



Research article

Thermal properties of lignocellulosic precipitates from neutral sulfite semichemical pulping process



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ABSTRACT

In a neutral sulfite semichemical (NSSC) pulping process, wood chips are pretreated with sodium sulfite and sodium carbonate solution. This pretreatment dissolves a part of hemicellulose and lignin from wood chips. The spent liquor (SL) that is produced in the pretreatment process contains a considerable amount of lignosulfonate and hemicelluloses, but SL is generally treated in the wastewater effluent system of the mills (i.e. lignocelluloses are wasted). In this paper, these lignocelluloses were separated from SL with organic solvents, and their thermal properties were determined. The results showed that the precipitates isolated from SL/acetone, SL/ethanol or SL/isopropyl mixtures with the weight ratio of 67/33 had the highest heating values of 18.61, 17.59 and 17.05 MJ/kg, respectively. The precipitates made from mixing acidified SL and solvents had lower heating values than those made from mixing untreated SL and solvents, which is likely due to the relatively high ash content of the precipitates made from mixing acidified SL and solvent. The theoretical and experimental heating values of precipitates were compared in this work. The precipitates displayed lower ignition temperatures compared with other biomass-based solid fuels, implying that the combustion of precipitates would require lower activation energies.

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1. Introduction

Fossil fuels are the primary energy resource in the world [1]. The uncertainties in the price of oil and environmental challenges associated with the use of oil-based materials are great concerns these days [2]. It is crucial to decrease the fossil fuel use by replacing it with biomass-based fuel for sustainable energy production.

Recently, the consumption of some paper products has declined very significantly, which severely impacted the pulping industry. Pulping processes are seeking for alternatives to increase their overall revenues. Forest biorefining has been proposed as a means to revisit pulping industry. Pulping processes can be converted to forest biorefining processes if their under-utilized biomass, e.g. hemicellulose or lignin, is effectively converted into value-added products [3]. In forest biorefining processes, hemicelluloses can be converted to ethanol or furfural [3,4], while lignin can be converted to phenol or used as energy source for instance [5,6]. Song et al. [7] reported a method for lignosulfonate conversion into phenol via heterogeneous nickel catalysts. In this process, the aryl-alkyl C—O—C linkages of lignin are cleaved in heterogeneous Ni-based catalytic systems in the temperature range of 473–513 K. It was noted that the use of diatomic and triatomic alcohols in this process resulted in a high lignosulfonate conversion. The conversion of

hemicelluloses and lignin to other value-added products is possible if they are in pure form and/or highly concentrated in solutions.

In the neutral sulfite semi-chemical (NSSC) pulping process, the majority of cellulose and hemicellulose of wood chips are collected and then converted to corrugated medium papers, while lignin (in lignosulfonate form) and the rest of hemicelluloses are wasted in the pulping spent liquors [2,8,9]. To convert the NSSC pulping process to an NSSC based forest biorefinery, the wasted lignocelluloses in the spent liquor (SL) should be converted to value-added products or energy [9]. As is, the concentrations of lignosulfonate and hemicelluloses in the SL are very low, which hampers the direct use of SL in producing value-added chemicals or fuel [8]. It is necessary to extract lignosulfonate and hemicelluloses from SL for further conversion of lignocelluloses to value-added chemicals or fuel.

In our previous studies, we reported that flocculation was a useful technique for isolating lignocelluloses from various spent liquors [9–12]. In one study, polyethylene imine (PEI) and poly diallyl dimethyl ammonium chloride (PDADMAC) were used for isolating lignocelluloses from SL [9]. However, polymers might be expensive, and flocculation processes may be ineffective in some systems. Acidification was claimed as a feasible method to isolate lignocelluloses from spent liquors [13,14]. More interestingly, the combination of polyethylene oxide treatment and acidification led to sufficient lignin isolation from pre-hydrolysis liquor (PHL) in one study [12]. In the first part of this work, we reported that lignocelluloses of SL could be isolated from SL with the help of solvents [15]. The combination of acidification and

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ethanol treatment was effective in hemicellulose extraction in another report [13]. In the past, different products were proposed to be produced from lignocelluloses extracted from pulping spent liquors [16–18]. Solvents were reported to be efficient in extracting lignocelluloses from pulping liquors, and thus can be used in forest biorefining to produce value-added products [13,15]. However, a solvent recovery unit may be necessary to have a cost effective biorefining process. The type of solvents will significantly impact the solvent recovery yield, the complexity of recovery process, and thus the overall cost of producing value-added products in forest biorefining. In the past, the use of ethanol and acetone for this purpose was reported to be promising due to their low boiling points and thus relatively efficient and less complicated recovery process. Our previous results also showed that adding solvents (e.g. ethanol and acetone) to the spent liquor of NSSC process at the ratio of 20/80 wt./wt. would result in a significant isolation of lignocelluloses from the spent liquor [15]. However, the potential application of extracted lignocelluloses was not clear, and the application would significantly impact the overall practicality and economic feasibility of the proposed process. To investigate the end-use application of the extracted lignocelluloses, it is essential to investigate the properties of the extracted lignocellulose. The first objective of this work was to study the thermal properties of precipitates obtained via solvent treatment of SL.

The elemental components of lignocelluloses impact their heating values, which is an important property of fuels [19]. It was reported that the increase in carbon, hydrogen and sulfur contents of lignocelluloses improved their heating values; while oxygen, nitrogen and ash contents negatively impacted the heating values [20]. It was also reported that the use of biomass-based fuel with low Cl and Si, but with a high Ca content led to equipment corrosion and slagging problems [21]. Furthermore, a high K and Na contents resulted in a low melting temperature for ash, which caused ash slagging and carbon deposition in the combustion unit of a boiler [22]. Another objective of this study was to determine and relate the elemental components of the extracted lignocelluloses with their thermal characteristics.

The work presented herein focused on analyzing the properties of lignocelluloses isolated from an NSSC spent liquor. The properties of precipitates that were isolated from SL via mixing SL with ethanol, acetone, and isopropyl were experimentally evaluated. The main novelty of this work is the thermal analysis of precipitates that are produced via solvent extraction from spent liquors. For the first time, the heating values and elemental compositions of the precipitates were experimentally and theoretically determined and compared. The paper also reports the heating values and ignition temperatures of the precipitates.

2. Materials and methods

2.1. Materials

The SL sample was supplied by an NSSC process located in Eastern Canada. During this process, mixed hardwood chips are treated with sodium sulfite and caustic alkali for 15–18 min at 180 °C [23]. At first, the SL was centrifuged at 3000 rpm for 15 min for removing undissolved materials. After centrifuging, the filtrate was separated and considered as the raw material for this study. Acetone (95 vol.%), ethanol (95 vol.%), isopropyl alcohol (95 vol.%) and sulfuric acid (98 wt.%) were procured from Fisher Scientific and used without further purification.

2.2. Sample preparation and mixing

In one set of experiments, the SL was mixed with ethanol, acetone and isopropyl alcohol with the weight ratios of 67/33, 50/50, 25/75 and 20/80, and kept at room temperature for 10 min. Afterward, the samples were centrifuged at 3000 rpm for 15 min, which isolated lignocelluloses from SL. The isolated precipitates were separated from the supernatants and dried in an oven at 80 °C for 24 h. Alternatively, the pH of the SL sample was decreased to 1.8 via adding sulfuric acid to the SL.

After acidification, the samples were centrifuged at 3000 rpm for 15 min. The precipitate was then collected (Sample 4). The supernatants were mixed with solvents with various ratios as explained above. The resulting precipitates were separated by centrifugation and dried at 80 °C for 24 h. The dried samples were used in subsequent tests.

2.3. Chemical compositions of precipitates and SL

In one set of experiments, 0.3–0.5 g dried precipitates made from acidifying SL (Sample 4) and from mixing solvents with untreated or acidified SL at the weight ratio of SL/solvent 67/33 were dissolved in 30–50 g of deionised water. The mixtures were placed in a water bath shaker (Boekel Scientific) and shaken at 50 rpm and 30 °C for 24 h. After mixing, the samples were filtrated using Whatman filter paper, Cat No#1001-070. The treated filter papers were placed in the oven at 60 °C for 48 h and the amounts of undissolved lignocelluloses remained on filter papers were determined. Alternatively, the compositions of dissolved lignocelluloses in SL and made solutions were determined. The lignosulfonate content of the mixtures was examined in accordance with the TAPPI UM 250 standard via UV spectrophotometry at 205 nm (Genesys 10S UV-vis, Thermo Scientific) [24]. The hemicelluloses content of the solutions was determined using an ion chromatography (IC) unit (Dionex ICS-5000⁺ DP, Thermo Scientific) equipped with Dionex CarboPac SA10 column, Thermo Scientific and pulsed amperometric detector (Thermo Scientific Electrochemical Detector). KOH was used as the eluent with the 1 mM concentration and 1 mL/min flow rate. In this set of experiments, 1 g of the solutions was mixed with 4% sulfuric acid (5 g) and placed in the thermal bath for 1 h at 121 °C. The total amount of monomeric sugars determined in this analysis was considered as hemicelluloses content of the precipitates [15]. Acetic acid and furfural concentration of the dissolved samples were determined using Varian Unity Inova 500 MHz Nuclear Magnetic Resonance (NMR) [25].

2.4. Ash content of precipitates

The ash content of the precipitates was quantified in accordance with ASTM D-1102-84 standard described by Rowell et al. [26]. At first, crucibles were placed in the muffle furnace (ThermoLyne 1400, ThermoFisher Scientific) at 575 °C for contamination removal. Then, the crucibles were weighted and filled with samples. The crucibles with samples were placed in the furnace at 575 °C, and ash content was determined based on the weight difference of empty and filled crucibles after the heating treatment.

2.5. Heating value analysis

In calorimetric analysis, the low heating value or net heating value of biomass is defined as energy generated via combusting biomass and contains moisture in vapor form in the combusted products at 0.1 MPa [22]. A 0.3–0.4 g of samples was combusted according to ASTM E711-87 using a Parr 6200 oxygen bomb calorimeter, which was attached to a Parr 6510 water handling system.

2.6. Elemental analysis

The elemental analysis of the precipitates was conducted using a Vario EL Cube Instrument (Germany) according to the procedure illustrated in the literature [27]. In this method, 5–10 mg of the samples was loaded in an integrated carousel of the instrument. First, the samples were flushed with a carrier gas (He). Subsequently, the samples were combusted, which was followed by the reduction of the burned gasses in order to determine the mass of elements in the samples [27].

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