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Short Communication

Hydrolytic depolymerization of hydrolysis lignin: Effects of catalysts and solvents

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HIGHLIGHTS

- Depolymerized hydrolysis lignin (DHL) was produced from HL for rigid PU foams.
- DHL with $M_w \sim 1000$ g/mole was obtained in water–ethanol mixture.
- Alkaline hydrolysis of HL at 10 wt.% NaOH loading produce DHL with $M_w \sim 850$ g/mole.
- Acidic hydrolysis of HL in water led to high yield of solid residues ~39 wt.%.
- Acidic catalyst in water–ethanol mixture improved DHL yield up to 75 wt.%.

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ABSTRACT

Hydrolytic depolymerization of hydrolysis lignin (HL) in water and water–ethanol co-solvent was investigated at 250 °C for 1 h with 20% (w/v) HL substrate concentration with or without catalyst (H_2SO_4 or NaOH). The obtained depolymerized HLs (DHLs) were characterized with GPC-*UV*, FTIR, GC–MS, ^{1}H NMR and elemental analyzer. In view of the utilization of depolymerized HL (DHL) for the preparation of rigid polyurethane foams/resins un-catalyzed depolymerization of HL employing water–ethanol mixture appeared to be a viable route with high yield of DHL ~70.5 wt.% (SR yield of ~9.8 wt.%) and with M_w *as* low as ~1000 g/mole with suitable aliphatic (227.1 mg KOH/g) and phenolic (215 mg KOH/g) hydroxyl numbers. The overall % carbon recovery under the selected best route was ~87%. Acid catalyzed depolymerization of HL in water and water–ethanol mixture lead to slightly increased M_w. Alkaline hydrolysis helped in reducing M_w in water and opposite trend was observed in water–ethanol mixture.

1. Introduction

Hydrothermal depolymerization and catalytic liquefaction of lignocellulosic biomass, have demonstrated promise for replacing petroleum derived chemicals with more sustainable alternatives (Huber et al., 2006), in accordance to the principles of green chemistry. Production of bio-derived polymers is very challenging due to the variability and complexity of the bio-based starting materials; this requires careful control of reaction conditions and the use of catalysts capable of selective bond cleavage (Barta et al., 2014). Lignocellulosic biomass composed of three biopolymers: cellulose, hemicellulose and lignin. Cellulose is a linear homopolymer of glucopyranose residues linked by β (1 → 4) glycosidic bonds (Shen et al., 2011) and is resistant to hydrolysis. Where, hemicellulose can be easily hydrolyzed by acid or base. Lignin is a naturally occurring aromatic biopolymer consisting of phenylpropanoid units. Large quantities of lignin are yearly available from numerous pulping mills and biorefinery industries (such as cellulosic ethanol plants). The presence of phenolic and aliphatic hydroxyl reactive groups in lignin and its large availability render a significant opportunity for the production of a wide range of renewable chemicals/materials using lignin.

Hydrolysis lignin (HL) – a by-product from pre-treatment processes in cellulosic ethanol plants (Yuan et al., 2011), is mainly composed of lignin up to 60% balanced with unreacted cellulose, mono and oligosaccharides. Extensive research was undertaken in the former Soviet Union to find uses for HL. However, unfortunately, the majority of HL was disposed for no valorization, either because the required modifications for HL utilizations were too expensive or because the HL-derived materials did not function well enough. Advances in the lignin depolymerization and the

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utilization of depolymerized lignin products have shown great promise in the valorization of this type of lignin.

Most of the current depolymerization/liquefaction processes are carried out heterogeneously, requiring rigorous conditions in terms of solvent, temperature and pressure (Long et al., 2012). Lignocellulosic biomasses can be easily depolymerized in the presence of acidic/basic catalysts in the presence of a suitable solvent. Hot-compressed or subcritical water has been used by many researchers for biomass liquefaction effectively (Cheng et al., 2010) however; the yield of water-insoluble oily products was lower when compared with the yield obtained employing sub-/supercritical alcohols (Yamazaki et al., 2006; Liu and Zhang, 2008). The high yield of oily products from using alcohols attributed to their low dielectric constant which helps to readily dissolve relatively high molecular weight products derived from biomass liquefaction (Yamazaki et al., 2006). Therefore, biomass solvolysis was found to be greatly affected by the type of solvent (Liu and Zhang, 2008). Lignin in woody biomass could be effectively depolymerized using water–ethanol mixture (Cheng et al., 2010) to produce low molecular weight products with more reactive aliphatic –OH groups and more accessible phenolic –OH groups for their further utilization either in polyurethane (PU) foams (Mahmood et al., 2013) or in phenolic foams (Zhuang et al., 2011).

Inspired from the above research work for the depolymerization of biomasses, in this study for the first time, depolymerization of HL was comprehensively studied. Both acidic and basic media using sulfuric acid (H_2SO_4) and NaOH as catalysts, respectively, were tested at 250 °C, 1 h for 20% (w/v) HL substrate concentration. Effects of solvent type (either water or water–ethanol mixture) were compared on the yield of products (DHL and SR) and the M_w of the DHL products.

2. Methods

2.1. Materials

Hydrolysis lignin (HL) used in this study was kindly provided by FPInnovations, a byproduct from its proprietary hardwood fractionation process for bioproducts (or called "TMP bio-process") (Yuan et al., 2011). The original HL composed of 56.7 wt.% lignin, 29.8 wt.% carbohydrates, 1.2 wt.% ash and 12.3 wt.% others, with elemental composition (on dry basis) of 62.8 wt.% carbon, 6.1 wt.% hydrogen, 4.0 wt.% nitrogen and 27.1 wt.% others (oxygen plus ash) (Yuan et al., 2011). The molecular weight of original HL was believed at least >20,000 g/mole, but unpredictable by using GPC-*UV* due to its insolubility in common organic solvents. The pH value of the original HL is neutral. Other chemicals used including NaOH, H_2SO_4, acetone, pyridine, acetic anhydride, dibromomethane, tetrahydrofuran (THF, HPLC grade) and ethanol, all CAS reagent grade, purchased from Sigma–Aldrich and used without further purification.

2.2. Depolymerization of hydrolysis lignin

The depolymerization of HL was carried out in 100 mL Parr autoclave reactor. In a typical run, reactor was charged with 10 g HL, 0.2–1.0 g of catalyst (NaOH 2–10 wt.% or H_2SO_4 2 wt.% of the HL substrate), and ~40 mL of solvent (water or 50/50 (v/v) water–ethanol mixture). The reactor was sealed, purged with nitrogen three times and finally pressurized to 2000 kPa (2 MPa) with N_2 to prevent the reactive material from boiling in the course of heating process. The reactor was heated under a fixed stirring rate (290 rpm) and allowed to run over a pre-specified length of time after reaching the required temperature i.e. 250 °C. After the reaction time elapsed (1 h), the reactor was immediately quenched with a water bath to stop further reactions. Once the reactor was cooled down to room temperature, the gaseous products inside the reactor were collected and analyzed by micro GC–TCD. The total gas yields were negligibly low (<1 wt.%) in all tests. The reaction mixture was then poured into a beaker, and the reactor was thoroughly rinsed with acetone in case of all experiments except where NaOH was used as a catalyst. When NaOH was employed as a catalyst, the reaction products were transferred into a beaker with the help of spatula and 5 mL of water, followed by the neutralization or slight acidification of sample using sulfuric acid, sonication and then dissolving in acetone. The combined reaction mixture was filtered through a Buchener funnel. The obtained solid residues (SRs) were dried with filter paper at 105 °C in an oven, and were weighed to obtain the yield of SRs. The acetone soluble filtrate was transferred to a pre-weighed Erlenmeyer flask to remove acetone, ethanol and water with a rotary evaporator at 45–60 °C under reduced pressure to obtain the depolymerized HL (DHL) products. The yield of DHL products was calculated based on the dry mass of input HL. Each experiment was repeated 2–3 to ensure that the experimental errors in the DHL yields be within ±5%.

2.3. Product characterization

The dried samples of original HL and DHL were analyzed directly by PerkinElmer Fourier Transform Infrared Spectroscopy (FTIR) with universal ATR accessory for their functionality changes in the range of 500–4000 cm^{-1} (scans = 16) with attenuated total reflectance (ATR). The molecular weights of DHLs were measured with a Waters Breeze GPC-*UV* (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using THF as the eluent at a flow rate of 1 mL/min with linear polystyrene standards for the molecular weight calibration curve. Proton nuclear magnetic resonance (^{1}H NMR) spectra for DHLs were acquired at 25 °C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16–32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from −2 ppm to 14 ppm (sw = 9000.9 Hz). Quantitative ^{1}H NMR analysis was realized, as described in Mahmood et al. (2013), using acetylated sample of DHL and Dibromomethane (CH_2Br_2) as an internal standard. Gas samples were analyzed via micro GC–TCD. The filtered sample of freshly prepared depolymerized HL (DHL) was dissolved in acetone to make a homogeneous solution of a concentration of approx. 0.1 wt.% for GC–MS analysis. GC–MS analysis was conducted with an Agilent 7890B GC coupled with a 5977A MSD using a 30 m × 0.5 mm × 0.25 μm DB-35 ms column with temperature programming as follows: a 2 min hold at an initial temperature of 60 °C followed by a 10 °C min^{-1} ramp to the temperature of 120 °C with a 0 min holding time and finally the temperature was raised to 280 °C with a 8 °C min^{-1} ramp with a 5 min hold. The elemental analysis of DHL and SRs was performed using a Thermo Fischer Flash EA 1112 series CHNS-O elemental analyzer.

3. Results and discussions

3.1. Effects of solvent type on non-catalytic HL depolymerization

Table 1 shows that using water alone as a solvent the depolymerization of HL resulted in ~68 wt.% yield of DHL with low M_w ~ 2030 g/mole and ~5 wt.% yield of SRs. Effective liquefaction of HL in water solvent could be ascribed to its unique properties such as lower dielectric constant and an enhanced solubility for organic compounds than ambient water (Cheng et al., 2010).