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Fundamental understanding of distracted oxygen delignification efficiency by dissolved lignin during biorefinery process of eucalyptus

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ABSTRACT

In this work, a fundamental understanding of oxygen delignification distracted by dissolved lignin was investigated. In the new biorefinery model of shortening kraft pulping integrated with extended oxygen delignification process, increasing content of residual lignin in the original pulp could result in enhanced delignification efficiency, higher pulp viscosity and less carbonyl groups. However, the invalid oxygen consumption by dissolved lignin could be increased with the increase of process temperature and alkali dosage. The normalized ultraviolet absorbance (divided by absorbance at 280 nm) also showed that the content of chromophoric group in dissolved lignin decreased with oxygen delignification proceeded, both of which indicated that dissolved lignin could enhance the invalid oxygen consumption. Therefore, a conclusion that replacement of the liquor at the initial phase of oxygen delignification process would balance the enhancement of delignification efficiency and invalid oxygen consumption was achieved.

1. Introduction

Lignocellulosic biomass is one of the most abundant resources that can be transferred into fuels, power, heat and value-added chemicals through the biorefinery process (Liu et al., 2015; Liguori and Faraco, 2016; Mattila et al., 2017). However, excess of residual lignin in cellulosic biomass is a barrier for enzymatic hydrolysis and further conversion to fermentable sugars (Draude et al., 2001). At present, using alkaline solution under harsh conditions is still the superior lignin elimination method in mill applications. To further improve biorefinery process performance, i.e. biomass utilization, energy and chemical cost, shortening the alkaline lignin elimination process integrated with extended oxygen delignification process (SKP-EOD) presented profound potentials as reported in our previous report (Jafari et al., 2014). In this new model of biorefiney process, high level of residual lignin in pre-oxygen delignified cellulose fibers will result in high concentration of dissolved lignin, which can activate more oxygen species for delignification and partial cellulose degradation. Therefore, further fundamental understanding of the oxygen delignification chemistry about the distracted efficiency by dissolved lignin will be beneficial for further improvement of biorefinery performance.

Oxygen delignification (OD) is a multi-phase of chemical reaction, with cellulose fibers as solid, and oxygen as gaseous, and alkali solution as liquid. The complex delignification chemistry starts with that the phenolic hydroxyl group in lignin is deprotonated to produce the phenolate anion which will be ready for oxygen attack (Asgari and Argyropoulos, 1998). Compared to the reaction between gaseous oxygen and solid lignin, the reaction access must be easier for dissolved oxygen and dissolved lignin. However, the activated oxygen species, including peroxy radicals, hydroxyl radicals, and hydroperoxy radicals, can work on delignification while cellulose degradation (Kratzl et al., 1974). Therefore, through investigation on the oxidized matter, which is the degradation products of lignin and saccharides, a suitable balance between delignification and cellulose degradation could be achieved. Small amount of unoxidized matter which can be dissolved in the very beginning of OD process could have positive effects on the OD stage, while larger quantities always decreased the delignification (Miller et al., 1991; Vuorenvirta et al., 2000), which will be more obvious for biorefinery model of SKP-EOD, since more dissolved lignin will be generated in the heating-up period before oxygen is introduced. During the whole OD process in mill application, dissolved matter, including the oxidized and unoxidized, has been shown to have different impact on delignification efficiency, chemical costs and pulp properties (Wilke et al., 2016, 2017). Unfortunately, above literatures investigate on the

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effect of dissolved matter on delignification process performance from a perspective of degradation products. Until now, there is no unanimous report regarding the chemical basis of dissolved matter involved chemical reaction.

Based on the comparison results of delignification degree, cellulose polymerization and carbonyl content, from a perspective of chemical basis, the present work firstly demonstrates that the high amount of lignin in alkaline liquor will enhance the invalid oxygen consumption followed by the decrease of chromophoric group. This fundamental understanding about distracted oxygen delignification efficiency will be helpful for the industrial application of new biorefinery model of SKP-EOD.

2. Materials and methods

2.1. Oxygen delignification

The original eucalyptus kraft pulp with initial kappa number (IKN) of 27.2 and 16.9 was made in laboratory according to previous report (Li et al., 2016), and labeled as A and B respectively. Oxygen delignification experiments were carried out with 20 g kraft pulp (based on oven-dried mass) at 10% consistency in a Parr reactor (4843, Parr Instrument Company, Illinois, USA). The procedure of oxygen delignification was as follows: $MgSO_4$ (0.2% based on oven-dried pulp) was added to pulp suspension and mixed for 5 min in a polythene bag by strong rubbing. Then, NaOH (3.0% based on oven-dried pulp) was added and mixed for another 5 min. After transfer of the pulp slurry to the reaction vessel, water was added into the polythene bag for adjusting pulp consistency to 10%. The vessel was heated to 100 °C in Parr reactor, and then the oxygen gas was introduced to the reactor until the pressure reached at 0.6 MPa. At the end of the reaction, the reactor was cooled to 40 °C with an ice water in 5 min. Pulp slurry were washed with deionized water and stored at 2 °C for the further testing. Process effluents were obtained by vacuum filtration and also stored 2 °C for the further testing. The footnotes, i.e. 15, 30, 60, 90, 135, with sample A and B represented the oxygen delignification time.

To understand the fundamental chemistry involved in the invalid chemical reaction between dissolved oxygen and lignin, a simulation process under laboratory scale was constructed. In the oxygen delignification process of kraft pulps with IKN 27.2, 10 mL of process effluent was filtered when the vessel was heated to 100 °C in Parr reactor and before oxygen was introduced. Followed was the injection of lignin solution into a sealed vessel, and removal of air by filtration of industrial oxygen. Process conditions, including reaction temperature and time, were the same with oxygen delignification. Through this simulation process, the reaction vessel could be directly linked to the gas chromatography, and therefore the residual oxygen and methanol generation could be quantitatively determined.

3. Sample analysis

The kappa number and intrinsic viscosity were determined by the TAPPI Method T 236 and SCAN-C 15:62 method, respectively.

The amount of carbonyl groups was according to the our previously report (Li et al., 2015): adding suitable amount of cellulose fiber into headspace sample vial with 5 g of SiO_2 and 1 mL of 0.5 g/L $NaBH_4$ solution filled with nitrogen, and then the vial was sealed with a septum. Place the vial in water bath for 60 min at 80 °C, and then cooled to room temperature, and 1 mL of 0.8 mol/L sulfuric acid was injected into the sealed vial by a syringe to neutralize the alkaline medium and react with $NaBH_4$ to release hydrogen which could be quantitatively by headspace gas chromatography.

The amounts of methanol in the process liquors was determined by direct adding 10 μL process effluent into a sealed headspace sample vial (20 mL) followed by heating up to a temperature of 105 °C, in which the equilibrated vapor was determined by a full evaporation headspace gas chromatographic technique developed previously (Li et al., 2007).

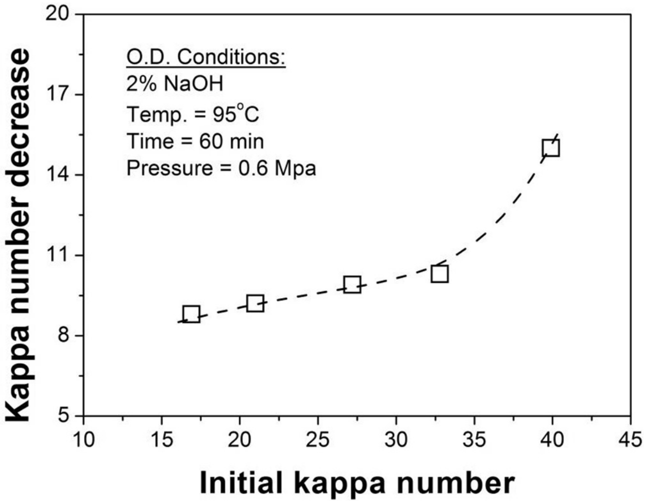

Fig. 1. Change of net kappa number decrease as function of initial kappa number of pre-oxygen delignified pulp fibers.

4. Results and discussion

4.1. Effectiveness of OD on pulps with different kappa numbers

Decrease of kappa number, which is a parameter for metering the remaining lignin in cellulose fibers, can reflect the delignification efficiency. Fig. 1 showed the change of kappa number decrease degree with kappa number of pre-oxygen delignified pulp. As can be seen, delignification efficiency could be improved when the initial kappa number (IKN) increased, and this is one of the main reasons for extending oxygen delignification process in place of kraft pulping process.

Based on the reported results previously (Li et al., 2016), the energy and alkali consumption in the integrated biorefinery process could be optimized when using a KP pulp with kappa number of ~27. In this paper, we deeply compared the viscosity change of oxygen delignified pulps with kappa number of ~27 and 16.9 (i.e. traditional kraft pulp number for hardwood). Fig. 2 showed the change of pulp viscosity with remained lignin during the delignification process. As can be seen, the oxygen delignified pulps prepared by the new biofinery model possessed high viscosity comparatively.

Carbonyl groups can be an oxidizing product during oxygen delignification process. In cellulose, it is a reaction spot for de-

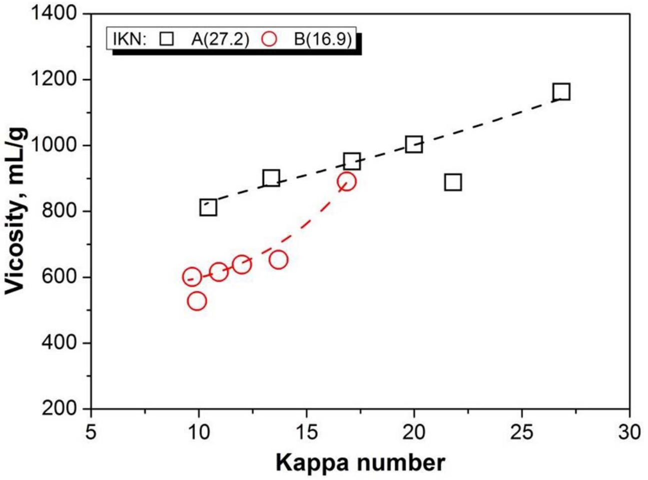

Fig. 2. Change of pulp viscosity as function of delignification degree.