KINETICS OF BAGASSE DELIGNIFICATION BY USING HIGH-BOILING SOLVENT

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Kinetic modeling of lignin removal under conditions of high-boiling solvent (HBS, i.e. 1,4-butanediol) auto-catalyzed pulping of bagasse has been studied. The experimental data were collected based on the absorption of dissolved lignin in black liquor at a wavelength of 320 nm, which can eliminate the interferences arising from furfural (F) and 5-hydroxymethyl furfural (HMF) generated during pulping. The results indicated that the delignification process consists of two distinct phases. The initial phase, involving a very fast reaction, is followed by a rather slow second phase. The delignification equation was determined as: $D=87.71\times C^{0.8982}\times (1-e^{-1.757t})\times 100\%$, which is valid within an HBS concentration range of 50% to 80% and can be used for predict the lignin removal from bagasse by HBS pulping.

Keywords: Black liquor; Delignification; High-boiling solvent; Bagasse

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INTRODUCTION

Bagasse, the byproduct of refining in the sugar industry, is one of the main herbaceous plant resources that is produced in large quantities worldwide every year (Xu et al. 2006). However, only a very small portion of the bagasse is reused to produce high-valued product, such as paper and bio-based products (Lei et al. 2010). A large amount of non-wood fiber has been burnt in the fields or on the road, and pollutants are released (Sun et al. 2002). Utilization of such agricultural residues for industrial products has potential advantage, especially for such low-cost and large quantity feedstocks. It is even more important for countries that lack of wood fiber (Rainey et al. 2009).

Traditionally, the environmental problems caused by chemical pulping, including soda-AQ pulping and kraft pulping, are difficult or expensive to avoid (Hamzeh et al. 2009). This is mainly due to the high content of ash and silicon in the non-wood materials. During the alkali pulping process, these elements can become co-dissolved with lignin into the spent liquor and cause deposits, lowering the coefficients of heat transfer, and causing pipeline blocking (Huang et al. 2008). To abate these problems, lots of effective methods have been tried (Hedjazi et al. 2008; Shukry et al. 2008).

Pulping processes utilizing organic solvents as cooking media, such as the Organocell process (Dahlmann et al 1990; Schroeter 1991), Alcell process (Ni et al 1998; Zhang et al. 1998), ASAM processes (Sheng et al. 2008; Al-Dajani et al. 2010), and

NAEM (Lohrasebi et al. 2001), have a long history and have achieved commercial or pre-commercial scale. The promise of value-added products from dissolved lignin and hemicelluloses has captured researchers' attention. Advantages for such processes include the simplicity of recovery, a lower silicon content in black liquor (Lavarack et al. 2005; Pasquini et al. 2005; Ruzene et al. 2009), and no requirement for a complex and expensive recovery boiler and lime kiln. Therefore, it is safe to believe that the organosolv pulping is an alternative to overcome problems related to chemical pulping methods.

The high-boiling solvent considered in this work is a newly developed aqueous solvent that can be used as delignification agent for raw materials (Kishimoto et al. 2001). The superiority of this solvent is due to its high boiling temperature (1,4-butanediol, 232 ^{o}C) and the lower pressure generated in the reactor during pulping. The delignification mechanism during HBS pulping has been studied thoroughly (Kishimoto et al. 2001, 2002, 2003a,b). However, there are few reports on the delignification kinetics during HBS pulping.

The objective of this paper is to elucidate the process of lignin removal during HBS pulping by a series of laboratory experiments using 1,4- butanediol/water media. Finally, a kinetic model for delignification was developed to predict the extent of delignification.

EXPERIMENTAL

Chemical Composition of Bagasse

The bagasse used in this study was received from Nanning City, Guangxi Province, China. Before pulping, the bagasse was screened, air-dried at room temperature, and stored in a polythene bag. Typical chemical compositions of the bagasse were analyzed according to China National Standards (GB), giving the following results: a moisture content of 7.82% (GB/T 2677.2-1993), a soluble content in ethanol-benzene of 1.94% (GB/T 2677.6-1993), lignin content of 21.0% (GB/T 2677.8-1993), and a pentose content of 21.1% (GB/T 2677.9-1994), respectively.

Pulping Process

The pulping was conducted in batch mode in a high-pressure stainless steel vessel. The desired temperature in the reactor was maintained with a thermo-stated oil bath. The bagasse to liquor ratio was 1:10 (oven dry bagasse and cooking liquor). The solvent systems used were 50/50, 60/40, 70/30, and 80/20 1,4-duanediol/water (v/v). The cooking time was varied from 10 to 210 min. The cooking temperature was fixed for all samples at 190 ^{o}C.

The digester was heated up using an oil bath to the desired temperature, and then the digester loaded with raw material was immersed. After the desired cooking time was reached, the vessel was removed immediately from the thermal oil bath and cooled under cold tap water. Then the spent cooking liquor was separated and collected by filtration.

Apparatus and Chemicals

A UV-Vis spectrophotometer (HACH DR5000, equipped with a 1-cm path length flow cell) was used for the absorption analysis.

All chemicals used in the experiments were from commercial sources.

RESULTS AND DISCUSSION

Analytical Method

The lignin content in the black liquor from HBS pulping was determined using UV spectroscopy according to the literature (Pasquini et al. 2005). The purified HBS lignin and F and HMF were prepared for the UV-vis spectroscopy, and results are shown in Fig. 1.

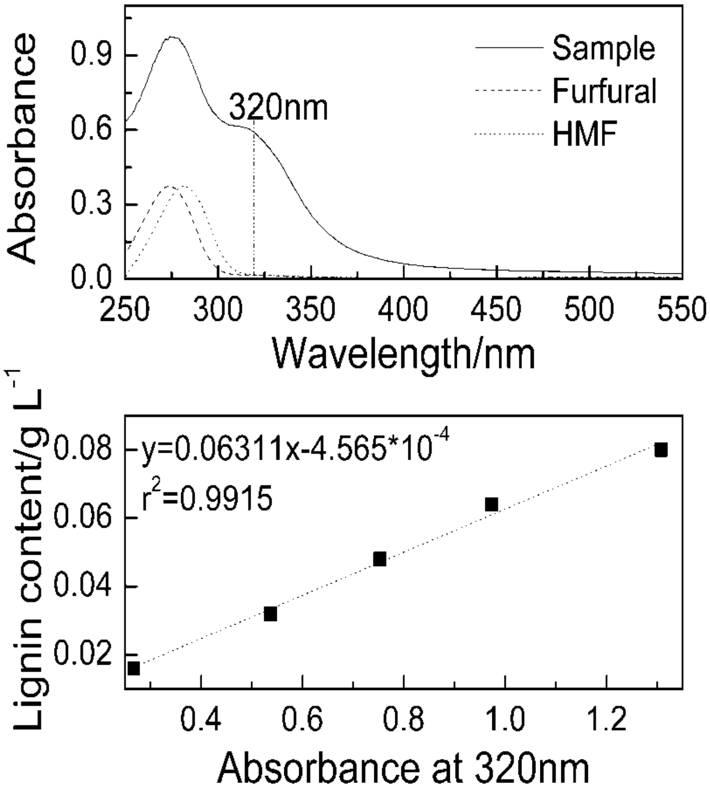

Fig. 1. spectra of lignin and F and HMF, and curve plot of lignin

It well known that furfural (F) and 5-hydroxymethyl furfural (HMF) are generated during pulping with HBS (Tu et al. 2008). As shown in Fig.1, both F and HMF absorb in the range 250 to 310 nm, which will interfere lignin absorption. However, a wavelength of 320 nm showed the absorption by lignin only, thus avoiding the interference from F and HMF. Therefore, the lignin content in black liquor can be determined at this wavelength.

The absorbance response plot for lignin determination was carried out by varying purified HBS lignin concentration in HBS solvent as shown in Fig. 1. The extent of delignification was determined according to Eq. 1,

$$D = \frac{[L]_1}{[L]_T} \times 100\% \tag{1}$$

where $[L]_1$ is the lignin content in black liquor, $[L]_T$ is the total lignin content in the raw material, and D is the extent of delignification.

Delignification Kinetics in the Black Liquor of HBS Pulping

To quantify the dissolved lignin content and investigate delignification kinetics in the black liquor during HBS pulping, a series of pulping tests were conducted under the conditions described above. The experimental parameters examined included reaction time and HBS concentration. The black liquor was collected and measured as described earlier.

The results shown in Fig. 2 indicate that dissolved lignin in black liquor increased steadily as HBS pulping proceeded under the conditions studied. When the applied HBS concentration increased from 50% to 80%, the delignification increased by more than 60%, suggesting that the HBS concentration has a profound impact on the extent of delignification. At the end of HBS pulping, the delignification typically ranged from 45% to 75% of total lignin in the raw material.

Most of the lignin removal occurred in the range 10 to 90 min of pulping. By extending pulping time to 210 min, the rate of delignification was decreased. The pulping conditions were divided into two phases, comprising an initial quick phase and a later slow phase, which is in agreement with the literature (Tu et al. 2008).

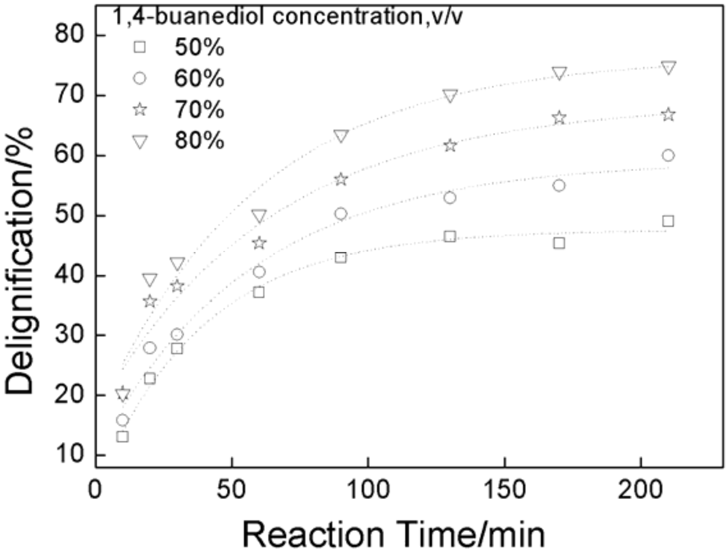

Fig. 2. Effect of reaction time and HBS charge on the lignin concentration

Kinetic Model Development

HBS pulping is a complex process, which includes mass transfer of HBS into the raw material and heterogeneous chemical reaction between different material components and the chemicals (Tu et al. 2008). The following apparent kinetic mechanism for dissolved lignin is proposed,

$$L_0 + HBS + H_2O \xrightarrow{k_1} L_1 \tag{2}$$

where L_0 is the lignin content, *HBS* is 1,4-butanediol solvent, and L_1 is the lignin content in black liquor.

From Eq. 2 the kinetic equation of delignification for HBS pulping can be derived as follows,

$$v_L = \frac{d[L]_1}{dt} = k_1 [L]_0{}^n C^m \tag{3}$$

where v_L is the rate of delignification, $[L]_1$ is the dissolved lignin concentration in the black liquor (g.L^{-1}), $[L]_0$ is the proto-lignin concentration (g.L^{-1}), C is the HBS concentration during pulping (%), K_1 is the rate constant of the chemical reaction ($K_1=f(1/T)$, g.L^{-1} min^{-1}), t is reaction time, and n and m are the power of each parameter.

During HBS cooking of delignification, the concentration of HBS in the cooking liquor was kept constant, it can be simplified as k_2 shown in Eq. 4; therefore, Eq. 3 can be simplified as Eq. 3a with Eq. 4,

$$\frac{d[L]_1}{dt} = k_2 [L]^n = k_2 ([L]_T - [L]_1)^n \tag{3a}$$

$$k_2 = k_1 C^m \tag{4}$$

where $[L]_T$ is the total content of lignin in raw material. Integrating Eq. 3a, one can obtain Eq. 5:

$$\int_0^{[L]_1} \frac{d[L]_1}{([L_T] - [L]_1)^n} = \int_0^t k_2 dt \tag{5}$$

Delignification by HBS has been interpreted as a first-order reaction in the literature (Kishimoto and Sano 2001). Thus, Eq. 6 can be derived from Eq. 5:

$$[L]_1 = [L]_T (1 - e^{-k_2 t}) \tag{6}$$

Additionally, the HBS concentration has the major effect on dissolved lignin, as shown in Fig. 2. Higher concentrations of HBS, in the range of 50% to 80%, resulted in more lignin removal.

Therefore, a concentration term of HBS should add to the Eq. 6, and the rate of delignification can be described from Eq.1 and Eq. 6 as follows,

$$D = K \times C^{a} \times \frac{[L]_1}{[L]_T} \times 100\% \quad (7)$$

where C is the HBS concentration, and "a" represents the exponent of C. Substituting Eq. 6 into Eq. 7, the following expression is obtained:

$$D = K \times C^{a} \times (1 - e^{-k_2 t}) \times 100\% \quad (8)$$

Using the experimental data, the least-square estimated of the parameters in Eq. 8 were estimated using nonlinear procedure of curve fitting toolbox in Matlab (R2010b, The MathWorks, Inc.). The fitting result is shown in Fig. 3.

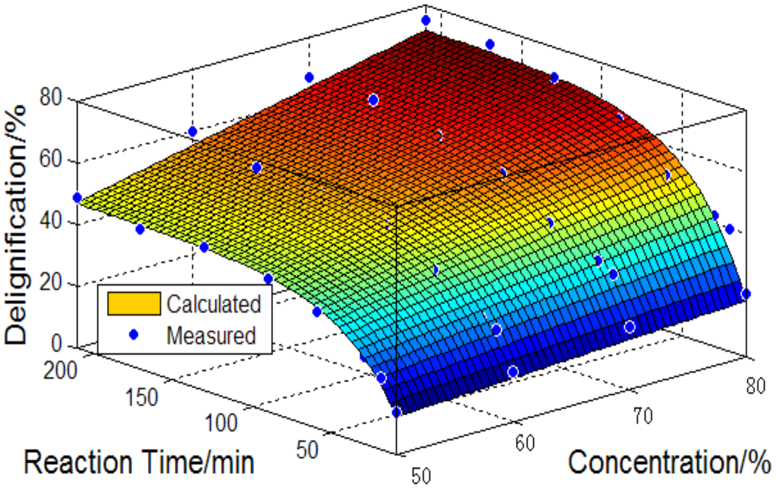

Fig. 3. Delignification as a function of reaction time and concentration; fitting results by Matlab

The plot shows that the model based on Eq. 8 fit the measured data very well (see Fig. 3). The parameters of K, a, and k_2 were 87.71, 0.8982, and 1.757, respectively, and R-square for this estimation was 0.9539.

Model Applications

In the HBS pulping process, the extent of lignin fragments removal and carbohydrate degradation was increased with elevated HBS concentration and prolonged cooking time, according to the experiment conditions. The delignification model is illustrated in Fig. 3.

As shown in Fig. 4, a linear regression was applied to estimate the parameters of the mathematical model based on Eq. 8. The regression coefficient of 0.9571 was calculated. Therefore, this kinetic model derived experimentally can be used to predict the lignin removal of bagasse in the HBS pulping within a range of 50% to 80% of HBS solvent. The good linear correlation between the model predictions and 32 independent experimental results supports the validity of the model, providing evidence of its suitability for application. With this model, the lignin content in the black liquor can be predicted from the cooking condition.

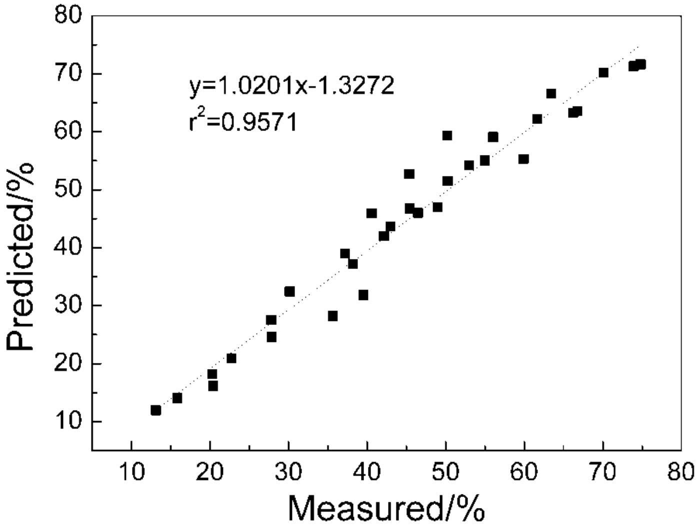

Fig. 4. Measured and model predicted delignification in the black liquor of HBS pulping

It has to be pointed out that the coefficients and constants of the developed model obtained were from the experimental data of HBS in the concentration range of 50% to 80%. However, further increases in the concentration to 90% resulted in the delignification decreasing rapidly, according to our experiments, which may caused by the lower value of $[H^+]$ (Tirtowidjojo et al 1988). Therefore, one needs to re-calculate the parameters when solvent concentrations are beyond this range.

CONCLUSIONS

The pulping of bagasse in autocatalyzed HBS (i.e. 1,4-buanediol media) lead to extensive delignification under the following conditions: 80% (v/v) aqueous 1,4-buanediol at a ratio of solid to liquor ratio of 1:10, temperature at 190 °C, and pulping time of 90 min. The typical delignification process is clearly characterized by an initial fast phase, followed by a slow second phase of delignification. A kinetic model of lignin dissolution by HBS was proposed and justified as follows: $D=87.71\times C^{0.8982}\times(1-e^{-1.757t})\times 100\%$.

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