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Catalytic effect of metal chlorides on analytical pyrolysis of alkali lignin

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ABSTRACT

The effect of KCl, $CaCl_2$ and $FeCl_3$ as additives on pyrolysis performance of alkali lignin was examined using thermogravimetric analyzer/Fourier transform infrared spectrometer (TG-FTIR) and pyrolysis–gas chromatography/mass spectrometry (PGC/MS). Notable differences of catalytic effects were observed after different metal chlorides were added. The yield of residual carbon and gases with low molecular weight increased remarkably with the addition of KCl. $FeCl_3$ and $CaCl_2$ had a promoting influence on the thermal cracking of alkali lignin, resulting in a decrease of the residual carbon formation by 2.7% and 3.5%. All additives played an active role in promoting the content of active phenols obtained from pyrolyzing the alkali lignin. During the catalytic pyrolysis process, the yields of small-molecule gases were in the order of $CO_2 > H_2O > CH_4 > CO$, the capability of catalytic thermal cracking of alkali lignin by three metal additives was ranked as such: $Fe^{3+} > Ca^{2+} > K^+$, and the ability of generating small-molecule gases by the additives was in the order of $K^+ > Fe^{3+} > Ca^{2+}$.

1. Introduction

As a promising material for producing renewable aromatic chemicals, lignin is one of the main components of biomass and includes various reactive functional groups such as $–OCH_3$, –OH, and –CO [1,2]. Pyrolysis is considered as an effective method to convert lignin into small molecules. However, lignin is very difficult to be thermal-degraded due to its complicated structure [3,4]. Therefore, lignin pyrolysis plays a crucial role in the process of the pyrolysis conversion of biomass.

Recently, many researchers focused on the catalytic pyrolysis of lignin. It was found that the dipping treatment of lignin with additives showed the capacity to promote the pyrolysis process [5–8]. Ben and Ragauskas [5] suggested that the presence of $NiCl_2$ and ZSM-5 zeolite as additives in Kraft lignin could almost eliminate the aliphatic hydroxyl and carboxyl groups and decrease the oxygen content in the bio-oil, resulting in the quality improvement of bio-oil. Collard et al. [6] assessed the effect of nickel and iron salts on the pyrolysis mechanisms of the main constituents of Beech wood. It was found that the nickel salts contributed to a significant decrease in tar production and a large increase in hydrogen production. Using the nickel-based catalysts to increase the gas yield and hydrogen production was also reported by Wu et al. [7]. Guo et al. [8] concluded that the additives of NaOH and Na_2CO_3 had a great catalytic effect on the pyrolysis and gasification process of alkali lignin.

Most of the reported relative studies have focused on the pyrolysis influence of the same type of metal-salts and only a few have examined the pyrolysis performance of lignin in the presence of different types of metal-salts. It is well known that three kinds of typical metal-salts of the alkali, alkali earth and transition metal-salts have different chemical activities. However, the comparative effects of these additives on the pyrolysis behavior of alkali lignin have not been reported. In this study, the main objective was to examine the effect of KCl, $CaCl_2$, and $FeCl_3$ as pyrolysis additives on alkali lignin by determining the thermal degradation, kinetics, and chemical structure with a thermogravimetric analyzer (TGA)/Fourier transform infrared (FTIR) spectrometer and chemical composition of pyrolysis vapors with a pyrolysis–gas chromatograph/mass spectrometer (PGC/MS). It is expected that the results will clarify the degradation pattern and product formation of lignin pyrolysis with different additives, which is also beneficial to the production of value-added chemicals from biomass pyrolysis.

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 w%, 13.9 w% and 14.5 w% 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

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Table 1
Ultimate analysis and proximate analysis 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.

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 w%, 0.47 w% and 0.16 w%, respectively.

2.2. Experimental methods

The NETZSCH STA449F3 (Germany) thermo-gravimetric analyzer was coupled with BRUKER TENSOR 27 Fourier transform infrared analyzer (TG-FTIR). With a flow rate of 50 mL/min and a heating rate of 10 K/min, nitrogen was used as a protection gas in the chamber. The pyrolysis temperature ranged from 303 to 1073 K. During the experiment, the FTIR mode number of 4000–600 cm^{-1}, 4-time scans s^{-1} and a resolution of 1 cm^{-1} were used.

The CDS 5150 pyrolyzer coupled with Shimadzu GCMS-QP2010Plus gas chromatography/mass spectrometry (PGC/MS) was used to observe the characteristics of the pyrolysis vapor. GC/MS had EI source, DM-5 (60 m × 0.25 mm × 0.25 μm) and NIST08 MS data base. A heating rate of 20 K/s, a holding temperature of 873 K and a time-duration of 10 s were used for the pyrolyzer. An inlet temperature of 525 K, a He gas flow rate of 1.0 mL/min and a flow split-ratio of 100:1 were used for the GC. A heating schedule for the column was pre-set as: remained at 323 K for 5 min, increased to 525 K at a rate of 10 K/min and then remained for 15 min. A junction temperature of 523 K, an ion temperature of 473 K, an EI source electron energy of 70 eV and a scan range of 40–450 μm were used for the MS.

2.3. Pyrolysis kinetic analysis method

The Coats–Redfern method [9] was used to analyze the kinetic characteristics of alkali lignin pyrolysis. The Coats–Redfern formula used to calculate the kinetic parameters of different order reactions is as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}, \qquad n=1 \tag{1}$$

Table 2
Kinetic parameters of alkali lignin pyrolysis.

Sample	T_s (K)	n	T_{max} (K)	w (%)	E (kJ mol^{-1})	A (min^{-1})	R^2
Lignin + K^+	354–416	1	401	59.9	55.2	2.3×10^5	0.953
	536–744	2	582		33.8	59.4	0.974
	960–1050	2	980		191.8	4.2×10^{10}	0.984
Lignin + Ca^{2+}	314–395	1	376	50.2	44.7	1.0×10^5	0.986
	577–774	2	623		24.5	10.8	0.976
	955–1050	2	935		225.0	7.9×10^{12}	0.979
Lignin + Fe^{3+}	333–395	1	374	51.0	43.9	5.8×10^4	0.964
	541–780	2	608		24.0	9.8	0.995
	935–1045	2	930		198.7	9.2×10^{11}	0.995
Lignin	325–400	1	388	53.7	33.7	6.3×10^2	0.987
	541–736	2	599		35.4	86.7	0.977
	943–1052	2	952		161.3	8.5×10^8	0.958

T_s: temperature section; n: reaction order; T_{max}: temperature of the maximum rate of weight loss; w: the final residual mass fraction; E: activation energy; A: pre-exponential factor; R^2: correlation coefficient.

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT}, \qquad n\neq1 \tag{2}$$

where α is the mass loss fraction, n is the reaction order, E is the activation energy (kJ mol^{-1}), A is the pre-exponential factor (min^{-1}), β is the heating rate (K min^{-1}), R is the universal gas constant (8.314 J $K^{-1}\cdot mol^{-1}$) and T is the temperature (K).

3. Results and discussion

3.1. Thermal gravimetric analysis

Fig. 1a showed that all the carbon residue of alkali lignin pyrolysis with and without additives were more than 50 w%. The carbon residue reduced with the addition of $CaCl_2$ and $FeCl_3$, while increased with the addition of KCl due to the strengthening of cross-linking reaction [10]. It is indicated that $CaCl_2$ and $FeCl_3$ had a promoting effect on the degradation of alkali lignin.

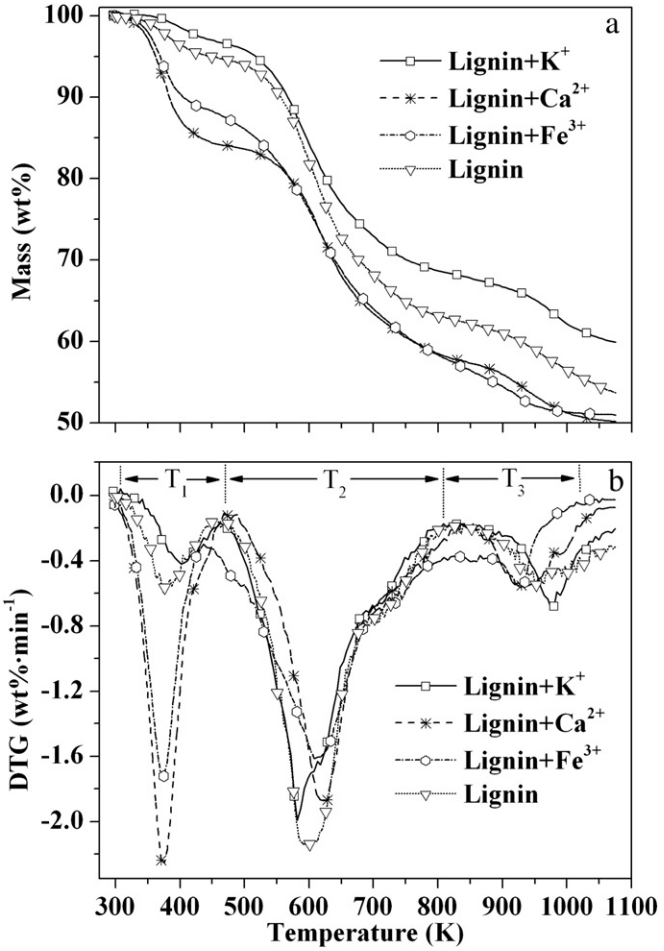

Fig. 1. The TG (a) and DTG (b) curves of alkali lignin pyrolysis.