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PRODUCTION OF PULP, ETC.

No Drawing.

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This invention relates to improvements in the production of pulp and treatment of residual liquors of the digestive operations for the regeneration of cooking liquors.

More particularly the invention relates to cyclic interrelated processes, employing three types of cooking liquors which may be characterized briefly as sodium sulfite type, sodium sulfid type and caustic soda type cooking liquors, and in which residual liquor from a sodium sulfite cooking process is treated to produce a cooking liquor for a sodium sulfid cooking process, and in which residual liquor from a sodium sulfid cooking process is treated to produce a cooking liquor for a caustic soda cooking process, and in which residual liquor from a caustic soda cooking process may be treated to produce a sodium sulfite cooking liquor. In these cyclic and interrelated operations some of the same soda is employed in one type of cooking liquor and then in another. Soda is employed as a sulfite of sodium in a sodium sulfite cooking process, then in part as sodium sulfid in a sodium sulfid cooking process, and thereafter in a caustic soda cooking process.

According to one embodiment of this invention, a sodium sulfite type of cooking process is carried out with a cooking liquor containing sodium sulfite, either alone or admixed with certain other ingredients. Residual liquor therefrom is concentrated and subjected to a reducing furnace treatment to convert some of the sodium-sulfur compounds into sodium sulfid, with the remainder of the soda largely present as sodium carbonate. A cooking liquor is produced, from the resulting product, which contains considerable sodium sulfid, and may contain other reagents, such as caustic soda or sodium sulfite, or both, etc. This cooking liquor is employed for a digestion treatment. Residual liquor from the latter cooking operation, in which the sodium sulfid containing liquor is employed, is treated to produce a cooking liquor which contains caustic soda as the primary active constituent and may be either substantially free from sodium sulfid or contain sodium sulfid in relatively smaller amount. This caustic soda liquor is employed

for a digestive treatment. The residual liquor from the caustic soda cooking operation may be treated to produce a sulfite of sodium type of cooking liquor. Soda is thus employed as a sulfite of sodium in the sulfite type of cooking process, then in part as sodium sulfid in the sulfid type of cooking process, and next largely as caustic soda, and then again in some cases as a sulfite of sodium. Sulfur is employed as a sulfite of sodium, next as sodium sulfid, and the residue is then largely reoxidized or removed, and may be recovered for further use, e. g. in the sulfite type of process or in the sulfid type of process, or in part in each of these types.

The sulfite of sodium type of cooking process may be an acid, a neutral or an alkaline sodium sulfite cooking process. That is, the cooking liquor may contain sodium monosulfite alone, or with smaller amounts of certain other ingredients; or it may be an alkaline liquor containing sodium sulfid or caustic soda or both, as well as sodium sulfite; or it may be an acid liquor containing sodium bisulfite, or a mixture of sodium monosulfite and sodium bisulfite, or even sulfur dioxide beyond the bisulfite stage, i. e. containing NaHSO_3 and H_2SO_3 . Cooking liquors containing only or mainly sodium monosulfite, or sodium monosulfite together with a lesser amount of sodium thio-sulfate, or with sodium sulfid or with caustic soda, etc., may be used, for example, cooking liquors such as described in our prior applications Ser. Nos. 481,147, filed June 28, 1921, 686,137, filed January 14, 1924, 711,857 filed May 8, 1924, or 704,176 filed April 4, 1924. Or the cooking liquor may be an alkaline cooking liquor containing sodium sulfite and caustic soda, or sodium sulfite, caustic soda and sodium sulfid, etc., for example, as described in our prior Patent No. 1,651,665. Or the cooking liquor may be an acid sulfite cooking liquor, e. g. sodium bisulfite, or a mixture of sodium monosulfite and sodium bisulfite, or even an excess of sulfur dioxide beyond the bisulfite state, i. e., a mixture of sodium bisulfite and sulfurous acid.

The sodium sulfid type of cooking liquor may be that of the ordinary so-called sulfate

process, in which the cooking liquor contains primarily caustic soda and a lesser amount of sodium sulfid as the active constituents; or it may be a modified process differing from the ordinary sulfate process cooking liquor by containing sodium sulfid as the primary cooking chemical and being made up e. g. mainly of sodium sulfid and sodium carbonate; or it may contain also some caustic soda or some sodium sulfite or various mixtures of these compounds. Cooking liquors such as described in our prior application Ser. No. 57,954 filed September 22, 1925, may be used, containing caustic soda and sodium sulfid together with sodium sulfite. The cooking liquor of the sodium sulfid cooking process need not contain sodium sulfid as the main constituent, but it nevertheless generally contains it in fairly large amounts.

The caustic soda type of cooking liquor, which is the third type of the series of cooking liquors, may be the ordinary soda process cooking liquor or a modified caustic soda liquor, or it may be an ordinary sulfate process cooking liquor, but sodium sulfid, if present therein, will be generally in smaller amounts than in the cooking liquor of the sodium sulfid process, and it may be absent therefrom. The caustic soda type of cooking liquor may contain some sodium sulfite, but in general it will be made up mainly of caustic soda, i. e., it will contain caustic soda as the predominant active constituent.

The residual liquor from the sulfite type of cooking process, especially when neutral or alkaline, may be directly and readily concentrated. If acid, it may be advantageously neutralized prior to concentration, by the addition thereto of alkaline residual liquor or of recovered alkaline compounds from one or another of the regenerative processes. After neutralization or having been made alkaline, the liquor may then be more advantageously concentrated, thus retaining sulfur more readily. The concentrated residual liquors, or the solids contained therein after drying, are subjected to a reducing furnace treatment which decomposes organic compounds and converts sodium-sulfur compounds to a considerable extent into sodium sulfid, so that the product of the reducing furnace treatment contains the sodium compounds mainly as sodium carbonate and as sodium sulfid, generally with a considerable amount of sodium sulfid. Some sulfur may be driven off (e. g. as combustible sulfur compounds) during this reducing heat treatment which can be recovered, e. g. from the furnace gases after oxidizing them, recovering sulfur trioxide and sulfur dioxide, e. g. for use in the sulfid and in the sulfite type of cooking liquors, respectively.

The furnace product containing the sodium compounds mainly as sodium carbonate and as sodium sulfid may be dissolved to form

a solution which may, in some special cases, be used directly as a cooking liquor, in which case the cooking liquor will consist mainly of sodium sulfid and sodium carbonate. In this case the sodium present as sodium sulfid and as sodium carbonate may advantageously be approximately equal. Instead of using the solution directly as cooking liquor, some of the sodium carbonate can be causticized with lime to form caustic soda, or sulfited e. g. by treatment with calcium sulfite, or in part causticized and in part sulfited, to give a cooking liquor containing sodium sulfid and caustic soda, or sodium sulfid and sodium sulfite, or sodium sulfid, caustic soda and sodium sulfite. The cooking liquors as employed should have the required activity for the result which is desired.

Residual liquor from such a cooking operation in which sodium sulfid is present, is concentrated and subjected to a furnacing treatment, which may be either reducing or oxidizing. If the furnacing operation is reducing, some sodium sulfid may be present in the furnace product. If the furnacing operation is oxidizing, the furnace product may be free from sulfid and may contain some sodium sulfate, or sodium sulfite, or both. Such reducing furnace product usually contains a higher amount of sodium carbonate and a lower amount of sodium sulfid than in the case of the reducing treatment of the sulfite type of residual liquor above referred to. In such case, by highly causticizing a solution of the recovered sodium compounds a relatively small or moderate amount of sodium sulfid may be present and accompanied by a large amount of caustic soda. When the furnacing operation is carried out under oxidizing conditions, the furnace product also will contain the sodium compounds largely as sodium carbonate, and, by highly causticizing a solution thereof, a cooking liquor can be produced consisting mainly of caustic soda. Some of the soda can be sulfited where sodium sulfite is desired in the caustic soda type of cooking liquor. For example, one part may be causticized, another part sulfited, and these admixed in proper ratio.

Residual liquor from the caustic soda type of cooking operation may be concentrated and organic matter decomposed. Organic compounds may be carbonized or burned preferably under oxidizing conditions, so that any sulfur residue thereof may be in part removed and in part oxidized to sulfate or sulfite. If sulfur compounds are absent from such caustic soda cooking liquor, oxidation or removal of sulfur is not required. The result of such heat treatment of residual liquor from the caustic soda type of digestion is to yield a furnace product in which sodium carbonate is the main sodium compound present, and from which sodium sulfid is absent or is present therein in only small amount. A solu-

tion of the sodium carbonate so produced can be readily sulfited e. g. with SO_2 gas to regenerate the sulfite of sodium type of cooking liquor. If this cooking liquor is to be an alkaline sulfite liquor, or a liquor containing mainly sodium monosulfite, some thiosulfate may also be present. If the cooking liquor is to be a highly acid sulfite solution, e. g. with a large excess of sulfur dioxide beyond the sodium bisulfite stage, the sodium carbonate solution, which is to be sulfited, is preferably free from sodium sulfid and thiosulfate.

Instead of operating the same number of digesters with each of the three types of cooking liquors, or instead of using all of the residual liquor from each type of cooking operation to produce cooking liquor for the next type of digestion of the cycle, part of the residual liquor from one type of cooking operation may be treated to regenerate similar cooking liquor for the same type of cooking operation, or residual liquors from different types of cooking operations may be admixed in regulated proportions and the admixed liquors then treated to regenerate one or another of the three types of cooking liquors. For example, in making cooking liquor for the sulfid-containing cooking operation, some residual liquor from the sulfid containing cooking operation may be employed for neutralizing an acid sulfite residual liquor, or for admixture with a neutral or an alkaline sulfite residual liquor, and the resulting admixed liquors may then be treated in the manner described for producing a sulfide-containing cooking liquor. The cycle has considerable flexibility, so far as the number of digesters cooked or relative amounts of pulp produced by the respective types of cooking operations are concerned.

The supply of soda and of sulfur to make up for losses may take place at various suitable points in the cycle. Where sodium sulfate is available, it may be added with advantage to the sulfite type residual liquor, or the dried product thereof, so that sodium sulfid will be produced therefrom during the reducing furnace treatment, thus supplying sodium and some sulfur to the cycle. Sulfur may be supplied in the form of sulfur dioxide by burning sulfur in air or by roasting iron sulfide or other sulfides. Sodium carbonate may be supplied and may be sulfited to form a sulfite of sodium, or be causticized to form caustic soda. Caustic soda, sodium sulfid, etc. may be supplied at any suitable point in the cycle.

A considerable amount of the sulfur which may be driven off in the form of oxidized compounds or of combustible sulfur compounds can be recovered for further use. Combustible gases from the reducing furnace treatment of sulfur-containing residual liquors can thus be oxidized or burned to convert combustible sulfur compounds, when

present, largely into sulfur dioxide or trioxide, or both, which can be recovered by scrubbing the gases, e. g. with residual liquor or with a solution of sodium carbonate. The gases from the oxidizing furnace treatment of residual liquors e. g. from the sulfid-containing cooking operation can similarly be scrubbed to recover sulfur compounds therefrom. In case sulfur is oxidized to sulfur trioxide, it can be recovered e. g. by scrubbing the gases with black liquor or with a sodium carbonate solution, as sodium sulfate, and the sodium sulfate can be returned to the cycle and utilized for supplying sodium sulfid to the sulfid type of cooking liquor.

As an example of a sodium sulfite type of cooking liquor which can be used in the sulfite type of cooking operation of the invention, we may mention a suitable volume of cooking liquor containing sodium monosulfite to the extent of about 35 to 40 per cent on the oven-dry weight of the wood, in the case of poplar wood, or to the extent of 40 to 50 per cent on the oven-dry weight of the wood, in the case of spruce wood.

As an example of cooking liquors containing both sodium monosulfite and sodium bisulfite, a cooking liquor may be used containing 1200 pounds of sodium monosulfite, and about 500 pounds of sodium bisulfite to 4000 pounds of wood (oven-dried basis), in the case of poplar wood, or about 1335 pounds of sodium monosulfite and about 550 pounds of sodium bisulfite to 4000 pounds of wood (oven-dried bases), in the case of spruce wood. Such liquors may also contain a relatively small amount of sodium thiosulfate and also of sodium sulfate. The sodium-sulfur compounds in the resulting residual liquor form some sodium sulfid for the sulfid type of cooking liquor, during the reducing furnace treatment.

As examples of an acid sulfite cooking liquor, beyond the bisulfite stage, the liquor may contain 990 pounds of sodium bisulfite and about 260 pounds of sulfurous acid (H_2SO_3) to 4000 pounds of wood (oven-dried basis) in the case of poplar wood, or about 1240 pounds of sodium bisulfite and about 325 pounds of sulfurous acid (H_2SO_3) in the case of spruce wood. Sodium sulfate may also be contained in such liquor.

A liquor containing about 1320 pounds of sodium besulfite to 4000 pounds of wood (oven-dried basis) in the case of poplar wood, or about 1650 pounds of sodium bisulfite to 4000 pounds of spruce wood (oven-dried basis) can be used and sodium sulfate may also be present in such liquors, e. g., to the extent of 200 or 300 pounds.

The sulfite type of liquor when alkaline may also contain some sodium carbonate, caustic soda or sodium sulfid. As an example of a liquor containing a large amount of sodium sulfite, and also containing consider-

able sodium sulfid, we may use a liquor containing about 1030 pounds of sodium monosulfite and about 640 pounds of sodium sulfid, together with about 870 pounds of sodium carbonate to 4000 pounds of poplar wood (oven-dried basis). In the case of spruce wood we may use about 2275 pounds of sodium monosulfite and about 700 pounds of sodium sulfid to 4000 pounds of wood (oven-dried basis). The cooking operation in such cases can be carried out, for example, at a temperature corresponding to a saturated steam pressure of 130-150 pounds per square inch and for a sufficient time to complete the cooking operation.

As examples of cooking liquors, relatively high in sodium sulfid, we may use, for example, a cooking liquor containing about 800 pounds of sodium sulfid and about 1090 pounds of sodium carbonate to 4000 pounds of poplar wood; or about 1000 pounds of sodium sulfid and about 1360 pounds of sodium carbonate to 4000 pounds of spruce wood. Or we may preferably use a cooking liquor also containing sodium sulfite; for example, liquor such as above described containing in addition to the sodium sulfid and sodium carbonate, about 320 pounds of sodium sulfite for poplar wood, and about 400 pounds of sodium sulfite for spruce wood.

As examples of cooking liquors containing caustic soda, as well as sodium sulfid in relatively large amount, we may use a cooking liquor containing about 600 pounds of sodium sulfid and about 800 pounds of sodium carbonate, together with about 200 pounds of caustic soda to 4000 pounds of poplar wood, or about 750 pounds of sodium sulfid, about 1000 pounds of sodium carbonate, and about 250 pounds of caustic soda to 4000 pounds of spruce wood; or about 250 pounds of NaOH, 750 pounds Na₂S, 400 pounds Na₂SO₃, 375 pounds of Na₂CO₃; or about 300 pounds NaOH, 600 pounds of Na₂S, 500 pounds of Na₂SO₃, 275 pounds of Na₂CO₃; or 400 pounds of NaOH, 600 pounds Na₂S, 400 pounds Na₂SO₃, and 200 pounds of Na₂CO₃, for poplar or spruce wood.

Such cooking liquors can be produced by treating the solution containing mainly sodium carbonate and a relatively high sodium sulfid content, with a regulated amount of lime to form the required amount of caustic soda from the sodium carbonate, and with calcium sulfite sufficient to form the required sodium sulfite from some of the sodium carbonate, or a properly proportioned mixture of lime and calcium sulfite may be employed, where the cooking liquor is to contain both caustic soda and calcium sulfite, as well as sodium sulfid.

As an example of a cooking liquor relatively high in caustic soda, we may use a cooking liquor containing about 640 pounds of caustic soda, and about 375 pounds of sodium sul-

fid to 4000 pounds of pine wood (oven-dried basis). Such a liquor contains a considerable amount of sodium sulfid, and illustrates a cooking liquor which may be produced from the furnace product obtained by treating sulfur-containing residual liquors under reducing conditions, or a cooking liquor which may be produced, e. g. from the sulfite type of residual liquor when the operation is carried out so that a relatively large amount of sodium carbonate is produced and a smaller amount of sodium sulfid, and by suitably causticizing the sodium carbonate. By admixing different proportions of the sulfite type of residual liquor and of the sulfid type of residual liquor, and subjecting the admixed products to reducing furnacing treatment under regulated and suitable conditions, the ratio of carbonate to sulfid in the furnace product can be somewhat controlled and therefrom a caustic soda cooking liquor can be produced of varying sodium hydroxide and sodium sulfid content. Example: 800 pounds NaOH, 150 pounds Na₂S, 200 pounds Na₂CO₃ for 4000 pounds of wood (oven-dried basis). These cooking liquors may contain some sodium sulfite.

Where the caustic soda cooking liquor is produced from the furnace product formed from the residual liquor of the sulfid type of cooking process, especially when carrying out the furnacing operation under oxidizing conditions, it may be free, or nearly so, from sodium sulfid. Example: 1000 pounds NaOH, 200 pounds Na₂SO₄, 200 pounds Na₂CO₃ for the same amount of wood.

It will thus be seen that the present invention includes cooking operations in which cooking liquors of three different types are employed; that residual liquor from the sulfite type serves to provide a recovered soda product containing a rather large portion of its sodium content as sodium sulfid, which is employed in a cooking liquor of the sodium sulfid type; while residual liquor from the sulfid type of cooking operation serves to provide a recovered soda product for preparing a cooking liquor of the caustic soda type, which is employed in a caustic soda cooking operation; and residual liquor from the caustic soda type of cooking operation provides a recovered soda product which is readily utilizable by sulfiting to form a cooking liquor of the sulfite type, which may be employed to produce pulp by a sulfite type of cooking operation, and to form a residual liquor which can be advantageously utilized in the further carrying on of the cycle. Soda may be thus employed in a cyclic manner, while sulfur may also be employed in a cyclic manner, serving as a sulfite, then as sulfid, then being in part removed or oxidized or both. Some sulfur may be recovered for reuse, e. g. as a sulfite, or as sulfate, or both.

The residual liquor from the caustic soda

type of cooking operation may be treated in any suitable manner. It may be evaporated to dryness and the solids subjected to a heat treatment under oxidizing conditions to yield a furnace product containing mainly sodium carbonate. Most of the sulfur contained in such residual liquor either is removed by the gases or converted into an oxidized compound by such treatment and thus conserved or fixed. Therefore some sodium sulfate may be present in the furnace product along with the sodium carbonate. This sodium sulfate may thus be present in the sulfite type of cooking liquor which may be readily prepared by dissolving the sodium compounds, clarifying as needed, and sulfiting the solution, e. g. by SO_2 gas. When residual liquor from the sulfite type of cooking operation is subjected to the reducing furnace treatment, this sodium sulfate is useful in forming some sodium sulfid for the sulfid type of cooking liquor. The sulfur which is fixed as sulfate is thus conserved. As stated, Na_2S is advantageously absent from the Na_2CO_3 solution which is to be sulfited, especially when the sulfite type of cooking liquor is to be of a highly acid character, since $\text{Na}_2\text{S}_2\text{O}_3$, which might otherwise be formed, is detrimental in such highly acid liquors and furthermore increases the sulfur requirements.

Instead of carbonizing or burning the organic compounds in the residual liquor coming directly from the caustic soda type of cooking operation, this residual liquor may be sulfited directly by SO_2 gas to decompose some of the compounds therein and form a sulfite of sodium liquor. Some of the organic compounds are thereby decomposed and some organic matter is precipitated. The completely sulfited or the partially sulfited liquor may be separated from the precipitate in any suitable manner, and the separated liquor, after further sulfiting if needed, be employed for cooking wood with the sulfite type of cooking liquor thus prepared, all as more particularly set forth in our U. S. Patent No. 1606501.

This residual liquor from the caustic soda type of cooking operation may be employed to scrub furnace gases which contain oxidized sulfur compounds, e. g. SO_2 . Such liquor may be further sulfited, if necessary, e. g., after separation from precipitated organic matter, in order to produce a cooking liquor containing the desired amounts and ratio of combined to uncombined SO_2 . Inasmuch as such employment of this residual liquor for the scrubbing operation may result in a liquor which contains some sodium thiosulfate, the sulfite type of cooking liquor thus prepared should have sufficient combined SO_2 to overcome or avoid the objectionable effects of $\text{Na}_2\text{S}_2\text{O}_3$, such as those when it is present in considerable amount in sulfite type of cooking liquors which contain

a high percentage of uncombined SO_2 and a relatively small amount of combined SO_2 . Cooking liquors which contain a mixture of sodium bisulfite and a considerable amount of sodium monosulfite may thus be prepared and safely employed, such moderate amount of $\text{Na}_2\text{S}_2\text{O}_3$ as they contain being useful in producing some Na_2S when the sulfite type of residual liquor is subjected to the reducing furnace treatment. Such sodium organic compounds as remain in the cooking liquor thus prepared, i. e. by direct sulfiting of such residual liquor with SO_2 , are present in the sulfite type of cooking operation and serve to form some Na_2CO_3 in the subsequent furnace treatment.

The following will serve to illustrate, in a general way, the employment of the three types of cooking liquors in a cyclic manner which has some advantages.

A solution of sodium carbonate is sulfited by means of SO_2 gas, which may be obtained by burning sulfur in any suitable manner, to form a solution which contains principally sodium monosulfite. This solution is employed in suitable amount for the cooking of wood chips and may contain around 20 to 30 parts of SO_2 (total) to 100 parts of wood (oven-dry basis). The digester may be gradually and slowly heated to the cooking temperature, e. g. around 165 to 180 deg. C., and the cooking liquor is adequately circulated and maintained at a suitable temperature until the cooking has been carried to the proper degree, when the digester is "blown" in the customary manner. When such a cooking liquor is employed, little if any SO_2 is released from the liquor, differing from the usual acid sulfite type of cooking operation in which calcium bisulfite is employed. By thus retaining the SO_2 in the liquor, special SO_2 recovery means are not necessary, and the cooking liquors can be readily prepared of ample strength and at a fairly high temperature thus facilitating the preparation of the cooking liquor and conserving heat units.

The residual liquor is separated from the pulp, and may then be neutralized or made moderately alkaline to litmus by the addition thereto of some residual liquor from the sulfid type of cooking operation, or by some of the solution of the recovered soda compounds of the furnace product obtained by the subsequent furnace treatment. The neutralized or alkaline residual liquor is then concentrated and the solids subjected to a reducing furnace treatment. Sodium sulfate, in amount sufficient to replace lost soda, may be added to the solids prior to the reducing furnace treatment. This furnace treatment is so carried out that the resulting soda product contains principally sodium carbonate and sodium sulfid, the operation being so regulated that a considerable amount of sul-

fur is retained as sodium sulfid in the soda product, thus avoiding the removal of an excessive amount of sulfur along with the furnace gases, e. g. as sulfur or as an oxidizable sulfur compound. The soda in the resulting furnace product is dissolved in water and the solution is causticized by sufficient lime to convert a large part of the sodium carbonate into sodium hydroxide, thus yielding a cooking liquor containing principally sodium hydroxide and sodium sulfid. The sodium sulfid content thereof will generally be quite high, e. g. around 30 to 50 parts Na_2S for each 70 to 50 parts NaOH . If desired, a moderate amount of Na_2SO_3 may be produced in or added to the cooking liquor. For example, by using some CaSO_3 along with the $\text{Ca}(\text{OH})_2$; or by sulfiting a portion of the soda solution prior to causticizing, or without causticizing the sulfited portion and with causticizing of the other portion of the soda solution and mixing the sulfited portion with the causticized portion. After separating the lime mud from the cooking liquor, the cooking operation is carried out therewith, this being a sulfid type of cooking operation. The residual liquor from such cooking operation is separated from the pulp, is concentrated in whole, or a portion thereof may be diverted for admixing with the residual liquor from the sulfite type of cooking operation as described above. The solids in the concentrated portion of the residual liquor are subjected to a furnace treatment, e. g. of a reducing type, so as to produce a furnace product containing mainly sodium carbonate, although a moderate amount of sodium sulfid may with advantage be present therein. In such treatment, a considerable amount of sulfur is removed along with the furnace gases.

Sodium compounds in the resulting furnace product, principally sodium carbonate, are dissolved in water, and the solution is causticized by treatment with a regulated amount of lime to convert nearly all of the contained sodium carbonate into sodium hydroxide. If desired some sodium sulfite may also be present in this cooking liquor, but generally the amount thereof will be small. This cooking liquor is the caustic soda type of cooking liquor. Where the solution of the recovered soda compounds contains some Na_2S , the cooking liquor thus prepared may have a small or moderate amount of Na_2S , but the principal active ingredient in the caustic soda type of cooking liquor is sodium hydroxide, considerable of the original sulfur content having been eliminated or displaced from its combination or association with soda. This highly caustic liquor is employed as a cooking liquor, being especially suitable for producing soft stock, e. g. pulp from deciduous woods, such as poplars, etc.

The cooking operation with the highly

caustic liquor may be carried out according to the cooking procedure of the usual soda process. The residual liquor therefrom is separated from the pulp, is concentrated and the solids may then be subjected to an oxidizing furnace treatment, for example, to convert most of the soda into sodium carbonate and to eliminate some of the sulfur residue and to oxidize such sulfur as remains with the soda. The sodium compounds are dissolved in water, the solution clarified, if required, and then may be sulfited to produce a cooking liquor which contains, for example, mainly sodium sulfite and sodium bisulfite, although the cooking liquor may contain some sodium sulfate, as stated. And the cycle may then be repeated.

Instead of employing sodium sulfate for replacing lost soda, sodium carbonate may be employed for this purpose, and it may be added at any suitable point, e. g. before causticizing to prepare the highly caustic liquor, or prior to sulfiting to prepare the sulfite type of cooking liquor.

Some of the sulfur accompanying the furnace gases may be recovered in the manner stated or in any other suitable manner, and the recovered sulfur be returned to the cycle.

Where the furnace gases carry both SO_2 and SO_3 , the SO_3 content may be largely absorbed in one liquor and the SO_2 content largely in another liquor, and the various compounds thus obtained can be returned to the cycle at their most advantageous points, respectively. By removing most of the SO_2 from the gases, e. g. by electrical precipitation, or by absorption in black liquor from the sulfid type of cooking operation, which is to be reduced to form a furnace product containing Na_2CO_3 and Na_2S , the SO_2 remaining in the gases is more readily available for sulfiting soda to form a sulfite of sodium for use in the sulfite type of cooking liquor. A solution of Na_2CO_3 , or black liquor from the caustic soda type of cooking, may be used to absorb SO_2 from the gases. Thus the recovery of the sulfur content is made more feasible and in a particularly advantageous manner.

By employing the three types of cooking liquors, various woods can be cooked in a very advantageous manner, to yield the particular types of pulps desired. Thus, spruce may be cooked by a sulfite type of cooking liquor to produce a "sulfite pulp"; pines may be cooked by the sulfid type of cooking liquors to produce "sulfate pulp" or "kraft pulp"; and poplar and other deciduous woods may be cooked with the caustic soda type of cooking liquors to produce "soda pulp".

The sulfur employed in the sulfite type of cooking liquors is utilized, at least in part, for preparing Na_2S . The Na_2S thus prepared is present in cooking liquor employed for digesting wood and the reaction between

the wood substance and the soda facilitates the subsequent production of a recovered soda product which contains a relatively smaller amount of Na_2S , and finally the residue of sulfur is in part separated from the soda and may be in part converted into an oxidized compound, being thus conserved and made again available in part, as Na_2S upon a further reduction treatment.

10 Instead of employing a mixture of sodium disulfite and sodium monosulfite in the sulfite type of cooking liquor, the liquor may be free from sodium bisulfite, or it may even be a mixture of sodium bisulfite and sulfurous acid. Sodium bisulfite solutions, free from sodium monosulfite, and from excess sulfurous acid, may be employed, if desired.

Where a relatively large amount of the alkaline types of pulps are desired, i. e. produced by the sulfid type and caustic soda type of cooking liquors, and a relatively small amount of pulp by the sulfite type of cooking liquors is desired, just enough of the soda from the furnace product resulting from the furnace treatment of residual liquor from the caustic soda type of cooking operation may be diverted and sulfited to produce the required amount of cooking liquor of the sulfite type, the remainder of the soda from such furnace product being causticized for either the sulfid type or the caustic soda type of cooking liquor, as conditions may justify. Such sulfur dioxide as is employed in producing the cooking liquor of the sulfite type is utilized as a sulfite for cooking wood and subsequently in the formation of some Na_2S . The employment of the soda successively in the two types of cooking operations, viz.: The sulfid type and the caustic soda type, is advantageous in that a soda product is thus obtained which is readily sulfited by SO_2 to produce the sulfite type of cooking liquor. Na_2SO_4 is advantageously employed for replacing lost soda as it provides some sulfur as well as soda. This is especially advantageous when SO_2 and SO_3 are reclaimed from gases of the furnace operations.

Where the sulfite type of cooking liquor is prepared by directly sulfiting residual liquor from the caustic soda type of cooking operation, the separated organic matter may advantageously be added to the material which is to be subjected to a reducing furnace treatment to form Na_2S for the sulfid type of cooking liquor.

In case a relatively large amount of pulp is to be produced by the sulfid type of cooking operation, a regulated portion of the black liquor from such cooking operation may be treated to produce a furnace product relatively high in sodium carbonate and containing only a moderate amount of sodium sulfid, by employing a reducing furnace treatment and adding no additional sodium-sulfur compounds thereto, or the furnace product may

be free from sodium sulfid and contain primarily sodium carbonate with perhaps some sodium sulfate where the furnace operation is of an oxidizing type. The soda compounds are dissolved and the solution highly causticized to produce a moderate amount of cooking liquor of the caustic soda type. Such cooking liquor is employed to produce pulp and the residual liquor thereby formed is treated to produce a cooking liquor of the sulfite type and the latter is employed for producing pulp and a residual liquor which is then utilized for producing additional amounts of sodium sulfid, e. g. by admixing with the portion of black liquor from the sulfid type of cooking operation which remains after the other portion has been diverted. Such residual liquor from the sulfite type of cooking operation should be admixed quite uniformly with all of this remaining portion of the black liquor to insure the production of a cooking liquor for the sulfid type of cooking operation, which is fairly uniform in its ratio of NaOH to Na_2S . Sodium sulfate sufficient to make up for soda losses may be employed for such purpose, e. g. by adding it in a uniform manner to the material which is to be subjected to the reducing furnace treatment for producing the Na_2S for the sulfid type of liquor. Operating in this manner, even where the losses of soda per ton of pulp are quite low, the ratio of NaOH to Na_2S can be kept quite suitable for the sulfid type of cooking, as the Na_2SO_4 is utilized to advantage, as well as the sulfur.

Where the sulfite type of cooking liquor is to have a high acid content, e. g. a mixture of NaHSO_3 and H_2SO_3 , and in case this type of cooking liquor is to be prepared by directly sulfiting, by means of SO_2 , residual liquor resulting from the caustic soda type of cooking operation, it is preferable to have the caustic soda type of cooking liquor free from Na_2S ; however, Na_2SO_4 may be present therein. When sufficient SO_2 has been thus dissolved in such a residual liquor to precipitate substantially all of the precipitable organic matter therefrom, it is advisable to separate the solution from the suspended matter and to thereafter continue the sulfiting until the liquor contains the desired ratio of combined to uncombined SO_2 . Since the liquor still contains some dissolved organic matter which may be capable of reacting with sulfite, it is advisable to have the cooking liquor contain more total SO_2 per unit of wood to be cooked than if the cooking liquor were free from organic compounds when charged. An increase of, for example, 10 to 15% in the total SO_2 over the usual practice will generally be sufficient for the purpose. When such highly acid liquors are employed, the cooking operation can be carried out in the usual acid sulfite cooking manner, relieving SO_2 and uti-

lizing it in any suitable way, e. g. for fortifying the raw acid liquor and thus raising the content of uncombined SO_2 therein.

Instead of preparing the sulfite type of cooking liquor from soda recovered from black liquor from the caustic soda type of cooking operation, sodium carbonate when freshly supplied for replacing lost soda may be sulfited in solution to prepare the sulfite type of cooking liquor. The black liquor from the caustic soda type of cooking operation may in such instances be utilized in any other suitable manner, e. g., for regenerating a cooking liquor containing caustic soda, either accompanied by or free from Na_2S . Operating in this manner, the sulfur and the sodium carbonate freshly supplied, are first employed in a sulfite type of cooking operation and the residual liquor thereby formed is utilized for the production of some sodium carbonate and some sodium sulfid. A cooking liquor of the sulfid type is then prepared and utilized for a cooking operation and the resulting black liquor is employed, at least in part, for the production of a cooking liquor containing a relatively high content of sodium hydroxide, which is employed in a cooking operation of the caustic soda type.

It will thus be seen that the cycle is capable of numerous variations; that various raw materials may be employed; that various grades and kinds of pulp may be produced; that the cycle may be carried out in an efficient and advantageous manner; that the soda and the sulfur of the cycle are utilized to good advantage; and various other features will be apparent to those skilled in the art.

Cellulosic materials other than wood may be pulped by one or more of the three types of cooking operations described herein.

We claim:

1. The method of producing pulp which comprises cooking wood with a cooking liquor containing a sulfite of sodium, treating constituents of the residual liquor under reducing conditions to form a product containing sodium sulfid, producing a cooking liquor containing such sodium sulfid and cooking wood therewith, treating residual liquor from such cooking operation to form a different cooking liquor containing caustic soda as its primary active reagent and cooking wood therewith, and treating residual liquor from such caustic soda cooking operation to regenerate a cooking liquor.

2. The process of producing pulp which comprises cooking wood with a cooking liquor containing sodium hydroxide and sodium sulfid, treating the constituents of the resulting residual liquor by a reducing furnace treatment to form a product containing sodium carbonate and a relatively small amount of sodium sulfid, dissolving the

soda compounds and treating the solution with lime whereby a preponderating portion of the sodium carbonate is converted into sodium hydroxide, separating the liquor from the lime mud, cooking wood with the cooking liquor, treating the constituents of the residual liquor by an oxidizing furnace treatment to form a product containing most of the soda in the form of sodium carbonate and free from large amounts of sodium sulfid, dissolving the sodium compounds, clarifying the solution and sulfiting the same to form a cooking liquor containing a sulfite of sodium, employing the cooking liquor to cook wood, mixing an alkaline liquor with the residual liquor thereby obtained, subjecting the constituents of the mixed liquor to a reducing furnace treatment, dissolving the sodium compounds and employing the sodium sulfid thereof in a cooking liquor for the cooking of wood.

3. The process of producing pulp from raw fibrous materials which comprises cooking a portion thereof in a liquor comprising sodium sulfite as the principal active reagent, cooking another portion in a liquor comprising sodium sulfide as the principal active reagent and cooking a third portion in a cooking liquor comprising caustic soda as the principal active reagent, utilizing a portion of the soda content repeatedly in each of the three liquors, first as sulfite, then as sulfide and then as hydroxide.

4. The process of producing pulp from raw fibrous materials which comprises cooking a portion thereof in a liquor comprising sodium sulfite as the principal active reagent, cooking another portion in a liquor comprising sodium sulfide as the principal active reagent and cooking a third portion in a cooking liquor comprising caustic soda as the principal active reagent, utilizing a portion of the soda content repeatedly in each of the three liquors, first as sulfite, then as sulfide and then as hydroxide, and utilizing a portion of the sulfur content repeatedly, first as sulfite and then as sulfide.

In testimony whereof we affix our signatures.

LINN BRADLEY.
EDWARD P. McKEEFE.