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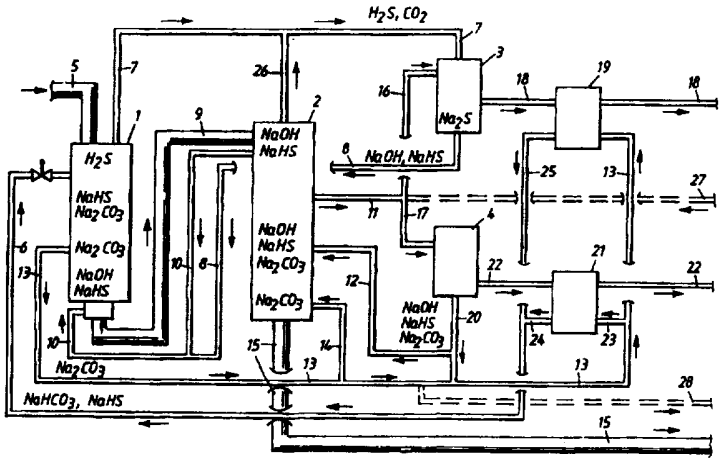
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(57) Abstract

A method of continuously producing paper pulp by integrating the process steps of impregnating fiber material and boiling the impregnated fiber material, the boiling being commenced with digesting liquor containing white liquor of high sulphidity. According to the invention the process includes a pretreatment of the fiber material in a tank (1) with a liquid containing alkali metal bicarbonate and alkali metal hydrogen sulphide. The pretreatment liquid is brought into contact with the fiber material under reducing pressure, whereby, through the pressure reducing and under the influence of heat in situ, said compounds from H_2S, CO_2 and alkali metal carbonate so that a part of the H_2S and HS^- formed is absorbed by or diffused into the fiber material, while said CO_2 is withdrawn from the tank. A liquor is formed during the pretreatment, which contains said alkali metal carbonate and which is withdrawn from the fiber material.

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HYDROGEN SULPHIDE PRETREATMENT OF LIGNOCELLULOSIC MATERIAL IN CONTINUOUS PULPING PROCESSES

The present invention relates to a method of producing in a continuous process paper pulp of cellulosic fiber material by integrating a plurality of process steps comprising impregnating fiber material and boiling the impregnated fiber material, the boiling being commenced in a concurrent digestion zone with digesting liquor comprising white liquor of high sulphidity.

White liquor consists of a water solution of the active digestion chemicals sodium hydroxide, NaOH, and sodium hydrogen sulphide, NaHS. The alkali in the white liquor is consumed during the digestion process by reacting with both lignin and carbohydrates including cellulose and hemicellulose. The sulphidity of the white liquor is dependent on several different circumstances in a sulphate factory and a general aim is to increase the sulphidity in the white liquor. The sulphidity can be increased by various environmental care measures, e.g. by increasing the closing degree of the chemical system in the factory and recovering sulphur from various gas discharges. In this way the sulphidity level can be increased from about 30% to about 45%. The sulphidity is a significant process variable and research is therefore directed to endeavouring to increase it further. An increase in the hydrogen sulphides, HS^-, in the digesting liquor results in a quicker digestion process, higher pulp yield and better pulp quality. This is because the sulphides are able to react with lignin through other reaction paths than hydroxyl ions so that the delignification occurs at higher speed and attacks on the carbohydrates are reduced.

SE-9202996-6 suggests a possibility of adding recovered hydrogen sulphide to the impregnation of wood chips prior to delignification. However, such an addition is

difficult to perform since it is a question of adding an exceptionally toxic gas to a chip bed which is under pressure. It is also difficult to take care of the excess hydrogen sulphide after impregnation.

US-3,841,962 describes a method of pretreating chips with a liquid produced using green liquor as raw material by crystallizing and separating the content of Na_2CO_3 out of the green liquor in order to obtain a remainder of NaHS and NaOH. This is supplied to the pretreatment tank, CO_2 also being added to effect carbonation and the formation of $NaHCO_3$ and H_2S in situ. After the pretreatment a liquid is withdrawn which contains remnants of $NaHCO_3$ and dissolved H_2S and CO_2. The problem is to dispose of this liquid. The pretreatment liquid is made of freshly produced green liquor which requires treatment to separate the Na_2CO_3, followed by addition of CO_2. The method limits the desired excess of H_2S at the treatment stage.

A limiting factor for increasing the sulphidity in white liquor is mainly the use of a soda boiler for recovering digestion chemicals and the necessary causticizing of the green liquor produced from melt from the soda boiler.

A process is known through SE-B-468 600 for obtaining white liquor of high sulphidity, i.e. having high sodium hydrogen sulphide content in relation to the sodium hydroxide content, directly from the evaporation reactor without the need for causticizing. According to this procedure hydrogen sulphide is recovered from the gas step extracted from a reactor and is returned to the reactor to be present at the thermal decomposition of the black liquor. Such a high partial pressure is thus established in the evaporation stage by hydrogen sulphide that the equilibrium reaction

$$Na_2CO_3 + H_2S \rightleftarrows Na_2S + CO_2 + H_2O$$

is displaced so far to the right that the formation of Na_2CO_3 is suppressed. Na_2S formed is dissociated in water to NaOH and NaHS. The recovery of hydrogen sulphide from the gas step occurs by the gas being allowed to pass a gas scrubber with an external absorption chemical, e.g. N-methyl pyrolidone or methyl di-ethyl amine, for selective and regenerative absorption of H_2S. The need for such an external chemical is drawback with this procedure and also requires a regeneration step to strip the hydrogen sulphide from the absorption chemical.

The object of the present invention is to provide an improved pretreatment of the fiber material with compounds containing sulphur, and an improved selectivity at commencement of the digestion by the use of a digesting liquid having as high sulphidity as possible.

Another object of the invention is to provide an improved pretreatment of the fiber material with compounds containing sulphur enabling total integration of the various process steps to be achieved, so that chemicals can be recovered and prepared to form active solutions for the various treatment steps without having to use convention causticizing and calcination in order to strip CO_2.

The method according to the invention is characterized in that the process also comprises an integrated pretreatment of the fiber material in a tank with a liquid containing alkali metal bicarbonate and alkali metal hydrogen sulphide as reaction components and being free from alkali metal hydroxide, said pretreatment liquid being brought into contact with the fiber material under reducing of pressure, whereby, initially through said pressure reducing and subsequently under the

influence of heat, the reaction components form H_2S, CO_2 and alkali metal carbonate in situ so that a part of the H_2S and HS^- formed is absorbed by and diffused into the fiber material, while said CO_2 is withdrawn from the vessel; and that in said pretreatment a liquor is formed containing substantially said alkali metal carbonate and which is withdrawn from the fiber material.

White liquor with high sulphidity can generally be manufactured for the digestion stage in the process according to the invention by allowing conventional white liquor to absorb H_2S gas or by adding to the white liquor elementary sulphur for forming polysulphide.

Green liquor can be added to a second digestion zone, e.g. a green liquor having low sulphidity. The invention offers an advantageous method of producing such low-sulphidity green liquor.

The pretreatment liquid can generally be manufactured from green liquor which has been allowed to selectively absorb H_2S and, as co-absorption to a lesser extent, CO_2, to obtain $NaHCO_3$ and NaHS in accordance with the following reactions:

$NaHCO_3$ and NaHS:

$$NaOH + H_2S \rightleftarrows NaHS + H_2O$$

$$Na_2CO_3 + H_2S \rightleftarrows NaHCO_3 + NaHS$$

$$2NaOH + CO_2 \rightleftarrows Na_2CO_3 + H_2O$$

$$Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3$$

The process step of recovering chemicals and energy from spent liquor and gases in the process is preferably also included, for the production of active liquors of said chemicals for the process.

Preferably at least a part of the liquor containing alkali metal carbonate is conducted to the recovery step to be brought into contact with combustion gas containing H_2S formed at gasification of spent liquor, for the production of a pretreatment liquid having said composition, which is transferred to said pretreatment step.

A surplus of H_2S is preferably formed at said treatment, which is conducted to the recovery step of the process to be present at gasification of said first part of spent liquor in the manufacture of white liquor of high sulphidity.

A second part of the spent liquor withdrawn from the delignified fiber material in the process is preferably gasified to produce a combustion gas and green liquor with low sulphidity.

A first part of said green liquor is preferably conducted to the digestion process to be present in a second digestion zone. Said first part of the green liquor having low sulphidity can be brought into contact with a sulphurous compound, the green liquor thus enriched with sulphur being supplied to the digestion process to be present in the second digestion zone and/or in an additional digestion zone downstream of the second digestion zone. The green liquor can suitably be brought into contact with hydrogen sulphide or polysulphide. The hydrogen sulphide may be obtained from said pretreatment and/or from a gas scrubber with absorption chemicals, said gas scrubber being supplied with combustion gas, preferably from said gasification of spent liquor for the production of white liquor having high sulphidity. Said polysulphide can be produced from liquid sulphur and H_2S which is absorbed therein, or from liquid sulphur and Na_2S originating from said gasification of spent liquor

for the production of white liquor of high sulphidity, said liquid sulphur being produced in a Claus apparatus in which H_2S is converted to elementary sulphur, and to which gas containing H_2S is supplied from said pretreatment and/or from a gas scrubber with absorption chemicals, said gas scrubber being supplied with combustion gas, preferably from said gasification of spent liquor for the production of white liquor having high sulphidity.

A second part of said green liquor is preferably brought into contact with combustion gas containing H_2S formed at gasification of spent liquor, to produce a pretreatment liquid of said composition which is conveyed to said pretreatment stage.

The white liquid has a sulphidity of over 40%, preferably over 70%.

The green liquor of conventional type which is used in the process has an NaHS content of about 30 g/l, calculated as NaOH, whereas the green liquor with low sulphidity produced through said evaporation at increased pressure, with the resultant displacement in reaction equilibrium, has an NaHS content of about 9-15 g/l.

The treatment liquid contains $NaHCO_3$ and NaHS in a quantity exceeding 80%, preferably 90%, of the chemical content, any remainder consisting substantially of Na_2CO_3.

The method according to the invention enables chemicals for the process steps of impregnation and digestion to be produced without the need of a soda boiler or of equipment for causticizing and thus a complicated calcium cycle. CO_2 formed in the process steps, including the recovery step, is removed from the system without calcium

treatment, namely by means of simple stripping with the combustion gas. Although it is preferred not to make use of conventional systems with soda boiler and causticizing, it lies within the scope of the invention to use such a system for recovering chemicals to be added to the digester.

According to a preferred embodiment the quantity of pretreatment liquid supplied for pretreating the fiber material, calculated with regard to alkali metal bicarbonate and alkali metal hydrogen sulphide, is such that, under the prevailing operating conditions, a controlled large surplus of H_2S is formed during the pretreatment and is conducted to said recovery to be present in the gasification of the spent liquor with a controlled, increased partial pressure.

The pretreatment liquid according to the invention is thus manufactured from recirculated liquor containing substantially Na_2CO_3 and a small amount of dissolved wood substance, and with the requisite addition of green liquor having low NaHS content for selective absorption of H_2S. The absorption, which may take place in several steps with the relevant liquids mixed or one by one, is designed for selective H_2S absorption and the least possible co-absorption of CO_2. The contact apparatus for gas-liquid is preferably designed with multi-step contact in counterflow in series in order to achieve a predetermined ratio between H_2S absorption and CO_2 absorption so that the pH value of the pretreatment step can be controlled. For this purpose atomised liquid is used with small drops which offer a large area and good mixing in the gas. The best selectivity of H_2S (co-absorption of CO_2) is achieved through extremely brief contact time, preferably 0.1-0.01 sec.

In further embodiment of the invention, gas containing H_2S is brought into contact with spent liquor so that H_2S is absorbed selectively by the spent liquor in order to obtain a spent liquor enriched with sulphur. Such a spent liquor may consist of black liquor, partially evaporated spent liquor from the digestion and/or spent liquor from the bleaching department, which is preferably alkaline. The gas containing H_2S suitably comes from said pretreatment. It may also consist of combustion gas from said gasification of spent liquor which results in white liquor having high sulphidity and/or gasification of spent liquor which results in green liquor with low sulphidity. It is suitable for the sulphur-enriched, partially evaporated spent liquor to be fully evaporated in order to obtain black liquor.

The black liquor enriched with sulphur may advantageously be gasified to produce white liquor having high sulphidity and/or green liquor with low sulphidity. It is also advantageous to treat the fiber material with the sulphur-enriched spent liquor before or in conjunction with said pretreating step, in which case spent liquor from this treatment is withdrawn from the fiber material and gasified directly or after evaporation.

The invention will be described in more detail in the following with reference to the drawing in which

Figure 1 shows schematically a flow chart of a process line for the manufacture of paper pulp with total integration of the actual process steps.

With reference to Figure 1 it shows schematically a flow chart of a process line for the manufacture of paper pulp from cellulosic fiber material, particularly wood, through total integration of the pretreatment, impregnation, digestion and recovery process steps. If

desired bleaching may also be included as a process step in this total integration, in which case the spent liquor evaporated at the recovery step may consist partly of spent liquor from the bleaching department which is supplied via a pipe 27. In the latter case Na_2CO_3 withdrawn from the pretreatment vessel may constitute the raw product for the bleaching department's requirement of NaOH after separate causticizing, to which said Na_2CO_3 can be transferred via a pipe 28. Pretreatment is performed in a tank 1 and impregnation and digestion in a tank 2. Evaporation of black liquor is performed in a first reactor 3 and a second reactor 4.

Chips are fed by an arrangement 5 to the top of the pretreatment tank. The temperature in the pretreatment tank lies within the interval 70-170°C, preferably within the interval 90-120°C. A pretreatment liquid is introduced via a pipe 6 into the upper part of the pretreatment tank 1, said pretreatment liquid containing $NaHCO_3$ and NaHS as the only reaction components, but being free from hydroxyl ions since these would react with sodium bicarbonate formed in an undesirable manner for the purpose of the invention. The pretreatment liquid in the pipe 6 has relatively high pressure, typically about 25 bar. The pressure in the pretreatment tank 1 is within the interval 0.5-8 bar, preferably within the interval 1-5 bar. When the pretreatment liquid enters the pretreatment tank it expands and development of gases and formation of carbonate commence through the following reactions:

$$NaHCO_3 + NaHS \rightarrow H_2S + Na_2CO_3$$
$$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O$$

Thanks to the formation of H_2S and CO_2 an approximately neutral or weakly acid pH value is obtained in the chips

suspension. The pH value generally lies within the interval 4-8, preferably 5-7.

The reactions continue down through the pretreatment tank 1 until all or substantially all sodium hydrogen sulphide and sodium bicarbonate have been converted to Na_2CO_3. CO_2 and excess H_2S rise in the tank and are fed out through a pipe 7. H_2S and HS^- are thus formed in situ, not merely outside but also in a favourable manner inside the chips. Part of the hydrogen sulphide and HS^- will penetrate into the chips through absorption and diffusion, respectively. In this pretreatment, thus, the hydrogen sulphide ion is given priority over the hydroxyl ion, which is particularly valuable since the hydroxyl ions have a much greater tendency to attack carbohydrates than lignin. Since OH^- is restrained during said pretreatment and HS^- is also selective towards lignin, a valuable increase in quality and yield is obtained. The duration of the pretreatment is over 10 minutes, preferably over 20 minutes. The acid chips are buffered by the sodium carbonate formed which dissociates at the high temperature, with displaced equilibrium towards hydroxyl ions in accordance with the following reactions:

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$$

The liquid containing carbonate is withdrawn at the lower part of the tank 1 and fed through a pipe 13. The chips treated in this way are transferred via a pipe 9 from the bottom of the tank 1 to the top of the tank 2 with the aid of liquid withdrawn from the upper part of the tank 2 and allowed to circulate through a pipe 10 to the bottom part of the tank 1. A pipe 8 is connected to the pipe 10 for the supply of high-sulphidity white liquor. Impregnation of the chips with digesting liquid takes

place in the upper part of tank 2, after which follows a concurrent digestion zone with digestion temperature, typically about 165°C. The liquid/chips ratio lies within conventional values and is typically about 4:1. Gas withdrawal can be carried out in conventional manner via a pipe 26 at the top of the tank 2, said pipe 26 joining the pipe 7 from the first tank. Alternatively this pipe 26 can be eliminated. Spent liquor is withdrawn after the digestion zone and supplied through a pipe 11 to arrangement for flashing and evaporation (not shown). After withdrawal of spent liquor a second digestion zone follows in which green liquor, i.e. NaOH, NaHS and Na_2CO_3, with low sulphidity is introduced into the tank 2 via a pipe 12 for continued delignification of the chips in counterflow and at a temperature of about 160-165°C. At the lower part of the tank 2 is a zone for buffering the chips with sodium carbonate. For this purpose a pipe 14 is arranged between the pipe 13 and the tank 2 in order to make use of a part of the carbonate obtained at said pretreatment. The delignified chips are fed out via a pipe 15 for continued treatment in conventional manner.

Arrangements are provided for the recovery of chemicals and energy from spent liquors and gases from the various steps of the process and for preparation of treatment liquids of these chemicals, said arrangements comprising in the embodiment shown a reactor 3 for production of white liquor of high sulphidity and a reactor 4 for production of green liquor with low sulphur content, as well as said flashing and evaporation arrangements. The gases produced in the reactors 3, 4 are conducted via pipes 18 and 22, respectively, to contact devices 19 and 21, respectively for liquid-gas (e.g. "absorbers") in order to bring the combustion gases containing H_2S into contact with the described liquor of carbonate and with green liquor of low sulphidity. Following evaporation to higher dry solids content, the spent liquor withdrawn

from the tank 2 is distributed in predetermined manner to the reactors 3, 4 via the pipes 16, 17.

The gas containing hydrogen sulphide is supplied from the tank 1 to the reactor 3 via pipe 7. The black liquor is evaporated in the reactor 3 under reducing conditions in the presence of H_2S to form a melt of substantially Na_2S and a combustion gas containing hydrogen sulphide. The reactor 3 operates at a relatively low pressure, about 1.5-6 bar, preferably 2-4 bar and the supply of H_2S entails that an increased partial pressure for this gas is obtained so that the equilibrium reaction

$$Na_2CO_3 + H_2S \rightleftarrows Na_2S + CO_2 + H_2O$$

is displaced to the right, thereby suppressing the formation of Na_2CO_3 and favouring the formation of Na_2S. The melt of Na_2S is cooled and dissolved in a suitable liquid to form white liquor, NaOH and NaHS, with high sulphidity. The white liquor produced is fed through the pipe 8 to the bottom of the tank 1. In the contact arrangement 19 sodium carbonate and green liquor with low sulphidity react selectively with hydrogen sulphide and, to a lesser extent, with carbon dioxide to form a solution containing $NaHCO_3$ and NaHS. This solution of sodium bicarbonate and sodium hydrogen sulphide is supplied at a specific pressure and temperature to the pretreatment tank 1 via the pipes 25 and 6 for pretreating the chips as described above. A pump (not shown) may be arranged in pipe 25 in order to achieve a high pressure if necessary.

The black liquor is evaporated in the reactor 4 under reducing conditions for the production of a combustion gas containing sulphur, which is cooled, and a melt of Na_2CO_3, Na_2S and NaOH, which is dissolved and cooled in a liquid to form green liquor, NaOH, NaHS and Na_2CO_3, which

is fed out via a pipe 20, and a combustion gas containing hydrogen sulphide. The green liquor from the reactor 4 has a lower content of NaHS than conventional green liquor since the remaining sulphur exists in the combustion gas as H_2S due to the prevailing high operating pressure during the evaporation. A first part of this green liquor is conducted to the vessel 2 via a pipe 12, while a second part is conducted to the contact arrangements 19, 21 for liquid-gas via the pipe 13 and a pipe 23, mixed with sodium carbonate withdrawn from the tank 1. In these contact arrangements 19, 21 the gas containing H_2S from the reactors 3 and 4 is brought into contact with the treatment liquids - alternatively individually - so that solutions are formed containing sodium bicarbonate and sodium hydrogen sulphide. These solutions are fed out via the pipes 24 and 25 and combined to be conducted in the common pipe 6 under high pressure, typically 25 bar, and at high temperature, to the tank 1 in which a pressure reducing occurs due to expansion of the liquid.

The evaporation temperature in the reactors 3, 4 is generally within the interval 500-1600°C, preferably 700-1300°C, and most preferably 800-1000°C. In the reactors the black liquor is thermally decomposed under reducing conditions through the supply of pure oxygen gas or gas containing oxygen, in a quantity corresponding to from close to 0 up to 80%, preferably up to 60%, of the stochiometrically required amount of oxygen for complete oxidation of the substances formed at decomposition.

Anthraquinone may be added to the tank 2 if desired, in the zones where the HS^- content of the digesting liquid is low. A pipe for the supply of anthraquinone may thus be connected to the pipe 12 for green liquor and/or to the pipe 14 for sodium carbonate.

Suitable equipment (not shown) is also provided in the pipe 7 for condensing condensate which may be used for cooling and dissolving melt and cooling gas at the reactor 3.

Suitable separation equipment is arranged in one or both of the pipes 13 and 20 for separating elements foreign to the process, from the wood.

The process steps of pretreatment, impregnation and digestion may be performed in one and the same tank or in separate tanks. The pretreatment tank may also be extended downwardly so that impregnation with the impregnation liquid occurs after the carbonate has been withdrawn.

The manufacture of white liquor may also be performed in two or more reactors, for reasons of capacity or in order to obtain white liquors having different sulphidity.

The second part of the black liquor can be divided via pipe 17 to supply two or more reactors for separate production of green liquor and pretreatment liquor containing sodium bicarbonate and sodium hydrogen sulphide. These two liquors can also be obtained in one and the same reactor which is provided with two separate liquid baths, where the gas produced in the reactor is allowed to pass through one liquid bath to form sodium hydrogen bicarbonate and sodium hydrogen sulphide.

The distribution of the black liquor to the various evaporation steps depends on the sulphidity of the liquor stock. 10-60%, preferably 20-40%, of the black liquor is supplied to the first evaporation step, i.e. to the reactor 3, while the rest is supplied to the reactor 4.

It is advantageous to arrange a contact device for gas-liquid in the pipe 7 for H_2S and CO_2 and to connect the pipe 16 for black liquor to this contact device, whereby the gas containing H_2S and CO_2 is brought into contact with the black liquor so that H_2S is absorbed selectively by the black liquor, while CO_2 can be withdrawn via a separate pipe. The black liquor thus enriched with sulphur is then conducted to the reactor 3 for evaporation in order to produce a melt consisting substantially of Na_2S. Said contact device can be supplied with partially evaporated spent liquor from the digestion instead of black liquor, after which the spent liquor thus enriched with H_2S is conducted to final evaporation in the evaporation plant to obtain black liquor which is then transferred to the reactor 3.

Spent liquor from the digestion can be used as liquid for cooling the combustion gas and for cooling and dissolving the melt formed in the reactor 3, particularly thin liquor, i.e. spent liquor which has not been evaporated and which has passed a first flash cyclone. A digesting liquid is thus obtained which consists of a mixture of white liquor and spent liquor. The condensate can at the same time advantageously be added at the outlet of the reactor 3 to encounter the melt and the combustion gas. Such a condensate may thus be obtained in said condensation equipment in the pipe 7 and/or condensate free from alkali from the evaporation plant which preferably contains sulphur compounds.

Although it is a particular advantage with the method according to the invention that spent liquor from the digestion need not be added separately for impregnation of the chips, such spent liquor may in certain cases be used.

The method according to the invention thus comprises a multi-stage process with total integration of the delignification and liquor recovery. Process chemicals for chips pretreatment, impregnation and digestion are produced continuously without the need of equipment for causticizing. CO_2 is stripped without having to use the complicated calcium cycle, namely together with the combustion gas and possibly with said contact device in the pipe 7. Necessary process chemicals are produced with predetermined compositions in each individual case, within an integrated gasification, liquor and gas treating system. The naturally acid chips are treated at a temperature of 70-170°C with expanded pretreatment liquid as the first process chemical containing sodium bicarbonate and sodium hydrogen sulphide, this expansion causing such a pressure decrease that H_2S and CO_2 are released and that H_2S and HS^- are formed in situ. Said release continuous through the pretreatment tank under the influence of heat. No external CO_2 or other chemicals are added to the pretreatment to assist in the reactions. SH^- ions are formed during the pretreatment, which are preferred to OH^-, after which the impregnation and digestion steps are commenced with digesting liquid of high sulphidity.

In most cases it is desirable to be able to distribute the sulphur in the process between high sulphidity white liquor and low sulphidity green liquor to the digester according to the current need for delignification and the sulphidity of the liquor material, the Na/S ratio. This desire is fulfilled with a preferred embodiment of the invention in which said first part of the green liquor having low sulphidity is brought into contact with a sulphurous compound, after which the green liquor thus enriched with sulphur is supplied to the digestion process to be present in the second digestion zone and/or in an additional digestion zone downstream of the second

digestion zone. One method is for the H_2S to be absorbed selectively in the low-sulphidity green liquor before being connected to the digester. Another method is to lead a flow of gas containing H_2S to a Claus apparatus for producing liquid sulphur in accordance with the following reactions:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$
$$2H_2S + SO_2 \rightarrow 3S_{(1)} + 2H_2O$$

Sulphurous residue gas is suitably conducted to the gasification step that produces white liquor having high sulphidity. Said flow of gas containing H_2S may be obtained from said pretreatment and/or from a gas scrubbing with a suitable absorption chemical for selective and regenerative absorption of H_2S, which is desorbed and conducted wholly or partially to the Claus furnace. These sources of H_2S can also be utilized in the first method mentioned above. $S_{(1)}$ is extracted from the Claus furnace and added to the low sulphidity green liquor, preferably together with a flow of Na_2S obtained from said gasification for the production of high sulphidity white liquor, to produce polysulphides according to the reactions:

$$Na_2S + S \rightarrow Na_2S_2$$
$$Na_2S_2 + S \rightarrow Na_2S_3, \text{ and so on.}$$

It is suitable to add $S_{(1)}$ directly to the liquor mixture containing Na_2S, at a temperature of 160-200°C. Polysulphide can also be produced most advantageously by absorbing H_2S, e.g. from one of said H_2S sources, in $S_{(1)}$. In this case the addition of high sulphidity liquor may be omitted.

Some of said green liquor poor in sulphide and/or the solution of Na_2CO_3 may be causticized if so desired.

The integration of the process steps proposed according to the invention entails valuable synergetic effects. Sulphur resources can be redistributed and utilized more efficiently according to the current requirement. All sulphur is available in active form, which offers an increase of about 7-10% over that obtained through the soda recovery unit method. A small quantity of NaOH, about 5% by weight of the melt, is obtained during gasification, i.e. green liquor of low sulphidity contains a relatively small proportion of NaOH. The neutralisation of the wood acid and buffering is achieved substantially by means of dissociated Na_2CO_3 solutions of high temperature, i.e. without consuming active digestion chemicals.

The method according to the invention is not limited to sodium as a basis. A potassium basis is also possible, or a combination of these.

If desired the digestion liquor may contain various additives such as an organic additive, e.g. a suitable alcohol.

In order to compensate for unavoidable losses of process chemicals suitable make-up chemicals such as Na_2SO_4 may be added and/or sulphate soap is returned.

The expression "white liquor having high sulphidity" in this description and in the following claims also includes a polysulphide-based digestion liquor.

The pressures stated above and in the appended claims relate to absolute pressure.

C L A I M S

1. A method of producing in a continuous process paper pulp of cellulosic fiber material by integrating a plurality of process steps comprising impregnating fiber material and boiling the impregnated fiber material, the boiling being commenced in a concurrent digestion zone with digesting liquor comprising white liquor of high sulphidity, characterized in that the process also comprises an integrated pretreatment of the fiber material in a tank (1) with a liquid containing alkali metal bicarbonate and alkali metal hydrogen sulphide as reaction components and being free from alkali metal hydroxide, said pretreatment liquid being brought into contact with the fiber material under reducing of pressure, whereby, initially through said pressure reducing and subsequently under the influence of heat, the reaction components form H_2S, CO_2 and alkali metal carbonate in situ so that a part of the H_2S and HS^- formed is absorbed by and diffused into the fiber material, while said CO_2 is withdrawn from the tank (1); and that in said pretreatment a liquor is formed containing substantially said alkali metal carbonate and which is withdrawn from the fiber material.

2. A method as claimed in claim 1, characterised in that the pretreatment occurs at a pH value of 4-8, preferably 5-7.

3. A method as claimed in claim 1 or 2, characterized in that the pretreatment is performed at a pressure within the interval 0.5-8 bar, preferably 1-5 bar, and at a temperature within the interval 70-170°C, preferably 90-120°C.

4. A method as claimed in any of claims 1-3, characterized in that the quantity of pretreatment liquid

supplied for pretreating the fiber material, calculated with regard to alkali metal bicarbonate and alkali metal hydrogen sulphide, is such that, under the prevailing operating conditions, a controlled large surplus of H_2S is formed during the pretreatment.

5. A method as claimed in any of claims 1-4, characterized in that said digesting liquor has a sulphidity of at least 40%, preferably at least 70%.

6. A method as claimed in any of claims 1-5, characterized in that a part of the alkali metal carbonate withdrawn from the pretreatment step is supplied to the end of the digestion process in order, through buffering action, to prevent precipitation of lignin on the fiber material.

7. A method as claimed in any of claims 1-6, said method also comprising recovery of chemicals and energy from spent liquors and gases in the process for manufacturing active liquors from said chemicals for the process, characterized in that said white liquor with high sulphidity is produced by gasification of a first part of spent liquor which is withdrawn from delignified fiber material in the process during simultaneous supply of H_2S to obtain a combustion gas and a white liquor of high sulphidity.

8. A method as claimed in claim 7, characterized in that a second part of spent liquor withdrawn from delignified fiber material in the process is gasified to produce a combustion gas and green liquor with low sulphidity.

9. A method as claimed in claim 7 or 8, characterized in that at least a part of the withdrawn liquor containing alkali metal carbonate is conducted to the

recovery of the process to be brought into contact with combustion gas containing H_2S formed at gasification of spent liquor, for the production of a pretreatment liquid having said composition, which is transferred to said pretreatment step.

10. A method as claimed in claim 9, characterized in that the contact between gas and liquid is designed, preferably as multi-stage contact in counterflow in series, for a predetermined ratio between H_2S absorption and CO_2 absorption, whereby this ratio can be utilised to control the pH value of the pretreatment step, that said liquid or liquor is atomised into small drops having a large area, and that said contact occurs over a brief period of time, preferably 0.1-0.01 sec.

11. A method as claimed in any of claims 7-10 in combination with claim 4, characterized in that the excess of H_2S formed at said pretreatment is conducted to the process recovery to be present in a controlled increased partial pressure at gasification of said first part of spent liquor in the manufacture of white liquor of high sulphidity.

12. A method as claimed in claim 8, characterized in that a first part of said green liquor is transferred to the digestion process to be present in a second digestion zone.

13. A method as claimed in claim 12, characterized in that said first part of the green liquor having low sulphidity is brought into contact with a sulphurous compound, and that the green liquor thus prepared and enriched with sulphur is supplied to the digestion process to be present in the second digestion zone and/or in an additional digestion zone downstream of the second digestion zone.

14. A method as claimed in claim 13, characterized in that the green liquor is brought into contact with hydrogen sulphide or polysulphide.

15. A method as claimed in claim 14, characterized in that said hydrogen sulphide is obtained from said pretreatment and/or from a gas scrubber with absorption chemicals, said gas scrubber being supplied with combustion gas, preferably from said gasification of spent liquor for the production of white liquor having high sulphidity.

16. A method as claimed in claim 14, characterized in that said polysulphide is produced from liquid sulphur and H_2S which is absorbed therein, or from liquid sulphur and Na_2S originating from said gasification of spent liquor for the production of white liquor of high sulphidity, said liquid sulphur being produced in a Claus apparatus in which H_2S is converted to elementary sulphur, and to which gas containing H_2S is supplied from said pretreatment and/or from a gas scrubber with absorption chemicals, said gas scrubber being supplied with combustion gas, preferably from said gasification of spent liquor for the production of white liquor having high sulphidity.

17. A method as claimed in claim 12 or 13, characterized in that a second part of said green liquor is brought into contact with combustion gas containing H_2S formed at gasification of spent liquor, to produce a pretreatment liquid of said composition which is conveyed to said pretreatment step.

18. A method as claimed in any of claims 7-17, characterized in that said spent liquor which is gasified

consists partially or entirely of spent liquor from the digester.

19. A method as claimed in claim 18, which also comprises a bleaching step, characterized in that said spent liquor which is gasified consists partially of spent liquor from the bleaching department.

20. A method as claimed in claim 19, characterized in that a part of the liquor withdrawn from the pretreatment step, which contains Na_2CO_3, is causticized separately in order at least partially to fill the bleaching department's requirement for NaOH.

21. A method as claimed in any of claims 7-20, characterized in that elements in the wood material that are foreign to the process are separated off at one or more points in the process, preferably from the liquor containing alkali metal carbonate withdrawn from the pretreatment and/or from the green liquor with low sulphidity.

22. A method as claimed in any of claims 7-21, characterized in that gas containing H_2S is brought into contact with spent liquor so that H_2S is absorbed selectively by the spent liquor in order to obtain a spent liquor enriched with sulphur.

23. A method as claimed in claim 22, characterized in that gas containing H_2S is brought into contact with spent liquor in the form of black liquor, partially evaporated spent liquor from the digestion and/or spent liquor from the bleaching department, so that H_2S is absorbed selectively by the black liquor, partially evaporated spent liquor, and spent liquor from the bleaching department, respectively, in order to obtain a black liquor enriched with sulphur, evaporated spent

liquor partially enriched with sulphur, and spent liquor from the bleaching department enriched with sulphur, respectively.

24. A method as claimed in claim 23, characterized in that gas containing H_2S is brought into contact with alkaline spent liquor from the bleaching department.

25. A method as claimed in any of claims 22-24, characterized in that said gas containing H_2S originates from said pretreatment step.

26. A method as claimed in any of claims 22-24, characterized in that said gas containing H_2S is present in combustion gas from said gasification of spent liquor for the production of white liquor having high sulphidity and/or gasification of spent liquor for the production of green liquor having low sulphidity.

27. A method as claimed in claim 23, characterized in that the sulphur-enriched, partially evaporated spent liquor is finally evaporated to obtain black liquor.

28. A method as claimed in any of claims 22-27, characterized in that the sulphur-enriched spent liquor is gasified for the production of white liquor and/or green liquor having high and low sulphidity, respectively.

29. A method as claimed in any of claims 22-27, characterized in that the fiber material is treated with the sulphur-enriched spent liquor before or in conjunction with said pretreating step, and that spent liquor from this treatment is withdrawn from the fiber material and gasified directly or after evaporation.

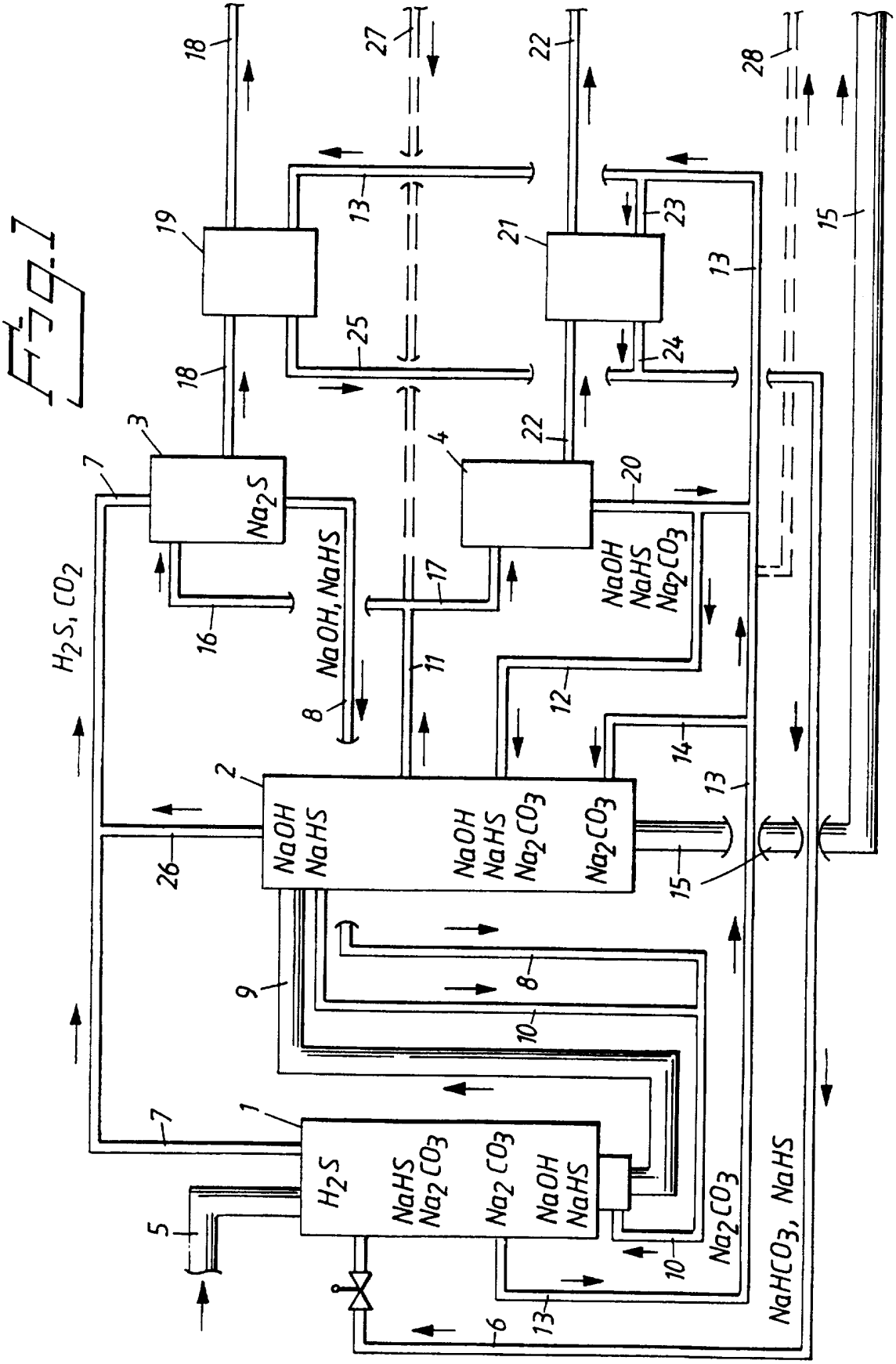
30. A method as claimed in any of claims 7-29, characterized in that anthraquinone is added to the digestion process.

31. A method as claimed in claim 30, characterized in that anthraquinone is added to the digestion process to be present in a zone or zones in which the sulphide content is low, preferably in a second digestion zone, to which green liquor is added.

32. A method as claimed in claim 9, characterized in that said withdrawn liquor containing said alkali metal carbonate is brought into contact with combustion gas obtained from the production of said white liquor having high sulphidity, and also combustion gas obtained from the production of said green liquor having low sulphidity.

33. A method as claimed in claim 9, characterized in that the liquor containing said alkali metal carbonate is brought into contact with combustion gas obtained from the production of said green liquor having low sulphidity, and that the combustion gas obtained from the production of said white liquor of high sulphidity is brought into contact with an absorption chemical in a gas scrubber for selective and regenerative absorption of H_2S, which is desorbed and returned to be present at said gasification of spent liquor for the production of white liquor having high sulphidity.

Fig. 1


H_2S, CO_2
Na_2S
NaOH, NaHS
NaOH
NaHS
Na_2CO_3
H_2S
NaHS
Na_2CO_3
$NaHCO_3$, NaHS

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 97/00686

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 1/06, D21C 3/02, D21C 11/04
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4113553 A (HANS OLOF SAMUELSON), 12 Sept 1978 (12.09.78) --	1-33
A	WO 9312288 A1 (CHEMREC AKTIEBOLAG), 24 June 1993 (24.06.93) -- --------	1-33

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"E" erlier document but published on or after the international filing date
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"P" document published prior to the international filing date but later than the priority date claimed
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 July 1997	06 -08- 1997
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Marianne Bratsberg Telephone No. +46 8 782 25 00

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Information on patent family members

International application No.
PCT/SE 97/00686

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