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Research article

Characterization of bio-oils and bio-chars obtained from the catalytic pyrolysis of alkali lignin with metal chlorides

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ABSTRACT

The pyrolysis experiments were carried out in a fixed bed reactor at a reaction temperature of 873 K and gas residence time of 1.0 s. The physicochemical properties of bio-oils and bio-chars obtained from alkali lignin pyrolysis with and without KCl, $CaCl_2$, and $FeCl_3$ additives were studied. The compositions of bio-oils were examined using gas chromatography–mass spectrometry (GC–MS). Characterizations of bio-chars were performed using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area and scanning electron microscopy (SEM) techniques. Adding KCl caused a sharp decrease in bio-oil yield while an increase in bio-char yield was found as a result. The addition of $CaCl_2$ and $FeCl_3$ significantly increased the yield of bio-oil and phenol content while inhibited the formation of char residues. The bio-char generated after $FeCl_3$ addition has a much high BET surface area. This result indicates that the addition of $FeCl_3$ in alkali lignin significantly improves the quality of both bio-oil and bio-char, which is beneficial to the usage of bio-oil for chemical materials and bio-char for activated carbon species.

1. Introduction

Lignin is a heterogeneous polymer consisting of phenylpropane units linked through ether or C–C linkages. Alkali lignin, which is an abundant, cheap and renewable resource in paper industry, can be converted into value-added products by pyrolysis. However, lignin decomposes slowly over a broad temperature range and has a lower yield of liquid fraction and a higher yield of char compared with cellulose and hemicelluloses [1,2].

Most previous studies focused on understanding the property and composition of the liquid pyrolysis products. It was found that phenols were the major products in liquid products [3–5]. Recently, due to the several poor properties of pyrolysis products, such as thermal instability, poor volatility, high oxygen content and high viscosity [6], many researchers explored the use of additives to enhance the properties of pyrolysis products. Li et al. [7] studied the influence of cotton stalks with NaCl, K_2CO_3, and $MgCl_2$ on microwave pyrolysis characteristics and found that these additives can simplify the bio-oil components and improve the quality of bio-oil obviously. Ben and Ragauskas [8] suggested that the presence of $NiCl_2$ and ZSM-5 zeolite as additives in kraft lignin could decrease the oxygen content in bio-oil and improve the quality of bio-oil. Ma et al. [9] used transition metal oxides (Co_3O_4, MnO_3, NiO, Fe_2O_3, and CuO) to control the selectivity to specific valuable products, such as vanillin, guaiacol, phenols and arenes.

Numerous studies have been carried out on the characterization of volatile products (gas and tar) produced from pyrolysis of lignin. However, there were very limited studies on the other important product-char. It was reported that bio-char had a condensed aromatic structure and reserve up to 50% of energy from starting biomass [10]. Sharma et al. [11,12] conducted very detailed characterization of lignin char and found the char yield decreased from 80 wt.% to 40 wt.% of lignin as the pyrolysis temperature increased from 523 to 1023 K. Mu et al. [13] discussed the challenges to use the bio-oil obtained from lignin and summarized the methods to improve the quality of bio-oil and bio-char from lignin pyrolysis. A recent study by Azargohar et al. [14] described the effect of temperature on the physicochemical characteristics of fast pyrolysis bio-chars and the result showed that these bio-char samples had a great potential for agricultural applications.

Although previous studies revealed the effect of metal-salt additives on the process of fast pyrolysis, most descriptions of pyrolysis did not give a good account for its effect on the physicochemical properties of pyrolysis products, such as bio-oil and bio-char. Our previous work has examined the catalytic effect of metal chlorides (KCl, $CaCl_2$, and $FeCl_3$) on the pyrolysis vapor of alkali lignin [15]. The aim of this study was to show the influence of KCl, $CaCl_2$, and $FeCl_3$ on physicochemical properties of bio-oils and bio-chars of alkali lignin and explore the formation mechanism of pyrolysis products from the alkali lignin with different metal additives.

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Table 1
Ultimate and proximate analyses of alkali lignin.

Ultimate analysis (wt.%)[b]					Proximate analysis (wt.%)[d]		
C	H	O[a]	N	S	A	VM	FC[a]
62.40 ± 0.14	6.14 ± 0.00	29.43 ± 0.23	0.26 ± 0.03	1.77 ± 0.06	6.21 ± 0.07	66.43 ± 0.21	27.36 ± 0.28

[a] By difference.
[b] daf basis.
[d] Dry basis.

2. Material and methods

2.1. Material preparation

Alkali lignin, CAS 9005-53-2, was purchased from Tokyo Chemical Industry (TCI). Particles with an average size of 20–45 μm were selected. Table 1 presented the composition of the alkali lignin.

Three kinds of metal chlorides of KCl (AR), $CaCl_2$ (AR), and $FeCl_3$ (AR) were selected as additives. Additive amounts were based on the mass ratio of 1:20 between the metal atom of K, Ca, Fe and the alkali lignin. It was calculated that the mass fractions of KCl, $CaCl_2$, and $FeCl_3$ were 9.6 wt.%, 13.9 wt.% and 14.5 wt.% in alkali lignin, respectively. The excessive impregnation method was used to add the additives. The additives were dissolved in the deionized water. The alkali lignin was impregnated with the additive solutions by ultrasonic immersing for 0.5 h and static immersion for 12 h. Then it was dried at 378 K for 6 h to remove absorbed water before the experiments. The mass fractions of K, Ca, and Fe in the resulting alkali lignin samples, detected by atomic absorption spectroscopy, were 0.09 wt.%, 0.47 wt.%, and 0.16 wt.%, respectively.

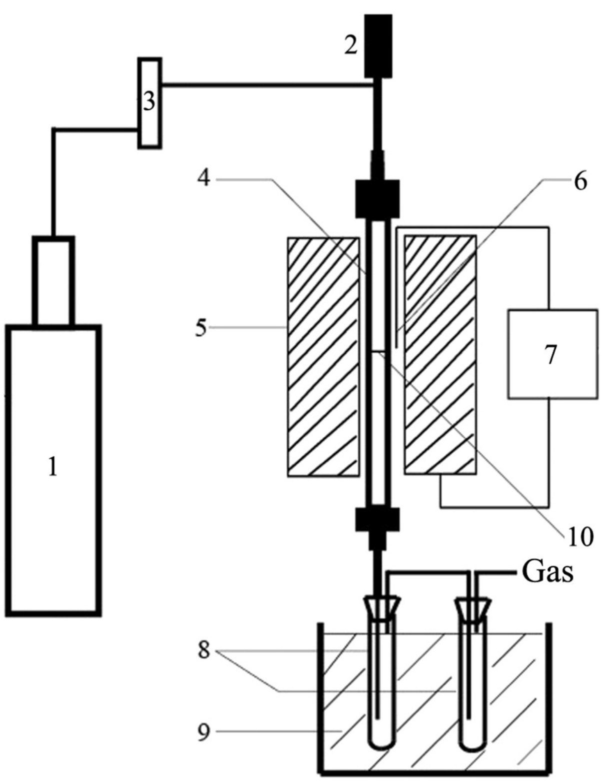

Fig. 1. Fixed bed reactor of alkali lignin pyrolysis. 1—nitrogen cylinder, 2—inlet valve, 3—gas flowmeter, 4—pyrolysis reactor, 5—heater, 6—thermocouple, 7—temperature control device, 8—bio—oil collection, 9—condensing system, 10—wire netting.

2.2. Experimental methods

Pyrolysis experiments (Fig. 1) were carried out in a fixed bed reactor (quartz tube reactor) [16]. The samples were continuously fed into the reactor. Under a constant N_2 flow of 1200 mL min^{-1}, these samples were heated at 873 ± 10 K for gas residence time of 1.0 s. The pyrolysis vapors were condensed into bio-oil and then collected by the condensing system with a collector. The bio-oil condensing system and collectors were weighed before and after the experiments to determine the quantity of the generated bio-oil. The quartz tube reactor was moved out of the heater when the temperature fell below 523 K, while the nitrogen was still supplied as a carrier gas until the pyrolysis residues cooling down to room temperatures to avoid the oxidation of the bio-char.

The compositions of bio-oils were measured using a Shimadzu GCMS-QP2010Plus. During the analysis process, 0.2 μL bio-oil was collected using a micro collection pin. The bio-oil was injected into GC–MS with an inlet temperature of 553 K, a He gas flow rate of 1.0 mL min^{-1} and a split-flow ratio of 30:1. A heating schedule was pre-set as: the temperature remained at 323 K for 5 min, increased to 553 K at a rate of 5 K min^{-1} and then remained for 15 min. A junction temperature of 553 K, an ion temperature of 523 K, an EI source electron energy of 70 eV and a scan range of 20–400 u were used for MS.

The X-ray diffraction (XRD) patterns of raw samples and bio-chars of alkali lignin were examined by the Shimadzu XRD-6000 and collected from 5–45° using Cu Kα radiation (60 kV, 80 mA) at a scanning rate of 2° min^{-1}. The specific surface areas of the bio-chars were measured in a Quadrasorb SI (USA) by nitrogen adsorption. Each sample was

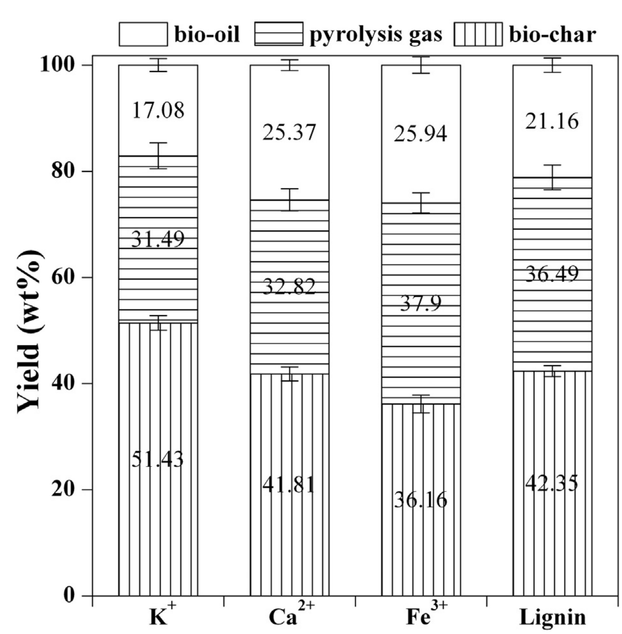

Fig. 2. The yields of pyrolysis products of alkali lignin with the additives of KCl, $CaCl_2$, and $FeCl_3$.