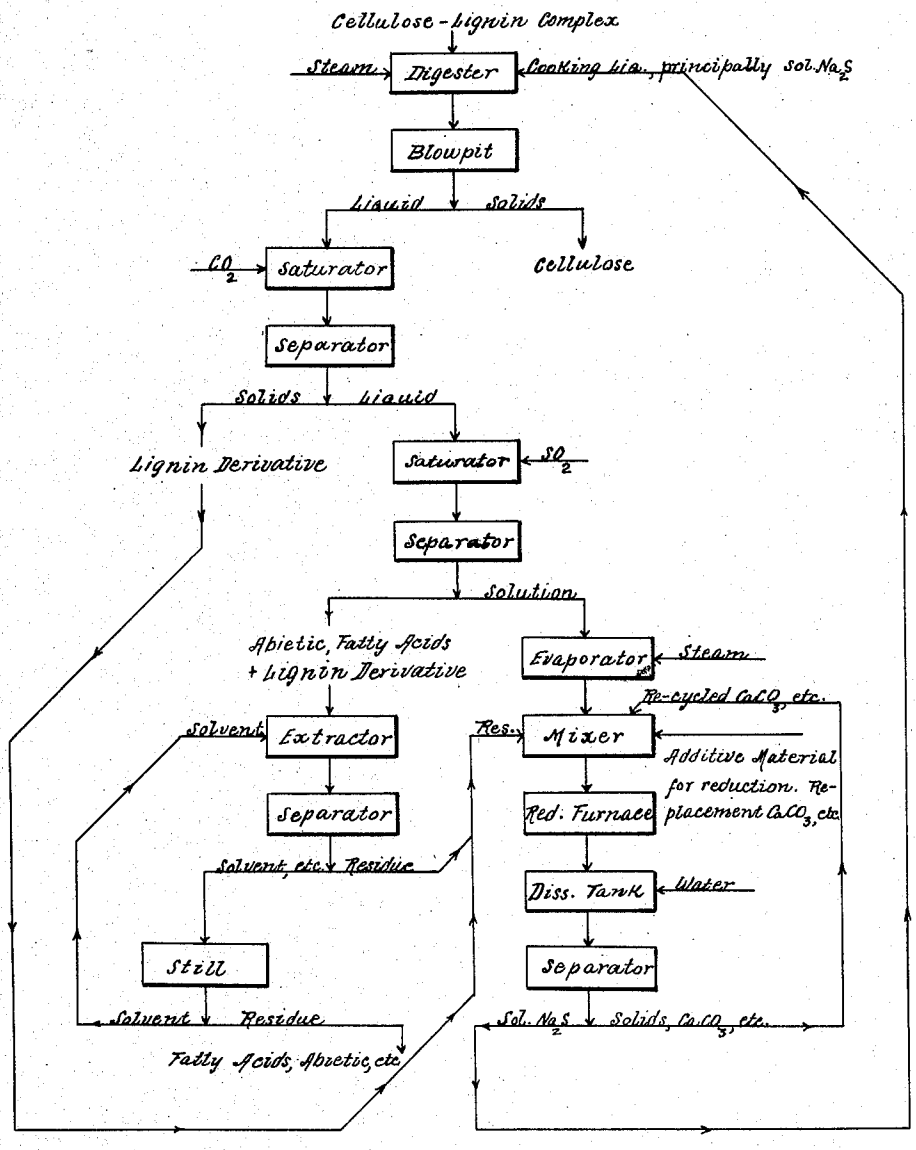
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METHOD OF REGENERATING A SPENT COOKING LIQUOR RESULTING FROM THE DIGESTION OF A CELLULOSE-LIGNIN COMPLEX

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METHOD OF REGENERATING A SPENT COOKING LIQUOR RESULTING FROM THE DIGESTION OF A CELLULOSE-LIGNIN COMPLEX

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The underlying chemical reaction upon which my process is based is the selective action of the alkaline metal sulphides upon the lignin ingredient of such complexes while the cellulose component is but slightly affected. Simultaneously, the components that would consitute the so-called "ether extract" of such complexes are saponified or emulsified by the action of the sulphide and thus pass into the lignin solution together with said lignin.

While these statements are but well known facts familiar to all that are skilled in the art yet little use has been made thereof because of the lack of a truly cyclic manner of recovering and reusing the all essential alkali metal sulphide. It is, therefore, in furnishing such a truly cyclic recovery and reuse that my process resides, not in the orthodox chemistry on which it is based.

The expression "alkali metal sulphide" includes, of course, both potassium and sodium sulphide. In general, the potassium salt is the better but the sodium salt the cheaper, but many of these complexes contain considerable potassium so that even though the process be started with sodium sulphide yet the re-cycled medium will ultimately become a mixture of salts of both sodium and potassium.

My process hence consists in digesting a comminuted form of the complex with a re-cycled solution of alkali metal sulphide at a temperature range corresponding to a gage pressure of from 20 to 125 pounds, depending upon the character of the complex, for such a time as shall be needed to liberate the cellulose component from the encrusting materials.

In the accompanying flowsheet I have set forth the various steps needed to accomplish the reuse of said sulphide and the process is best followed and understood by the complete explanation of said drawing. However, a brief synopsis will first be given. Separation is first made between the solid and liquid components of the completed digestion. The spent cooking liquor is then acidified with sulphur dioxide, thus converting the resident alkali metal salts substantially into sulphates and sulphites, chiefly the latter. This is accompanied by the separation of sulphur and of a modified form of lignin, as well as the ingredients constituting the "ether extract." The resultant solution, after removal of the ingredients above mentioned, is then evaporated and the resident salts converted to sulphide by a reducing furnace operation in the presence of solid carbon or of materials that will yield solid carbon. The

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reduced salts are dissolved in water and then constitute the cooking liquor as originally employed.

While this is the essence of the process, a number of additional steps appear in the drawing. They are introduced to facilitate the above described series of reactions and to the extent to which they contribute additional revenue from by-products are of much commercial importance. However, the fundamental reactions are still the essential ones and the supplementary steps merely aid in the operation. It will be evident that the total amount of material rendered insoluble in said acidification could be commingled with the concentrated solution, prior to the furnace operation and the identical cooking liquor thus reconstituted.

In order to elucidate more fully the flowsheet, I shall combine this description with a preferred version of my process as applied to the resinous stump wood of certain pines that are rich in resinous material, such as the southern pine, the sugar pine and the ponderosa pine. Such wood will contain over 20% of resinous material and included in the ether extract will be a varying amount of fatty acids, partly free and partly as fats, chiefly oleic acid.

This raw material is chipped as in conventional pulp work and then digested for a period of 5 hrs. at a pressure of 85 lbs. gage, with an adequate amount solution to cover same. The cooking liquor will contain approximately 50% of the bone dry weight of wood as Na_2S. When digestion is completed the pulp is separated from the spent cooking liquor and the latter saturated with a gas containing a substantial portion of CO_2, such as spent boiler stack gases, or lime kiln gas.

The saturation is effected by scrubbing or by blowing the compressed gas through the liquid. A heavy precipitate of a modified form of lignin is separated and removed in the "separator," which may be a settler, a filter, or a centrifuge, as desired. On the drawing this lignin is seen later on commingled with the mix for the furnace, but if a better commercial use is desired such use can be replaced by almost any substance that will yield solid carbon in the furnace operation, such as waste vegetable matter.

The time for such saturation cannot be specified but it is continued until a filtered sample of the liquor yields almost no additional precipitate with fresh CO_2. The reason for this preliminary saturation with CO_2 is to obtain resinous and fatty acid components in the next step, in

a more concentrated form than would be the case if commingled with all this lignin which has now been removed.

The liquor, purified by the removal of said lignin, is next saturated with a gas containing a substantial amount of SO_2, such as the spent gas from the reducing furnace operation, roaster gas from the roasting of metallic sulphides, or purer forms of SO_2. The absorption is virtually quantitative and is continued until the liquor shows no alkaline reaction when the separation of the resinous and fatty acids will be found complete. This is likewise done by test. Commingled with the resinous and fatty materials will also be a certain amount of highly degraded lignin.

After separation from the liquor, this "ether extract" is purified by the use of a selective solvent which will leave the lignin behind. As the separated acids are soluble in virtually all types of fat solvents the greatest variation is possible. Any of the alcohols, acetone, or chlorinated derivatives are acceptable. Also ethers and the light petroleum distillates. On the drawing I have shown the cyclic use of such a solvent by the use of a still which is, of course, conventional. The lignin residual is sent to the furnace as in the former case.

The residual solution from the SO_2 saturation is next evaporated to the highest degree compatible with retaining a fluid material. It is then mixed with the separated lignin residuals, or in lieu thereof with a substance that will yield solid C in the furnace step. The operation in the furnace is entirely reducing, so a reducing flame is used as the source of heat and an excess of solid C is maintained. This excess is cyclically returned from the dissolving step. I have also shown the use of $CaCO_3$ in the furnace charge. This is not absolutely essential and may be omitted. It will be seen that it is also cyclically returned. In the furnace operation it becomes converted to CaS, but in the lixiviation step it becomes reconverted to $CaCO_3$. Its advantage is largely mechanical, as it makes a smooth operation. About 50% on the charge is desirable but is altered to suit conditions.

The temperature of the reduction is carried as low as possible for the double reason of lessened attack on the furnace lining and of volatilization losses. The composition of the resultant cooking liquor, which should be essentially a solution of alkali metal sulphides, is the best warrant for an adequate temperature. Any increase in unreduced alkali metal sulphites and/or sulphates is the signal that the temperature must be increased.

The output of the furnace is discharged directly into water where its soluble ingredients dissolve. Separation is then made, by settling or otherwise, of the solids which are chiefly $CaCO_3$, excess C, and minor decomposition products. In as much as impurities are continually introduced in the raw material, the cyclic load is gradually rendered more and more impure. It must, therefore be discarded periodically or else a small amount must be split off consistently and replacement material added to make good the loss. Unless the content of alkali salts in the raw material is adequate there will likewise be a need for some replacement of the sodium sulphide with which the operation was commenced. This is most conveniently covered by adding the corresponding sulphate to the mixer.

Any type of furnace may be used for this reduction but I prefer the use of a rotary furnace,

similar to a cement kiln. A separate fire box will be needed and the discharge end of the furnace must be closed in order to insure a reducing atmosphere within the furnace.

The temperature in the dissolving tank should be near boiling. If it drop too low there is danger of carbonates appearing in the cooking liquor which is the sign of undecomposed Na_2S being returned with the cyclic load. A little does no harm but the content should be substantially sulphide, so any increase in carbonate means lack of temperature in the dissolver. Separation of the solids may be in any conventional manner.

In the event that the lignin complex contain non-saponifiable material, such as waxes, these will as already stated be emulsified. If the spent cooking liquor be centrifuged before saturation with the gas, such an emulsion will generally be obtained in concentrated form and the danger of having it become intermixed with much separated lignin will have been obviated. An illustration would be found if the raw material be the straw of the fiber flax, or the "tow" conventionally made therefrom. In this case the wax would be a substance very similar to beeswax, and it would be obtained from the centrifuge in a very concentrated form easy to subject to additional refining.

While not represented on the drawing, it is obvious that concentration by evaporation could be introduced anywhere before the furnace without changing any other sequence. If it preceded the first saturation then a "soap" would rise to the surface of evaporator storage tank, and such soap could be easily skimmed off. The composition of said soap would be higher in fatty acids and lower in abietic than the material remaining in solution and subject to recovery after saturation with SO_2. A partial fractionation could thus be obtained.

It is also obvious that the furnace gases could be made the source of both the SO_2 and the CO_2 needed in the saturation steps and that the above result would be obtained if the spent cooking liquor were passed counter-current to the furnace gases, lignin being separated after the first saturation with CO_2, and fatty material from the latter saturation. After the gases had contacted the liquor the SO_2 resident therein would have been quantitatively absorbed and only CO_2 would remain for the subsequent use of the gas in saturation.

Inasmuch as cellulose-lignin complexes with additive ingredients of resins, fats, fatty acids, and waxes run almost the entire gamut of the vegetable world it is evident that the two illustrations given herein represent but an exceedingly small fraction of the total field. In general, therefore, it may be said that "trial and error" must be the means whereby a process, conceived within the limits of this disclosure, is made adaptable to any type of raw material falling within the scope of my process. Such adaptations, or modifications, will be found to represent little except a sound knowledge of the chemistry involved and will suggest themselves to any operator.

Having thus fully described my process, I claim:

1. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient which comprises; neutralizing said liquor with sulphur dioxide; removing the materials rendered insoluble by said neu-

tralization; evaporating the neutralized liquor; commingling it with material containing carbon; incinerating the mixture in a reducing atmosphere to convert resident alkali metal salts to sulphide; lixiviating said reduced incinerated material to obtain a solution of alkali metal sulphide suitable for another digestion of cellulose-lignin complex.

2. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient which comprises; commingling said spent cooking liquor with carbon dioxide as long as a precipitate of lignin is produced thereby; separating the lignin from the residual solution; neutralizing said resultant solution with sulphur dioxide and removing the ingredients rendered insoluble by such neutralizing procedure; evaporating the neutralized liquor after separation of the insoluble ingredients; commingling it with material containing carbon; incinerating said mixture in a reducing atmosphere to convert resident alkali metal salts to sulphide; lixiviating said reduced incinerated material to obtain a solution of alkali metal sulphide suitable for the digestion of a cellulose-lignin complex.

3. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient set forth in claim 1; with the added step that calcium carbonate be added to the mixture being incinerated; the solids from the lixiviation step, containing said calcium carbonate and excess carbon, being cyclically returned to the mixture before incineration.

4. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient set forth in claim 2; with the added step that emulsified solids suspended in the spent cooking liquor be separated prior to the treatment with carbon dioxide recited therein.

5. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient which comprises; removing any emulsified substances suspended in said spent liquor; saturating the residual liquor with carbon dioxide as long as any lignin is precipitated; removing said lignin; saturating the liquor after such lignin removal with sulphur dioxide until liquor is no longer alkaline; separating the material rendered insoluble in such saturation; evaporating the neutralized liquor and commingling it with lignin previously separated and a cylic return of solids from a future lixiviation step; incinerating said mixture in a reducing atmosphere to convert resident alkali metal salts to sulphide; lixiviating said reduced incinerated material to obtain a solution of alkali metal sulphides suitable for the digestion of a cellulose-lignin complex and residual solids; and returning the solids to the mixture to be incinerated as previously specified.

6. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient as set forth in claim 5; with the added step that calcium carbonate be made an ingredient of the solids cyclically returned from the lixiviating step.

7. The method of regenerating a spent cooking liquor resulting from the digestion of a cellulose-lignin complex with an alkali metal sulphide as the sole, active ingredient as set forth in claim 5; with the added step that saturation with CO_2 and SO_2 as disclosed therein be effected by passing the spent cooking liquor counter current to the gases obtained by the oxidation of the volatile products obtained in the incineration step.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,689,534	Richter	Dec. 4, 1928
1,743,080	Bradley et al.	Jan. 7, 1930
1,797,678	Bradley et al.	Mar. 24, 1931
1,860,803	Bradley et al.	May 31, 1932
1,864,619	Richter	June 28, 1932
2,201,797	Scott	May 21, 1940