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Recovery of lignocelluloses from pre-hydrolysis liquor in the lime kiln of kraft-based dissolving pulp production process by adsorption to lime mud

Jing Shen [a,b,*], Pedram Fatehi [b,c,*], Pendar Soleimani [b], Yonghao Ni [b]

[a] Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040, China
[b] Department of Chemical Engineering and Limerick Pulp and Paper Centre, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3
[c] Department of Chemical Engineering, Faculty of Engineering, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1

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ABSTRACT

Dissolved lignocelluloses from the pre-hydrolysis liquor (PHL) of kraft-based dissolving pulp production process were recovered by adsorption to lime mud produced in the causticizing plant of the kraft process. The adsorption of lignocelluloses was a fast process, and could be completed within one hour. The addition of polydiallyldimethylammonium chloride (PDADMAC) significantly increased the amounts of adsorbed lignin and hemicelluloses, which more than doubled at the PDADMAC dosage of 0.1% (based on the weight of PHL). The measured heating values of the adsorbed lignocelluloses indicate that adsorption of lignocelluloses to lime mud may result in the energy saving of the lime kiln. The process proposed in this study could also be adapted to decrease inhibitor concentrations (lignin and acetic acid) if the dissolved hemicelluloses in the PHL were used to produce value-added products, e.g., ethanol, xylitol, based on the fermentation process.

1. Introduction

The utilization of the forest biorefinery concept has received great attentions due to the shortage of oil supply and the environmental concerns (Zhu and Pan, 2010). The main objective of forest biorefinery is to produce viable platforms for producing value-added chemicals and biofuels in order to substitute for the oil-based products (Jahan et al., 2009; van Heiningen, 2006). Pre-hydrolysis kraft-based pulping is a commercial process to produce dissolving pulp. In this process, the majority of hemicelluloses and a part of lignin are separated from the wood chips and dissolved in the pre-hydrolysis liquor (PHL) (Liu et al., 2011; Saeed et al., 2010; Shi et al., 2011). Currently, the PHL is mixed with black liquor and burned in the recovery boiler. However, due to the low concentrations of the dissolved lignocelluloses in the PHL, this is not the most desirable way of handling PHL. PHL contains acetic acid and furfural, which are the by-products of hemicelluloses degradation during the pre-hydrolysis process (Saeed et al., 2011; Tunc and van Heiningen, 2008) and, together with lignin, are the main inhibitors of ethanol and xylitol fermentations.

Adsorption can remove inhibitors from PHL. Lime mud is readily produced in the causticizing plant of the kraft process and burned in the lime kiln to produce lime. In this study, lime mud (made of mainly calcium carbonate) was introduced as an adsorbent for dissolved lignocelluloses in PHL, and the performance of lime mud on adsorbing the lignocelluloses of two industrially produced PHLs was experimentally evaluated. Also, the addition of a cationic polymer, i.e., polydiallyldimethylammonium chloride (PDADMAC), to improve the adsorption performance of lime mud was explored. Finally, the heat value of lignocelluloses-modified lime mud was evaluated.

2. Experimental

2.1. Materials

The PHL was produced via steaming (saturated steam at 170 °C) of wood chips (70% wt. maple, 20% wt. poplar, and 10% wt. birch) for 30 min (Shi et al., 2011). The pre-hydrolysis liquors (PHL1 and PHL2) produced on different dates and the lime mud were provided by a mill located in Eastern Canada. To remove large particles and impurities, the PHLs were filtered using Whatman® qualitative filter papers (GE Healthcare UK Limited, UK) and Nylon 66 membrane with a pore size of 0.45 μm and diameter of 47 mm (Supelco Analytical Group, USA). Lime mud was used as received. Polydiallyldimethylammonium chloride (PDADMAC) with a molecular weight of 400–500 kDa was obtained from Sigma–Aldrich Co.,

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* Corresponding authors. Address: Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Material Science and Engineering College, Northeast Forestry University, Harbin 150040, China (J. Shen). Tel.: +86 506 450 5583; fax: +86 506 453 4767.

E-mail addresses: jingshen.china@gmail.com (J. Shen), pfatehi@lakeheadu.ca (P. Fatehi).

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(USA) and diluted to 4% wt. prior to use. Sulfuric acid (4 N) was purchased from Fisher Scientific Inc. (USA) and diluted to 4% wt. prior to use.

2.2. Lime mud analysis

The hydrodynamic size of lime mud particles was measured in a 0.1% lime mud suspension by quasi-elastic light scattering (QELS). The data was obtained with a ZetaPlus Brookhaven (Holtsville, NY, USA) and analyzed with 90plus/BI-MASS software. The scattering angle and operating wavelength were 90° and 658 nm, respectively. The mean diffusion coefficient was obtained based on dynamic light scattering (DLS) measurement. The apparent hydrodynamic sizes of the lime mud particles were calculated with the Stokes–Einstein Equation (Feitosa et al., 2006). The zeta potential was calculated by measuring the electrophoretic mobility, using the Smoluchwski's approximation, with a ZetaPlus Zeta potential analyzer (Brookhevan, Holtsville, NY, USA) (Fatehi et al., 2010; Onesippe and Lagerge, 2008; Reis et al., 2003).

For SEM analysis of lime mud particles, a Scanning Electron Microscope (JEOL, JSM-6400, Japan) was used. The sample was coated with carbon prior to analysis, and the accelerating voltage was set at 15 kV.

2.3. PHL treatment

In the experimental work, 1 g lime mud (dry weight) was added to 20 g PHL1 or PHL2 (mentioned in Section 2.1), and the mixture was shaken at 150 rpm and 26 °C in a 125-mL Erlenmeyer flask for 1 h or 24 h. The lime mud treated PHLs were then filtered though Nylon 66 membrane filters to collected the filtrates, and the filter cakes were also carefully and completely collected. Subsequently, the filter cakes were dried at 105 °C in the oven for 4 h, and incinerated in a muffle at 575 °C for 6 h to completely remove the adsorbed lignocelluloses. The weight of the filter cake after incineration was measured as W. Also, 1 g original lime mud (without any treatment) was incinerated under the same conditions, and its weight after incineration was measured as W_0. The yield (Y) of the undissolved lime mud during the PHL treatment process was determined according to the following equation:

$$Y = W/W_0 \times 100\%$$

2.4. Dissolved lignocelluloses analysis

The lignin content of the PHLs was measured by using a UV/Vis spectrometric method at a wavelength of 205 nm according to Tappi UM 250 (Liu et al., 2011; Saeed et al., 2010; Shi et al., 2011).

The hemicelluloses content of the PHLs was measured using an ion chromatography unit equipped with CarboPac® PA1 column (Dionex-300, Dionex Corporation, USA) and a pulsed amperometric detector (PAD) (Liu et al., 2011; Saeed et al., 2010; Shi et al., 2011). To convert oligomeric sugars of the PHLs to monomeric sugars, the PHLs were hydrolyzed using 4% (wt.) sulfuric acid at 121 °C for 1 h in an oil bath (Neslab instruments Inc., Portsmouth, NH, USA). The acid-hydrolyzed PHLs were then diluted, and the monomeric sugar content was measured. The concentration of sugars after this additional hydrolysis stage reflects the total sugar (hemicelluloses) content of the samples. The oligomeric sugar content of the PHLs was determined by considering the monomeric sugar and total sugar contents of the samples before and after this additional acid hydrolysis stage. Meanwhile, the same analysis was conducted before and after filtration to determine if the sugars were adsorbed on the filters during filtrating of PHLs or not.

The acetic acid and furfural contents of the PHLs were determined by using a Varian 300 ^{1}H-NMR-spectrometer. Calibration curves were established for both furfural and acetic acid in the NMR analysis. The detailed experimental procedures were described by Saeed et al. (2011).

2.5. Heat value analysis

The heat induced from the incineration of lignocelluloses-modified lime mud was estimated by the heat value calculations based on the adsorbed amounts of the lignocelluloses on lime mud and the heat values of the lignocelluloses obtained in the literature (van Heiningen, 2006). However, as the boiling points of acetic acid and furfural are 118 and 160 °C, respectively, they will readily evaporate in an open system e.g., lime kiln. Thus, theoretically, the adsorbed acetic acid and furfural cannot contribute to energy savings of the lime kiln. These two components were not considered when conducting the heat value calculations. The experimental evaluation of the heat generated induced from the incineration of lignocelluloses-modified lime mud was experimentally determined by differential scanning calorimetry (DSC) (2910 Modulated DSC, TA Instruments) under air flow (Kumar and Pratt, 1996). This method is based on heat flow as a function of programmable temperature with the area being proportional to the heat of combustion (Sadek and DeBot, 1988).

3. Results and discussion

3.1. A proposed process for recovering lignocelluloses in PHL using lime mud

Fig. 1 shows a process scheme for adsorbing dissolved lignocelluloses in PHL on lime mud. Part of the lime mud produced in the

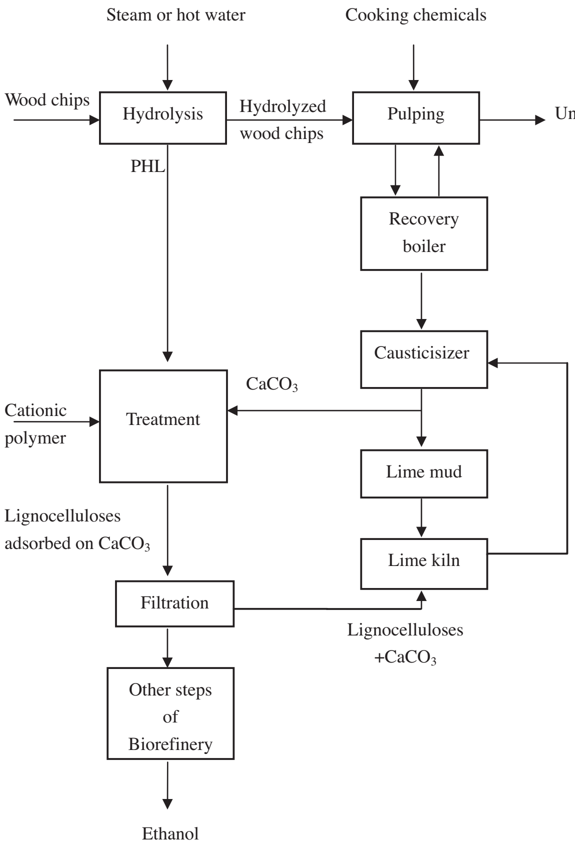

Fig. 1. Proposed process for recovering the dissolved lignocelluloses of PHL using lime mud.