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Research paper

Physico-chemical characterization of carbons produced from technical lignin by sub-critical hydrothermal carbonization

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ABSTRACT

Morphology, physical and chemical properties of carbonaceous materials (CMs) synthesized by hydrothermal carbonization (HTC) of a technical lignin, HP-L™, derived from a bio-refinery waste-stream is reported. The technical lignin, HP-L™, was hydrothermally carbonized at four processing temperatures; 200, 250, 300 and 350 °C. The yield of derived CMs was highest at the lowest processing temperature (200 °C), and decreased with increasing temperature. L350, obtained at 350 °C was further chemically activated with KOH. SEM analysis showed that lignin exhibited agglomerated structures with some vesicles at elevated temperatures. Overall, major structural changes in the HP-L™ lignin only occurred after 300 °C. Vibrational spectroscopy showed bands due to lignin functionalities disappeared at 350 °C. This was supported by deconvolution and peak analysis using NMR, which revealed the evolution of a more condensed structure characterized by aromatic C when temperature reached 350 °C. Unlike carbohydrates and other biomass types which can easily be hydrothermally carbonized at temperatures (160–220 °C), HP-L™ lignin remains relatively unchanged up until 350 °C where significant aromatization occurs. 350 °C is therefore the desired temperature for the hydrothermal treatment of HP-L™ lignin.

1. Introduction

Lignin is a major waste stream from emerging bio-refineries and the established pulping industry. On weight basis, it represents approximately 30% of biomass and is the most abundant aromatic biopolymer. Yet, to-date, lignin remains heavily underutilized and large-scale use is limited to as energy source heat. Therefore, valorizing lignin is a great opportunity to improve the economics of the bio-refinery process [1] and so greater research effort is being made to develop value added products for lignin. Obtaining carbonaceous materials (CMs) derived from lignin are potential added-value products since CMs have found applications in adsorbents, gas storage, electrodes, catalyst supports, carbon fixation, water purification and carbon fuel cells [2–5].

Carbonaceous materials have special morphologies, pore structures (nano, meso and macropores), and are rich in surface functionalities which can greatly improve their hydrophilicity and chemical reactivity. Additionally, these properties of CMs can be "tuned" via choice of precursor type, method of synthesis and various secondary treatments such as addition of heteroatoms to either their surface or structural framework [6]. To make these methods of manufacturing CMs sustainable, it is imperative to reduce their environmental and energy footprints. The use of renewable precursors for the synthesis of CMs is therefore attractive especially when compared to traditional precursors such as coal since the latter requires high energy processes such as pyrolysis, chemical vapor deposition (CVD), arc-discharge methods and laser ablation [7]. In contrast, hydrothermal carbonization (HTC) process, although not novel, is a facile, low-energy, low-cost and environmentally friendly route for manufacturing novel functionalized carbonaceous materials [8]. CMs produced by HTC exhibit well-controlled morphology, composition and structure with specific surface functional groups such hydroxyl, aldehyde and carboxyl groups [8]. Although, HTC-derived CMs have limited texture (surface area and porosity), these properties can be enhanced by activation and "doping" with heteroatoms such as nitrogen or sulfur [9].

The synthesis of such CMs notably from module compounds of simple and complex carbohydrates (glucose, xylose, fructose, cellulose,

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starch) have been reported in literature [10–12]. A major hurdle to the commercialization of the HTC process is the relative high cost and sustainability of these model compounds (glucose, cellulose, etc.) when used at the commercial scale as feedstocks. Consequently, bio-refinery waste-streams like lignin can be valorized and their environmental footprint also reduced.

Unlike carbohydrate precursors, only a few studies on HTC of lignin have been reported [13,14]. Importantly, lignin is a more complex heterogeneous biopolymer consisting of three mono-lignols: p-coumaryl, coniferyl and sinapyl alcohol connected by various bonds [ether (β-O-4′, α-O-4′); carbon-carbon linkages (β-β′, β-5′, and 5-5′) [15]. Structurally, lignin varies by species, subcellular location, plant tissue and methods of extraction. During extraction, new linkages such as enol ethers may be formed and quinone methide intermediates may produce additional C—C bonds [16,17]. Consequently, lignin derived from chemical and physical extraction processes are inherently heterogeneous, highly polydisperse and exhibit complex and variable functional groups [18]. These extracted lignins are often denoted as technical lignins and differ both physically and chemically from native lignin. As result of the just mentioned significant differences in lignin structure, functionality, reactivity and heterogeneity, industrial utilization of this biopolymer presents significant challenges [19]. Our earlier study demonstrated differences in the morphology of CMs obtained by HTC of different types of commercial lignin: Mascoma lignin, ammonium and sodium lignosulfonate lignins. HTC derived CMs from Mascoma lignin exhibited spherical morphology (diameters from 50 to 250 nm), whilst CMs from ammonium and sulfonate lignins were highly agglomerated [20]. Thus, it is imperative to physically and chemically characterize CMs synthesized by HTC from different technical lignins.

In this paper, we report the effect of HTC process conditions on the morphology, and physical and chemical properties of CMs synthesized from a precursor bio-refinery lignin waste-stream, HP-L™ lignin. The effect of KOH activation on surface area and pore characteristics were also studied. HP-L™ lignin is a waste-stream produced by Lignol Innovations Inc. (Lignol) via a proprietary modified organosolv pretreatment method for lignocellulose biomass to produce cellulosic ethanol, purified lignin and furfural from hardwoods. It has high water-insolubility, high phenolic content, low molecular weight and relative purity (i.e. low carbohydrate content, ash and free of sulfur) [21]. Recently, Lignol Innovations Inc. received up to $30 million in funding from the US Department of Energy (US DOE) to build a commercial demonstration cellulosic ethanol plant in Commerce City, Colorado. Additional funding for another bio-refinery plant at Ferndale, PA was also provided by US DOE. To the best of our knowledge, results presented in this paper represent the first reported investigation of the HTC of HP-L™ lignin.

2. Materials and methods

2.1. Materials

The lignin used in this study (HP-L™ lignin) was supplied by Lignol Innovations Inc. (Lignol Energy Corporation, Burnaby, BC, Canada). The precise composition of HP-L™ lignin material is given in Table 1. Potassium hydroxide (KOH) pellets was purchased from Fisher Scientific (Pittsburgh, PA).

Table 1
Composition of HP-L™ lignin.

Properties	HP-L™
Ash	< 0.5%
Carbohydrates	< 1%
Sulfur	< 0.5 ppm
Hildebrand solubility δ	~20
Polar solvent (e.g. acetone)	100%
Klason lignin (determined in the lab)	99.47%

Table 2
Process conditions and product yields of CMs obtained from the hydrothermal carbonization of Lignin.

Sample	Initial Mass (g)	Max. Pressure (MPa)	Max. Temp. (°C)	Process Time (mins)	Final mass (g)	Yield (%)
L200	5	1.48	200	60	4.4	88
L250	5	4.41	250	60	4.4	88.6
L300	5	8.72	300	60	5.5	78.6
L315	5	10.44	315	60	3.3	66
L335	5	13.88	335	60	2.8	56.4
L350	5	20.58	350	60	2.1	42

2.2. Hydrothermal carbonization of precursor lignin

The investigations reported were conducted in two phases. Phase 1 was a preliminary investigation to screen HTC processing temperatures which were later used in Phase 2, which was the main investigation. In phase 1 for which only limited data are presented, the effect of six temperatures (200, 250, 300, 315, 335 and 350 °C) on yield was determined (Table 2). From these results, four processing temperatures of 200, 250, 300 and 350 °C were selected for use in Phase 2. Samples are designated as L-temp, e.g. L-200–lignin samples hydrothermally carbonized at 200 °C.

HTC of lignin was carried out in an autoclave (Parr Instruments, Model 4766), with a Pyrex-glass liner (Fisher Scientific, Hampton, NH). Temperature was controlled by varying the voltage applied to the heater of the autoclave and gauge pressure (psi) was recorded using an analog pressure meter connected to the interior of the autoclave by an air-tight feed-through. Similarly, temperature was monitored with a thermocouple (and a digital meter) inserted through the feed through. Approximately 5 g of oven-dried lignin was dispersed in 70 mL distilled water and HTC was carried out at one of the experimental temperatures. Experiments above 300 °C showed tiny droplets of oil products. After each HTC experiment, the set-up was cooled down and the water (with oily products on top if present) was decanted. The resulting solid products which are hereafter described as carbonaceous materials were recovered by filtration after washing several times with copious amounts of distilled water. The CMs were dried overnight at 103 ± 3 °C and weighed. The percentage yield was calculated as: Yield (%) = (Final weight/Initial weight) ×100.

2.3. Activation of CMs

Activation was carried out in a Lindberg Blue M tube furnace by mixing CM with potassium hydroxide (KOH) in a ratio of 1:4 (weight basis) in a porcelain crucible. The mixture, under constant flow of nitrogen gas, was heated at a rate of 10 °C/min to 700 °C and held at this temperature for 2 h. After carbonization, the activated carbons were cooled to room temperature and transferred into beakers containing 0.1 M hydrochloric acid (HCl), stirred for 1 h and washed with deionized water until the pH of washing solution reached 6–7. They were then dried in oven at 103 ± 3 °C.

2.4. Elemental analysis of lignin and CMs

Carbon, hydrogen and nitrogen contents of the HP-L™ lignin precursor and CMs were determined using a Perkin Elmer 2400 analyzer as per ASTM- D5373 standard. Approximately 1–3 mg of each sample was used for the measurement. Sulfur (S) was analyzed separately and oxygen (O) was calculated by difference.