(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 025 807 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
18.02.2009 Bulletin 2009/08

(51) Int Cl.:
D21C 11/00 *(2006.01)*

(21) Application number: **07397025.3**

(22) Date of filing: **25.07.2007**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

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(54) **Method to recover chemicals in mechanical pulping**

(57) The present invention refers to a method to recover chemicals in mechanical pulping by evaporating mechanical pulping or recycled fibre plant effluent and burning the received concentrate under oxidative atmosphere to yield sodium carbonate. According to the invention said sodium carbonate is dissolved into water together with CaO in order to convert said sodium carbonate into sodium hydroxide at least partly.

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Description

[0001] This invention relates to a method to recover chemicals in mechanical pulping by evaporating mechanical pulping or recycled fibre plant effluent and burning the received concentrate in a temperature of at least 850 °C under oxidative atmosphere to yield sodium carbonate, the flue gases formed during the combustion are cooled by mixing a colder medium into the flue gases to reach a temperature of 700 to 600°C in order to prevent formed sodium carbonate to stick on surfaces, further cooling of the flue gas and sodium carbonate fume is carried out by converting its heat content into steam, and subsequently sodium carbonate ash is removed from the cooled flue gas flow and dissolved in water for reuse in impregnation prior to refining and/or in peroxide bleaching.

[0002] Bleaching may require a higher pH than is reached only with a sodium carbonate solution. According to the invention higher pH solution is generated from a sodium carbonate solution by recausticizing i.e. mixing CaO into the solution or alternatively by electrolytic decomposition of $N_{a2}CO_3$ into NaOH and CO_2. The recausticizing can be complete or partial depending on the pH requirement in peroxide bleaching. Alternatively calcium carbonate can be fed into the combustion furnace where it is calcined into CaO, or also ferric oxide as iron ore or titanium ore, ilmenite or any other autocaustizicing chemical can be fed to the furnace mixed with the concentrate or separately.

[0003] Wood can be processed chemically or mechanically to produce fibers suitable for papermaking. In chemical processes, lignin binding the fibers of wood together is dissolved in a chemical process at an elevated temperature and pressure. The chemical solution may be either acidic or basic. In an alkaline cooking process known as sulphate or kraft cooking NaOH and Na_2S are used as cooking chemicals. Pulp yield prior to bleaching is about 50%. Dissolved wood substances and cooking chemicals are recovered from the fiber in a washing system as a solution having a total solids content above 10%, the remainder being water. This spent liquor is concentrated by evaporation, whereupon it is combusted in a chemical recovery boiler under reducing conditions. The heat content of organic material dissolved from wood is recovered as high-pressure steam, from which electricity and process steam of a lower pressure is produced, generally by means of a turbogenerator. The chemicals form a melt at the bottom of the recovery boiler, which melt is dissolved in water. The solution having Na_2CO_3 and Na_2S as main components is converted by a conventional causticizing process into cooking chemicals suitable for reuse.

[0004] A cost-effective production of kraft pulp requires the above-described combustion of spent liquor and recovery of chemicals by causticizing. However, the equipment required is very costly.

[0005] Mechanical defibration or refining processes yield a bleached product at 90 to 97 % yield calculated on dry wood. A thermo mechanical pulping process, i.e. a TMP process, is frequently integrated with a paper mill. The chemical oxygen demand, i.e. COD, of the wastewater is 50 to 80 kg/ton TMP pulp produced. This wastewater is sent to a biological purifying process in conjunction with other wastewaters of the paper mill.

[0006] Chemi thermo mechanical refining or CTMP plants are not equally often integrated with a paper mill, but rather, the produced pulp is bleached, dried and transported for use elsewhere. The chemical oxygen demand of wastewater from this process may be twice or more compared to conventional mechanically refined pulp, whereby also the costs of waste water treatment in a biological treatment plant is roughly at least doubled. Furthermore, spent chemicals cannot be recovered, but instead, they are often dumped in nearby waterways thus forming a potential environmental hazard. In addition to be expensive, it is known that the operation of a biological treatment plant is problematic due to extractives dissolved from wood into the wastewater. An original function of the extractives is to protect wood against decay and microbes.

[0007] The CTMP-process produces fibres at a high yield of above 90%. The fibres in numerous applications can replace kraft pulp. In addition to the high fibre yield, the investment costs in relation to production capacity are considerably lower than in a sulphate pulping process.

[0008] In a CTMP plant, chips are traditionally impregnated with a Na_2SO_3 solution. Typically, chemical consumption in impregnation is about 20 kg / ton pulp or higher. After refining, the pulp is bleached by using at least 20 kg H_2O_2/ton pulp together with an equal amount of NaOH. Further, up to 20 kg sodium silicate per ton pulp is generally used as an inhibitor.

[0009] Today, also silicate free inhibitors are commercially available and are in industrial use.

[0010] Two mills are known to use oxidized green liquor as impregnating chemical i.e. using sodium carbonate as active chemical.

[0011] In US patent 6,945,181 a method to burn wastewaters from mechanical and chemi mechanical refining followed by fibre bleaching is described.

[0012] In said patent it is assumed that produced sodium carbonate solution can be used as sole alkali source in alkaline peroxide bleaching. However, it has been found that sometimes in bleaching for certain fibre grades higher pH is favourable than what can be achieved with sodium carbonate. In addition to mechanical pulping this may apply to other alkaline and organic material containing wastewater from a recycled fibre plant or any other plant using caustic and producing wastewater containing alkaline and organic material.

[0013] According to this invention said problem can be solved by carrying out causticizing (partial or complete) in a

carbonate ash dissolving vessel by adding CaO into it and to have normal causticizing reaction to proceed. Formed $CaCO_3$ is separated in a filter or centrifuge resulting in partly causticized liquor for bleaching.

[0014] Alternatively calcium carbonate can be fed into the combustion furnace where it is calcined into CaO. Also ferric oxide as iron ore, titanium oxide as titanium ore, sodium borate, ilmenite or any other autocaustizicing chemical can be fed to the furnace mixed with concentrate or separately.

Example:

[0015] In order to test partial recausticizing laboratory tests were carried out.

[0016] Oxidized green liquor from a running BCTMP mill was used for the tests. Said liquor had following analysis:

Total sodium	3.9 mol/l
SO_4	0.54 mol/l(a) or 0.40 mol/l(b) *
S_2O_3	0.025 mol/l
Dregs	30 mg/l
Causticity	33 %

[0017] Both laboratory grade CaO and mill CaO from a kraft pulp mill was used.

[0018] Lime was added into 1 l green liquor heated to 85 °C and mixed for 60 min

[0019] Lime dosage about 50 % of equivalent

[0020] Results are reported in the table below.

Test	Mill CaO	Lab CaO	settling	causicity %
1a	20 g/ 1 l		20 min	56
1b		18 g / 1 l	5 min	47
2a	20 g/ 1 l		20 min	59
2b		18 g / 1 l	15 min	62

[0021] The reults confirm that partial recausticizing is a real possibility.

[0022] Used calcium carbonate can be reused by drying it and by feeding it into a concentrate combustion furnace to be converted into calcium oxide or by mixing it into evaporated wastewater as moist and by feeding it into final concentrators and further into a furnace.

Claims

1. A method to recover chemicals in mechanical pulping by evaporating mechanical pulping or recycled fibre plant effluent and burning the received concentrate in a temperature of at least 850 °C under oxidative atmosphere to yield sodium carbonate,
the flue gases formed during the combustion are cooled by mixing a colder medium into the flue gases to reach a temperature of 700 to 600°C in order to prevent formed sodium carbonate to stick on surfaces,
further cooling of the flue gas and sodium carbonate fume is carried out by converting heat content of the flue gas and sodium carbonate fume into steam, and
subsequently sodium carbonate ash is removed from the cooled flue gas flow and dissolved in water for reuse in impregnation prior to refining and/or in peroxide bleaching,
characterized in that said sodium carbonate is dissolved into water together with CaO in order to convert said sodium carbonate into sodium hydroxide at least partly.

2. The method as claimed in claim 1, **wherein** limestone is mixed into concentrated wastewater resulting in a mixture to be fed into a concentrate furnace wherein limestone is converted into calcium oxide, and
the produced mixture of sodium carbonate and calcium oxide is mixed into water in order to have causticizing reactions to proceed.

3. The method as claimed in claim 1 or 2, **wherein** an autocausticizing agent, such as ferric oxide, titanium oxide or

sodium borate is mixed into the wastewater concentrate.

4. The method as claimed in claim 1, **wherein** Na_2CO_3 is converted into NaOH via an electrochemical method.

5. The method as claimed in claim 2, **wherein** sodium carbonate and lime are separated simultaneously from a flue gas stream exiting the concentrate furnace.

6. The method as claimed in claim 5, **wherein** solid sodium carbonate and lime are mixed with water to start a causticizing reaction to convert sodium carbonate into sodium hydroxide.

7. The method as claimed in claim 2, **wherein** limestone is out sourced or is recycled from separation of calcium carbonate from sodium hydroxide.

8. The method as claimed in claim 7, **wherein** recycled limestone is added into an intermediate concentrate before final concentration.

9. The method as claimed in any of the preceding claims, **wherein** calcium carbonate formed during causticizing is separated from the solution by a filter or a centrifuge.

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EUROPEAN SEARCH REPORT

Application Number
EP 07 39 7025

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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EPO FORM 1503 03.82 (P04C01)

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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