

Method of Black Liquor Combustion to Remove Silicon from Wheat Straw Pulping

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The effects of aluminium sulphate and sodium aluminate on physical and chemical properties of wheat straw pulp black liquor were studied. Results showed that the expansion rate was enhanced by increasing the aluminum salt content; furthermore, the effect of sodium aluminate was better than that of aluminum sulfate. The maximum desilication rate of 92.31% was reached with the addition of 3% sodium aluminate. A rheometer showed that aluminum salt had little impact on the viscosity of thick black liquor, so even at a high temperature it could be conveyed by pumps in paper mill at 110 °C. The effect of aluminium salt on the silicon removal rate during black liquor combustion was also studied. The experimental results showed that both aluminium sulphate and sodium aluminate helped to remove silicon. The desilication rate of sodium aluminate reached 62.33%, higher than that of aluminum sulphate. SEM-EDX illustrated that the aluminum and silicon ions were formed into insoluble precipitates. It was optimal to use 3% sodium aluminate as desilication agent.

Keywords: Thick black liquor; Rate of inflation; Rheometer; Desilication; SEM – EDX

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INTRODUCTION

There are abundant non-wood cellulosic resources in Asia and Africa. With increasing demand for paper, it is necessary to use non-wood resources efficiently for pulping and papermaking. Wheat straw is a kind of grass-like plant which grows widely around the world and has advantages such as a short growth cycle, tolerance toward high ambient temperatures, resistance to cold weather, and others (Stone and Nicolas 1995; Talebnia and Karakashev 2009). Wheat straw pulp is a good raw material for pulping and papermaking.

In the chemical pulping process, about 50% of the dissolved organic material formed in the cooking liquor comes from fibrous raw material. Alkaline pulping waste liquor is called black liquor (Zhan 2009). The chemical makeup of black liquor is complex in that it contains different organic and inorganic polymers. Silicon material in wheat straw black liquor has caused problems in the alkali recovery system, referred to as “silicon interference” (Isono and Ono 1967; Rao *et al.* 1988; Tutus and Eroglu 2004; Taylor and McGuffie 2007). These issues are as follows: during the evaporation process, the viscosity of black liquor containing sodium silicate increases more rapidly than that of black liquor without sodium silicate. When processing black liquor that contains silicon, inorganic scale forms readily on the evaporation equipment. Sodium silicate has a high melting point, resulting in high energy consumption during black liquor combustion. When adding lime into green liquor for causticization, sodium silicate reacts with lime

and generates calcium silicate, and the particles of sodium silicate are too fine to be easily precipitated and filtered. Accordingly, white mud wrapped with fine particles is hard to wash, which results in alkaline liquor being excessively washed away. Therefore, eliminating or reducing silicon interference is key to improving the efficiency of the alkali recovery system.

The solids content of black liquor is usually expressed as a percentage. Low solids black liquor from the extraction section has a solids content in the range of 8 to 20%; moderate concentrations of black liquor from the multi-effect evaporator system has a solids content between 20 and 40%; and thick black liquor, examined in this study, comes from the recovery furnace. The solids content of thick black liquor is usually in the range of 40 to 60%.

Currently, many researchers are working on a variety of desilicating processes and have achieved some theoretical and practical success (Eroglu and Deniz 1998; Vehmaan-kreula 2000; Tutus and Eroglu 2001). Carbon dioxide (Xia *et al.* 2013) or sulfuric acid (Ono and Tsuji 1967) can also be used to remove silicon using the seeding method. The decrease in pH due to the introduction of CO₂ and sulfuric acid leads to the formation of silicic acid colloid. However, the pH value of green liquor is decreased, requiring the addition of NaOH to return to the original pH.

However, the cited studies mainly have focused on dilute black liquor for desilication, *etc.* Aluminum salt as a desilicating agent for thick black liquor from straw pulp has been only rarely studied (Tutus and Eroglu 2003). The purpose of this research is to study the effect of aluminum desilicating agents on the viscosity of thick black liquor, its isothermal volume expansion coefficient (VIE), and desilication rate, with an expectation to provide some data and basic theories of aluminum salt for pilot plant testing of the alkali recovery system.

EXPERIMENTAL

Materials

The thick black liquor from non-wood pulp was provided by a paper mill in China. Its composition was as follows: solids content of 54.12%, SiO₂ content of 3.85%, a VIE of 2.36 mL/g, and a pH of 10.33.

The Effect of Black Liquor Expansion

Black liquor was obtained by weighing the amount into 300 mL beakers. Aluminum sulfate and sodium aluminate were added to the black liquor and heated for 10 min at 200 °C in the furnace. The amounts of aluminum salts added were 1%, 2%, 3%, and 6% of the relative solid content, respectively. After the black liquor was naturally cooled to room temperature, the solid contents were measured by vacuum oven (Kemeny and Chazin 1973). The black liquor's volume isothermal expansion coefficient (VIE) was measured using a muffle furnace (Wang and Cheng 1997).

The effect of black liquor expansion was represented by VIE's expansion rate (Eq. 1).

$$X = \frac{B_2 - B_1}{B_1} \times 100\% \quad (1)$$

In Eq. 1, X is the expansion rate (%), B_1 is VIE of the blank sample (without aluminum salts) in mL/g, and B_2 is the VIE of thick black liquor with added aluminum salts in mL/g.

Rheometer Set

The viscosity of thick black liquor was measured at a shear rate of 20 S-1, and the test temperatures were changed from 70 °C to 120 °C in two different amounts of aluminum black liquor.

Black Liquor Combustion Process

The whole process included 4 steps. The first step was evaporation carbonization. In this step, the thick black liquor was dried in an oven for 12 h at 105 °C. The second step was carbonization of dried black liquor. From this, 20 g of dried black liquor was wrapped with double quantitative filter paper, put into a 50 mL porcelain crucible, and then heated in the furnace. The carbonization was completed until smokeless at 300 °C. The third step was silicon removal. Carbonized black liquor was ground slightly by mortar and then put into a 50 mL corundum crucible (main ingredient Al_2O_3), which was taken to a muffle furnace where an alkali recovery boiler combustion process was simulated at 1050 °C. The last step was the detection and removal of silicon. The black liquor melt was directly added into 500 mL of cooling water, forming green liquor. Then, the solution was filtered with a vacuum pump to obtain the insoluble precipitate. Elemental composition of precipitate was analyzed by Hitachi S-4800 SEM-EDAX spectrum analysis. The silicon content of filtered green liquor was measured by the silicon molybdenum blue method (Tong and Lu 2005).

Calculation of the Desilication Rate in Black Liquor Combustion Method

5 mL of green liquid was put into a 50 mL beaker with a pipette, and its absorbance value was measured, which reflected the silicon content. The desilication effect of thick black liquor was represented by removal rate of silicon content in green liquor (Eq. 2):

$$Y = \frac{C_1 - C_2}{C_1} \times 100\% \quad (2)$$

In Eq. 2, Y is the desilication rate (%), C_1 is the absorbance value of the green liquor when the desilication agent is not added, and C_2 is the absorbance value of the green liquor when the desilication agent is added.

RESULTS AND DISCUSSION

The Effect of Aluminum Salts on Black Liquor VIE

Black liquor Isothermal Volume Expansion Coefficient (VIE) is the volume expansion number of per gram of solid after combusting. When the temperature was increased to 300 °C, the majority of the organics in black liquor were dehydrated and carbonized rapidly, and the inorganics formed the framework of carbonization. In the process of carbonization, the volatilization of gas led to the formation of pores in the carbonization. A greater VIE value correlated with a higher void amount in pore

formation. The isothermal expansion volume index was related to viscosity, silicon content, and ash of black liquor and other factors. The isothermal expansion volume index of straw pulp black liquor was low due to its high ash content and viscosity (Miller and Clay 1989). VIE values were used in the furnace operation, which represented the dryness of the black liquor and cushion looseness degree in black liquor combustion indirectly. Higher VIE values favored the combustion of black liquor. VIE values have garnered more attention as an indicator of combustion of black liquor in recent years.

The effect of aluminum salts as desilication agents on the expansion rate of wheat straw pulp thick black liquor was studied, and the results are shown in Fig. 1.

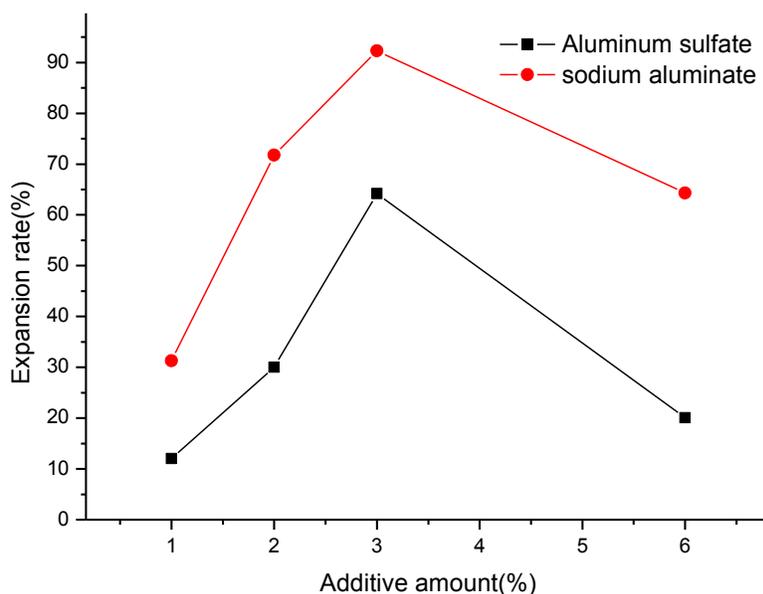


Fig. 1. The influence of aluminum salts loading on expansion rate

Figure 1 shows that the expansion rate of black liquor increased with increasing aluminum sulfate or sodium aluminate loading. This demonstrated that aluminum salt was conducive to increasing the expansion of black liquor. It is generally considered that the main factor which affected the value of VIE is the proportion of inorganic and organic compounds (Alén 1994; Wang 1995). The expansion ratio is also an indicator to control the loose degree of cushion in alkali recovery boiler combustion, which demonstrates that increasing the amount of inorganics in black liquor would improve the VIE of thick black liquor.

With the increase in the amount of aluminum salt, the swelling rate of black liquor reached a maximum value when the aluminum salts or aluminium sulphate loading was 3%, and the maximum swelling rates were 64.19% and 92.31%, respectively. At the same time, the effect of sodium aluminate on expansion ratio was better than that of aluminum sulfate. A related reference (Liu 2003) showed that the increasing content of SiO_2 can decrease the VIE value. Aluminum ions can be partly transformed into aluminate ions in the alkaline conditions of black liquor. Then partial aluminate ions and silicate ions may form a water-insoluble precipitate. The effect of sodium aluminate was seen to be better than aluminum sulfate on the swelling rate at the same molar mass. However, when the amount of aluminum salt was higher than 3%, the black liquor

swelling rate began to decrease, which indicated that the excessive inorganics had a negative effect on swelling rate.

Effects of Aluminum Salts on the Viscous Flow Temperature

Viscous flow temperature is the initial temperature or softening temperature of the non-crystalline polymer transformed from a high elastic state to the viscous flow state. Highly concentrated black liquor from wheat straw, which contains lignin and other polysaccharide polymers, is a complex polymer and meet the viscous flow characteristics of polymer (Sandquist 1983; Souml 1988). It follows that one can characterize the flow characteristics of the black liquor by viscous flow temperature. Generally, the force between the liquid molecules is complex, and the viscosity of the fluid changes with temperature (Zaman and Fricke 1994). In order to study viscous flow temperature effects, the viscosity of original black liquor with 54.68% solid content, added aluminum sulfate, and sodium aluminate was measured at different temperatures, respectively. The results are shown in Fig. 2 and 3.

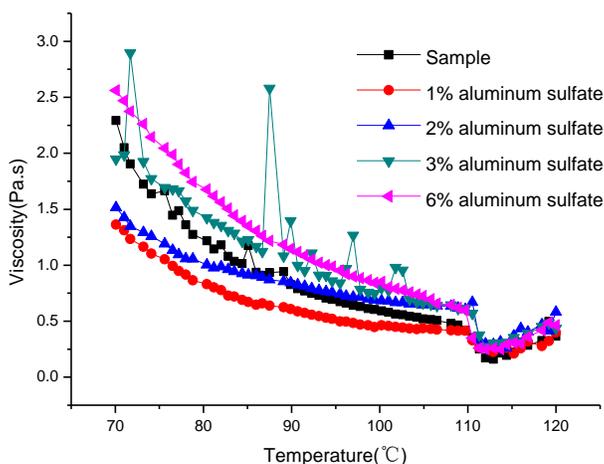


Fig. 2. The effect of aluminum sulfate on viscous flow temperature of the thick black liquor

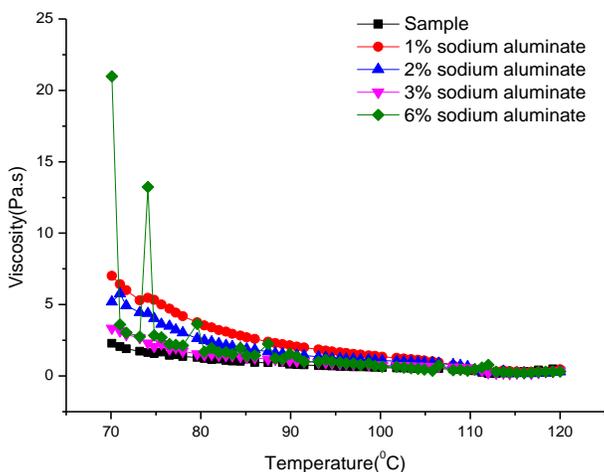


Fig. 3. The effect of sodium aluminate on viscous flow temperature of the thick black liquor

As shown in Figs. 2 and 3, the viscosity of original black liquor and black liquor with the addition of aluminum decreased with increasing temperature. Rising temperature could increase the energy of the polymer, which would make the molecule move faster and reduce intermolecular friction. On the other hand, rising temperature can make lignin and other long-chain carbohydrate molecules degrade into shorter chain molecules. It would weaken the strength of the network structure of black liquor and irreversibly reduce the viscosity of black liquor (Branch *et al.* 1991). Under all these factors, rising temperature can reduce the viscosity of black liquor significantly.

In comparison with the black liquor without adding aluminum salts, the viscosity of black liquor decreased when aluminum sulfate loading was 1% and 2%. However, it had an opposite effect when the addition of aluminum sulfate was 3% and 6% (Fig. 2). A phenomenon occurred that resulted in the viscosity of black liquor being gradually reduced with the increasing amount of sodium aluminate (Fig. 3). The viscosity of black liquor was higher than that of the black liquor without sodium aluminate added. However, Figs. 2 and 3 show that the viscosities of black liquor with added aluminum salts were similar to that of the sample at a high temperature, indicating that aluminum salts had little influence on the viscosity of the thick black liquid.

There was an abnormal phenomenon when the temperature of black liquor rose to 110 °C. The viscosity of thick black liquid decreased suddenly. This could be explained by the partial degradation of lignin and other polysaccharide polymers; in that situation, a large number of gases in the black liquor at this temperature, such as water, hydrogen sulfide, and methyl mercaptan, caused the viscosity to suddenly decrease. This could provide a theoretical basis for the pumping of thick black liquor in paper mills.

Effects of Aluminum Salt on Silicon Removal Rate of Thick Black Liquor

Aluminum salts were added into thick black liquor and burned at 1050 °C. The residue was poured into water, resulting in green liquor. Then 5 mL of green liquor was filtered by vacuum and transferred into a beaker. The desilication rate of aluminum salt on the thick black liquor was calculated. Sodium aluminate (NaAlO_2) can react with Na_2SiO_3 and generate a complex precipitate of sodium aluminosilicate during combustion (Eq. 3) (Zhan 2009).

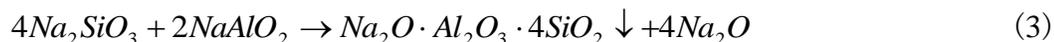


Figure 4 shows that the desilication rate increased with increasing aluminum salt loading. When the additive amount was increased from 1% to 3%, the desilication rate increased quickly. The desilication rate began to increase slowly when the additive amount was beyond 3%.

Figures 5 through 7 show the SEM-EDAX test results for the blank samples (without aluminum salts addition), 3% aluminum sulfate, and 3% added sodium aluminate, respectively. Aluminum elements were not detected for Fig. 5 but are depicted in Figs. 6 and 7. When aluminum salts were not added, the mass fraction of silicon element was 10.77%, as shown in Table 1. When 3% aluminum sulfate was added, the mass fraction of the silicon element was 21.68%, as shown in Table 2. When 3% sodium aluminate was added, the mass fraction of silicon element was 23.2%, as shown in Table 3. This further indicates that sodium aluminate had a better desilication effect than aluminum sulfate. These results indicate that aluminum salts engaged in the mentioned chemical reaction (Eq. 3).

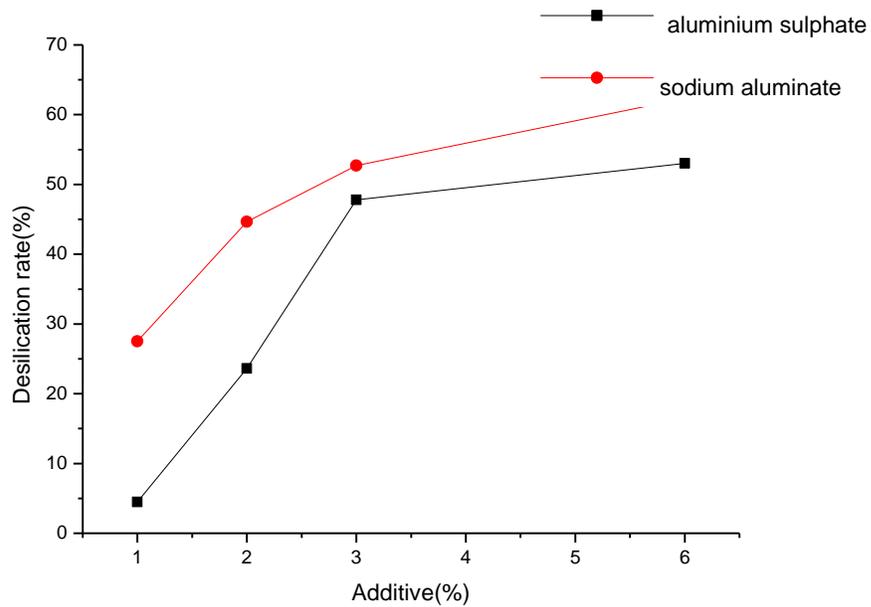


Fig. 4. Effect of aluminum salt on removal silicon rate

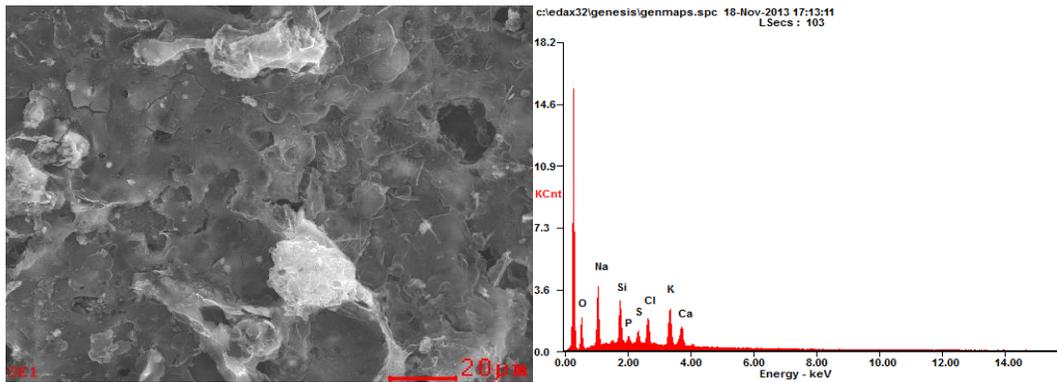


Fig. 5. SEM-EDAX analysis of precipitate of the blank sample

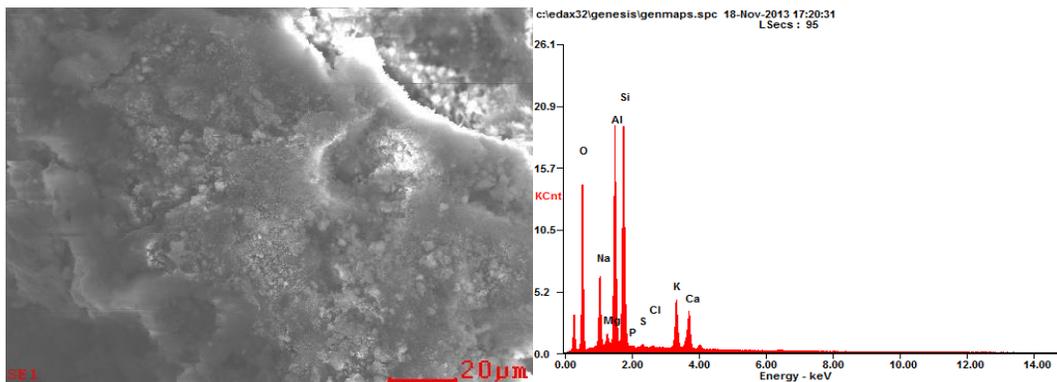


Fig. 6. SEM-EDAX analysis of precipitate under 3% aluminum sulfate loading

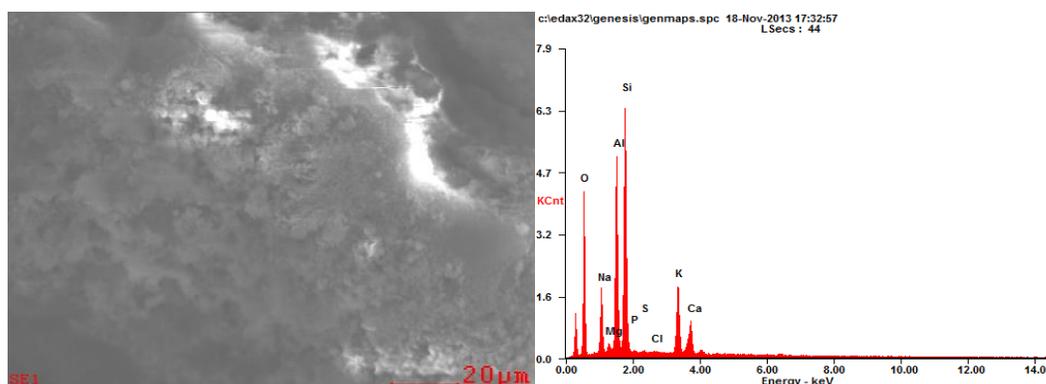


Fig. 7. SEM-EDAX analysis of precipitate of 3% sodium aluminate

Table 1. Spectrum Stave of Precipitate of the Blank Sample

Element symbols	O	Na	Si	P	S	Cl	K	Ca
Percentage (%)	29.28	23.99	10.77	2.02	3.72	8.39	14.06	7.76

Table 2. Content of Elements of Precipitate of 3% Aluminum Sulfate

Element symbols	O	Na	Mg	Al	Si	P	S	Cl	K
Percentage (%)	39.59	8.89	1.13	17.01	21.68	0.17	0.37	0.24	6.12

Table 3. The Content of Elements of Precipitate of 3% Sodium Aluminate

Element symbols	O	Na	Mg	Al	Si	P	S	Cl	K
Percentage (%)	38.70	7.71	0.79	15.82	23.20	0.27	0.25	0.24	8.90

CONCLUSIONS

1. Two kinds of aluminum salts had similar effects on the expansion rate trend of thick black liquor: the expansion rate reached a peak value when the additive was increased to 3%, it decreased when more aluminum salt was present. Sodium aluminate had a better effect on the expansion of thick black liquor than that of aluminum sulfate, reaching 92.31% when the sodium aluminate loading was 3%.
2. The results of using a rheometer detector showed that aluminum salts had a negative effect on the viscosity of black liquor when the temperature was in the range of 70 to 110 °C. When the temperature increased, this negative effect became weaker. Viscosity of the black liquor sample was similar to the black liquor with added aluminum salt, providing a theoretical basis for a plant to pump thick black liquor.
3. Both sodium aluminate and aluminum sulfate had an effect on silicon removal. Increasing the loading of aluminum salt also increased the silicon removal rate. The silicon removal effect of sodium aluminate was better than that of aluminum sulfate. The precipitates were detected by SEM-EDAX, and the results indicated that the chemical reaction between aluminum ions and silicon generated a type of water-insoluble precipitate.

4. Considering the effect of aluminum salt on desilication and the physicochemical properties of thick black liquor from wheat straw pulping, adding 3% sodium aluminate and pumping black liquor at 110 °C were the optimum conditions.

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