

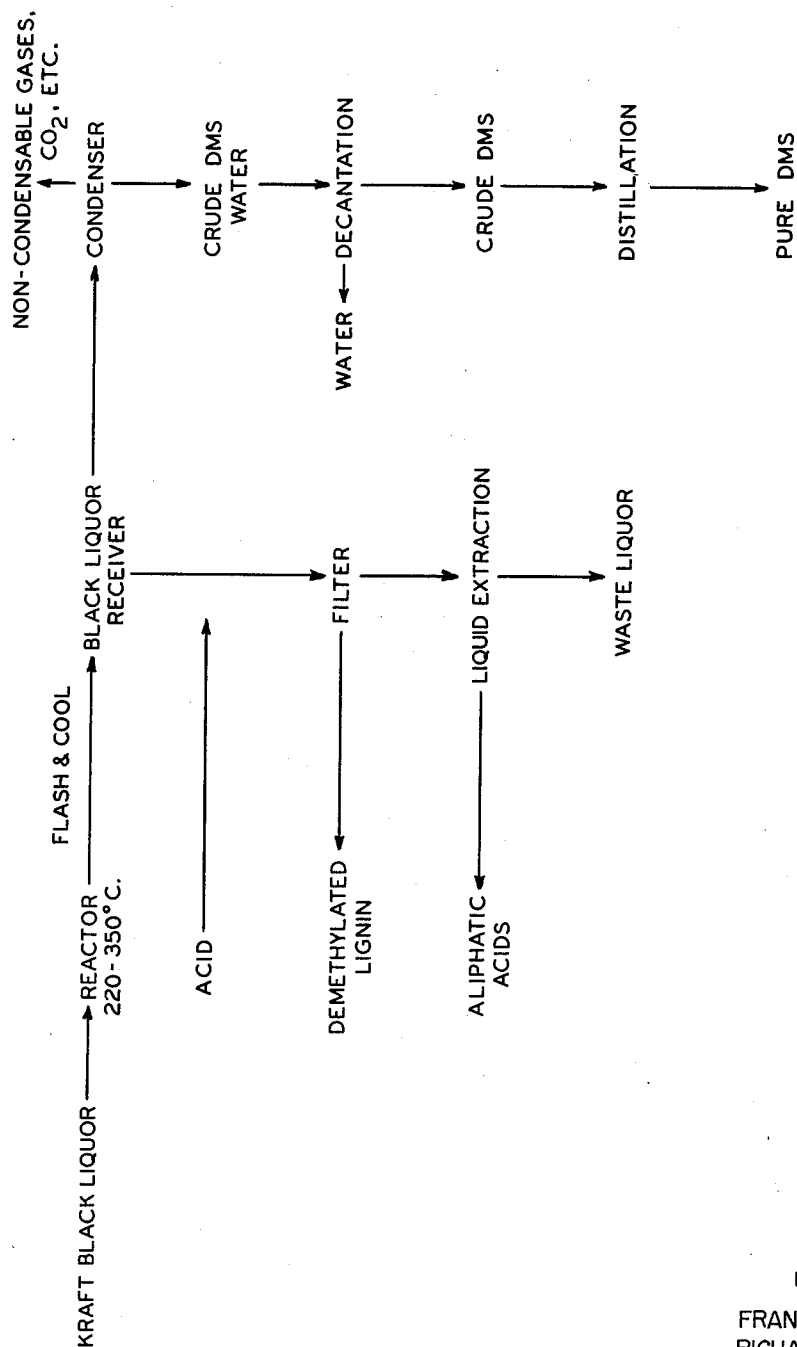
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TREATMENT OF KRAFT BLACK LIQUOR AND PRODUCT

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TREATMENT OF KRAFT BLACK LIQUOR
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This invention relates to a process for treating residual black liquor from the kraft pulping process whereby dimethyl sulfide is produced, lignin contained in the black liquor is modified and the aliphatic acid content in the black liquor is substantially increased.

It is well known from the teachings of Hagglund et al. in Reissue Patent No. 24,293 and Cisney et al. in Patent No. 2,816,832 that dimethyl sulfide can be produced in substantial quantities from residual black liquor of kraft pulping processes. According to these teachings, however, in order to obtain any appreciable amounts of dimethyl sulfide it is necessary that sulfur in certain forms be added to the black liquor. The sulfur is added by Hagglund et al. in the form of inorganic sulfidic sulfur, i.e. sulfides or bisulfides, while Cisney et al. utilizes elemental sulfur for addition to the black liquor wherein the elemental sulfur forms sulfides in reaction with alkali present in the black liquor.

We have found, however, that if black liquor from kraft pulping not having sulfur in any form added is heated to 220 to 350° C. at a pressure not less than the vapor pressure of the black liquor at the existing temperature and maintained in that temperature range for a period of time varying with the temperature that the yield of dimethyl sulfide obtained is substantially the same or greater than the yields obtained by practicing the methods of Hagglund and Cisney. We have also found that the production of dimethyl sulfide during this heating is accompanied by the demethylation of lignin and the formation of certain low molecular weight aliphatic acids.

During heating of kraft black liquor at temperatures between 220° and 350° C. at a pressure not less than the vapor pressure of the black liquor at the existing temperature, whatever sulfides or bisulfides may be present in the liquor are little affected by the treatment. The sulfur ingredient of the dimethyl sulfide produced is chiefly supplied by other sulfur compounds present in the waste liquor. It has been found, however, that while it is not necessary to have any sulfidic sulfur present it is desirable to do so. Our experiments indicate that considerable quantities of dimethyl sulfide can be produced from kraft black liquor which does not contain any sulfide or bisulfide but in which the sulfidic sulfur has been oxidized for example prior to concentrating to avoid sulfur losses in that operation. In these cases, however, although substantially the same quantities of dimethyl sulfide may be formed as when sulfidic sulfur is present, the formation of dimethyl sulfide proceeds at a very slow rate. When some sulfidic sulfur is present the rate of formation of dimethyl sulfide is greatly increased.

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The quantity of sulfide or bisulfide necessary to increase the rate of formation is very small and kraft black liquor before or after concentrating has been found to contain more than enough sulfidic sulfur for this purpose. The action of the sulfidic sulfur is thought to be merely that of a reaction initiator.

Heating of liquors containing some sulfidic sulfur, although increasing the rate of formation of dimethyl sulfide, does not, as mentioned hereinbefore, greatly affect the yield as most of the sulfur in the dimethyl sulfide comes not from the sulfidic sulfur but from other sulfur compounds, such as thiosulfates, sulfites, sulphates, etc. which are formed during digestion of wood or subsequent handling of the liquor, i.e. during washing, storage, evaporating, etc. For example, a typical partially concentrated kraft black liquor from the pulping of pine wood containing 4.27 g./l. of sulfidic sulfur was heated under the process of this invention. The equivalent of 7.24 g./l. of sulfur was recovered in the dimethyl sulfide while the black liquor still contained 3.08 g./l. of sulfidic sulfur.

During the heating of the black liquor methoxy groups are removed from the lignin. These methoxy groups react with the sulfur compounds within the liquor to form the dimethyl sulfide. Besides being demethylated the lignin also undergoes other changes which are not fully understood but which result in a substantial increase in the concentration of certain low molecular weight aliphatic acids, such as acetic, propionic, glycolic, oxalic, and lactic acids, which acids will be referred to as aliphatic acids throughout the disclosure and claims of this specification, and a considerable reduction in the pH of the liquor. These changes and their significance will be more fully shown after the following description of the complete process of this invention.

The complete process of this invention is shown in the drawing which forms a part of this specification. The single figure of the drawing is a flow diagram of the process.

The process is carried out with black liquor from a kraft cook, say of pine pulp, as the sole starting material. This black liquor may be obtained from the digesters, the washers, the evaporators or any source. For several reasons however, it is best that the liquor be concentrated to a solids content of greater than about 25%. These reasons are to reduce the heat requirements of the reactor, to reduce the size of the reactor, and to increase the rate of formation of dimethyl sulfide. Liquors having a solids content of over 55 to 60% are generally less satisfactory, however, due to the difficulties encountered in handling the liquor. In a typical case a partially concentrated black liquor from the kraft pulping of pine wood from which the tall oil skimmings have been removed may contain 30-35% solids and have a sulfidic sulfur content of 4 to 6 g./l. calculated as the sulfide ion. This material is delivered to a suitable reactor, either of a continuous or batch type, without modification or addition of any chemicals and is there heated to 220° to 350° C. at or above the vapor pressure of the black liquor. The temperature is maintained for a time sufficient to produce substantial quantities of dimethyl sulfide or to effect a desired degree of demethylation of the lignin. The time required is variable dependent on the temperature em-

ployed. To effect substantial production of dimethyl sulfide and demethylation of lignin maintenance of the temperature for approximately 1 minute to several hours will be required with the shorter period of time being applicable to the use of higher temperatures and vice versa. Preferably temperatures between 280 and 320° C. will be used with time of 1 to 50 minutes.

At the end of the desired heating period the pressure is relieved, the liquor being allowed to pass via coolers to a receiver where it should arrive with a temperature near the boiling point of the black liquor at atmospheric pressure. As the pressure is relieved the more volatile components of the liquor particularly the dimethyl sulfide is flashed into vapor.

The part of the liquor which remains liquid is collected and discharged under suitable control to a filter, being acidified enroute to the filter to cause precipitation of the lignin and liberation of the aliphatic acids from their salts. The precipitated lignin is then recovered by filtration. The filtrate from which the lignin has been removed is subjected to a process, such as liquid extraction, for separating the aliphatic acids.

If desired a two stage acidification process may be used resulting in savings in acid. During the first stage the liquor is acidified to a pH of approximately 9.5 which will cause approximately 95% of the lignin to be precipitated. After removing this precipitated lignin by filtration the liquor is further acidified to precipitate the final quantities of lignin and to produce the aliphatic acids from their salts.

The vapors and gases flashed from the liquor are conducted to a cooler where the noncondensable gases, such as carbon dioxide, are removed and the condensable dimethyl sulfide and water vapor condensed. The water and dimethyl sulfide, being practically mutually immiscible, form two layers with the dimethyl sulfide floating on the aqueous condensate. The dimethyl sulfide is separated from the water by decantation to obtain a crude dimethyl sulfide. Pure dimethyl sulfide is then obtained by distillation of the crude dimethyl sulfide.

While effecting as great or greater yield of dimethyl sulfide as the previously known methods of Hagglund and Cisney the present method has several important advantages. The production of dimethyl sulfide is accompanied by very little if any production of methyl mercaptan. This eliminates the need for conversion of the methyl mercaptan to dimethyl sulfide or its removal from the dimethyl sulfide. The addition of sulfur compounds prior to heating, as in Hagglund and Cisney, increases the concentration of sulfur in the liquor thus favoring the reaction of a single atom of sulfur combining with a single methoxy group to form the mercaptan rather than combining with two methoxy groups to form dimethyl sulfide.

A very significant effect of the reaction as carried out according to this invention in relation to the recovery of lignin and aliphatic acids is the lowering of the pH. The pH of the liquid fraction has been found to decrease as much as 2.5 pH units during the heating of the liquor. A higher percentage of the lignin may thus be precipitated with the same addition of acid now used for precipitating lignin from untreated black liquor or the same percentage of lignin may be precipitated with a lesser addition of acid. In either case an economy is realized. Also more aliphatic acids are liberated with the same quantity of acid.

It is apparent that some of the carbohydrate material breaks down during the heating to yield aliphatic acids, since the concentration of these acids is increased by a significant amount, up to 25%.

Besides being demethylated the lignin contained in the liquor undergoes certain changes which result in the production of a novel type of lignin. While these changes are not fully understood the modified lignin produced by the process of this invention possesses characteristics which make it of much greater value than normal lignin.

For example, the moist sodium salt of this modified lignin has been found to be a very effective oxygen-scrubber. In most applications where normal lignin is used this modified lignin may also be used more easily or effectively.

The chemical structure of the lignin produced by this process will vary considerably with the conditions under which the black liquor is treated. The modified lignin from kraft pulped pine will contain 0.1 to 12% by weight of methoxy groups compared to 13 to 15% for normal kraft pine lignin, 0.5 to 2% of sulfur compared to 1.0 to 3.0% for normal kraft pine lignin, and up to 50% more acidic groups than normal kraft pine lignin. Although not definitely established, it appears the lignin of this process has a wide range of molecular weights whereas normal kraft pine lignin has a very uniform molecular size.

Similar results are obtained using black liquor from the kraft pulping of hardwoods. Hardwood lignin, however, contains a much higher initial methoxy content than pine lignin. Thus hardwood lignin which contains approximately 21% methoxy groups when demethylated may contain a higher percentage of methoxy groups than normal pine lignin. For example in subjecting kraft liquors from the pulping of hardwoods to the process of this invention lignin containing up to 18% methoxy groups were produced.

The changes in the chemical structure of the lignin causes great changes in the physical and chemical characteristics of the lignin. For example, compared to normal kraft pine lignin, pine lignin modified by this process has greater solubility in many organic solvents such as ethanol, hexanol, methyl acetate, acetone, epichlorohydrine, dioxane, triethylphosphate, dimethyl sulphone, and mixtures such as 1:1 methanol-benzene, increased reactivity with organic and inorganic compounds such as formaldehyde and oxygen, a more spherical particle shape, and a much greater ether extractability, up to 30% while normal lignin has no ether extractability.

The lignins from this process are greatly superior to lignins modified by the methods of Hagglund and Cisney which contain high percentages of sulfur, up to 15%, and have little if any solubility in most organic solvents.

The modified lignins produced by the process of this invention will form salts. All substances which will form salts with normal lignin will also form a salt with the modified lignin by the same processes. For instance, by precipitating the modified lignin from the black liquor at high pH, about 9.0 to 10.0, the sodium salt is obtained. Other modified lignin salts can be obtained by the same method generally used in producing normal lignin salts, i.e. by reacting lignin in solution at a proper pH with the appropriate positive ion and precipitating the lignin salt formed at a pH above that at which the salt will be decomposed.

From the many runs which have been made the following are chosen as typical.

Example 1

Concentrated black liquor from a kraft cook of pine wood containing 35.35% solids after skimming off of the tall oil soaps was heated to (1) 220° C. and held at that temperature for (2) 36 minutes under a pressure of (3) 800 p.s.i. This heating lowered the pH of the liquor from 11.90 to (4) 11.15. This liquor was flashed to remove gases and vapors and the pH of the liquid fraction was reduced to 9.5 by the addition of (5) 85 ml. of 31° Bé. sulfuric acid for precipitating the major portion of the lignin. The liquor was filtered and acidified again to precipitate the remaining lignin and to liberate the aliphatic acids from their salts. The liquor was again filtered to remove the lignin precipitated and the aliphatic acids were extracted. The total yields of dry lignin and pure dimethyl sulfide expressed as percentages of black liquor solids were, respectively, (6) 34.5 and (8) 0.22. The percentage reduction of the methoxy groups on the lignin was (9) 12%. The aliphatic acid yield expressed in

grams per liter of the liquor heated was (7) 24.8. The procedure conformed generally to the flow diagram and to the description in connection therewith.

The details of Example 1 are tabulated below together with corresponding details of Examples 2 to 8. In Examples 2 through 8 the starting material and procedure were the same as for Example 1 with the exception of the indicated variations.

Example	(1) Temp., ° C.	(2) Time, Min.	(3) Pressure, p.s.i.	(4) Dep. pH	(5) Acid demand per liter to pH 9.5 ml. 31% Bé. H ₂ SO ₄	(6) Lignin Yield, Percent BLS	(7) Aliphatic acid Yield	(8) DMS Yield, Percent BLS	(9) Percent Red. OCH ₃
1	220	36	800	11.15	85	34.5	24.8	0.22	12
2	220	109	700	10.45	55	30.6	25.1	1.01	40
3	250	14	800	10.75	65	33.9	24.2	1.38	33
4	250	30.5	900	10.15	65	31.3	25.8	2.03	49
5	250	73	900	10.7	55	29.1	25.8	2.21	80
6	270	15	950	10.2	65	30.8	25.9	2.63	68
7	270	30	950	9.9	20	28.4	22.6	2.81	72
8	300	17	1,350	9.7	30	28.4	22.6	3.08	94
Control	None	None	None	11.9	85	34.9	20.9	0.0	0

While certain preferred embodiments of the invention have been illustrated and described in detail, it is to be understood that changes may be made therein and the invention practiced in other forms. It is not therefore, the intention to limit the patent to the specific details illustratively described but to cover the invention broadly in whatever form its principles may be utilized.

We claim:

1. The method of treating residual black liquor of the kraft pulping process having a small initial ratio of sulfidic sulfur to total solids inherently present and a considerably larger initial ratio of chemically combined, non-sulfidic sulfur to total solids inherently present, which comprises heating such black liquor, concentrated to a solids content of 25 to 60%, to, and maintaining it in, the range of 220° to 350° C. under a pressure which is at all times at least as great as the vapor pressure of the black liquor at the existing temperature of the black liquor, thereby producing a quantity of dimethyl sulfide whose sulfur content is derived chiefly from the initially non-sulfidic sulfur of the black liquor, and separating and recovering from the back liquor the dimethyl sulfide so produced.

2. The method of claim 1 in which a substantial portion of the sulfidic sulfur is oxidized prior to the concentration of the black liquor.

3. The method of treating residual black liquor of the kraft pulping process having a small initial ratio of sulfidic sulfur to total solids inherently present and a considerably larger initial ratio of chemically combined, non-sulfidic sulfur to total solids inherently present, which comprises heating such black liquor, concentrated to a solids content of 25 to 60%, to, and maintaining it in, the range of 220° to 350° C. under a pressure which is at all times at least as great as the vapor pressure of the black liquor at the existing temperature of the black liquor, thereby producing a quantity of dimethyl sulfide whose sulfur content is derived chiefly from the initially non-sulfidic sulfur of the black liquor, an increased yield of low molecular weight aliphatic acids, and a modified lignin product, and recovering from the black liquor a desired product so produced.

4. The method of treating residual black liquor of the kraft pulping process having a small initial ratio of sulfidic sulfur to total solids inherently present and a considerably larger initial ratio of chemically combined, non-sulfidic sulfur to total solids inherently present, which comprises heating the black liquor, concentrated to a solids content of 25 to 60%, to 220° to 350° C. and maintaining it in that temperature range for a period of

the order of one-quarter hour to two hours while maintaining it under a pressure which is at all times at least as great as the vapor pressure of the black liquor at the existing temperature of the black liquor, thereby producing a quantity of dimethyl sulfide whose sulfur content is derived chiefly from the initially non-sulfidic sulfur and exceeds the total initial sulfidic sulfur content of the black liquor, an increased yield of low molecular weight ali-

phatic acids, and a modified lignin product, and recovering from the black liquor a desired product so produced.

5. The method of treating residual black liquor of the kraft pulping process having a small initial ratio of sulfidic sulfur to total solids inherently present and a considerably larger initial ratio of chemically combined, non-sulfidic sulfur to total solids inherently present, to produce and recover dimethyl sulfide, a modified lignin, and an increased yield of aliphatic acids, which method comprises heating the black liquor, concentrated through evaporation to a solids content of 25 to 60%, to the range of 220° to 350° C. and maintaining it in said range for a period of the order of one-quarter hour to two hours, while maintaining it under pressure which is at all times at least as great as the vapor pressure of the black liquor at the existing temperature of the black liquor, thereby producing dimethyl sulfide whose sulfur content is derived chiefly from the initially non-sulfidic sulfur and exceeds the initial sulfidic sulfur content of the black liquor, reducing the pressure on the heated black liquor to a pressure not substantially above atmospheric pressure to cause flashing of vapors from the black liquor at a temperature not substantially above the atmospheric boiling point of the black liquor, separating the flashed vapors from the liquid fraction, acidifying the liquid fraction to cause the precipitation of the lignin and conversion of aliphatic acid salts into aliphatic acids, filtering out the lignin and extracting the aliphatic acids from the filtrate, condensing the water and dimethyl sulfide vapors flashed from the liquid fraction, and separating the condensed dimethyl sulfide from the condensed water.

6. A modified lignin product, obtained from black liquor from the kraft process of pulping wood having a small initial ratio of sulfidic sulfur to total solids inherently present and a considerably larger initial ratio of chemically combined non-sulfidic sulfur to total solids inherently present, by heating such black liquor, concentrated to a solids content of 25 to 60%, to, and maintaining it in, the range of 220° to 350° C. under a pressure which is at all times at least as great as the vapor pressure of the black liquor at the existing temperature of the black liquor, and separating the modified lignin product from the black liquor by acidifying the liquor to precipitate the modified lignin product therefrom, said modified product being characterized by having a sulfur content between 0.5 and 2.0% by weight and having, when compared to the kraft lignin from which the modified lignin was prepared, a substantially reduced methoxy content, greater acidic group content, greater ether extractable content, increased reactivity toward oxygen and formaldehyde, and substantially increased solubility in

each of acetone, hexanol, and 1:1 mixture of methanol-benzene.

7. A modified lignin product as set forth in claim 6, wherein the black liquor is from the kraft process of pulping hardwood.

8. A modified lignin product as set forth in claim 6, wherein the black liquor is from the kraft process of pulping pine wood, and wherein the methoxy content is reduced from 12 to 94% as compared with the unmodified product.

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