Influence of Alkali and Alkaline Earth Metallic Species on the Phenolic Species of Pyrolysis Oil

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Bio-oil as an important renewable energy product has been successfully made from corn stalks and lignin *via* a fast pyrolysis process. This study investigated the effects of alkali and alkaline earth metallic species (AAEMs) on phenolic products in corn stalk and lignin pyrolysis oil. Corn stalks were demineralized with 0.5 M HCl, and lignin was doped with 0.2wt%, 2wt%, and 20wt% KCl and $CaCl_2$, respectively. The pyrolysis experiments were conducted in a fixed bed tubular furnace ranging from 450 °C to 600 °C. It was found that AAEMs exert positive effects on the formation of char and gas and inhibit the production of bio-oil. The effect of KCl on the product distribution from lignin is somewhat stronger than $CaCl_2$. Moreover, the content of P, HP, GP, and SP decreases after removal of AAEMs. KCl can promote the polymerization of light molecular aromatic hydrocarbons to increase the SP yield at 600 °C, whereas the effect on increase in P and HP content is relatively weaker than $CaCl_2$. KCl and $CaCl_2$ play notable roles in demethxylation and demethoxylation in increasing phenol content and removing the R group from the ring.

Keywords: Phenolic species; AAEMs; Corn stalk; Lignin; Fast pyrolysis; Biomass

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INTRODUCTION

With the increasing depletion of fossil fuel resources and the serious threat of global warming, interest in using environmentally friendly, renewable energy has grown in recent years. As one of the mostly carbon-neutral, low in sulfur, and low in nitrogen renewable energy resources, biomass has great prospects of helping to overcome the challenges mentioned above. Pyrolysis oil (bio-oil), which is obtained by liquefaction of biomass, has advantages in storage, transport, and increased energy density compared to more traditional forms of biomass energy. Therefore, significant research has been done on transformation and utilization technologies for bio-oil (Kawser and Ani 2000; Balat *et al.* 2009; Bridgwater 2012; Jeong *et al.* 2016; Rashid *et al.* 2016). Bio-oil, which is abundant in organic compounds such as phenols, can be used in the production of higher value chemicals. For example, phenolic-rich pyrolysis oil can be used as alternative to phenol to synthesize phenolic resin (Gao *et al.* 2012), used in cosmetics as a photo stabilizer (Andersen *et al.* 2010; Soltani *et al.* 2016), and used to synthesize dyes (Kristanti *et al.* 2016).

The phenolic compounds in bio-oil are produced primarily by pyrolysis liquefaction from the lignin component of biomass; phenolics comprise about 20% of the bio-oil from biomass pyrolysis, while the content is above 55% in lignin pyrolysis oil (Lv

et al. 2013; Shen *et al.* 2015; Liu *et al.* 2016). In addition, it was also reported that the phenolic compounds are mainly phenol, 4-vinyl phenol, 2-methoxy-4-vinyl phenol, and 2,6-dimethoxy phenol (Ohra-aho *et al.* 2005; Patwardhan *et al.* 2011; Zhou *et al.* 2013). The high yield of phenolic compounds is attributed to the special structure of lignin—the three primary monomers (p-coumaryl, coniferyl, and sinapylalcohol) are linked by carbon–carbon bonds and ether bonds (*e.g.* β–5 and 5–5), wherein the unsaturated carbon–carbon bonds are important functional groups that can serve as links in the polymerization of lignin to produce aromatic hydrocarbon compounds (Saiz-Jimenez and De Leeuw 1986; Ralph *et al.* 2004; Zakzeski *et al.* 2010). As one of the most abundant terrestrial polymers, lignin accounts for about 20wt% of lignocellulose depending on feedstock type.

In addition to the three primary structural components of biomass, the presence of metals (potassium, calcium, sodium, magnesium, *etc.*) plays significant roles in thermal conversion of biomass including lignin (Wang *et al.* 2006; Fahmi *et al.* 2007; Patwardhan *et al.* 2010). To study the catalytic effects of alkali and alkaline earth metals (AAEM) during pyrolysis, three different methods were used in prior research: (i) based on different inherent AAEMs contained in different biomass; agricultural residues that contain higher amount of AAEMs than wood residues produced the lowest liquid yields and highest water and gas yields (Oasmaa *et al.* 2010), (ii) removal of AAEMs in biomass by acid leaching; light oxygenates and non-condensable gas yields were promoted while char production was inhibited after removing the inherent AAEMs in red oak and switchgrass using sulphuric acid (Dalluge *et al.* 2014) and large increases in the yields of organic pyrolysis oil and pyrolytic sugar were observed for all acetic acid leached biomasses (pine wood, wheat straw, hay, bagasse, and cellulose) (Oudenhoven *et al.* 2015), and (iii) other AAEMs are involved in biomass pyrolysis; TG analysis showed the char formation increased with increased potassium concentration, and analytical Py-GC/MS also revealed that potassium catalyzed the formation of C6 and C2C6 lignin derivatives that result from impregnated HF-demineralized samples with different concentrations of KCl (Eom *et al.* 2012). Wood samples that were soaked in sodium and potassium hydroxides yielded more phenolic compounds upon their pyrolysis; NaOH is slightly more effective for the production of guaiacol, cresols, and 4-ethylguaicol, whereas KOH is slightly better for the production of phenol, cis-isoeugenol and transisoeugenol (Di Blasi *et al.* 2009). Similar results have been found from Kleen and Gellerstedt (1995) that sodium, both as an exchanged counter-ion and as added inorganic salt, does not change the absolute amount of lignin products to any noticeable degree but has a clear catalytic effect on the distribution pattern of lignin pyrolysis products. AAEMs exerts effects on the distribution of pyrolysis products and phenolic compounds of biomass. However, fewer research investigations have been carried out on pyrolysis of lignin doped with AAEMs. The effect of minerals on the primary pyrolysis product distribution of lignin (doped with NaCl, KCl, MgCl$_2$, and CaCl$_2$) was investigated, and no significant differences were observed in the speciation resulting from these samples, apart from an approximately 1 wt % increase in the char yield (Patwardhan *et al.* 2011). The cited authors also found that the yield of alkylated phenols increased with temperature, whereas the yield of methoxylated phenols reached a maximum at 600 °C

Therefore, temperature is also generally considered to be an important factor in biomass pyrolysis. Many papers on the fast pyrolysis of biomass are available in the literature (Patwardhan *et al.* 2011; Zhou *et al.* 2013; Song *et al.* 2015). The trend in distribution of pyrolysis products is similar when comparing untreated and water (or

organic acid) washed biomass with increasing temperature. For example at 500 °C to 900 °C, the yield of solid and liquid products decreased while the yield of gaseous products increased (Song *et al*. 2015).

The phenolic-form compounds in pyrolysis oil can be used to produce high value-added chemicals. To investigate how the inherent AAEMs catalyze the generation of phenolic products, corn stalk was demineralized by HCl and compared with raw untreated corn stalk. The influence of potassium and calcium in untreated and KCl and $CaCl_2$ doped lignin pyrolysis was studied, and the distribution of pyrolysis and phenolic products was compared. Enhanced knowledge of the influence of AAEMs in biomass and lignin pyrolysis could lead to new process insights for enhanced production of phenolic products for fuels and chemicals.

EXPERIMENTAL

Materials

Representative agricultural residue corn stalks were obtained from Zibo, Shandong Province, China. The dried corn stalks were milled and pulverized to a particle size of 300 μm and heated at 105 °C for 24 h to remove moisture.

The lignin component (alkali processed) was purchased from Sigma Corporation (St. Louis, USA) and used as a commercial sample in the study. Potassium chloride (powder) and calcium chloride (sheet) were used as substitutes for the inherent potassium (K) and calcium (Ca) elements in biomass. The chloride salts were ground to 300 μm before being doped with lignin.

Methods

The powdered maize stalk was washed in distilled deionized water at 25 °C with stirring for 2 h, adding 0.5 M HCl solution to reduce the mineral content. In the treatment, 1 g of sample was impregnated in 20 mL acid solution. After 2 h, the demineralized sample was filtered with deionized water until it reached a stable conductivity, and then it was dried in an oven at 105 °C for 24 h. The treated sample was sealed in desiccators prior to analysis and investigation. To investigate the effects of potassium and calcium on lignin pyrolysis, the lignin component was prepared by doping with alkaline chloride salts. The lignin was doped with 0.2wt%, 2wt%, and 20wt% KCl (AR 98%) and $CaCl_2$ (AR 95%), respectively. These mixtures were stirred in mechanical agitation before experiments.

The pyrolysis experiments were conducted in a fixed bed tubular furnace (Fig. 1). The experimental unit mainly consisted of a tubular reactor (with an inner diameter and length of 55 mm and 680 mm), a temperature controller, two steps collector bottles, and a gas collector bag. Nitrogen (purity > 99.999%) was used as a carrier gas and to provide an oxygen-free atmosphere.

Accurately weighed 2.00 g of samples were put into porcelain boats with dimensions of 50 mm × 20 mm × 10 mm. Each of the porcelain boats was filled half way. The furnace was turned on and heated to the desired temperature controlled by the electrical controller. After the tubular reactor had been filled with nitrogen gas (the flow rate of 300 mL/min), the feeding side of the tube was opened, and then the sample boat was rapidly pushed into the heat zone for pyrolysis. The sample was quickly heated in the furnace with a heating rate of 1000 °C/s. The gas product passed through two cooling

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bottles and a gas collector bag, wherein the condensable gases were cooled into tar and collected in the cooling bottles. The incondensable gases were captured in the gas bag. The tar cooling bottles were put in an ice and water bath to improve the efficiency of condensation. The process was continued until the volume of the gas collector bag was no longer changing, at which point it was time to insert a new boat. The reaction time of a boat was about five minutes.

The liquid product was dissolved with equal quality ethanol and taken from cooling bottles using an injector. Then the liquid was filtered through a FitMax Syringe Filter (25 mm 0.22 μm Nylon 100/pk) and injected into a GC-MS sample bottle for analyzing. The yields of char were obtained by the ratio of the mass of the char in boats after the reaction to that of raw material in boats before the reaction. There was not any coke on the reactor wall at all. The gas yield was obtained by subtracting the yield of bio-oil and coke from the overall yield of products (be closed to 100%).
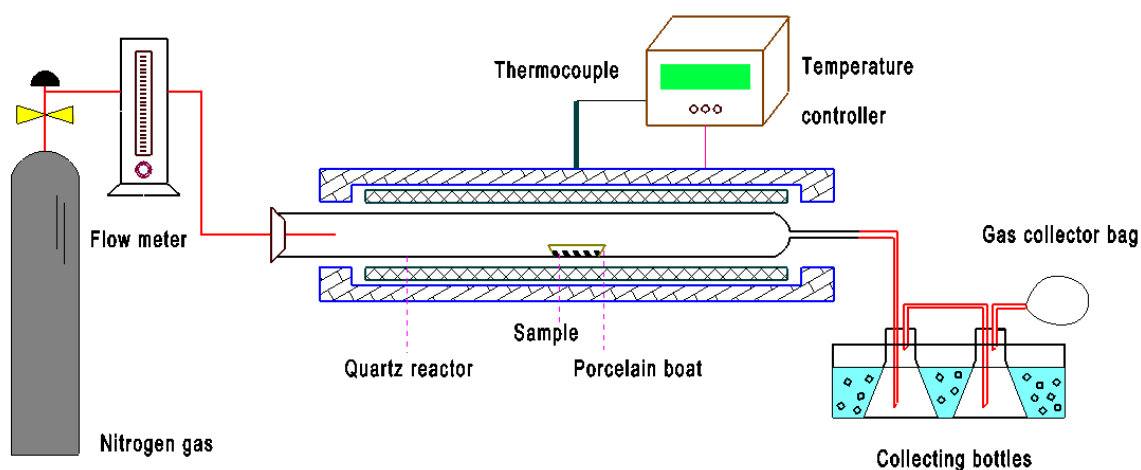

Fig. 1. Fixed bed tubular furnace

Characterization

Proximate analysis was carried out according to GB/T 28731 (2012). The volatile matter, fixed carbon, and moisture contents of raw and treated maize straw samples were measured as shown in Table 1. The elemental analysis of raw and treated samples was carried out using a EURO EA3000 Analyzer (LEEMAN LABS INC., Hudson, USA). Table 1 also shows the basic elemental composition of the samples. The proximate and ultimate analyses were conducted with the dried samples.

The inherent AAEMs concentration of the raw and acid-washing samples were assessed using inductively coupled plasma mass spectrometry (ICP-MS), as described previously (Patwardhan *et al.* 2010; Jiang *et al.* 2015). Briefly, the sample was digested in a mixture of 2 mL H_2O_2 (30%), 1 mL HF (38%), and 10 mL HNO_3 (65%) in a microwave digestion system. The AAEMs content in the mixture was measured by ICP-MS. The measurement was repeated three times. The results are presented in Table 2.

Analytical gas chromatography-mass spectrometer (GC-MS) experiments were performed with the Agilent 6890/5973 device (Agilent, USA) with a split ratio of 60:1 and injection temperature of 280 °C. The DB-1701 GC capillary column was 60 m × 0.25mm × 0.25 μm. Helium (99.999% high purity) was the carrier gas with a flow rate of 1 mL/min. The GC oven temperature was programmed to increase from 40 °C to 240 °C with a rate of 5 °C/min, followed by a hold for 5 min at 240 °C. The transfer line was set

at 280 °C, and the MS ion source (Aux) was set at 250 °C with 70 eV electron energy. Data analysis was performed by comparing the spectra of the components with the database of known components stored in the GC-MS Nist-05 library. The run time was 45 min.

Table 1. Proximate and Ultimate Analyses of Raw and Treated Corn Stalk

Name	Proximate Analysis			Elemental Analysis			
	Volatiles	Fixed carbon	Ash	C	H	N	S
RCS	74.43	19.22	6.35	43.21	5.28	1.55	0.4
AWCS	76.18	20.38	3.44	44.47	5.37	1.21	0.36
RCS, raw corn stalk; AWCS, acid-washed corn stalk							

Table 2. AAEMs Content and Demineralization Efficiency of Raw and Treated Corn Stalk

| Sample	AAEMS (mg/kg, by dry weight)				Demineralization Efficiency (%)			
	Na	Mg	K	Ca	Na	Mg	K	Ca
RCS	157.05 ±1.04	3327.01 ±2.01	21405.13 ±1.87	4825.03 ±2.31	-	-	-	-
AWCS	47.56 ±0.69	58.32 ±0.87	101.65 ±3.37	166.75 ±1.51	69.71	98.2	99.5	96.5
RL	75420.13 ±0.22	193.8 ±1.93	15771.26 ±1.48	204.15 ±1.87	-	-	-	-
RCS, raw corn stalk; AWCS, acid-washed corn stalk; RL, raw lignin sample								

RESULTS AND DISCUSSION

Distribution of Pyrolysis Products

The distributions of the pyrolysis products of raw corn stalk (RCS) and acid-washed corn stalk (AWCS) are shown in Fig. 2. It can be observed that temperature significantly affected the distribution of biomass pyrolysis products. For RCS, the yield of pyrolysis oil first increased and then decreased, with the temperature increasing from 450 °C to 600 °C, and the highest yield was 31.4% at 550 °C. The yields of char and gas yield were different from pyrolysis oil yield. Char yield decreased and gas yield increased with increasing experimental temperature. The trends of pyrolysis products indicated that temperature promoted the depolymerization of biomass to generate heavy condensable molecules that can be transformed into pyrolysis oil. After 550 °C, the secondary cracking of heavy condensable molecules was promoted, so that the gas yield increased.

For AWCS, using the distribution of RCS pyrolysis products as the basis for comparison, missing AAEMs had a great influence on the distribution of products. The pyrolysis oil yield of AWCS, which was higher than that of RCS, increased from 25.3% to 39.8% with increasing temperature. The highest yield was achieved at 600 °C, which differed from RCS. The same trends were observed for incondensable gas yield and char yield of RCS and AWCS. Meanwhile, the yields of both were suppressed by acid-washing. It is concluded that the removal of AAEMs promoted the thermal decomposition of corn stalk and increased liquid product yield. The char yield and gas yield were both reduced after acid-treated corn stalk. The results are in accordance with the literature (Jensen *et al.* 1998; Song *et al.* 2015).

The distributions of raw and metal salts doped lignin pyrolysis oil are listed in Table 3. Increases in K and Ca proportion enhanced the formation of gas and char. At 500 °C, the char yield increased from 54.56% to 65.41% with the increasing proportion of K, and it increased to 60.96% with that of Ca. Increasing the K and Ca proportions resulted in an increase in yield of gas from 17.45% for RL to 20.78% and 24.86% for 20wt% KCl and CaCl$_2$, respectively. The bio-oil yield changes were different from char and gas, which were reduced from 22.53% to 13.69% and 17.58% by the effect of 20wt% KCl and CaCl$_2$, respectively. Accordingly, the effect of KCl on the distribution of lignin pyrolysis products was somewhat stronger than CaCl$_2$, especially for bio-oil and char yields. A low content of CaCl$_2$ did not exert notable influence on lignin pyrolysis. It is in agreement with the results of Eom *et al.* (2012), who found Ca ions did not cause significant changes in the formation of pyrolysis compounds during adding CaCl$_2$ to lignocellulosic biomass pyrolysis.
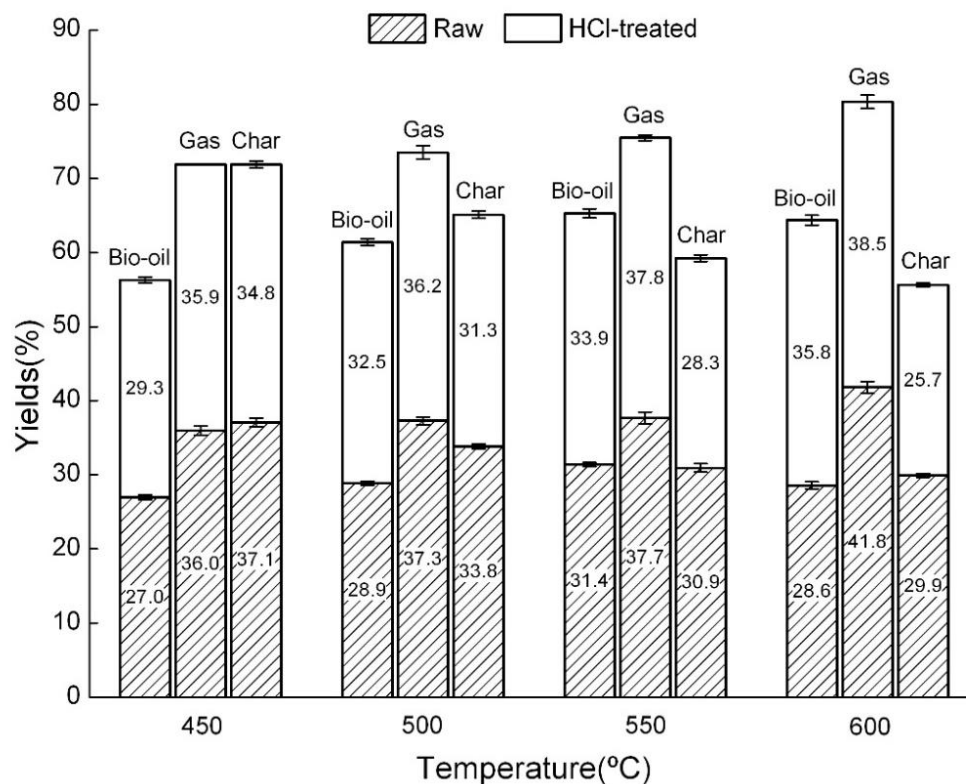
Fig. 2. Distribution of pyrolysis products in raw and acid-washed corn stalk at different temperatures

Table 3. Distribution of Raw and Treated Lignin Pyrolysis Products

Temperature	Production	Yields (%)						
		Raw	0.2wt%KCl	2wt%KCl	20wt%KCl	0.2wt%CaCl$_2$	2wt%CaCl$_2$	20wt%CaCl$_2$
450 °C	Bio-oil	19.03	16.32	13.67	13.41	18.03	17.32	16.59
	Gas	14.42	16.43	18.45	19.14	15.21	15.68	16.64
	Char	63.19	65.10	66.04	67.93	63.27	64.24	66.1
	Closure	96.64	97.85	98.16	100.48	96.51	97.24	99.33
500 °C	Bio-oil	22.53	19.05	14.22	13.69	19.78	19.22	17.58
	Gas	17.45	19.08	21.33	20.78	21.33	22.24	24.86
	Char	57.56	61.51	62.65	65.41	57.95	58.01	59.96
	Closure	97.54	99.64	98.20	99.88	99.06	99.47	102.4
550 °C	Bio-oil	21.58	19.25	15.41	13.88	19.31	18.49	16.11
	Gas	19.34	20.78	22.72	25.12	22.2	23.6	25.14
	Char	57.08	58.65	61.43	62.2	57.14	57.22	58.07
	Closure	98.00	98.68	99.56	101.2	98.65	99.31	99.32
600 °C	Bio-oil	20.09	17.65	14.93	12.1	17.45	17.05	15.77
	Gas	24.46	26.50	29.31	30.33	23.1	24.49	24.68
	Char	55.38	56.11	56.97	60.09	56.15	56.44	57.90
	Closure	99.93	100.26	101.21	102.52	96.7	97.98	98.35

Catalytic Effects of AAEMs on Yields of Phenolic Products

The phenolic compounds obtained from pyrolysis oil can be divided into four classes of species: P (phenols), HP (hydroxy phenols), GP (guaiacols), and SP (syringls). Figure 3 presents the catalytic effects of AAEMs on the phenolic content at different temperatures. As can be seen, the phenolic compounds rich in the bio-oil were mainly P and GP, whereas the content of HP and SP were relatively low within the range 450 °C to 600 °C.

As shown in Fig. 3, AAEMs had catalytic effects on the phenolic content. The content of P, HP, and GP was noticeably restrained after the removal of AAEMs, but the change of SP content was not remarkable. In particular, the effect of AAEMs on the distribution of phenolic compounds was somewhat stronger when the experimental temperature was below 550 °C. The possible reason is that AAEMs in comparison to temperature has the most predominate effect on thermal conversion of phenolic compounds below 550 °C. Moreover, phenolic production was sensitive to temperature. The content of P increased with an increase in temperature, while that of GP and SP was decreased. These interesting phenomena suggested that AAEMs have positive effects on breaking the intermolecular hydrogen bridges and promoting the transformation of macromolecules into small aromatic ring phenols in pyrolysis process, as previously noted (Wang *et al.* 2006). On the other hand, the increase of phenolic compounds may have been because inorganic constituents increased at the expense of the lignin content (Eom *et al.* 2012).
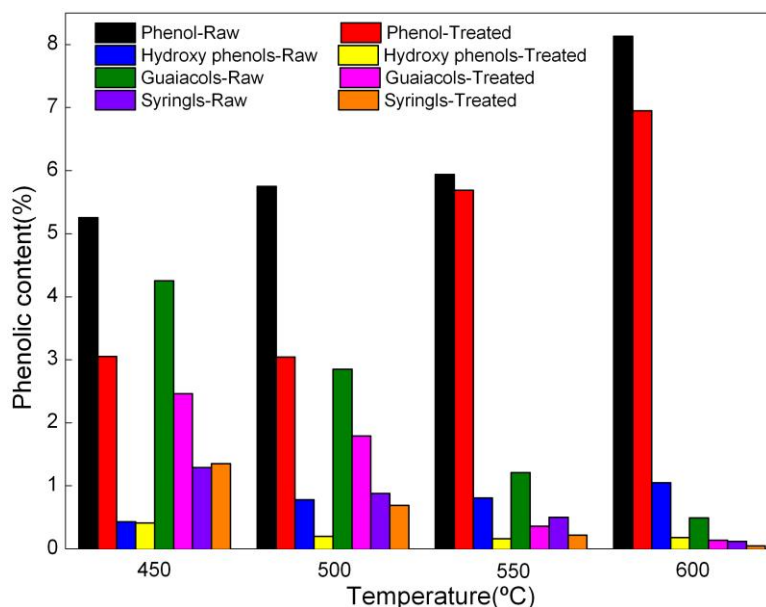
Fig. 3. Phenolic content in raw and acid-washed corn stalk pyrolysis oil at different temperatures

The Effects of Potassium and Calcium on Phenolic products in Lignin Oil

Potassium and calcium are the highest content alkali and alkaline earth metallic species typically found in corn stalk, and phenolic compounds are mainly obtained from the lignin component. To better understand the effects of AAEMs on the phenolic compounds in pyrolysis oil, the catalytic effects of K and Ca on phenolic products were investigated. The mass of metal salts and lignin was based on the initial contents of K, Ca, and lignin in corn stalk. As reported, lignin content is approximately 10~20wt % in corn stalk (Pordesimo *et al.* 2005; Zhang *et al.* 2010). K and Ca account for about 10~20wt% and about 2~5wt% of lignin, respectively, while pure lignin contains a few K (1.5wt%) and Ca (0.02wt%), based on Table 2. Thus, KCl and $CaCl_2$ were prepared as 0.2wt%, 2wt% and 20wt%, respectively.

Reduction reactions, involving the production of catechol (HP), appear to be involved in lignin pyrolysis before the formation of phenol (P). Such reduction reactions principally involve removal of the R group from the ring, demethylation, or demethoxylation from GP and SP (Dorrestijn and Mulder *et al.* 1999; Hosoya *et al.* 2008; Zakzeski *et al.* 2010). Thus, in the following study, P and HP were classified as phenolic compounds with no methoxyl side chains.

The phenolic content in raw and KCl-doped lignin pyrolysis oil at different temperatures is shown in Fig. 4. The content of phenolic compounds in raw and metal treated lignin pyrolysis oil at 500 °C is listed in Table 3.

SP, which has two methoxyl side chains, is sensitive to temperature. SP content reduced with temperature increased from 450 °C to 550 °C and was lower than others. On the other hand, SP content decreased a little in the presence of KCl and $CaCl_2$. This can imply that the demethoxylation of syringyl units was slightly promoted by the potassium (Eom *et al.* 2012). However, SP were detected in KCl-lignin oils at 600 °C,

which may be due to the fact that KCl promoted polymerization of light molecular aromatic hydrocarbon in bio-oil.

GP content was inhibited notably by the increasing temperature, as seen from Fig. 4. On the other hand, it is shown in Table 4 that the GP content such as 2-methoxyl-phenol and 2-methoxyl-4-methyl-phenol was promoted by the effect of KCl at 500 °C. With $CaCl_2$ involved, the total content of GP had no obvious trend except at 450 °C, while the content of 2-methoxyl-phenol and 3-hydroxy-4-methoxy-benzaldehyde dropped with the increase of the proportion of KCl. This strange phenomenon may be because the aromatic hydrocarbons in the bio-oil are accompanied by the re-polymerization reaction during pyrolysis at 500 °C to 600 °C. Meanwhile, it can be concluded that the effect of Ca on the total content of GP is somewhat weaker than K. These results of K and Ca on phenolic compounds are in agreement with prior reports in the literature (Hosoya *et al.* 2008; Eom *et al.* 2012).

As shown in Fig. 4, the total content of P and HP was significantly influenced by KCl and $CaCl_2$. For the effect of KCl, the total content of P and HP was increased notably, which was consistent with the increasing proportion of KCl (Di Blasi *et al.* 2009; Eom *et al.* 2012).

The content had a striking upward trend from 13.04% to 15.23% at 450 °C, 17.20% to 22.63% at 500 °C, 32.77% to 37.49% at 550 °C, and 43.79% to 60.78% at 600 °C. Similarly to the influence of KCl, $CaCl_2$ exhibited a positive influence on the increase of P and HP content. P and HP yields were also affected by $CaCl_2$ as can be seen from Fig. 4. According to Table 4, among all kinds of P and HP, only phenol increased remarkably with the role of KCl and $CaCl_2$. This could be explained by the reason that KCl and $CaCl_2$ play notable roles in demethxylation and demethoxylation, or removing the R group from ring. This effect of $CaCl_2$ was somewhat stronger than KCl, based on the changes of P, HP, GP, and SP content, as seen from Fig. 4.

Table 4. Content of Main Phenolic Compounds in Raw and Metal-Treated Lignin Pyrolysis Oil at 500 °C

| Compounds name	Phenolic compounds content (%)						
	Lignin	0.2wt% KCl	2wt% KCl	20wt% KCl	0.2wt% CaCl$_2$	2wt% CaCl$_2$	20wt% CaCl$_2$
Phenol	11.09	11.94	13.09	16.00	11.48	12.96	15.54
Phenol, 2-methoxy-	43.63	42.90	43.55	45.18	42.96	41.97	41.30
Phenol, 2-methyl-	2.67	3.72	4.13	3.53	3.46	4.16	4.50
Phenol, 4-methyl-	0.94	0.82	1.14	0.84	0.75	1.08	0.86
Phenol, 3-methyl-	1.65	1.56	1.96	1.57	1.48	2.01	2.71
Phenol, 2-methoxy-4-methyl-	2.10	2.25	2.62	2.90	2.35	1.02	3.00
Phenol, 2,5-dimethyl-	0.85	0.92	1.37	0.70	0.81	0.60	1.07
Phenol, 3,4-dimethoxy-	0.23	0.30	0.22	0.17	0.20	0.18	0.13
Benzaldehyde, 3-hydroxy-4-methoxy-	0.99	0.78	0.99	1.02	1.11	0.91	0.53
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.62	0.57	0.74	0.55	0.42	0.50	0.58
Ethanone, 1-(2-hydroxy-5-methoxy-4-methylphenyl)-	0.13	0.16	0.31	0.25	-	-	-
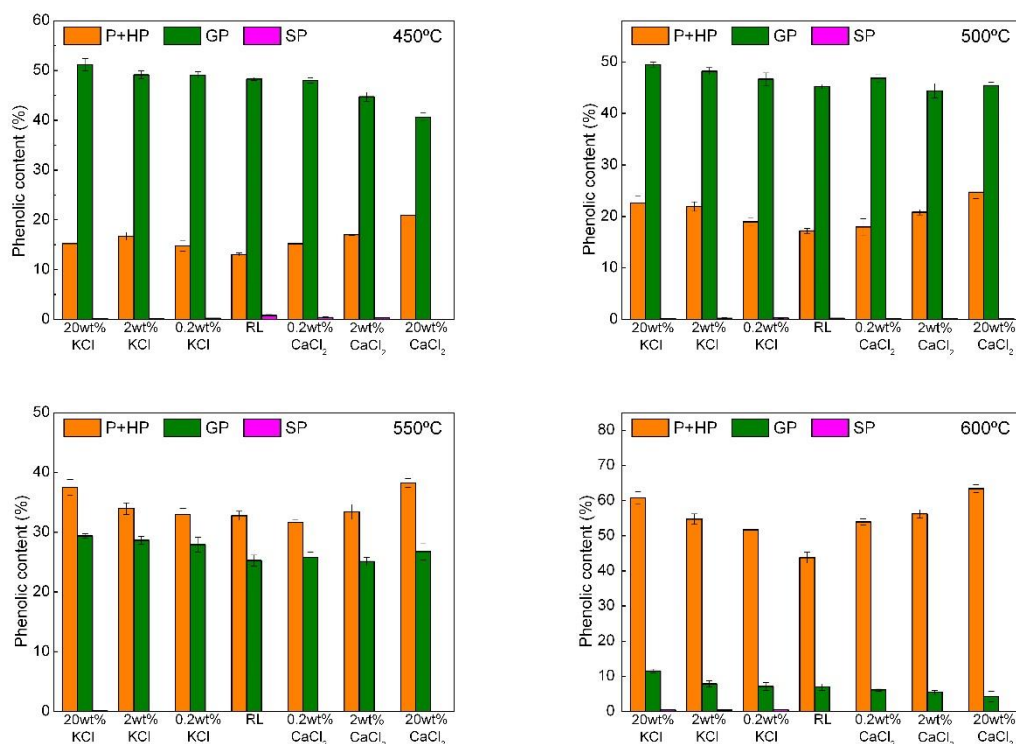
Fig. 4. Phenolic content in raw and KCl-doped lignin pyrolysis oil at different temperatures

CONCLUSIONS

1. Alkali and alkaline earth metallic species exerted effects on the distribution of corn stalk pyrolysis products and phenolic products. AAEMs showed positive effects on the formation of char and gas, while they had a passive effect on yielding bio-oil. The effect of KCl on the production distribution was somewhat stronger than that of CaCl$_2$.

2. Comparing the phenolic content in raw and salts doped corn stalk pyrolysis oil, the phenolic content was promoted by the effect of AAEMs, especially for phenols and guaiacols. The positive influence of AAEMs was relative dominate when the experiment temperature below 550 °C.

3. The influence of potassium and calcium on phenolic products in lignin oil was investigated. The content of P and HP increased and that of GP decreased. Such effects were ascribed to the influence of KCl and CaCl$_2$, whereas CaCl$_2$ exhibited more positive effects on the formation of P and HP. The effect of KCl can promote the polymerization of light molecular aromatic hydrocarbon, which can explain why KCl promoted the production of SP at 600 °C. The increase in phenol content can be concluded that KCl and CaCl$_2$ play notable roles in demethxylation and demethoxylation, or removing the R group from a ring.

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