



Catalytic depolymerization of organosolv sugarcane bagasse lignin in cooperative ionic liquid pairs

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ABSTRACT

Lignin has been considered as a promising sustainable feedstock for high value-added aromatic chemical production. Here, we propose a novel and efficient process for lignin depolymerization in the presence of cooperative ionic liquid pair, which affords excellent catalytic activity and char inhibition capability. Under the optimized reaction condition, 66.7% lignin conversion is achieved, yielding 14.5 wt.% phenolic monomer, numerous volatile products (identified by GC–MS) and negligible char formation. The structural evolution of the sugarcane lignin was intensively investigated via comparative characterization of raw and regenerated lignin using HSQC, ¹H NMR, FT-IR, GPC and elemental analysis. All three structural lignin units are degraded in this process, where, H-lignin is found to be the most susceptible. Satisfactory lignin depolymerization performance was found for the cooperative ionic liquid system, even after the fifth run, demonstrating a reasonable reusability.

1. Introduction

The requirement of sustainable development has led to significant attention on non-food derived biomass as a promising, renewable alternative for fossil resources [1]. Thus, exploration of chemical approaches for efficient utilization of this renewable feedstock would have significant economic and environmental advantages [2,3]. As a major component, lignin accounts for about 30 wt.% of the weight, and 40% of the energy of lignocellulosic biomass [4]. Furthermore, it contains numerous functional groups, such as, aromatic, phenolic, hydroxyl, ester, ether, carbonyl and carboxyl groups, indicating its potential as a suitable starting material for versatile chemicals and high-quality bio-fuel [5–9]. However, due to its complex chemical bonding and matrix structure, the efficient conversion of this natural polymer is still a significant challenge.

Lignin is a three-dimensional amorphous polymer and consists of phenylpropanoid monomers, which includes coniferyl, sinapyl, and *p*-coumaryl alcohols. These structures bond together via C–O chemical linkages (such as β-O-4, α-O-4, 4-O-5, etc.) and C–C [4], therefore, considerable efforts have been undertaken towards selective cleavage of

these bonds. It has been demonstrated that lignin could be degraded in a solution of NaOH, yielding 10% of phenolic monomers at 573 K [10]. Huang and co-workers found that the phenolic monomer yield could be significantly increased when lignin was depolymerized over MgAlOx in supercritical ethanol, an excellent formaldehyde scavenger [11,12]. Compared with the conventional base catalyzed process, the ether linkage is much easier to break with an acid catalyst. As such, numerous investigations have been undertaken with Lewis and Brønsted acid catalysts, such as, sulfate acid, Al₂O₃–SiO₂, zeolite, metal chloride, metal acetate, metal triflate, etc. [13–18]. However, severe char formation over heterogeneous catalysts and complex separation of homogeneous catalysts are still big barriers for achieving effective reaction systems. As efficient catalysts and/or solvents, room temperature ILs are widely employed in lignin depolymerization. Ekerdt claimed that the β-O-4 linkage in lignin can be efficiently cleaved with [Hmim]Cl as both solvent and catalyst [19]. Prado's study demonstrated that lignin depolymerization was significantly promoted when hydrogen sulfate was used as the anion of the IL [20]. SO₃H-functionalized IL was also used as a catalyst for sugarcane lignin depolymerization, 13.5% of phenolic monomer could be obtained in a

Abbreviations: IL, ionic liquid; [bmim]Cl, 1-butyl-3-methylimidazolium chloride; [bsmim][HSO₄], 1-(4-sulfobutyl)-3-methylimidazolium; [bmim][CF₃SO₃], 1-butyl-3-methylimidazolium trifluoromethanesulfonate; THF, tetrahydrofuran; D₂O, deuterium oxide; DMSO, dimethyl sulfoxide; *p*-CA, *para*-coumaric acid; PB, *para*-benzoic acid; H-lignin, *para*-hydroxy-phenyl lignin; G-lignin, guaiacyl lignin; S-lignin, syringyl lignin; GPC, gel permeation chromatography; ¹H NMR, proton nuclear magnetic resonance spectroscopy; FT-IR, Fourier transform infrared spectroscopy; EA, elemental analysis; GC-TCD, gas chromatography-thermal conductivity detector; GC–MS, gas chromatography–mass spectrometry; GC-FID, gas chromatography-flame ionization detector; HSQC, heteronuclear single-quantum coherence

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70% aqueous ethanol solution. No obvious char formation was observed, which was attributed to the electron-rich imidazolium cation, which is an excellent capping reagent and carbocation scavenger [21]. These studies clearly indicate that functionalized ILs have great potential for the valorization of lignin and inhibit char formation.

Previously, we found that cooperative IL pairs (for example [bmim]Cl/[bSmim][HSO₄]) show improved performance, comparing to single IL in cellulose conversion. The synergistic effect between IL catalyst ([bSmim][HSO₄]) and solvent ([bmim]Cl) resulted in five times greater conversion than cellulose solubility in the IL solvent alone, which was attributed to improve cellulose dissolution, resulting in enhanced *in-situ* degradation, which substantially promoted reactor efficiency [22–24]. The cooperative IL pair was found to be efficient for carbohydrate conversion and delignification for numerous untreated lignocellulosic biomass sources, such as bagasse, corn stove and rice straw [25]. Inspired by these works, we propose here a novel and efficient process for organosolv sugarcane bagasse lignin depolymerization using cooperative IL pairs, consisting of [bSmim][HSO₄] (IL catalyst) and [bmim][CF₃SO₃] (IL additive, an excellent IL solvent for lignin dissolution [26]).

2. Material and method

2.1. Materials

THF (HPLC grade) was purchased from Acros (Beijing, China). ILs [bSmim][HSO₄] and [bmim][CF₃SO₃] were synthesized and characterized according to reported procedures [27–29]. Other reagents were supplied by Guanghua Chemical Factory Co. Ltd (Guangzhou, China), all of which are of analytical grade and were used without further purification. Sugarcane bagasse was kindly donated by Local Sugar Corporation (Guangzhou, China). Composition analysis using the TAPPI method (T249 cm-85 for carbohydrate and T222 om-88 for lignin) showed that it consists of 46.47% cellulose, 33.35% hemicellulose, 18.96% lignin and 1.22% ash. The sugarcane bagasse was milled and sieved to a particle size between 40 and 60 mesh followed by drying under vacuum at 353 K overnight prior to use.

2.2. Organosolv lignin separation

The lignin was separated according to the reported procedure [30] with minor modification. Typically, 5.0 g of dry bagasse, 60 mL aqueous ethanol solution with a volumetric concentration of 80%, and 2.0 mmol concentrated sulfuric acid were charged into a 100 mL stainless autoclave (Dalian Tongda Reaction Kettle Factory, Liaoning, China). Air was displaced from the autoclave by purging with 10 bar of N₂ three times, after which, it was heated to 353 K for 24 h. Then, it was removed from the furnace and cooled to room temperature under flowing water. The product mixture was filtered and the solid fraction was washed thoroughly with an 80% aqueous ethanol solution (10 mL × 4). The filtrate and the ethanol solution used for solid washing were combined in a 500 mL beaker, to facilitate lignin precipitation, 300 mL deionized water was added. The obtained lignin was collected on a 0.45 μm Millipore filter, washed thoroughly with deionized water, dried under vacuum at 333 K for 12 h, after which, it was sieved to 20–80 mesh for further use.

2.3. Lignin depolymerization with cooperative IL pairs

All lignin depolymerization experiments were carried out in a 100 mL stainless autoclave (Dalian Tongda Reaction Kettle Factory, Liaoning, China). In a typical procedure, the reactor was charged with 0.5 g lignin, 3.0 mmol acidic IL [bSmim][HSO₄], 5.0 g [bmim][CF₃SO₃], 50 mL H₂O, sealed and purged with N₂ three times to remove air. The reactor was heated to the designated reaction temperature (483–523 K) at an average speed of 7.0 K min⁻¹ and held for specific

reaction times (15–45 min) at the final temperature. When the reaction time elapsed, the reactor was removed from the furnace and cooled to room temperature in flowing water.

2.4. Product separation and analysis

Gaseous products were collected in a gas bag and identified by GC-TCD, the weight of this fraction was found to be less than 1.0 wt% of the lignin in each experiment, hence, it was considered to be negligible. The liquid fraction was collected after reaction and filtered using a 0.45 μm Millipore filter. Collected solid was washed with deionized water (2 mL × 3). The filtrate and water used for residual solid washing were collected, 40 mL chloroform was used for volatile organic product extraction (10 mL × 4). The raffinate was diluted with 200 mL deionized water to precipitate unreacted lignin and partially decomposed fractions. The precipitated solid fraction, defined here as regenerated lignin, was obtained *via* a combination of filtration, water washing and vacuum drying at 333 K for 12 h. The liquid fraction was submitted to a rotary evaporator for water removal, then, it was dissolved in 20 mL dichloromethane. Rotary evaporation of the solvent and drying under vacuum at 353 K for 12 h, allowed for recycling of the cooperative IL pairs, which would be utilized in consecutive runs.

The chloroform soluble fraction (volatile product) was qualitatively analyzed on an Agilent 7890 B gas chromatograph equipped with a HP-5 MS 5% phenyl methyl silox capillary column (30 m × 0.25 mm × 0.25 μm) coupled to an Agilent 5977 mass spectrometer. The injector was maintained at 523 K with 1.0 mL min⁻¹ helium as the carrier gas. The initial oven temperature was 323 K (held for 3 min), then ramped at 15 K min⁻¹ to 523 K (held for 1 min before cooling). The degree of lignin depolymerization (conversion) was calculated by weight comparison between regenerated and original lignin (0.5 g). The quantitative analysis of the volatile products was conducted on an Agilent 7890 B gas chromatograph using a FID (GC-FID). The same column and temperature program as the GC-MS analysis was adopted with dimethyl phthalate as the internal standard.

2.5. Comparative characterization of original and regenerated lignin

The HSQC spectra of original and regenerated lignin were obtained on a Bruker Avance III 600 MHz spectrometer. The same method and conditions as that used in a previous study [31] were adopted. ¹H NMR spectra were recorded on a Bruker AV-400 spectrometer, where d₆-DMSO was used as solvent. FT-IR spectra were obtained from lignin containing KBr discs on a Bruker Tensor 27 FT-IR spectrophotometer in the range 400–4000 cm⁻¹. The average molecular weight of original and regenerated lignin was measured by GPC on an Agilent 1260 using a RID detector. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹, using polystyrene standards for molecular weight calibration. Elemental analysis was conducted on a Vario EL III elementary analyzer, with oxygen content calculated according to mass conversation, based upon the assumption that the samples only contain of C, H, O, N and S.

3. Results and discussion

3.1. Catalytic depolymerization of sugarcane bagasse lignin

Table 1 shows the catalytic depolymerization performance of lignin under various conditions. Generally, subcritical water is a good self-catalyst for the acid-base catalytic process due to enhanced dissociation of H⁺ at temperatures above 473 K [32], 36.4% lignin conversion is achieved under the hydrothermal conditions. However, most of the lignin is converted to the undesirable product, char, caused by the carbocation mechanism [4]. When IL [bmim][CF₃SO₃] is present, lignin conversion increases to 45.2% without any obvious char formation. As a natural macromolecule, lignin contains intensive hydrogen as well as

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