ABSTRACT

Presented is a process wherein spent pulping liquors used in the Alkaline Sulfite Process for pulping wood and having a pH of about 9 to 12 are coked in the liquid phase in a coking zone at about 450°F to 750°F and autogenous pressure of 100 to 3000 psig for 0.5 minute to 6 hours. The gases, liquid effluent and coke which form are separated. The coke is washed for removal of salts and dried with flue gas. Next, the dried coke and the gas are burned to produce steam, supply heat for coking and to generate SO₂ in the flue gas. Some of the effluent is flashed in a flashing zone to produce water for washing the coke followed by heat exchange of the bottoms from the flashing zone with the spent liquors to preheat the same. Other portions of the effluent are recombined and reconstituted for use as pulping liquor.

No pH reduction is necessary prior to coking and the COD of the effluent is normally about 75 percent less than that of the starting liquors.

2 Claims, 2 Drawing Figures
FIG. 2

ALKALINE SULFITE LIQUOR

% COD REMOVAL

0 10 20 30 40 50 60 70 80 90 100 110 120

MINUTES OF AUTOCLAVE

2 HRS.

600°F 1700psi

550°F 1100psi
3,884,751

COOKING OF SPENT PULPING LIQUORS USED IN THE ALKALINE SULFITE PROCESS

BACKGROUND OF THE INVENTION

This invention relates to the treatment of spent liquors used in the Alkaline Sulfite Process for pulping wood.

The above-mentioned process is described in Canadian Pat. No. 847,218, issued July 21, 1970 to Canadian International Paper Company. In this process the "hot pH" of the cook is maintained at around 9-12 during the cooking by adding alkali thereto. Conventional sulfite pulping is carried out well on the acid side or, more recently, under slightly alkaline conditions of up to pH 9.

A competitive process, the Kraft pulping process, operates in the same alkaline pH range of 9-12 as does the alkali sulfite pulping process. Alkaline sulfite pulping combines the advantages of Kraft and conventional sulfite pulping while minimizing the disadvantages associated with each. The brighter pulp and minimal atmospheric emission of malodorous sulfur compounds associated with sulfite pulping are combined with the higher strength associated with Kraft pulp. Disadvantageously, however, no commercial process exists for disposal of or chemical recovery from the spent pulping liquors of the alkali sulfite process in contrast to the extensive spent Kraft liquor processing technology. The present process provides such a means of handling spent alkaline sulfite pulping liquors.

BRIEF SUMMARY OF THE INVENTION

Spent pulping liquors used in the Alkaline Sulfite Process for pulping wood and having a pH of about 9 to 12 are coked in the liquid phase in a coking zone at about 450°F to 750°F and autogenous pressures of 100 to 3000 psig for 0.5 minute to 6 hours. The gases, liquid effluent and coke formed are separated. The coke is washed for metal ion and partial sulfur removal and dried with flue gas. Next, the dried coke and the gas are burned to produce steam, supply heat for coking and to generate SO₂ in the flue gas. Some of the effluent is flashed in a flashing zone to produce water for washing the coke followed by heat exchange of the bottoms from the flashing zone with the spent liquors to preheat the same. The portions of the effluent are recombined and reconstituted to supply pulping liquor to the pulp operating.

No pH reduction is necessary prior to coking and the COD of the effluent is normally about 75 percent less than that of the starting liquors.

BRIEF DESCRIPTION OF THE DRAWINGS

The process of this invention will be better understood by reference to the accompanying drawings in which:

FIG. 1 illustrates diagrammatically a preferred embodiment of the present invention; and

FIG. 2 illustrates a curve showing COD removal versus time when coking alkaline sulfite liquor.

DESCRIPTION OF PREFERRED EMBODIMENT

In the physical embodiment of the invention diagrammed in the drawing, spent alkaline sulfite liquor is raised to coking pressure of 1000-1100 psig by pump 10 and preheated through exchanger 11, flowing to fired heater 12 where its temperature is raised to the coking temperature of 550°F. The heated liquor then flows through line 14 to the coker hold drum 15, which provides the necessary residence time for completion of the coking reactions as well as some settling of the coke particles to produce a clear effluent which leaves the hold drum through line 16. Upon pressure reduction through valve 17, a portion of the effluent is vaporized and separated from the vaporized liquid in flash drum 18. The unevaporated liquid flows from flash drum 18 through line 19 and cooled by heat exchange with incoming feed in exchanger 11. From exchanger 11, the liquid phase effluent passes through line 20 to point 21 where it is combined with other liquid streams from the process.

That portion of the clear coker effluent which was vaporized in flash drum 18 passes to surface condenser 22. Fixed gases are taken overhead through line 23 and reduced to substantially atmospheric pressure by control valve 24. At point 25 they are combined with de-pressurized gas produced by the coking reactions taking place in hold drum 15. The combined gas stream is then brought to the fired heater 12 through line 26 where sulfur-containing compounds as well as other combustible gases are incinerated.

Condensate from surface condenser 22 is conveyed by line 27 to coke washer 28 where sodium ions and other pulping chemicals retained on the coke are recovered by washing. From coke washer 28, the condensate stream, now containing chemicals recovered from the coke, passes through line 29 and is combined at point 21 with the liquid phase material from which it was separated in flash drum 18.

A settled coke slurry is removed from the bottom of hold drum 15 through line 30 and dewatered in dewatering device 31. Device 31 may be a liquid cyclone or other suitable device for solid-liquid separation. Overflow passes to coke washer 28. Here, as described previously, condensate from line 27 washes occluded sodium and other pulping chemicals from the coke.

Washed coke settles to the bottom of 28 and is again dewatered in dewatering means 34, a liquid cyclone or other device similar to 31. Overflow from 34 joins the main washings stream through line 35 at point 36. Dewatered coke is carried by line 37 to coke dryer 38 where hot flue gas from fired heater 12 through line 48 evaporates residual water from the coke to produce a dry granular solid. The dried coke is removed from the bottom of dryer 38 and conveyed by line 49 to fired heater 12 where it is burned to provide process heat for the coking operation as well as to raise steam for general plant use.

Flue gas exits from dryer 38 through line 39 and passes to SO₂ recovery absorber 40. Here sulfur dioxide generated by the combustion of sulfur-containing coke from line 49 and the sulfur compounds contained in the combined gas stream in line 26 are absorbed in the combined liquid effluent from coking, which is charged to absorber 40 through line 41. Pollutant-free flue gas exits from absorber 40 through line 42 and is vented to the atmosphere. The liquid effluent passes from absorber 40 to causticizer 44 through line 43. In causticizer 44 lime is added to convert sodium carbonate, produced by reaction with CO₂ from the coking reaction, to sodium hydroxide required for the high pH sulfite pulping liquor. Removal of lime mud in clarifier 45 and in filter 46 results in a reconstituted pulping liquor which is recycled to the digesters through line 47. Clar-
ifier 45 and filter 46 are employed to remove solids generated by causticization. As mentioned above, CO₂ produced by coking as well as that picked up during flue gas contacting for SO₂ recovery, converts NaOH present in the spent liquor to Na₂CO₃ and/or NaHCO₃. Addition of lime then converts these carbonates to hydroxide with the formation of CaCO₃. The latter is insoluble and must be removed prior to using the reconstituted pulping liquor.

In an example of the successful practice of the invention, spent Alkaline Sulfite Process liquor was coked at 550°F under 1100 psig for 2 hours with the results tabulated below.

**TABLE 1**

<table>
<thead>
<tr>
<th></th>
<th>Wt % Yield</th>
<th>Wt % Dissolved Solids</th>
<th>COD</th>
<th>Wt % Ash</th>
<th>Wt % C</th>
<th>Wt % Sulfur</th>
<th>Wt % Na</th>
<th>Wt % Ca</th>
<th>Wt % N</th>
<th>Wt % H₂</th>
<th>pH</th>
<th>Gross Heat of Combustion BTU/lb</th>
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<tr>
<td>Spent Liquor</td>
<td>20.3</td>
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<td>156.5</td>
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<td>(74.8% H₂O)</td>
<td>2.14</td>
<td>28.18</td>
<td>59.8</td>
<td>4.1</td>
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**TABLE 2**

<table>
<thead>
<tr>
<th></th>
<th>Wt % Yield</th>
<th>Wt % Dissolved Solids</th>
<th>COD</th>
<th>Wt % Ash</th>
<th>Wt % C</th>
<th>Wt % Sulfur</th>
<th>Wt % Na</th>
<th>Wt % Ca</th>
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<td>156.5</td>
<td>9.46</td>
<td>5.6</td>
<td>1.59</td>
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<td>0.05</td>
<td>0.007</td>
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<td>Coker</td>
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<tr>
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<td>Gas</td>
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<td></td>
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</tbody>
</table>

The gas produced is high in carbon dioxide, produced no doubt from decarboxylation of wood sugars and the like. The washed dry coke produced normally has a gross heating value of around 12,200 BTU/lb and usually contains about 3.7 percent sulfur. This coke is burned in a heater to produce high pressure process steam and also to supply heat for the liquid phase coking. Sulfur dioxide is contained in the flue gases from the heater and absorbed in the coker effluent to make sodium sulfite (a pulping chemical). The fortified effluent with such added chemical fortification as required is recycled to the wood pulp digester.

It is also seen from the table that the bulk of the sodium is retained in the effluent from the coker. The pH of the coker effluent has been reduced from 11.9 to 9.4. This no doubt comes about from the reaction of CO₂ (in the produced gas) with sodium hydroxide. When SO₂ (from the flue gas) is absorbed in the effluent from the coker it reacts preferentially with NaOH rather than Na₂CO₃. Thus the effluent from the coker, either before or after absorption of SO₂ should be causticized, preferably with lime, to bring the final fortified coker effluent up to a pH suitable for alkaline sulfite wood pulping.

The graph of FIG. 2 has a curve showing COD removal against time when coking alkaline sulfite liquor at 550°F and 1100 psig.

In another example of the described process, spent Alkaline Sulfite Process liquor was coked at 60°F under 1700 psig for 2 hours with the results tabulated below.

**What is claimed is:**

1. In the coking of spent pulping liquors used in the Alkaline Sulfite Process which have a pH of about 9 to about 12; the steps of:
   - coking said liquors in the liquid phase in a coking zone at about 450°F to about 750°F under a pressure of about 100 to about 3000 psig for about 0.5 minute to about 6 hours to form gases including CO₂, liquid effluent and coke; separating said gases, said effluent and said coke; flowing said gases to a combustion zone wherein malodorous sulfur compounds are converted to SO₂ vaporizing a portion of said effluent and cooling the remainder by heat exchange with incoming liquor to preheat said liquor; flowing said vaporized portion of said effluent to a conditioning zone; condensing said portion to form a condensate; washing said coke with said condensate to remove sodium ions and other
pulping chemicals retained on said coke; combining said condensate now containing chemicals recovered from said coke, with the cooled effluent and conveying the combined stream to an SO₂-containing absorbing zone; drying said coke with flue gas, burning said coke in a combustion zone to provide useful heat, to incinerate aforementioned sulfur-bearing gases and to generate an SO₂-bearing flue gas; then flowing said flue gas to said SO₂ absorbing zone; venting off the pollutant-free flue gas obtained thereby; flowing said liquid stream to a causticizing zone, and adding lime to said stream to convert sodium carbonate produced therein by reaction with CO₂ produced by said coking to NaOH and clarifying said stream to remove solids resulting from causticizing, thereby forming new cooking liquor having a pH suitable for alkaline sulfite pulping.

2. The process of claim 1 including the steps of dewatering said coke after washing same.