Effects of pH and Suspended Matter on the Physico-Chemical Properties of Black Liquor from Alkali-Oxygen Pulping of Rice Straw

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Black liquor (BL) can be regarded as the energy and alkali resource of the pulping mill. In this work, the effects of the characteristics of black liquor derived from the alkali-oxygen pulping of rice straw were studied. Through analyses of the chemical and physical properties, especially the thermodynamics properties, which depend on suspended matter and alkalinity, it was shown that the removal of the suspended matter from the black liquor could effectively improve its thermodynamic properties, particularly in making its solids content reach up to more than 56% at the turning point of its viscosity. Moreover, sodium salt played an important role in the presence of macromolecules and silica in the BL. When the BL was adjusted to pH = 11 with NaOH, the filtered BL had the lowest silica content, the highest volumetric isothermal expansivity (VIE), was more susceptibility to thermal cracking, and was more suitable for processing for alkali recovery.

Keywords: Rice straw; Alkali-oxygen pulping; Black liquor; Suspended matter; Thermodynamics property

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INTRODUCTION

Rice straw, as a low-cost, easily acquired, and environmentally friendly raw material, is widely abundant, especially in many developing countries. However, compared with the pulping of wood, the pulping of rice straw has many disadvantages. For instance, rice straw black liquor (BL) has a higher viscosity and a higher concentration of silica, leading to unsmooth jetting of the BL into the recovery furnace at the threshold value of BL viscosity. Unlike the concentration of 65% or more for wood BL (Belov *et al.* 2012) maintaining higher thermal capacity, the biggest obstacle is the extremely low solids concentration, commonly below 50%. Therefore, it is difficult to employ an alkali recovery process in the pulping of rice straw.

Rice straw BL is noted for a sharply rising viscosity with increasing solids content. This increase can be at least partly attributed to the presence of a large amount of silicate (Roberts 1982). Rice straw BL has the highest silica content among fiber materials commonly used in papermaking. Desilication of straw BL by means of acidification with stack gas and sulfuric acid (Xu *et al.* 2015) is considered an effective method. It can help reduce and even eliminate silicon disturbance during chemical recovery of straw BL, but the increment in the solids concentration is limited, being within 3% to 5%.

Another reason for the unique viscosity of straw BL is the presence of much more xylan (Lisboa *et al.* 2005), which could cause the viscosity of straw BL to greatly increase once evaporated to approximately 45% of the solids concentration (Zhang *et al.*

2012). Unlike troublesome and incombustible silicate, a large amount of xylan must be burnt as an important part of fuel in BL. The viscosity of straw BL could be lowered by degradation of xylan to smaller molecules with the aid of oxidation, to attain an added value of approximately 5% of the solids concentration.

Additionally, there is much suspended matter, including fines from fractured fibers and non-fibrous cells, prominent in straw BL. The fines undoubtedly have a negative impact on the recovery of BL, but eliminating them is not of vital importance because most of the fines can be recovered from BL with the help of a BL filter unit, or removed together with the precipitated silica during desilication. An integrated result of the aforementioned efforts to reduce the viscosity (Llamas *et al.* 2007) is that it is hard to make the solids concentration of straw BL reach more than 52% (Nikkanen 1993) and even lower than 50% for rice straw BL in particular. To resolve this problem, many scholars have attempted to find convenient and economic methods such as heat treatment (Louhelainen *et al.* 2002), flocculation (Chen *et al.* 2002), and coagulation (Huang *et al.* 2007) of BL from rice straw pulp. Therefore, it is still urgent to improve the performance of the alkali recovery process radically, or the properties of straw BL, compared unfavorably with those of wood BL, will always be a major impediment to the straw pulping industry.

In comparison with the BL from the traditional alkaline pulping of straw, some typical features of the BL from alkali-oxygen pulping of straw are closer to those of the former treated by both desilication and oxidation, which is known to have a reasonable silica content (Tutus and Eroglu 2004) and a lower viscosity (Tutus and Eroglu 2003). In fact, the process of alkali-oxygen pulping delignifies straw into the desired pulp, while the depositing of dissolved silica in pulp and the oxidative degradation of carbohydrates and lignin in the BL would take place almost simultaneously. This result is preferable, as alkali-oxygen pulping relieves traditional straw BL of additional treatment by desilication and viscosity reduction. Unfortunately, such a pulping method, superior to the traditional alkali pulping in both pulp quality and BL characteristics, has not yet been used as a replacement in industrial applications with real significance. One important reason is that the BL from alkali-oxygen pulping of straw is currently poorly understood.

To resolve the problems associated with silicate, many treatments have been adopted, including electrocoagulation treatment (Rastegarfar *et al.* 2015), flue gas desiliconisation (Qiu *et al.* 2006), and membrane filtration (Liu *et al*., 2004). Particularly, membrane filtration can force low-molecular weight substances such as SiO_2 and NaOH to flow through the membrane, but not the macromolecular groups or suspended matter (Hellsten *et al.* 2013). However, this method is not convenient for industrial application and is rarely used to treat BL.

Rice straw can be easily pulped with an alkali-oxygen method (Persson *et al.* 2010), which can largely reduce the silica content of the BL from straw at its end point of pulp reaction when the pH of BL is below 10 (Chen and Hayashi 1997), with the silica content being less than 0.5 g/L in the resultant BL (Chen and Hayashi 1999). But, for traditional pulp such as Soda-AQ, since the high silicon content, the viscosity of the resultant BL increase rapidly once evaporated to approximately 44% of the solids concentration (Zhang *et al.* 2012). Pulping with oxygen, in combination with sodium hydroxide, can effectively improve the properties of black liquor for alkali recycling. However, in contrast with traditional pulp BL, there still is much confusion about the BL from alkali-oxygen pulp. Hence, this study was to study how the suspended matter, as well as sodium salt, influences the properties of the BL. Much attention was paid to the relationship between the thermodynamic properties and pH environment, as well as suspended matter.

EXPERIMENTAL

As shown in Table 1, the experimental methodology consisted of determining the chemical composition, volumetric isothermal expansivity (VIE), heating value (HIV), and viscosity parameters of these liquors, which reflect their thermal characteristics.

Samples

All BL samples were separated from rice straw pulp cooked with alkali-oxygen in the Pulping and Papermaking Research Center of Yunnan Province, China, in which recovery was approximately 97%. The obtained BL had *ca.* 10% solids content, 9.26 pH, and 3 g/L SiO_2 content.

Pretreatment of the BL

Except for the part that remained as the original BL, the rest of the BL, which was retained overnight, was present in the up-layer of the supernatant and the sediment layer of the precipitate. Decanted carefully, solid precipitate was sufficiently washed and centrifuged to remove the suspended matters. The washed precipitate was freeze-dried as P1, and the supernatant, including the washed part, served as centrifuged BL. In the decanted supernatant layer, suspended matter with particle sizes greater than 0.45 μm were trapped through membrane filtration and then freeze-dried as P2 after being washed with distilled water twice. The liquid that passed through the membrane was evenly divided into four parts. Three of them were, with the addition of NaOH, adjusted to pH 11, 12, and 13 and named C1, C2, and C3, respectively. The rest (filtered BL) was saved as filtered original BL.

Physical Characterization of the BL

The heating value (HV) was evaluated using a C2000 calorimeter made by IK, a company in Germany. Following this method, a calorimetric bomb (model C-5010, IK Company, Germany) was used to determine the heat of combustion of these black liquors.

Volumetric isothermal expansivity (VIE), which expresses the quality of dehydration and expansion of carbonization, which greatly affects the combustion performance, was determined as follows: (a) the black liquor was concentrated to 40% to 60% solids content in a crucible, in which the volume is V_o (mL); (b) approximately 2 to 3 g of oven-dry sample was weighed as M (g), burned in a muffle furnace at 300 °C for 1 h, and, after cooling, weighed as G_1; (c) the crucible was filled with silica sand ρ (mL/g), weighed as G_2. VIE is defined as:

$$\mathrm{VIE} = \frac{\left[Vo-(G2-G1)/\rho\right]}{M}(mL/g) \tag{1}$$

Chemical Characterization of the BL

The methods adopted are shown in Table 1.

Table 1. Experimental Methods Used in Characterization of the Black Liquor

Property	Techniques and Equipment	Technique References
Solids content (%)	Drying of a determined mass of black liquor sample in an electric oven under controlled temperature (105 °C) until reaching a constant mass	TAPPI T650 om-15
Organic/inorganic materials (%)	Liquor combustion followed by dust analysis	TAPPI T625 cm-14
Silicon (%)	Calcined at 1000 °C after treatment with concentrated sulfuric acid and nitric acid	TAPPI T32 cm-11
HV heating value (J/g)	Heating with a complete oxidizing liquor in an adiabatic calorimetric bomb	TAPPI T684 om-11
Viscosity (η)	Viscosity measurements at various solids contents and temperatures with SNB-1 viscometer at 60rd/min rotor speed	(Zhang *et al.* 2011)
VIE (mL/g)	Concentrated black liquor total solids content to 40% to 60% take about 2 to 3 g oven dry samples burned in a muffle furnace at 300 °C for 1 h	(Wang and Cheng 1997)
TG (%/min)	Thermo-balance using a heating rate of 10 $K\cdot min^{-1}$, with nitrogen (flow rate: 55 $cm^3\cdot min^{-1}$) in the temperature range from 50 to 350 °C using a a Jupiter Thermo Gravimetric Analyzer STA 449C (Netzsch, Germany)	(Leite *et al.* 2012)

Determination of the Viscosity of the BL

The viscosity of each BL sample was determined using a SNB-1 viscometer, made by the Hengping Company in China. By evaporating the BL in a beaker set in a hot water bath with the help of continuous stirring, each sample was concentrated to the solids content at which its viscosity reached more than 400 mPa·s. The values of the viscosity corresponding to *ca*. 20%, 30%, 40%, 50%, and 60% of the solids content were recorded at 50, 60, 70, 80, and 90 °C on the viscometer, respectively. Because of the rapid increase that occurred at *ca*. 50% to 65%, more points were adopted in this range.

RESULTS AND DISCUSSION

The thermal properties of BL correlate with all aspects of BL's characteristics to varying degrees. Research on the BL from alkali-oxygen pulping of rice straw has mostly focused on the proportions of inorganic and organic material in the solid, which are closely relevant to its calorific value, the effect of alkalinity and suspended matter in its viscosity variation, thermolysis, and other thermal properties.

The inorganic and organic contents of the BL are shown in Table 2. The composition, both inorganic and organic, expressed as the mass percentage of this content to total dry solids, and SiO_2, expressed as the mass percentage of this content to inorganic, were obtained from a series of (at least) two tests, with a standard deviation lower than 5%.

Table 2. Characteristics of the Black Liquor

	Inorganic content (%)	Organic content (%)	Organic/Inorganic	SiO_2 (%)	VIE (mL/g)	HV (J/g)
The stock solution						
pH = 11	25.08	74.92	2.99	2.60	5.69	9766
pH = 12	25.50	74.50	2.92	3.09	5.04	9623
pH = 13	28.44	71.56	2.52	3.04	4.72	9322
original BL	24.32	75.68	3.12	2.39	5.80	9839
After removing suspended matter						
pH = 11	25.46	74.54	2.93	0.59	24.66	9753
pH = 12	27.60	72.40	2.62	1.10	17.11	9539
pH = 13	36.61	63.39	1.73	2.10	7.95	8877
original BL	26.32	73.68	2.80	1.19	16.23	9609

Relationship of HV of the BL to Its Inorganic and Organic Content

The original BL shown in Table 2 had 75.68% organic content and 2.39% SiO_2. The higher proportion of organic material in the solids and lower silica content, compared with those from traditional alkali pulping of rice straw, were essentially in agreement with the results previously reported for alkali-oxygen pulping of rice straw. As shown in Table 2, the variation of the mineral material percentage in the solid was consistent with the pH, with the exception of an opposite trend of silica content.

It is well known that filtration can remove suspended matter such as fines from pulp, as well as insoluble mineral particles such as silica and insoluble macromolecules like lignin and carbohydrates. On one hand, different pH environments affect the filtration and change the BL’s characteristic. First, the addition of NaOH gave the BL a slight increase in inorganic content. After the removal of suspended matter, as more NaOH was added, the inorganic content increased to a larger extent. However, compared with the stock solution without adjusting the pH environment, the pH 11 sample showed unexpected results: the inorganic content of the stock solution at pH 9.26 increased by approximately 2%, but it only increased by 0.38% at pH 11. Second, from the results shown in Table 2, the most important change was what happened to the silica content after removing the suspended matter. Silica content decreased by 77% at pH 11, 64% at pH12, and 30.92% at pH 13. Third, the trend for the organic material was inverse to that for the inorganic material.

On the other hand, compared with the BL after removing suspended matter, the stock solution’s HV decreased by approximately 10%. Notably, among BL samples at various pH environments, the BL at pH 13 after filtration showed unusually low organic proportion, being approximately 6% below normal, as in the case of the BL before filtration. Correspondingly, its HV was also extraordinarily low (8.877 kJ/g). Based on the HV of the BL before filtration, the heat losses after filtration appeared to decline from pH 11 to 13, being 0.13%, 0.87%, and 4.8%, respectively. If the ratio of HV loss to organic loss is thought of as being heat capacity per gram of the lost organic matter, the corresponding values were 0.34, 0.41, and 0.59 J/g, respectively. In short, its heat capacity increased with increasing loss of organic material. This implies that some lignin was prone to being filtered out of the BL because it had a much higher heat capacity than other organic materials, such as carbohydrates, in BL.

In the filtered BL samples, when tests were carried out at pH 11, only a minute amount of the organic content was separated from the solution. This can interpreted as indicating that almost all of the organic content in the BL had passed through the membrane filter. The greater removal of the organic material from the solution phase of the original BL after filtration could be explained by the formation of some lignin precipitate because of its lower pH. But such an explanation does not account for the fast increase in lignin removal from solution as the pH increased to over 12. A rational explanation for this is that the membrane made of mixed cellulose ester might start to swell as soon as the alkalinity of the BL became strong enough. Such swelling is bound to result in the constriction of the membrane pores, although this action is probably very limited. Thus, part of the soluble lignin macro-molecules smaller than 0.45 μm would be trapped on the membrane, even if the pores of the membrane had a delicate construction. This may be the reason why so much loss of the organic material in the BL occurred at pH 13.

Relationship of VIE of the BL to its SiO_2 and Organic Contents

The VIE represents the thermal expansion magnification of the BL solid. As the VIE increases, the burning efficiency of the solid also increases. The VIE values in Table 2 reveal three evident characteristics. First, lowering the silica content could greatly reduce interference with the thermal expansion of the BL solid. The maximum VIE (24.7 mL/g) was obtained at the minimum silica content (0.59%), being more than four times that of the unfiltered BL. Then, a higher organic proportion in the solid could increase the VIE to a certain extent. Finally, addition of soda to the BL would have a limited negative impact on the thermal expansion of the BL solid.

Overall, the relationship between the VIE and the composition in the BL is very complicated. It is hard to correlate the amount of silica or organic content, *etc*., in the BL with its VIE quantitatively. However, there seems to be a critical point or region of the silica content that could cause a sharp rise in the VIE. Compared with the slow increase of the VIE value beyond 2% silica content, the value halving the silica in the original BL could nearly triple its VIE. In the recovery boiler, higher than 2% silica content could make trouble for the thermal expansion of BL for burning. Compared with silica, the effects of the inorganic and organic materials on the VIE of the BL was the opposite, but the impact magnitude originating from them could not be described only by the available data and should be further studied.

Based on the aforementioned data, it is clear that inorganic materials could affect the thermodynamic properties, and the silica content had a particular negative impact on the VIE of the BL. The rate of organic to inorganic (I/O) content of the BL was positively proportional to its HV. In addition, different pH environments had different effects on the thermodynamic properties of the BL. Moreover, adjustment of the pH environment to 11 with NaOH would largely improve this thermodynamic character. However, addition of more sodium hydroxide, to pH =13, increased the inorganic content of the BL, which caused the HV to decrease even more than others.

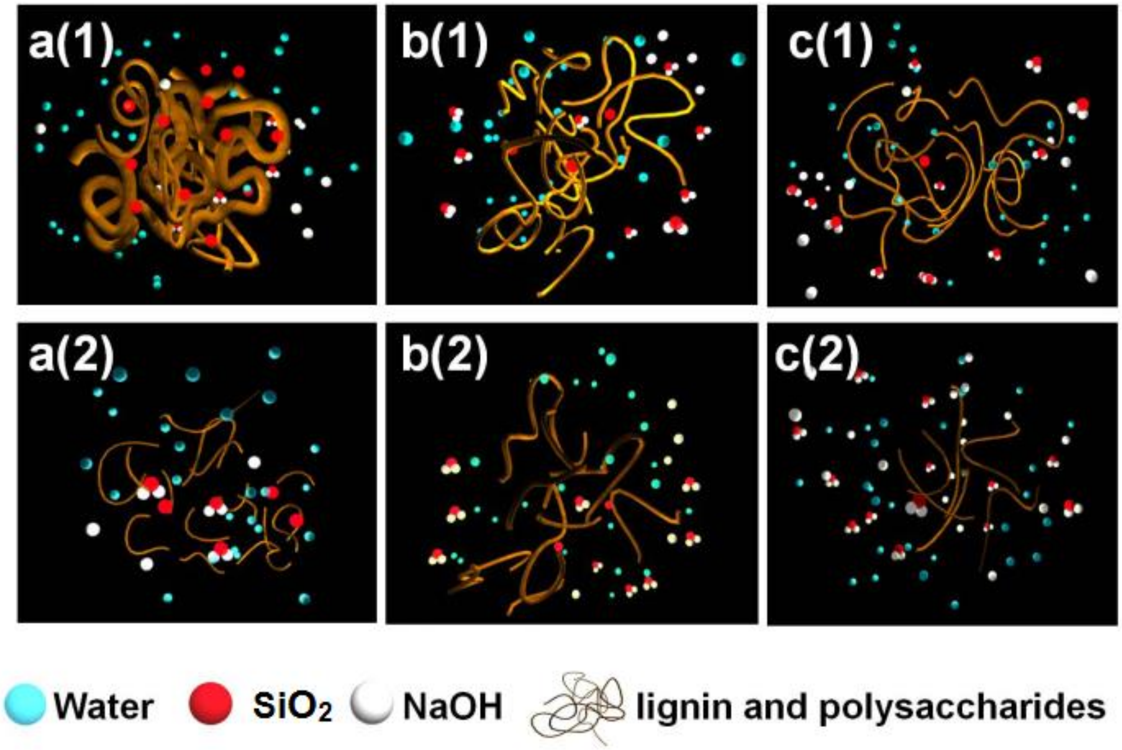

Fig. 1. A diagram of the existence of macromolecules and silica dependent on alkalinity in the BL. Parts a, b, and c show BL at pH 11, 12, and 13, respectively; (1) and (2) are the original BL and filtered BL, respectively.

On the basis of the data in Table 1, the existence of macromolecules and silica in the BL under various alkalinities are graphically displayed in Fig. 1. Cardoso *et al.* (2009) characterized the existential state of lignin and carbohydrate polymers in black liquor, which are intertwined with salt ions and water in a very intricate way. As shown in this figure, SiO_2 is involved in the BL, serving as the adhesives of the connection, and is distributed among the gaps of the lignin and polysaccharides. Silica combines with NaOH to dissolve in the liquor, which loosens the connection. As a result, the filtered BL with the maximum addition of NaOH at pH 13 showed the highest silica and inorganic contents, directly resulting in a large decrease in its HV. Although high-molecular weight of lignin as well as polysaccharides could filter through, this still cannot account for the substantial heat loss.

In addition to influencing the silicon and inorganic contents, NaOH also has an effect on the structure of lignin, which has been shown by Frederick (1987): when pH > 12.5, phenol groups are ionized and the lignin structure becomes soluble, forming compact and spherical structures; when 11.5 < pH < 12.5, partial lignin dissolved in the BL and shapeless and voluminous chains structures are formed. Morphological changes in lignin in the BL from pH 11 to 13 should follow this pathway. As shown in Fig. 1, the lignin at pH 13 would become slenderer and unconstrained.

Effect of Temperature and Solid Content on the Viscosity of the BL

Viscosity variation of the original BL with or without precipitate

The viscosity of BL is a key indicator of alkali recovery because it may dictate the maximum value of solids content of BL. Normally, BL injected into the recovery furnace would have a viscosity of 300 to 500 mPa·s at approximately 105 °C (Adams and Frederick 1987) to keep it spraying smoothly. Under this premise, the solids content should be concentrated to the maximum possible to increase the heat efficiency of the furnace to the utmost. It is, in general, desired that BL in the furnace should contain more than 50% solid content to ensure an acceptable heat recovery efficiency of the alkali recovery system, or else fuel such as additional heavy oil should be added to compensate for the low heat value of the BL. Unfortunately, it is not an easy thing for the concentration of the solid content of straw BL to reach 50% or more (Zhang *et al.* 2012).

As for the BL from alkali-oxygen pulping of rice straw, a relationship between the viscosity and solid content of the BL was investigated at temperatures from 50 to 90 °C. Figure 2 is the curve of the viscosity *vs*. the solid content of the original BL.

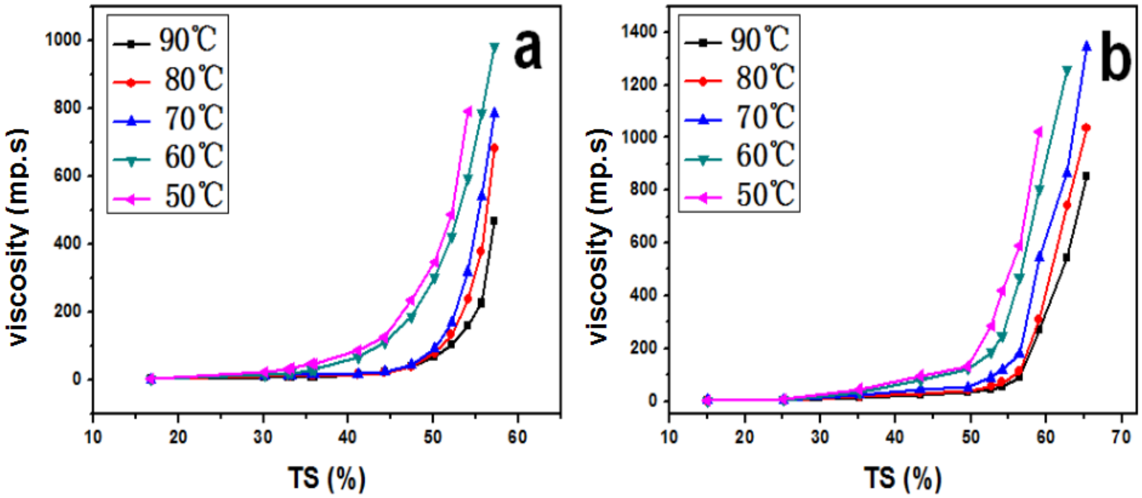

Fig. 2. (a) Apparent viscosity of original BL at various total solid concentrations (TS) with various temperatures; (b) apparent viscosity of BL after removing suspended matter at various total solid concentrations (TS) with various temperatures

It is clear that the viscosity of the BL increased very slowly until it reached 45% solid content. When temperature reached 70 ºC, the viscosity appeared low, even at the high solid content. A further increase in the solid content *ca*. 50% resulted in a rapid increase of viscosity at 50 ºC to 70 ºC but still gentle rising at 70 ºC to 90 ºC. There always was a turning point, no matter which temperature the curve was from.

The BL in Fig. 1 contained a certain amount of precipitable suspended matter. The viscosity variation of the BL, which loses this precipitate after centrifugation and filtration, is presented in Fig. 2. In comparison with Fig. 1, the most significant result is that not only did the viscosity of the BL decrease at the same solid content, but the turning point of the viscosity occurred later at about 52.5%. It is conceivable that removing the precipitable suspended matter would alleviate thermal mass flow resistance, as the flow of the BL as a fluid becomes easier without the interference from rigid granules with it.

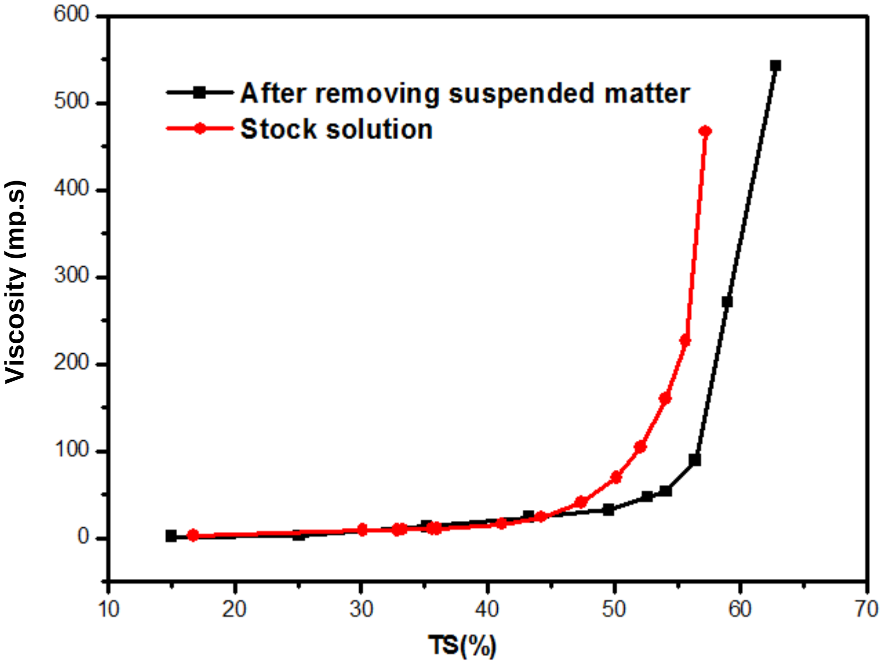

Fig. 3. Apparent viscosity of BL at various total solid concentrations (TS) with T=90 °C

Moreover, to study the behavior of BL during the industrial alkali recovery, the curves of the viscosity at 90 °C, which is the closest to the true state of the industrial process, were chosen for comparison. Similar to Fig. 1a and b, the turning point of viscosity from Fig. 2 has largely increased from *ca*. 50% to 56%, which are both beyond the BL solid content, within 45%, of traditional straw pulping (Liu *et al.* 2013). Additionally, the filtered BL appeared to have better viscosity properties than the stock solution, as the turning point of BL occurred at *ca*. 50% and 57%, respectively.

Viscosity variation of the BL pH-adjusted with NaOH

Traditional BL in alkali recovery displays an alkalinity, in which the pH is often beyond 11 without the addition of extra caustic soda. The pH of the BL from alkali-oxygen pulping is usually lower than the former (Cao 2002). Because of the neutralization of organic acid produced by oxidation in pulping with NaOH, the pH of pulp environment reduce. Whether adjusting the original BL pH with or without addition of NaOH could cause different operation in alkali recovery, which is worth discussing.

The decanted supernatant after natural sedimentation for an overnight was separately adjusted into three BL samples with pH = 11, 12, and 13 with solid NaOH, to observe the effect of OH^{-} ions on the BL. Also, the BL was passed through a 0.45-μm membrane filter. Figures 3(a), (b), and (c) present the variation of the viscosity with solid contents at pH = 11, 12, and 13, respectively. In brief, these tests all showed similar viscosity trends.

As expected for both liquors, the viscosity increased slowly until 51% TS, above which point the viscosity increased rapidly. This result agrees with the results related by Frederick *et al.* (2004), in which low TS, < 50%, may lead to the appearance of Newtonian fluid mechanics characteristics, while liquor would change to non-Newtonian fluid mechanics properties when TS > 50%. The point at which viscosity turns rapidly is very important for industry, especially for alkali recycling.

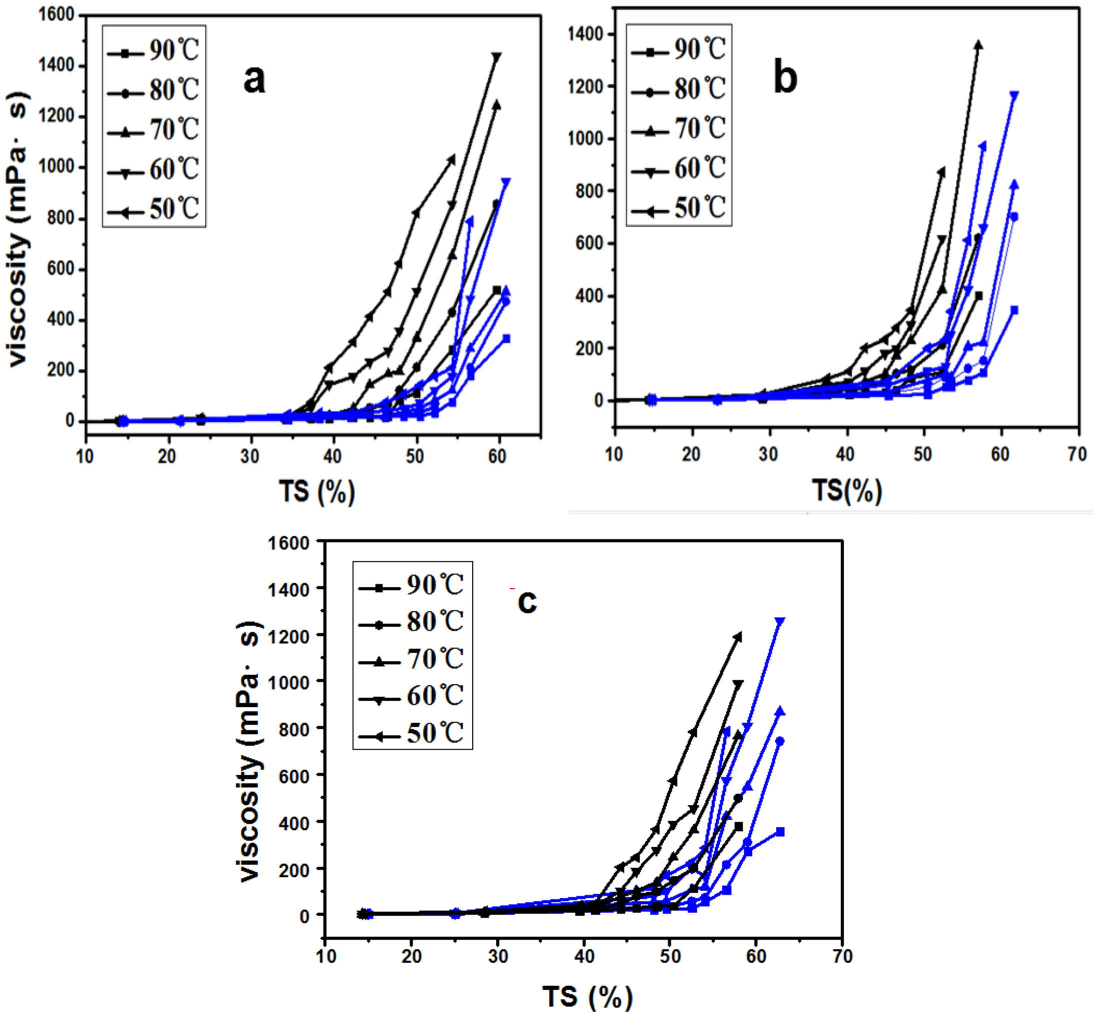

Fig. 4. The viscosity of BL adjusted to different pH environments (pH = 11 (a), pH = 12 (b) and pH = 13 (c)) with various total solid concentrations (TS) at given temperatures. In all samples, the black is for stock solution and the blue for solution after removing suspended matter.

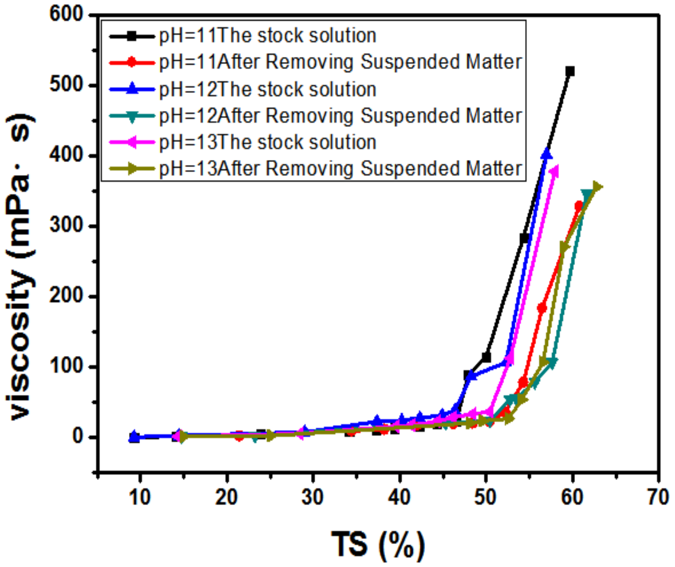

Fig. 5. Apparent viscosity of BL at various total solid concentrations (TS) at 90 °C

Note that the turning point of BL that removed suspended matter over the size of 0.45 μm appeared at the higher solid content at the same temperature compared with the stock solution. The reason for the improved viscosity of the BL should be attributed to the elimination of the interference from the rigid granules, as stated above. The presence of the smaller particles appeared at a higher kinetic energy as the temperature increased, with the result that the viscosity of the infiltrated BL at 90 °C approached that without the tiny suspended matter under the same conditions. It is conceivable that the difference in viscosity between the two might become smaller if the BL is heated to *ca*. 105 °C in commercial evaporation units.

There, of course, existed some difference among a, b, and c in Fig. 3. The increase in pH from 11 to 13 could narrow the gap of the solid content between 50 and 90 °C at the same viscosity. This means that increasing the alkalinity could help increase the viscosity of the BL, which is especially effective for the BL at lower temperatures. However, considering that the three factors pH, T, and suspended matters, which all impact viscosity, were simultaneously changeable merely by changing pH, it is difficult to state that a proper alkalinity is worth recommending.

According to the aforementioned results, for the BL from alkali-oxygen pulping of rice straw, it can at least be said that there is no need to worry about bottlenecks existing in traditional straw pulping. The BL obtained from traditional straw pulping is difficult to evaporate to more than 50% TS, while the BL of alkali-oxygen pulping of rice straw has approximately 60% TS. Such a large increase in TS may be ascribed to the deposition of silica in the BL onto pulp fibers and oxidative degradation of the organic substances in the BL during alkali-oxygen pulping, then removal of precipitable granules by natural sedimentation and the subsequent membrane filtration of 0.45-μm fines, which facilitated a TS of up to 60%. Even without membrane filtration, natural sedimentation caused BL TS to reach 56%. Thus, many drawbacks associated with traditional straw BL, for example, silicon interference and the addition of extra heavy oil, should not occur in alkali recycling of the BL from alkali-oxygen pulping of rice straw.

It should be pointed out that the reason for the apparent effect of the precipitable granules and fines in the BL on its viscosity is complicated. Compared with other components like ash, xylan, and fines, SiO_2 must have a greater impact on viscosity. In a wet colloid, surface of the silica particles contains silanol groups (Si-O-H) and silica particles and lignin molecules are connected to form hydrogen bonds (Zhang *et al.* 2013). As the content of SiO_2 increased, the number of the colloid groups increased, which made the viscosity of BL increase rapidly.

On the other hand, with the addition of NaOH, creation of the colloid in the BL would be more difficult because the partial dissolution of the SiO_2. As a consequence, addition of the NaOH has an effective influence on BL and this paper has given a general range, but the correct identification of its optimum pH point still needs to be studied in the future.

TG Analysis

Based on connection of the solid content with viscosity of the BL from alkali-oxygen pulping of rice straw, there should be a basic understanding of the thermal decomposition of the BL. The results of thermo-gravimetric analysis (TGA) of BL, which is a method to explore the thermodynamic properties, are shown in Figs. 6, parts (a) and (b). In this figure, the mass loss from both the original BL and the filtered BL occurred between 50 °C and 150 °C and between 225 °C and 300 °C. In the first temperature range, the DTG peaks primarily resulted from loss of water and the escape of many labile groups through decomposition (Bassilakis *et al.* 2001). In the second temperature range, the DTG peaks were primarily caused by the pyrolysis of the organic groups of lignin, polysaccharides, *etc*. (Jiang *et al.* 2010). Therefore, more attention should be paid to the variation of mass loss in the later range, which displayed the pyrolysis properties of main organic group lignin.

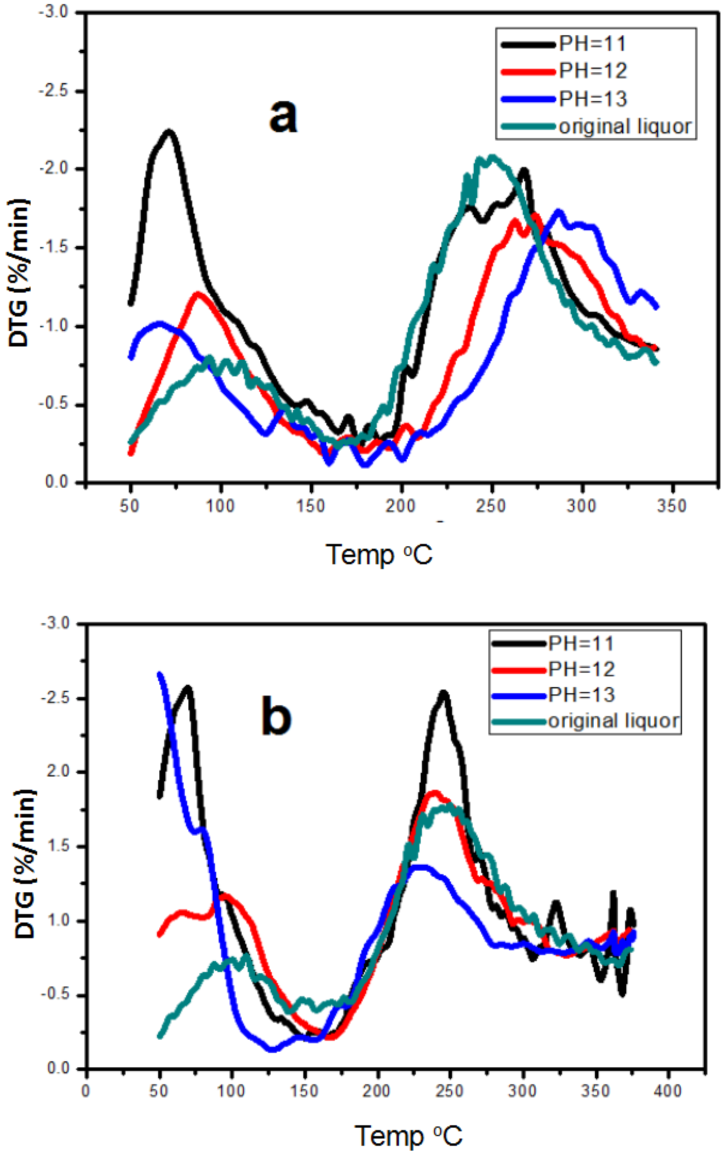

Fig. 6. TG curves with derivative mass loss of black liquor samples at a heating rate of 10 Kmin^{-1} in different pH (11, 12, 13); (a) organic BL; (b) that filtered by 0.45-μm micro-filtration membrane

From the peak points in Fig. 4 (see also Table 3), it is clear that with an increase in pH, the values of the stock solution's temperature increased from 250.4 to 278.4 °C. In contrast, the filtered BL appeared with lower temperatures, around 242 °C with an exception of 235.4 °C at pH = 13, whose inorganic content increased by 10% after filtered. The appearance of such an unusual temperature may result from catalytic effects of sodium compounds in black liquor during pyrolysis (Kuang *et al.* 2008). In addition, the DTG of the filtered BL slightly decreased, but that at pH = 11 increased to the maximum (-2.61%/min).

Table 3. The Peak Point of the DTG Curves of Stock Solution and Filtered BL

Peak point of the DTG	Stock solution		After filtered	
	T (°C)	DTG (%/min)	*T* (°C)	DTG (%/min)
Original liquor	250.4	-2.2	243.3	-1.86
pH = 11	267.5	-2.0	242.4	-2.61
pH = 12	273.6	-1.71	242.4	-1.51
pH = 13	278.4	-1.71	235.4	-1.51

The aforementioned performance of the thermodynamic properties were, to some extent, consistent with the VIE (see also Table 1) on the index used to evaluate the thermal expansion, which was determined above. Nor did the VIE of the filtered BL rapidly increase, but the maximum DTG, -2.61%, originated from the filtered BL at pH 11 with the maximum VIE of 24.66 mL/g. This means that the thermal expansion of the BL affected its decomposition rate. Furthermore, there did not seem to be any apparent connection between the peak point and the addition of NaOH until pH 12, as the values of the BL after filtration were similar, at *ca*. 243 °C in Table 1. An over-dosage of NaOH to pH 13 in the filtered BL would, however, help to accelerate the thermal decomposition of the organics. A large difference of *ca.* 20 °C in the peak point between the BL before and after filtration probably correlated with the existing magnitude of silica to a significant degree. Research by Miller *et al.* (1989) and Xu *et al.* (2015) shows that silica has a direct impact on the thermodynamic properties. Combining the peak points of the DTG curve in Fig. 4 with silica content in Table 1, there should be a level value of silica content in BL, at approximately 2.6%. When the silica content was greater than this value, the peak point of the decomposition temperature increased rapidly, *i.e.*, the pyrolysis of the BL became difficult with increasing silica. Because the thermal decomposition is sensitive to the existing magnitude of silica in BL, a reasonable explanation should be further studied.

CONCLUSIONS AND FURTHER WORK

From the assessment of the BL from alkali-oxygen pulping of rice straw, it can be inferred that suspended matter and pH affect the thermodynamics property obviously.

1. The black liquor after removing suspended matter had better quality than the original, possessing low SiO_2 content, larger VIE, a turning point of viscosity up to 55%, and a negligible loss of HV, reduced less than 5%.
2. Different alkalinities had different effects on the properties of the black liquor. Adjusted to pH = 11 with NaOH, the filtered BL appeared to have the lowest silica

content, highest VIE, and greater susceptibility to thermal cracking, which is more favorable for the alkali recovery on the premise that DTG has lightly increased.

3. The large increment of *ca.* 10% of TS and the outstanding improvement of the thermal properties for the BL should owe much to the oxidative degradation of organics during alkali-oxygen pulping, the significant reduction of silica, which is mostly deposited on the pulp, and the removal of suspended matter through filtration. Combined alkali-oxygen pulp and removing suspended matter could indeed decrease the troubles encountered like in alkali recovery of the BL from traditional alkaline pulping of straw.

ACKNOWLEDGEMENT

This research was supported by the National Natural Science Foundation of China (21276119).

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Article submitted: August 12, 2015; Peer review completed: February 18, 2016; Revised and accepted: March 1, 2016; Published: March 24, 2016.
DOI: 10.15376/biores.11.2.4252-4267