Slow pyrolysis of prot, alkali and dealkaline lignins for production of chemicals

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HIGHLIGHTS

- Optimisation of slow pyrolysis parameters for alkali, prot and dealkaline lignin.
- Maximum biooil yield (34.1 wt.%) obtained alkali lignin at 450 °C.
- Ca. 35 wt.% of guaiacols obtained form prot lignin at 300 °C.
- Maximum yield (92%) of phenolic compounds from dealkaline lignin at 350 °C.
- Relative contents of each phenolic compound changes significantly with pyrolysis temperature.

ARTICLE INFO

ABSTRACT

Effect of different lignins were studied during slow pyrolysis. Maximum bio-oil yield of 31.2, 34.1, and 29.5 wt.% was obtained at 350, 450 and 350 °C for prot lignin, alkali lignin and dealkaline lignin respectively. Maximum yield of phenolic compounds 78%, 80% and 92% from prot lignin, alkali and dealkaline lignin at 350, 450 and 350 °C. The differences in the pyrolysis products indicated the source of lignins such as soft and hard wood lignins. The biochar characterisation revealed that the various ether linkages were broken during pyrolysis and lignin was converted into monomeric substituted phenols. Bio-oil showed that the relative contents of each phenolic compound changes significantly with pyrolysis temperature and also the relative contents of each compound changes with different samples.

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1. Introduction

Concern over depletion of fossil fuel and global warming has led to an increasing interest in utilisation of biomass to biofuels/biochemicals (Butler et al., 2011). Biomass-derived fuels are environmentally friendly because the CO_2 released from their combustion are reused by plants for photosynthesis (Zhang et al., 2007). Lignin is a major component of lignocellulosic biomass, which is a three-dimensional (Chakar and Ragauskas, 2004) amorphous aromatic polymer comprised of various linked phenylpropane units, such as hydroxyphenyl (H), guaiacyl (G), and syringyl (S). The compositional variations in these units depend upon the type of biomass feedstocks (i.e., hardwood, softwood, and herbaceous biomass) (Boerjan et al., 2003). Chemical structure and abundance of lignin varies with its source species (Mu et al., 2013). Abundant industrial lignin is obtained as by-product from pulping and enzymatic hydrolysis or fermentation processes of biomass for ethanol synthesis (Windt et al., 2009). However presently, these lignin residues are disposed of as waste or burned to generate steam as a low-grade fuel which is a low value use. A minor fraction is used to produce low value products such as dispersants and adhesives, while most lignin has not been used more profitably because of its complex structure (Windt et al., 2009).

Hydrothermal liquefaction of prot lignin has been carried out using methanol and ethanol at various temperatures (200, 250 and 280 °C) and residence times of 15, 30 and 45 min and liquid product yield (85%) comprising substituted phenols and aromatic ethers (Singh et al., 2014). Hydrodeoxygenation (HDO) of dilute alkali extracted corn stover lignin catalysed by noble metal catalyst

(Ru/Al$_2$O$_3$) and acidic zeolite (H$^+$-Y), to produce lignin-substructure-based hydrocarbons (C$_7$–C$_{18}$), primarily C$_{12}$–C$_{18}$ cyclic structure hydrocarbons in the jet fuel range has been carried out (Wang et al., 2015a). Pyrolysis of the lignin residues obtained by dilute acid and alkali pre-treatment of corn stove and rice straw to phenol derivatives was carried out in a fixed-bed pyrolysis reactor at 800 °C (Jung et al., 2015). The effect of temperature on pyrolysis products of Alcell lignin and Asian lignin was investigated using pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS). For both lignins, the maximum yield of phenolic compounds was obtained at 600 °C (Jiang et al., 2010).

Pyrolysis behaviour of alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL) isolated from the same pine wood was analysed by TG-FTIR and Py–GC/MS. AL and MWL decompose more readily, while polymerisation is the primary reaction during KL pyrolysis. The phenol yields are maximised at 600 °C, and G-type compounds are the majority products. AL and MWL produce more phenols at low temperature (Wang et al., 2015b). Effect of lignin source and reaction temperature on thermochemical conversion of three lignin samples (maple lignin, rice straw lignin and rice husk lignin) prepared by Klason method were examined using TG-FTIR and Py–GC/MS. Guaiacol-type and syringol-type compounds were the predominant products for maple lignin regardless of the reaction temperature, while these products were only dominated for rice straw lignin and rice husk lignin under lower temperature. The production of phenol-type compounds and aromatic hydrocarbons was promoted with the increased temperature due to the enhancement of demethoxylation and dehydroxylation reactions under higher temperature (Shen et al., 2015).

In the open literature there are very few studies on the pyrolysis of different types of lignins on nature of products and most of studies used a very small amount of lignin (in mg scale) and have been carried out using analytical pyrolysis techniques like TG-FTIR and Py–GC/MS. The novelty of the manuscript is to study the slow pyrolysis of various lignins and understand the product distribution, and extensive analysis of pyrolysis products.

In this manuscript, we report the slow pyrolysis of three different kinds of lignin (prot lignin, alkali lignin, dealkaline lignin) at different temperatures to understand the effect of product distribution and detailed characterisation of products. The feedstock and pyrolysis products were analysed by using various analytical techniques such as TGA, ^{1}H NMR, FT-IR, total organic carbon etc., Identification of compounds in bio-oils was done by gas chromatography/mass spectrometry (GC–MS).

2. Methods

2.1. Materials

Three types of lignins (prot lignin, alkali lignin and dealkaline lignin) were used in this study. Alkali and dealkaline lignin used in this research were obtained from Sigma Aldrich and Tokyo Chemical Industry Co. Ltd respectively. Prot lignin was procured from Asian Lignin Manufacturing™ (ALM) in the form of Protobind™ 1000, a renewable product obtained from agricultural fibrous feedstocks. The properties of the prot lignin are presented in our earlier studies (Singh et al., 2014)

2.2. Characterisation techniques

The thermo-gravimetric analysis was carried out in Shimadzu DTG-60 instrument. Moisture content has been obtained using HR-83 Mettler Toledo Halogen Moisture Analyser. The ^{1}H NMR spectra have been recorded in the Bruker Avance 500 Plus instru-

ment using CDCl$_3$ as a solvent. Powder X-ray diffraction patterns were collected on Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu Kα radiation source. Diffraction patterns in the 2–80° region have been recorded with a 0.04 step size (step time = 4 s). The FT-IR spectra were recorded on Nicolet 8700 FTIR spectrometer with the sample powder diluted in KBr. SEM images have been collected on FEI Quanta 200 F, using tungsten filament doped with lanthanum hexaboride (LaB$_6$) as an X-ray source, fitted with an ETD (Everhart Thornley Detector), which preferentially work as a secondary electron detector. The sample for SEM has been subjected to disperse on a carbon paper coated adhesive followed by gold coating. The organic fraction of the bio-oil was analysed using gas chromatography–mass spectrometry (GC/MS, Agilent 7890 B). The carrier gas was He and column flow rate was 1 ml min^{-1}. A HP-1 column (25 m × 0.32 mm × 0.17 μm) was used for the separation. Oven isothermal program was set at 50 °C for 2 min, followed by a heating rate of 5 °C min^{-1} till 280 °C where it was held for 5 min. The injected volume was 0.4 μL in a split less mode. TOC analysis of feed and bio-char was performed using Shimadzu TOC-L unit with solid sample module SSM-5000A. Volatile matter has been calculated by measuring the weight loss in the sample after placing it in a muffle furnace at 950 ± 50 °C for 2 min similar to ASTM D3175.

2.3. Experimental procedure

Slow pyrolysis of all lignin has been performed in a fixed bed glass reactor (length: 28 cm; i.d. 3.4 cm) under atmospheric pressure of nitrogen as shown in Supplementary Fig. S1. Briefly 10 g of the lignin feed was loaded into the reactor and the reactor was purged with nitrogen to remove the inside air. The nitrogen flow rate during pyrolysis was 50 cm^3 min^{-1}. The starting temperature was the ambient room temperature at 25 °C and the heating rate to reach the pyrolysis temperature was set at around 20 °C min^{-1}. Once final pyrolysis temperature was attained, the reactor was maintained at the required temperature for a period of 1 h to ensure that all condensable vapours were collected. Biomass bed temperature as indicated using thermocouple has been taken as the pyrolysis temperature and another thermocouple indicated the skin temperature of the reactor. The vapours formed after the reaction was condensed using cooling water maintained at 4 °C (Krishna et al., 2015).

Water in the bio-oil was removed by the addition of anhydrous sodium sulphate and diethyl ether was used to recover the organic fraction. The experiments have been carried out in duplicates/triplicate and average results have been reported. The deviations in the experimental results are within ±1%. The remaining solid after the reaction left in the reactor is termed as bio-char. Various equations to calculate the yield of various fractions are given below (Krishna et al., 2015).

Bio-oil yield, wt.% = [((Weight of measuring cylinder with biooil) − (Weight of empty measuring cylinder))/(Weight of feed)] * 100

Bio-char yield, wt.% = [((Weight of reactor after reaction) − (Weight of empty reactor))/(Weight of feed)] * 100

Gas yield, wt.% = 100 − (Bio-oil yield, wt.% + Bio-char yield, wt.%)

Conversion to liquid and gaseous products, % = 100 − (Bio-char yield, wt.%)

3. Results and discussion

The ultimate and proximate analysis of the three selected lignins are shown in Table 1. The contents of carbon and hydrogen in prot lignin and alkali lignin were higher than that in dealkaline