Quantitative comparison of surface properties of enzymatic hydrolysis lignin before and after degradation

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ARTICLE INFO

ABSTRACT

The high value utilization of lignin is attracting increased attention because of environmental problems and resource depletion. Although these are numerous reports describing the modification and degradation of enzymatic hydrolysis lignin (EHL), quantitative characterization is lacking. In this work, EHL was efficiently degraded using $H_3PW_{12}O_{40}/ZrO_2$ (HPW/ZrO_2) as catalyst. Following degradation, the total hydroxyl group content and phenolic hydroxyl group content, measured by acid-base titration and ultraviolet spectrophotometry, were increased by 259% and 152%, respectively. Hansen solubility parameters were calculated using the specific retention time of probe solvents, measured by inverse gas chromatography (IGC), quantitatively characterizing changes in surface properties.

1. Introduction

Lignin is an important renewable biomass, second in abundance only to cellulose (Laurichesse and Avérous, 2014; Peng and She, 2014; Podkościelna et al., 2017). Although very large quantities of lignin are produced, most are burned to provide energy (Aro and Fatehi, 2017; Klapiszewski et al., 2017). Enzymatic hydrolysis lignin (EHL) is derived from the residues of the bio-ethanol production process (Guo et al., 2013). EHL has the same complicated three-dimensional reticular structure as other types of lignin but retains many functional groups, including hydroxyl groups, because of the relatively mild processing conditions (Azadfar et al., 2015; Jing et al., 2015). Most current studies focus on the structure and catalytic degradation of EHL, with the aim of improving reactivity and increasing value-added application (Gao et al., 2016; Jiang et al., 2016, 2015; Li et al., 2018). For example, EHL is employed as a sorbent to remove heavy metal ions from waste water and can be also used as the additive to produce bio-based materials (Jin et al., 2010; Lu et al., 2012). Acidic catalysts such as phosphotungstic acid (HPW) and its derivatives have been shown to readily degrade cellulose and lignin by cleavage of, for example, ether linkages and double bonds (Demesa et al., 2017; Zheng et al., 2018). Although HPW is an effective catalyst for the degradation of lignin, it is difficult to recover and recycle (Patel and Singh, 2014). This drawback can be overcome by impregnation of the HPW into the surface of ZrO_2, a

process which also improves catalytic efficiency (Wang et al., 2012).

The structural changes, such as increasing numbers of hydroxyl groups, brought about degradation of EHL alter the surface properties and thus have an important effect on the performance of lignin/polymer composites (Jiang et al., 2015; Jin et al., 2010; Jing et al., 2015). Quantitative study of the surface properties of EHL is, therefore, necessary to improve the preparation and performance of composites. Hansen solubility parameter (HSP) can be used to quantitatively characterize polar substances and has previously been used to quantify the surface properties and structural characteristics of lignin (Ni et al., 2016; Ramanaiah et al., 2012). HSP can be measured by many methods, such as swelling, group contribution and inverse gas chromatography (IGC) method. But it is subjective to predict HSP by observing the solubility of polymers in solvents using swelling method and group contribution method group contribution method requires a known structure (Gharagheizi et al., 2011; Ni et al., 2016). Neither is applied to the determination of HSP of blends. IGC is a rapid, direct and sensitive method for measuring physicochemical properties and determining Hansen solubility parameters compared with other methods (Marcus, 2016; Nastasović et al., 2014; Niederquell et al., 2018). In IGC, a chromatography column is packed with the sample of interest and probe solvents are injected into the column at different temperatures (Shi et al., 2004). IGC has been widely used for the characterization of polymers, medical materials and biomass materials (Adamska et al.,

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2016; Reddy et al., 2013; Srinivas et al., 2009).

In the present study, EHL was catalytically degraded using HPW/ZrO$_2$ at 60 °C for 6 h. The total hydroxyl group content and phenolic hydroxyl group content were measured before and after degradation to correlate structural changes with changes in surface properties. Specific retention times were determined by IGC and used to calculate physicochemical parameters and Hansen solubility parameters of EHL before and after degradation, thereby quantitatively characterizing the changes in surface properties. Hansen solubility parameters of EHL before and after degradation can be used to select suitable solvents or additives for biomaterials and to provide reference data for the relationship construction between structure and properties of lignin composites.

2. Material and methods

2.1. Materials

EHL was prepared from bioethanol residue powder using the alkali-solution and acid-isolation method (Jin et al., 2011). H$_3$PW$_{12}$O$_{40}$, ZrO$_2$, ethanol and probe solvents were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China).

2.2. Lignin preparation

The EHL used in these reactions was prepared using the acid-precipitation method. Bioethanol residue powder was dissolved in 1 M NaOH solution and insoluble material was removed by centrifugation. The filtrate was treated with 2 M hydrochloric acid to pH 4 and then filtered. The filter cake was washed with distilled water to neutral and then vacuum dried at 0.08 MPa and 45 °C.

2.3. Preparation of catalysts

HPW/ZrO$_2$ composite (1:4 w/w) was prepared using the sol-gel technique (Salavati et al., 2012). Briefly, a mixture of zirconia support and HPW solution in ethanol (4 mL of ethanol solution per g of zirconia support) was stirred under reflux at 80 °C for 12 h. Excess ethanol was removed at 78 °C under vacuum. The resulting solid material was dried at 120 °C for 24 h and ground to a fine powder. The final product was then calcined at 200 °C for 4 h.

2.4. Degradation of EHL

EHL decomposition reactions were carried out in a round bottomed flask, equipped with a reflux condenser and a stirrer. The flask was charged with EHL (5 wt%) and ethanol/water (2:1 v/v, 30 mL) and placed in a water bath at 60 °C. The contents were then stirred for 15–20 min. HPW/ZrO$_2$ catalyst (25 wt%) was added and the mixture was stirred for 6 h. After cooling to room temperature, the catalyst was removed by filtration and washed with distilled water. The combined filtrates were evaporated using a rotary evaporator and the residue was dried under vacuum at 45 °C for 24–48 h to give catalytically degraded lignin.

2.5. Determination of hydroxyl group content

Chemical titration was used to measure the total hydroxyl content of the lignin and the phenolic hydroxyl content of the lignin samples was determined using UV differential spectrophotometry (Zhang et al., 2017).

2.6. Inverse gas chromatography

Retention times, used to calculate Hansen solubility parameters, were measured using an Agilent 6890 N gas chromatograph (Agilent

Table 1
Total hydroxyl group content and phenolic hydroxyl group content of EHL and DEHL.

Hydroxyl group content	EHL	DEHL
Total hydroxyl group content (mmol/g)	4.45	15.99
Phenolic hydroxyl group content (mmol/g)	2.65	6.62

Technologies, Santa Clara, CA, USA), equipped with a flame ionization detector. The injector and detector were operated at 200 °C. High purity nitrogen was used as the carrier gas and the nitrogen flow rate was maintained at 20 mL/min. Solvent-rinsed stainless steel chromatography columns (2000 mm, 1/8 in O. D.) were packed with Chromosorb 6201 that had been coated with lignin using concentrated acetone solutions. After packing, the columns were conditioned in a stream of nitrogen at 130 °C for about 8 h. Probe solvents were injected manually using a 0.5 μL Hamilton syringe to determine retention times at 383.15, 393.15, 403.15, 413.15 and 423.15 K. Each probe solvent was injected at least three times and the average retention time, t_R, was used to calculate Hansen solubility parameters of EHL before and after degradation.

3. Results and discussion

3.1. Hydroxyl group content

The hydroxyl group content of EHL and the degradation product of EHL (DEHL) were measured by acid-base titration and UV spectrophotometry (Table 1). Lignin is rich in ether linkages together with C=O and C=C bonds.(Hu et al., 2006) When the temperature is increased within a certain range in the presence of catalyst, ether or ester bonds can be broken and new hydroxyl groups formed (Korntner et al., 2015). Both total hydroxyl group content and phenolic hydroxyl group content increased after degradation of EHL. This provided a more favorable species for the preparation of bio-based materials, for example production of polyurethanes (Monteil-Rivera et al., 2013).

3.2. Specific retention volume

Retention time was determined using IGC and the specific retention volume, V_g^0, was calculated using Eq. (1),

$$V_g^0 = 273.15 JF \frac{\Delta t}{mT} \tag{1}$$

where $\Delta t = t_r - t_m$, t_r is the retention time of the adsorbing probe solvent, t_m is the mobile phase (n-pentane) hold-up time (dead time, min), F is the flow rate under ambient conditions (mL/min), m is the mass of the solvent on the column packing (g) and T is the column temperature (K). The factor J, which corrects for the influence of the pressure drop along the column, is given by,

$$J = \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \tag{2}$$

where P_i and P_0 are the inlet and outlet pressure, respectively (Zhao et al., 2018).

With homologous probe solvents other than alcohols, the value of V_g^0 increased with increasing the molecular weight (Table 2), indicating that the molecular weight of nonpolar and weakly polar probe solvents can influence the interaction with lignin. V_g^0 values of homologous alcohols decreased with increasing molecular weight, likely because of the formation of more hydrogen bonds between the alcohols and the hydroxyl groups of lignin. As the temperature increased, the interaction (mainly adsorption) between the probe solvent and lignin was reduced and the retention time of the probe solvent in the column decreased, so V_g^0 values decreased with increasing temperature for all probe solvents.

Retention diagrams, in which ln V_g^0 is plotted *versus* 1/T, for selected