Rheological Properties of Thick Kraft Black Liquor at High Temperature with the Addition of Sodium Aluminate

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In kraft recovery systems, there is a trend toward increasing solids content of the black liquor injected to the furnace. Higher solids contributes to combustion efficiency and stable boiler operations. However, the presence of silica can adversely affect the viscosity of the mixture in such cases. Sodium aluminate, which was used as a desilicating agent during the black liquor combustion, had an excellent effect on the removal of silicon from the bamboo kraft black liquor (BKBL) to solve the problems presented by silicon. The apparent viscosities of thick BKBL with the addition of varied sodium aluminate loading were studied with a rotational rheometer. The thick BKBL behaved as a pseudo-plastic fluid that exhibited shear-thinning. However, shear-thickening appeared when the shear rate exceeded 30 s^{-1} at 98 °C, which would influence the flow stability of BKBL in pipelines. When the loading was 1.5 wt.%, sodium aluminate promoted the flow and droplet formation of thick BKBL by reducing its structural strength. The Ostwald-de Waele model provided an ideal fit to the apparent viscosity data. Hence, it could be used to accurately predict apparent viscosity changes in thick BKBL.

Keywords: Shear-thinning; Black liquor; Apparent viscosity

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INTRODUCTION

Bamboo is a non-wood fiber raw material that is abundant in China. Compared to the straw pulping process, the bamboo kraft pulping process is more environmentally friendly (Sun and Hui 2002). The properties of bamboo pulp are very close to those of hardwood pulp. Bamboo kraft paper is delicate and soft with a strong toughness and a smooth, bright surface. The quality of bamboo kraft paper is superior to that of straw pulp paper. Hence, bamboo is considered a favorable papermaking material (Xu *et al.* 2016a).

However, the silicon content of bamboo kraft black liquor (BKBL) is much higher than that of hardwood pulp black liquor. This characteristic leads to a series of silicon-related problems in recovery systems, such as the reduction of their evaporation and combustion efficiencies (Miller *et al.* 1989; Karlsson *et al.* 2013). The viscosity of black liquor increases with increasing silicon content, which negatively impacts pipeline transportation and the atomization of BKBL. Furthermore, the silicon present in the green liquor decreases the alkali recovery rate. According to previous research, a new method was proposed to remove silicon from black liquor (Xu *et al.* 2015a,b). Sodium aluminate

($NaAlO_2$), which has typically been used as a desilicating agent, was added into black liquor before combustion. The Na_2SiO_3 in the black liquor can react with $NaAlO_2$ to produce $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ during the black liquor combustion. The $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ forms a precipitate, which can be filtered after the combustion products are dissolved in water. The decrease of silicon content in green liquor is beneficial to the causticizing process (Xu *et al.* 2015b).

Black liquor, an aqueous mixture which consists mostly of lignin, polysaccharides, resinous compounds, and inorganics such as sodium salts and small amounts of calcium, potassium, magnesium, silicon, and irons salts (Liu *et al.* 2013; Zhang *et al.* 2013), is the by-product extracted from papermaking materials during the pulping process (Trung *et al.* 2015). In the recovery unit of the pulp and paper industry, black liquor is used as an energy source (Samistraro *et al.* 2015), which is burned in a furnace after being concentrated to a solids content above 60 wt.%. One of the most important development directions is the burning of black liquor at a solid content of above 80 wt.% in recovery systems, due to its higher combustion efficiency and stability. Further, the discharge amount of SO_2 can be lowered greatly, and an environmentally protective effect can be achieved when the black liquor is burned at a high solid content (Llamas *et al.* 2007). However, BKBL at a high solid content (above 70 wt.%) exhibits relatively high viscosity and reduced flowability at room temperature.

Several studies have investigated the main influencing factors on the rheological properties of black liquor (Moosavifar *et al.* 2009; Zhang and Chen 2016). The viscosity of black liquor was related to the temperature, solid content, shear rate, and organic components (Söderhjelm and Hausalo 1996), *etc*. Zaman and Fricke (1995) studied viscoelastic properties of high solids softwood kraft black liquor. The Power-Law Model, Cross Model, and Carreau-Yasuda Model were used to describe the relationship between dynamic viscosity and shear rate, which provided the theoretical basis for the design of alkali recovery furnace (Zaman and Fricke 1995). Further, the relationship between apparent viscosity and shear rate could be described by the Ostwald-de Waele model (Alabi *et al.* 2012; Singh *et al.* 2016). According to previous research (Xu *et al.* 2016b), BKBL exhibits a shear-thinning phenomenon only when the solid content is above 50 wt.% during the shearing process. The study of the rheological properties of thick BKBL with the addition of sodium aluminate is essential to provide a theoretical support for the method of black liquor combustion used to remove silicon from bamboo pulping.

The temperature of the BKBL from the evaporators was approximately 120 °C and gradually reduced along the flow direction. Considering the above conditions, this paper focuses on the rheological properties of thick BKBL at above 70 °C and sodium aluminate's effect on them. The apparent viscosities of 70.19 wt.% BKBL and 79.87 wt.% BKBL with varied sodium aluminate loading were studied with a rotational rheometer. The experimental data were fitted according to the Ostwald-de Wale to explore the variation law of apparent viscosity.

EXPERIMENTAL

Materials

The BKBL was kindly supplied by Chitianhua Pulp and Papermaking Co., Ltd., Guizhou, China. The solid content was 70.19 wt.%. The total alkali content was 25.01 wt.%. The total sulfur content was 4.43 wt.%. The fuel value was 11.18 MJ/kg.

Sodium aluminate ($NaAlO_2$) was supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China.

Specimen preparation

The thick black liquor was dried at 80 °C in a vacuum drying oven until the solids concentration reached 79.87 wt.%. Sodium aluminate (0.5 wt.% and 1.5 wt.%, based on the solid weight in black liquor) was added into the BKBL with different solid contents (70.19 wt.% and 79.87 wt.%). The mixtures were stirred at 260 rpm for 10 min at 40 °C.

Rheology measurement

The apparent viscosities of BKBL were measured with an AR2000ex rotational rheometer (TA Instruments, New Castle, USA) at 70 °C and 98 °C. The jig of the rheometer was a stainless steel parallel plate with a diameter of 25 mm. The measuring space was 700 μm. The shear rate ranged from 0.1 s^{-1} to 100 s^{-1}. Silicone oil, which has a low density and viscosity, was used to cover the mixtures to prevent water evaporation. The silicone oil did not mix with the black liquor and had a negligible effect on torque generation.

Methods

The apparent viscosity data obtained from the rotational rheometer was fitted according to the Ostwald-de Wale model, which was often used to describe the relationship between apparent viscosity (η_a) of black liquor and shear rate (γ). The formula (Eq. 1) was as follows,

$$\eta_a = K \times \gamma^{n-1} \tag{1}$$

where K is the consistency index ($Pa \cdot s^n$), n is the power law index, η_a is the apparent viscosity (Pa·s), and γ is the shear rate (s^{-1}).

RESULTS AND DISCUSSION

Rheological Properties of Thick BKBL at High Temperature

The relationship between shear rate and apparent viscosity of BKBL (without additives) with varied solid contents and temperatures is shown in Fig. 1. Clearly, the apparent viscosities of BKBL with two different solid contents both decreased with an increased shear rate at 70 °C.

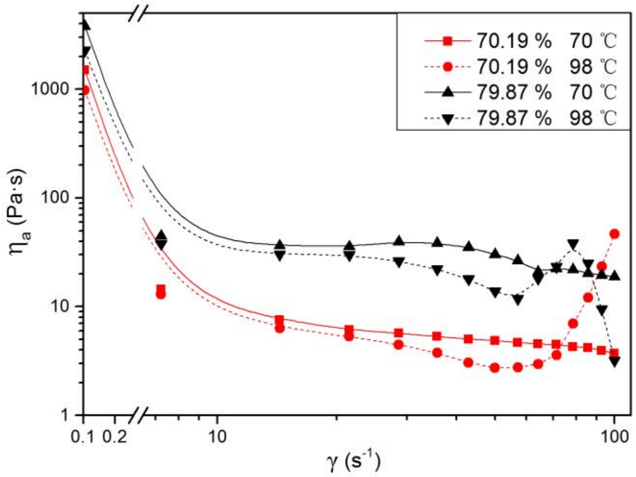

Fig. 1. Apparent viscosity *vs.* shear rate for BKBL with different solid contents at different temperatures

Also, Fig. 1 indicates that BKBL exhibited shear-thinning at this temperature, which is one of the prominent features of pseudo-plastic fluid (Yang *et al.* 2007). Within the test range, the first Newtonian zone did not appear in the curves; such a zone might be located when the shear rate was below 0.1 s^{-1}. In the shear rate range of 0.1 s^{-1} to 10 s^{-1}, the apparent viscosities showed a sharp decline. Then, the apparent viscosities exhibited a slow reduction and tended to be constant in the range of 10 s^{-1} to 100 s^{-1}, where the second Newtonian zone was located.

The shear-thinning phenomena could be explained as follows: when black liquor was in a stationary state, a complex and amorphous structure could be formed by the intertwining macromolecules due to the presence of lignin and the degradation products of celluloses and hemicelluloses. This structure generates resistance to the flow of black liquor (Marcelo *et al.* 2009). Under the shear forces, these chaotic macromolecules were straightened or snapped constantly and tended to be parallel to the stress direction. Meanwhile, the network structure of the black liquor was destroyed. The reduced resistance effect on flowing further lowered the apparent viscosity of black liquor.

According to the curves at 98 °C in Fig. 1, BKBL exhibited the shear-thinning phenomenon in the range of 0.1 s^{-1} to 30 s^{-1}. Nevertheless, shear-thickening behavior appeared when the shear rate continued to increase. The apparent viscosities increased, reached peak values, and then decreased rapidly. Under the shear force, the amorphous macromolecules in thick BKBL moved faster due to the higher temperature. Some macromolecules gathered together and formed a new network structure, which resulted in the increase of apparent viscosities. When the shear stress increased to a certain degree, the network structure was destroyed and the viscosities began to decrease.

As shown in Fig. 1, the η_a values of the 79.87 wt.% BKBL were much larger than those of the 70.19 wt.% BKBL. Therefore, achieving the combustion of BKBL at high solid content requires the development of new techniques to overcome the problems related to its high viscosity. The apparent viscosities were reduced with rising temperature due to the increased kinetic energy of the macromolecules and the larger space for molecular movement. Hence, an increased temperature might be a solution to solve the problems of thick BKBL during the alkali recovery process.

Effects of Sodium Aluminate on the Apparent Viscosity of BKBL

Figures 2 through 5 show the apparent viscosities of BKBL with the addition of sodium aluminate. At 70 °C, the sodium aluminate had no distinct influence on the apparent viscosities of BKBL according to the rheological curves. However, the shear rates that corresponded to peak values would be affected when sodium aluminate was added to the BKBL at 98 °C. A possible reason is that the sodium ions broke the aggregation of lignin in BKBL, as has been demonstrated in previous research (Zaman and Fricke 1996). The binding force among the molecules was weakened upon the addition of sodium aluminate to the BKBL. The network structural strength was reduced with increased sodium aluminate loading. Structures in the mixture that were responsible for the observed high viscosity were destroyed at a lower shear rate. Hence, with increased sodium aluminate loading, the shear rates that corresponded to the peak values of viscosity exhibited a certain decrease.

The obtained rheological data were fitted according to the Ostwald-de Waele model (Eq. 1). The fitted curve results are listed in Table 1.

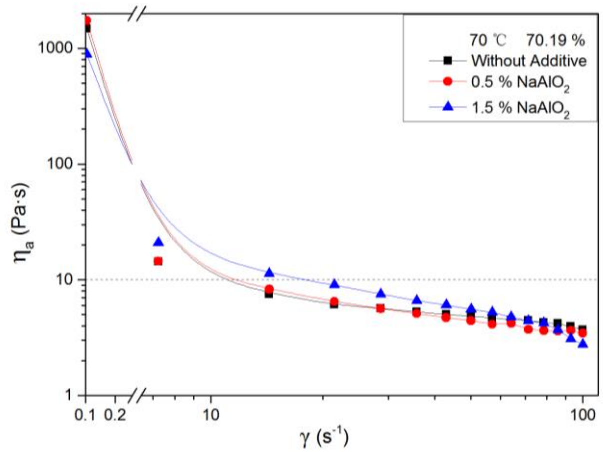

Fig. 2. Apparent viscosity *vs.* shear rate for 70.19 wt.% BKBL with the loading of sodium aluminate at 70 °C

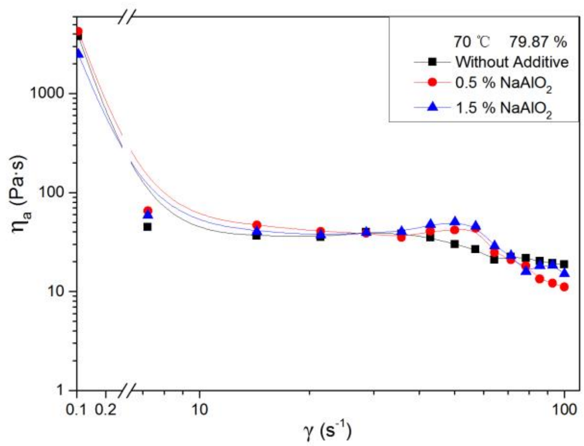

Fig. 3. Apparent viscosity *vs.* shear rate for 79.87 wt.% BKBL with the loading of sodium aluminate at 70 °C

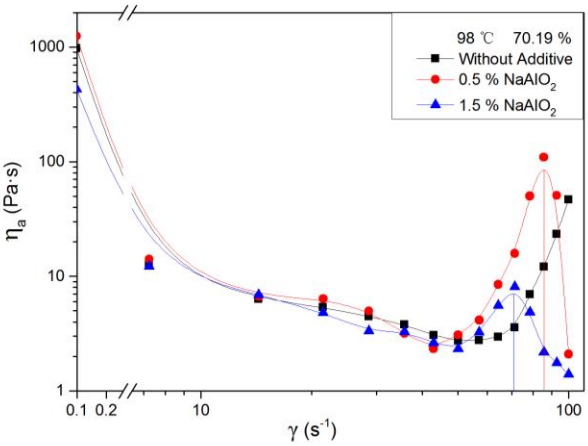

Fig. 4. Apparent viscosity *vs.* shear rate for 70.19 wt.% BKBL with the loading of sodium aluminate at 98 °C

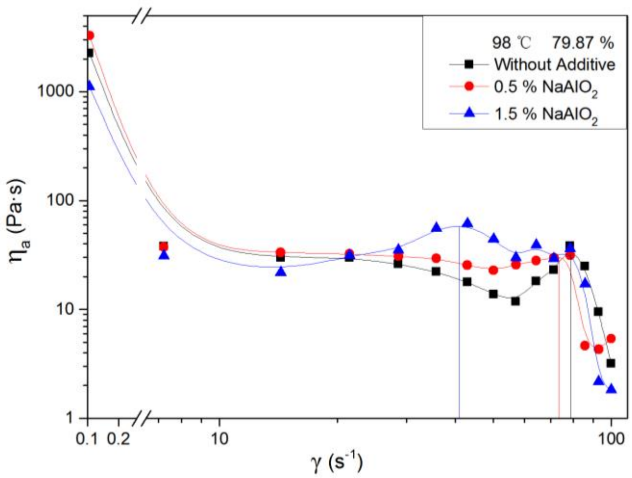

Fig. 5. Apparent viscosity *vs.* shear rate for 79.87 wt.% BKBL with the loading of sodium aluminate at 98 °C

Table 1. Fitted Curve Results from the Relationship between Apparent Viscosity and Shear Rate Using the Ostwald-de Waele Model

Temperature (°C)	Solid Contents (%)	Adding Amount (%)	*K* ($Pa \cdot s^n$)		*n*		R^2
			Value	Standard Error	Value	Standard Error	
70	70.19	0	141.4920	8.1854	-0.0357	0.0255	0.99995
70	70.19	0.5	152.3808	7.5079	-0.0725	0.0217	0.99997
70	70.19	1.5	125.6336	2.2035	0.1381	0.0077	0.99997
70	79.87	0	483.7208	35.9645	0.0926	0.0329	0.99970
70	79.87	0.5	561.5352	31.0036	0.1052	0.0244	0.99981
70	79.87	1.5	427.8383	26.1830	0.2232	0.0270	0.99923
98	70.19	0	121.1451	30.4936	0.0984	0.1088	0.99673
98	70.19	0.5	182.9427	61.8542	0.1702	0.1462	0.98768
98	70.19	1.5	66.3253	3.5323	0.1935	0.0230	0.99961
98	79.87	0	329.1804	24.3539	0.1450	0.0328	0.99948
98	79.87	0.5	416.1391	34.4554	0.0853	0.0367	0.99965
98	79.87	1.5	259.2852	22.9067	0.3535	0.0390	0.99344

As shown in Table 1, the *K* values of the BKBL with 0.5 wt.% additive were greater than those of the BKBL without additive. In contrast, BKBL showed the lowest *K* values when the additive loading was 1.5 wt.%, indicating the weakest structural strength (Sandhu and Siroha 2017). Hence, using 1.5 wt.% sodium aluminate loading was considered due to its favorable effect on the flow and atomization. All *n* values were less than 1, which indicated that thick BKBL was a pseudo-plastic fluid. Furthermore, the Ostwald-de Wale model provided an ideal fitting to the experimental data with high determination coefficients (R^2 values were greater than 0.98) and could be used to accurately predict apparent viscosity changes of thick BKBL.

From what has been discussed above, it can be concluded that the BKBL, even at a high solids content, exhibited shear-thinning at 70 °C. The shear-thickening phenomenon will influence the flow stability of BKBL in pipelines. During the black liquor combustion process, sodium aluminate promoted the droplet formation of BKBL when its loading was 1.5 wt.%.

CONCLUSIONS

1. The thick bamboo kraft black liquor (BKBL) was a pseudo-plastic fluid that exhibited shear-thinning phenomena. Shear-thickening appeared when the shear rate exceeded 30 s^{-1} at 98 °C. An increased temperature resulted in the reduction of apparent viscosity.
2. The addition of sodium aluminate had only small effects on the measured viscosity of black liquor, which would not bring additionally negative effects on the transport operation in the efficient silicon removal process.
3. Sodium aluminate had no distinct influence on the apparent viscosities of BKBL at 70 °C. In the shear-thickening zone, the shear rates that corresponded to peak values would be affected when sodium aluminate was added to the BKBL at 98 °C. When the loading of sodium aluminate was 1.5 wt.%, it was conducive to the flow and atomization of thick BKBL by reducing the structural strength of BKBL.
4. The Ostwald-de Waele model could be used to accurately predict apparent viscosity changes of thick BKBL.

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