Fuel 223 (2018) 366–372

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Effect of structural characteristics on the depolymerization of lignin into phenolic monomers

Cheng Chen[a], Dongxue Jin[a], Xinping Ouyang[a,b,*], Lisha Zhao[a], Xueqing Qiu[a,b,*], Furong Wang[a]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] Guangdong Provincial Engineering Research Center of Green Fine Chemicals, Guangzhou 510640, PR China

ARTICLE INFO

Keywords:
Lignin
Molecular weight
Depolymerization
Phenolic monomers

ABSTRACT

The structure of lignin is one of the key factors affecting its depolymerization into phenolic monomers. Four lignin fractions with different molecular weight were obtained by using ultrafiltration membrane technology, and the characteristics of lignin factions with different molecular weight were determined by gel permeation chromatography (GPC), potentiometric titration, FT-IR and NMR. It is found that wheat alkali lignin with low molecular weight contained more content of phenolic hydroxyl, methoxyl function groups, and β-O-4 linkages, which was relatively prone to depolymerize into phenolic monomers with a higher yield, although the more content of carbonyl was reported to facilitate the depolymerization of lignin. With the increase of molecular weight of lignin, the depolymerization was more difficult, and the YMC decreased. Lignin fraction with low molecular weight was favorable for depolymerization into syringyl and alkyl syringyl, while the high molecular weight lignin was prone to depolymerize into guaiacyl and alkyl guaiacyl products. Boric acid was proved effective to avoid repolymerization and improve the YMC, and the dosage of boric acid was determined by the content of hydroxyl groups in lignin.

1. Introduction

Lignin is the most abundant source of aromatic chemicals in nature, which has attracted a great deal of attention over the past few decades because the depolymerization of lignin can produce phenol derivatives as value-added chemicals, and alternative fuels [1]. It is generally considered that lignin is a highly branched and recalcitrant phenolic macromolecule consisting of phenylpropanoid units linked by C—O or C—C bonds. The complex and ill-defined structure of lignin is a typical waste in current biorefinery processes and pulping industry that is combusted as a low value fuel to produce heat and power for the industry [2]. Currently, a large number of researches have been directed towards a profound understanding of catalysis, solvent effects and depolymerization processes in order to devise pathways to break down the biopolymer into monophenolic compounds [3–5]. However, the efficiency of depolymerization of lignin still faces great challenges. For better valorization of lignin, it is important to investigate the effect of the structural characteristics of lignin on the depolymerization of lignin. Shuai et al. [6] reported that biomass pretreatment with formaldehyde caused the formation of 1,3-dioxane structures with lignin side-chain hydroxyl groups, preventing lignin condensation. As a result, the yields of monophenolic compounds were three to seven times compared to those obtained without formaldehyde pretreatment.

Zhu et al. [7] investigated that the oxidization of C_α—OH to benzylic ketone (C_α=O) facilitated the cleavage of the C_α—C_β bond due to a greater decomposition rate constant and a lower barrier for the decomposition-determining step. However, the reduction of C_α—OH to benzylic hydrogen (C_α—H) resulted in no C_α—C_β bond being cleaved. The aromatic aldehyde would be obtained from the model compounds containing C_α—OH or C_α—OCH_3, while the model compound containing C_α=O would produce aromatic ester. Zhu et al. [8] also reported that the *β*-O-4 bonds in compounds without a benzylic alcohol group were cleaved directly and quickly to form two aromatic monomers in near-quantitative yield. However, both dehydrogenation and dehydroxylation occurred for the model compounds containing a benzylic alcohol group, and resulted in more complicated products distribution. In our previous work, some structural factors, including functional groups and lignin subunit type, affecting the depolymerization of lignin were investigated by using lignin model compounds. Shu et al. [9] studied the hydrogenolysis of three typical lignins with different structures, dealkaline lignin, sodium lignosulfonate and organosolv lignin. The results showed that organosolv lignin was more sensitive for hydrogenolysis due to its high unsaturation degree.

Up to now, the yield of monophenolic compounds reported is

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* Corresponding authors at: School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China.
E-mail addresses: ceouyang@scut.edu.cn (X. Ouyang), cexqqiu@scut.edu.cn (X. Qiu).

https://doi.org/10.1016/j.fuel.2018.03.041
Received 6 November 2017; Received in revised form 26 January 2018; Accepted 7 March 2018
0016-2361/

usually less than 13% even under harsh conditions of degradation of lignin [10]. Xiao et al. used a nano-structured MoO_x/CNT and gave the yield of monophenols as high as 47 wt% by the hydrogenolysis of enzymatic mild acidolysis lignin [11]. Although Shuai et al. reported that the hydrogenolysis of native lignin with high-syringyl subunits after the pretreatment of formaldehyde from transgenic poplar could produce 78 mol% of monophenols [6], the use of extracted lignin led to monomer yield typically 5 to 20 mol%. Therefore, the conversion of technical lignin into phenolic monomers is still a huge challenge. Repolymerization reactions are believed to be one of the main problems in the production of phenolic monomers with low yields [12]. Therefore, decreasing the repolymerization reactions during lignin depolymerization is another key issue to improve the yields of monophenolic products [13].

One strategy that has been proved effective to solve this problem involves hydrogen donor solvents. Cheng et al. [14] investigated that formic acid was employed in the depolymerization of alkali lignin and organosolv lignin in a water-ethanol (50/50, v/v) medium at 300–350 °C, obtaining 70–80% degradation yields. Another strategy involves that boric acid protecting agent was used to shift the product distribution to lower molecular weight compounds and increase product yields beyond 85%. It was found [15] that besides the catalytical action, boric acid could protect the phenolic OH groups and thus reduce concurrent repolymerization reactions during hydrothermal lignin depolymerization, and hence increased the yield of monophonic compounds. However, the effect of boric acid on the yield of monophenolic compounds in the depolymerization of different lignin structure is not quite clear.

In the present work, four lignin fractions with different molecular weight separated from wheat alkali lignin were investigated to explore the effect of molecular structure of lignin on monophenolic yields of depolymerization. In addition, the effects of boric acid on the depolymerization of lignin with different molecular weight were also explored for providing theoretical guidance for depolymerization of lignin.

2. Experimental

2.1. Materials

Wheat alkali lignin (WAL) recovered from alkali pulping spent liquors was provided from Shandong Quanlin Paper Group Co., China. To remove carbohydrates from the black liquor, 2 M hydrochloric acid was added to adjust pH to 2–3. After being stirred at 50 °C for 30 min, the mixture was separated by vacuum filtration. The resulting lignin was washed with water for three times, and dissolved in 10% sodium hydroxide solution. WAL was further separated into four fractions using ultrafiltration apparatus (Wuxi Membrane Science and Technology Co., China) by hollow fibre membranes with molecular weight cut-off 2.5, 5 and 10 kDa. The operation was under a pressure of 1.5 MPa and temperature of less than 45 °C. The obtained four mixtures were acidulated using 2 M hydrochloric acid at pH 2, and the precipitates were washed with deionized water for three times and then dried at 50 °C to obtain four purified fractions lignin, respectively. The flow chart of ultrafiltration process was shown in the Scheme 1.

All other chemicals were purchased from Aladdin Chemistry Co., Ltd, China.

2.2. Hydrogenolysis depolymerization of lignin

0.3 g of lignin, 10 mL of ethanol, 10 mL of water, 0.06 g of Pd/C (5%) and 1 mL of formic acid (99% wt) were added into a 100 mL of stainless steel autoclave (Beijing Shijishenglang Chemical Machinery Co., Ltd., China). The catalytic reaction was carried out at 300 °C for 120 min with a stirring speed of 400 rpm. And then the autoclave was cooled down to room temperature with cooling water. The depolymerized products were acidified with sulfuric acid at pH of 2.5. After filtration, the filtrate was extracted three times with ethyl acetate. The organic phase was dried and then dissolved with methanol.

2.3. Characterization of lignin and depolymerized products

The molecular weight distributions of lignin samples were determined by a Waters 1515 gel permeation chromatograph instrument (Waters Corp., USA). The chromatographic column was made up in series by Ultrahydragel™ 120, Ultrahydragel™ 250 and Ultrahydragel™ 500 columns with the pore size of 120, 250 and 500 Å, respectively. The samples were dissolved in THF with the concentration of 1 mg/ml, and THF was also used as a mobile phase at a flow rate of 1 mL/min. The effluent was monitored at 254 nm with a BECKMAN UV-detector. The columns were calibrated using polystyrene standards in the range of 92–66000 g/mol.

The mean particle size and its distribution of each lignin fraction were determined by using dynamic light scattering (DLS) measurements at 25 °C on a particle size analyzer (Zetasizer Nano-ZS, Malvern Instruments, U.K.) equipped with a Hydro EV wet dispersion unit, where 0.3 g of lignin samples were dissolved in 20 mL of ethanol/water (1:1, v/v) and then transferred to 30 mL sample bottle for the measurement after standing for 0.5 h.

Elemental analysis was carried out on a Vario EL III (Perkin Elmer Corp., USA) in the CHNS mode using helium as the carrier gas. The amount of oxygen was calculated by difference measurements. The degree of unsaturation was calculated using the following equation.

$$\text{Degree of unsaturation} = C_m + 1 - H_m/2 \tag{1}$$

where C_m and H_m are the molar quantities of carbon and hydrogen, respectively. The degree of unsaturation was not affected by the oxygen content.

The content of phenolic hydroxyl group and carboxyl group in the WAL were measured using 809 Titrando automatic titrator (Metrohm Corporation, Switzerland) by non-aqueous potentiometric titration [16], and the content of methoxyl group in the WAL and the oxidized lignin was determined by modified Zeisel method [17]. The standard deviation calculated was based on 5 measurement values.

The FT-IR spectra of four lignin fractions were obtained on a BRUKER spectrometer. The region between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} at 20 scans were recorded. The spectra were analyzed by Nicolet software to compare the absorbance corresponding to each functional group.

Heteronuclear single quantum coherence (HSQC) spectra were recorded at 400 MHz on a Bruker Avance DRX-400 superconducting NMR spectrometer (Bruker Co., Germany) at room temperature (300 K). Approximately 5 mg of sample was dissolved in deuterated dimethyl sulfoxide and transferred to a 5 mm NMR tube, and spectra were acquired with 90° pulses using an acquisition time of 250 ms and a relaxation delay of 3.0 s, $^1J_{C\text{-}H}$ of 145 Hz, 16 scans and the acquisition of 8192 data points (for ^1H) and 256 increments (for ^{13}C). The pulse widths of ^1H and ^{13}C were p1 = 6.9 μs and p3 = 12.9 μs. The spectral widths of ^1H and ^{13}C were 20 ppm and 240.00 ppm, respectively (16,025.6 and 48275 Hz). HSQC correlation peaks were assigned by comparing with the literature [18–20], which were performed using the MestReNova v10.0.0 software default processing template.

The depolymerized products were identified by gas chromatography-mass spectrometry (GC–MS, GCMS-QP2010, Shimadzu Co., Japan) equipped with an electron impact ion source (ionization energy at 70 eV). The capillary column was DB-5 column (30 m × 0.32 mm × 0.25 mm). The column temperature was programmed to keep at 50 °C for 2 min, ramp to 280 °C at 10 °C/min, and then hold at 280 °C for 5 min. Helium was used as a carrier gas at 0.6 mL/min. The injector temperature and ion source were set to 260 and 200 °C, respectively. The aromatic monomers were identified by comparing their mass spectra with those in a computer library (NIST) followed by comparing their retention time with those of standard