Abstract: The present invention relates to a process for producing substantially pure hydrogen sulphide (H₂S). The present invention also relates to a process for producing a new pre-treatment mixture, which is to be used in a pre-treatment step before cooking in processes for producing kraft pulp. The present invention also relates to a process for producing kraft pulp, said process comprising the above mentioned processes.
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KRAFT PULPING PROCESS

TECHNICAL FIELD

The present invention relates to a process for producing substantially pure hydrogen sulphide (H₂S). The present invention also relates to a process for producing a new pre-treatment mixture, which is to be used in a pre-treatment step before cooking in processes for producing kraft pulp. The present invention also relates to a process for producing kraft pulp, said process comprising the above-mentioned processes.

BACKGROUND OF THE INVENTION

There are several methods known disclosing pre-treatment of wood chips with H₂S before the cooking in processes for producing kraft pulp. This pre-treatment is used in order to increase the kraft pulp yield as the H₂S will prevent degradation of the carbohydrates. However, none of these methods has been commercialized, i.e. adapted to large scale production of pulp probably due to safety reasons as H₂S is a very toxic and also very explosive gas and also due to problem of obtaining a safe environment when having a large scale production. Furthermore, there is not available any effective or economic recovery cycle for the H₂S, which is applicable to a kraft mill process.

H₂S is, as mentioned above, a very toxic and explosive gas and therefore has to be handled with care. There are different processes available for obtaining H₂S. US 3560329 discloses that H₂S can be obtained from black liquor, however the disclosed process has problems with fouling which is caused by non-soluble lignin in the evaporation train. CA 923255 also discloses a process for obtaining H₂S, wherein the black liquor is treated with flue gases and thereafter the obtained gas mixture is purified by using an absorption/desorption process to purify the gas mixture. The problem with said process is that also solid substances are obtained, which requires expensive and advance equipment. Furthermore, this process also requires the addition of additional substances, which makes the process more complicated. Hence, the processes used for producing or regenerating H₂S are often very complex as they comprise many steps and consumes large amount of energy. It has been suggested that H₂S can be made from green liquor by formation from hydrogen sulphide ions. However, available processes provide products comprising large amounts of impurities and therefore large amounts of gas will be needed to obtain the desired yield of the pulp.
WO 2004/092478 discloses a method for the pre-treatment of chips that are fed to a kraft process, the method is characterized in that the chips before heating in a closed pre-treatment step are formed into a slurry with an acidic treatment fluid, after this the acidified chips are drained and then heated with a sulphide-rich alkali impregnation liquor and therefore $H_2S$ is formed locally. The disadvantage with this process is the relative modest yield increase caused by the inefficient formation of $H_2S$. Also, the process cannot be completed since suitable sulphide-rich liquors are not available in kraft mills of today.

A.R. Procter (Pulp and Paper Canada Vol. 77, Nov 12/December 1976), US 3520 773 and US 3841962 discloses hydrogen sulphide pre-treatment of lignocellulosic materials in alkaline pulping processes. The processes disclosed do not give as high pulping yield as when high pressure $H_2S$ is applied. Additionally, the processes are very complex and require many process steps, this makes the energy demand large, mainly because of the crystallization step.

Hence, there is a need for having a safe and sustainable process solution for producing kraft pulp in large scale when using $H_2S$ in a pre-treatment step, which will provide both good pulp yield and be applicable in large scale and which only requires a minimum amount of added chemicals. Furthermore, in order for the $H_2S$ treatment to be as efficient as possible there is a need for the pre-treatment solution to have a buffering capacity and also for the partial pressure for the $H_2S$ to be as high as possible and that the time and temperature to be high enough and the reaction time to be long enough so that the reactions should have time to occur. Also, in order to minimize any effect on the rest of the process and the Na/S ratio in the recycling process, the $H_2S$ used in the pre-treatment should be prepared within the process.

The present invention, besides from overcoming the problems mentioned above, also aims to fulfill these requirements.

**SUMMARY OF THE INVENTION**

The present invention provides a process for producing substantially pure hydrogen sulphide ($H_2S$). The substantially pure $H_2S$ is, according to the present invention, in gaseous form. The advantage of having a substantially pure $H_2S$ is that the process equipment used in the kraft pulp mill will be cheaper and simpler as the total pressure can be minimized. Also, with said process, it will be possible to have a closed system for
producing pulp, i.e. in the sense that almost all chemical substances used are recycled so there will be almost no emissions to the environment, which will provide a safer environment within the mill. Furthermore, another advantage of having the present invention within a kraft pulp mill, is that it will be much easier to control the total process system compared to a case when the H$_2$S is formed in-situ.

The present invention is also providing a process for producing pre-treatment mixture and the use of said pre-treatment mixture in a process for pre-treating wood before the kraft cooking process. The wood can be in the form of chips, shives, saw dust etc. The pre-treatment mixture has a high content of H$_2$S and a high buffering capacity. When the produced pre-treatment mixture is used in a pre-treatment process, said process will be very effective due to the high partial pressure of H$_2$S and the sufficiently high reaction temperature, i.e. a temperature in the range of from 100 to 180 °C, such as from 120 - 160 °C, such as 140 °C. Hence, the process for producing the pre-treatment mixture uses an efficient and short recirculation process of pre-treatment mixture which will provide a high concentration of H$_2$S in the recirculated liquor and therefore reduce the charge of fresh H$_2$S (g) to the pre-treatment process, which in turn will reduce the size of the needed stripper for H$_2$S generation, and thereby reduce the costs.

The present invention will also provide a large scale kraft process comprising the two processes mentioned above, said process has a cheap and simple equipment as this process only needs one “main process equipment” when forming H$_2$S (g). Hence, the present invention provides a process integrating the processes disclosed above for producing pulp, more specifically kraft pulp. The obtained pulp is provided in excellent yield and also has good pulp properties.

**DEFINITIONS**

The terms "kraft process" and "sulphate process" are used interchangeably within the present application and describes a technology for chemically treating wood in order to liberate fibers from each other. The process entails treatment of wood, e.g. in the form of chips, with a mixture of sodium hydroxide and sodium hydrosulphide, known as white liquor, which degrades lignin and makes it soluble.

The terms "hydrogen sulphide" and "dihydrogen sulphide", are used interchangeably herein to denote the chemical compound with the formula "H$_2$S". It is a colorless, very
poisonous and flammable gas with the characteristic foul odor of expired eggs perceptible at concentrations as low as 0.00047 parts per million.

The term "green liquor" as used herein is intended to mean the dissolved melt of sodium carbonate and sodium sulphide from the recovery boiler in the kraft process. An example of a composition of a green liquor of a kraft mill is a composition comprising 3.36 mol/kg Na\textsuperscript{+}, 0.20 mol/kg K\textsuperscript{+}, 0.68 mol/kg OH\textsuperscript{-}, 0.60 mol/kg HS\textsuperscript{-}, and 1.13 mol/kg CO\textsubscript{3}\textsuperscript{2-}. The term "sulphide-lean green liquor" as used herein is intended to mean green liquor comprising almost no sulphur, such as less than 10 % of the originating sulphur content of the green liquor, such as less than 9, 8, 7, 6, 5, 4, 3, 2 or 1% of the originating sulphur content of the green liquor.

The term "short recirculation" as used herein is intended to include the internal loop of H\textsubscript{2}S containing impregnation liquor around the H\textsubscript{2}S pre-treatment process step. It includes the pre-treatment vessel, piping and the impregnation liquor storage vessel.

In the present application the term "closed system" is intended to include a system which has almost no emissions of H\textsubscript{2}S to the surroundings. Further, all surplus H\textsubscript{2}S from the chip impregnation is collected and re-circulated in the short recirculation. This has both the advantage of lower emissions to the environment and substantially lower chemical costs.

The term "stripper" as used herein is intended to mean a kind of distillation column wherein a gas is desorbed from a liquid by using a stripping agent, example of a stripping agent is steam (vapour). Stripping is a physical separation process where one or more components are removed from a liquid stream by a vapor stream

The term "main process equipment" is used for equipment in which a process step is conducted. The main process equipment includes process parts such as pumps, mixers, heat exchangers etc.

The term "substantially pure H\textsubscript{2}S" as used herein is intended to mean H\textsubscript{2}S gas consisting less than 15 weight% impurities, such as less than 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2 or 1 weight% impurities. The impurities are for example carbon dioxide and steam. Example of a substantially pure H\textsubscript{2}S is a H\textsubscript{2}S gas consisting of 90 weight% H\textsubscript{2}S and 10 weight% CO\textsubscript{2}.
In the present context is the abbreviation (g) intended to mean gas and the abbreviation (aq) intended to mean dissolved in water.

The abbreviation "TTA" means Total Titratable Alkali and is the sum of the concentration of all bases present in liquor which can be titrated with strong acid (in total 3 inflexion points). Examples of such bases are NaOH, Na$_2$S and Na$_2$CO$_3$ (as NaOH) measured by titration according to SCAN 30:85. SCAN is an international standard for processes/analytical methods used within the technical field.

The abbreviation "ΕΑ" stands for Effective Alkali and is the concentration of strongly alkaline constituents determined by titration of a sample of white or green liquor. It is determined by titration with strong acid to the first inflexion point in the procedure SCAN 30:85. In practice this is considered to be the concentration of hydroxide ions.

In the present context, the term "recirculated liquor" is intended to mean the used pre-treatment liquor prior to the make-up charge of green liquor and H$_2$S.

In the present context, the term "bar(a)" means the absolute pressure in bar.

It is to be understood that even though exact values are given in the present context, these values also include tolerances.

**BRIEF DESCRIPTION OF THE FIGURES**

- **Figure 1**: Process for producing substantially pure H$_2$S(g)
- **Figure 2**: Process for pre-treatment of wood before cooking
- **Figure 3**: High-yield kraft pulping process

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention relates to a process for producing substantially pure H$_2$S, wherein said process comprises the steps of:

- a) treating a green liquor with an acid to form an alkali-lean green liquor;
- b) adding the obtained alkali-lean green liquor from a) to a vessel;
- c) adding steam to said vessel;
- d) removing sulphur-lean green liquor from said vessel;
- e) treating the removed sulphur-lean green liquor with an acid;
- f) adding the obtained liquor from step e) to said vessel;
g) removing steam from the gas phase; and
h) removing the substantially pure H₂S from the vessel.

The steps a)-f) will result in gas formation and separation of the gas from the liquors.

According to one embodiment of the present invention the separated gas from a)-f) may be treated in a condenser in step g) in order to obtain substantially pure H₂S (g) in step h).

According to the process of the present invention the word "treating" means mixing, injection etc., as there are different methods to obtain the result of each step, e.g. in step a) treating means mixing.

According to one embodiment of the present invention, step a) is performed at a temperature of from 60 to 95°C, such as from 80 to 85°C.

According to one embodiment of the present invention, the pressure of the vessel is from 0.05 to 1 bar(a), such as from 0.15 to 0.3 bar(a). According to one embodiment of the present invention, the temperature of the vessel is from 25 to 95°C.

According to one embodiment of the present invention, the ratio of steam flow and H₂S production flow is from 10 to 40, such as from 15 to 20.

According to one embodiment of the present invention, said green liquor is obtained from the recovery cycle of the kraft pulping process and wherein said green liquor comprises a molar ratio of Na₂CO₃/Na₂S of ≥ 1.5.

According to one embodiment of the present invention, a distillation column is used as a vessel, such as a stripper.

According to one embodiment of the present invention, the acid of step a) and/or step e) is carbon dioxide.

Figure 1 shows a schematic representation of the process of the present invention for producing substantially pure H₂S (g). Part of the green liquor flow of the pulp mill is treated with an acid, such as carbon dioxide. The acid neutralizes the hydroxide ions in the green liquor and alkali-lean green liquor is formed. Thereafter, the alkali-lean green liquor is introduced to the main process equipment, preferably a stripper with a packed
bed. To the stripper a sulphur-lean green liquor is also added, which is formed from a treatment of the bottom product of the stripper with an acid such as carbon dioxide. The two liquors will react and H₂S (g) will be obtained. The obtained H₂S (g) will be stripped of using a stripping agent, such as steam. The gaseous product will exit the stripper and the substantially pure H₂S will be obtained after removal of steam. According to one embodiment of the present invention the substantially pure H₂S will also consist of CO₂ (g) and H₂O (g). The stripper is preferably operated in such a way that the concentration of CO₂ (g) is minimized.

The process of producing substantially pure H₂S is, according to the present invention, preferably performed using a stripper as equipment. However, person skilled in the art are aware of other suitable equipment.

The driving force of the stripper is the difference in partial pressure in the vapor phase and the amount of substances in the liquid phase. According to the present invention, simultaneous chemical reactions will take place in the stripper, i.e. a reactive distillation. Furthermore, it has been found that stripping of H₂S is more effective at lower total pressures because this reduces the partial pressure of H₂S in the stripper. A reduction of the total pressure enables a reduction in either stripping steam flow or the reflux flow of sulphide-lean green liquor. The low pressure of the stripper also improves the safety as a leakage would not cause a hazardous environment outside the stripper. In this way, the zone in which pressurized H₂S is handled can be minimized.

The reaction of the stripper is the following: NaHS + NaHCO₃ ⇌ Na₂CO₃ + H₂S (g).

According to one embodiment of the present invention, the stripper has the following process data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S yield</td>
<td>95 %</td>
</tr>
<tr>
<td>H₂S production</td>
<td>900 kg/h</td>
</tr>
<tr>
<td>Feed temperature</td>
<td>85°C</td>
</tr>
<tr>
<td>Feed green liquor</td>
<td>46000 kg/h</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.2 bar(a)</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>Steam</td>
<td>16000 kg/h</td>
</tr>
<tr>
<td>CO₂</td>
<td>1700 kg/h</td>
</tr>
</tbody>
</table>
The obtained gas composition consists of about 90 % \( \text{H}_2\text{S} \) and about 10 % \( \text{CO}_2 \).
However, the stripper can be operated in many ways, as well known to a person skilled in the art.

5 The present invention also relates to a process for producing a pre-treatment mixture, said process comprises the steps of:
   i. adding substantially pure \( \text{H}_2\text{S} \) to a liquor; and
   ii. adding a green liquor to the obtained liquor from step i;
wherein said liquor of step i) is a liquid obtained from a kraft pulping process and wherein said liquor comprises \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{HS}^- \), \( \text{H}_2\text{S} \), \( \text{CO}_3^{2-} \) and dissolved wood components.

In said process, step i. and step ii. do not have to be carried out in any specific order, i.e. step ii. might be carried out before step i. and step i. might be carried out before step ii.
However, the lead time between said steps might be long.

10 According to one embodiment of the present invention, the liquor of step i) has been used in earlier pre-treatment processes.

According to one embodiment of the present invention, the obtained pre-treatment mixture comprises sulphur so that the total amount of sulphur is greater than 1 mol S/kg wood, such as greater than 1.5 mol S/kg wood. According to one embodiment of the present invention said sulphur is in the form of \( \text{HS}^- \) or \( \text{H}_2\text{S} \).

According to one embodiment of the present invention, the pH of the recirculated liquor is in the range of from 5 to 9, such as from 6 to 8.

According to one embodiment, the total titratable alkali (TTA) of the pre-treatment liquor is from 1 to 10 %, such as from 3 to 6 %.

30 According to one embodiment, the temperature of the pre-treatment liquor is from 100-180°C, such as 130-160°C.

The present invention also relates to a process for the pre-treatment of wood wherein said wood is treated with the pre-treatment mixture produced as disclosed above. The wood might be in the form of chips, shives, saw dust etc.
Figure 2 shows a schematic representation of the part of the present invention wherein the pre-treatment of wood with $H_2S$ prior to kraft cooking is taking place. Wood is added to the pre-treatment vessel wherein the wood is treated with a buffer solution, which comprises recirculated buffer solution, green liquor and $H_2S$. After the pre-treatment process, the used pre-treatment liquor is displaced to the recirculation cycle (wherein a pre-treatment liquor storage vessel can be incorporated). The treated wood thereafter undergoes kraft cooking (either in the pre-treatment vessel or in a separate digester). The re-circulated pre-treatment liquor is rich in $H_2S$ (aq) and is re-used in subsequent pre-treatments after necessary make up of green liquor and $H_2S$ (g).

The present invention also relates to kraft processes comprising the processes of the present invention as disclosed above for producing high-yield kraft pulp.

Kraft processes are highly alkaline processes comprising NaOH and $Na_2S$ as the active chemicals in the cooking liquor. This is a difference compared to sulphite processes wherein $SO_2$, water and a base cat-ion are used as cooking chemicals, example of a sulphite process is disclosed in e.g. SE383866. Many different bases can be used in the sulphite process (Ca, Mg, Na and $NH_3$). The composition of the resulting spent cooking liquors and the corresponding regeneration of cooking chemicals therefore differ between sulphite and kraft processes.

The chemical recovery of used kraft cooking liquor (black liquor) starts with evaporation of water followed by incineration of organic material in a recovery boiler which also regenerates cooking chemicals in the form of a melt which mainly consists of $Na_2S$ and $Na_2CO_3$. This melt is dissolved in weak liquor (water and some alkaline components) and clarified to give *kraft green liquor*. Example of a green liquor composition is a composition comprising 80-100 g $Na_2CO_3$, 40-50 g $Na_2S$, 3-6 g $Na_2SO_4$, 5-20 g NaOH and 5-10 g other dissolved Na compounds per litre (calculated as $Na_2O$). The green liquor is processed further to produce the white liquor used for cooking.

The "sulphite green liquor" from a sodium based process is very different from kraft green liquor. Even though the brown liquor (in analogy to black liquor for the kraft process) is burned in a kraft type furnace the resulting melt consisting of sodium sulphide and sodium carbonate is much richer in sulphur.
The kraft process according to the present invention can be used either for a continuous or a batch digester. An example of such a process is a process comprising a pre-treatment of wood prior to kraft cooking with \( \text{H}_2\text{S} \) in diluted kraft green liquor with a TTA of 2-8 % on wood and liquor to wood ratio of 3-8 kg/kg. Example of such a process is shown in figure 3. The wood are pre-treated with the present pre-treatment mixture according to the present invention before they are fed into the sulphate cooking process as shown in figure 3.

The wood material, for example in the form of chips can be obtained according to methods known to a person skilled in the art. The wood chips may also prior to said pre-treatment step be pre-treated with steam to improve the impregnation with pre-treatment liquor. After the pre-treatment, the pre-treatment liquor will be displaced to the pre-treatment liquor vessel by another liquor (batch case) or in the continuous case first displaced using counter-current washing in the pre-treatment vessel, and then pumped to the digester in a standard manner.

Re-use of impregnation liquor, which therefore is saturated with \( \text{H}_2\text{S} \) (aq) limits the need for makeup \( \text{H}_2\text{S} \) (g) at steady state for a given yield increase after cooking compared to a standard kraft process. Without the re-use of impregnation liquor, the necessary make up for the same yield increase would be about doubled.

The key to the relatively low make-up need is the internal loop of impregnation liquor which after the impregnation phase is displaced together with needed makeup liquor to the impregnation liquor vessel. After a few cooks a steady state concentration of \( \text{H}_2\text{S} \) (aq) in the liquor will be attained.

Hence, the present invention is based on the finding that in order to be able to scale-up pre-treatment processes comprising \( \text{H}_2\text{S} \), it is important to have a substantially pure \( \text{H}_2\text{S} \) and to reduce the amount of \( \text{CO}_2 \), the reduction of \( \text{CO}_2 \) will also reduce the total pressure of the process at a constant partial pressure of \( \text{H}_2\text{S} \). According to the present invention the \( \text{CO}_2 \) is reduced since the amount of added \( \text{CO}_2 \) will be minimised and the stripper should be operated in such a way that the equilibrium and kinetics favours the formation of \( \text{H}_2\text{S} \) (g) and suppresses the formation of \( \text{CO}_2 \) (g) from present \( \text{CO}_3^{2-} \).
It is necessary to have a steady flow of $H_2S$ to the pre-treatment mixture and thereby to achieve the desired yield of the pulp. As mentioned above, in order to minimize the effect on the rest of the process, especially in regard to the Na/S balance in the recycling process, it is necessary for the $H_2S$ that is used in the pre-treatment step to be prepared within the kraft process.

In figure 3 the process system for producing high yield kraft pulp is schematically presented incorporating both production of substantially pure $H_2S$ (g) and the production of high yield pulp based on $H_2S$ pretreatment using this substantially pure $H_2S$ as a make-up chemical.

Hence, the present invention provides a process for producing kraft pulp, which has taken the whole process system of the kraft pulping process under consideration. Furthermore, the processes according to the present invention can be integrated into a large scale kraft pulping process without any need of additional process equipment installations (except those mentioned in the present invention). Also, the present invention relates to a process for producing substantially pure $H_2S$ and also to a kraft pre-treatment process, wherein the pre-treatment liquor is recirculated in a closed system. The pre-treatment liquor is rich in $H_2S$ due to unconsumed gas from earlier pre-treatments, and the need for fresh make-up $H_2S$ is therefore reduced.

The present invention is further illustrated by the non-limiting example below.

**EXAMPLE**

**Pilot plant: $H_2S$-impregnation in diluted green liquor followed by kraft cooking**

The whole process was performed in a digester system wherein liquors were allowed to be transferred between vessels and $H_2S$ gas could be charged to the system.

2400 grams of spruce chips was first steamed to maximize the impregnation efficiency. Thereafter, the impregnation liquor was pumped to the impregnation vessel in a volume corresponding to a liquor to wood ratio of 5:1. The impregnation liquor used was diluted industrial kraft green liquor corresponding to a total of 4 % TTA. After 5 minutes liquor circulation in room temperature, fresh $H_2S$ gas was charged (25 g/kg chips) to the vessel.
The temperature of the vessel was increased to 140°C during 15 minutes and H₂S was allowed to react with the chips at 140°C for 40 minutes.

The free liquor in the digester was displaced through the digester top to the impregnation liquor vessel charging liquors from the bottom of the digester using the following sequence: a) make-up chemicals needed to retain correct strength of the impregnation liquor (this liquor was also displaced to the impregnation liquor vessel), b) water to make sure there would not be any cooking liquor transferred to the impregnation liquor vessel and c) cooking liquor to hydraulic fill the digester (21.5 % EA).

Temperature was then increased to cooking temperature (170°C) and a standard circulation cook was performed until a Kappa number of 30-32 was reached (H-factor 1700, residual alkali 5-6 g/l). For the first cook a yield increase of about 1% (on wood) was obtained compared to a standard reference cook without the H₂S impregnation.

After multiple (5) H₂S impregnation steps reusing the displaced impregnation liquor, an equilibrium of H₂S was built in the impregnation liquor vessel, and at this steady state a pulp yield increase of 5% (on wood) was obtained after cooking. Using a conventional bleaching sequence this increased yield was remained.

A mill scale process for recycling of pre-treatment liquor and charging of necessary make-up H₂S (internally produced from green liquor in the stripper) can be achieved for batch digesters by using the process as disclosed in this example (the digester is used both for the pre-treatment and the cooking phase). For continuous digesters, there will be a need for a separate pre-treatment vessel (as shown schematically in Figure 2) prior to the digester, which could be in the form of a standard pre-impregnation vessel (used in 2-stage cooking), in which a counter-current washing zone at the bottom is incorporated.
CLAIMS

1. A process for producing substantially pure $\text{H}_2\text{S}$, wherein said process comprises the steps of:
   a) treating a green liquor with an acid to form an alkali-lean green liquor;
   b) adding the obtained alkali-lean green liquor from a) to a vessel;
   c) adding steam to said vessel;
   d) removing sulphur-lean green liquor from said vessel;
   e) treating the removed sulphur-lean green liquor with an acid;
   f) adding the obtained liquor from step e) to said vessel;
   g) removing steam from the gas phase; and
   h) removing the substantially pure $\text{H}_2\text{S}$ from the vessel.

2. Process according to claim 2, wherein the pressure of the vessel is from 0.05 to 1 bar(a), such as from 0.15 to 0.3 bar(a).

3. Process according to claim 1 or claim 2, wherein the ratio of steam flow and $\text{H}_2\text{S}$ production flow is from 10 to 40, such as from 15 to 20.

4. The process according to any one of claims 1 to 3, wherein said green liquor is obtained from the recovery cycle of the kraft pulping process and wherein said green liquor comprises a molar ratio of $\text{Na}_2\text{C}_3\text{O}_3/\text{Na}_2\text{S}$ of $\geq 1.5$.

5. A process according to any one of claims 1 to 4, wherein a distillation column is used as a vessel, such as a stripper.

6. A process according to any one of claims 1 to 5, wherein the acid of step a) and/or step e) is carbon dioxide.

7. A process for producing a pre-treatment mixture, said process comprises the steps of:
   i. adding substantially pure $\text{H}_2\text{S}$ to a liquor;
   ii. adding a green liquor to the obtained liquor from step i);
wherein said liquor of step i) is a liquor obtained from a kraft pulping process and wherein said liquor comprises $\text{Na}^+$, $\text{K}^+$, $\text{HS}^-$, $\text{H}_2\text{S}$, $\text{C}_3\text{O}_3^{2-}$ and dissolved wood components.
8. Process according to claim 7, wherein the liquor of step i) has been used in earlier pre-treatment processes.

9. Process according to claim 7 or claim 8, wherein the obtained pre-treatment mixture comprises sulphur so that the total amount of sulphur is greater than 1 mol S/kg wood, such as greater than 1.5 mol S/kg wood.

10. Process according to any one of claims 7 to 9, wherein the pH of the recirculated liquor is from 5 to 9, such as from 6 to 8.

11. Process according to any one of claims 7 to 10, wherein the total titratable alkali (TTA) of the pre-treatment liquor is from 1 to 10 %, such as from 3 to 6 %.

12. Process according to any one of claims 7 to 11, wherein the temperature of the pre-treatment liquor is from 100-180°C, such as 130-160°C.

13. A process for the pre-treatment of wood wherein said wood is treated with the pre-treatment mixture produced according to any one of claims 7 to 10.

14. A process for producing a high-yield kraft pulp, said process comprises a process according to any one of claims 1 to 6 and/or a process according to any one of claims 7 to 13.
Figure 2