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(54) Title: METHOD FOR RECYCLING SULPHUR IN A PULP PRODUCTION PROCESS

(57) Abstract: The invention relates to a method for recycling sulphur in a process for producing paper or paperboard. In the method of the invention, (a) the bisulphite formed from the sulphur recovered in the process cycle is converted to bisulphate by means of an oxidant, the bisulphate being further used as a recycled acid in different process steps, and/or (b) the bisulphite formed from sulphur recovered from the process cycle is converted into sulphur dioxide by means of an acidic substance, the sulphur dioxide being further used in different process steps.



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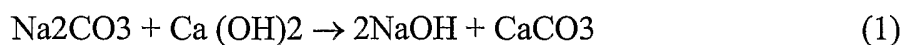
Method for recycling sulphur in a pulp production process

The invention relates to a recycling method of sulphur for treating sulphur-containing compounds contained in gases recovered from a pulp process, especially from a chemical pulp process, in order to produce sulphur-containing products usable and recyclable in the process.

State of the art

In recent years there have been a special focus on an efficient and environmentally friendly use of energy in preparation processes of pulp from raw wood. Thus, for instance, in chemical pulp process, the use of additives has increased and efforts have been made to minimise emissions both of malodorous reduced sulphur compounds and of sulphur dioxides. The emission limits imposed by air protection authorities are becoming increasingly stringent, therefore it is a target nowadays to recover the sulphur dioxide generated in malodorous sulphur compound combustion and other process steps. Sulphur dioxide can be purged from flue gases e.g. in gas scrubbers in which sulphur dioxide is converted into sodium bisulphite by means of sodium hydroxide in a manner known *per se*.

Processes include the sulphate process as being currently the most frequently used chemical pulp process. In this process, the alkaline cooking liquor, i.e. white liquor, contains approximately three parts of sodium hydroxide, NaOH, and one part of sodium sulphide, Na₂S. The process includes as an essential part the recovery of the cooking chemicals and certain by-products. After the cooking, the pulp is scrubbed, the fatty and rosin acids derived from wood extractives contained in the pulp being separated from the wash liquor, i.e. the black liquor. During pulp digestion, the major portion of wood lignin is dissolved in the cooking liquor, which is combusted in a soda recovery boiler, where the sulphur and sodium contained in the cooking liquor are also recovered. A great part of the water of black liquor is evaporated, after which the residue is combusted in a soda recovery boiler. In the soda recovery boiler, the organic substance is removed by combustion and the inorganic portion of black liquor remains, which at this stage consists mainly of sodium carbonate, Na₂CO₃, and sodium sulphide Na₂S. The obtained molten salts are dissolved into water from the soda recovery boiler, resulting in "green liquor". The green liquor is fed to causticisation, where sodium carbonate reacts with calcium hydroxide in the aqueous solution:



The produced calcium carbonate is further regenerated in a lime kiln by burning it into calcium oxide, which is slaked with water, forming calcium hydroxide:



The white liquor obtained from causticisation contains principally sodium hydroxide and sodium sulphide. The composition of such white liquor has a notable impact on the properties of the pulp to be digested. Since the process is in principle closed in this respect as well, i.e. the cooking chemicals are not consumed during the process, it is crucial to maintain the sulphur:sodium ratio of the chemical cycle in balance. Nowadays, in controlling said balance the major problem is the excess sulphur which originates from sulphuric acid introduced into the process. Cellulose mills have several different subprocesses producing sulphur, one of the main ones being the tall oil production process. In addition sulphur is introduced into the process e.g. from the wood itself, from water, from the fuel oil of the lime kiln and from magnesium sulphate used in oxygen bleaching.

During sulphate pulp cooking, among wood additives, resin fatty acids and resin acids are saponified into sodium salts, i.e. soap, and there will also be residual unsaponified organic components, depending on the species of raw wood used. These soaps are further micellised, with a certain amount of unsaponified substances dissolved into the micelles. Usually pulp digestion is followed by a scrubbing step, the solution removed from this step, black liquor, comprising soap micelles rising to the surface of the liquor in the form of raw soap. The soap formed is separated from black liquor by decantation, after which it can be split into tall oil by means of sulphuric acid and heat. Consequently, splitting signifies an acid treatment, in which the soap separated from the surface of black liquor is cooked together with sulphuric acid, corresponding acids being produced from the water-soluble sodium salts of fatty and resin acids, the mixture of acids being referred to as raw tall oil. The reaction occurring during splitting has the following formula:



In practice, the sulphur acid addition should be such that the pH will decrease below 4. The tall oil obtained during splitting is separated from the pulp press water phase, which is recycled to the chemical circulation system of the pulp mill.

Waste acid from e.g. a chlorine dioxide reactor, derived e.g. from the well-known Mathieson process, can be used as the splitting acid, which is in fact frequently done. Since the aqueous phase produced during splitting is recycled to the chemical circulation system, sulphur in dissolved form will also enter the chemical circulation system. Along with waste acid, a notable amount of sulphur will enter the process, because waste acid contains sodium sulphate or sodium sesquisulphate in considerable amounts besides sulphuric acid. This waste acid also contains chlorine compounds, i.e. sodium chloride and sodium chlorate, which cause corrosion problems. Depending on the wood species and the site of growth, tall oil splitting may introduce sulphur into the process at a rate of 2 to 4 kg/t of pulp. The sulphur loss of a modern pulp mill, i.e. the sulphur that is not recycled but is removed from the chemical circulation system, can be compensated with sulphurous chemicals generated during the preparation of bleaching chemicals, whose amount even exceeds the sulphur demand of the pulp mill. Especially splitting of tall oil soap introduces a considerable excess of sulphur into the process.

Further sulphur is additionally introduced in the process also in the step of applying a soluble magnesium compound during oxygen delignification, typically magnesium sulphate.

It will then be necessary to remove excess sulphur from the process. If excess sulphur is removed from the process in the form of sodium sulphate, the removed sodium has to be compensated with fresh liquor, resulting in increased sulphur removal cost. In the control of the chemical balance of a sulphate pulp mill, it is essential to control the ratio of sulphur to sodium, i.e. the sulphidity. Tall oil soap splitting is a major cause of imbalance in the sulphidity of a sulphate pulp process. If excess sulphur is removed e.g. in the form of fly ash, sodium will escape simultaneously, requiring compensation with fresh liquor introduced into the process.

At modern sulphate cellulose mills, sulphurous gases are collected from many different sources. The amount of sulphurous compounds thus formed has typically

been approx. 2 kg/t of pulp, however, using e.g. black liquor evaporation, the amount may rise to 5 kg/t, even to 10 kg/t of pulp. Sulphurous compounds can be incinerated and the sulphur dioxide formed can be absorbed into a NaOH solution, yielding a sodium bisulphite solution.

WO patent specification 9411571 discloses soap acidification by means of a large excess of sodium bisulphite solution relative to the soap amount for the recycling of sulphur with a view to reuse in tall oil production. However, it will be necessary to further acidify soap by means of sulphuric acid in order to complete cooking. A bisulphite solution as such is not very acidic, having a pH slightly below 5. The pH of splitting acids should be less than 4.

The sodium bisulphate solution has also been used for partly replacing sulphur dioxide water in the last step of a chemical pulp bleaching process for decomposing residual chlorine dioxide, or depending on the step, hydrogen peroxide, and for final acidifications. Acidification with sulphur dioxide water also improves dewatering during pulp drying.

Such mills that do not produce chlorine dioxide by the Mathieson process still use sulphur dioxide as the reducing agent, in the form of i.a. sulphur dioxide water for decomposing residual chlorine dioxide and peroxide as above and for acidification of the final pulp. Due to the hazardous handling of commercially available sulphur dioxide in liquid form, it would be preferable to produce sulphur dioxide directly at the mill.

FI 64408 describes a method in which a bisulphite solution is treated with an acidic waste solution derived from chlorine dioxide production and containing both sulphuric acid and sodium sulphate – which is in practice in the form of an acidic sodium bisulphate solution. The waste solution also contains chlorous compounds, which may cause corrosion problems in the process equipment. The method further comprises the evaporation and crystallisation of the solution remaining after sulphur dioxide formation for precipitating sodium sulphate, and the remaining sulphuric acid which contains chloride being returned to the chlorine dioxide production process. The residual solution, which contains chloride, among other substances, may also cause corrosion and cleaning problems in the post treatment apparatus.

Object of the invention

The object of the present invention is to provide a simple and efficient recycling process of recovered sulphur originating from a chemical pulping process, especially from the chemical circulation system of the pulp mill, without the need of introducing additional sulphur in any notable amounts from the outside, whereby problems with the sulphidity of the process can be avoided.

A further object of the invention is to provide a sulphur recycling method with which the sulphur-sodium balance of a process can be further improved.

The invention also provides an improved method of recycling sulphur, in the treatment steps of which corrosive treatment solutions can be avoided or less corrosive solutions can be used, such as acid solutions containing chlorides.

The invention also provides further alternatives for treatment solutions/reagents used in pulp processes and sulphur recycling methods, these treatment solutions/reagents enabling to replace e.g. previously used solutions containing chlorides and/or other corrosive substances.

Description of the drawings

- Figure 1 illustrates the pH decrease in an oxidation treatment during the course of oxidation
- Figure 2 is a schematic view of an embodiment of the invention for the recycling of sulphur.
- Figure 3 is a schematic view of another embodiment of the invention for the recycling of sulphur.

Description of the invention

It was surprisingly found in conjunction with the present invention that it is possible to treat a bisulphite solution, which is produced from sulphur recovered during a

preparation process of a pulp, especially a chemical pulp, such as a sulphate pulp process, in such a way that the sulphur can be recycled to the process very efficiently and even, if desired, used further in the treatments of the invention.

Thus the invention provides a method for recycling sulphur in a process for producing pulp, especially chemical pulp, whereby

(a) bisulphite, which is produced from sulphur recovered from the process cycle, is converted by means of an oxidant to bisulphate, which is then further used as recycled acid in various steps of the process, and/or

(b) bisulphite, which is formed from sulphur recovered from the process cycle, is converted by means of an acidic agent to sulphur dioxide, which is further used in various steps of the process.

In case the method does not include treatment (a), but only treatment (b), the acid treatment is performed with an acidic agent other than an acidic waste solution obtained from chlorine dioxide production.

Owing to the invention, the bisulphite solution obtained from recycled sulphur can be used for more versatile sulphur recycling purposes and, furthermore, both treatments (a) and (b) can be mutually utilised so that products from one of the treatments (a) and (b) can be used in the other treatment (a) or (b). Sulphur and also sodium are very efficiently recycled in the process, i.e. the method enables to reduce the amount of sulphur compounds introduced into the process and simultaneously to decrease the demand of sodium hydroxide. This also allows a better control of the balance ratio of sulphur:sodium during the chemical circulation system and the entire process.

The method further enables to use and to produce treatment agents which contain less corrosive substances, such as chlorides.

In this context, the expression “is further used as recycled acid in various steps of the process” or “is further used in various process steps” signifies that the bisulphate product obtained from the treatment (a) and/or the sulphur dioxide obtained from the treatment (b) and possibly the mother liquor remaining from step (b) is used as a reagent, e.g. as an acidic agent (“acid source”), in one or more steps

of the process and/or as a raw material for preparing one or more reagents for use in the process, such as magnesium sulphate used in the pulp oxygen delignification or pulp bleaching, or chlorine dioxide used in pulp bleaching. The products obtained from these treatments can be used for said purposes continuously or whenever needed. Thus the method of the invention may further comprise, in addition to treatments (a) and/or (b), other process steps for recycling/using the products obtained from treatments (a) and/or (b).

The invention relates to a process for preparing pulp, especially chemical pulp. Pulp obtained from the process can be used e.g. for producing paper or paperboard. Hence the terms "pulp production process" or "process" in this context cover in a broad sense the actual preparation process of a pulp, preferably a chemical pulp, preferably a sulphate process, including any steps for producing the pulp, any steps for further processing the obtained pulp, such as processes for producing paper or paperboard, and, in a manner known in the art, any other processes related to a pulp preparation process, such as a chlorine dioxide process, and any process steps related to the further processing of products other than pulp, which products are formed and obtainable from these processes, such as the conventional process step included to a sulphate process for the acid treatment of tall oil soap separated from the pulp, i.e. the splitting treatment in order to produce tall oil. Thus products obtained from treatments (a) and/or (b) of the invention can be used in any preparation step and/or treatment steps for which they are suitable.

"Acid treatment" generally denotes a treatment performed with any acidic agent, typically an aqueous solution of an acidic agent having a pH below 6, preferably below 4, such as 2.

"Recycling" means that at least a portion of the sulphur or of the products treated according to the method is recycled to the process cycle.

"Bisulphite scrubber" means treatment of sulphur dioxide obtained from sulphur combustion with an alkaline agent, typically sodium hydroxide or an agent containing sodium hydroxide, in order to produce a bisulphite solution.

The "mother liquor" used in the application, which is obtained from step (b), means a reaction mixture remaining after sulphur dioxide has formed, the reaction mixture containing any unreacted bisulphite derived from the bisulphite solution used as the

starting material, and, typically, the acid treatment solution, the composition of which may naturally vary depending on the treatment agent and amount used. The mother liquor is thus usually acidic.

The bisulphite solution used in treatments (a) and (b) is typically an aqueous solution of sodium bisulphite as known in the art. Thus the bisulphate solution obtained in treatment (a) and the acidic mother liquor obtained in treatment (b) are usually in the form of an aqueous solution. If necessary, the solutions can be concentrated, for instance, preferably by evaporating in order to produce the solution concentration and/or volume suitable for the specific purpose of use.

The method of the invention can utilise the sulphur which is recovered from the process, especially sulphur contained in the malodorous gases (e.g. TRS gases). In one preferred embodiment, at least part of the sulphur recovered from the process, e.g. a sulphate pulp process, preferably the malodorous gases, are incinerated in order to convert the sulphur compounds contained therein into sulphur dioxide, and at least part of the obtained sulphur dioxide is used for preparing bisulphite, preferably a sodium bisulphite solution, by means of an alkaline agent, preferably sodium hydroxide, in a manner known in the art.

According to a further embodiment, the sodium bisulphite solution mentioned above is used in the method, whereby

(a) at least a portion of the obtained sodium bisulphite solution obtained is subjected to an oxidation treatment in order to oxidise at least a portion of the bisulphite to bisulphate, and the bisulphite-containing reaction mixture is further used in the process, and/or

(b) at least a portion of the obtained sodium bisulphite solution is subjected to an acid treatment in order to convert bisulphite to sulphur dioxide for further use in the process, and the mother liquor remaining from the treatment is optionally further used in the process.

In one preferred embodiment, the method includes merely the treatment (a). Furthermore, the method may include the treatment (a) and optionally the treatment (b).

In a second preferred embodiment, the method includes at least the treatment (b) and optionally the treatment (a). In that case, if the treatment (a) is not included into the method, the treatment (b) is limited as defined above and in claim 1.

An especially preferred method of the invention comprises both the treatment (a) and the treatment (b), whereby said combination enables to improve further the recycling of sulphur. Then the amount or feed stream of the bisulphite solution can be selected for each treatment according to the need in each case. The proportional ratio (feed stream (a)) (feed stream (b)) may vary within the range 1:99 and 99:1, and the proportion of the feed stream (a) is preferably larger than that of feed stream (b). If the process comprises the two treatment lines (a) and (b), the bisulphite solution can be divided between the treatment lines (a) and (b). In addition, treatment lines (a) and (b) can be arranged in parallel and they may operate simultaneously, periodically or alternately, according to the needs of each process.

Treatment (a) and/or (b) of the invention may further be arranged in the process cycle for operating continuously or periodically as needed in each case.

The products obtained from the treatment (a) and/or (b) of the invention can be used in various steps of the process for replacing partly or totally substances that would otherwise have to be brought into the process cycle from the outside, e.g. for replacing partly or completely an acid, e.g. sulphuric acid, introduced from the "outside" for use in any acid treatment step.

Accordingly, the bisulphate solution obtained in treatment (a) of the sulphur recycling method of the invention can be used as an acidic agent in one or more acid treatment steps of the process, alone or together with another acidic substance.

In a preferred embodiment, the method comprises a process step, in which tall oil soap is recovered and subjected to acid treatment in order to produce tall oil, whereby the acid treatment is carried out by using a bisulphate solution obtained from the treatment (a), alone or together with a second acidic agent. The treatment can be carried out using methods known in the art.

Further the bisulphate solution obtained from the treatment (a) can be recycled to the treatment (b), in other words, the bisulphate solution can be used as the acidic

agent to produce the sulphur dioxide in the treatment (b). In that case the bisulphate solution can be used alone or together with an additional acid. The treatment can be performed using methods known in the art. The production can be carried out in analogy with known methods.

In a second preferable embodiment the bisulphate solution obtained from the treatment (a) can be used as a raw material for preparing sulphates used in the process, e.g. in the oxygen delignification step (bleaching step) for preparing magnesium sulphate used as a reagent.

In the treatment (b), sulphur dioxide is formed during the reaction between bisulphite and the acidic agent. The treatment can be carried out in analogy with the known prior art. The sulphur dioxide formed can be recycled for use in the process. In one preferred embodiment, the sulphur dioxide produced in treatment (b) is brought into contact with water for preparing sulphur dioxide water for use in the process. The preparation and use of sulphur dioxide water in a sulphate cellulose process is well known in the art, and thus, for said preparation, reference is made to the prior art.

The sulphur dioxide obtained in treatment (b) can be further used as a raw material in the preparation of chlorine dioxide intended for pulp bleaching. The process for producing this chlorine dioxide can be arranged in connection with a pulp bleaching process in a manner known in the art.

The mother liquor which may contain the acid treatment solution and/or any unreacted bisulphite which remains from treatment (b) can also be used as an acidic agent for the purposes of use described above. In one embodiment the method further includes a process step, wherein tall oil soap is recovered from the process and is subjected to an acid treatment in order to produce tall oil and wherein the acid treatment is performed with the use of the mother liquor remaining from treatment (b) alone or together with another acidic substance, preferably together with a bisulphate solution obtained from the treatment (a). The treatment can be carried out in analogy with the known practice.

The mother liquor remaining from treatment (b) may be further recycled to treatment (a). In that case it can be added to a "fresh" bisulphite solution fed into

treatment (a), after which the mixture obtained is oxidised in order to produce a bisulphate solution.

Optionally, the mother liquor obtained in treatment (b) can be combined with the previously oxidised bisulphate solution from treatment (a), and then the mixture obtained can be used in the acid treatments of the process, e.g. for tall oil splitting.

In one embodiment the bisulphate solution obtained from the treatment (a) is used as an acidic agent in the treatment (b) for producing sulphur dioxide from the bisulphite solution, and the mother liquor remaining from the treatment can be recycled to the oxidation treatment (a), if desired, in order to produce bisulphate from the unreacted bisulphite contained in the mother liquor and/or combined with the previously oxidised bisulphate solution for use of the mixture as an acidic agent in the acid treatments of the process, preferably for tall oil production.

The invention thus provides new highly useful alternatives for recycling sulphur in a pulp production process, e.g. a sulphate cellulose process.

The invention further provides the use of the bisulphate solution obtained in treatment (a) and/or the mother liquor obtained in treatment (b) as an acidic agent in acid treatments of the various steps of the process, preferably in tall oil splitting. It further provides the use of the bisulphate solution obtained in the treatment (a) as a raw material in the preparation of the reagents, preferably magnesium sulphate, used in the process.

The treatments (a) and (b) of the invention and the embodiments of recycling the products obtained in the treatments to other process steps of the method are explained in further detail below.

Detailed description of the invention

Treatment method (a) of the invention is based on the finding that in connection with a process for producing pulp, especially chemical pulp, recycled sulphur is oxidised with an oxidant to form a bisulphate solution which is usable in the process. The recycled sulphur is thus oxidised to a bisulphate solution by means of an oxidant.

We have now surprisingly also found that raw tall oil can be cooked by using recycled sulphur obtained from the chemical circulation system of the process, such as a pulp mill. The bisulphate solution obtained with the method of the invention is considerably more acidic than e.g., a bisulphite solution, its acidity being sufficient for splitting soap into raw tall oil even in one single step. In a mill this allows a significant reduction of the amount of sulphuric acid introduced from the outside to the process for the said purpose or for any other acid treatment.

The bisulphate solution can also be used for preparing the reagents required in the process, such as sulphate compounds, e.g. magnesium sulphate used in bleaching.

In treatment (a) oxidation is carried out by using an oxidant. The oxidant used in the method of the invention may be any conventional oxidant, such as hydrogen peroxide, oxygen, air, ozone or e.g. organic peracids, such as peracetic acid or performic acid. Oxygen, air or hydrogen peroxide are preferably used. Optionally it is also possible to use for the oxidation a peroxide-containing solution derived from any other process step, such a filtrate containing residual peroxide obtained from pulp bleaching.

It is evident to those skilled in the art that the oxidation conditions and the amount of the used are selected depending on the oxidant and the desired oxidation degree in a manner known in the art.

The bisulphate formed in the oxidation treatment decreases the pH of the bisulphite solution, having a very favourable effect on the further use of the solution in the process. Thus bisulphite may be oxidised partly or totally, preferably partly, in order to obtain the bisulphate content, preferably the pH value of the reaction mixture, which is suitable for the use in question.

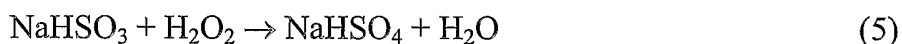
In one embodiment the bisulphite solution is oxidised until the desired pH is achieved for the reaction solution. The oxidation degree required can be determined e.g. in terms of the pH desired for the reaction solution. The determination can be performed in a manner known in the art, by calculatory means and/or experimental means, depending i.a. on the used oxidant.

The pH drop achieved as a result of the oxidation reaction is illustrated with an example (figure 1). The figure shows that the pH of a bisulphite solution containing

10 g/l drops rapidly from its initial value of a little above four when hydrogen peroxide is added. The pH of the bisulphite solution drops significantly even with a small amount of peroxide.

The pH of the bisulphate solution obtained can be brought to a level suitable for tall oil cooking or any other acid treatment, to the range $\text{pH} < 2$, preferably $\text{pH} < 1.5$, so that, with the use of hydrogen peroxide, for instance, the amount of hydrogen peroxide is more than 0.1, preferably 0.2 times the stoichiometric amount required for the oxidation of bisulphite.

In the method of the invention, the bisulphite obtained from the process cycle can be oxidised to bisulphate with e.g. hydrogen peroxide as the oxidant, as shown in equation (5). In that case, only water will remain as a surplus reaction product. At the same time, the pH of the solution decreases substantially. Sulphurous acid (H_2SO_3) has the acid constants $\text{pK}_{\text{a}1} = 1.8$ and $\text{pK}_{\text{a}2} = 6.8$, whereas sulphuric acid has accordingly $\text{pK}_{\text{a}1} = -3$ and $\text{pK}_{\text{a}2} = 1.8$.



In the method of the invention, e.g. hydrogen peroxide consumption for stoichiometric oxidation of bisulphite has the pulp ratio of 1:3 of H_2O_2 : NaHSO_3 , i.e. peroxide consumption is of the order of 0.33 kg of H_2O_2 /kg of NaHSO_3 .

However, it is preferably not necessary to oxidise bisulphite completely in order to achieve a sufficiently low pH, but partial oxidation is also sufficient.

When oxygen or air is used as the oxidant the reaction is preferably conducted under overpressure, e.g. over 6 bar, preferably approx. 10 bar, in an autoclave and at an elevated temperature. Furthermore, oxygen or air can further advantageously be fed through a mixing device in order to achieve a good contact between the gas and the liquid. The use of such pressurised oxidation results in a fast reaction.

Optionally, the bisulphate solution obtained in accordance with the invention may be prepared already in the bisulphite scrubber, whereby sulphuric acid and bisulphate is also produced into the bisulphite solution. In that case, the materials used in the process equipment should withstand any corrosion caused by the oxidant

and the oxidation reaction $\text{SO}_2 \rightarrow \text{SO}_3$. The bisulphate solution produced then also contains a certain amount of sulphuric acid, i.e. the solution is slightly more acidic.

In other words, the method of the invention allows conversion of the recycled sulphur of the process from a sodium bisulphite form into a sufficiently acidic bisulphate form for it to be suitable i.a. for tall oil splitting. With bisulphite used as such, tall oil will be split only partly and final splitting will require an additional acid from the outside, e.g. sulphuric acid. The method of the present invention does not necessarily require extra sulphuric acid, or, if used, the required amount is less than e.g. when a bisulphite solution is used.

It is known that tall oil soap can be split by means of an acid which is brought from the outside of the process, such as sulphuric acid or waste acid from a chlorine dioxide process, providing sufficiently low pH. The pH of bisulphite obtained directly from the process is not sufficient as such for this purpose. When a bisulphite solution is oxidised to bisulphate in accordance with the invention, this pH range can be reached. It is important to decrease the pH to be low enough for the fatty acids, which are weak acids, to convert them into an acid form and separated. A bisulphate solution having a pH below 2 would convert a major portion of the fatty acids into the acid form. When the pH is about 2 units below the pKa value of the fatty acid, which is typically of the order of 4, the major portion of the fatty acids is in acid form and not as a salt.

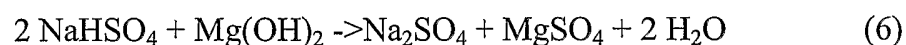
In one embodiment of the invention, splitting is performed in a one single step using a sodium bisulphate solution prepared in accordance with the invention as the splitting acid, the oxidant being used in a stoichiometric amount. In some cases it may be advantageous to use an excess of oxidant. Optionally, the bisulphate may be only partly oxidised. Splitting can also be performed with the use of a mixture, e.g. a mixture of sulphuric acid and bisulphate, or a mixture of bisulphate and the mother liquor obtained from treatment (b). This sulphuric acid may also be prepared from sulphur dioxide obtained from recycling step (b) by means of hydrogen peroxide, by oxidising first the sulphur dioxide to sulphur trioxide and further to sulphuric acid. It is previously known to prepare sulphuric acid by oxidising sulphur dioxide directly to sulphur trioxide. The procedure of the invention avoids investments in a separate sulphuric acid plant.

In one embodiment of the invention, tall oil soap splitting is performed in two or more steps. In a two-step method, the first step may comprise a bisulphate solution prepared in accordance with the invention and the second step any other acid, such as e.g. fresh sulphuric acid or waste acid from a chlorine dioxide reactor, or a mixture of acids. Optionally, the first step may involve the use of a sodium bisulphite solution derived directly from the process or carbon dioxide, and the sodium bisulphate solution of the invention used only in the second step. In that case a smaller amount of the bisulphate and thus the peroxide will be needed compared to a single-step method. Optionally, in two-step tall oil soap cooking, the bisulphite solution characteristic of the invention is used in both the steps. The mother liquor obtained in treatment (b) can also be used in one or both of said steps.

A magnesium compound used in oxygen delignification (oxygen bleaching) can be prepared by utilising the sulphur recovered in a sulphate process cycle, whereby the use of magnesium sulphate from the outside can be avoided, which external magnesium sulphate would increase the sulphur load.

Sulphur-free raw materials of a magnesium compound may comprise e.g. magnesium hydroxide, magnesium oxide or magnesium carbonate. Technical MgO is one preferable magnesium source.

In one embodiment of the invention, the magnesium compound is dissolved e.g. in the bisulphate solution obtained from the sulphate process using the reaction equation (6), yielding magnesium sulphate.



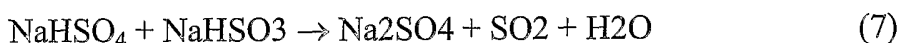
One optional way for preparing magnesium sulphate is performing the reaction already in the gas scrubber, where the gas containing SO₂ is scrubbed with water containing an oxidant, such as hydrogen peroxide, and Mg(OH)₂. In that case, peroxide consumption will be in the range from 0.28 to 0.33 kg/kg of MgSO₄.

Because MgSO₄ contains 26.6% of sulphur, the method of the invention produces a sulphur amount less than 0.26 to 0.8 kg/t of pulp, with the amount of MgSO₄ dosed in oxygen bleaching being 1 to 3 kg per ton of pulp.

In the treatment (b) of the invention, the acid treatment can be carried out with any acidic agent suitable for the process, such as an acid introduced from the outside, e.g. sulphuric acid, or optionally with an acidic agent recycled in the process, such as an acidic waste liquid of the process, which may derive from a process for preparing chlorine compounds, such as chlorine dioxide, or compounds other than chlorine compounds, included in the overall process. The amount of acid needed for producing sulphur dioxide depends i.a. on the acidic substance used, its concentration and the bisulphite solution composition and concentration, and it can be determined by calculatory or experimental means by a person skilled in the art.

If necessary, the sulphuric acid to be used can be prepared from bisulphate obtained in treatment (a).

The acid treatment (b) may further include the use of the bisulphate solution from treatment (a) as follows:



Treatment (b) may produce sulphur dioxide for use in the preparation of e.g. sulphur dioxide water at the final end of the bleaching line. The preparation and use of sulphur dioxide water are well known in the art. For this purpose, it would be possible to use e.g. 2 to 3 kg of SO₂/t of pulp, i.e. 1 to 1.5 kg of S/t of pulp, corresponding to 2 to 3 kg of recycled sulphur in the form of sodium bisulphate and sodium bisulphite.

Since both the bisulphate and the bisulphite solution contain water, and water also forms during the reaction, 50% of water, preferably 70% of water can be evaporated from the amount of the two solutions, and then the pH of the solution drops.

Using the bisulphate solution obtained in treatment (a), bisulphate can be used for sulphur dioxide formation in a stoichiometric amount or in an excess amount. In case of an excess of sodium bisulphate, the excess is typically more than 40%, preferably more than 60% and more preferably over 70%. Preferably an excess of sodium bisulphate solution is used for completing the reaction (7), the remaining mother liquor being also particularly advantageous for use in acid treatments, such as in tall oil soap splitting. Bisulphate can be used also together with sulphuric acid introduced in the process.

The acidic substance used in treatment (b) can further comprise merely sulphuric acid introduced into the process, and/or an acidic solution from the Mathieson process or sodium sesquisulphate formed as a by-product in the preparation of chlorine dioxide, when a methanol process is used.

Acid treatment (b) is performed at a raised temperature, preferably below 100 °C, thus avoiding excessive water evaporation. If necessary, the reaction can be carried out by using stripping in order to facilitate the conversion of bisulphite into sulphur dioxide.

The mother liquor remaining after sulphur dioxide formation can be recycled in the process, e.g. in tall oil soap splitting, and/or as in treatment (a) above and as defined in claim 1.

The recycling, recovery and reuse of sulphur in a pulp production process, e.g. a sulphate pulp process in accordance with the invention, are exemplified by means of a number of preferred embodiments shown in figures 2 and 3.

In the operation of the invention, the equipment needed for the oxidation reaction is simple. The equipment comprises substantially a mixing vessel, in which the reaction between the bisulphite containing recycled sulphur from the sulphate process and the oxidant takes place. The equipment may also comprise an oxidant dosing apparatus and an intermediate storage container for the bisulphate produced as a reaction product, from where the bisulphate solution can be redirected to the desired process point, such as tall oil soap splitting or magnesium sulphate production, for instance.

In the embodiment of figure 2, the bisulphate solution is prepared in accordance with the invention by oxidising the sodium bisulphite derived from the bisulphite scrubber 4 in the mixing vessel 1 by means of an oxidant, which is brought to the mixing vessel 1. The sodium bisulphate prepared in the mixing vessel is conducted e.g. to a raw tall oil cooking reactor 5 or to a reactor 6 for preparing magnesium sulphate. In reactor 6, magnesium sulphate is prepared from a magnesium reactant introduced in the process from the outside, and from sodium bisulphate prepared from recycled sulphur in accordance with the invention. The magnesium sulphate thus produced is used in oxygen bleaching 7. The filtrate from the oxygen bleaching

is further conducted to an evaporating plant 8 and from there to the soda recovery boiler 9. Raw soap is separated from the liquor coming from the scrubbing plant 11 and going to the evaporating plant 8 during the preparation of raw tall oil, the raw soap being conducted to a cooking reactor 5, where it reacts into raw tall oil by means of bisulphate. Raw tall oil 12 is removed from the process from the tall oil cooking reactor 5 and the remaining sulphur-containing pulp press water is conducted through the evaporating plant 8 to the soda recovery boiler 9 for combustion of organic compounds and sulphur. In the soda recovery plant 9, the sulphur compounds are burned to sodium sulphide. From the soda recovery boiler 9, an aqueous solution of sodium carbonate and sodium sulphide, green liquor, is conducted to causticisation 13, where sodium carbonate is converted into calcium carbonate and the sodium hydroxide-sodium sulphide solution thus produced, white liquor, is recycled to the pulp digestion 10. The remaining calcium carbonate is further regenerated in the lime kiln 14, forming calcium oxide. The major sulphur dioxide source is the malodorous gas combustion 15, where reduced sulphur compounds, mainly H_2S , methyl mercaptane, dimethyl mercaptane and dimethyl dimercaptane, are incinerated to sulphur dioxide and are further conducted to the bisulphite scrubber 4. Likewise, besides malodorous gas combustion, sulphur dioxide from any other sources can be recovered. In the bisulphite scrubber 4, sulphur dioxide is absorbed into the $NaOH$ solution, producing sodium bisulphite. The sodium bisulphite produced in the bisulphite scrubber is further fed to oxidation in the mixing vessel 1 in accordance with the invention.

Further in figure 3, the recycling method comprises an apparatus for incinerating gases containing malodorous sulphurous compounds (TRS gases), e.g. a lime kiln 14 and a bisulphite scrubber 4, to which the sulphur dioxide formed during combustion is conducted in order to form a bisulphite solution, preferably a sodium bisulphite solution. The apparatus may further comprise, besides an oxidation apparatus 1, an acid treatment apparatus 17 for sulphur dioxide formation. In use, a portion of the bisulphite flow is fed to the sulphur dioxide generator 17, to which an acid treatment solution is added, e.g. an acid introduced from the outside or a bisulphate solution oxidised in the apparatus 1 by means of an oxidant, alone or combined with one or more other acidic substances. Depending on its composition, the mother liquor can be recycled to the oxidiser 1, where unreacted bisulphite can be oxidised together with fresh bisulphite. Optionally, the mother liquor can be subjected to acid treatments of the process, wherein it can be used alone or together with bisulphite from oxidation 1, for instance, for tall oil soap splitting, and then

also sodium can be recovered. The sulphur dioxide generated in the apparatus 17 can be conducted to a process 18 for preparing sulphur dioxide water.

Due to the method of the invention the use of a waste acid from e.g. a chlorine dioxide production process 16, such as a Mathieson process, or from a process using hydrogen peroxide as the reducing agent, can be partly or completely avoided.

The following is a detailed description of a number of features specific for the invention by means of examples, however, without limiting the invention to these:

Example 1

A sodium bisulphite solution NaHSO_3 obtained from a sulphate pulp mill in a concentration of 43 g/l and with pH 4 was oxidised by adding a 50% hydrogen peroxide solution. Table 1 shows the pH variation of the solution as a function of the peroxide addition. A rate of 12 g/l of $\text{Mg}(\text{OH})_2$ was readily dissolved in a bisulphite solution to which 11 g/l of H_2O_2 had been added, the final solution containing 24.9 g/l of MgSO_4 . The solution also contained sodium sulphate.

The magnesium sulphate solution thus prepared had exactly the same function in oxygen bleaching and peroxide bleaching as pure magnesium sulphate introduced from the outside. The accompanying sodium sulphate was not observed to cause any negative effects.

Table 1

Hydrogen peroxide content g/l	pH
0	3.99
0.9	2.88
2.5	2.35
5.0	1.82
7.4	1.33
10.2	0.75
11.0	0.68

Example 2

4 l of a sodium bisulphite solution obtained from a sulphate pulp mill, NaHSO_3 , in a concentration of 210 g/l, was taken and placed in an autoclave with a volume of 8 l. The autoclave was equipped with a gas-circulating stirrer, with oxygen used as the gas. The autoclave temperature was regulated to 80 °C and it was supplied with pure oxygen so as to generate an overpressure of 10 bars in the autoclave.

The consumption of supplied oxygen and the pH were measured. Table 2 shows the development of the pH as the oxygen consumption proceeds.

Table 2

Oxygen consumption (% of theoretical)	pH
0	5.18
59.5	2.22
78.5	1.47
94.3	1.02
98.1	0.92
100	0.88

The pH of the bisulphite solution decreases rapidly to below three at the initial stage of the oxidation and decreases further as the oxidation proceeds. The increased acidity is clearly due to the almost total oxidation of bisulphite to bisulphate. The test shows that the use of oxygen as the oxidant allows the appropriate pH range to be reached, the recycled solution being then apt for reuse in the splitting of tall oil soap, for instance.

Example 3

A process solution of sodium bisulphite having a volume weight of 1169 g/l, pH 5.6 and a SO_3^{2-} proportion of 15% was oxidised with hydrogen peroxide (50 w%) to sodium bisulphate. After oxidation, the solution contained 263 g/l of sodium bisulphate. This solution was used for splitting tall oil soap.

400 g of tall oil soap was measured in a 2 l vessel. When mother liquor was used for splitting, it was added at this stage. Using sulphuric acid, as in the comparative test, 300 g of water was also added. The insulated vessel was heated to a temperature of 100 °C and the acidic solution used was added until the pH decreased to below 3. With the use of a sodium bisulphate solution, 50% of the required amount of sulphuric acid was compensated with this.

When the pH had dropped to below 3, the sample was boiled for about 15 minutes at a temperature of 100 °C. After this the product was poured into an extraction funnel. At the end of 30 minutes, three phases separated: tall oil, lignin and mother liquor. Tall oil was separated and recovered and the volume, volume weight and pH of the solution were measured, after which the tall oil yield was calculated. In part of the tests, the phases were separated by centrifugation. These test are marked with an asterisk.

By calculating, 50 g of sulphuric acid is needed for each 400 g of tall oil. If 50% of the sulphuric acid were replaced with a theoretical amount of sodium bisulphate, the amount would be 6.12 g, and with a 230 g/l solution, 266 ml is required. The bisulphate prepared from the process liquor had a theoretical content of 263 g/l, so that the corresponding required amount would be 233 ml.

The amount of tall oil soap varied slightly from one test to another, being consistently a little above 400 g.

In the tests two different industrial tall oil soap samples, a and b were used. Table 3 shows a comparison of the splitting using sulphuric acid, and in table 4 the splitting has been performed with a mixture of sodium bisulphate and sulphuric acid, in which bisulphate has been produced by oxidising the bisulphite solution obtained from the process by means of oxygen. In table 4, the acid ratio means the ratio of sulphuric acid obtained from sodium bisulphate to the added sulphuric acid.

Table 3

Test no	Raw soap	H ₂ SO ₄ kg/t of raw soap	Yield %	Acid number value mg KOH/g	Soap number mg KOH/g

1	a	94.2	68	152	0.6
2	a*	109	68	152	0.4
3	b	104	63	153	0.6
4	b*	106	64	156	0.4
Mean value		103	66	153	0.5

Table 4

Test no	Raw soap	Total H ₂ SO ₄ kg/t of raw soap	Acid ratio NaHSO ₄ /H ₂ SO ₄	Yield %	Acid number mg KOH/g	Soap number mg KOH/g
6	a*	122	0.539	75	157	0.9
7	b	137	0.539	74	157	1.5
8	b*	129	0.539	74	158	0.9
Mean value		129	0.539	74	158	1.1

The raw tall oils thus prepared had excellent acid number values corresponding to the fat and rosin acid content, which should have a value > 150. The average soap value, which corresponded to the soap amount in raw tall oil, meets the requirements on high-quality industrial tall oil. The yield was much better than with the use of sulphuric acid (cf. table 3).

Example 4

As in example 3, the entire sulphuric acid demand was replaced by a bisulphate solution obtained from the process. The salt proportion apparently increases the volume weight of the water phase and thus improves tall oil separation. Then the overall oxygen consumption decreases relative to the use of sulphuric acid.

The values of tall oil yield corresponded to the values given in table 4.

Example 5

Raw tall oil soap was treated as in example 3 in a two-step process, where the soap was first preneutralised with a sodium bisulphate solution and the final acidification was performed with sulphuric acid. These results are shown in table 5.

Table 5

Test no	Raw soap	Total H ₂ SO ₄ kg/t raw soap	Acid ratio NaH- SO ₄ /H ₂ SO ₄	Yield %	Acid number mg KOH/g	Soap number mg KOH/g
9	A	99.1	0.799	76	155	1.4
10	A*	95.2	0.896	76	156	0.8
12	A*	130	0.479	80	158	0.4
13	b	132	0.517	76	156	1.0
14	b*	130	0.523	73	155	0.7
Mean value		118		75	156	1.1

The results show that a replacement of over 50% of the sulphuric acid with sodium bisulphate results in a substantial decrease of the overall acid consumption per ton of tall oil.

Example 6

500 ml of the process solution containing 120 g of sodium bisulphite was poured into a reaction vessel equipped with a stirrer. The solution was heated to 80 °C and 104 g of 95% sulphuric acid was added slowly drop-wise during 70 minutes at constant temperature. The produced sulphur dioxide was first fed through methanol and then through water and the dissolved sulphur dioxide amounts were analysed. The sulphuric acid feed was calculated per time unit and the same was done for sodium bisulphite conversion into sulphur dioxide. The results are shown in table 6.

Table 6

Time min.	H ₂ SO ₄ calc. mol	H ₂ SO ₄ surplus %	SO ₂ formed g	SO ₂ formed mol	SO ₂ conversion %
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0			0	0	
10	0.144		3.8	0.0593	5.1%
20	0.288		16.5	0.258	22.3%
30	0.432		25.6	0.400	34.7%
40	0.576	-0.2%	43.5	0.679	58.9%
50	0.720	25%	59.6	0.930	80.7%
60	0.863	50%	64.3	1.004	87.0%
70	1.007	75%	66.3	1.035	89.7%

The results indicate that an almost stoichiometric amount of sulphuric acid and bisulphite yields an about 60% conversion of sulphur dioxide.

When sulphur dioxide is prepared in stoichiometric amounts, the mother liquor is preferably fed to the oxidation treatment for converting it into bisulphate. If, again sulphuric acid is used, e.g. 40% or more preferably over 70%, the mother liquor can be used for different acidifications, most preferably for tall oil soap splitting.

Claims

1. A method for recycling sulphur in a process for producing pulp, **characterised** in that
 - (a) bisulphite, which is produced from the sulphur recovered from the process cycle, is converted by means of an oxidant to bisulphate which is then further used as a recycled acid in various steps of the process, and/or
 - (b) bisulphite, which is produced from the sulphur recovered from the process cycle, is converted by means of an acidic agent, which is other than an acidic waste solution derived from chlorine dioxide preparation process, to sulphur dioxide which is then further used in various steps of the process.
2. A method as defined in claim 1, **characterised** in that the method comprises the treatment step (a).
3. A method as defined in claim 2, **characterised** in that the sulphur recovered from the process cycle is partly or totally converted to bisulphate.
4. A method as defined in claim 2, **characterised** in that hydrogen peroxide, ozone, organic peracids, oxygen, a peroxide-containing solution obtained from any other process step or mixtures of these, preferably hydrogen peroxide, oxygen and/or air, is used as the oxidant.
5. A method as defined in claim 4, **characterised** in that, when hydrogen peroxide used as the oxidant, it is used in an amount more than 0.1, preferably more than 0.2 times, of the stoichiometric amount required for the oxidation of bisulphite.
6. A method as defined in claim 2, **characterised** in that the sulphur recovered from the process cycle is converted into bisulphate by means of an oxidant after it has first been converted into bisulphite form in a bisulphite scrubber.
7. A method as defined in claim 2, **characterised** in that the sulphur recovered in the process cycle is converted in a bisulphite scrubber into bisulphate by means of an oxidant.

8. A method as defined in any of the preceding claims, **characterised** in that the oxidant is used in an amount which provides a bisulphate-containing reaction solution having a pH below 4, preferably below 2, most advantageously below 1.2.
9. A method as defined in any of the preceding claims, **characterised** in that the bisulphate solution obtained from the treatment (a) is used as an acidic agent in one or more acid treatment steps of the process, alone or together with another acidic agent.
10. A method as defined in any of the preceding claims, **characterised** in that the bisulphate solution obtained from the treatment (a) is used as the raw material for preparing magnesium sulphate used as a reagent in the bleaching steps of the process.
11. A method as defined in any of the preceding claims 2 to 10, **characterised** in that the method further comprises a process step for splitting tall oil soap, wherein bisulphate obtained from the treatment (a) as defined in any of claims 1 to 10 forms at least part of the used splitting acid.
12. A method as defined in claim 11, **characterised** in that splitting takes place in one or more steps, at least one of which uses said bisulphate, either alone or together with other acids.
13. A method as defined in claim 11 or 12, **characterised** in that in addition to the bisulphate obtained from the treatment (a) as defined in claims 1 to 10, a further acid or carbon dioxide is also used as the splitting acid.
14. A method as defined in claim 13, **characterised** in that the further acid is sulphuric acid or bisulphite.
15. A method as defined in claim 11, **characterised** in that for the use as the splitting acid in the treatment (a) oxidation is carried out with hydrogen peroxide, which is used in an amount exceeding 0.15, preferably over 0.20 g/g of bisulphite.
16. A method as defined in any of the preceding claims 2 to 15, **characterised** in that the method comprises a further process step for preparing magnesium sulphate, which is used in the bleaching of pulp, preferably sulphate pulp, wherein bisulphate

obtained from the treatment (a) as defined in any of claims 1 to 10 is used as the sulphate raw material and wherein the bisulphate is reacted with an oxidant and a magnesium compound introduced into the process from the outside.

17. A method as defined in claim 16, **characterised** in that the magnesium compound is a sulphur-free magnesium compound, preferably magnesium hydroxide, magnesium oxide or magnesium carbonate, most advantageously a technical magnesium oxide, the magnesium compound being dissolved in a bisulphate solution, which has been prepared by treatment (a) defined in accordance with any of claims 1 to 10.

18. A method as defined in claim 1 to 17, **characterised** in that the method comprises at least the treatment (a) and optionally the treatment (b).

19. A method for recycling sulphur in a pulp production process, **characterised** in that the method comprises the treatment (a) as defined in any of claims 2 to 10, and the treatment (b), wherein bisulphite formed from sulphur, which is recovered from the process cycle, is converted with an acidic agent into sulphur dioxide for further use in the process, and the remaining mother liquor is optionally further used in various steps of the process.

20. A method as defined in claim 19, **characterised** in that the sulphur compounds contained in the malodorous gases, which are recovered from the process, are incinerated to sulphur dioxide and the obtained sulphur dioxide is converted with an alkaline agent, preferably with sodium hydroxide, to a bisulphite solution, preferably to a sodium bisulphite solution, and

(a) at least a portion of the obtained bisulphite solution is subjected to an oxidation treatment in order to oxidise at least a portion of the bisulphite to bisulphate, and the obtained reaction mixture is then further used in the process, and

(b) at least a portion of the obtained bisulphite solution obtained is subjected to an acid treatment in order to convert bisulphite to sulphur dioxide for further use in the process, and the mother liquor remaining from the treatment is optionally further used in the process.

21. A method as defined in claim 19 or 20, **characterised** in that the method further comprises a process step as defined in any of claims 9 to 17.
22. A method as defined in any of claims 1 to 18 or 19 to 21, **characterised** in that the bisulphate solution from treatment (a), an acid, such as a sulphuric acid, an acidic process waste solution derived from a process for producing chlorine compounds, or an acidic process waste solution not derived from a process for producing chlorine compounds, preferably a sulphuric acid which is introduced into the process from outside and/or a bisulphate solution obtained from the treatment (a), is used as the acidic agent in the acid treatment (b).
23. A method as defined in claim 1, **characterised** in that the method comprises at least the treatment (b) and optionally the treatment (a) as defined in accordance with any of claims 1 to 10.
24. A method as defined in any of the preceding claims 1 to 18, 19 to 22 or 23, **characterised** in that the process comprises the recovery step of tall oil soap, which is subjected to an acid treatment for producing tall oil, wherein the acid treatment is carried out by using the remaining bisulphite solution after treatment (b), alone or together with another acidic agent, preferably together with the bisulphate solution obtained from the treatment (a).
25. A method as defined in any of the preceding claims 1 to 18, 19 to 22, 23 or 24, **characterised** in that the sulphur dioxide obtained from the treatment (b) is fed into water in order to produce sulphur dioxide water for use in the process.
26. A method as defined in any of the preceding claims 1 to 18, 19 to 22, 23, 24 or 25, **characterised** in that the sulphur dioxide obtained from the treatment (b) is used as a raw material for the production of chlorine dioxide intended for pulp bleaching.
27. A method as defined in any of the preceding claims 1 to 18, 19 to 22, 23 or 24 to 26, **characterised** in that the acidic mother liquor remaining after treatment (b) is recycled to the treatment (a) by adding it into the bisulphite solution to be oxidised, and the mixture obtained is oxidised in order to produce a bisulphate solution.

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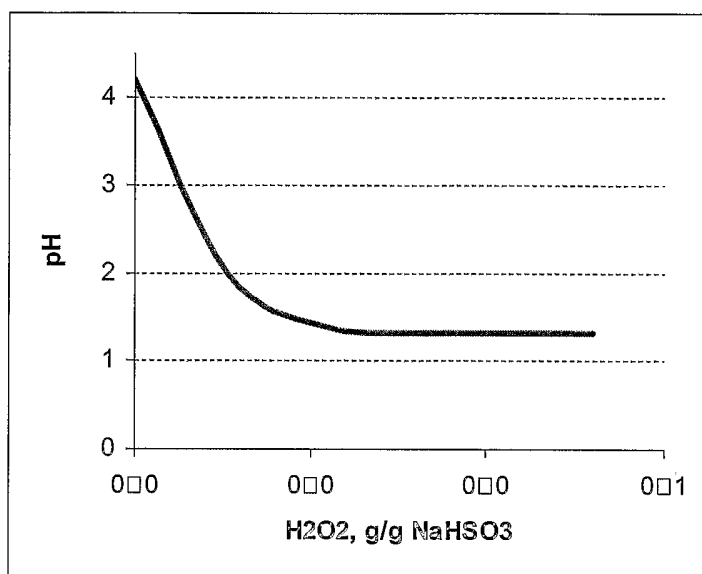


Figure 1

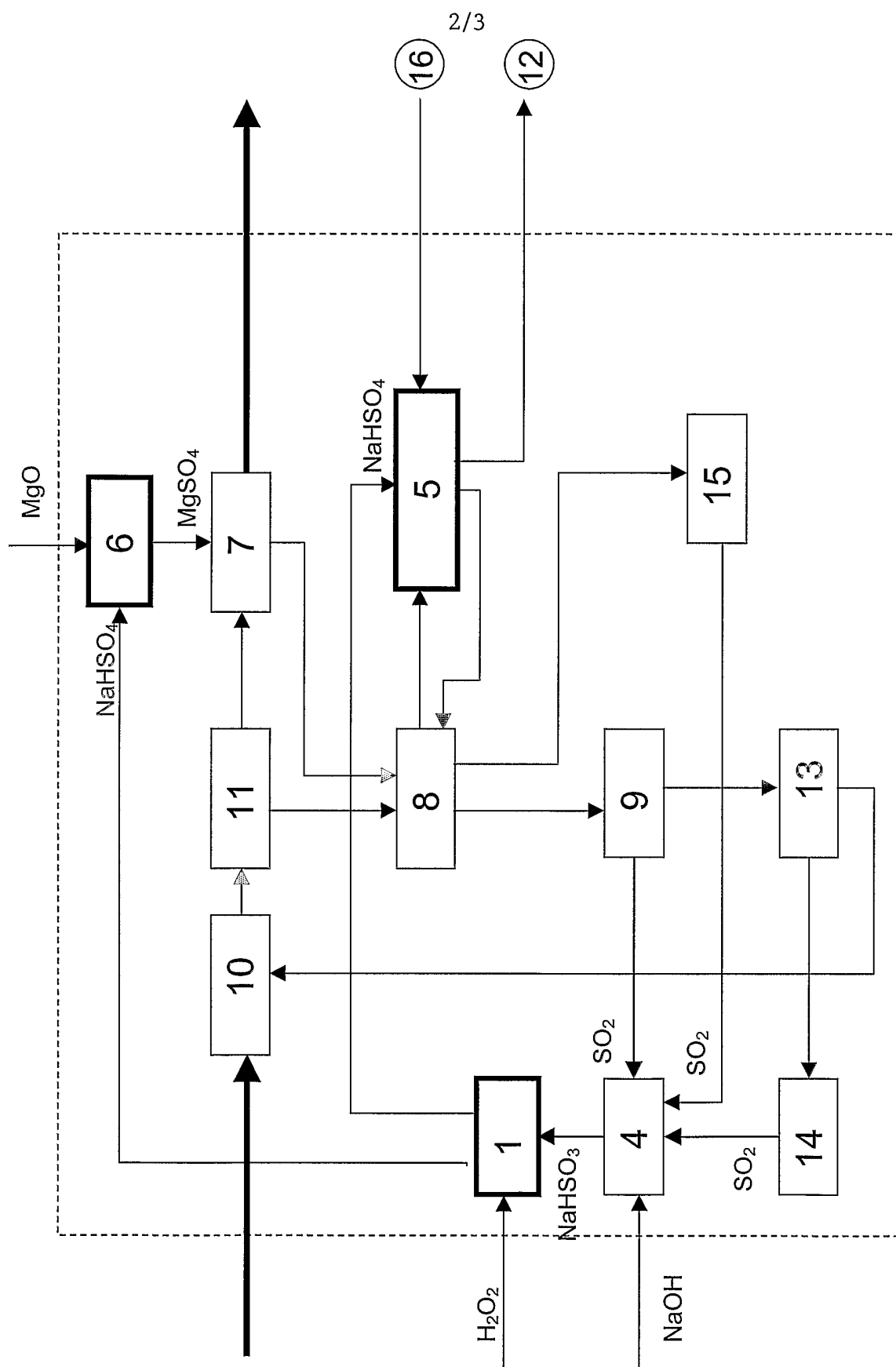


Figure 2

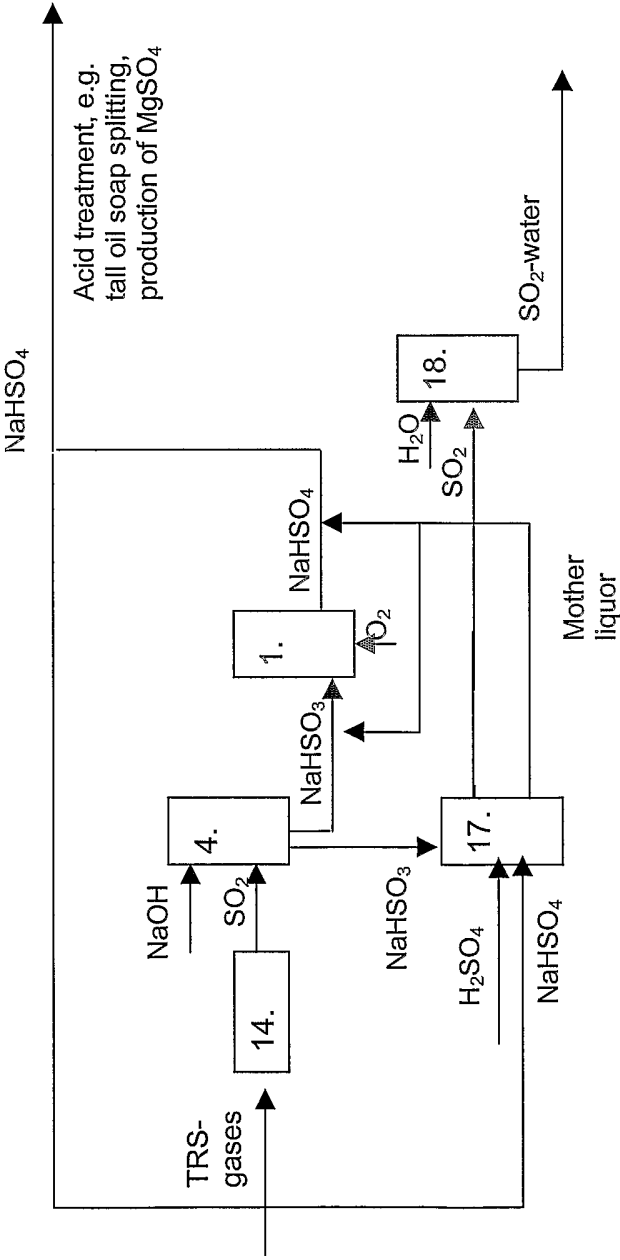


Figure 3