Novel and Efficient Diethylene Glycol/H_2O Solvent for Lignin Dissolution

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Novel lignin solvents were developed by adding H_2O to diethylene glycol (DEG). The solubility of lignin in the DEG/H_2O solvents was determined at 25 °C, and the effect of mass ratio of H_2O to DEG on lignin solubility was investigated. The DEG/H_2O solvents exhibited highly efficient capacity for lignin dissolution, even at room temperature. The possible dissolution mechanism is proposed to be the interaction between the DEG and lignin. In addition, the DEG/H_2O solvents hardly disrupt the structure of lignin.

Keywords: Lignin; DEG/H_2O solvent; Dissolution mechanism; Thermostability; Structure

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INTRODUCTION

Lignin is one of three main components (cellulose, hemicellulose, and lignin) of lignocellulosic biomass, and it protects cellulose and hemicellulose by providing hydrophobicity, mechanical strength, and indigestibility to plant cell walls (Ragauskas *et al.* 2006; King *et al.* 2009; Kim *et al.* 2011; Hossain and Aldous 2012). Lignin is composed of three types of monolignols including coniferyl alcohol, paracoumaryl alcohol, and sinapyl alcohol. The relative ratios of each of these monolignols depend on the origin of the biomass, and it is also the only native biopolymer on the earth that contains aromatic phenolpropanoid monomers (Metzger *et al.* 1992; Pu *et al.* 2007; Hossain and Aldous 2012). With the increasing depletion of petroleum resources, rising environmental awareness, and health concerns, the exploitation of low-cost and biorenewable bioresources such as lignin have received great attention (Graca *et al.* 2012; Rozite *et al.* 2013). Lignin could be utilized in polymer matrices for high performance composite applications (Gosselink *et al.* 2004), and lignin is a potential resource to produce value-added chemicals as an alternative to the petrochemical industry (Thielemans *et al.* 2002; Saake and Lehnen 2007; Faruk *et al.* 2012; Fernandes *et al.* 2013).

Currently, the dominant method to isolate lignin is kraft pulping, which accounts for about 90% of the total production capacity (Azadi *et al.* 2013). However, kraft pulping technology employs high temperatures and harsh alkaline conditions, and it causes environment pollution. Therefore, ongoing efforts have still been made to develop efficient lignin solvents till now. In recent years, Due to their distinct advantages such as chemical and thermal stability, non-detectable vapor pressures, and chemical tunabilities, imidazolium-based ionic liquids (ILs) have been developed as promising solvents for lignin dissolution and the isolation/extraction of lignin from lignocellulosic biomass (Tadesse and Luque 2011; Dupont and Souza 2012; Ji *et al.* 2012; Sun *et al.* 2013; Xu *et al.* 2015a; Xu *et al.* 2015b). More recently, Wang *et al.* (2014) investigated lignin dissolution in dialkylimidazolium-based IL aqueous solution at 60 °C, and the maximum lignin solubility (39.8 g/100 g) was obtained in 70% [C_2mim][CH_3COO] aqueous solution.

The goal of this work was to develop novel lignin solvents. Lignin solvents were prepared by adding H_2O to diethylene glycol (DEG). H_2O was used because it is the greenest solvent, and it also decreases viscosity and cost. The solubility of lignin in the DEG/H_2O solvents was determined at 25 °C. The effect of mass ratio of H_2O to DEG on lignin solubility and the possible dissolution mechanism was investigated. In addition, the lignin generated from the DEG/H_2O/lignin solution was characterized to examine its chemical structure and thermostability.

EXPERIMENTAL

Materials

The kraft lignin with a moisture content of 5% was purchased from Sigma-Aldrich (Shanghai, China) and was dried under vacuum for 24 h in the presence of P_2O_5 before the experiments. Diethylene glycol (DEG) was purchased from Shanghai Jingchun Biotechnology Co. Ltd.

Dissolution of Lignin in the DEG/H_2O Solvent

In a typical dissolution experiment, water, at a given mass ratio, was added into DEG to gain DEG/H_2O solvent. Lignin was added into a 20-mL colorimetric tube which contained 2.0 g of DEG/H_2O solvent, and the tube was sealed with parafilm. The tube was then immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory, Gongyi, China), and the bath temperature was controlled to be 25 ± 0.5 °C. The lignin/DEG/H_2O mixture was heated and stirred at 25 °C. At each step of the procedure, additional lignin was not added until all the lignin present had been completely dissolved, based on observations using a polarizing microscope (Nanjing Jiangnan Novel Optics Co. Ltd., Nanjing, China). When lignin became saturated to the point that no more lignin was dissolved further within 1 to 2 h, its solubility (expressed by gram per 100 g of solvent) at 25 °C was calculated from the amount of the solvent and lignin added.

Measurements ^{13}C NMR Spectra

The ^{13}C NMR spectra for DEG in the DEG/D_2O (R = 0.5:1) solvent and the DEG/D_2O (R = 0.5:1)/lignin (8.0%) solution were performed at room temperature on a Bruker DMX 400 spectrometer (Karlsruhe, Germany). Deuterated water (D_2O) was used as a deuterated solvent and co-solvent in place of H_2O for the convenience of ^{13}C NMR measurements due to the similarity of D_2O to H_2O. Chemical shifts were given in ppm downfield from TMS.

Characterization of the Regenerated Lignin

To obtain regenerated lignin, lignin was dissolved in DEG/H_2O(R=0.6:1) solvent for 1 h at 25 °C to obtain a lignin solution with 10.0% of solubility. Lignin was then precipitated from the DEG/H_2O/lignin solution by rapidly mixing with distilled water. The powdery dark-brown fine lignin precipitate was then filtered, washed thoroughly with distilled water, and dried at 60 °C in a vacuum oven. The regenerated lignin was employed for the measurements of FTIR spectroscopy and GTA.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus spectrometer (ThermoScientific, Waltham, MA, USA) with KBr pellets. A total of 16 scans were taken for each sample at a resolution of 2 cm^{-1}. Thermogravimetric analysis (TGA) was carried out with a Netzsch STA 449 C thermal analyser (Self, Germany) using alumina crucibles. The sample mass was 10 to 15 mg per measurement. The measurements were carried out under flowing N_2 at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Effect of H_2O Addition on the Dissolution of Lignin in DEG

Table 1 gives the solubility of lignin in the DEG/H_2O solvents at 25 °C. DEG displayed a powerful dissolution capacity for lignin (> 88%), and the addition of H_2O to DEG clearly affected lignin solubility. At the mass ratio range from 0:1 to 0.6:1, high lignin solubility was obtained (> 90%) (Table 1). Such high efficiency lignin solvents have not been documented before. It should also be pointed out that, within the mass ratio range from 0.3:1 to 0.6:1, although the increase in lignin solubility was observable due to the addition of H_2O, one ought not to draw a conclusion that the dissolution capacity of the DEG/H_2O solvents for lignin must be higher than that of DEG in that both DEG/lignin and the DEG/H_2O lignin solutions are too viscous to be stirred. At the same time, it is also noted that the further addition of H_2O to DEG decreased lignin solubility (Table 1), which was attributed to the decreased DEG concentration in the DEG/H_2O solvent. The findings indicate that DEG in the DEG/H_2O solvent dominates lignin dissolution, and H_2O in the DEG/H_2O solvent dilutes the DEG. Compared with neat DEG, the DEG/H_2O solvents can achieve nearly the same effect of lignin dissolution, and thus are economical from a practical application perspective.

Table 1. Solubility of Lignin in the DEG Aqueous Solution at 25 °C

R	Solubility (g of lignin per 100 g of solvent)
0:1	>88
0.3:1	>96
0.5:1	>91
0.6:1	>90
0.7:1	>28
0.8:1	1.5
1:1	Insoluble

R is the mass ratio of H_2O to DEG.

Interaction between Lignin and DEG and Possible Dissolution Mechanism

To further investigate the possible dissolution mechanisms of lignin in the DEG/H_2O solvent, ^{13}C NMR measurements of DEG were carried out in a DEG/H_2O solvent and a DEG/D_2O/lignin solution at room temperature. D_2O was used as the deuterated solvent and co-solvent in place of H_2O for the convenience of ^{13}C NMR measurements due to the similarity of D_2O with H_2O. The schematic structure and numbering of C atoms in DEG are shown in Fig. 1. The ^{13}C NMR spectra and data are given in Fig. 2 and Table 2, respectively. In Table 2, $\Delta\delta$ was calculated using Eq. 1,

$$\Delta\delta = \delta_{\mathrm{obsd}} - \delta_{\mathrm{obsd,0}} \tag{1}$$

where δ_{obsd} is the chemical shift values of the C atoms of DEG in DEG/D_2O(R=0.5:1)/lignin solution, and $\delta_{obsd,0}$ represents the chemical shift values of the C atoms of DEG in DEG/D_2O(R=0.5:1) solvent.

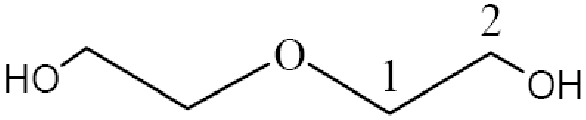

Fig. 1. The schematic structure and numbering of DEG

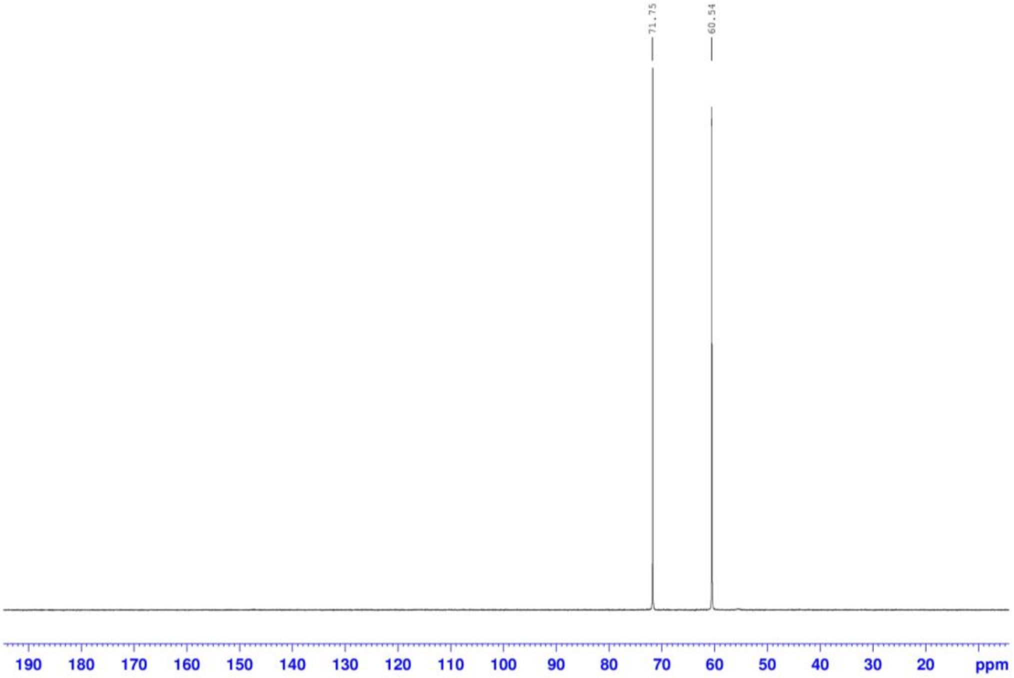

Fig. 2. The ^{13}C NMR spectra of DEG in DEG/D_2O(R=0.5:1) solvent (above) and DEG/D_2O(R=0.5:1)/lignin solution (below)

Table 2 indicates that when lignin concentration was increased, the signals of the C1 and C2 atoms of DEG moved downfield, indicating an increase in chemical shift. Thus, during lignin dissolution, lignin probably interacted with the oxygen atoms of DEG through hydrogen bonding, which decreases the electron cloud density of the C1 and C2 atoms, thus causing their chemical shifts downfield. This result showed that the interaction between lignin and DEG dominates the dissolution of lignin.

Table 2. The ^{13}C NMR Chemical Shifts (δ (ppm) relative to TMS) of DEG in DEG/D_2O(R=0.5:1) Solvent and DEG/D_2O(R=0.5:1)/Lignin Solution

Lignin Concentration (wt.%)	δ (ppm)	
	C1	C2
0	71.24	59.99
8.0	71.75	60.54
$\Delta\delta$	0.51	0.55

Structure and Thermal Properties of the Regenerated Lignin

Thermogravimetric analysis and FTIR spectroscopy were used to examine the structure and thermostability of the regenerated lignin from DEG/H_2O(R=0.6:1)/lignin solution by addition of water after 1 h of dissolution at 25 °C. The FTIR spectra of the original and the regenerated lignin are shown in Fig. 3. The two spectra were quite similar, and no new peaks were observed in the regenerated lignin. This result indicated that no chemical reaction took place during the dissolution and regeneration of lignin. The FTIR spectra of the original and the regenerated lignin were similar to previously published results, and all the group bond vibrations for lignin can be seen in the original and regenerate lignin (Xiao *et al.* 2001; Tejado *et al.* 2007; Pinkert *et al.* 2011).

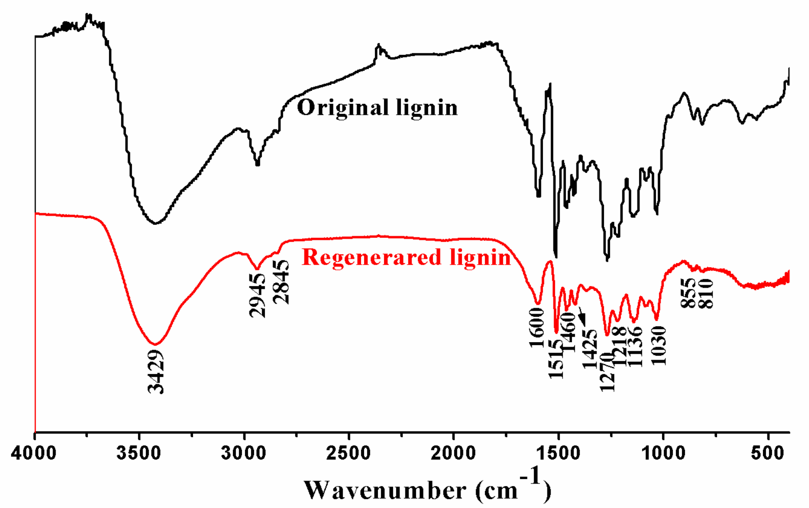

Fig. 3. FT-IR spectra of the original lignin and the regenerated lignin from DEG(R=0.6:1)/lignin solution by addition of water after 1 h of dissolution at 25 °C

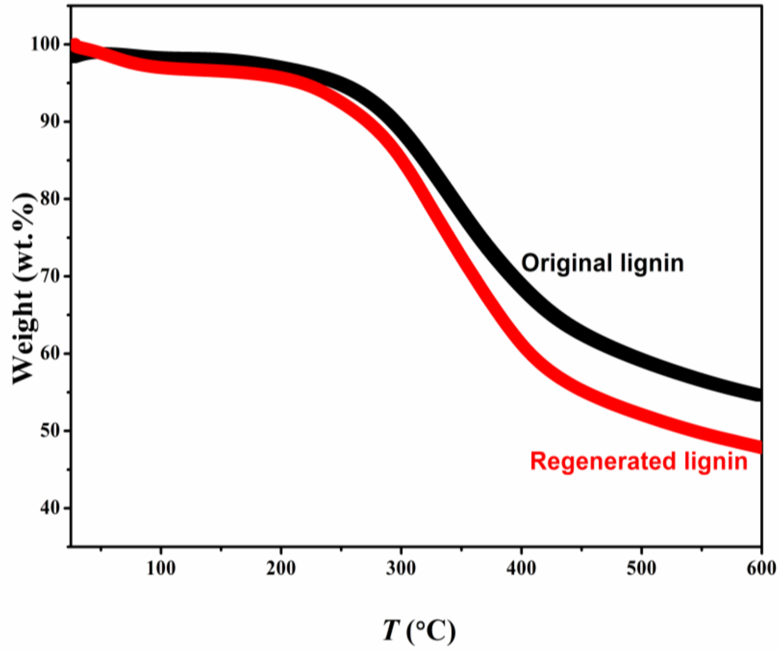

Fig. 4. Thermal decomposition profiles of the original lignin and the regenerated lignin from DRG(R=0.6:1)/lignin solution by addition of water after 1 h of dissolution at 25 °C

The TGA curves of the original and regenerated lignin nearly overlapped within 300 °C (Fig. 4). The regenerated lignin exhibited an onset temperature of decomposition (265 °C) that was very similar to the original lignin (272 °C). This result indicated that the lignin regenerated from DEG/H_2O(R=0.6) solvent had good thermal stability and did not degrade during its dissolution and regeneration.

CONCLUSIONS

1. Powerful lignin solvents were developed by adding H_2O to DEG.
2. At the mass ratio range from 0 to 0.7, the DEG/H_2O solvent displayed a strong capacity to dissolve lignin (> 88 %).
3. The lignin regenerated from the DEG/H_2O/lignin solution exhibited the same structure as the original lignin and had a good thermal stability similar to the original lignin.

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