Thermogravimetric Mass Spectrometry of Lignin Pyrolysis under the Co-action of CaO and $K_2HPO_4 \cdot 3H_2O$

Falin Chen,[a] Jinfang Yao,[a] Yuyu Lin,[a,]* Mingyan Gu,[a,]* and Shang Li [b]

The pyrolysis processes of lignin under the action of CaO and $K_2HPO_4 \cdot 3H_2O$ alone or in coordination were studied by thermogravimetric mass spectrometry (TG-MS). The experimental results showed that after addition of CaO, CaO immobilized the "CO_2-like active intermediates" produced during lignin pyrolysis, which reduced the amount of CO_2 emission in the first stage and lowered the temperature of CO_2 emission in the second stage. After addition of $K_2HPO_4 \cdot 3H_2O$, lignin pyrolysis was remarkably advanced. $K_2HPO_4 \cdot 3H_2O$ catalyzed methyl breakages in the first two pyrolysis stages, and it hindered the release of volatile matter in the third stage to promote the formation of more coke. $K_2HPO_4 \cdot 3H_2O$ catalyzed the reactions toward formation of aromatic ring products and phenols. After addition of CaO and $K_2HPO_4 \cdot 3H_2O$, the initial pyrolysis stage was milder than that with $K_2HPO_4 \cdot 3H_2O$ alone, and the weight loss peak was sharper in the second stage. In the pyrolysis stage, the trend of CH_4, CO, M/Z = 46, toluene, and furfural emission showed that there was a synergistic effect between $K_2HPO_4 \cdot 3H_2O$ and CaO.

Keywords: Calcium Oxide (CaO); Dipotassium hydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$); Lignin; Pyrolysis

*Contact information: a: School of Energy and Environment, Anhui University of Technology, Ma' Anshan 243002, Anhui, China; b: The 71st Research Institute of China Shipbuilding Industry Corporation, Shanghai, 201108, Shanghai, China; *Corresponding authors: linyuyu88@126.com; gumy@ahut.edu.cn*

INTRODUCTION

The catalytic pyrolysis of biomass is the selective conversion of biomass into high-value chemicals or high-quality bio-oil under the action of catalysts (Wang 2010; Ren *et al*. 2013; Liu *et al*. 2016; Yang *et al.* 2019). It is an important way to utilize biomass and has attracted the attention of researchers (Luo *et al*. 2017; Wang *et al*. 2018).

The researchers studied the effects of CaO, phosphate, Al_2O_3, MgO, SiO_2, ZnO, CuO, Fe_2O_3, HZSM-5 and MCM-41 on the biomass pyrolysis products, and found all of these catalysts have an important impact on the products of biomass pyrolysis (Shen *et al.* 2016; Behrens *et al.* 2017; Ma *et al.* 2018; Li *et al.* 2016).

Phosphorus acid and phosphate have been widely used in the study of biomass catalytic pyrolysis process (Lu *et al*. 2013; Zhang *et al*. 2014; Li *et al*. 2016). Li (2016) found that K_3PO_4 could reduce the activation energy of rice husk pyrolysis reaction and change the pyrolysis reaction paths. Fu *et al.* (2008) found that H_3PO_4 could reduce the yield of biomass pyrolysis tar and levoglucosan (LG), but it increased the production of coke and levoglucosenone (LGO). Zhang *et al*. (2014) found that KH_2PO_4, K_2HPO_4, and K_3PO_4 could promote the formation of phenolic products in poplar pyrolysis, while K_2HPO_4 and KH_2PO_4 could increase the yield of small molecule acids during pyrolysis.

CaO is also widely used as a catalyst in biomass catalytic pyrolysis (Wang *et al*. 2010; Lin 2011; Yuan *et al.* 2013). In a small fluidized bed experiment of biomass pyrolysis oil, it was found that the relative content of high oxygen content substances, such as levoglucosan, formic acid, and acetic acid, decreased significantly after adding CaO (Lin *et al*. 2010). Yu *et al*. (2014) found that the addition of CaO in the pyrolysis of pine sawdust had a great influence on the reaction process. Veses *et al*. (2014) studied the co-pyrolysis behavior of pine with CaO in a spiral reactor. It was found that the liquid product yield did not change much, but the organic phase yield increased, the oxygen content decreased, and the calorific value increased from 22.4 to 30.2 MJ/kg. Acids, furans, guaiacol, ethyl methoxyphenol, and other phenols with high oxygen content decreased, while phenols with low oxygen content, low molecular weight chain carbonyl components (aldehydes or ketones), and cycloketones increased.

From the above discussion, K_2HPO_4 can increase the yield of phenolic products while increasing the yield of acids. CaO can significantly reduce the yield of acids. Therefore, it was assumed that the interaction of K_2HPO_4 and CaO would produce some beneficial synergistic effects on biomass pyrolysis (Lin *et al.* 2019). A thermogravimetric-mass spectrometry (TG-MS) study was conducted relative to the cellulose pyrolysis with the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$. The results showed that after the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, the amounts of some species generated, such as H_2, CH_4, CO, phenol, increased compared with those generated in the pyrolysis with single catalyst. Therefore, CaO and $K_2HPO_4{\cdot}3H_2O$ exhibited a strong synergistic effect in the pyrolysis process. Zhao and Lin *et al.* (2018) also found after the mixture of $K_3PO_4{\cdot}3H_2O$ and CaO was added, the emission of HNCO, CH_3CN during camphor pyrolysis decreased compared with those generated in the pyrolysis with single catalyst. However, the combinative effects of CaO and $K_2HPO_4{\cdot}3H_2O$ on biomass or its three major components need to be further explored. In this paper, TG-MS was used to investigate the formation behavior of small molecules in the pyrolysis of lignin, one of the major components of biomass, under the co-action of CaO and K_2HPO_4. The results could provide a further clarification for the biomass pyrolysis of biomass under the combinative effect of CaO and K_2HPO_4.

EXPERIMENTAL

Materials

The CaO, $K_2HPO_4{\cdot}3H_2O$, and lignin samples from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) were used in the experiment. Before the experiment, lignin samples were dried to constant weight at 80 °C in a N_2 atmosphere. Sample configurations are shown in Table 1, labeled as Samples 1, 2, 3, and 4. The quality of lignin in each group was guaranteed to be the same during the experiment.

Table 1. Laboratory Samples

Sample Number	Sample Composition	Mass Ratio
1	Lignin	1:0
2	Lignin + CaO	1:1
3	Lignin + $K_2HPO_4{\cdot}3H_2O$	1:1
4	Lignin + CaO + $K_2HPO_4{\cdot}3H_2O$	2:1:1

Methods

The TG-MS system was composed of a Netzsch STA 449C thermogravimetric (TG) analyzer (STA 449C; Thermogravimetric analyzer, Bavaria, Germany) and a Netzsch QMS 403 mass spectrometer (QMS 403; Mass spectrometer, Bavaria, Germany). The connecting pipes between TG and MS were heated by gradient heating, *i.e.*, along the exit of the TG furnace to the entrance of the MS instrument at 220 °C, 240 °C, and 260 °C to prevent the condensation of gas products. The experimental samples were placed in the aluminium oxide crucible of the thermogravimetric analyzer. After the mass spectrometer signal was stabilized, the temperature programme started, and the mass spectrometer began to record on-line. The argon flow rate was 50 mL/min, the heating rate was 20 °C/min, and the temperature range was 50 to 900 °C.

RESULTS AND DISCUSSION

Analysis of TG/DTG Curve of Pyrolysis

Figure 1 shows the TG and DTG curves for different samples. It can be seen that the pyrolysis of lignin occurred over a wide temperature range, which can be divided into three stages. The first stage was from 50 to 203 °C, and the peak temperature of DTG was 119 °C. Free water and bound water in lignin volatilized, lignin underwent vitrification and began to depolymerize, and some waxy components softened. The second stage was from 203 to 592.6 °C, with the peak temperature at 328.4 °C. This stage was the main weight loss stage. Most of the weight loss occurred in this region. The functional groups such as C-C, C=C, C-O-C, C=O, -OH, methoxy ($-OCH_3$), and so on, which connected the structural units of phenylpropane, broke up and produced condensable volatile components such as alcohols, aldehydes, ketones, and acids. Gases, such as H_2, CH_4, CO, and CO_2, were also generated. In the third stage, from 592.6 to 900 °C, the DTG curves showed two peaks at 701.9 °C and 761.5 °C, corresponding to the carbonization stage. The C=O bonds, C-C bonds, and C-H bonds further broke, condensed, and reorganized. Benzene rings underwent different degrees of chain-breaking or aromatization, and more stable amorphous carbon formed, accompanied by a small amount of small molecular gas emissions.

In the second stage of pyrolysis, there were two peaks at 119 °C and 430 °C in DTG curves after adding CaO, and the second peak temperature range was 400 to 460 °C, which was due to the dehydration and decomposition of $Ca(OH)_2$ formed during the preparation of CaO samples or the initial stage of pyrolysis. In addition, the temperature range of the third stage changed from 563 to 810 °C, with two peaks of 647 °C and 701.6 °C in the DTG curve. The reason for the advancement of this interval was that CaO reacted with carboxylic acid precursors and other "CO_2-like active intermediates" generated during lignin pyrolysis to form calcium carboxylate or organic calcium salts, and then decomposed to form amorphous $CaCO_3$, which further decomposed at 563 °C. After the addition of $K_2HPO_4{\cdot}3H_2O$, there was no obvious weight loss peak in the third stage of pyrolysis. The $K_2HPO_4{\cdot}3H_2O$ promoted the formation of more coke in the third stage. After adding CaO with $K_2HPO_4{\cdot}3H_2O$, the weight loss peak in the second stage of pyrolysis was sharper during 400 to 460 °C, which was caused by the reaction of $K_2HPO_4{\cdot}3H_2O$ with CaO to produce more $Ca(OH)_2$. In addition, there were two apparent peaks at 663 °C and 728 °C in the DTG curve, and the peak temperature and weight loss rate were lower than that of adding CaO alone. This is because $K_2HPO_4 \cdot 3H_2O$ could delay the third stage of volatile matter emission and promote the formation of more coke.

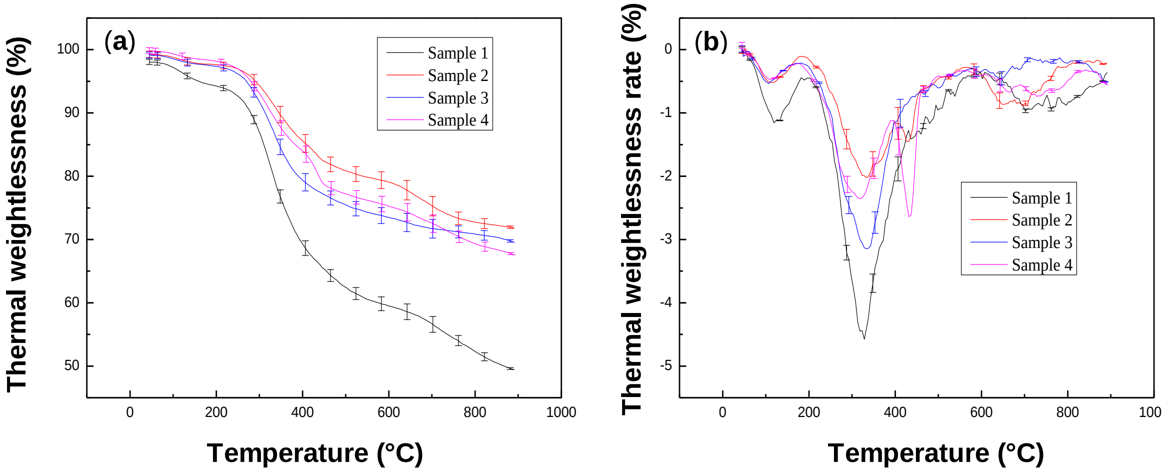
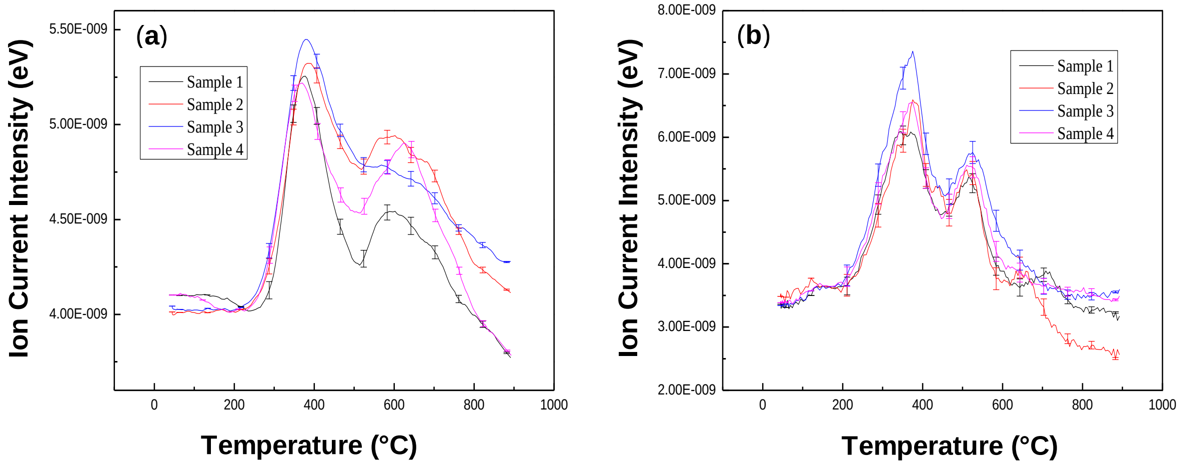


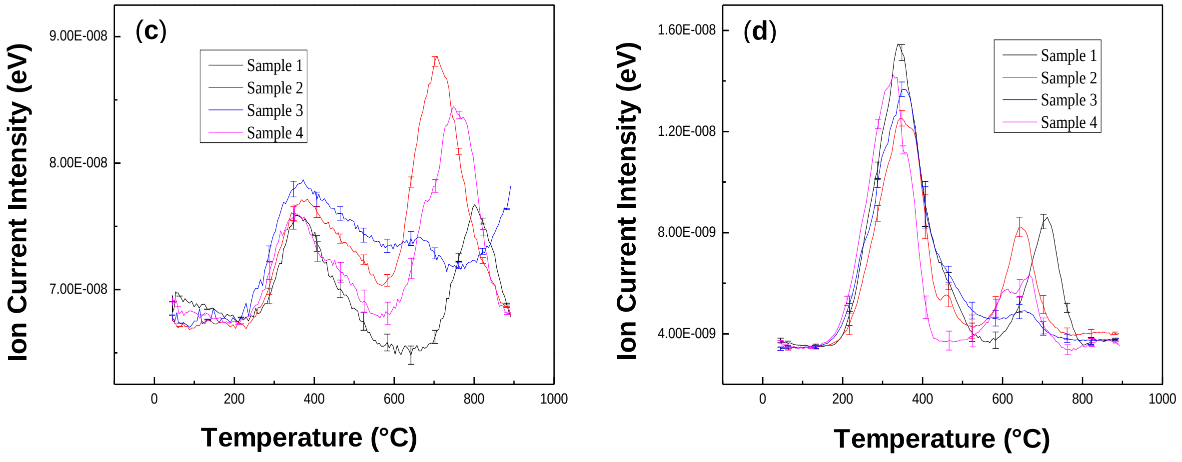
Fig. 1. The pyrolysis (a) TG and (b) DTG curves of samples

Mass Spectrometric Analysis of Exfoliated Gases in Pyrolysis Process

Figure 2 shows the ionic flow intensity curves of H_2, CH_4, and other gases during sample pyrolysis.

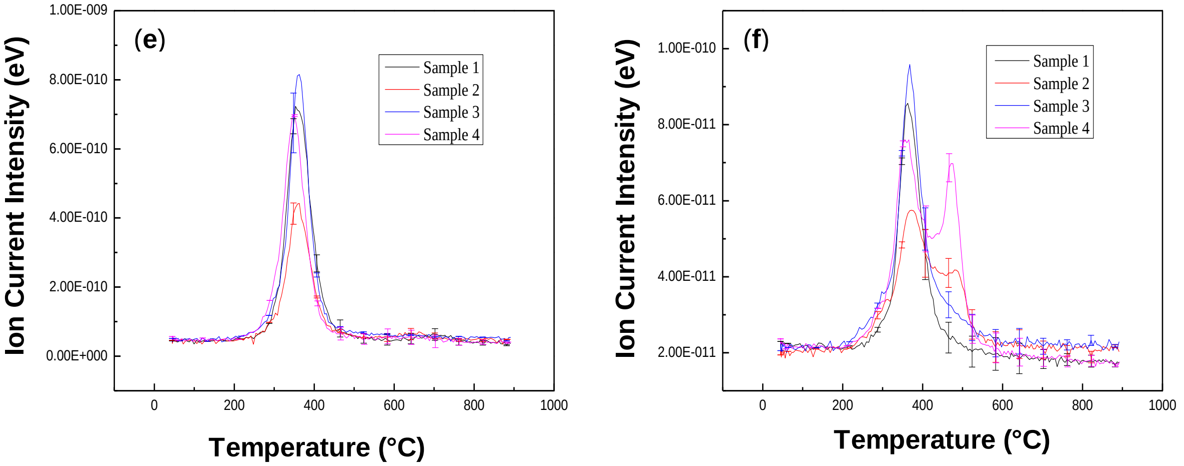


(a) M/Z = 2 (b) M/Z = 16



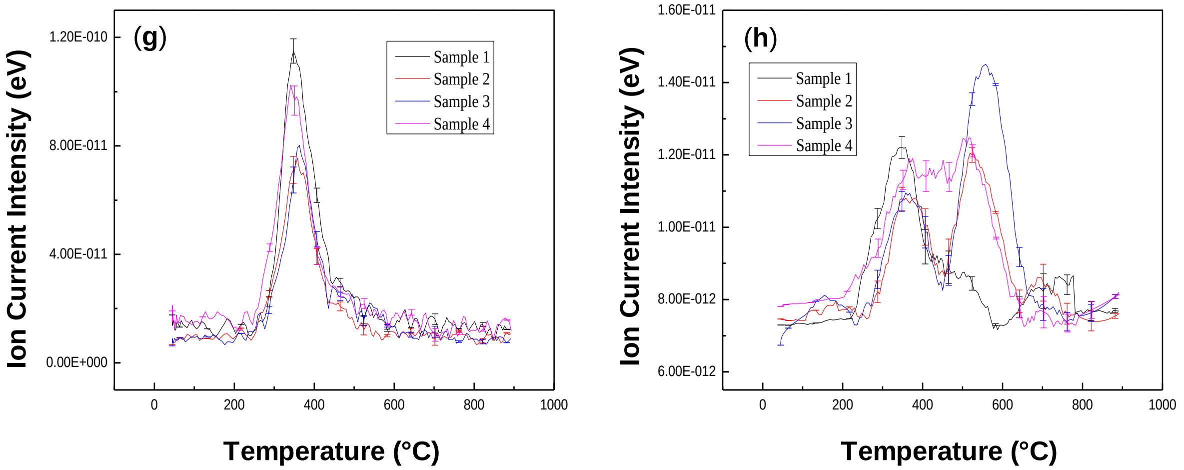
(c) M/Z = 28

(d) M/Z = 44



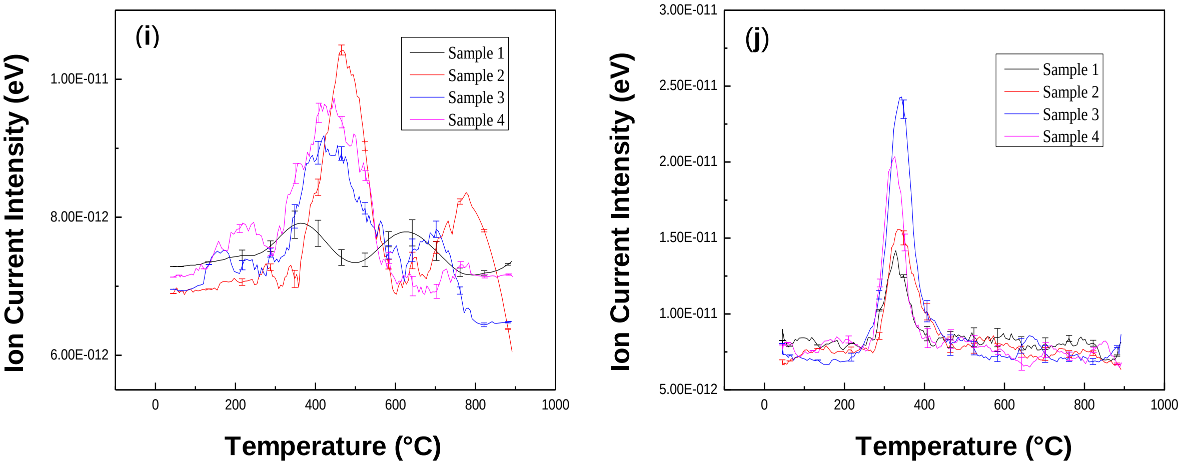
(e) M/Z = 46

(f) M/Z = 58



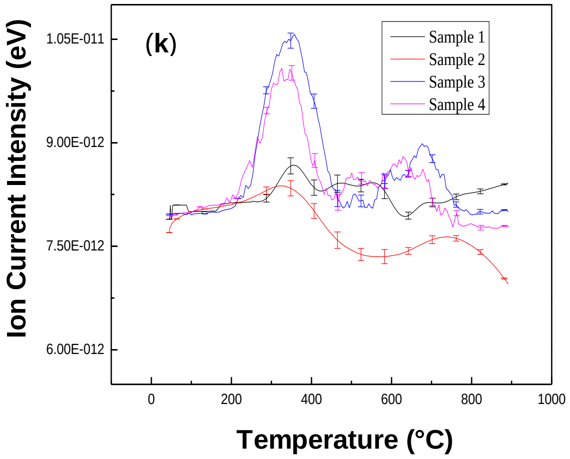
(g) M/Z = 60

(h) M/Z = 78



(i) M/Z = 92

(j) M/Z = 94



(k) M/Z = 96

Fig. 2. Mass spectrometric ion flow intensity curves of H_2, CH_4, and other gases during pyrolysis of samples

The ion current intensity can qualitatively explain the change of gas component concentration, and *M*/*Z* represents the nuclear-mass ratio.

Figure 2(a) exhibits the emission curve of $M/Z = 2$ (H_2). There were two emission temperature ranges: 229 to 518 °C and 518 to 900 °C for the lignin alone, with the peak temperatures at 372.7 °C and 602.4 °C, respectively. After CaO was added, the initial emission temperature slightly shifted to 217 °C, the peak temperature was 392.2 °C, and the amount of H_2 emission increased. After adding $K_2HPO_4{\cdot}3H_2O$, the initial temperature of H_2 emission changed to 203 °C, the peak temperature changed to 392.2 °C, and the amount of H_2 emission increased. The results showed that both CaO and $K_2HPO_4{\cdot}3H_2O$ can promote hydrogen evolution during pyrolysis. When $K_2HPO_4{\cdot}3H_2O$ and CaO were added together, the amount of H_2 precipitated at 203 to 515 °C was similar to that of lignin pyrolysis without any catalysts, and was lower than that of lignin pyrolysis with any single catalyst. The amount of H_2 precipitated at 515 to 900 °C was larger than that of lignin pyrolysis alone. The variation trends in the whole range indicated that the role of $K_2HPO_4{\cdot}3H_2O$ and CaO was not additive, but synergistic.

Figure 2(b) shows the emission curve of $M/Z = 16$ (CH_4). The emission temperature ranged from 203 to 465 °C, 465 to 637 °C, and 637 to 796.5 °C for pure lignin, with the peak temperatures at 377.5 °C, 528.5 °C, and 711.9 °C, respectively. The breakage of the methoxyl group with side chain of phenylpropane contributed greatly to the first stage of emission. Secondary fracture or pyrolysis of volatile matter contributed greatly to the second stage of emission, and the peak value of the third stage appeared due to the reformation of carbon skeleton structure at high temperature. After adding CaO, the emission temperature ranges for CH_4 were 203 to 465 °C, 465 to 617.3 °C, and 617.3 to 796.5 °C, and the peak temperatures were 382.5 °C, 528.6 °C, and 637.1 °C, respectively. The increase of CH_4 indicated that CaO promoted the demethylation reaction in pyrolysis process. The reason for the advance of the initial emission temperature in the third stage was also because of the decomposition of calcium carboxylate salts. At the same time, there was an unobvious peak in the range of 422 to 461 °C for the CH_4 curve, with a peak temperature of 432 °C. This was because the decomposition of $Ca(OH)_2$ caused a h-containing atmosphere, which contributed to the formation of CH_4. With the addition of $K_2HPO_4{\cdot}3H_2O$, there were two emission temperature ranges: 183.2 to 460 °C and 460 to 700 °C, with peak temperatures of 377.5 °C and 528.5 °C, respectively. The third emission stage disappeared, and the emission amount of CH_4 increased in the first two stages. This indicated that $K_2HPO_4{\cdot}3H_2O$ could catalyze methyl fracture in the first two stages of lignin pyrolysis, and it could hinder the emission of volatile products and simultaneously promote the formation of char in the third stage. When the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, the CH_4 emission curve was similar to the first two intervals when CaO was added alone.

Figure 2(c) shows the emission curve of M/Z = 28 (CO). There were two emission temperature ranges: 203 to 617 °C and 617 to 900 °C, with the peak temperatures of 353.1 °C and 801.5 °C, respectively. The CO emission in the first temperature range mainly came from the fracture of ether or carbonyl between the main chains and side chains, and the emission in the second temperature range came from the fracture of diaryl ether bonds or the reforming of aromatic rings. In addition, the reaction between CO_2 and C might cause the generation of CO during the temperature rise from 617 to 900 °C. After the addition of CaO, the emission temperature ranges were 203 to 567.9 °C and 567.9 to 900 °C, and the emission amount increased. In the second stage, the initial emission temperature was advanced, which was also due to the decomposition of calcium carboxylate. With the addition of $K_2HPO_4{\cdot}3H_2O$, the CO precipitate temperature ranges were 203 to 608.6 °C and 608.6 to 731.5 °C. In the first stage, the amount of CO increased. The results showed that $K_2HPO_4{\cdot}3H_2O$ catalyzed the decarbonylation and C-O-C bond cleavage reactions in the first temperature range. In addition, CO precipitated after 731.5 °C. $K_2HPO_4{\cdot}3H_2O$ remarkably changed the decomposition reaction path or activation energy of aromatic ring skeleton at high temperature, which promoted the CO emission at high temperature. When CaO and $K_2HPO_4{\cdot}3H_2O$ were mixed, the emission temperature ranges were 203 to 564 °C and 564 to 900 °C, with peak temperatures of 351 °C and 748 °C, respectively. The amount also increased remarkably in the second temperature range. The emission amount was remarkably higher than the arithmetic average of that with CaO and $K_2HPO_4{\cdot}3H_2O$ added alone. The results showed that CaO and $K_2HPO_4{\cdot}3H_2O$ had strong synergistic effects during the pyrolysis process.

Figure 2(d) provides the emission curve of M/Z = 44 (CO_2). There were two emission intervals at 175 to 568 °C and 568 to 801 °C, with the peak temperatures of 338.3 °C and 711.9 °C, respectively. The fracture decomposition of the alkyl ether bond and the carboxyl group on the side chain of phenylpropane contributed a lot to the first stage, and the secondary decomposition of the pyrolysis semi-coke product contributed a lot to the second stage. When CaO was added, the emission temperature ranges changed to 161.6 to 528.6 °C and 528.6 to 766.4 °C, with peak temperatures at 343.3 °C and 642 °C, respectively. In the first range, the amount of CO_2 decreased, and in the second range the initial emission temperature decreased. This was because CaO reacted with carboxylic acid in lignin to produce "CO_2-like active intermediates" in the first stage. At the same time, amorphous $CaCO_3$ was formed by decomposition of calcium carboxylate or organic calcium salt, and then it continued to decompose at a lower temperature. After adding $K_2HPO_4{\cdot}3H_2O$, the emission temperature ranges became 133.6 to 587.5 °C and 587.5 to 761.4 °C, and the peak temperatures were 348.1 °C and 651.9 °C, respectively. The initial emission temperature in the first range decreased, and the emission amount in the second stage decreased substantially. The results showed that $K_2HPO_4{\cdot}3H_2O$ reduced the activation energy of initial decarboxylation reaction in the first range, and it hindered the volatile emission and reduced the CO_2 yield at high temperature range. After the mixture of CaO and $K_2HPO_4 \cdot 3H_2O$ was added, two peaks appeared in the second stage at 326.1 and 668.3 °C, indicating that the mixed catalysis of CaO and $K_2HPO_4 \cdot 3H_2O$ could remarkably change the reaction pathway in the high temperature stage, thus changing the CO_2 emission pathways.

Figure 2(e) shows the emission curve of $M/\underline{Z}$ = 46 (CH_3CH_2OH, CH_3-O-CH_3, or HCOOH). The three possible products originated possibly from the decomposition of phenylethanol, benzoic acid, the hydrogenation, or the collisions of small oxygen-containing free radical fragments generated by the fracture of long straight side chains of lignin macromolecules. It was observed that M/Z = 46 had a large emission range at 247.9 to 499.1 °C for the lignin pyrolysis alone, with the peak temperature at 353 °C. After adding CaO, there was no obvious change in the initial and peak temperatures of emission, but the emission amount decreased. This was due to the suppression of these reactions by CaO or the formation of calcium carboxylate salts. With the addition of $K_2HPO_4 \cdot 3H_2O$, the initial emission temperature decreased; however, the total amount of emission increased. This was because $K_2HPO_4 \cdot 3H_2O$ reduced the activation energy of oxygen-containing side chains and catalyzed the occurrence of such reactions. At the same time, $K_2HPO_4 \cdot 3H_2O$ provided the required active hydrogen for the formation of the three products. When the mixture of CaO and $K_2HPO_4 \cdot 3H_2O$ was added, the initial emission temperature of M/Z = 46 decreased and the emission amount did not change much. The trend of emission showed that the effect of $K_2HPO_4 \cdot 3H_2O$ and CaO was not additive but synergistic.

Figure 2(f) corresponds to M/Z = 58 (acetone). Acetone mainly comes from the addition reaction of free radical fragments with C=O group and the alkyl radical fragments produced during lignin pyrolysis. It was seen that the emission temperature range of acetone was 253.8 to 523.6 °C, with the peak temperature at 362.9 °C. After adding CaO, the emission amount decreased. At the same time, a second emission temperature range appeared at 460 to 582 °C, with the peak temperature around 479.2 °C. This second range may have been caused by the h-containing environment from the decomposition of $Ca(OH)_2$, which is helpful for the generation of acetone. After the addition of $K_2HPO_4 \cdot 3H_2O$, the initial emission temperature decreased to approximately 203 °C with the increase of emission amount, which indicated that $K_2HPO_4 \cdot 3H_2O$ catalyzed the reaction that produced small molecule products in the main stage of lignin pyrolysis. When the mixture of CaO and $K_2HPO_4 \cdot 3H_2O$ was added, the emission amount in the first stage decreased slightly, while the acetone precipitated greatly at 427 to 599 °C, with a peak temperature of 476.1 °C. The amount was remarkably higher than that in the second peak formed by adding CaO alone. This was attributed to strong synergistic effects of CaO and $K_2HPO_4 \cdot 3H_2O$ in the pyrolysis process.

Figure 2(g) is for M/Z = 60 (CH_3COOH, $HCOOCH_3$, or propanol). There was a single emission temperature range: 241.6 to 523.6 °C for M/Z = 60 during lignin pyrolysis alone. After adding CaO, the initial emission temperature did not change much, but the emission amount decreased. The decrease was also because CaO immobilizes "CO_2-like active intermediates". With the addition of $K_2HPO_4 \cdot 3H_2O$, the initial temperature of thermal decomposition did not change much, and the amount of emission also decreased. When the mixture of CaO and $K_2HPO_4 \cdot 3H_2O$ was added, the emission amount decreased, but it was still larger than that with a single catalyst. This indicated that CaO and $K_2HPO_4{\cdot}3H_2O$ have synergistic effects.

Figure 2(h) corresponds to *M*/*Z* = 78 (benzene). There were two emission intervals for benzene: 203 to 427 °C and 427 to 614 °C for the lignin pyrolysis alone, with the peak temperatures at 341.3 °C and 500 °C, respectively. After CaO was added, the amount of emission increased dramatically in the second interval. The results indicated that CaO catalyzed the dehydration of phenol to form benzene. With the addition of $K_2HPO_4{\cdot}3H_2O$, the emission temperature ranges were 239 to 447 °C, 447 to 753 °C, with the peak temperatures of 367 °C and 550 °C, respectively. The emission in the second stage increased greatly, indicating that $K_2HPO_4{\cdot}3H_2O$ might catalyze the reaction to formation of aromatic ring products in the pyrolysis stage of lignin. When the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, the emission temperature ranged from 203 to 437 °C and 437 to 653 °C. In the second stage, the emission amount increased, but the amount was lower than the average of that with single catalyst. This also indicated that the two catalysts have synergistic effects.

Figure 2(i) is for *M*/*Z* = 92 (toluene). No obvious toluene emission occurred during lignin pyrolysis alone. When CaO was added, toluene increased during the whole pyrolysis process. With the addition of $K_2HPO_4{\cdot}3H_2O$, toluene increased remarkably in the range of 316 to 673 °C with a peak temperature of 490 °C but the emission amount was still much lower than that of other products. This suggested that $K_2HPO_4{\cdot}3H_2O$ catalyzed the generation of aromatic hydrocarbons. When the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, the formation interval and quantity of toluene changed little compared with that with $K_2HPO_4{\cdot}3H_2O$ alone.

Figure 2(j) pertains to *M*/*Z* = 94 (phenol). Phenol precipitated in the range of 241.8 to 421.3 °C for lignin pyrolysis alone, with the peak temperature of 328.4 °C. When CaO was added, the initial and peak emission temperatures did not change much and the amount of emission increased slightly. With the addition of $K_2HPO_4{\cdot}3H_2O$, the initial emission temperature decreased to approximately 203 °C, and the amount of phenol increased remarkably. This indicated that $K_2HPO_4{\cdot}3H_2O$ strongly catalyzed the demethylation of methoxyphenol to form phenol during lignin pyrolysis. When the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, phenol increased in the temperature range of 252.4 to 432 °C.

Figure 2(k) is for *M*/*Z* = 96 (furfural). No obvious furfural emission was observed during lignin pyrolysis alone. After CaO addition, furfural emission was also not observed. When $K_2HPO_4{\cdot}3H_2O$ was added, two emission temperature ranges were observed at 210 to 480 °C and 553 to 777 °C, with peak temperatures of 358 °C and 678 °C, respectively. The results indicated that $K_2HPO_4{\cdot}3H_2O$ catalyzed the formation of furfural during lignin pyrolysis. When the mixture of CaO and $K_2HPO_4{\cdot}3H_2O$ was added, the amount of furfural emission was higher than the average of that with the two single catalysts. The results also indicated that CaO and $K_2HPO_4{\cdot}3H_2O$ have synergistic effects.

CONCLUSIONS

1. When CaO was added, the emission of H_2, CH_4, CO, benzene, toluene, and phenol increased, while the emission of *M*/*Z* = 46 (CH_3CH_2OH, CH_3-O-CH_3, or HCOOH) and acetone decreased. CaO immobilized the "CO_2-like active intermediates"

produced during lignin pyrolysis, thus reducing the amount of CO_2 emission in the first stage and lowering the temperature of CO_2 emission in the second stage.

2. When $K_2HPO_4 \cdot 3H_2O$ was added, the pyrolysis was remarkably advanced, and the amount of H_2, CO, CH_4, $M/\underline{Z} = 46$ (CH_3CH_2OH, CH_3-O-CH_3, or HCOOOH), acetone, and benzene emission increased, while the amount of $M/Z = 60$ (CH_3COOH, $HCOOCH_3$, or propanol) and CO_2 decreased. $K_2HPO_4 \cdot 3H_2O$ could catalyze the formation of aromatic ring products and catalyze the demethylation of methoxyphenols to form phenol during lignin pyrolysis.
3. After adding CaO and $K_2HPO_4 \cdot 3H_2O$, the initial stage of thermogravimetry was more moderate than that of lignin pyrolysis alone or with $K_2HPO_4 \cdot 3H_2O$ addition singly. In the third stage, there were two unobvious peaks at 663 to 728 °C. The peak temperature and weight loss rate was lower than those when CaO was added alone. This is because $K_2HPO_4 \cdot 3H_2O$ can delay the volatile emission in the third stage and promote the formation of more coke. In the pyrolysis stage, the emission trend of CH_4, CO, M/Z = 46, toluene, etc. showed that there was a synergistic effect between $K_2HPO_4 \cdot 3H_2O$ and CaO, which indicated that the components of bio-oil from biomass pyrolysis might be regulated by a combinative usage of the two catalysts.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51506128, 51776001) and the University Natural Science Research Project of Anhui Province (KJ2019A0081).

REFERENCES CITED

Behrens, M., Cross, J. S., Akasaka, H., and Ohtake, N. (2017). “A study of guaiacol, cellulose, and Hinoki wood pyrolysis with silica, ZrO_2&TiO_2 and ZSM-5 catalysts,” *Journal of Analytical and Applied Pyrolysis* 125, 178-184. DOI: 10.1016/j.jaap.2017.04.004

Fu, Q. R., Argyropoulos, D. S., Tilotta, D. C., and Lucia, L. A. (2008). “Understanding the pyrolysis of CCA-treated wood: Part II. Effect of phosphoric acid,” *Journal of Analytical and Applied Pyrolysis* 82(1), 140-144. DOI: 10.1016/j.jaap.2008.02.007

Li, F. Y., Zhang, L., Li, X. L., Xie, Y., Wang, Y., and Wang, J. F. (2016). “Biomass co-pyrolysis with calcium dihydrogen phosphate improving carbon fixation of biochar,” *Transactions of the Chinese Society of Agricultural Engineering* 32(12), 201-205. DOI: 10.11975/j.issn.1002-6819.2016.12.029

Li, F. Y., Zhang, L., Li, X. L. Xie, Y., Wang, Y., and Wang, J. F. (2016). “Biomass co-pyrolysis with calcium dihydrogen phosphate improving carbon fixation of biochar,” *Transactions of the Chinese Society of Agricultural Engineering* 32(12), 201-205. DOI: 10.11975/j.issn.1002-6819.2016.12.029

Li, K. (2016). *Experimental Study on the Pyrolysis Characteristics of Lignocellulosic Biomass Impregnated with Ammonia Source and Potassium Salts*, Ph.D. Thesis, University of Science and Technology China, Hefei, Anhui, China.

Liu, J. M., He, Y. F., Ma, X. X., Liu, G. Q., Yao, Y., Liu, H., Chen, H., Huang, Y., Chen, C., and Wang, W. (2016). "Catalytic pyrolysis of tar model compound with various bio-char catalysts to recycle char from biomass pyrolysis," *BioResources* 11(2), 3752-3768. DOI: 10.15376/biores.11.2.3752-3768

Lin, Y. Y. (2011). *Experimental Investigation on Biomass Fast Pyrolysis in the Presence of CaO for in-situ Deoxygenation of Bio-oil*, Ph.D. Thesis, Shanghai Jiao Tong University, Shanghai, China.

Lin, Y. Y., Zhang, C., Zhang, M. C., and Zhang, J. (2010). "Deoxygenation of bio-oil during pyrolysis of biomass in the presence of CaO in a fluidized-bed reactor," *Energy & Fuels* 24(10), 5686-5695. DOI: 10.1021/ef1009605

Lin, Y. Y., Zhu, L. T., Wang, H. J., Gu, M. Y., Wang, J. L., and Chu, H. Q. (2019). "Thermogravimetric and mass spectrometry analyses of cellulose pyrolysis under the synergistic effect of CaO and $K_2HPO_4{\cdot}3H_2O$," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 42(1), 10-16. DOI: 10.1080/15567036.2019.1587049

Lu, Q., Zhang, Z. B., Yang, X. C., Dong, C. Q., and Zhu, X. F. (2013). "Catalytic fast pyrolysis of biomass impregnated with K_3PO_4 to produce phenolic compounds: Analytical Py-GC/MS study," *Journal of Analytical and Applied Pyrolysis* 104(11), 139-145. DOI: 10.1016/j.jaap.2013.08.011

Luo, J., Shao, J. A., Yang, H. P., Chen, Y. Q., Yang, M. F., and Chen, H. P. (2017). "Research progresses on production of light olefins from catalytic pyrolysis of biomass," *Chemical Industry and Engineering Progress* 36(5), 1555-1564. DOI: 10.16085/j.issn.1000-6613.2017.05.001

Ma, H., and Wu, S. B. (2018) "Research Progresses on Catalytic Pyrolysis of Lignin," *China Pulp & Paper* 37(9), 59-63. DOI: CNKI:SUN:ZGZZ.0.2018-09-017

Ren, X. Y., Gou, J. S., Wang, W. L., Li, Q., Chang, J. M., and Li, B. (2013). "Optimization of bark fast pyrolysis for the production of phenol-rich bio-oil," *BioResources* 8(4), 6481-6492. DOI: 10.15376/biores.8.4.6481-6492

Shen, H. H., Jin, J., Lin, Y. Y., Guo, M. S., Hou, F. X., and Li, S. (2016). "Influence of CaO on soybean protein pyrolysis characteristics and NH_3 and other nitrogenouscom pounds release," *Chemical Industry and Engineering Progress* 35(7), 2263-2267. DOI: 10.16085/j.issn.1000-6613.2016.07.045

Veses, A., Aznar, M., Martínez, I., Martínez, J. D., López, J. M., Navarro, M. V., Callén, M. S., Murillo, R., and García, T. (2014). "Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts," *Bioresource Technology* 162, 250-258. DOI: 10.1016/j.biortech.2014.03.146

Wang, D. H. (2010). *Investigation on the Mechanism of Deoxygenation of Catalytic Pyrolysis of Biomass,* Ph.D. Thesis, Southeast University, Jangsu, China.

Wang, D. H., Xiao, R., Zhang, H. Y., and He, G. Y. (2010). "Comparison of catalytic pyrolysis of biomass with MCM-41 and CaO catalysts by using TGA–FTIR analysis," *Journal of Analytical and Applied Pyrolysis* 89(2), 171-177. DOI: 10.1016/j.jaap.2010.07.008

Wang, S., Cao, B., Liu, X. L., Xu, L. J., Hu, Y. M., Afonaa-Mensah, S., Abomohra , A. E., He, Z. X., Wang, Q., and Xu, S. N. (2018). "A comparative study on the quality of bio-oil derived from green macroalga *Enteromorpha clathrata* over metal modified ZSM-5 catalysts," *Bioresource Technology* 256, 446-455. DOI: 10.1016/j.biortech.2018.01.134

Yang, Y., Luo, Z. Y., Li, S. M., Lu, K. Y., and Wang, W. B. (2019). "Catalytic pyrolysis of hemicellulose to produce aromatic hydrocarbons," *BioResources* 14(3), 5816-5831. DOI: 10.15376/biores.14.3.5816-5831

Yu, W. J., Ying, H., Jang, J. F., and Wang, Y. J. (2014). "Research on pyrolysis dynamics of pine sawdust under pressure and with CaO as catalyst," *Biomass Chemical Engineering* 48(3), 19-24. DOI: 10.3969/j.issn.1673-5854.2014.03.004

Yuan, L., Liu, Y. Q., Wang, D., and Zang, Y. H. (2013). "Effects of catalyst CaO on fast pyrolysis of pine for the production of bio-oils," *Biomass Chemical Engineering* 47(4), 1-6. DOI: 10.3969/j.issn.1673-5854.2013.04.001

Zhang, Z. B., Dong, C. Q., Ye, X. N., Lu, Q., and Liu, Y. Q. (2014). "Preparation of levoglucosenone by catalytic pyrolysis of cellulose over solid phosphoric acid," *CIESC Journal* 65(3), 912-920. DOI: 10.3969/j.issn.0438-1157.2014.03.021

Zhang, Z. B., Lu, Q., Ye, X. N., Xiao, L. P., Dong, C. Q., and Liu, Y. Q. (2014). "Selective production of phenolic-rich bio-oil from catalytic fast pyrolysis of biomass: Comparison of K_3PO_4, K_2HPO_4, and KH_2PO_4," *BioResources* 9(3), 4050-4062. DOI: 10.15376/biores.9.3.4050-4062

Zhao, B., Jin, J., Lin, Y. Y., Li, S., Li, H. L., and Zhang, J. C. (2018). "Interconnection effect of CaO and tripotassium phosphate trihydrate on the pyrolysis characteristics of camphor powder and the release of NO_x precursor," *Chemical Industry and Engineering Progress* 37(3), 956-961. DOI: 10.16085/j.issn.1000-6613.2017-1089

Article submitted: August 15, 2019; Peer review completed: November 17, 2019; Revised version received: January 30, 2020; Accepted: February 2, 2020; Published: March 25, 2020.
DOI: 10.15376/biores.15.2.3356-3367