Full Length Article

Reductive de-polymerization of kraft lignin with formic acid at low temperatures using inexpensive supported Ni-based catalysts

Shanhua Huang, Nubla Mahmood, Yongsheng Zhang, Matthew Tymchyshyn, Zhongshun Yuan, Chunbao (Charles) Xu*

Department of Chemical and Biochemical Engineering, Faculty of Engineering, Western University, London, Ontario N6A 5B9, Canada

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ABSTRACT

This work aimed to explore inexpensive supported Ni-based catalysts for de-polymerization of kraft lignin with formic acid at lower temperatures. In this study, kraft lignin was de-polymerized in water–ethanol mixture 50/50 (v/v) with formic acid as an *in-situ* hydrogen source in the presence of Ni-based catalysts ($Ni_{10\%}$/Zeolite and FHUDS-2), compared with an expensive Ru-based reference catalysts ($Ru_{5\%}$/C). At 200–300 °C for 1–3 h with or without catalyst, Kraft lignin (KL, M_w ~10,000 g/mol) was effectively de-polymerized to low M_w (M_w 1000–3000 g/mol) de-polymerized lignin (DL) products at a very high yield (85–95 wt%). Generally, at all temperatures tested, the presence of a supported metal catalyst could effectively reduce the M_w of the DL product although it did not yield significant effects on the product yield. The effects of catalyst were more evident at a lower temperature. For instance, $Ni_{10\%}$/Zeolite exhibited excellent activity for de-polymerization of KL, producing DL of M_w = 3150 g/mol at 93.5($\pm$ 4.1) wt.% yield at a low temperature (200 °C) for 1 h. Among all catalysts examined, the two inexpensive Ni-based catalysts (although at a loading double that of the expensive Ru catalysts), i.e., FHUDS-2 (a W-Mo-Ni industrial catalyst) and $Ni_{10\%}$/Zeolite demonstrated to be the most effective catalysts for sulfur-removal, reducing the sulfur content from 1.52 wt% in KL to 0.47 wt% in DL with $Ni_{10\%}$/Zeolite and to ~0 wt% in DL with FHUDS-2 catalyst at 300 °C.

1. Introduction

Kraft lignin (KL) is a by-product from kraft pulping mills, generated in a large quantity of ~50 Mt/year worldwide, mainly used as a solid fuel for producing heat and electricity in the mills. KL can be efficiently separated from "pulping black liquor" via acid precipitation processes, such as the LignoBoost process [1] and the LignoForce process [2].

Utilization of crude KL for chemicals or fuels is challenging due to its low reactivity caused by its large molecular weight and highly branched molecular structure. De-polymerization of lignin by breaking the C-O-C bonds (β-O-4 ether linkage, the dominant bonds among lignin macromolecule) proved to be a viable approach to increase its reactivity, miscibility and compatibility with other chemicals or to utilize it for liquid fuels [3–6]. Cheng et al. [3] conducted catalytic hydrothermal liquefaction of kraft lignin and employed $Ru_{10\%}$/Al_2O_3 and $Ni_{10\%}$/AC as catalysts. De-polymerized lignin (DL) with a low molecular weight, M_w < 2000 g/mol, was obtained at a high yield of > 90 wt%, The DL can be utilized to substitute phenol at up to 75–90 wt% in the preparation of bio-phenol-formaldehyde (BPF) resins [3], or as bio-polyols for the synthesis of lignin-based polyurethane foams [4].

De-polymerization of lignin can be realized using hydrolytic, oxidative or reductive approaches [4]. The reductive de-polymerization of lignin using reducing agent such as hydrogen has shown promise for conversion of lignin into high-value aromatic chemicals and liquid fuels. De-polymerization of lignin and lignin model compounds using homogeneous and heterogeneous catalysts have been reported [5,6]. Reductive de-polymerization often employs a metal catalyst and high-pressure hydrogen. Xin et al. [7] reported reductive de-polymerization of enzymolysis lignin via mild hydrogenolysis over Raney nickel. The DL products have enhanced solubility in organic solvents due to reduced molecular weights and de-oxygenation. Song et al. [8] reported that reduced nickel-based catalysts were effective in the hydrogenolysis of the C-O-C bonds (β-O-4 ether linkage) in lignin.

However, reductive lignin de-polymerization processes as discussed above generally require a high-pressure external hydrogen source. Supplying of high-pressure H_2 gas to the reactor and recycling/purification of the un-reacted hydrogen gas would result in high infrastructure costs. Using formic acid as an internal hydrogen source to substitute external hydrogen can thus be advantageous due to its less

requirement on infrastructure. It has been demonstrated that catalytic reductive de-polymerization in ethanol/formic acid solvent could be a promising approach to production of liquid oil products rich in de-methoxylated phenolics [9,10].

The authors of the present work have recently demonstrated efficient de-polymerization of KL using formic acid as internal hydrogen source in water-ethanol mixture at 300 °C under high pressure 12–15 MPa, leading to ~90 wt% yield of DL (with M_w ~1500 g/mol) [11]. As continued efforts to the previous study, this work aimed to explore inexpensive supported Ni-based catalysts for de-polymerization of kraft lignin with formic acid at lower temperatures. In this study, kraft lignin was de-polymerized in water-ethanol mixture 50/50 (v/v) with formic acid as an *in-situ* hydrogen source in the presence of two inexpensive Ni-based catalysts ($Ni_{10\%}$/Zeolite and FHUDS-2), compared with an expensive Ru-based reference catalyst ($Ru_{5\%}$/C). It should be noted that in this study the loading of the Ru-based catalysts was kept half of that of the Ni-based catalysts, which was actually on purpose, as explained below. Normally noble metal catalysts (Pt, Pb, Rh and Ru, etc.) are more active than group VIII metals (Fe, Ni, Mo, Co, etc.), but the major problem of using noble metal (such as Ru) catalysts is its extremely high price, more than 100 times that of nickel. Should the same loadings be used for the Ni and Ru catalysts in the experiments, there would be a possibility that the Ni-based catalysts were not as effective as the Ru-based reference catalyst, which would make the comparison not favorable for the inexpensive Ni catalysts. Thus, in designing the experiments, the loading of the Ni-based catalysts was on purpose kept double that of the Ru-based catalysts. Should the performance of Ni-based catalysts be superior to the Ru reference catalysts, the inexpensive Ni-based catalysts (although at a higher loading that of the reference catalysts) would then be selected as cost-effective alternatives to the noble metal catalysts the target process.

2. Materials and experimental methods

2.1. Materials

Kraft lignin (KL) was supplied from FPInnovations, whose M_w and M_n determined by GPC-UV are ~10,000 g/mol and ~5000 g/mol, respectively. The KL contains 0.57 wt% ash (on a dry basis) and 1.57 wt% sulfur (on a dry-ash-free basis). In this study, ethanol, acetone and formic acid were all ACS reagent grade solvents from Caledon Lab Chemicals, and used as received. For GPC analysis for the liquid products, HPLC grade tetrahydrofuran (THF) containing 0.03 wt% stabilizer of 2,6-di-t-butyl-4-methyl-phenol was used as the eluent. An in-house prepared zeolite-supported metal catalyst ($Ni_{10\%}$/Zeolite) (whose preparation methods are detailed in the following section), and two commercial catalysts ($Ru_{10\%}$/C and FHUDS-2) were tested in this work as references.

2.2. Catalyst preparation

Two commercial catalysts were employed in this work for lignin de-polymerization, namely, $Ru_{5\%}$/C obtained from Sigma Aldrich and FHUDS-2 (a proprietary W-Mo-Ni catalyst supplied by Fushan Research Institute of Petroleum & Petrochemicals), and they were used as received.

$Ni_{10\%}$/Zeolite catalysts was prepared in-house by incipient wetness impregnation using aqueous metal salt solutions of $Ni(NO_3)_2 \cdot 6H_2O$. The zeolite (X-zeolite) was purchased from Sigma-Aldrich. Both nickel-based catalysts, $Ni_{10\%}$/Zeolite and FHUDS-2, were calcined in N_2 at 550 °C for 1 h followed by 3-h reduction in hydrogen at the same temperature. The $Ru_{5\%}$/C, supplied by Sigma-Aldrich, was used directly without further reduction. All the catalysts were then crushed and sieved to particle size less than 300 μm for the experiments. BET surface area of the fresh catalyst was measured by nitrogen isothermal adsorption at 77 K on a Quantachrome Autosorb-1 instrument. Prior to the

Table 1
Textural properties (BET specific surface areas, total pore volume and average pore size) of the fresh catalysts.

Catalyst	BET specific surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
FHUDS-2	230	0.28	5
$Ru_{5\%}$/C	961	0.82	3
$Ni_{10\%}$/Zeolite	9	0.03	16

measurements, all samples were de-gassed under N_2 purge at 523 K for 6 h. The textural properties (BET specific surface areas, total pore volume and average pore size) of the fresh catalysts used in this study are displayed in Table 1.

2.3. De-polymerization of kraft lignin

Reductive KL de-polymerization was conducted in a 100 mL Parr pressure reactor. In a typical run, 5.0 g KL, 0.5 g Ni-based catalyst (10 wt% of the lignin), 3 mL of formic acid (FA) and 30 mL water/ethanol mixture (1:1 v/v) were loaded into the reactor. It should be noted that the loading of the Ru-based reference catalyst ($Ru_{5\%}$/C) in each run was purposely reduced to 0.25 g, half of that for the Ni-based catalysts ($Ni_{10\%}$/Zeolite and FHUDS-2), as explained previously. The reactor was purged with N_2 and then pressurized to 2.0 MPa with N_2 before heating at around 10 °C/min to the specified temperature (200–300 °C) under 290 rpm stirring. After the preset reaction time (1–3 h) had elapsed, the reaction was stopped by quenching the reactor in an ice-water bath. The gaseous products were collected in a gas bag and analyzed with a Micro-GC for the compositions of H_2, CO, CO_2, CH_4, and C_2-C_3. The reaction mixture was then washed out from the reactor with acetone, and filtered to obtain solid residue and an acetone-soluble fraction. The acetone-soluble fraction was evaporated on a rotary evaporator under reduced pressure at 40–60 °C to recover acetone, ethanol and water solvents. After evaporation, the resulted liquid phase was designated as de-polymerized lignin (DL), vacuum dried at room temperature overnight. The solid residue (SR) after filtration was oven dried at 105 °C for 24 h. The DL and SR yields in this work were calculated by the weight percentage of the weights of DL and the SR products in relation to the dry weight of KL, respectively.

Effects of catalysts, temperature, and reaction time were investigated, and the results reported in this work are average values from 2 to 3 replicate runs. Standard deviation values were shown as errors or error bars in some Tables and Figures.

2.4. Characterization of lignin and lignin-derived products

2.4.1. Characterization of the lignin-derived products

Inficon 3000 Micro-GC with TCD detectors was used to analyze the H_2, O_2, N_2, CO, CO_2, CH_4 and C_2 gases compositions of the gas products. Molecular weights and distributions of the DL products were determined by gel permeation chromatography (GPC) on a Waters Breeze GPC instrument [1525 binary HPLC pump; UV detector at 270 nm; Waters Styragel HR1 column at 40 °C], where THF was used as the eluent at the flow rate of 1 mL/min, and polystyrene standards were used for calibration of the GPC setup. Thermo Fischer Flash EA 1112 series CHNS-O elemental analyzer was used to determine the C, H, N, S and O composition of the DLs. ^{1}H-NMR spectra of KL and DLs were acquired on Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe, using acetylated samples of the KL and DLs, prepared in the procedure detailed elsewhere [12]. The ^{1}H-NMR spectra acquisition parameters were 16–32 scans with a 2 s recycle delay, 3.6 min acquisition time, a 45-degree tip angle (pw = 4.8 μs), 2–14 ppm spectral width and sw = 9000.9 Hz. Qualitative ^{1}H-NMR analysis was conducted using D_6-