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## Hydrothermal conversion of lignin to substituted phenols and aromatic ethers

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### HIGHLIGHTS

- Hydrothermal liquefaction of lignin was performed using ethanol & methanol.
- Maximum liquid yield (85%) was observed at low reaction temperature of 200 °C.
- The major liquid products are substituted phenols and aromatic ethers.
- The maximum organic carbon conversion was found to be 72%.

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### ABSTRACT

Hydrothermal liquefaction of lignin was performed using methanol and ethanol at various temperatures (200, 250 and 280 °C) and residence times of 15, 30 and 45 min. Maximum liquid product yield (85%) was observed at 200 °C and 15 min residence time using methanol. Increase in temperature was seen to decrease the liquid products yield. With increase in residence time, liquid yields first increased and then decreased. FTIR and <sup>1</sup>H NMR showed the presence of substituted phenols and aromatic ethers in liquid products and breakage of β-O-4 or/and α-O-4 ether bonds present in lignin during hydrothermal liquefaction was confirmed through FTIR of bio-residue. In comparison to the existing literature information, higher lignin conversion to liquid products and maximum carbon conversion (72%) was achieved in this study.

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### 1. Introduction

The growing interest in biofuels from lignocellulosic feedstock can provide a path towards replacing petroleum-based fuels with sustainable biofuels which have the potential to lower greenhouse gas (GHG) emissions. Lignocellulose consists mainly of plant cell wall materials and is a complicated natural composite with three main biopolymers, cellulose (40–50%), hemicellulose (15–25%) and lignin (15–35%).

The lignocellulosics-to-ethanol process makes use of the cellulose and hemicelluloses, leaving behind lignin as waste. In addition, the pulp and paper industry also generates huge amounts of lignin. Presently, lignin is being utilised as a low-grade boiler fuel to provide heat and power to the process. However, the aromatic structure of lignin suggests that it may be a good source of valuable

bulk and specialty chemicals like aromatics (Benzene, Toluene, and Xylene, etc.), phenols, aromatic ethers, vanillin, etc., if broken into smaller molecular units by the development of appropriate thermochemical method/catalytic technology. Lignin-derived products find application as fuels, solvents, chemical reagents, and polymers. However, lignin depolymerisation with selective bond cleavage is the major challenge for converting it into value-added chemicals.

Superior to pyrolysis technology, high-pressure direct liquefaction technology has the potential to produce liquid oils that is not miscible in water, with much higher calorific values and a range of chemicals including vanillin, phenols, aldehydes, and organic acids, etc. (Huber et al., 2006). The process is best suited for wet materials as the drying of feedstock is not necessary and water is used as one of the reactants.

Methanol and ethanol have lower boiling as well as critical points than water. Due to the lower dielectric constants of these solvents, high molecular weight products produced as a result of

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reaction of cellulose and hemicellulose readily dissolve in them (Mazaheri et al., 2010). Liquefaction in organic solvents other than water produces a higher yield of water insoluble oily products making methanol and ethanol promising solvents for the liquefaction of biomass to produce valuable hydrocarbons (Zhou et al., 2012).

Beauchet et al. used aqueous alkaline solution to depolymerise Kraft lignin, Indulin AT into gas fraction (mainly CO<sub>2</sub>), methanol, acetic acid and formic acid, aromatic monomers (19.1 wt.%) and oligomers (polyaromatic molecules) and modified lignin (45–70 wt.%) (Beauchet et al., 2012). Gosselink et al. used supercritical fluid consisting of carbon dioxide/acetone/water (300–370 °C, 100 bar) for converting organosolv hardwood and wheat straw lignins to a phenolic oil and monomeric aromatic compounds (10–12%) (Gosselink et al., 2012). Yuan et al. used hot-compressed water–ethanol medium for depolymerisation of alkaline lignin into oligomers using NaOH as the catalyst and phenol as the capping agent at 220–300 °C. The optimal process condition as reported in their study was 260 °C for 3 h (Yuan et al., 2010). Song et al. studied the conversion of native birch wood lignin into monomeric phenols like propylguaiacol and propylsyringol with total selectivity >90% at a lignin conversion of about 50%, over nickel-based catalysts common alcohols as solvents (Song et al., 2013).

In the present investigation, lignin depolymerisation was studied in organic solvents viz. ethanol and methanol under various temperatures (200, 250 and 280 °C) and residence times of 15, 30 and 45 min. The lignin and its reaction products were analysed using various physicochemical characterisation methods such as TG, Powder X ray Diffraction (XRD), FTIR, NMR, and Total Organic Carbon (TOC) to understand and confirm the formation of monomeric ligninophenols from macromolecular lignin.

## 2. Methods

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 lignin are presented as Table S1 in Supplementary materials.

Hydrothermal liquefaction of lignin was carried out in stainless steel tubular reactor (35 ml). The thermocouples were placed in the skin and heart of the reactor. In a typical hydrothermal liquefaction experiment, the reactor was loaded with lignin and ethanol/methanol (1:10 by weight). Then the reactor was purged five times with nitrogen to remove the inside air. The temperature was then raised to required point at heating rate of 10 °C min<sup>-1</sup> and kept for a specific residence time. After the specified reaction time, the reactor was taken out of the furnace and was immediately submerged into a water bath to stop the further reaction. After cooling to room temperature, the reaction contents were filtered and washed with the respective solvent (ethanol/methanol). Upon removal of the solvent in a rotary evaporator under reduced pressure, the liquid products were obtained and weighed. The solid residue was dried in the oven and after drying weight of solid residue was noted. The liquid and solid products obtained were then analysed.

Lignin and reaction products obtained after the hydrothermal upgradation (HTU) of lignin were analysed by powder XRD, and FTIR. The thermogravimetric analysis was carried out in Perkin-Elmer TG instrument. The gross calorific value of lignin has been found out using Parr 6300 Bomb Calorimeter. The bio-oil samples were analysed using FTIR and NMR. Powder XRD pattern of lignin was collected on a Bruker D8 advance X-ray diffractometer. The <sup>1</sup>H NMR spectra of the liquid samples have been recorded in the Bruker Ultra shield 500 plus instrument and DMSO-d<sub>6</sub> has been used as solvent. The FTIR spectra were recorded on a Nicolet 8700 FTIR

spectrometer. TOC analysis of lignin and bio-residue was performed using Shimadzu TOC-L unit with solid sample module SSM-5000A.

## 3. Results and discussion

The presence of organic solvents is known to improve the solubility of lignin and its decomposition products (Kang et al., 2013). Moreover, methanol can be used as a hydrogen donor in lignin liquefaction, which is in favour of low oxygen content oil production (Barta et al., 2010). Maximum liquid product yield was observed at low temperature and effect of various reaction conditions is explained below (Fig. 1a and b).

### 3.1. Effect of temperature

The reaction temperature is an important factor for the product distribution. The maximum liquid product yield was observed at 200 °C for both ethanol and methanol. Raising the temperature would promote the decomposition of lignin and repolymerisation of the intermediates simultaneously. The maximum liquid product yield was observed at 30 min residence time so this residence time has been considered to see the effect of temperature on liquid product yields. With the increase of temperature from 200 to 280 °C the yield of liquid products obtained by hydrothermal liquefaction of lignin using ethanol decreased. At 200 °C the liquid yield was maximum at 81% and with increase of temperature to 250 °C liquid product yield decreased to 75%. Further decrease of liquid product yield at 65% was observed at 280 °C. The similar trend of decrease in liquid product yield with increase in temperature was also observed at residence times of 15 and 45 min respectively for hydrothermal liquefaction of lignin using ethanol. Solid bio-residue yield increased with increase in temperature and similar result was found by Ye et al. where yield of liquid products decreased with increasing temperature from 225 to 300 °C for lignin depolymerisation in ethanol–water. This was attributed to the formation of solid residue through side reactions such as repolymerisation of lignin decomposition intermediates. This indicates that lower temperature favoured depolymerisation reaction whereas with the increase of temperature formation of higher reactive radicals promoted repolymerisation (Ye et al., 2012). Similar phenomenon is observed in coal liquefaction. Similar effect of temperature on liquid products yield was observed in case of hydrothermal liquefaction of lignin using methanol. Maximum liquid products yield (85%) was observed at 200 °C and liquid products yield gradually decreased with the increase of temperature.

### 3.2. Effect of residence time

The maximum liquid product yield was observed at 200 °C and 30 min residence time for hydrothermal liquefaction of lignin using ethanol and the effect of residence time at different temperatures is discussed below. At 200 °C the effect of residence time on liquid products yield is negligible and liquid yield was constant at all residence times of 15, 30 and 45 min respectively. At 250 °C the liquid product yield first increased with increasing residence time from 15 to 30 min. With the further increase of residence time to 45 min the liquid product yield decreased. The liquid product yield was 60%, 75% and 55% at residence time of 15, 30 and 45 min respectively. Similar trend of decrease in liquid product yield with increase of residence time was observed at 280 °C. The liquid product yield was 42%, 65% and 41% at residence time of 15, 30 and 45 min respectively. During lignin degradation, cracking reactions and condensation occur simultaneously. After a certain reaction time when most of the easily cleaved bonds in lignin molecule

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