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Effect of shortening kraft pulping integrated with extended oxygen delignification on biorefinery process performance of *eucalyptus*

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HIGHLIGHTS

- Use of kraft pulps with high residual lignin content can improve biomass utilization and oxygen delignification efficiency.
- Hexenuronic acid and methanol formation can be reduced in the integrated biorefinery processes.
- Effectiveness of energy and alkali consumption can also be enhanced.

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ABSTRACT

The aim of this work was to study the impact of shortening kraft pulping (KP) process integrated with extended oxygen delignification (OD) on the biorefinery process performance of *eucalyptus*. Data showed that using kraft pulps with high kappa number could improve the delignification efficiency of OD, reduce hexenuronic acid formation in kraft pulps. Pulp viscosity for a target kappa number of ~10 was comparable to that obtained from conventional KP and OD process. The energy and alkali consumption in the integrated biorefinery process could be optimized when using a KP pulp with kappa number of ~27. The process could minimize the overall methanol formation, but greater amounts of carbonate and oxalate were formed. The information from this study will be helpful to the future implementation of short-time KP integrated with extended OD process in actual pulp mill applications for biorefinery, aiming at further improvement in the biorefinery effectiveness of hardwood.

1. Introduction

At present, biorefinery can be implemented when it is incorporated with pulp production, which was considered as only a process for producing fibers and energy before (Paananen and Sixta, 2015). Reports about biorefinery were mostly focused on fraction technologies for value-added chemicals so far, such as bioethanol (Zhou and Runge, 2015) and sugars (Liu et al., 2015). Thus comparatively less attention was paid for the main process, i.e., pulping process, in biomass-based biorefinery. However, improvement on raw materials utilization, effectiveness of chemical use, and energy conservation in kraft pulping process will be beneficial for the whole biorefinery process.

In mill practice, oxygen delignification (OD) has become an indispensible process for removal of residual lignin that remains in pulps after alkaline pulping. Due to the recoverability of its spent liquor, the OD process effectively offsets downstream bleaching chemical requirements while reducing the pollution load in elemental chlorine free (ECF) bleaching effluent (Hartler et al., 1970). Compared to the last phase of kraft cooking step, OD process is more selective and the presence of high quantity of residual lignin in pulps can protect cellulose from degradation (Bajpai, 2012). Therefore, it is expected that shortening alkaline pulping time, followed by enhanced OD for pulps with high kappa number, would further improve the overall performances in terms of raw material utilization, pollution control, and energy savings.

As reported in our previous work, shortening alkaline pulping time could reduce the generation of methanol (Zhu et al., 2000) and organic sulfur compounds, such as methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS) (Yoon et al., 2001) in pulping liquors. In addition, reducing the alkaline pulping time also reduced the formation of hexenuronic acid groups

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(HexA) in hardwood pulps (Chai et al., 2001a) that are associated with yellowness reversion (Cadena et al., 2010). Moreover, it also made the use of anthraquinone (a cooking assistant agent) more effective (Chai et al., 2007). Despite the positive findings in short-time pulping, limited work was reported for compensate of extended oxygen delignification on raw materials utilization, chemical efficiency and energy consumption. Moreover, *eucalyptus* has been proved to be one of the most suitable wood species for kraft pulping process and chemical pulp-based biorefinery (Pereira et al., 2012). Therefore, extensive research on its utilization in kraft pulping process aiming at improving the biorefinery performance is necessary.

In 2007, van Heiningen group (Ji and Van Heiningen, 2007; Ji et al., 2007) firstly proposed a continuous stirred tank reactor (CSTR) technology for the study of reaction kinetics during OD, in which the process was performed at a constant and relatively low alkali concentration. Recently, they have applied the CSTR technology to the delignification of high kappa number pulp (Jafari et al., 2014). The results showed that the degree of lignin removal from the kraft pine pulp with a kappa number of 65 could be greater than 70%, compared to only 50% in the conventional OD process. In addition, there was a 2% additional gain of pulp yield due to a shortened pulping time. According to reaction kinetics, OD should improve the reaction rate at the initial reaction phase when the pulp contains high lignin content. However, because of the cost issues related to chemical, energy and water usage, CSTR technology has not been adopted for industrial application. Therefore, it is useful to examine in greater detail the OD process applied to high kappa number pulp in an existing batch-type reactor.

In this work, the impact of high kappa number pulp on the effectiveness of the OD process was investigated. *Eucalyptus* pulps with different kappa numbers obtained from the KP processes were used to evaluate the delignification efficiency, chemicals use, energy consumption and pulp properties for the entire pulping/delignification process. It is also the first time to provide a comprehensive overview on the advantages of the integrated pulping and oxygen delignification process if the kraft pulping is terminated at a higher kappa number.

2. Methods

2.1. Experimental materials

The *eucalyptus* chips (approximately 3 cm × 2 cm × 3 mm) used in this study was originated from the hybridization of *Eucalyptus urophylla* and *Eucalyptus grandis* and with the age of 6 years, and obtained from Leizhou Forestry Bureau in Guangdong Province, China. Some visible bark and knots were manually removed. The chips were washed with tap water, air-dried at room temperature, and sealed in double-decked polyethylene plastic bags to maintain the equilibrium moisture content of the chips.

2.2. Pulping

All of the pulping experiments were carried out in batches in a laboratory digester (Greenwood 2110-2, USA) system with circulating cooking liquor. The total volume of the digester was 10 L. One thousand grams of wood chips (based on oven-dried mass) were put into the digester. The effective alkali (EA) charge ([NaOH] + 1/2 [Na_2S] expressed as NaOH) was maintained at 20% of oven-dry wood; i.e., 20 g of EA/100 g chips. The sulfidity was maintained at 25% (sulfidity = [Na_2S]/([Na_2S] + [NaOH]) all expressed as NaOH). The liquor-to-wood ratio was 4:1 in all of the experiments. The cooking liquor (white liquor) was prepared in the lab using sodium hydroxide and sodium sulfide. The remainder of the water in the system was made up by the water in the wood chips and with de-ionized water. The cooking temperature was increased from room temperature to 160 °C at a rate of 80 °C/h and then held at 160 °C for 30, 40, 50, 65, and 90 min, respectively.

2.3. Oxygen delignification

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 information of the parameters such as alkali charge, oxygen pressure, reaction temperature and time are listed in Table 1. The procedure of oxygen delignification was as the 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, the specific charge of 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 the specific temperature 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.

The reacted pulp slurry was removed from Parr reactor to a Buchner funnel with a stainless steel filter screen (200-mesh). The effluents were obtained by the vacuum filtration. The pulp cake from filtration was weighed and placed in a 5 L beaker. After adding the deionized water to obtain 1% of pulp consistency, it was mixed for 5 min by a mechanical agitator at 2000 rpm (IKA RW20, Staufen Germany). The pulp slurry was filtered by vacuum filtration, and then stored at 2 °C for the further testing.

2.4. Sample analyses

The yield of kraft, oxygen delignified pulps were determined by the weight and moisture content of the collected pulps. The kappa number and intrinsic viscosity were determined by the TAPPI Method T 236 and SCAN-C 15:62 method, respectively. The hexenuronic acids (HexA) content in the pulps was measured by TAPPI Method T282 pm-07 (Chai et al., 2001a).

The amounts of methanol in the process liquors was determined by direct adding 10 μL black liquor 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).

The amount of carbonate in the process liquors was determined by adding 1 mL black liquor into a sealed headspace sample. After injecting 1 mL of sulfuric acid solution (2 mol/L) into the vial, the carbonate is converted into carbon dioxide and released to the headspace and then determined by a headspace gas chromatographic method (Chai et al., 2001b).

The determination process of oxalate in the process liquor was as following: 5 mL of sample solution was directly mixed with

Table 1
Process conditions of oxygen delignification.

Kappa number from kraft pulping	Reaction temperature (°C)	Reaction time (min)	Oxygen pressure (MPa)
39.0	85–115	0–90	0.6
32.8			
27.2			
21.0	90–110	0–60	
16.9			