Insight into the effect of ZnCl$_2$ on analytical pyrolysis behavior of cellulolytic enzyme corn stover lignin

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ABSTRACT

The target of this work is to investigate the effect of impregnated ZnCl$_2$ on the analytical pyrolysis behavior of waste cellulolytic enzyme corn stover lignin (CECL). Pyrolysis of CECL in a thermogravimetric analyzer coupled with Fourier transform infrared spectroscopy (TG-FTIR) exhibited that ZnCl$_2$ promoted the formation of solid product, resulted in high activation energies (114–236 kJ/mol). The evolution amount of CO$_2$ and H$_2$O increased 2–3 times with ZnCl$_2$. Pyrolysis in a pyrolyzer coupled with gas chromatography/mass spectrometry (Py-GC/MS) showed that 4-vinylphenol and 4-vinylguaiacol exhibited high peak areas, and the formation of most monomeric phenols was substantially suppressed by ZnCl$_2$. A possible mechanism was provided considering that ZnCl$_2$ promoted the formation of char and non-condensable gases while suppressed the formation of bio-oil. The substantial evolution of gases could be responsible for the highly porous structure of activated carbon prepared with ZnCl$_2$. Our work provides a foundation towards understanding the effect of ZnCl$_2$ on lignin pyrolysis.

1. Introduction

Lignin is a polymer of phenylpropane units connected with ether and carbon-carbon linkages [1,2]. As the second most abundant component in biomass, lignin is a promising material to replace fossil resources for the production of high-value functional carbon materials, fuels and chemicals [1–3]. In cellulosic ethanol industry, cellulolytic enzyme lignin (CEL) is produced as the main waste by-product, and high-value use of this waste residue can greatly improve the economic competitiveness of the cellulosic ethanol process [4,5]. However, due to its heterogeneous and robust structure, efficient use of lignin remains a grand challenge compared with that of carbohydrates [6].

Pyrolysis represents a promising thermo-chemical route to convert lignin into a range of high value-added products including bio-char, bio-oil and non-condensable gases [1]. The bio-char with abundant surface functional groups while limited surface area can be upgraded to high-value functional carbon materials, like activated carbon. Activated carbon with highly porous and large surface areas has great potential in the application fields of environment protection, energy storage, and catalysis, etc. [3]. Activated carbon can be prepared by physical activation or chemical activation, and chemical activation involves pyrolysis and activation at relative low temperature (450–650 °C) in one step [7,8]. The most widely used chemicals for chemical activation include zinc chloride (ZnCl$_2$), phosphoric acid (H$_3$PO$_4$), and potassium hydroxide/carbonate (KOH/ K$_2$CO$_3$). As one of the commonly used activation chemicals, ZnCl$_2$ (the melting and boiling points are 263 and 732 °C, respectively) can intrude into the lignin matric and remain in a liquid state throughout the pyrolysis process. As a result, the rearrangement of carbon molecules will not be inhibited, producing char with well-developed microporous and mesoporous structure [9–11]. In spite of being toxic, ZnCl$_2$ can be fully removed by appropriate acid treatment and washing [12].

Besides bio-char, pyrolysis of lignin also produces bio-oil and non-condensable gases. Bio-oil contains abundant phenolic compounds which are precursors for renewable aromatic chemicals and drop-in fuels. Reported work showed that the formation of bio-oil and non-condensable gases during pyrolysis of biomass was greatly impacted by adding metal-salts. Wang et al. examined the effect of KCl, CaCl$_2$ and FeCl$_3$ on pyrolysis performance of alkali lignin, finding a strong selective enrichment of phenols in pyrolysis vapors with the catalysts [13]. Collard et al. investigated the effect of nickel and iron salts on the pyrolysis of beech wood, reporting a significant decrease in tar production and an increase in H$_2$ production in the presence of nickel salts [14]. Wu et al. also reported that the gas yield and hydrogen production for pyrolysis/gasification of the three main components of biomass was promoted by nickel-based catalysts [15]. Despite the significant efforts

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devoted to the performance of $ZnCl_2$ on properties and applications of obtained char, its effect on bio-oil and non-condensable gases production has not been well elucidated, leading to a lack of comprehensive understanding of the mechanisms of $ZnCl_2$ on lignin pyrolysis [9–11,16].

The target of this work is to investigate the effect of impregnated $ZnCl_2$ on the pyrolysis behavior of waste cellulolytic enzyme corn stover lignin (CECL), mainly focusing on the evolution of bio-oil and non-condensable gases. Our results will enhance the understanding of $ZnCl_2$ on lignin pyrolysis and give a guidance on promoting the commercial use of CECL, bringing added-value to the cellulosic ethanol process. Considering that the pyrolysis behavior is tightly related to the structure of sample, we first characterized the structure of CECL in terms of the distribution of elements, functional groups, building blocks (p-hydroxyphenyl unit, guaiacyl unit, and syringyl unit) and interunit linkages. Thermogravimetric analyzer coupled with fourier transform infrared spectroscopy (TG-FTIR) and pyrolyzer coupled with gas chromatography/mass spectrometry (Py-GC/MS) were then introduced for investigating the catalytic effect of $ZnCl_2$ on pyrolysis behavior of CECL mainly focusing on the evolution information of bio-oils and non-condensable products. Finally, a possible mechanism of $ZnCl_2$ on CECL pyrolysis was proposed.

2. Materials and methods

2.1. Materials

The chemicals used in this study were purchased from the Nanjing Reagent Co. and used as received. The cellulolytic enzyme corn stover lignin (CECL) was obtained from Yanghai Co. (Jinan, China) as the by-product derived from a cellulosic ethanol biorefinery process. The CECL has trace amount of ash.

Additive amount of $ZnCl_2$ was based on the mass ratio of 1:15 ($ZnCl_2$: lignin). An excessive impregnation method was used to add the catalyst. In brief, certain amount of $ZnCl_2$ was dissolved in the deionized water, then CECL was added and dispersed by ultrasonic for 0.5 h. Just after that, the impregnated lignin was heated with 1000 rpm stirring to remove water, and then stored in desiccator for following pyrolysis experiments.

2.2. Methods

2.2.1. Characterization of the lignin

Elemental analysis of the lignin was performed on a Vario Micro analyzer. C, H, N contents were measured and the O content was calculated by difference.

FTIR spectra of the lignin was recorded on a FTIR spectrophotometer (Bruker Vector 22) using KBr pellet containing about 1% samples. The scan was conducted in the range from $4000 \, cm^{-1}$ to $400 \, cm^{-1}$.

^{13}C NMR spectra were obtained on 100 mg lignin dissolved in 0.6 mL of dimethylsulfoxide-d6 (DMSO-d_6) using a Bruker AV500 spectrometer. The spectrum was recorded from 2000 scans with 220 ppm sweep width and 1 s pulse delay at room temperature, and the peak at 39.5 ppm of DMSO-d6 was used as internal standard.

2.2.2. TG-FTIR

A thermogravimetric analyzer (Setsys-1750, Setaram) coupled to an FTIR spectrophotometer (Bruker Vector 22) was employed to investigate the mass loss of lignin and on-line formation of gas products. About 20 mg lignin sample was placed into the furnace and heated from 30 to 900 °C at a heating rate of 10, 20 and 40 °C/min under a nitrogen flow of 60 mL/min to maintain an inert atmosphere. The FTIR instrument was connected to the thermogravimetric analyzer by a flow cell which was heated to 280 °C to prevent condensation of the non-condensable products. The scanning range of FTIR was set at $4000–400 \, cm^{-1}$.

2.2.3. Py-GC MS

Fast pyrolysis analyzer (CDS5250) was coupled with the GC–MS (Agilent 5975C) to identify the volatile products of fast pyrolysis of lignin [17–19]. 0.5 mg lignin sample was loaded in the pyrolysis tube, and the pyrolysis temperature was set to be certain temperature (500, 700 °C) with the flash heating rate of 20000 °C/s. The residence time for the sample was 20 s. The evolved volatiles were identified by GC–MS, the condition of which was set to be: the injector temperature was kept at 300 °C; the chromatographic separation was performed with a HP-5MS capillary column; the oven temperature was programmed from 50 °C (2 min) to 290 °C (1 min) with 8 °C/min heating rate; the mass spectra were operated in EI mode at 70 eV. The mass spectra were obtained from m/z 50 to 650. The chromatographic peaks were identified according to the NIST MS library and previously published work [18,20].

2.2.4. Isoconversional method

The isoconversional method was applied to calculate the activation energy regardless of the reaction mechanism. The isoconversional method used in this work was Starink method [21],

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = C_s - 1.0037\frac{E}{RT}$$

Where β is the heating rate, T is the Kelvin temperature, Cs is constant, E is the activation energy, and R is the universal gas constant. For a given conversion rate α, the activation energy was determined from the slope of regression for points of $\ln(\beta/T^{1.8})$ and $1/T$ at different heating rates.

3. Results and discussion

3.1. Structural analysis of CECL

Elementary analysis of CECL revealed that the lignin mainly contains C (60.71 wt%), H (6.12 wt%), O (31.29 wt%), and N (1.88 wt%). O content in CECL was higher than most reported lignins, especially lignins from wood (20–30%), because CECL contained abundant p-coumaric acid units and ferulic acid units which widely exist in grass lignin, as revealed by following ^{13}C NMR analysis [2].

Fourier transform infrared spectroscopy (FTIR) is used for qualitative analysis of functional groups in CECL (**Fig. S1**). Bands were assigned according to published work [22,23]. Apparent absorption peaks could be identified for hydroxyl groups ($3425 \, cm^{-1}$, 1 in Fig. 1), methyl and methylene groups ($2920 \, cm^{-1}$, 2; and $1470–1460 \, cm^{-1}$, 6), C—O in unconjugated carbonyls ($1715–1705 \, cm^{-1}$, 3), and aromatic ring skeleton vibration ($1605–1595 \, cm^{-1}$, 4; $1510–1505 \, cm^{-1}$,5; and $1430–1425 \, cm^{-1}$, 7). According to signals in fingerprint area (bands below $1500 \, cm^{-1}$), CECL showed intense peaks of guaiacyl rings ($1270 \, cm^{-1}$, 10; and $1215 \, cm^{-1}$, 11) and syringyl rings ($1120 \, cm^{-1}$, 12; and $1325 \, cm^{-1}$, 9). Peak assignments of CECL indicated a characterization of grass lignin.

Fig. 1 shows the ^{13}C NMR spectrum of CECL, and signals were assigned according to published work [24]. The very weak signals in the region between 102 and 90 ppm indicated few carbohydrate impurities in CECL.
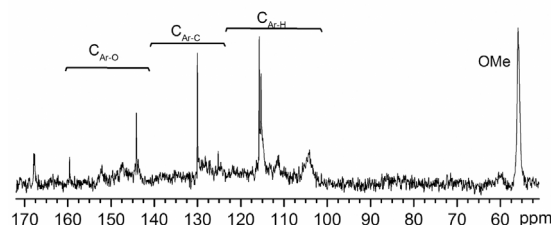

Fig. 1. ^{13}C NMR spectrum of CECL.