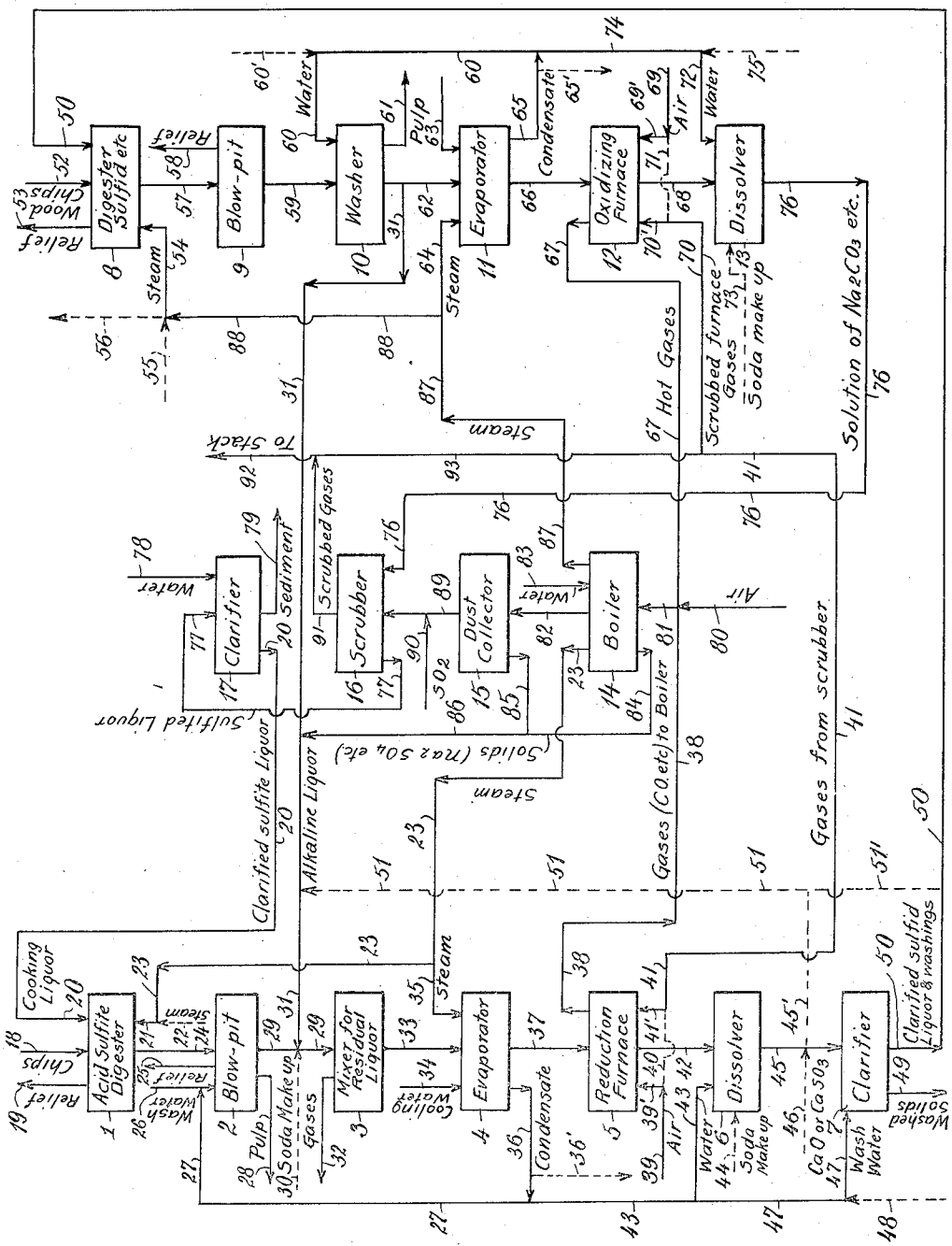
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PRODUCTION OF CHEMICAL PULP, ETC

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PRODUCTION OF CHEMICAL PULP, ETC.

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This invention relates to the production of chemical pulp, and to the treatment of residual liquors for the regeneration of cooking liquors.

More particularly the invention relates to cyclic and interrelated operations, in which two or more different kinds or types of sulfur-containing cooking liquors are employed, of which soda is the base, some of the same sulfur being employed in one type of cooking liquor as a sulfite and in another type as a sulfid, and with successive employment of some of the same soda as a sulfite in one type and as sulfid in another type of liquor, although the soda and the sulfur may in part be present as other compounds.

Among the particular improvements which the invention presents are operations or steps employing interrelated acid-sulfite processes and sulfid processes, in which cooking liquors for one type of cooking process are regenerated (at least in part) from residual liquors of another type of cooking process, and vice versa. The acid sulfite cooking processes to which the invention particularly relates are those in which a relatively high content of combined sulfite is employed, more particularly cooking liquors in which the combined sodium is equal to or greater than that corresponding to sodium bisulfite, the cooking liquors being free from any large excess of sulfur dioxide or sulfurous acid and in general being made up of mixtures of sodium monosulfite and sodium bisulfite. The sulfid type of cooking liquors to which the invention more particularly relates are regenerated cooking liquors in which the sodium present as sodium sulfid equals or exceeds in amount that present as sodium hydroxide, in case the latter also is present.

According to one embodiment of the present invention, residual liquor from an acid sulfite cooking process, in which the cooking liquor is a mixture of sodium monosulfite and bisulfite, and which already contains a high ratio of sodium to sulfur, is treated with some alkaline soda compound and concentrated, and the resulting product is subjected to a reducing furnacing treatment under regulated conditions to produce a furnace product containing a considerable proportion of the sodium as sodium sulfid, with the remainder of the sodium present mainly as sodium carbonate. A solution of the sodium compounds of the furnace product is prepared which is utilized, either directly or after modification or further treatment, as a cooking liquor in the sulfid type of cooking process. Residual liquor from the sulfid type of cooking operation is concentrated, and the resulting product is subjected to a suitable heating or furnacing operation to decompose organic compounds and to form a product containing the soda largely as sodium carbonate; and a solution of the resulting sodium compounds is prepared and subjected to a regulated sulfiting treatment to regenerate a suitable cooking liquor containing sodium sulfite and bisulfite which is then utilized in the acid-sulfite type of cooking operation of this invention.

In the treatment of residual liquor from such acid-sulfite cooking operation, the alkaline compound or compounds added to react with acid therein and to more firmly fix sulfur therein, may be sufficient only to neutralize the acid, but may advantageously be somewhat in excess thereof. Other and additional suitable sodium compounds may be added, as desired, e. g. to increase the ratio of sodium to sulfur compounds in the liquor. The alkaline compound added and utilized for combining with acid of the residual liquor may be contained in alkaline residual liquor from the sulfid type of cooking operation or present in one of the furnace products which contains sodium carbonate or sodium carbonate and sodium sulfid, as its main alkaline constituents. By utilizing residual liquor from the sulfid type of cooking process, or a regenerated solution containing sodium sulfid and sodium carbonate, the content of sulfur compounds will be increased as well as the content of sodium.

The invention also includes improvement in the carrying out of the furnacing operation of the regenerative treatment, so that the heat of the hot gases may be employed for generating steam for the cycle, and so that some sulfur as well as soda compounds may

be advantageously recovered for reuse in the cyclic and interrelated processes.

The cooking liquor used in the sulfid type of cooking process of the invention may vary considerably in its composition. When it is produced solely by a regenerative treatment of a sulfite type of residual liquor, and it contains a sufficiently high proportion of sodium sulfid, it may be used directly for a cooking operation, and in this case will be made up mainly of sodium sulfid and sodium carbonate. With cooking liquors of this kind, i. e., containing little or no sodium hydroxide or sodium sulfite, it is desirable to have a considerable amount of sodium carbonate present, for example, an amount such that the sodium present as sodium carbonate is approximately equal to that present as sodium sulfid. For example, for poplar wood the cooking liquor may contain about 800 pounds of sodium sulfid and about 1087 pounds of sodium carbonate for 4000 pounds of wood (oven-dry basis); and for spruce wood the cooking liquor may contain about 1000 pounds of sodium sulfid and about 1359 pounds of sodium carbonate to 4000 pounds of wood (oven-dry basis). In such cooking liquors the sodium or sodium oxide equivalent of the sodium sulfid and the sodium carbonate is approximately equal. With such cooking liquors the amount of sodium sulfid charged into the digester, when chemical pulp is desired without a further cooking or chemical or other treatment, should be at least about 18 per cent on the oven-dry weight of wood treated and preferably 20 per cent or more. In such a cooking liquor, the sodium carbonate appears to be active to some extent and to assist in the cooking operation, but the sodium sulfid is mainly relied upon. The percentages above referred to are for poplar wood; for wood such as spruce, a larger amount of active chemical is required, as illustrated in the above example.

Instead of using (for cooking liquor) a solution containing mainly sodium sulfid and sodium carbonate, such as is obtainable directly by dissolving the soda content of the product from the reducing furnace treatment of the neutralized liquor from the sulfite type of cooking operation, the liquor may have some of its sodium carbonate converted into caustic soda, so that the cooking liquor will contain, for example, around ten parts of sodium sulfid for every two to ten parts of sodium hydroxide, and so that the total of sodium sulfid and sodium hydroxide will amount to at least around 16 to 18 per cent on the weight of the wood (oven-dry basis) when poplar wood is used, and larger amounts of Na_2S and NaOH for other woods, such as spruce. The presence of caustic soda enables the amount of sodium sulfid to be reduced. The caustic soda may be readily formed from sodium carbonate by causticizing with lime, for example, by treating the solution of sodium carbonate and sodium sulfid with a regulated amount of lime, as a part of the regenerative treatment.

A further improvement in the sodium sulfid type of cooking liquor may be made by the formation therein or the addition thereto of sodium sulfite, for example, from 5 to 15 parts of sodium sulfite for 10 parts of sodium sulfid. The sodium sulfite appears to combine with some of the sulfur of the sodium sulfid during the cooking operation. Cooking liquors containing Na_2SO_3 along with Na_2S and NaOH produce pulp which is more easily bleached to a good white than when sodium sulfid alone or sodium sulfid and sodium carbonate are employed without other active reagents. Such amounts of sodium sulfite may be readily produced therein by mixing and thoroughly agitating the solution of sodium carbonate and sodium sulfid with the required amount of freshly prepared calcium monosulfite, for example, during or as a part of the clarification. The reaction of such calcium monosulfite with some of the sodium carbonate produces sodium sulfite in solution and a precipitate of calcium carbonate which aids in the clarification of the liquor.

By treating the solution containing sodium carbonate and sodium sulfid with both lime and calcium sulfite, in appropriate and regulated amounts, a cooking liquor can be produced which contains both caustic soda and sodium sulfite in addition to sodium sulfid; for example, with the sodium sulfid present in preponderating amount; that is to say, that more sodium is present as sodium sulfid than as sodium hydroxide or as sodium sulfite.

Where the sodium carbonate and sodium sulfid liquor contains considerably more sodium as sodium carbonate than as sodium sulfid, the addition of sufficient lime, or calcium sulfite, or both, permits of the ready reproduction of cooking liquors which contain a preponderating amount of the sodium in the form of caustic soda, or in the form of sodium sulfite, or of admixed caustic soda and sodium sulfite, with a relatively smaller amount present as sodium sulfid. Such cooking liquors can be used in cooking processes in which a preponderance of sodium sulfite is desired, or in which a preponderance of caustic soda is desired, or a preponderance of caustic soda and sodium sulfite over the sodium sulfid content.

In the liquors of the cooking operations of this invention, some other sodium compounds may be present, such as sodium sulfate, sodium thiosulfate, etc., but these are advantageously kept low in amount. They serve to combine some sulfur which is again available as sodium sulfid after a reducing furnace treatment.

As examples of cooking liquors which con-

tain sodium sulfite or caustic soda or both in addition to sodium sulfid and sodium carbonate, we give the following examples. These examples indicate the weight of sodium sulfid and of other sodium compounds mentioned, which are present in cooking liquor for each 4000 pounds of wood (oven-dry basis).

For poplar wood the cooking liquor may contain about 800 pounds of sodium sulfid, about 1087 pounds of sodium carbonate, and about 322 pounds of sodium sulfite (Na_2SO_3). For spruce wood the cooking liquor may contain about 1000 pounds of sodium sulfid, about 1359 pounds of sodium carbonate and about 400 pounds of sodium sulfite.

Where caustic soda is present in the cooking liquor, there may be present, for example, for poplar wood, about 600 pounds of sodium sulfid, about 815 pounds of sodium carbonate, and about 205 pounds of caustic soda. For spruce wood there may be present about 750 pounds of sodium sulfid, about 1020 pounds of sodium carbonate, and about 255 pounds of caustic soda.

The following examples show the amount in pounds of sodium sulfid, sodium carbonate, sodium sulfite and caustic soda, where all these are present, either alone or with small amounts of sodium sulfate, sodium thio-sulfate, etc., each example being for about 4000 pounds of wood, oven-dry basis.

Wood	Sodium sulfid	Sodium carbonate	Sodium sulfite	Caustic soda	Na_2O as sodium sulfate	Na_2O as sodium thiosulfate
Poplar, Exhibit 1	600	300	322	205	80	40
Spruce, Exhibit 2	750	375	402	256	100	50
Poplar, Exhibit 3	640	544	258	164	127	64
Spruce, Exhibit 4	800	600	322	205	159	80
Poplar, Exhibit 5	711	966	144	92	71	71
Poplar, Exhibit 6	400	200	300	400	60	50
Pine, Exhibit 7	615	265	498	316	104	52
Pine, Exhibit 8	500	200	350	450	75	50

Where the regenerated solution, containing mainly sodium sulfid and sodium carbonate, regenerated entirely or in part from residual liquor of the sulfite type of cooking process, is of suitable composition and ratio of sulfid to carbonate, such cooking liquors can be directly produced therefrom by subjecting it to a regulated causticizing and sulfiting treatment, for example, by using lime and calcium sulfite in regulated amounts and with conversion of the required amounts of sodium carbonate into sodium sulfite and caustic soda and with formation of calcium carbonate. Where, however, the ratio of sodium carbonate to sodium sulfid is such that the liquor would not yield cooking liquor of the desired composition, appropriate additions may be made, or a part only of the regenerated liquor utilized with additions of fresh material. Sodium sulfite, for example, can be added, which may be made by subjecting to a sulfiting treatment a solution of the sodium carbonate produced by the oxidizing furnace treatment hereinafter referred to, and this sodium sulfite may be added and be present in the cooking liquor. In this way the desired ratio of sodium sulfite to sodium sulfid can be obtained. An excess of sodium carbonate may or may not be present in such cooking liquor. A portion of the

$$Na_2CO_3Na_2S$$

liquor may be causticized to the required extent, another portion thereof may be sulfited and these two portions mixed after such treatments to form cooking liquor of the desired composition.

In the cooking liquor of the acid sulfite type of cooking process of the present invention, as pointed out above, an excess of free sulfur dioxide beyond that corresponding to sodium bisulfite is avoided and while an amount of SO_2 corresponding to sodium bisulfite can be used, we consider it more advantageous in the cyclic and inter-related processes of the invention, to have a considerable amount of sodium monosulfite present in admixture with sodium bisulfite. In regenerating the acid sulfite type of cooking liquors from the sulfid type of residual liquors, the greater part of the sulfur content of the latter can be eliminated or oxidized during the oxidizing furnace treatment, but some sodium sulfid or thiosulfate may be present in the finished furnace product. Sodium thiosulfate may also be formed in the liquor when there is any sulfid present in the liquor which is sulfited, particularly if the sulfiting is done with sulfur dioxide. The presence of sodium thiosulfate is objectionable in a highly acid sulfite of sodium cooking liquor, but by having a sufficient amount of sodium monosulfite present in the cooking liquor in addition to the sodium bisulfite, a limited amount of sodium thiosulfate may be present therein without such objection, in the way of sulfur separation, darkened stock, etc., as when it is present in a highly acid sulfite liquor having insufficient combined SO_2. Accordingly, when sodium thiosulfate is present in a regenerated acid sulfite type of cooking liquor, it is advantageous to regulate the composition of the cooking liquor so that it contains both sodium monosulfite and sodium bisulfite, and so that a sufficient amount of sodium monosulfite is present therein.

We give below a series of examples showing the charges of sodium sulfite and of sodium bisulfite in cooking liquors which may be used. In certain of these the cooking liquor is a sodium bisulfite cooking liquor, and in such case sodium thiosulfate preferably is absent. Such a liquor may be used, for example, at the outset, or where, by special treatment during regeneration, thiosulfate is absent. In the other cooking

liquors of the examples it will be noted that sodium sulfite is present in addition to sodium bisulfite. The amounts of chemicals in the following examples are present in cooking liquors employed for treating 4000 pounds of wood (oven-dry basis). The volume of liquor and amount of chemicals required for a large digester charge will, of course, be adjusted to suit the amount and kind of wood charged thereinto.

Wood	Sodium sulfite (Na_2SO_3)	Sodium bisulfite ($NaHSO_3$)	Sodium sulfate (Na_2SO_4)	Sodium thiosulfate ($Na_2S_2O_3$)
Poplar, Example 1	1,200	495		
Poplar, Example 2	1,067	440		
Spruce, Example 3	1,333	550		
Poplar, Example 4	800	660	338	62
Spruce, Example 5	1,000	825	422	67
Poplar, Example 6	640	792	229	
Spruce, Example 7	800	990	286	
Poplar, Example 8	1,321	229		
Spruce, Example 9	1,651	286		
Poplar, Example 10	1,400	165	366	102
Spruce, Example 11	1,800	165	457	127

Cooking liquors which contain a very high ratio of sodium to sulfite (high combined SO_2) release no considerable amount of sulfur dioxide when the digester is relieved to promote liquor circulation during the cooking operation, and the residual liquors produced therefrom release little if any sulfur dioxide when the digester contents are blown into a blowpit. Such liquors avoid such a liberation of sulfur dioxide as takes place when highly acid liquors are employed, i. e., containing a large excess of sulfur dioxide, and thus it is unnecessary to provide an elaborate sulfur dioxide recovery system such as commonly used in the usual and common acid sulfite cooking process using highly acid cooking liquor. Accordingly, a much higher proportion of the sulfur content of the cooking liquor is retained in the residual liquor and is thus available for the production of some sodium sulfid during the subsequent treatment of constituents of this residual liquor.

In order to make advantageous use of its sulfur content during the subsequent treatment of the residual liquor, even though it be not strongly acid, sufficient alkaline residual liquor from the sodium sulfid type of cooking process or from another suitable alkaline cooking process, or sufficient other alkaline constituents, for example recovered soda compounds, are added to react with the acid and to fix or combine some of the sulfur as a sodium compound, so that the treated residual liquor is rendered neutral or alkaline, i. e. to litmus. In case organic matter separates out when residual liquor is thus treated, this may be removed in any suitable manner or it may be allowed to remain with the liquor, or it may be redissolved by the addition of a regulated amount of strong alkali, such as caustic soda.

The liquor after neutralization or being made alkaline is concentrated and the constituents therein are decomposed under suitable reducing conditions, so that a relatively large amount of the sulfur content of the residual liquor will be retained in the product as sodium sulfid. The remainder of the sodium compounds will be mainly converted into sodium carbonate.

The reducing furnace operation, moreover, may be so carried out that the gases resulting therefrom are utilized. By regulating the reducing conditions, the resulting gases contain carbon monoxide, and may contain a combustible sulfur compound or even elemental sulfur. Such compounds as COS, CS_2 and H_2S, and also elemental sulfur, yield sulfur dioxide or sulfur trioxide or a mixture of both when burned by the addition of further air. In order to advantageously recover sulfur from the furnace gases, and also to utilize their heat value, these gases are employed as fuel, and then are subjected to treatment for the recovery of sulfur dioxide and of sulfur trioxide therefrom, which are thus made available for utilization in the process and correspondingly reducing the amount of fresh sulfur or sulfur compound otherwise supplied to make up for losses.

The sulfur lost may be replaced either by burning sulfur, or in the form of sulfur dioxide from some other source, or it can be supplied in part by adding sodium sulfate before the reducing furnace treatment. Sulfur dioxide can be employed in forming the sulfite type of cooking liquor, and the sulfur content of the resulting residual liquor can then be utilized to a considerable extent in the regenerated sodium sulfid type of cooking liquor. This sulfur dioxide can be to some extent recovered from the process, in part in the manner above described, and in part from the gases and solids given off during the regeneration treatment to which the sodium sulfid type of residual liquors are subjected.

The combustible matter in the residual liquor from the sodium sulfid type of cooking operation is advantageously burned under high temperature and oxidizing conditions having a regulated excess of air. The heat thus produced can be utilized in a boiler to generate steam for the cooking process. This oxidizing burning treatment serves to separate from its combination with soda, a considerable part of which sulfur which is converted into sulfur dioxide or sulfur trioxide or a mixture of both, and such oxides can be recovered from the furnace gases. The oxidation treatment also converts a considerable part of the remaining sulfur which is thus present in the furnace product in the form of sodium sulfate. Such furnace product will contain a high percentage of sodium carbonate, which can be dissolved and readily sul-

fited to form the sulfite of sodium type of cooking liquor. The sodium sulfate present therein will aid in supplying sodium sulfid when the sulfite type of residual liquor is treated to regenerate the sodium sulfid type of cooking liquor.

The hot gases from the two types of furnaces, that is, the reducing type of furnace and the oxidizing type of furnace, are advantageously mixed, and a further amount of air, if required, supplied to burn combustible constituents which the mixed gases contain, and the resulting hot gases can be passed through a steam boiler to utilize their heat. Some solids collect in the various gas passages, e. g. of the boiler, which usually are high in sodium sulfate. A further amount of solids may be collected from the gases, and these solids also are usually high in sodium sulfate and can advantageously be added to the cycle before the reduction treatment which produces sodium sulfid. The furnace gases may also contain a considerable amount of sulfur dioxide and of sulfur trioxide. Sulfur dioxide can be recovered by scrubbing the gases with a sodium carbonate solution. Sulfur trioxide when present will form sodium sulfate, while sulfur dioxide will form sodium sulfite. These can be returned to the process, the sodium sulfite for use in the sulfite cooking operation, and the sodium sulfate to produce additional sodium sulfid during the reducing furnace treatment. By employing two separate scrubbing treatments, a considerable separation of the SO_3 from the SO_2 may be effected and advantage taken of such separation.

Where the sulfiting of the sodium carbonate liquor for the regeneration of the sulfite type of cooking liquor is carried out in part by scrubbing the hot gases of the furnaces with the liquor and in part by sulfur dioxide formed by the combustion of fresh sulfur, these operations can be so regulated that the amount of sodium sulfite and of sodium bisulfite in the resulting cooking liquor can be controlled. The sodium carbonate liquor can be used first for scrubbing the hot furnace gases (advantageously after removing a large part of the SO_3 content thereof) and the sulfiting can then be completed by passing the partially sulfited liquor over an absorption tower into which a suitable mixture of sulfur dioxide and nitrogen, resulting from the combustion of sulfur in air, is introduced, the temperature thereof being controlled so as to get good absorption without unduly cooling the liquor.

Instead of recovering sulfur dioxide or sulfur trioxide or both from the furnace gases by using a sodium carbonate solution, this recovery can be effected by using milk of lime, or an aqueous suspension of calcium carbonate (preferably recently precipitated), and bringing the gases into contact with the milk of lime or the aqueous suspension so that sulfur dioxide and sulfur trioxide will be absorbed and forming calcium sulfite and calcium sulfate. If there is any acetic acid in the furnace gases it may form calcium acetate, which may remain in solution, or may react with sodium compounds, such as sodium sulfite or sodium sulfate when present to form calcium sulfite or calcium sulfate, leaving sodium acetate in solution. The calcium sulfate and calcium sulfite, where both are present, may be separated from the solution and employed for treating some of the liquor containing sodium carbonate and sodium sulfid to convert sodium carbonate into a corresponding amount of sodium sulfate or sodium sulfite, or both, and form calcium carbonate.

The admixed calcium sulfite and calcium sulfate, where both are present, may be employed together for treating a sodium carbonate solution, or the calcium sulfate and calcium sulfite may be separately utilized by treating the mixture with only enough sodium carbonate to react with the calcium sulfate, leaving calcium sulfite behind with the calcium carbonate thus formed. The solution of sodium sulfate can now be separated, and may be added to the residual liquor from the sulphite type of process, so that it will be subjected to the reducing furnace treatment. The mixture of calcium sulfite and calcium carbonate may be employed for sulfiting some sodium carbonate, and the resulting sodium sulfite may be employed in a cooking liquor. By separating the sulfate and the sulfite radicles in this way, the sulfate radicle is employed in that part of the cycle where it is best used, and the sulfite radicle is transferred to that part of the process where it is best used. The calcium sulfite may, however, be used for sulfiting some sodium carbonate of the liquor which is to be used in the sulfid type of cooking process, where this cooking liquor is to contain sodium sulfite, as well as sodium sulfid. The sulfate radicle which is returned to the process may be in part recovered as sodium sulfid for the sulfid type of cooking process, while part of the sulfur of the sulfate radicle may be transferred, separated and recovered as the sulfite radicle from the furnace gases so that it may be utilized in producing sodium sulfite.

The inter-related processes of the invention and the novel steps and features of the regenerative and interrelated processes will be further described and illustrated in connection with the accompanying drawing, which is a flow-sheet in a more or less conventional and diagrammatic manner and with certain of the operations indicated thereon. It will be understood that the invention is illustrated by but is not limited to the particular operations and sequence of operations illustrated in the flow-sheet. Moreover, certain of the features

of the invention are not limited to use in the particular cycle and sequence of steps of the inter-related processes, but are of more general application and are so claimed in certain of the method claims.

In the flow-sheet, a suitable acid sulfite type of digester is indicated at 1. The wood chips are indicated as entering at 18, and the cooking liquor through 20, this cooking liquor being that regenerated from the sulfid type of process as herein described. The relief line indicated at 19 may be employed to promote circulation of the cooking liquor by the steam which enters through 21. The steam may come from the waste-heat boiler through the line 23, or other steam may be supplied through the line 22. When the cooking operation has been completed, the contents of the digester are blown through the line 24 into the blow-pit 2, provided with relief 25. Wash water, which may be the condensate from the evaporator 4, enters at 26, or other water may be employed. The washed pulp is separated at 28 and the mixture of residual liquor and wash water passes through the line 29 into the mixer 3. Sodium compounds to make up for losses may be added at 30, for example, sodium sulfate or other suitable sodium compound.

An alkaline liquor is added at 31 to neutralize uncombined sulphur-containing acids in the residual liquor. This alkaline liquor may be a portion of the residual liquor from the sulfid type of digestion process, as indicated by the line 31, or some of the liquor from the dissolver 6 or from the clarifier 7, may be employed, as indicated by the line 45′, 50 and 51′. Part of the alkaline material for neutralizing the acidity may come in part from each of these sources, thus providing flexibility and control.

The admixture of acid residual liquor and alkaline liquor is agitated and thoroughly mixed in the tank or mixer 3. Any liberated gas, such as carbon dioxide, may escape as indicated at 32. Lines 84, 85 and 86 show the return of solids collected from the gas passages of the boiler 14 and dust collector 15. The solids thus returned are generally high in sodium sulfate content and are thus incorporated and admixed with the liquors for treatment in the subsequent reduction step to form sodium sulfid.

In case the admixed liquors contain an objectionable amount of suspended solids, the liquor may be clarified before passing it from the mixer 3 to the evaporator 4.

The evaporator 4 may be any suitable type of multiple effect evaporator and is advantageously equipped with means for forcing a rapid circulation of liquor through the heating portion of the most highly concentrated effect. A regulated amount of caustic soda may be added to the mixed liquors to redissolve precipitated organic compounds, and this when so employed is preferably added after carbon dioxide has been permitted to escape, which carbon dioxide may be produced by interaction between the acids of the residual liquor and the sodium carbonate of the alkaline liquor added, and preferably after removal of most of the suspended organic matter.

Cooling water is shown entering the evaporator through 34, and steam enters through 35. Condensates leave through 36, that which is not reused being rejected through 36′. The steam is shown as entering through 23 and 35 and being obtained from the boiler 14. Any other suitable source of steam may be employed in whole or as a part thereof in case it should be needed.

The hot and highly concentrated liquor passes through 37 into the reduction furnace 5, in which the organic matter is consumed and a furnace product containing mainly sodium carbonate and sodium sulfid is produced. Any suitable type of furnace may be employed for this step, and it is an advantage to so conduct the operations in the furnace 5 that a high percentage of the soda in the furnace product is present as sodium sulfid, and that the amount of sodium sulfate is small. A product which carries about 40% to 50% of its sodium in the form of sodium sulfid and about an equal amount in the form of sodium carbonate is quite suitable. The ratio of sulfid to carbonate will vary somewhat due to operating conditions. Polysulfides are advantageously absent in the furnace product.

Air in regulated amount is shown entering the furnace 5 through 39 and 39′. 41 and 41′ represents the introduction of a regulated amount of gases from the scrubber 16, carrying carbon dioxide, nitrogen, etc. Line 40 shows how some of these returned gases may be admixed with air to give a modified air. By the use of such returned gases, in regulated amount most of the carbon can be oxidized to CO_2 or CO, advantageously the latter, in furnace 5. A high ratio of CO is desirable for retention of sulfur and the formation of sodium sulfid, and the CO can be burned to CO_2 for heat utilization in boiler 14. The returned gases aid in restraining the temperature in 5 and are thus of additional advantage. The gases from 5, which are generally and advantageously combustible, e. g. containing considerable CO, are shown passing through 38 and thence through 81 into boiler 14. Oxygen for the combustion of CO, and of sulfur or unoxidized sulfur compounds, e. g. CS_2, COS, H_2S, may enter through line 80 as air, in case more oxygen is required than enters with the gases coming from furnace 12 through line 67. The amount of air thus added can be controlled so as to convert CO to CO_2, oxidize sulfur compounds to SO_2 or SO_3, and the heat

thus generated can be utilized in generating steam in boiler 14.

Furnaces 5 and 12 may be so arranged as to receive their respective charges of residual liquor in the form of atomized liquor, one operating with an insufficient supply of air and the other with an excess supply of air, the furnace 5 being operated so as to conserve sulfur therein and yield a furnace product high in sodium sulfid, while the furnace 12 is operated so as to drive off a considerable amount of sulfur and yield a furnace product high in sodium carbonate and low in sodium-sulfur compounds, and with such sulfur compounds as present being largely in the form of sodium sulfite or sodium sulfate. The returned gases referred to may, at least in part, being introduced adjacent the highly heated walls, and roof, so as to maintain, as well as feasible, these portions of the furnace at safe working temperatures.

The furnace product from 5 is shown passing through 42 into dissolver 6, and water or condensate from 4 enters through 43. Line 44 shows how some caustic soda or sodium sulfid, for examples, may be added to the liquor in the dissolver 6, for instance when these are available for replacing lost soda in whole or in part. Also lime, calcium sulfite, etc., may be there introduced. When the liquor in the dissolver is of appropriate strength, it passes through 45 into clarifier 7, of any suitable kind.

Some lime, sufficient to convert the required amount of sodium carbonate into caustic soda, or/and $CaSO_3$ sufficient in amount to convert the required amount of sodium carbonate into sodium sulfite may be added through 46, and thoroughly admixed with the liquor. Prior to adding such calcium compounds, a regulated portion of the liquor from 6 may be diverted through 45′. The liquor is clarified in 7, separated from the solids, and the solids washed by introducing water through 47. The washed solids leave through 49 and the clarified liquor and washings leave through 50. The washings may, if desired, be kept separate and returned to the dissolver 6. Some of the clarified liquor may be diverted through 51′ as stated.

The clarified liquor from 7, consisting mainly of sodium sulfid as active cooking reagent (with which may be present a moderate amount of either or both sodium sulfite or caustic soda) and which may contain considerable sodium carbonate (but preferably free from sodium polysulfid and free from or low in sodium thiosulfate) is shown passing through 50 into digester 8 where it is employed as a cooking liquor, the predominating amount of digesting being due to the sodium sulfid. Wood chips enter the digester 8 through 52. 53 is a relief line which may be employed to assist in circulating the cooking liquor. Steam enters at 54, and may come through 55, from any suitable source, or through 88 and 87 from the boiler 14. Surplus or unused steam from the boiler 14 is shown passing beyond through 56 to any other suitable point or usage.

When the sodium sulfid digestion step has been completed, the contents are discharged through 57 into blowpit 9, provided with relief 58. The stock is then delivered through 59, advantageously after thinning with some residual liquor while in the blow-pit or being removed therefrom, into the washing device, of any suitable kind but preferably one that will wash the stock and remove the liquor in an economical manner and produce a weak black liquor containing all or nearly all of the soda without an excessive dilution. Water for washing the stock enters through 60, which may be fresh water supplied through 60′, or condensate from the evaporator 11 through lines 65 and 60. The washed pulp passes out through 61, and the black liquor (and chosen washings) passes through 62. A portion may be diverted through 31 for admixing with the acid residual liquor in 3.

The liquor is concentrated to a high point in a suitable type of evaporator 11, e. g., a multiple-effect evaporator. Steam is shown entering through 64, coming from the boiler 14. Any other suitable steam supply may be adapted as needed. The condensates leave through 65, any surplus being removed through 65′.

The highly concentrated liquor leaves the evaporator through 66 and is charged into the oxidizing or burning furnace 12. This furnace may be of any suitable type. It may operate by atomizing or spraying the strong and hot black liquor into it, the water being evaporated and the organic matter decomposed and carbon burned to CO, and preferably to CO_2 to a large extent at least. An excess of air over that theoretically required for complete combustion may be introduced, e. g., through 69 and 69′. Some of the products of combustion may be returned to the furnace, e. g. through 70 and 70′, coming from the scrubber 16 through 91, 93 and 70. Some of these returned gases may be admixed with air by passing through line 71, thus giving a modified air which may serve to suppress the flame temperature in the furnace so as to aid in maintaining the furnace at a safe working temperature. Another portion of such returned gases may be introduced into the furnace adjacent the hot walls, roof, etc., as a further means of maintaining safe working temperatures, these hot gases absorbing heat as their temperatures are raised. The mixture of hot gases from this furnace may be passed directly, so as to lose little temperature, into the boiler 14 and onward, being utilized in generating steam for use in the cycle of operations.

The soda product of the furnace, mainly sodium carbonate (with some sodium sulfate and little if any Na_2S) passes through 68 into dissolver 13. Water is shown entering through 72, which may be fresh water through 75 or condensate through 74 and 65. 73 shows how sodium carbonate, sodium sulfite, caustic soda, etc., may be added in amount sufficient to supply a portion or all of the soda required due to losses.

When the solution is of appropriate strength it passes through 76 into scrubber 16 and is therein employed to absorb sulfur compounds from the gases, advantageously carrying sulfur dioxid in considerable amount and little or no sulfur trioxid. The liquor may be herein converted into cooking liquor containing the required amount of combined and uncombined sulfur dioxid, e. g., a solution which contains both sodium monosulfite and bisulfite. Sulfur for supplying the sulfur dioxide required, in addition to that already in the gases coming from the dust collector 15, is shown as SO_2 entering at 90. This may be obtained by burning sulfur in air to form a mixture of SO_2 and nitrogen, these gases passing through 90; or iron sulfides or other suitable sulfides may be roasted to form SO_2 and this SO_2 be passed through 90. The scrubbed gases leave the scrubber through 91, and the unreturned gases pass out through 92, e. g. to a suitable stack.

The sulfited liquor containing the desired amount of combined and uncombined sulfur dioxide, and which may also contain some acetate or other soluble organic acid radicles removed from the gases by the scrubbing operation, passes through 77 into the clarifier 17 and the clarified liquor passes through line 20 to the digester 1. Water is shown entering at 78 to wash the sediment removed from the liquor in 17, and the washed sediment leaves through 79, the washings being added to the liquor.

The hot gases entering the boiler carry some soda and also some sulfur oxides, a part of which comes from the furnace 5 and a part from the furnace 12. Some sodium sulfate is caught in the boiler flues, etc. This is removed through 84, as stated above. Water enters the boiler through 83 to be converted into steam. Steam leaves through 23 and 87. The somewhat cooled gases leave through 82 carrying some soda, etc. 15 is a dust collector advantageously of the dry-type, operating at above the dew point. The dry solids collected here contain a considerable percentage of sodium sulfate. These are removed through 85 and returned to 3 as stated.

This dust collector may be of any suitable type, but it is advantageously so operated as to recover substantially all of the soda, which is primarily present as sodium sulfate in many cases, and permit the sulfur dioxide to pass on to the scrubber 16 along with the gases which pass from 15 through 89 into 16. An electrical precipitation apparatus may serve as the dust collector, and it may with advantage be operated at a temperature considerably above the dewpoint of the gases, and thus recover nearly all of the soda as a dry product, which, as stated, contains considerable percentages of sodium sulfate.

Thus a considerable amount of the sulfur which is eliminated from soda, e. g. by the oxidizing combustion treatment in furnace 12, is collected as sodium sulfate and is returned to the mixer 3 to be employed for the production of sodium sulfid. And a further amount of sulfur as sulfur dioxide, which may come in part from the reducing furnace 5 and in part from the furnace 12, is collected in the scrubber and thus serves to make cooking liquor containing sulfites. In one type of cooking liquor the sulfur is active as sodium sulfid, while in the other it is active as an oxy-sulfur compound, i. e. a sulfite. And the cycle of operations is so carried out that the sulfur is in one instance employed as a sulfite while in another instance it is employed as a sulfid, and the two types of cooking operation and their residual liquor treatment cooperate in an advantageous manner.

The inter-related processes of the present invention are not limited to processes in which the cooking operations are carried so far that chemical pulp is produced. The cooking operations may be of relatively short duration, and with less chemicals than will completely pulp the wood and produce chemical pulp, and the cooking operation may be stopped when the wood has been sufficiently softened to lend itself to a mechanical treatment, whereby a strong pulpy mass is produced with high yield of product. The digestion steps of the inter-related processes may thus be partial digestion steps in which the wood is softened and only partially cooked, and in which the subsequent treatment of the partially cooked or underdone pulp is a mechanical treatment, or a treatment by some other pulping process, which may be a chemical pulp-making step.

The product thus made by the sulfid type of cooking operation, when the process is carried out at a temperature around 120° to 150° C., and with only sufficient chemicals to partially cook the wood may be employed for board manufacture. During such preliminary or partial cooking operations, the sodium sulfid appears to act upon certain more readily reactable constituents of the wood, and is itself converted to a considerable extent into sulfur-containing organic compounds of such a character that sulfur can be readily driven off when combustible constituents of the concentrated liquor are subjected to a suitable burning under oxidizing condi-

tions. The residual liquor from such a sodium sulfid type of cooking operation appears to behave differently from other alkaline residual liquor from pulp-making operations. In particular, it appears to intumesce to a less extent when the residual liquor is dried and the organic compounds are decomposed. This appears to explain why the soda is so easily recovered therefrom. With residual liquors produced by partial cooking operations of the kind above mentioned, additional fuel may be employed in the burning operation, if necessary or desirable, especially when the amount of organic matter in the residual liquor is not sufficient to generate the desired amount of heat.

When the sodium sulfid type of cooking operation is carried to completion, that is, so far as to produce chemical pulp, the pulps produced are sometimes dark, particularly where the cooking liquor contains sodium sulfid and sodium carbonate, without, or with only small amounts of, caustic soda or sodium sulfite. Such pulps may be given an auxiliary treatment to improve their color, or to improve their bleachability. For example, such pulp, after separation from the residual liquor and washing, may be washed with a weak acid liquor, and for this purpose, residual liquor from an acid sulfite cooking operation may be employed, particularly a liquor which still has a distinct acid reaction. Or the pulps may be treated with hot liquor which contains a small amount of caustic soda, or a hot solution containing sodium sulfite may be employed. Some of the dark colored compounds are thus removed from the pulp or are changed into other forms or compounds with resulting improvement in appearance and in some cases in quality of the pulps produced. The pulps produced when the sodium sulfid is accompanied by a considerable amount of sodium sulfite are of better color and quality, particularly where a rather large charge of sodium sulfite is also present.

Some of the pulps obtained by the sodium sulfid type of cooking operation do not bleach readily to a high white by a single stage bleaching treatment, using chloride of lime bleaching liquor. Such pulps may be more readily bleached by first treating them with about ten to fifteen per cent of bleach (35% available chlorine), then washing the resulting pulp products and adding a sufficient further amount of bleach thereto and finishing the bleaching operation in the second stage with final washing of the bleached product.

Pulps may be obtained from raw cellulosic materials other than wood, in accordance with the cycle of the present invention.

This application is in part a continuation of our applications Serial Nos. 686,137, filed January 14, 1924; 704,176, filed April 4, 1924, and 456,187, filed March 28, 1921.

We claim:

1. The process of producing pulp from wood which comprises digesting wood in a cooking liquor containing most of its soda in the form of a sulfite of sodium, subjecting resulting residual liquor to a treatment including a reducing furnacing operation adapted to yield a product containing sodium carbonate and a relatively large amount of sodium sulfide, utilizing sodium sulfide of the furnace product in an alkaline cooking liquor to cook an additional amount of wood, subjecting residual liquor from the second cooking operation to a treatment including a furnacing operation adapted to yield a product containing sodium carbonate and a lesser proportion of sodium sulfide than was present in the alkaline cooking liquor, subjecting the furnace product to a treatment including a sulfiting operation adapted to produce a cooking liquor containing an amount of sodium mono-sulfite at least equivalent to any sodium thio-sulfate which may be present; and repeating the cycle, utilizing this cooking liquor in the first named cooking operation.

2. The process of producing pulp from wood which comprises digesting wood in a cooking liquor containing sulfite of sodium and free from excess sulfur dioxide, subjecting residual liquor therefrom to a treatment including a reducing furnacing operation adapted to give a furnace product including sodium carbonate and a relatively large amount of sodium sulfide, subjecting the furnace product to a treatment including causticizing of sodium carbonate therein to produce an alkaline cooking liquor containing sodium hydroxide and sodium sulfide, digesting wood with the liquor so formed, subjecting residual liquor from this second cooking operation to a treatment including a furnacing operation adapted to drive off sulfur and produce a furnace product having sodium carbonate and substantially less sodium sulfide than was present in the alkaline cooking liquor, subjecting the furnace product to a treatment including a sulfiting operation to produce a cooking liquor containing an amount of sodium mono-sulfite at least equivalent to any sodium thiosulfate which may be present; and repeating the cycle, utilizing the cooking liquor so formed.

3. The process of producing pulp from wood which comprises digesting wood in a cooking liquor containing an acid sulfite of sodium and free from excess sulfur dioxide, separating the residual liquor from the pulp, neutralizing the liquor by the addition of an alkaline sodium compound, concentrating and treating the residual liquor to decompose organic compounds under reducing conditions to obtain a soda product containing mainly sodium carbonate and a relatively high content of sodium sulfid, forming there-

from a cooking liquor relatively high in sodium sulfid and cooking wood therewith, separating the pulp from the residual liquor thus produced, concentrating and subjecting the residual liquor to treatment under oxidizing conditions to decompose organic compounds and obtain a recovered soda product containing mainly sodium carbonate, and sulfiting a solution of such sodium carbonate to form an acid sulfite cooking liquor containing more sodium sulfite than sodium thiosulfate, and cooking wood with such liquor.

4. The method of producing pulp which comprises cooking wood with a cooking liquor containing sodium sulfid as its primary cooking chemical, cooking wood with an acid sulfite cooking liquor containing a sulfite of sodium, and treating residual liquor from one of said processes to produce cooking liquor for the other process and vice versa.

5. The method of producing pulp which comprises cooking wood with a cooking liquor containing sodium sulfid, cooking wood with a cooking liquor containing sodium bisulfite and sodium monosulfite, and treating residual liquor from each of said processes to regenerate cooking liquor for the other process.

6. The method of producing pulp which comprises digesting wood with a cooking liquor containing sodium bisulfite as the principal cooking reagent and a lesser amount of sodium mono-sulfite, digesting wood with an alkaline cooking liquor containing alkaline sodium compounds and treating residual liquors from each of said processes to regenerate cooking liquor for the other process.

7. The method of producing pulp which comprises digesting wood with an acid cooking liquor containing sodium bisulfite as the principal cooking reagent, treating residual liquor therefrom to form a non-acid-liquor containing a sodium-sulfur compound, digesting wood with the non-acid cooking liquor so formed, treating residual liquor from this second cooking operation to form a product containing alkaline sodium compounds, subjecting this product to a treatment including sulfiting to form a cooking liquor for use in the first named digesting operation containing sodium bisulfite and more sodium monosulfite than sodium thiosulfate; and repeating the cycle using the cooking liquor so formed.

8. The process of treating residual liquor resulting from cooking wood with a cooking liquor which contains sodium sulfite and sodium bisulfite, which comprises adding thereto a non-sulfur-containing compound of sodium which is capable of reacting with an acid constituent therein, and subjecting the treated liquor to concentration and solid constituents thereof to a reducing furnace treatment whereby a product is formed which contains sodium carbonate and sodium sulfid.

9. In claim 8, the improved step which includes employing an alkaline residual liquor for treating the residual liquor from the acid sulfite type of cooking operation.

10. In claim 8, the improved step which is characterized by regulating the addition of alkaline sodium compound to the acid sulfite type of residual liquor, whereby the treated liquor is rendered non-acid in character.

11. The method of producing pulp which comprises cooking wood with a cooking liquor containing sodium sulfid, subjecting residual liquor from such process to treatment including concentration and furnacing to form a product containing relatively less sodium sulfid than the cooking liquor from which it is derived and containing the sodium thereof mainly as sodium carbonate, sulfiting a solution of the resulting sodium compound so as to produce a cooking liquor containing most of its soda in the form of a sulfite of sodium, and cooking wood therewith.

12. A cyclic process for producing pulp from wood, which comprises cooking a portion of the wood in a liquor comprising a sulfite of sodium, separating the residual liquor from the resulting pulp and subjecting it to a treatment which includes a furnacing of the solid constituents thereof under reducing conditions, cooking a second portion of the wood in a liquor comprising sodium hydroxide and a sodium-sulfur compound derived at least in part from the said solid constituents, separating a residual liquor from the resulting pulp, subjecting the residual liquor to a treatment which includes furnacing the solid constituents thereof under conditions adapted to drive off sulfur compounds therefrom, subjecting gases from the furnaces to a treatment to remove suspended solids including sodium-sulfur compounds, adding such compounds to the solid constituents of the sulfite residual liquor, subjecting the gases from the precipitation treatment to a scrubbing with a liquor capable of absorbing sulfur dioxide.

13. In claim 12, the further improvement whereby the dust recovery treatment is conducted at a temperature above the dew-point of the gases.

14. In claim 12 a further improvement whereby sodium carbonate recovered from the second furnacing treatment is utilized for scrubbing the gases and the sodium sulfite formed thereby is utilized in producing a cooking liquor suitable for use in the first cooking treatment, and subsequently digesting a portion of wood by means of cooking liquor thereby produced.

15. The improvement in the production of cooking liquors from furnace products containing soda mainly as sodium carbonate and with a small amount of sodium sulfid, which comprises sulfiting a solution of such compounds under conditions to form a liquor

containing sodium bisulfite and sodium monosulfite, with the amount of sodium monosulfite in excess of the amount of any sodium thiosulfate which may be present.

16. The improvement in the treatment of residual liquors from pulp-making processes in which a sodium sulfid-containing cooking liquor is employed, which comprises subjecting the residual liquor to concentration and to furnacing under conditions to drive off sulfur and to form a product containing the sodium compounds mainly as sodium carbonate, and recovering sulfur dioxide from the furnace gases by absorbing it in a solution containing the sodium carbonate so produced, thereby producing a sulfite of sodium, and digesting wood with liquor containing the sulfite thus recovered.

17. The method of producing pulp which comprises cooking wood with a cooking liquor containing sodium sulfid, subjecting resulting residual liquor to concentration and constituents thereof to a furnacing treatment under conditions to drive off most of the sulfur therefrom, recovering a sodium sulfate from furnace gases so formed, adding it to residual liquor from a sulfite cooking process, and subjecting such sulfite residual liquor to a furnacing treatment under reducing conditions to form a product containing sodium sulfid and regenerating cooking liquor for the first mentioned cooking operation from soda contained in such product.

18. The improvement in the treatment of residual liquors from a pulp making process in which a sodium sulfur compound is employed, which comprises subjecting constituents obtained from the residual liquors of such a process to a furnace treatment to remove the greater part of the sulfur therefrom, and returning furnace gases for admixture with air to pass through said furnace during the treatment, whereby the treatment can be regulated.

19. The improvement in the treatment of residual liquors from a pulp making process, which comprises subjecting constituents thereof including sodium and oxy-sulfur compound to a reducing furnace treatment under conditions to produce a product containing a large amount of sodium sulfid, and returning furnace gases to such reduction furnace for admixture with the air to aid in regulating the treatment.

20. The improvement in the treatment of residual liquors, which comprises subjecting solids of a residual liquor including a sodium-sulfur compound produced by a cooking process in the manufacture of pulp to an oxidizing furnace treatment, subjecting constituents of residual liquor from a sulfited sodium cooking process to a reducing furnace treatment, admixing resulting gases from said furnacing operations and burning combustible material therein, collecting non-gaseous material from the gaseous products of combustion and returning the same for treatment in the reduction step of the process.

21. In a process for producing chemical pulp from wood, the steps which include employing sodium as a sulfite in an acid sulfite type of cooking liquor which contains sodium bisulfite but is free from excess sulfurous acid beyond the bisulfite combination, and subsequently employing some of the same soda as an alkaline sodium-sulfur compound in an alkaline cooking liquor.

22. In a process for producing chemical pulp from wood, the steps which include employing sulfur as a sulfite of sodium in an acid sulfite type of cooking liquor which contains sodium bisulfite but is free from excess sulfurous acid beyond the bisulfite combination, and subsequently employing some of the same sulfur as an alkaline sodium-sulfur compound in an alkaline cooking operation.

23. In a cyclic process for producing chemical pulp, the steps which include cooking wood and a cooking liquor which contains sodium bisulfite but is free from sulfurous acid beyond the bisulfite state, and cooking wood with an alkaline cooking liquor which contains an alkaline sodium-sulfur compound, some of each type of the cooking liquors being regenerated from soda contained in residual liquor from the cooking operation with the other type of cooking liquor.

24. In claim 23, the further steps characterized by mixing some residual liquor from one type of cooking operation with some residual liquor from the other type of cooking operation, subjecting constituents of the mixed liquors to a furnacing treatment whereby alkaline sodium compounds are obtained, preparing a solution which contains these sodium compounds, and employing some of the solution in the preparation of cooking liquor for one of the cooking operations.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.