	27.9	1.1
2	30	25.4	9.9
3	60	24.4	13.5

Example 3

[0043] A sample of the wood chips according to example 1 was treated in batch mode using chlorine dioxide gas at 5.5 volume % at a temperature of about 50°C and a pressure of about 100 kPa for 30 minutes. The treated chips were then cooked under Kraft pulping conditions at an H factor of 600. The resulting Kappa Number after cooking was 38.

Example 4

[0044] A sample of the wood chips was treated in batch mode using chlorine dioxide gas at 2.5 volume % at a temperature of about 50°C and a pressure of about 100 kPa for 60 minutes. The treated chips were then cooked under Soda-Antraquinone conditions at an H factor of 1600. The resulting Kappa Number after cooking was equal to 37. Untreated chips cooked at an H-factor of 1600 under the same Soda-AQ conditions had a final Kappa Number of 64. Thus, a Kappa No. reduction of 42 %.

[0045] From the above examples it is evident that the kappa number after cooking was substantially lower at a constant H factor when the lignocellulose containing materials were pre-treated with chlorine dioxide containing gas prior to the cooking process.

[0046] This means that a given kappa number after cooking can be achieved at a lower H factor when using lignocellulose containing materials that have been pretreated with chlorine dioxide according to the invention as compared to untreated chips.

Claims

1. A process for the removal of lignin from lignocellulose containing material **characterised in that** the material prior to a pulping process is treated with a delignifying gas comprising gaseous compounds containing oxygen atoms.

2. A process according to claim 1 **characterised in that** the materia prior to a pulping process is treated with a gas containing chlorine dioxide, nitrogen oxides, carbon dioxide or sulphur dioxide or mixtures thereof.

3. A process according to any of the preceding claims **characterised in that** the material prior to a pulping process is treated with a gas containing chlorine dioxide.

4. A process according to any of the preceding claims, **characterised in that** the pulping process is a chemical pulping process.

5. A process according to any of the preceding claims, **characterised in that** the chemical pulping process is a kraft, a soda anthraquinone (soda-AQ) or sulfite pulping process.

6. A process according to claim 3, **characterised in that** the charge of chlorine dioxide containing gas is from about 0.5 kg active Cl_2 per tonne oven dry lignocellulosic material up to about 300 kg active Cl_2 per tonne oven dry lignocellulosic material.

7. A process according to claim 3, wherein the concentration of chlorine dioxide in the gas is from about 0.05 up to about 100 % by volume.

8. A process according to claim 3, wherein the pressure in the treatment with the chlorine containing gas is maintained from about 100 mmHg abs up to about 2000 mmHg abs.

9. A process according to claim 3, wherein the temperature in the treatment with the chlorine dioxide containing gas is maintained from about 25 up to about 200 °C.

10. A process according to claim 3, wherein the lignocellulose containing material prior to the treatment with the chlorine containing gas is subjected to steaming and/or evacuation.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 85 0037

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	GB 567 774 A (FOWLER, G.B.) 2 March 1945 (1945-03-02) * page 5, line 40 - line 55 *	1-5,10	D21C1/00 D21C1/04
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A	DATABASE WPI Section Ch, Week 198908 Derwent Publications Ltd., London, GB; Class F09, AN 1989-059880 XP002137869 & SU 1 416 576 A (LENINGRAD FORESTRY ACAD), 15 August 1988 (1988-08-15) * abstract *	1-6	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 May 2000	Bernardo Noriega, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 85 0037

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82