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PRODUCTION OF PULP

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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 cooking liquors are employed, some common constituent being present in each cooking liquor, and with successive employment of such constituent, first in one type of cooking liquor and then in another type of cooking liquor.

In the cooking of wood chips, three digesting processes have been commonly used; one known as the soda process, wherein the chips are cooked in a solution of caustic soda; another known as the sulfite process, wherein the chips are cooked with a solution of acid sulfite or bisulfite; and the other known as the sulfate process, wherein the chips are cooked with a solution of sodium hydroxide and sodium sulfide. Recently there have come into use a number of processes using sodium monosulfite as a digestive reagent. These recent processes are our own invention and are covered in separate applications.

Residual liquor from each of the three various digesting processes referred to above has been treated to regenerate cooking liquors for the same digestive process or has been run to waste, according to the market value of the chemicals and the cost and feasibility of regenerating the cooking liquor from the residual liquor. Frequently it has been necessary or desirable to carry out two or more different types of digesting processes side by side in the same pulp mill. Thus the conventional acid sulfite process has been carried out side by side with the conventional soda or the conventional sulfate process when it was desired to mix short fibred pulp with long fibred pulp, in the manufacture of book paper. Sometimes market conditions demand different types of pulp from the same woods and to meet such demand the pulp mill may be devoted partly to one digesting process and partly to another or others. In such cases, prior to our invention, the mill has been divided practically into two separate plants, and the residual liquor from

each digesting process has been run to waste or regenerated separately to produce a cooking liquor for use in the same digesting process.

We have discovered that such different types of digesting processes as contain a common constituent, e. g. sodium or sulfur, may be interrelated and residual liquor from one digesting process may be treated to produce a cooking liquor for a different digesting process more economically than for the same digesting process. Thus in the case where an acid cook is carried out beside an alkaline cook, the residual liquors from the two digesting processes may be admixed, e. g. so as to neutralize each other and precipitate organic matter. The precipitated organic matter may be removed from the resulting liquor and the resulting liquor may be used for a third type of digesting process, namely a monosulfite digestion; or it may be divided and each portion of the liquor treated to regenerate a cooking liquor suitable for the acid and alkaline digesting processes respectively. Where a neutralized and clarified liquor is used in a monosulfite digesting process, the residual liquor therefrom may be treated as a whole or it may be separated into two or more portions and treated to regenerate cooking liquors for either one or both the acid and alkaline digesting processes.

Frequently at some stage in the treatment of a residual liquor, the intermediate product is better suited for producing a different type of cooking liquor than for producing that type which was used in the digesting process from which the residual liquor was obtained. For example, where an alkaline residual liquor is treated by means of sulfur dioxide to precipitate organic matter therefrom, and the precipitated organic matter is removed from the resulting liquor, as described in our co-pending application, Serial No. 434,720 filed January 3, 1921, a substantial portion of the sodium constituent of such a residual liquor may be thereby converted into a sulfite of sodium. The resulting liquor is therefore adapted with very little treatment for use in a sulfite, either bisulfite or monosulfite, digesting process. And, similarly, where an

acid sodium sulfite residual liquor is neutralized or made slightly alkaline, e. g. by means of added sodium hydroxide or/and sodium carbonate, normal sodium sulfite is produced, so that the resulting liquor is easily adapted for use in a normal sodium sulfite digesting process or even in a modified soda process. Where the dried residue of a sulfite-containing residual liquor is treated by furnacing, some of the sodium and sulfur are easily recovered as sodium sulfide. This compound may be used in a sulfate or a modified sulfate digesting process more advantageously than in the original sulfite digesting process. Numerous other instances might be cited in which it is advantageous to combine and interrelate different digesting processes according to our invention. However, it would be cumbersome, if not impossible, to enumerate within the limits of this specification all of such combinations, and it is believed that the following examples will adequately serve to illustrate how the invention may be practiced.

According to the present invention we may treat black liquor from a soda or modified soda pulp process, i. e., using a digesting liquor containing sodium hydroxide in solution, with sulfur dioxide or an acid sulfite such as sodium bisulfite, in amount regulated so as to bring about a separation of substantially all of the precipitable organic matter from the solution and so as to convert reactive sodium compounds of the liquor into the form of sodium sulfite or/and sodium bisulfite in solution. The organic matter present in such black liquor is of such a character that much of it can be precipitated from solution by treatment of the liquor with sulfur dioxide or sodium bisulfite. The precipitated organic matter may be separated from the treated liquor by filtration, sedimentation, etc. Such treated and clarified liquor will now contain a considerable portion of the sodium of the original cooking liquor in combination with sulfur dioxide, that is, as a sulfite of sodium in the solution or liquor; and this liquor will moreover be freed from a large part of the precipitable organic matter. The sulfite of sodium liquor thus produced, by treatment of such a black liquor in the manner above described, may be made use of, according to the present invention, in carrying out a sulfite digesting process to produce pulp. In case the clarified liquor does not have the desired amount of sodium sulfite or uncombined sulfur dioxide, we add more sodium sulfite or/and uncombined sulfur dioxide thereto. So also, the clarified liquor may be concentrated to give a more concentrated sulfite liquor for use; or/and the black liquor may be concentrated by any suitable means to a suitable concentration before the addition of the sulfur dioxide thereto, so that organic matter will be removed

from a more concentrated liquor, and so that a more concentrated sulfite liquor will be produced by the sulfur dioxide treatment. Instead of adding all of the sulfur dioxide at once to the black liquor, it may be added in stages; for example, sufficient sulfur dioxide may be added to convert the reactive sodium compounds for the most part into sodium sulfite, or with a sufficient excess of suitable acid to render the liquor acid to litmus and bring about a more complete separation of organic matter from the solution, the solution separated from precipitated organic matter and then concentrated either before or advantageously after neutralization, and a further amount of sodium sulfite or/and uncombined sulfur dioxide added to the liquor, e. g. to give the desired amounts of combined and uncombined SO_2 for use in a sulfite type of digesting process to produce pulp from wood, etc.

If the treated and clarified liquor still contains an objectionable amount of soluble organic compounds, after the addition of the sulfur dioxide in whole or in part, sodium sulfite contained in the liquor may be recovered to a considerable extent by concentration of the neutral or alkaline liquor until sodium sulfite crystallizes out on cooling, leaving the soluble organic compounds in the mother liquor. The crystallized sodium sulfite thus recovered, together with additional sodium sulfite, if desired, can then be dissolved in water and the resulting solution may be treated, if desired, with uncombined sulfur dioxide for the purpose of producing an acid sulfite solution appropriate for use in an acid sulfite of sodium digesting process (with such additions thereto as may be necessary to make up for losses). Sulfur dioxide for so treating such a black liquor can, at least in part, be obtained from cooking liquor employed in the acid sulfite digesting process, by recovering sulfur dioxide from the digester in a manner which will be readily understood.

The acid sulfite of sodium cooking liquor produced as above described, and with appropriate adjustment and regulation of its strength and acidity, can be used to advantage in the carrying out of an acid sulfite digesting process; so that black liquor from a sodium hydroxide type of digesting process is thus made available to advantage in the production of a cooking liquor for a sulfite of sodium type of digesting process.

The sulfite type of digesting process, which is carried out according to the present invention in conjunction with a sodium hydroxide type of digesting process, makes use of a sulfite liquor containing uncombined sulfurous acid together with sodium sulfite or bisulfite, instead of calcium bisulfite. The digestion of the wood chips with the sulfite liquor may thus be carried out with a liquor containing sulfurous acid and sodium bisulfite, and

the digestion can be carried out in much the usual way by heating with direct steam at a pressure around fifty to eighty pounds and for a suitable period of time, for example, from 3 to 10 hours. Upon completion of the cook in the sulfite type of digesting process, when carried out with sulfurous acid and sodium sulfite or bisulfite, free sulfur dioxide may be "blown" or relieved from the digester, e. g. at the end of the cook, and the pulp is separated from the residual liquor.

The residual liquor from the calcium bisulfite process, as commonly practiced, is run to waste. According to the present invention, however, the residual liquor may be advantageously treated for the separation and recovery of organic matter therefrom, and for the recovery of the soda contents of the liquor in a form available for use in the carrying out of a soda pulp process.

According to one method of treatment of the residual liquor from the sulfite type of digestion, we treat the liquor with a compound of an alkali or of an alkaline earth, to neutralize the acidity and to combine with the reactive sulfur dioxide of the liquor. We regard it as more advantageous to use an alkali compound than an alkaline earth compound, so that the alkali sulfite will remain in solution instead of the alkaline earth sulfite being precipitated. The liquor which has been more or less neutralized or made alkaline is then concentrated. It is advantageous to evaporate this liquor by spraying it into hot gases to produce a concentrated liquor; and this concentrated liquor may be again sprayed into hot gases to obtain a substantially dry product; or a substantially dry product may be obtained by one evaporation treatment, by proper regulation of the operation. The substantially dry product, especially when organic matter has not been removed, can be burned so as to utilize the fuel value of the organic matter which it contains, leaving an alkaline ash which can then be dissolved in a suitable amount of water and the solution causticized, either with or without the addition of further amounts of causticizable sodium compounds, to produce a caustic liquor suitable for use as a cooking liquor in a soda pulp process or a modified soda process. The caustic liquors produced by the above procedures can be further clarified if necessary before use.

Instead of neutralizing the residual liquor of the sulfite type before concentrating, the liquor may be similarly concentrated without neutralization and a dry product obtained containing substantially all of the organic matter of the liquor, and this dry product can be burned to utilize its fuel value and to give an ash which can be treated in the manner above described, that is, by dissolving the soluble sodium compounds and causticizing the solution with lime to give a caustic

soda liquor for use in a soda pulp process or a modified soda pulp process. The organic matter present in residual liquor of the sulfite type is so large in amount that it provides a large amount of combustible material, which can replace to an important extent fuel now commonly supplied from other sources for carrying out the operations of the pulp mill. When acid residual liquor of the sulfite type is neutralized or rendered alkaline before concentration, and the neutralized or alkaline liquor is concentrated by a spray evaporation treatment, organic matter may be left with the liquor so that it will be present in the dry product, and its fuel value made available as above described.

In the concentration of residual liquor of the sulfite type, and particularly if the liquor is not neutralized before concentration, as well as in the burning of the dry product produced therefrom, sulfur dioxide and other sulfur compounds may be contained in the resulting gases and may be recovered therefrom and made available for further use.

We have found that black liquor from digesting processes in which an alkaline liquor, e. g. one supplied with sodium hydroxide, is used for cooking wood, is an excellent absorbent for sulfur dioxide, inasmuch as such black liquor usually contains a considerable quantity of uncombined alkali and compounds of alkali with organic constituents which are replaceable by sulfur dioxide. The treatment of such black liquor with sulfur dioxide is therefore an advantageous treatment for the separation of organic matter from the black liquor and for the production of alkali sulfite or/and bisulfite in solution. The black liquor can thus be used to advantage for absorbing and recovering sulfur dioxide from the liquor used in the digesters in the acid sulfite type of digesting process, for example, sulfur dioxide relieved from the digester during or at the end of the cook, sulfur dioxide from the blow-pit, or sulfur dioxide from a subsequent treatment of the residual liquor; while sulfur dioxide itself is not only recovered advantageously in this way but it serves to bring about separation of organic matter from the black liquor. Organic matter thus separated from black liquor can be treated for the production of valuable products, or it may be burned.

It will thus be seen that a soda or modified soda pulp process and a sulfite type of digesting process (using sulfurous acid and sodium monosulfite or bisulfite) can advantageously be carried out in conjunction with each other, by operating in the manner above described, so that residual liquor from the soda or alkali sulfite pulp process is used in the production of a sulfite type of cooking liquor for this sulfite type of digesting process, and so that the sulfite type of residual liquor is used in making a caustic soda type of cooking liquor

for use in a soda or modified soda pulp process. Residual liquors of either or both processes can thus be used to advantage, while organic matter of the residual liquors can also be recovered at least in part and used as a valuable by-product of the process, or burned for its fuel value.

As another example of how our invention may be practiced, a digesting process using a cooking liquor comprising caustic soda, and sodium sulfide, with or without a tri-oxy-sulfur compound of sodium, may be combined or interrelated with a digesting process using a liquor containing sodium sulfite and sodium thiosulfate. Such digesting processes are disclosed in our applications Serial No. 713,257, filed May 4, 1924 and Serial No. 704,176, filed April 4, 1924, respectively. Thus spruce wood may be cooked with a liquor which contains caustic soda and a lesser amount of sodium sulfide, either with or without sodium sulfite or/and sodium thiosulfate, and the resulting residual liquor therefrom may be suitably concentrated, for example to about 10° to 15° Baumé (more or less) at about 135° F., and the concentrated liquor may be then subjected to a regulated sulfiting treatment, e. g. with sulfur dioxide or sodium bisulfite or both to precipitate organic matter and to convert a considerable portion of the contained sodium compounds into sodium sulfite, some of the sodium content of the treated liquor being present as sodium thiosulfate. The residual liquor may contain some sodium thiosulfate and this together with that formed, if any, when sodium sulfide of the residual liquor is converted by the sulfiting treatment into sodium thiosulfate, provides sodium thiosulfate in adequate amount for a cooking liquor in accordance with the process described in our application Serial No. 704,176, filed April 4, 1924. The sulfiting treatment may be continued until the liquor has been rendered moderately or slightly acid to litmus and thus considerable organic matter may be precipitated from the solution. When the sulfited liquor is sufficiently warm this precipitated organic matter coagulates and it may be removed from the liquor by sedimentation, filtration, etc. It is advisable to promptly remove the liquor from the precipitated organic matter after the sulfiting treatment in order to avoid redissolving precipitated organic matter which may occur to some extent upon prolonged standing. The separated liquor may be used as a cooking liquor, after adjustment if needed, using a digester which is constructed so as to withstand the action of the acid liquor. Or the acid liquor may be neutralized or rendered alkaline in any suitable manner, e. g. by adding the required amount of sodium hydroxide or/and sodium carbonate, sodium sulfide, etc., so that the neutralized liquor is alkaline to litmus and only

slightly to moderately alkaline to phenolphthalein.

The naturalized liquor generally contains a relatively large amount of sodium sulfite and usually a lesser amount of sodium thiosulfate. The method of using such a cooking liquor for the production of pulp from wood is more fully set forth in our patent application Serial No. 704,176, filed April 4, 1924. This cooking liquor, e. g. derived from such black liquor, may advantageously be employed for the production of pulp from short fibred woods, e. g. non-coniferous woods. The residual liquor or red liquor resulting from such sulfite type of pulping operation may be used, at least in part, for making up the cooking liquor which contains caustic soda, a sodium tri-oxy-sulfur compound, and sodium sulfide. The red liquor may contain some unconsumed sodium sulfite which may be so added to the cooking liquor, thus securing the advantage which such material imparts to the alkaline cooking liquor.

The remaining portion of the red liquor, if any, may be concentrated, the dried matter carbonized in a rotary furnace, e. g. such as is usually used in soda process mills, under reducing conditions, or it may be charred and then smelted in much the same way as is usually followed in sulfate process mills. An aqueous solution of the recovered soda compounds generally contains substantial amounts of sodium carbonate and of sodium sulfide, which solution when treated with lime yields cooking liquor which contains caustic soda and sodium sulfide. By a partial sulfiting treatment of the cool uncausticized aqueous solution with sulfur dioxide, the cooking liquor may be provided with the desired amount of tri-oxy-sulfur compound, e. g. sodium thiosulfate.

The organic matter precipitated by the sulfiting treatment contains considerable sodium compounds. This precipitated material may be regained and added to the other material undergoing treatment in a rotary furnace or/and smelter and thus the organic matter may be destroyed and the sodium content recovered to a considerable extent along with that from other material undergoing treatment.

The relatively strong short fibred pulp and the long fibred pulp, obtained by the combined or interrelated cooking operations above described, may be mixed and the mixture of pulps used for the production of strong and well formed papers. Or the pulps may be bleached and used in any manner customary in the art. Such combined or interrelated operations are particularly advantageous where the long fibred woods are resinous coniferous woods, e. g. such as those which grow in the southern portion of the United States of America, and the short fibred woods are the gums and other non-

coniferous trees which grow abundantly in the same region.

In the combined or interrelated operations the soda and the sulfur are used to special advantage, the amount of water to be removed by evaporation may be considerably reduced and the use of recovery apparatus may be modified in an advantageous manner, with the result that the expense may be reduced and the loss of soda and sulfur may be decreased. By using some of the digesters in a mill for cooking coniferous woods with the strongly alkaline cooking liquor, and using the black liquor therefrom for the production of a cooking liquor which contains a sulfite of sodium, and using some of the sulfite type of residual liquor for the regeneration or production of the strongly alkaline cooking liquor and some of the sulfite type of residual liquor for mixture with a strongly alkaline liquor, a number of advantages are obtained.

The following is another specific application of our process to a "multiple-liquor mill". A digestion of wood may be effected by means of a cooking liquor which contains mostly sodium sulfite (Na_2SO_3) as the digesting reagent and with but little or no sodium thiosulfate present in such cooking liquor, as more fully described in our applications Serial No. 481,147, filed June 28, 1921, and Serial No. 711,857, filed May 8, 1924. The resulting residual liquor may be separated from the resulting fibrous material, then suitably cooled, and enough sulfur dioxide absorbed therein or/and sodium bisulfite added thereto to produce an acid cooking liquor which contains the desired amounts of free and of combined SO_2 . This acid cooking liquor may then be employed for a digestion of wood (etc.). The acid cooking liquor may range from one that is slightly acid, through liquors of moderate acidities up to and including those which are strongly acid. When such liquors contain moderate amounts of thiosulfate, it may with advantage contain both Na_2SO_3 and NaHSO_3 .

The excess sodium sulfite (Na_2SO_3), i. e. that which was not consumed in the first digestion treatment, remaining in the first residual liquor serves to supply some soda and combined sulfur dioxide for the acid sodium sulfite cooking liquor made in this manner. Then an acid sodium sulfite cooking liquor digestion (e. g. of wood) is carried out, the second resulting residual liquor is separated from the resulting fibrous matter, and such latter residual liquor (together with wash waters if desired and with or without addition of alkaline material thereto) may be subjected to a concentrating treatment and the solids thereafter furnaced under strongly reducing conditions adapted to form mostly sodium carbonate and sodium sulfide from the sodium compounds. These

two compounds (Na_2CO_3 and Na_2S) are dissolved in water to form a liquor, this liquor is causticized (e. g. by lime) to form an alkaline digesting liquor which contains caustic soda (advantageously in preponderating amount), and sodium sulfide as its sole or as its principal digesting reagents, and such alkaline cooking liquor is employed to digest wood, etc., e. g. to form chemical pulp, and to form an alkaline sulfur-bearing residual liquor.

The latter residual liquor may then be concentrated and the solids furnaced to convert most of the sodium compounds into sodium carbonate, the latter being either free from or accompanied by but a small amount of sodium sulfide. If the amount of sodium sulfide being produced is objectionably large, the material undergoing treatment in the furnace may be subjected to a regulated and controlled oxidation treatment, e. g. by subjecting it for a short time to suitable oxidizing conditions in the furnace; or we may treat the sodium sulfide in solution with oxygen; or we may remove the sulfide sulfur from the solution as hydrogen sulfide, e. g. by treating the solution of the recovered sodium compounds with carbon dioxide or sodium bicarbonate and heating and agitating the carbonated solution, burning it to form sulfur dioxide and utilizing the sulfur dioxide to convert the sodium in the treated solution into sodium sulfite, all as more fully described in our co-pending application Serial No. 248,960, filed January 23, 1928. The dissolved sodium compounds, from the furnace product, may thus be treated to form a sulfite of sodium cooking liquor which is low in or may even be substantially free from sodium thiosulfate, with little if any NaHSO_3 present.

Such an operation is for a "three-liquor mill". A similar operation could be performed in a two-liquor mill using an acid sulfite cook similar to the second cook in the above cycle and treating the solution of the sodium compounds of the last mentioned furnace product with a sufficient amount of sulfur dioxide to regenerate an acid sulfite cooking liquor and digesting wood therewith.

In order to further illustrate the invention, the following example is described. This particular arrangement of pulp making operations, employing a strongly alkaline cooking liquor in one instance, and a mildly alkaline or a moderately acid cooking liquor in another instance, with utilization of the residual liquor from the first mentioned digesting process to supply a regenerated cooking liquor for the other digesting process, and vice-versa, is of special advantage. The wood cooked by the strongly alkaline cooking liquor may be either deciduous or coniferous wood, and the wood cooked by the mildly alkaline or the moderately acid cook-

ing liquor may also be either deciduous or coniferous wood; and the same of a different wood may be cooked by the two digesting processes.

Example: Around 10,000 pounds (oven-dry basis) of deciduous wood, such as aspen, poplar, gum, maple, birch, chestnut, etc., is treated in a suitable digester with about 500 to 600 cubic feet of cooking liquor which contains about 1400 pounds of sodium hydroxide, about 700 pounds of sodium sulfide, and may contain about 400 to 800 pounds of sodium sulfite, and may also contain around 200 to 300 pounds of sodium thiosulfate. The liquor and chips are gradually heated, e. g. by the direct or the indirect method or in part by each method, and the chips are digested for a suitable period of time so as to produce the quality of pulp desired. This may require around 3 to 5 hours, more or less, at a temperature of around 170 to 175 degrees C.

At the termination of the digesting period, the fibrous material and the resulting residual liquor may be blown from the digester into a blow-pit, in the usual manner, or removed therefrom in any other suitable manner, and the residual liquor separated from the resulting pulp. This liquor is termed "black liquor". It usually has a moderate amount of washings with it owing to the use of wash water in the separation of the black liquor from the pulp.

The black liquor may be concentrated and the residue furnaced according to the conventional methods of the soda process or the sulfate process to recover the soda principally in the form of sodium carbonate. This sodium carbonate may be dissolved in water and the resulting solution may be sulfited to produce a sulfite of sodium type of cooking liquor. When the cooking liquor is to contain little if any sodium bisulfite, the solution can be sulfited hot, e. g. at or around the boiling point, and it may be well agitated during the sulfiting treatment so as to aid in decomposing sodium sulfide, if any is present, so as to form hydrogen sulfide and so as to eliminate hydrogen sulfide from the solution, thereby producing a cooking liquor which contains but little if any sodium thiosulfate, when cooking liquor of that quality is desired. If it is desired to increase the amount of loosely combined or uncombined SO_2 in the regenerated cooking liquor, it may be cooled after substantially all of the sodium carbonate and sodium sulfid have been reacted upon by the sulfite radicle, and then subjected to further sulfiting by means of sulfur dioxide or sulfur dioxide and sodium bisulfite to produce a regenerated cooking liquor of the desired quality and composition. Thus cooking liquors which contain little or no loosely combined SO_2 , and ranging in composition up to and including those which contain a relatively large amount of uncombined

SO_2 , may be regenerated from the black liquor in the manner described.

Alternatively, the black liquor (in whole or in part) may be sulfited in any suitable manner and at any suitable concentration so as to precipitate substantially all of the precipitable organic matter of the black liquor, thereby forming a sulfite of sodium. By treating the black liquor at a partially concentrated state, with sufficient SO_2 to convert only a part of the sodium sulfite into sodium bisulfite, substantially all of such organic matter is precipitated or thrown out of solution. If the black liquor be warm enough, the precipitated organic matter coagulates. The precipitated organic matter is separated from the treated solution and the latter may be further treated with sodium sulfite or sodium bisulfite or sulfur dioxide or any two or more of these reagents so as to produce a regenerated cooking liquor of the sulfite of sodium type and having a suitable portion of its sulfur dioxide content present as a sulfite of sodium. When the black liquor contained a considerable amount of sodium sulfide and of sodium thiosulfate, before treatment with sulfur dioxide, etc., to precipitate organic matter, the resulting regenerated cooking liquor of the sulfite of sodium type generally contains a substantial amount of sodium thiosulfate. In such case, the regenerated cooking liquor should be provided with a sufficient amount of combined SO_2 , e. g. as normal sodium sulfite, to overcome or nullify the tendency of the loosely combined sulfur content of the sodium thiosulfate to objectionably darken the resulting pulp to such an extent as to render the pulp commercially unbleachable. The precipitated organic matter may be furnaced along with the residue resulting from removal of water from the residual liquor which results from the digesting step by means of the sulfite of sodium type of cooking liquor.

Regenerated cooking liquor produced as described above may be used, for example, in a digesting process such as the following:

Around 10,000 pounds (oven-dry basis) of spruce wood, or other suitable coniferous wood, may be digested in a suitable digester by means of a suitable amount of cooking liquor which is supplied with around 1500 pounds of sodium sulfite and around 3000 pounds of sodium bisulfite, more or less, the digester contents being gradually and slowly heated up to the active digesting temperature and the heating being continued until the desired degree of digestion has been obtained. The digester may be relieved as required, care being taken to avoid removing an objectionable amount of SO_2 from the digester. In some cases some sulfur dioxide may be relieved from the digester and regained and utilized in producing a cooking liquor.

Upon termination of the digesting step, the

fibrous material and the resulting residual liquor may be blown from the digester, and the residual liquor separated from the resulting fibrous material. This residual liquor may have some washings admixed therewith.

This residual liquor, either after or without having been treated by an available alkaline material so as to neutralize any free acid therein, may be concentrated to remove water and form a dry residue which contains sodium organic compounds, etc. These sodium organic compounds may be decomposed so as to obtain the soda in form capable of being utilized in producing a regenerated cooking liquor containing sodium hydroxide and sodium sulfid as its principal digesting reagents; and the cycle may be repeated two or more times.

One of the simplest methods of treating the dried residue from the residual liquor resulting from the digesting step with the sulfite of sodium type of cooking liquor, is to carbonize the organic matter and smelt the inorganic residue so as to obtain the soda principally in the form of sodium carbonate and sodium sulfide, the former compound usually being present in preponderating amount. These compounds may be dissolved in water to form a solution. Some of this solution may be utilized in neutralizing or rendering alkaline the residual liquor from the acid cooking step, in case such treatment is desired. The bulk of the solution is causticized by means of lime so as to produce a regenerated cooking liquor which is strongly alkaline. Such cooking liquor may have added thereto or produced therein some sodium sulfite or/and some sodium thiosulfate. Thus, some of the residual liquor from the sulfite type of digestion may be added to the alkaline solution either before, during or after the causticizing treatment.

Another method of treating the dried residue which contains the sodium organic compounds, especially when such dried residue is obtained by a regulated spray evaporation and drying operation so as to avoid objectionably decomposing sodium organic compounds, is to so treat the residue as to obtain organic acid or acids, or organic esters, or organic acid anhydrides, and to convert the sodium content into a sodium compound or compounds which can be thereafter treated so as to produce a regenerated cooking liquor which contains sodium hydroxide, etc. Thus the dried residue may be treated with SO_2 , or a sulfur-chlorine compound, or with a sodium compound which results from a regulated heating of sodium bisulfate to remove water therefrom, in case an anhydride or anhydrides are desired, the volatile compound or compounds being removed from the other constituents. Or the dried residue may be treated with an organic compound of a vola-

tile alcohol and a strong mineral acid such as sulfuric acid, phosphoric acid, hydrochloric acid, etc. For example ethyl sulfate, ethyl phosphate, ethyl chloride, or a hydrogen-bearing or acid compound such as ethyl hydrogen sulfate. The volatile organic compound resulting from such interaction may be removed from the inorganic residue by volatilization and the volatile material may be cooled to condense a valuable organic liquid.

Another method is to treat the dried sodium organic residue by means of an alcoholic solution of sulfur dioxide, so as to convert sodium content into a sulfite of sodium, and leave the organic acid content of the residue in the alcoholic solution, either as a free acid or as an ester or as a mixture of these. Thus SO_2 may be dissolved in ethyl alcohol or methyl alcohol or a mixture thereof and this material brought into intimate contact with the dried residue, whereupon a sulfite of sodium results and the resulting alcoholic solution can be removed from the inorganic residue. The liquid may be fractionated so as to remove the alcohol from ingredients having a different boiling point, and the alcohol may be reused for another treatment accompanied with the required amount of sulfur dioxide. In order to facilitate the separation of the sulfite of sodium from the alcoholic solution of the organic matter, it appears to be very desirable to have a regulated amount of water present, perhaps so as to form a crystalline sulfite of sodium, and to have enough SO_2 present in the alcoholic solution to convert the sodium content into and acid sulfite of sodium, e. g. enough to convert all of the reactive soda into sodium bisulfite, NaHSO_3 .

The sodium compounds recovered from the dried product by the above described methods may be used to form a suitable cooking liquor by causticizing with lime. In the case where the sodium is recovered as a sulfite, this causticizing may be only partial so that a part of the sulfite is utilized in the liquor. Sodium sulfid may be added to the liquor or formed therein.

When the dried sodium organic residue is treated to produce sodium sulfite or bisulfite or to produce sodium sulfate, these oxy-sulfur compounds of sodium, one or more, may be furnaced in the presence of carbon, under reducing conditions, so as to convert the soda into a mixture of sodium carbonate and sodium sulfide. This mixture can be dissolved in water to form a solution; and then by causticization with lime, the alkaline cooking liquor can be made. If sodium chloride is formed, it can be converted into sodium carbonate in any suitable manner and the latter may be causticized, or the sodium chloride can be electrolyzed to provide sodium hydroxide and chlorine, the latter

being useful for bleaching the pulp produced.

The volatile organic compound or compounds may be produced in rather large amounts by the methods outlined, and may constitute a valuable by-product of the pulp-making operations.

According to another method of treating the dried sodium organic material, such material may be subjected to a destructive or dry distillation step in a suitable vessel or retort, e. g. by means of heat externally applied or/and internally applied such as by means of an electric current developed within or passed through the dried carbonaceous material. High frequency currents may be induced within the carbonaceous material, according to the method developed by Dr. Northrop of Princeton and Trenton, N. J., thereby developing the required amount of heat and temperature to effect the destructive distillation of the material.

The gases driven off from the material contain hydrocarbons and may contain carbon monoxide. If necessary carbon monoxide may be separately generated and then admixed with the hydrocarbon gases so as to provide the desired and regulated amount of carbon monoxide in proportion to the hydrocarbons. The mixture of hydrocarbons and the carbon monoxide may be treated with elementary chlorine and the resulting mixture treated in the presence of a suitable agent to cause the reactions to take place, e. g. in the presence of sunlight or a catalyst such as aluminium chloride.

The reactions result in the production of a ketone or a mixture of ketones and hydrochloric acid, and these being volatile they are removed from the residue and the liquid condensed and the hydrochloric acid recovered in any suitable manner. This acid may be used for any suitable purpose, or marketed. Thus it may be used to treat alcohol such as ethyl alcohol to make an ethyl chloride and the latter can be used to treat some of the sodium organic residue to produce an ester or esters.

By heating the ester or esters and passing them in contact with carbon heated to a suitable temperature, the ester is decomposed into a ketone and carbon monoxide. This mixture may supply the carbon monoxide which is to be chlorinated to form a chloride such as carbonyl chloride, and the mixture may be treated with the hydrocarbon or hydrocarbons in the presence of a suitable catalyst and thus produce an increased amount of ketone or ketones. Methane may be treated with carbonyl chloride in the presence of a suitable catalyst and produce a ketone or ketones and hydrochloric acid. The methane may be obtained from any suitable source, e. g. natural gas or/and the gases from the destructive distillation treatment.

Although the examples specifically de-

scribed above have been concerned with producing chemical pulp, yet any or all of the digesting processes may be so regulated as to produce a partially digested wood, especially by the sulfite type of digestion, and this material may be disintegrated thereafter by mechanical means so as to produce what may be termed a semi-chemical pulp or pulps.

In addition to the above specific examples, we have disclosed in co-pending applications various other cyclic processes in which two or more digesting operations are combined and each of the residual liquors therefrom is treated to regenerate cooking liquor for another digesting operation.

In our co-pending application Serial No. 456,187 filed March 28, 1921, we have disclosed how an acid sulfite process may be combined with a soda process or a modified soda process using a small amount of normal sodium sulfite, each of the residual liquors being treated so as to regenerate cooking liquor for the other digesting operations.

In our co-pending applications, Serial Numbers 704, 176, filed April 4, 1924; 120,141, filed July 2, 1926; 120,242 filed July 2, 1926; 133,289, filed September 2, 1926; 133,290, filed September 2, 1926; 120,513, filed July 3, 1926; 133,291, filed September 2, 1926; 133,292, filed September 2, 1926; 133,293, filed September 2, 1926; 133,294, filed September 2, 1926; 248,960, filed January 23, 1928; 266,863, filed April 2, 1928; 276,501, filed May 9, 1928; and 267,476, filed April 4, 1928, we have disclosed numerous other examples including an acid sodium sulfite digesting process combined with a soda process, a sulfate process, a modified sulfate process, a monosulfite process, etc.; or a monosulfite process combined with a soda process, a sulfate process, a modified sulfate process, etc.; or a monosulfite-sulfide process combined with a soda process, etc.; and with regeneration by furnacing, together or separately, with one or more of the residual liquors subjected to a reducing furnacing, while others may be subjected to an oxidizing furnacing, or with all subjected to a reducing furnacing. In its broadest aspect the invention claimed herein includes all of the above and to that extent this application is to be considered a continuation in part thereof. In particular, this application is a continuation in part of our co-pending applications Serial No. 456,187, filed March 28, 1921; Serial No. 713,257, filed May 14, 1924; and Serial No. 248,960, filed January 23, 1928.

We claim:

1. The cyclic process of producing pulp, which comprises a digesting treatment of cellulosic material with a suitable digestive reagent, subjecting residual non-fibrous material to a treatment adapted to produce such a digestive reagent, the latter treatment comprising a digesting treatment of a cellulosic material with an intermediate digestive

reagent produced from such residual non-fibrous material.

2. The cyclic process of fibre liberation which comprises digesting cellulosic material with a cooking liquor containing a suitable digestive reagent, separating residual liquor from the resulting fibrous material and subjecting the residual liquor to a treatment adapted to regenerate a cooking liquor of the type used in such digesting step, said treatment comprising a digesting treatment of raw cellulosic material with an intermediate digestive reagent derived at least in part from the residual liquor.

3. The cyclic process of producing pulp which comprises digesting cellulosic material with a digestive reagent of one type, subjecting residual non-fibrous material to a treatment adapted to decompose a salt thereof and to form an inorganic compound adapted for use in producing a digesting reagent of another type, digesting cellulosic material with the latter reagent and treating residual non-fibrous material to produce a digesting reagent of the first mentioned type.

4. The cyclic process of fibre liberation which comprises digesting cellulosic material with a cooking liquor containing a reactive compound of an inorganic base, separating residual liquor from resulting fibrous material and subjecting the residual liquor to a treatment adapted to decompose an organic compound thereof, and to form an inorganic compound suitable for use as a digestive reagent in a different type of cooking liquor, including such inorganic compound in such a cooking liquor, digesting fibrous material therewith and treating resulting residual liquor to regenerate a cooking liquor suitable for use in the first name digesting step.

5. The cyclic process of fibre liberation which comprises digesting cellulosic material with a cooking liquor containing a reactive sodium compound, digesting cellulosic material with a cooking liquor of a different type containing active sodium compounds, treating residual non-fibrous material from each digesting process to convert a sodium compound thereof into a compound adapted for use in the other digesting step, producing cooking liquors containing such compounds respectively and repeating the digesting processes using such regenerated liquors.

6. A process of fibre liberation, which comprises digesting raw cellulosic material in an acid cooking liquor containing a soluble sodium compound, digesting raw cellulosic material in an alkaline cooking liquor containing a soluble sodium compound, and recovering sodium compounds from the waste acid cooking liquor resulting from one digestion and using the same in the formation of the alkaline cooking liquor for the other digestion.

7. A process of fibre liberation, which

comprises digesting raw cellulosic material in an acid cooking liquor containing a soluble sodium compound, digesting raw cellulosic material in an alkaline cooking liquor containing a soluble sodium compound, and recovering sodium compounds from the waste cooking liquor resulting from one digestion and using the same in the formation of the cooking liquor for the other digestion, and vice versa.

8. A process of fibre liberation, which comprises cooking raw cellulosic materials, one batch in an acid liquor and another batch in an alkaline liquor, and using as the basic compound for the liquor of each batch, those soluble inorganic compounds recovered from the other liquor after the raw material is cooked therewith.

9. A process of fibre liberation, which comprises cooking raw cellulosic material in two batches, one in an acid liquor containing sodium compounds and the other in an alkaline liquor containing sodium compounds, and forming each cooking liquor with sodium compounds recovered from the other liquor after the cooking therewith has been completed.

10. A process of fibre liberation, which comprises recovering sodium compounds from waste alkaline cooking liquor, forming an acid cooking liquor from such compounds and cooking cellulosic material therewith, recovering sodium compounds from the acid waste liquor resulting therefrom, and forming an alkaline cooking liquor from such recovered sodium compounds.

11. A process of fibre liberation, which comprises digesting raw cellulosic materials in successive batches, one in an alkaline cooking liquor and the other in an acid cooking liquor, and forming each liquor with inorganic compounds derived and recovered from the other liquor after the cooking operation therewith.

12. In the production of pulp, deriving a sodium compound from residual liquor formed in producing such pulp with an alkaline cooking liquor, acidifying such compound in solution with available sulfur dioxide, and cooking cellulosic material with such acid solution.

13. In the production of pulp, a cyclic process comprising digesting cellulosic material with an acid cooking liquor which includes a sodium-sulfur compound derived at least in part from the hereinafter-mentioned alkaline cooking liquor, and digesting cellulosic material with an alkaline cooking liquor which includes an alkaline sodium-sulfur compound derived at least in part from said acid cooking liquor.

14. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor of one type which includes a sulfite of sodium, digesting cellu-

losic material in a cooking liquor of different type which includes another active sodium compound, treating residual liquor from each digesting operation to convert sodium compounds thereof into compounds adapted for use in the cooking liquor for the other digesting step, producing cooking liquors containing such compounds and repeating the digesting operations using such regenerated cooking liquors.

15. The process of fibre liberation which comprises digesting cellulosic material in one type of cooking liquor containing a sulfite of sodium, digesting cellulosic material in a cooking liquor of a different type containing another reactive sodium compound, treating residual liquor from one of such digesting operations to convert a sodium compound thereof into a compound adapted for use in producing cooking liquor of the other type, the process including removal of a sulfur-bearing constituent from liquor of the first-mentioned digesting step and subsequently utilizing such sulfur in a digesting operation carried out with cooking liquor of the first-mentioned type.

16. The cyclic process of fibre liberation which comprises digesting cellulosic material in one type of cooking liquor containing a sulfite of sodium, digesting cellulosic material in a cooking liquor of a different type containing sodium hydroxide, treating residual liquor from each of such digesting steps to convert a sodium compound thereof into a compound adapted for use in cooking liquor for the other digesting step, producing cooking liquors containing such respective compounds and repeating the digesting operations using such regenerated cooking liquors.

17. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor containing a sulfite of sodium as the predominating digestive reagent, digesting cellulosic material in a cooking liquor of a different type containing a strongly alkaline sodium compound as the predominating digestive reagent, treating residual liquor from each digesting operation to convert a sodium compound thereof into a compound adapted for use in the other type of cooking liquor, producing cooking liquors containing such respective compounds and repeating the digesting operations using such regenerated cooking liquors.

18. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor containing an acid sodium sulfite, digesting cellulosic material in a strongly alkaline cooking liquor, treating residual liquor from each digesting step to convert sodium compounds thereof into compounds adapted for use in the other digesting step, producing cooking liquors containing such respective compounds and repeating the

digesting operations using such regenerated cooking liquors.

19. The cyclic process of fibre treatment which comprises digesting cellulosic material in a cooking liquor of one type, digesting cellulosic material in a cooking liquor of a different type, treating residual liquor from one digesting step by precipitation of organic matter and clarification, treating residual liquor from the other digesting step by drying and furnacing, and regenerating from one residual liquor a cooking liquor suitable for use in the other digesting step.

20. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor of one type, digesting cellulosic material in a cooking liquor of a different type, and treating residual liquor from each digesting step to regenerate a cooking liquor suitable for use in the other digesting step, one of such regenerating treatments comprising precipitation of organic matter from the residual liquor.

21. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor of one type, digesting cellulosic material in a cooking liquor of a different type, and treating residual liquor from each digesting step to regenerate a cooking liquor suitable for use in another digesting step, one of such regenerating treatments comprising precipitation of organic matter by means of a reagent adapted to form a digestive compound in the liquor.

22. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor containing sodium hydroxide, treating residual liquor resulting therefrom with the sulfite radicle to convert a sodium compound thereof into a sulfite of sodium, forming a cooking liquor containing such sulfite of sodium, digesting cellulosic material with such cooking liquor and treating the resulting residual liquor to regenerate a cooking liquor suitable for use in the first-named digesting operation.

23. The cyclic process of fibre treatment which comprises digesting cellulosic material in a cooking liquor containing sodium hydroxide, treating residual liquor resulting therefrom with sulfur dioxide to convert a sodium compound thereof into a sulfite of sodium, forming a cooking liquor containing such sulfite of sodium, digesting cellulosic material with such cooking liquor, drying the resulting residual liquor, decomposing organic matter, dissolving resulting sodium compounds and treating the resulting solution to form a cooking liquor suitable for use in one of the digesting steps, and digesting cellulosic material with such cooking liquor.

24. The cyclic process of fibre liberation which comprises digesting cellulosic material in a cooking liquor of one type, burning combustible matter derived from the resulting re-

sidual liquor, treating inorganic material derived therefrom to form a cooking liquor of a different type, digesting cellulosic material in such latter cooking liquor, and treating residual liquor therefrom to produce a cooking liquor for use in the first-named digesting operation.

25. The improvement in the sulfite process, which comprises treating the effluent liquor from an alkaline cooking operation with sulfur dioxide to produce a cooking liquor for use in a sulfite process, and supplying such liquor to a sulfite process.

26. The improvement in the sulfite process, which comprises treating black liquor from an alkaline cooking operation with an acid sulfite to bring about precipitation of organic matter and the formation of a solution containing a sulfite of sodium, and supplying the resulting liquor to a sulfite process.

27. The method of treating effluent liquor from an acid alkali-metal sulfite cooking operation, which comprises treating such liquor with alkaline sodium compounds derived from such a liquor by a furnacing treatment to decompose organic matter thereof.

28. The improvement in the recovery of sulfur dioxide from acid sulfite cooking processes and liquors which comprises absorbing such sulfur dioxide in the residual liquor from an alkaline pulp-making process.

29. The improvement in the recovery of sulfur dioxide from gaseous mixtures containing the same which comprises passing such gaseous mixtures into intimate contact with an alkaline residual liquor resulting from the cooking of wood with an alkaline cooking liquor.

30. In the manufacture of chemical wood pulp, recovering sodium compounds from the alkaline waste liquor used in producing such pulp, forming a solution thereof, acidifying such solution with sulfur dioxide, and cooking cellulosic material with such acid solution.

31. In the manufacture of chemical wood pulp, cooking cellulosic material in a sulfurous acid solution of a sodium salt, cooking cellulosic material in an alkaline solution of another sodium compound, neutralizing the waste acid cooking liquor with the waste alkaline cooking liquor, recovering sodium compounds from the resulting liquor in an alkaline solution, and cooking cellulosic material therewith.

32. In the manufacture of chemical wood pulp, a cyclic process comprising cooking cellulosic material with an acid solution of sodium-sulfur compounds recovered from the waste hereinafter-mentioned alkaline cooking liquor, and cooking cellulosic material with an alkaline solution of sodium-sulfur compounds recovered from the waste first mentioned acid cooking liquor.

33. In the manufacture of chemical wood

pulp, a cyclic process comprising cooking cellulosic material with an acid solution of sodium-sulfur compounds recovered from the waste hereinafter-mentioned alkaline cooking liquor, cooking cellulosic material with an alkaline solution of sodium-sulfur compounds recovered from the waste said acid cooking liquor, and making up losses in sodium during such cyclic operation by adding soluble sodium compounds to the alkaline cooking liquor.

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