Feb. 2, 1971 H. W. NELSON ET AL 3,560,329

PROCESS FOR LOW SULFIDE CHEMICAL RECOVERY

Filed Dec. 27, 1968 2 Sheets-Sheet 1

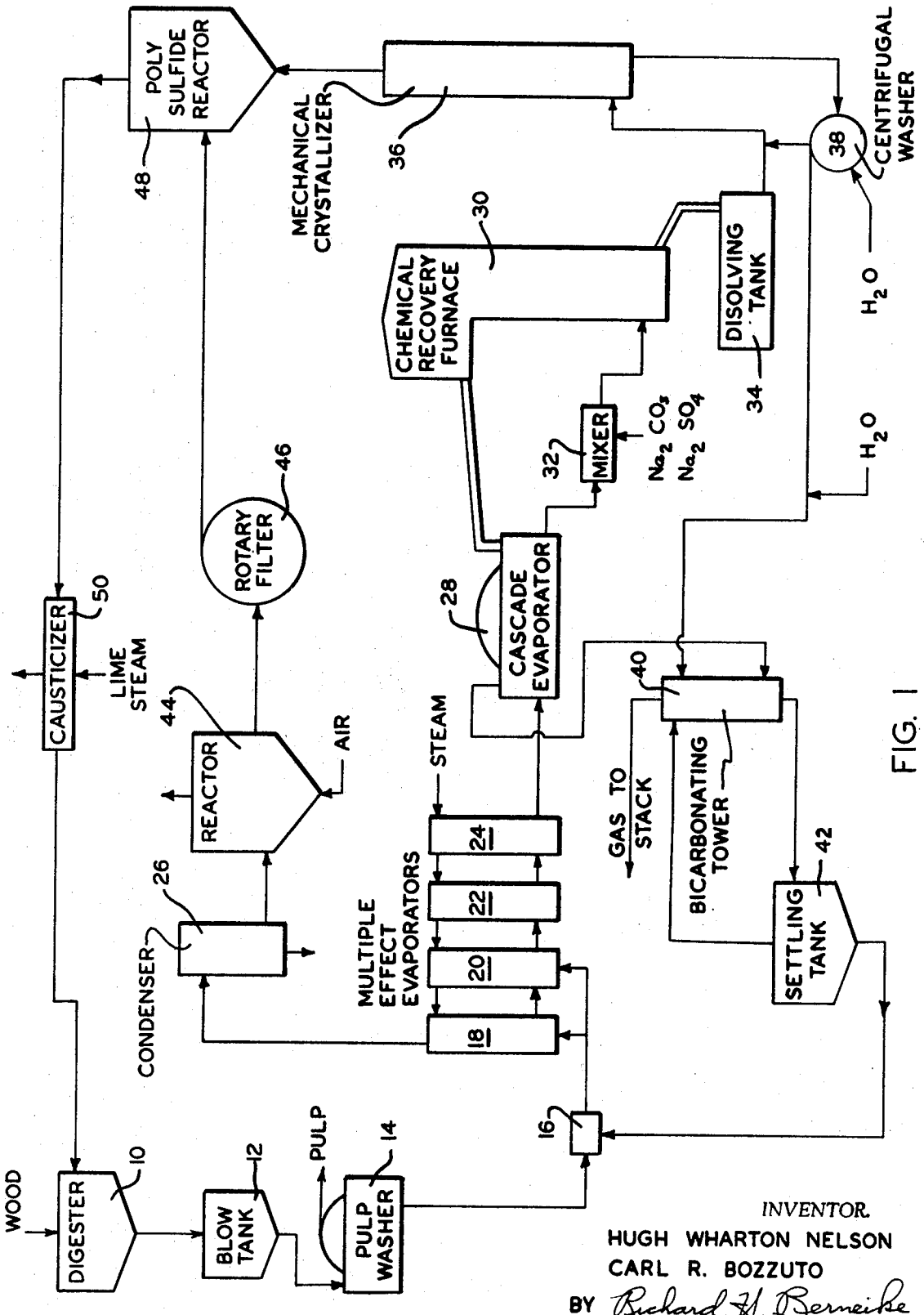


FIG. 1

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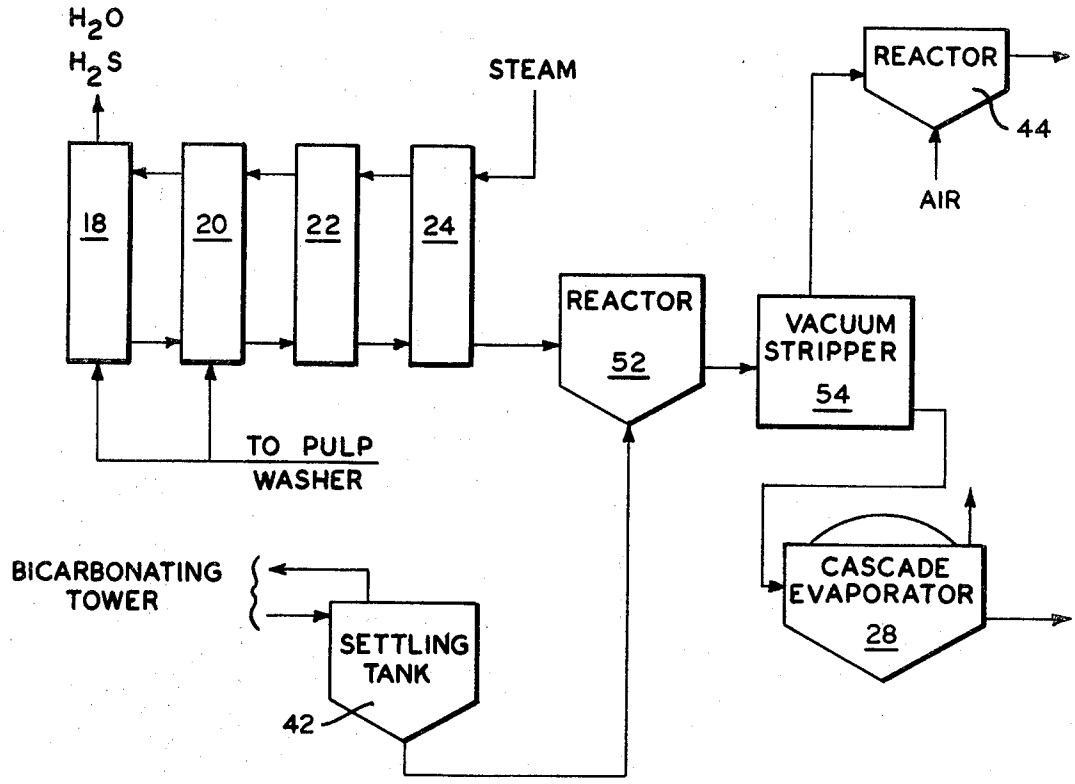


FIG. 2

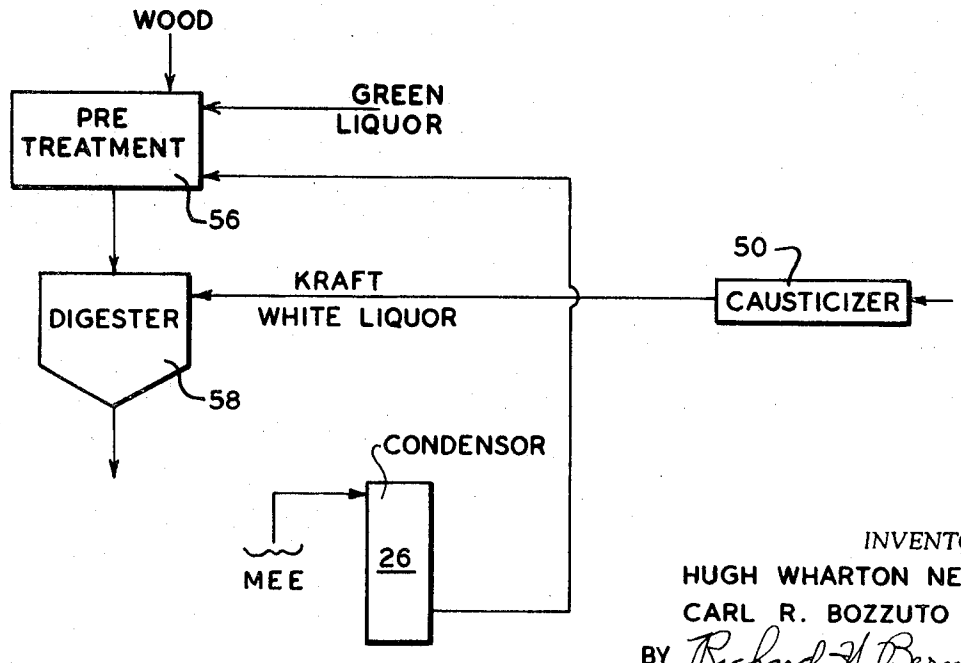


FIG. 3

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PROCESS FOR LOW SULFIDE CHEMICAL RECOVERY

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Int. Cl. D21c 11/12
U.S. Cl. 162—30 7 Claims

ABSTRACT OF THE DISCLOSURE

A paper pulping and chemical recovery process is described which is particularly adapted to pulping with high sulfidity liquors such as those used in the polysulfide process. The sulfidity of the black liquor is reduced by reaction with sodium bicarbonate slurry to release hydrogen sulfide for reuse either directly or indirectly in the pulping process. The resulting low sulfidity black liquor is then burned in the normal manner to provide green liquor. Sodium carbonate is crystallized from the green liquor and used to produce the sodium bicarbonate which is reacted with the black liquor. The remaining green liquor is treated in the conventional manner to provide fresh cooking liquor.

BACKGROUND OF THE INVENTION

In the manufacture of paper pulp by the sulfide or kraft process, it is an economic necessity to recover chemicals from the spent cooking or black liquor for reuse in the pulping process. Recovery systems for this purpose which involve the burning of the liquor in chemical recovery furnaces have been in use for many years. However, the burning of black liquor in chemical recovery furnaces creates several problems such as external corrosion of the furnace walls (particularly in modern higher temperature furnaces), sulfur loss and the resulting air pollution, and the danger of smelt-water explosions. The sulfur content of the black liquor and the smelt is at the root of these problems. The higher the sulfur content in the kraft process, the worse the problems become.

Many variations of the kraft process developed over the past few years to increase the pulping yield have also increased the problems of chemical recovery. Two examples are the polysulfide pulping process and an even newer process wherein the wood is pretreated with hydrogen sulfide in an alkaline solution. Both of these processes have very high sulfur content in the cooking liquor and the resulting spent liquor. This high sulfur content increases all of the furnace problems previously mentioned to the point where they are incompatible with the present day kraft recovery systems. Furthermore, these new developments require chemical recovery processes which include provisions for the regeneration of substantial amounts of hydrogen sulfide or elemental sulfur for reuse directly or indirectly in the pulping process.

SUMMARY OF THE INVENTION

The present invention is directed to a paper making system and process and more particularly to the processing

of the spent cooking or black liquor to remove sulfur therefrom prior to combustion in a chemical recovery furnace. This reduces the sulfidity of the black liquor and smelt in the furnace thus reducing the potential for corrosion, sulfur loss, air pollution and explosions. It also provides sulfur in whatever form is desired for use in producing fresh cooking liquors. This sulfur removal is accomplished by reacting the sodium sulfide in the black liquor with sodium bicarbonate to release hydrogen sulfide which can be processed as desired depending upon the particular pulping process being used. The sodium bicarbonate is obtained by extracting a portion of the sodium carbonate from the recovery furnace smelt and reacting it with carbon dioxide from the flue gases. The objects and advantages of the invention will be more fully understood from the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic flow diagram illustrating one embodiment of the invention;

FIG. 2 is a schematic flow diagram illustrating a modified portion of the system of FIG. 1;

FIG. 3 is a schematic flow diagram illustrating a modification of another portion of the system of FIG. 1.

DETAILED DESCRIPTION

The present invention is particularly adapted for use with the polysulfide paper pulping process and FIG. 1 illustrates the invention as applied to such a process. However, the invention is also applicable to other pulping processes, particularly those producing a high sulfidity black liquor, as will be discussed hereinafter. In the following description of a specific embodiment, some actual typical compositions and flow rates are given, and they are based upon the production of 100 air-dried tons of pulp per unit of time at 64 percent yield.

The wood which has been prepared for pulping is fed to the digester **10** along with the cooking liquor which is commonly referred to as white liquor. Typical flow rates and compositions into the polysulfide digester are as follows:

	Pounds
Wood	282,000
Water	282,000
White liquor:	
NaOH	58,000
Na_2S	26,000
Na_2SO_4	2,600
Na_2CO_3	13,600
$Na_2S_2O_3$	600
S	14,200
H_2O	729,000

After the normal polysulfide digestion process has been carried out, the pulp-liquor mixture is transferred to a blow tank **12** in which gases are vented. The pulp-liquor mixture from the blow tank **12** is then transferred to a pulp washing system **14** in which the weak black liquor is washed from the pulp. Coming from the pulp washing system **14** will be about 180,000 pounds of oven-dried

pulp which is equivalent to 100 tons of air-dried pulp. Typical composition and flow rates for the weak black liquor coming from the pulp washing system are as follows:

	Pounds
Na_2S	19,300
NaHS	3,900
Na_2SO_4	2,500
Na_2CO_3	13,000
S	13,500
Lignin	81,000
Na	32,000
H_2O	935,000

The next step in the chemical recovery process is to add an aqueous sodium bicarbonate slurry to the weak black liquor at mixing point **16**. The source of this sodium bicarbonate will be described hereinafter but typical specific compositions and flow rates are as follows:

	Pounds
$NaHCO_3$	89,300
Na_2CO_3	8,000
H_2O	146,000

The mixture of the weak black liquor and sodium bicarbonate is fed from the mixing point **16** to the multiple effect evaporators **18, 20, 22** and **24**. A small proportion of antifoam compound, such as Dow Corning Antifoam Agents A and Q, may be necessary to prevent foam over. These multiple effect evaporators serve two primary purposes in the process. First, they serve to evaporate water from the weak black liquor so as to concentrate the liquor in preparation for burning in the chemical recovery furnace. Secondly, the following reaction of the sodium bicarbonate with the sodium sulfide is carried out in the multiple effect evaporators:

$$2NaHCO_3+Na_2S \rightarrow H_2S+2Na_2CO_3$$

This reaction is substantially instantaneous and can readily be carried out in the evaporators. The vapor coming from evaporator **18** has the following typical composition and flow rates:

	Pounds
H_2O	884,000
H_2S	15,500
CO_2	2,900
Noncondensable gas	1,000

This vapor mixture is passed to a condenser **26** in which substantially all of the water is removed. The remaining gas containing primarily hydrogen sulfide will be utilized as described hereinafter.

The liquid stream coming from evaporator **24** contains about 55 percent solids and has the following typical composition:

	Pounds
Na_2S	6,100
Na_2SO_4	2,500
Na_2CO_3	116,000
$NaHCO_3$	13,400
Lignin, etc.	102,000
H_2O	197,000

It has a greatly decreased sodium sulfide and mercaptan content due to prior reaction with sodium bicarbonate so that preoxidation of the black liquor is not necessary to prevent sulfur loss during later evaporation. This liquid stream is passed to a direct contact evaporator such as a cascade evaporator **28** in which the black liquor is directly contacted with the flue gases from the recovery furnace **30**. The black liquor coming from the cascade evaporator **28** has a solids content of about 68 percent.

This strong black liquor is passed to a mixer **32** at which point additional make-up sodium carbonate and sodium sulfate are added as needed to replace sodium and sulfur losses from the system. The strong black liquor is then passed from the mixer **32** to the chemical recovery furnace **30** in which the combustibles in the black liquor are burned and in which the sodium sulfate and organic sulfur are reduced to sodium sulfide.

The smelt formed in the chemical recovery furnace is drained therefrom into a dissolving tank **34** in which the smelt is dissolved in water. A typical composition and flow rate for the solution coming from the dissolving tank, which is commonly referred to as green liquor, is as follows:

	Pounds
Na_2S	26,500
Na_2SO_4	2,800
Na_2CO_3	156,000
H_2O	552,000

The solution from the dissolving tank **34** is passed to a crystalizer **36** in which part of the sodium carbonate is crystalized from the green liquor. This crystalizing operation can best be carried out in this particular instance by cooling the green liquor rather than by heating to evaporate water. The use of cooling crystalization will conserve steam that would otherwise be required for the evaporation of excess water such as in a continuous low temperature vacuum crystalizer. Also, large decahydrate crystals, $Na_2CO_3.10H_2O$, will be formed rather than the small monohydrate crystals, $Na_2CO_3.H_2O$. By forming these large crystals, less green liquor will be carried from the crystalizer with the crystals and the crystals will be easier to wash. This crystalization can be accomplished, for example, by cooling a 25 percent green liquor solution to 73° F. which will effect the selective crystalization. The remaining green liquor solution is withdrawn from the crystalizer and processed as will be described hereinafter to produce fresh cooking liquor.

The sodium carbonate crystals withdrawn from the crystalizer, about 65,160 pounds on the previously identified basis, are then passed to a conventional centrifugal washer **38** in which the crystals are washed to remove the remaining green liquor solution. The wash water separated from the crystals is returned to the crystalizer as shown in FIG. 1. The solids coming from the centrifugal washer will contain about 64,200 pounds of sodium carbonate together with about 109,000 pounds of water. To this is added 96,000 additional pounds of water prior to introduction of the sodium carbonate into the top of the bicarbonating tower **40**. These bicarbonating towers are conventional pieces of apparatus used for carbonating and bicarbonating operations. In general they are liquid-gas absorption towers which are specially constructed so as to permit the downward gravitational travel of the growing sodium bicarbonate crystals. This may be done, for instance, by having trays within the tower which simulate a single, very large bubble cap with downward sloping floors. Also introduced into the top of the bicarbonating tower is a recycled water stream containing about 80,200 pounds of water and perhaps about 2,000 pounds of sodium carbonate. This means that there is about 19 percent sodium carbonate in the water at the top of the tower and that substantially all of the sodium carbonate will be in solution at this point. Introduced into the bottom of the bicarbonating tower **40** is the flue gas stream from the cascade evaporator **28** which contains large amounts of carbon dioxide. This gas is passed up through the sodium carbonate solution and the following reaction takes place:

$$Na_2CO_3+CO_2+H_2O \rightarrow 2NaHCO_3$$

As the less soluble sodium bicarbonate is formed in the

bicarbonating tower, it is crystalized out of solution. The resulting slurry is passed from the bicarbonating tower to a settling tank **42** in which significant amounts of water are removed from the sodium bicarbonate slurry. The removed water containing a small amount of unreacted sodium carbonate is recycled to the bicarbonating tower. The sodium bicarbonate slurry from the settling tank **42** is then passed to mixing point **16** for mixing with the weak black liquor.

In the FIG. 1 embodiment of the invention relating to polysulfide pulping, the gas stream from the condensor **26**, which contains primarily hydrogen sulfide, is passed to a reactor **44** in which the hydrogen sulfide is converted to elemental sulfur. This conversion may be accomplished by any one of the many processes available. One such process is the Claus reaction which is a gas phase, catalytic reaction which takes place at relatively high temperatures. The oxygen in this reaction converts the hydrogen sulfide to sulfur and water. Another process for converting the hydrogen sulfide to sulfur is by the use of organic chelated iron compounds which serve as catalysts in the reaction. This is a liquid phase reaction which takes place at room or slightly elevated temperatures. By passing air or oxygen along with the hydrogen sulfide bearing stream through the liquid in the reactor, the catalytic compounds are continuously converted back to their original active oxidizing state. One such catalyst is commercially sold under the trademark "Cataban" by Rhodia, Inc.

In the case of the liquid phase production of elemental sulfur from the hydrogen sulfide, the sulfur which is removed from the reactor **44** is passed to a rotary filter **46** in which the liquid is removed from the sulfur. The liquid from the filter **46** is recycled to the reactor **44** while the solid sulfur is washed free of residual liquid catalyst and passed to a polysulfide reactor **48**. Also introduced into the polysulfide reactor **48** is the sulfide rich green liquor coming from the crystalizer **36**. In the polysulfide reactor **48**, the sulfur is reacted with the sodium sulfide in the green liquor to produce polysulfides by the following reaction:

$$Na_2S+nS\rightarrow Na_2S_n+1$$

wherein n is normally from 2 to 4. The amount of polysulfide produced in this conventional reaction will depend upon the various proportions of sulfur to green liquor and the various operating conditions. The polysulfide green liquor coming from the polysulfide reactor **48** is passed to the causticizer **50** as is conventionally done with kraft green liquor. In the causticizer, the following reaction takes place:

$$Na_2CO_3+Ca(OH)_2\rightarrow CaCO_3+2NaOH$$

The calcium carbonate coming from the causticizer is calcined in the conventional manner to produce calcium oxide which is then slaked for reuse in the causticizer. The white liquor from the causticizer **50** is reintroduced into the digester **10** to complete the cycle.

In might happen that the additional sodium carbonate created in the multiple effect evaporators by the reaction of the sodium bicarbonate with the sodium sulfide would accelerate fouling of the heat transfer surfaces. If this should present an operating problem, the alternate system illustrated in FIG. 2 could be utilized. In this system the weak black liquor without any additional sodium bicarbonate is passed to the multiple effect evaporators. In this instance, the vapors coming from the evaporators will contain hydrogen sulfide, which must be recovered, along with considerable water. The concentrated black liquor coming from the multiple effect evaporators is then passed to a reactor **52** together with the sodium bicarbonate from the settling tank **42**. Thus the reaction of the sodium bicarbonate with the sodium sulfide takes place in the reactor **52** rather than in the multiple effect evaporators. The black liquor from the reactor **52** containing the hydrogen sulfide reaction products is passed to the vacuum stripper **54** in which the hydrogen sulfide is stripped from the black liquor and passed to the reactor **44**. In practice the operations in **52** and **54** might be combined in a single vessel since the desulfurizing reaction is ionic and rapid. This modified arrangement for reacting the sodium bicarbonate with the sulfide may exhibit several additional advantage over the scheme illustrated in FIG. 1, such as (1) a higher desulfurizing efficiency due to the more concentrated black liquor, (2) less foaming troubles with the more concentrated black liquor, and (3) the hydrogen sulfide from the vacuum stripper would contain less water than when the stripping is done in the multiple effect evaporators.

The system illustrated in FIG. 3 is an alternate to the polysulfide pulping arrangement of FIG. 1. In this FIG. 3 arrangement, the hydrogen sulfide gas either from the multiple effect evaporators or from the vacuum stripper **54** or from both is passed to a pretreating vessel **56** together with a quantity of green liquor and the wood to be pulped. Such a pretreating process is described on pages 27 and 28 of the Oct. 21, 1968, issue of Pulp and Paper. The pretreated wood from the vessel **56** is then passed to a conventional kraft digester **58** which corresponds to the digester **10** of FIG. 1. Such pretreatment of the wood increases the yield of pulp by around 6 percent.

It can be seen from the above description of the invention including the several modifications that the problems associated with high sulfidity in the chemical recovery furnace are avoided by routing a portion of the sulfur around the chemical recovery furnace. It also can be seen that the system lends itself to a variety of pulp digesting techniques of which the above are merely illustrative.

While these preferred embodiments of the invention have been shown and described, it will be understood that they are merely illustrative and that changes may be made without departing from the scope of the invention as claimed.

We claim:

1. A method of processing and recovering chemicals from sodium-sulfide containing black liquor of a pulping process comprising the steps of:

(a) reacting said sodium sulfide in said black liquor with sodium bicarbonate in an amount sufficient to produce sodium carbonate and hydrogen sulfide;

(b) separating said hydrogen sulfide from said black liquor;

(c) removing water from said black liquor to produce a more concentrated strong black liquor;

(d) combusting said strong black liquor in a chemical recovery furnace to produce flue gases containing carbon dioxide and smelt containing sodium carbonate and sodium sulfide;

(e) dissolving said smelt to produce green liquor;

(f) separating at least a portion of said sodium carbonate from said green liquor;

(g) reacting said removed sodium carbonate with carbon dioxide and water to produce sodium bicarbonate for reaction with said black liquor in step (a); and

(h) causticizing at least a portion of said green liquor to produce fresh cooking liquor for said pulping process.

2. A method as recited in claim **1** wherein said step (f) of separating sodium carbonate from said green liquor comprises crystalizing said sodium carbonate from said green liquor solution.

3. A method as recited in claim **1** wherein said carbon dioxide reacted with said sodium carbonate in step (g) comprises said carbon dioxide in said flue gases.

4. A method as recited in claim **1** wherein said step (c) of removing water from said black liquor includes contacting said flue gases from said chemical recovery furnace with said black liquor.

5. A method as recited in claim 4 and further including the step of conducting said flue gases after contact with said black liquor into contact with said removed sodium carbonate in step (g) whereby said carbon dioxide in said flue gases reacts with said sodium carbonate.

6. A method as recited in claim 1 and further including the step of converting said hydrogen sulfide separated from said black liquor in step (b) into elemental sulfur, reacting said elemental sulfur with said green liquor to produce a polysulfide green liquor and causticizing according to step (h), said polysulfide green liquor to convert sodium carbonate therein to sodium hydroxide to form polysulfide white liquor.

7. A method as recited in claim 1 including the step of combining said green liquor and said hydrogen sulfide separated from said black liquor in step (b) for pretreatment of wood in said pulping process.

References Cited

UNITED STATES PATENTS

2,824,071	2/1958	Gray et al.	163—36
3,331,733	7/1967	Venemark	162—30
3,347,739	10/1967	Tomlinson	162—30
3,366,535	1/1968	Cann	162—30

FOREIGN PATENTS

87,098	8/1936	Sweden	162—36

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