Journal of Environmental Sciences Vol. 7, No. 1, pp. 101—106, 1995 ISSN 1001—0742

Hydraulic and carbonizing actions of sulfuric acid to straw pulp and paper black liquor

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Abstract—A study on hydraulic and carbonizing actions of sulfuric acid to straw pulp and paper black liquor is presented in this paper. The results show that when black liquor is heated and pressurized (130—165℃, 0.2—0.6mPa), sulfuric acid has acid separating, dewatering and carbonizing actions to lignin, as well as hydrolytic and dewatering actions to pentosan in black liquor with pH in the range of 1.5—4. After black liquor is hydrolyzed and carbonized with sulfuric acid, the recovery rate of lignin is over 99%, while the rate of transforming theoretically contained pentosan to furfural is higher than 62%. By hydrolyzing and carbonizing black liquor with sulfuric acid, a new technology for multi-purpose utilization of black liquor is expected to be developed.

Keywords: straw pulp paper; black liquor; sulfuric acid.

1 Introduction

In the process of making paper with alkali or sulfate, pulped waste liquor—black liquor is generally treated in this way, namely, adding sulfuric acid to black liquor, then separating lignin from acidified black liquor under normal pressure and low temperature (60—70℃) so as to put it to multi-purpose use. But this method only suits the treatment of low concentration black liquor (0.1—7 Be′), in which the eliminating rate of COD is about 60%. Besides, deposited matter is difficult to be separated from acidified black liquor, and recovering organics and sodium sulfate from black liquor is also difficult due to its low concentration. Therefore the method needs further improvement (NEPA, 1988).

In this paper, a study is give on acid separating, dewatering and carbonizing of organic (lignin); hydrolyzing and dewatering of pentosan; transforming pentosan to furfural in high concentration black liquor (7—14 Be′) under high pressure and temperature. A new technology is expected to be developed so that major organics and inorganics can be recovered.

2 Experimental method

2.1 Devices and reagents

Stainless steel reactor (pressurized from 0 to 1.6mPa); ZD-3 automatical electrometric titration outfit; CS 501 super constant temperature water bath; H_2SO_4 (96% C.P.) as a catalyst.

2.2 Black liquor and its component analysis

Black liquor of reed pulp with alkali comes from Lukou Making Paper Mill in Zhuzhou, China, and its major components are shown in Table 1.

Table 1 Analysis of black liquor components

Specific weight, 15℃	12.75Be'
pH	11.01
COD_{Cr}	198800mg/L
Colority, dilution metering	15318
Basic capacity, NaOH	17.67g/L
Total solid capacity	200.67g/L
Organic capacity	124.893g/L
a. lignin	54.101g/L
b. theoretically contained furfural	9.41g/L
c. organic acid, CH_3COOH	15.1g/L
Inorganic capacity	75.744g/L
a. ash	2.042g/L

2.3 Analytical approach

Analysis of furfural and organics in black liquor accords with the standard of GB1926-80, while analysis of the other substances is conducted by the method offered in Environmental Monitoring and Analytical Approach by China Environment Protection Agency (NEPA1983).

3 Experimental results and discussion

3.1 The pH titration curve of black liquor

Black liquor contains the following substances: lignin, pentosan, HCOOH, CH_3COOH, lactic acid, NaOH, Na_2S, Na_2SiO_3, Na_2CO_3, and so on. The consumption of H_2SO_4 is a major consumed quota, when black liquor is treated with H_2SO_4 to separate, hydrolyze and carbonize the above substances. The purpose of this experiment is to examine the effect of concentrations of black liquor and H_2SO_4 on consumed amount of H_2SO_4, when the pH of black liquor changes.

3.1.1 The relation between black liquor pH and temperature

100ml black liquor (12.75 Be', 1#) and 100 ml water (2#) are taken out respectively, and the effects of temperature on pH are examined. The results are illustrated in Fig. 1.

3.1.2 The pH titration curve of black liquor

When black liquor is agitated and heated to 60℃ (keeping constant temperature), water and black liquors of different concentrations are titrated with H_2SO_4, respectively. The results are illustrated in Fig. 2.

In Fig. 2, curve 1 stands for 100ml water, curve 2 for 100ml 12.75 Be' black liquor, curve 3 for the mixture of 100ml 12.75 Be' black liquor and 40.1 ml water (specific weight 9.46Be') and curve 4 for the mixture of 100 ml 12.75Be' black liquor and 81.8 ml water (specific gravity

7. 64Be′), and all of the above liquors are titrated with 96% H_2SO_4; curve 5 stands for the mixture of 100 ml 12. 75Be′ black liquor and 81. 8 ml water (specific gravity 7. 64Be′) titrated with 15. 4% H_2SO_4 (transformed to 96% H_2SO_4 in Fig. 2).

Fig. 2 shows that the consumed amount of H_2SO_4 increases with the increasing of diluting amount of black liquor (100ml, 12. 75Be′) from the comparison of curve 2, 3 and 4; the consumed amount of H_2SO_4 increase with the decreasing of H_2SO_4 concentration from the comparison of curve 4 and 5, which is more obvious especially when the pH of the liquors decreases.

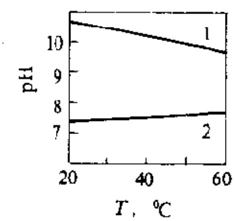

Fig. 1 pH vs. temperature in black liquor

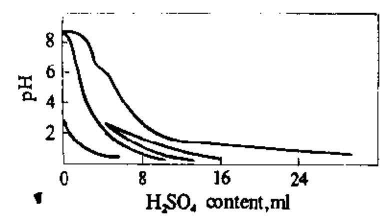

Fig. 2 pH vs. H_2SO_4(96%) added in black liquor

3. 2 The experiment of acid separating, dewatering, carbonizing and hydrolyzing of black liquor when it is pressured and heated

Take 100ml black liquor with 12. 75Be′ respectively, agitate and heat them to 60℃ and add different amount of 96% H_2SO_4 to each with the pH of black liquor being controlled. Then put them in the reactor to react for 80 min respectively under deferent pressures, and take out black liquor from the reactor and filter black liquor by intermediate rate quantitative filter paper (Φ100) in the vacuum of 0. 03 mPa. And then dry and weight the filter cake and observe its colour and carbonizing state. Finally measure the volume of the filter liquor and the amount of furfural in filter. The results are illustrated in Fig. 3.

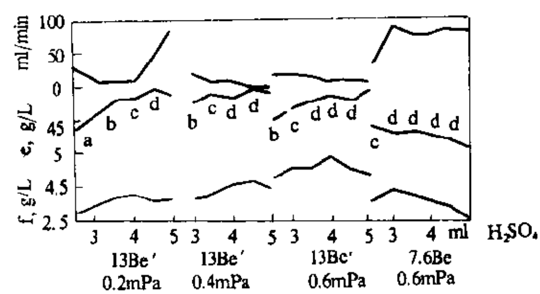

Fig. 3 The amount of 96% H_2SO_4 added in black liquor vs. the yield of furfural and sediment dried and filter rate

a. deep yellow and brown colour of dry sediment;

b. brown colour of dry sediment;

c. light brown and black colour of dry sediment;

d. filter rate of deep brown and black colour of dry sediment, ml/min;

e. the yield of dry sedimen, g/L;

f. the yield of furfural, g/L

3. 3 The experiment of treating black liquor under the optimal conditions

According to Yang (Yang, 1991) and the experiment, the optimal conditions of treating black liquor are as follows: 0. 6 mPa, 164℃, pH 2(i. e. $1m^3$ black liquor mixed with 40L 96% H_2SO_4), 80min. The results obtained under the optimal experiment conditions are illustrated in Table 2.

Table 2 The results obtained under the optimal experiment conditions

COD of filter liquor, mg/L	55260
Eliminating rate, %	72.1
Amount of furfural in filter liquor, g/L	6.15
Amount of lignin in filter liquor, g/L	0.1
Filter rate, ml/min	15.1
Yield of dry sediment, g/L black liquor	72.0
Colour of dry sediment, g/L black liquor	Deep black
Amount of organic acid in filtrate, g/L filtrate	24.5
pH of filter	2.31

3.4 Discussion

3.4.1 It is shown in Fig. 3 that with H_2SO_4 being used as a catalyst, the chemical reaction formula of transforming pentosan into furfural in black liquor is as follows:

$$(C_6H_8O_4)n + H_2O \xrightarrow{\text{Hydrolyzing}} nC_5H_{10}O_5 \xrightarrow{\text{dewatering}}$$

$$nC_5H_4O_2 + n(3H_2O) \xrightarrow{\text{decomposing}} \text{organic acid or acid polymer}$$

When the pH value of black liquor ranges from 1.5 to 5, the rate of above reaction and the yield of furfural increase with the decreasing pH value. But when the pH value of black liquor is below 1.5, the yield of furfural decreases with the increasing decomposing rate of furfural. Besides, the dewatering rate of pentosan and the yield of furfural increase with the increasing reacting temperature in the range of 130—165℃. When the temperature is above 165℃, the increase of the yield of furfural is not obvious because of its decomposing rate, and the energy consumption is increasing. When black liquor is diluted, the yield of furfural increases with the decreasing oxidizing and decomposing rate of furfural, but it has no more recovering value as the concentration of furfural in liquor is too dilute.

Compared with the present production of furfural, the hydrolytic reaction of pentosan with H_2SO_4 in black liquor is liquid phase reaction, and the liquid ratio is large. Therefore, the yield of furfural (the theoretically contained furfural) can reach 62% or more.

3.4.2 It is also shown in Fig. 3 that the field of dry sediment (formed mainly through acid separating, dewatering and carbonizing organics such as lignin in black liquor) increases with the decrease of pH value of black liquor and the increasing reacting temperature which is below 156℃. But when the temperature is above 160℃, the field of dry sediment decreases with the increase of temperature. The above phenomena can be explained in the following way: there is a lot of alkaline lignin colloid and a bit of water glass colloid ($Na_2O.SiO_2$); when sulfuric acid is added to black liquor, the sodium element of alkaline lignin exchanges with the hydrogen ion of sulfuric acid, thus forming non-soluble hydrogen lignin that deposites in black liquor, and the amount of sediment increases with the decreasing pH value. It is well known that the concentrated sulfuric acid has very strong dewatering and carbonizing actions on carbohydrate, while the results from our experiment prove that the diluted sulfuric acid has the same action under the conditions of high temperature and pressure, and with the temperature increasing, these actions are getting more intensified. Therefore, when the temperature is above 160℃, the lignin and other organics in black liquor are dewatered and carbonized to such an extent that it turns into carbon residue, thus decreasing the yield of dry sediment. This conclusion is also indicated by the change of dry sediment colour illustrated in Fig. 3. The ash in black liquor mainly consists of silicon dioxide which exists in the form of $Na_2O. SiO_2$. When sulfuric acid is added to black liquor, there will be depositions of silicic acid in the black liquor (the equivalent potential point of silicic acid ranging from pH 4 to pH 5). During the titration of pH to black liquor, it is also found that when the pH value of black liquor drops to 7, black liquor begin to foam; when the pH value of black liquor drops to 5. 5, the viscosity of black liquor greatly thickens, so much that it is difficult to agitate; when the pH value drops to 4, the viscosity of black liquor is getting thin and agitating operation can be normally performed. Therefore if the pH value is controlled above 4, it will be difficult to perform separating operation. With the further drop of pH, both acid separation of sulfuric acid and condensation of lignin are getting strong, which makes the filter rate of reacting liquor increase. But, when the pH value of black liquor continues to drop, sulfuric acid has stronger dewatering action due to its increasing consumption, which makes the actions of oxidizing condensation and carbonation of lignin get intensified. Hence, it weakens the condensing action of lignin and the filterability of reacting liquor. This rule is also reflected in Fig. 3.

3. 5 The technological process of black liquor hydrolyzed and carbonized with sulfuric acid

According to the results of our experiment and references (Yang, 1991; Zhou, 1991; Yang, 1989), we propose the above technological process of black liquor hydrolyzed and carbonized with sulfuric acid (Fig. 4).

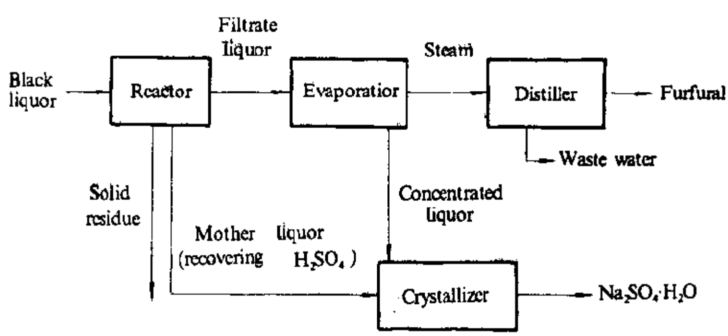

Fig. 4 The technological process of black liquor hydrolyzed and carbonized with H_2SO_4

Furfural, sodium sulfate and lignin or carbon residue of lignin (used to make active carbon of high quality) can be recovered from black liquor in the above technological process. 6 kg furfural, 80kg sodium sulfate and 70 kg carbon residue can be obtained from $1m^3$ black liquor with 13Be′ under the following conditions: 0. 6mPa, 80min and pH 2. The removal ratio of COD from treated black liquor is over 95%. Besides, some organic acids produced in the reactor can be recovered in the form of vinegar salt with gaseous neutral reaction in evaporator. The organic acid (2% — 3%) in the waste water discharged from the bottom of the distiller can also be recovered in the form of vinegar salt with the way by Chen (Chen, 1992) or the way of electrodialysis. As a result, the concentration of COD in the wastewater drops below 200mg/L.

4 Conclusion

Under the condition of 0.2—0.6mPa, 130—165℃ and pH 0.5—5, sulfuric acid mainly has the action of hydrolyzing, dewatering and carbonizing on black liquor. Besides it also has the action of acid separation in normal temperature.

When 7—13Be′ of black liquor is treated with sulfuric acid under heated and pressured conditions, the optimal conditions of recovering furfural, sodium sulfate and carbon residue of lignin are: pH 2, 0.6mPa and 80min; the optimal conditions of recovering lignin (main products), furfural and sodium sulfate (by-product) are: pH 3.0, 0.2mPa and 80 min.

While the above method is applied to treat black liquor for multi-purpose utilization. Both black liquor and sulfuric acid concentration have great effect on the consumed amount of sulfuric acid. The thicker the black liquor and sulfuric acid, the smaller the consumed amount of sulfuric acid and energy are. Therefore, a thicker black liquor and thicker sulfuric acid would be much better in the treatment of black liquor with sulfuric acid.

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(Received May 11, 1993)