Experimental Study on Pyrolysis of Rice Straw Catalyzed by CaO/Al₂O₃-Phosphate Mixture

Lianlian Xu · Zhongwen Xu · Feng Zhang · Yinmei Yuan · Bin Cheng · Chuang Zhang · Ping Chen · Xiangyong Huang · Yuyu Lin · Mingyan Gu

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Abstract
CaO and phosphates showed synergistic effects in the regulation of pyrolysis products in the pyrolysis of when they were directly mixed with camphor wood. The alkyl phenol yield increased during the pyrolysis process of corn straw fermentation residue directly mixed with KH₂PO₄ supported by γ-Al₂O₃. Rice stalks from agricultural crops are often disposed as waste. However, the potassium phosphate impregnated raw straw pyrolysis with CaO and Al₂O₃ has not been reported. This paper studied the synergistic effects of CaO or Al₂O₃ and three potassium phosphates (i.e., KH₂PO₄, K₂HPO₄·3H₂O, and K₃PO₄·3H₂O) in the rice straw pyrolysis through pyrolysis–gas chromatography-mass spectrometer (Py-GC/MS) experiments. The results showed that CaO/Al₂O₃ and potassium phosphates showed synergistic effects in the regulation of the types or contents of phenols, ketones, aldehydes, etc. and increased the contents of phenols, aldehydes, acids, and levoglucosan (LG) from most samples and increased those of ketones compared with those catalyzed by potassium phosphates alone. They were suitable for the production of ketone-rich and acid-low bio-oil, which is an important precursor for the preparation of power or jet fuel. The highest contents of ketones (HCK) reached 56.65% and 56.02% in the pyrolysis of K₃PO₄·3H₂O impregnated rice straw with CaO or Al₂O₃, respectively. The lowest contents of acids and acetic acid (LCA) were nearly or equal to 0, respectively. HCK and LCA were respectively significantly higher and lower than the values reported in the literatures for biomass catalytic pyrolysis using CaO/Al₂O₃ and potassium phosphates alone or in combination. Dehydration reactions, etc. were further promoted under the co-catalysis of the two catalysts, and some phenols could be converted to benzene products, etc. For 50% K₃PO₄·3H₂O impregnated sample, the yields of furans reduced sharply after CaO addition. For most impregnated samples except 50% K₂HPO₄·3H₂O and 30% and 50% K₃PO₄·3H₂O samples, the contents of total furans and furfural increased after Al₂O₃ addition.

Highlights
CaO/Al₂O₃ and potassium phosphates showed synergistic effects in the regulation of the types or contents of phenols, ketones, aldehydes, etc. They were suitable for the production of ketone-rich and acid-low bio-oil, which was an important precursor for the preparation of power or jet fuel. Dehydration reactions, etc. were further promoted under the co-catalysis of the two catalysts, and some phenols could be converted to benzene products, etc. The lowest contents of acids and acetic acid were nearly or equal to 0, respectively.

Keywords CaO · Al₂O₃ · Potassium phosphate · Catalytic pyrolysis · Rice straw · Py-GC/MS

Introduction
With the fossil energy reduction, environmental degradation, and other problems, more and more attention has been paid to the development and utilization of renewable
energy [1–8]. Biomass has the advantages of renewability, low cost, abundant reserves, and carbon neutrality, providing about 10% of global energy consumption [9–16]. Pyrolysis is an important biomass utilization technology to convert biomass directly into solid, liquid, and gaseous products in the absence of oxygen under high temperatures. The pyrolysis liquid containing many valuable chemicals is normally called bio-oil [17–23]. However, the primary pyrolysis bio-oil has many harmful properties, such as high oxygen content, acidity, viscosity, and low heating value [19, 24–29]. The use of catalysts within the pyrolysis process, known as catalytic pyrolysis, can selectively convert biomass into high-value-added chemicals or high-quality bio-oil. It has attracted the attention of many researchers [30–36]. The commonly used catalysts are metal oxide catalysts, metal salt catalysts, molecular sieve catalysts, etc. [37–40].

Metal oxides have large pore structure and good catalytic characteristics, and mainly includes CaO, Al₂O₃, NiO, Fe₂O₃, MgO, and ZnO [38, 41]. Lu et al. [41] used pyrolysis–gas chromatography–mass spectrometer (Py-GC/MS) to study the effects of metal oxides, such as CaO, Fe₂O₃, NiO, MgO, and TiO₂, on the polar pyrolysis process. The results showed that CaO significantly reduced the content of acids, phenols, and anhydrosugar, and increased the content of ketones. Fe₂O₃, NiO, MgO, and TiO₂ reduced the content of linear aldehydes and increased the content of ketones. Chen et al. [42–44] found that CaO, Al₂O₃, and NiO effectively reduced the oxygen content of bio-oil and improve the quality of bio-oil. Lin et al. and Wang et al. [45, 46] found that by the co-pyrolysis of biomass and CaO, the oxygen content of bio-oil decreased, and the water content increased. Veses et al. [47] studied the pyrolysis characteristics of pine with CaO and found that CaO increased the calorific value of bio-oil during the catalytic process. Acids, furans, and phenols with high oxygen content decreased, while the contents of phenol, small molecular ketones, and cyclic ketones with low oxygen content increased. Mahadevan et al. [48] found that after CaO addition, acids decreased, and the contents of furans and ketones increased.

Phosphate can provide a lot of acidic sites or active sites and plays a great catalytic role in the process of pyrolysis [49]. Zhang et al. [49, 50] used Py-GC/MS to study the catalytic pyrolysis of poplar wood by phosphates and found that K₃PO₄, K₂HPO₄, and KH₂PO₄ promoted the generation of phenols. And the selectivity of phenols from high to low was K₃PO₄, K₂HPO₄, and KH₂PO₄. Lu et al. [51] found that K₃PO₄ inhibited the devolatilization of cellulose to form organic volatiles, while promoted the decomposition of lignin to generate phenolic compounds. Potassium phosphates promoted the hetero-cleavage reaction of holocellulose, etc. to generate free radicals, which were H donors for the formation of phenolic products in the process of lignin pyrolysis. The pyrolysis pathway of lignin changed significantly; the fractures of some side chains and the removals of hydroxyls and carbonyls were enhanced under the catalysis of potassium phosphates, which led to the increase of specific phenolic products such as phenol. The yields and distributions of phenols varied under different potassium phosphates and catalyst ratios. In addition, K₃PO₄ showed strong alkalinity relatively and inhibited the formation of acid products, which promoted the polymerization of phenolic products in the process of biomass pyrolysis. And the yield of phenolic products increased further after K₂HPO₄ addition. Li et al. [52] found that K₂PO₄ was beneficial to reduce the reaction activation energy of rice husk pyrolysis and change the pyrolysis transformation path of rice husk.

Both metallic oxides and potassium phosphates are useful catalysts in the biomass pyrolysis. Phosphate can increase the yield of phenolic products, while K₂HPO₄ can increase the yield of acids. CaO can reduce the yield of acids and phenols with high oxygen content while increase the yields of phenols with low oxygen content. Therefore, it was assumed that the interaction of CaO and phosphate would produce some beneficial synergistic effects on biomass pyrolysis to decrease the production of smalls acids and selectively regulate the distributions of pyrolysis products such as phenols simultaneously [53]. In our previous studies, thermogravimetric-mass spectrometry (TG-MS) studies were conducted to investigate cellulose pyrolysis with the mixture of CaO and K₂HPO₄·3H₂O [53]. The results showed CaO and K₂HPO₄·3H₂O exhibited a strong synergistic effect in the regulation some products such as H₂, CH₄, CO, and phenol in the cellulose pyrolysis process. TG-MS studies were also conducted to investigate lignin pyrolysis with the mixture of CaO and K₂HPO₄·3H₂O. The emission trend of CH₄, CO, toluene, etc. also showed that there were some synergistic effects between K₂HPO₄·3H₂O and CaO [54]. Py-GC–MS studies were used to study camphor wood pyrolysis with the mixture of CaO and phosphates; CaO and phosphates showed synergistic effects in the pyrolysis of camphor wood. CaO and calcined K₂HPO₄·3H₂O together reduced the relative contents of 3-methoxy-2,5,6-trimethylphenol and 3-methoxy-1,2-benzenediol significantly, while enhanced those of isoeugenol, trans-isoeugenol, and furfural. CaO and calcined K₂HPO₄·3H₂O together increased the relative contents of phenols and cyclopentanones. Acids were relatively low in the products by co-catalysis [55]. Therefore, it can be further assumed that metallic oxides and potassium phosphates would show certain beneficial synergistic effects in the biomass pyrolysis process. Besides, Wang et al. [56] found that the alkyln phenol yield in bio-oil significantly increased to about 50% during the catalytic pyrolysis process of corn straw fermentation residue (CSFR) with KH₂PO₄ supported by γ-Al₂O₃.

Potassium phosphate can be added to biomass by direct mixing and impregnation. In the impregnation process,
potassium phosphate can penetrate into the pores of biomass particles, disperse evenly, and contact with biomass fully, and the catalytic cracking reaction is more intense. Lu et al. [34] found that the products of biomass pyrolysis catalyzed by phosphate impregnation and phosphate direct mixing are quite different. In our previous work, CaO and calcined phosphate were mixed first and then mixed with biomass. In Wang et al.’s work [56], the KH2PO4 solution was slowly added to γ-Al2O3 granules according to the isopyknic impregnation; the impregnated γ-Al2O3 granules were then placed in the open air at room temperature for 24 h and finally calcined in a muffle furnace at 715 °C for 8 h. And then, the sample of CSFR (15 g) and the catalyst (15 g) were loaded in a quartz sequentially, forming an up-layer of catalyst and a bottom-layer of CSFR sample. All potassium phosphates were not mixed by impregnation method in the previous study.

Rice stalks from agricultural crops are often disposed as waste [57, 58]. Cao et al. [59] studied the pyrolysis of rice straw with different types of catalyst such as metal salts (FeCl3, CuCl2, MgCl2, and MnCl2), metal basic oxides (MgO, CaO, MgCO3, and CaCO3), acidic metals (ZnO, ZrO2, CeO2, and TiO2), and zeolite catalysts (ZSM-5, Y-zeolite, mordenite, and SBA-15). The results showed that Y-zeolite effectively produced phenolic monomers as compared to basic (MgO), acidic (CeO2), and metal salt (MgCl2) catalyst. Moreover, lower molecular weight in the catalytic bio-oil was observed as compared to non-catalytic bio-oil. Ma et al. [60] studied the pyrolysis of rice straw (RS) and wheat straw (WS) with basic (MgO and CaO) and acidic (ZSM-5 and Y-zeolite) catalysts. The results showed that catalysts such as basic metal oxide are encouraged to formation of phenolic and ketone compound, while acidic catalysts were encouraged to formation of aromatic hydrocarbons. Moreover, higher amount of aromatic hydrocarbon (52.9%) was found with RS using Y-zeolite, whereas higher amount of phenolics (48.5%) was obtained with WS using CaO catalysts. However, the potassium phosphate impregnated raw straw pyrolysis with CaO and Al2O3 has not been reported.

Therefore, in this paper, CaO and Al2O3 were selected to study their synergistic effects with potassium phosphates in the rice stalk pyrolysis, and the biomass was impregnated with potassium phosphate and then mixed with metal oxide. The way of adding catalyst is different, and the catalytic process is different, and the pyrolysis products are also different, and then the synergistic effects are different to some extent. The product distributions of rice straw pyrolysis with CaO or Al2O3 and three potassium phosphates (i.e., KH2PO4, K2HPO4·3H2O, and K3PO4·3H2O) and the synergistic effects are investigated using Py-GC–MS, so as to provide a basis for the production of valuable bio-oil in the pyrolysis of biomass with the joint catalysis of CaO/Al2O3 and potassium phosphates and the further studies of the synergistic effects of metallic oxides and potassium phosphates.

### Experimental

#### Experimental Materials and Preparation

The biomass used in the research was rice straw purchased from Jiaxing City, Zhejiang Province. First, the rice straws were crushed by a shredder and then were screened through standard sample screening. Rice straws with particle size of 160–200 mesh (0.075–0.1 mm) were selected for this experiment. Before each experiment, the biomass was dried in a drying oven at 105 °C for 12 h. The proximate and elemental analyses of the rice straw are shown in Table 1. The O content was obtained by subtraction using the formula: O (wt.%) = 100-C-H-N-S.

Metal oxides (CaO and Al2O3) and potassium phosphates (KH2PO4, K2HPO4·3H2O, and K3PO4·3H2O) were purchased from Sinopharm Chemical Reagents Co., Ltd. Before the experiment, the sifted metal oxides (160–200 mesh) were placed in muffle furnace for calcination. The calcination time was 4 h. The calcination temperatures were 800 °C and 600 °C for CaO and Al2O3, respectively.

As illustrated in the introduction, potassium phosphates were added to biomass by impregnation method. The impregnation method was as follows: firstly, a certain amount of potassium phosphates was weighed and put into distilled water, then 2 g of camphor wood was added. The mixture was stirred by magnetic stirrers for 12 h in order to ensure sufficient contact with the solution. Finally, the mixture was placed in a drying oven for 12 h at 120 °C and sealed for use. Three main impregnation ratios were selected: 10%, 30%, and 50%. Calcined CaO and Al2O3 were mechanically mixed with rice straw samples impregnated with KH2PO4, K2HPO4·3H2O, and K3PO4·3H2O at the ratios of 0:1, 0.5:1, 1:1, and 1.5:1, and then sealed and bagged. During the pyrolysis experiment, the biomass mass in each experiment is 1 mg.
Instruments and Methods

The pyrolysis–gas chromatography-mass spectrometry test rig (Py-GC/MS) used in this study consisted of a Pyroprobe 5200 HP-R (CDS Analytical) and GCMS-QP2020 (Shimadzu, Japan). Samples were placed in the middle of the quartz tube, and quartz wool was placed at both sides of the quartz tube to avoid the escape of the particles. Helium (99.999%) was the carrier gas with a flow rate of 0.99 mL/min and a split ratio of 1:50. As illustrated in previous studies [38, 51, 55], the GC oven program was maintained at 50 °C for 2 min, then 10 °C/min to 200 °C followed by 15 °C/min to 280 °C, and finally 5 min at 280 °C. The ion source temperature of the mass spectrometer was 250 °C, and the mass spectrometer was operated in EI mode at 70 eV with a mass scanning range (m/z) of 28–400 amu. The standard mass spectrometry library used was NIST2014. For each product, the changing of its relative content among the detected products can be determined by comparing its peak area% values. The relative peak areas were determined by the ratio of the absolute peak areas of products to the total absolute peak area of all products.

Results and Analysis

In this study, rice straw, KH2PO4, K2HPO4·3H2O, and K3PO4·3H2O were represented by Rs, K1, K2, and K3, respectively. Rice straw sample with 30 wt.% K3PO4·3H2O impregnation was represented as 30% K3-Rs, and other samples were expressed according to this method.

Fig. 1 The thermograms of the pyrolysis without catalyst and with catalyst
Fig. 2 Phenols in the products of rice straw pyrolysis co-catalyzed by CaO and potassium phosphates. a Phenols. b 2-Methoxy-4-vinylphenol. c Mequinol. d 2,6-Dimethoxy-phenol. e 4-Ethyl-2-methoxy-phenol. f Phenol. g p-Cresol. h 3-Methyl-phenol. i 3-Methoxy-1,2-benzenediol. j 2-Methyl-1,3-benzenediol.
Co-catalytic Pyrolysis by CaO and Potassium Phosphates

As illustrated above, calcined CaO was mechanically mixed with rice straw samples impregnated with KH$_2$PO$_4$, K$_2$HPO$_4$·3H$_2$O, and K$_3$PO$_4$·3H$_2$O, respectively, in the mass ratios of 0:1, 0.5:1, 1:1, and 1.5:1, in which 0:1 indicated no addition of CaO. The pyrolysis products were divided into phenols, ketones, acids, aldehydes, furans, saccharides, etc. The contents were represented by the relative peak areas. Figure 1 shows some thermograms of the pyrolysis with and without catalyst. Only a few thermograms were displayed.

Phenols

Figure 2 shows the contents of phenols. $R$ is the mass ratio of CaO to impregnated biomass. The total content of phenols from Rs sample was 16.63%. For the Rs samples, the total yields of phenols slightly decreased and then increased with the increase of CaO addition ratios. The contents of 2-methoxy-4-vinylphenol and mequinol were high in the Rs sample pyrolysis. After CaO addition, phenol, p-cresol, and 3-methyl-phenol increased and 2-methyl-1,3-benzenediol decreased markedly. When $R$ was greater than or equal to 1, 2-methyl-1,3-benzenediol was not detected.

It could be seen that except for 10% KH$_2$PO$_4$ addition samples (10% K1-RS), potassium phosphates alone
promoted the generation of phenols, which was in accordance with Zhang et al.’s studies [50, 61, 62]. With 50% K₃PO₄·3H₂O impregnation only, the total yields of phenols reached the highest value of 27.69%. Under most impregnation ratios, the contents of phenols were in the descending order of K₃PO₄·3H₂O, K₂HPO₄·3H₂O, and KH₂PO₄, and the values increased with the increase of impregnation amount [63]. The contents of 4-ethyl-2-methoxy phenol, phenol, and p-cresol all increased after potassium phosphate impregnation only. After 50% KH₂PO₄ impregnation alone, the content of 2-methoxy-4-vinylphenol increased from 3.14 to 4.19%, with the highest value in phenols, and that of 4-ethyl-2-methoxy phenol increased from 0.72 to 2.55%. After 50% K₃HPO₄·3H₂O impregnation only, the content of 2,6-dimethoxy phenol increased from 1.21 to 1.77% and that of phenol increased from 1.05 to 2.17%. After 50% K₃PO₄·3H₂O impregnation only, the content of mequinol increased from 2.18 to 3.94%, and that of 2-methyl-1, 2-phenylenediol decreased to 0. This was because potassium phosphate could further promote the deoxidation, demethylation, demethoxylation reactions, etc. and also promote the removal of alkyl side chains on benzene ring in some phenols [64].

The total contents of phenols co-catalyzed by CaO and potassium phosphates generally decreased compared with those catalyzed by potassium phosphates.

Fig. 3 Ketones in the products of rice straw pyrolysis co-catalyzed by CaO and potassium phosphates. a Ketones. b 1-Hydroxy-2-propanone. c Acetone. d 1,2-Cyclopentanediene. e 2-Hydroxy-3-methyl-2-cyclopenten-1-one. f 1-(Acetyloxy)-2-propanone. g 2-Butanone
alone. The total contents of phenols decreased obviously from 27.69 to 17.57% with the increase of $R$ when co-catalyzed by CaO and 50% K$_3$PO$_4$·3H$_2$O. This was because CaO could further catalyze dehydration reactions, etc. to convert phenols to form benzene products, etc. Some phenols from some impregnated samples were further promoted after CaO addition, such as 2-methoxy-4-vinylphenol from the pyrolysis of 10% K1-Rs, mequinol from the pyrolysis of 50% K2-Rs or 30% K3-Rs, and p-cresol and 3-methyl-phenol from the pyrolysis of K2-Rs. Some phenols from some impregnated samples were inhibited after CaO addition in general, such as 2-methoxy-4-vinylphenol and 4-ethyl-2-methoxy-phenol from the pyrolysis of K3-Rs samples, 4-ethyl-2-methoxy-phenol from the pyrolysis of 50% K1-Rs and 50% K2-Rs, 2,6-dimethoxy-phenol and phenol from the pyrolysis of 50% K3-Rs, etc. The yields of 3-methyl-phenol, 3-methoxy-1,2-benzenediol, and 2-methyl-1,3-benzenediol from the pyrolysis of 50% K3-Rs, 50% K2-Rs, and most impregnated samples were even be reduced to 0 after CaO addition. The yields of some phenols from some impregnated samples reached the highest value at certain $R$, such as phenol from 30% K1-Rs, 10% K2-Rs, and 30% K3-Rs samples at $R = 0.5$, and p-cresol from 30% K2-Rs and 50% K3-Rs samples at $R = 0.5$ and 10% K2-Rs and 10% K3-Rs samples at $R = 1$. CaO and potassium phosphates showed synergetic effects in the regulation of the type of phenols.
Ketones

Figure 3 shows the contents of ketones. Ketones mainly come from the ring-opening reaction of cellulose, and acids are partially converted into ketones under catalytic pyrolysis \[65\]. The yields of ketones showed the highest value, with 34.47% in the products from the pure rice straw pyrolysis, indicating that rice straw was suitable for the preparation of ketone-rich bio-oil. After CaO addition only, the total yield of ketones increased significantly, with maximum value of 45.05% at \( R = 1 \). It could be seen from Fig. 3b–f that the relative contents of most ketones except 1,2-cyclopentanedione increased after CaO addition only. The yields of 1-hydroxy-2-acetone showed the highest value in the ketones, with 10.86% from pure rice straw pyrolysis and maximum content 13.05% at \( R = 1 \).

\( \text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O} \) and \( \text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} \) alone promoted the formation of ketones, while \( \text{KH}_2\text{PO}_4 \) inhibited the formation of ketones. This is because \( \text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} \) and \( \text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O} \) are alkaline, while \( \text{KH}_2\text{PO}_4 \) is acidic. Alkaline environment is conducive to the production of ketones. After \( \text{KH}_2\text{PO}_4 \) impregnation alone, the yields of 2-hydroxy-3-methyl-2-cyclopentene-1-one decreased, the yield of 1-acetyloxy-2-propanone decreased, and the yields of acetone and 1,2-cyclopentanediol did not change much.

High impregnation amount of \( \text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} \) reduced the contents of 1-hydroxy-2-acetone and 1,2-cyclopentanediol. \( \text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} \) increased the content of 2-hydroxy-3-methyl-2-cyclopentene-1-one, but had little effect on 1-acetyloxy-2-propanone. After 50% \( \text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O} \) impregnation only, the yields of 2-hydroxy-3-methyl-2-cyclopentene-1-one increased from 1.48 to 2.35% and those of 1,2-cyclopentanediol and 1-acetyloxy-2-propanone decreased to 0.

The total contents of ketones co-catalyzed by CaO and potassium phosphates further increased generally compared with those catalyzed by potassium phosphates alone. From \( R = 0 \) to \( R = 1.5 \), the contents of ketones increased from 44.62% to the highest value 56.65% from the pyrolysis of 10% K3-Rs. The highest content of ketones (HCK) was significantly higher than the values reported in the literatures for biomass catalytic pyrolysis using CaO/\( \text{Al}_2\text{O}_3 \) and potassium phosphates alone or in combination \[41, 48–50, 55\]. CaO and potassium phosphates showed synergistic effects in the regulation of the type of ketones and were suitable for the production of ketone-rich bio-oil, which is an important precursor for the preparation of power or jet fuel \[65, 66\].

Acids

Figure 4 shows the contents of acids. CaO alone significantly reduced the total content of acids from 8.44 to 3.45% at \( R = 0 \) to \( R = 1.5 \). This is because CaO can effectively react with acids or their precursors to generate calcium carboxylates, which can decompose into ketones such as acetone, as shown in Eqs. (1) and (2).

\[
\text{CaO} + 2\text{RCOOH} \rightarrow (\text{RCOO})_2\text{Ca} + \text{H}_2\text{O} \tag{1}
\]

\[
(\text{RCOO})_2\text{Ca} \rightarrow \text{CaCO}_3 + \text{RCOR} \tag{2}
\]
Acids mainly contain acetic acid. As shown in Fig. 4b, CaO alone significantly reduced the total contents of acid products from 4.67 to 2.33% at $R = 0$ to $R = 1.5$.

K$_3$PO$_4$·3H$_2$O alone significantly reduced acids. After 50% K$_3$PO$_4$·3H$_2$O impregnation, the yields of acids decreased to 2.39% and those of acetic acid decreased to 0. Except for 10% and 30% KH$_2$PO$_4$, the contents of acetic acid decreased after potassium phosphate addition alone.

The total contents of acids from the pyrolysis of rice straw co-catalyzed by CaO and potassium phosphates further decreased significantly compared with those catalyzed by potassium phosphates alone. For 50% K2-Rs and 50% K3-Rs, the contents of acids decreased to nearly 0. Except for 10% and 50% K1-Rs, the contents of acetic acid could decrease to 0 after CaO addition. The lowest contents of acids and acetic acid (LCA) were in general lower than the values reported in the literatures for biomass catalytic pyrolysis using CaO/Al$_2$O$_3$ and potassium phosphates alone or in combination [41, 48–50, 55]. CaO and impregnated potassium phosphates together showed stronger synergistic effects in decreasing acids and were suitable for the production of acid-low bio-oil.

**Aldehydes**

Figure 5 shows the contents of aldehydes. CaO alone reduced the total content of aldehydes from 24.67 to 16.71% and those of hydroxy-acetaldehyde from 16.41 to 9.93% at $R = 0$ to $R = 1.5$. The contents of hydroxyl-acetaldehyde, succinaldehyde, and pentanal all decreased after CaO addition alone.
Potassium phosphates alone reduced aldehydes; the higher the impregnation amount, the more the reduction of aldehyde content. K$_3$PO$_4$·3H$_2$O showed the highest reduction effects. 50% K$_3$PO$_4$·3H$_2$O alone reduced the yield of total aldehydes to 1.36%. Hydroxy-acetaldehyde and succinaldehyde from the pyrolysis of 10%, 30% K$_2$-Rs, and 10% K$_3$-Rs, and pentanal from the pyrolysis of 30% K$_3$-Rs. Some aldehydes from some impregnated samples showed fluctuated trends with the increase of $R$. CaO and potassium phosphates showed synergistic effects in the regulation of the type of aldehydes.

**Furans**

Figure 6 shows the contents of furans. CaO alone increased the total content of furans. This is because CaO promotes the depolymerization, ring opening, and dehydration of xylan and 4-O-methylglucuronic acid units. 50% KH$_2$PO$_4$ alone increased the yields of total furans to 9.52% from 5.31% in the pyrolysis products of pure rice straw. For 50% K$_3$-Rs sample, the yields of furans reduced sharply after CaO addition.

**Levoglucosan**

Levoglucosan (LG) is an important product in the biomass pyrolysis. Figure 7 shows the contents of LG. CaO alone changed the yields of LG a little.

Most potassium phosphates alone reduced LG in general [67]. K$_3$PO$_4$·3H$_2$O showed the highest promotion effects. This is because alkaline environment induced by K$_3$PO$_4$·3H$_2$O is harmful for the production of LG [68]. 30% and 50% KH$_2$PO$_4$ impregnation increased the yields of LG.

The contents of LG co-catalyzed by CaO and potassium phosphates decreased generally compared with those catalyzed by potassium phosphates or CaO alone. For 50% K$_2$-Rs and all the K$_3$-Rs samples, they could decrease to 0 after CaO addition.

**Co-catalytic Pyrolysis by Al$_2$O$_3$ and Potassium Phosphates**

**Phenols**

Figure 8 shows the contents of phenols. The contents of total phenols, 4-ethyl-2-methoxy phenol, 3-methoxy-1,2-benzenediol, and 2-methyl-1,3-benzenediol decreased after Al$_2$O$_3$ addition alone. The contents of most phenols co-catalyzed by Al$_2$O$_3$ and potassium phosphates decreased generally compared with those catalyzed by potassium phosphates alone. Other samples had fluctuated value content of total aldehydes. The decrease is also because CaO can further catalyze dehydration and deoxidation reactions. The yields of pentanal from the pyrolysis of 30% and 50% K$_1$-Rs and 10% K$_2$-Rs further increased after CaO addition in generally.

Some aldehydes from some impregnated samples were generally inhibited after CaO addition, such as hydroxy-acetaldehyde from the pyrolysis of most samples, hydroxy-acetaldehyde from the pyrolysis of 10%, 30% K$_2$-Rs, and 10% K$_3$-Rs, and pentanal from the pyrolysis of 30% K$_3$-Rs. Some aldehydes from some impregnated samples showed fluctuated trends with the increase of $R$. CaO and potassium phosphates showed synergistic effects in the regulation of the type of aldehydes.
Fig. 8 Phenols in the products of rice straw pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates. a Phenols. b 2-Methoxy-4-vinylphenol. c Mecquino. d 2,6-Dimethoxy-phenol. e 4-Ethyl-2-methoxy-phenol. f Phenol. g p-Cresol. h 3-Methyl-phenol. i 3-Methoxy-1,2-benzenediol. j 2-Methyl-1,3-benzenediol.
catalyzed by potassium phosphates alone. For certain samples, three small phenols, i.e., phenol, p-cresol, and 3-methyl-phenol, reached its highest value at certain R, such as phenol at $R = 1, 1.5, 1.5, 0.5$ for 30% and 50% K1-Rs samples and 10% and 50% K2-Rs samples, respectively. For 50% impregnation samples, the yields of total phenols decreased maximumly from 27.69 to 8.17% at $R = 0$ to 1.5. The yields of 2-methyl-1,3-benzenediol from all the samples decreased to 0 after $\text{Al}_2\text{O}_3$ addition. The yields of 3-methoxy-1,2-benzenediol from 30 and 50% K2-Rs samples decreased to 0 after high CaO addition amounts. $\text{Al}_2\text{O}_3$ and potassium phosphates showed synergistic effects in the regulation of the type of phenols.

Ketones

Figure 9 shows the contents of ketones. The contents of total ketones increased a lot after $\text{Al}_2\text{O}_3$ addition alone. The contents of ketones co-catalyzed by $\text{Al}_2\text{O}_3$ and potassium phosphates increased a lot compared with those catalyzed by potassium phosphates alone. The highest content of ketones (HCK) was 56.02% at 50% $\text{K}_3\text{PO}_4\cdot3\text{H}_2\text{O}$ impregnation and $R = 0.5$, which was higher than the values reported in the literatures for biomass catalytic pyrolysis using $\text{CaO}/\text{Al}_2\text{O}_3$ and potassium phosphates alone or in combination [44, 49, 50, 56].

The contents of 1-hydroxy-2-propanone from 10% K1-Rs sample, 30% and 50% K2 samples, and all K3-Rs samples;
Fig. 9 Ketones in the products of rice straw pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates. a Ketones. b 1-Hydroxy-2-propanone. c 1,2-Cyclopentanediione. d 2-Hydroxy-3-methyl-2-cyclopenten-1-one. e 1-(Acetyloxy)-2-propanone. f 2-Butanone
1,2-cyclopentanedione from 30 and 50% K2-Rs samples and 10% and 30% K3-Rs samples; and 1-acetyloxy-2-propanone from 50% K2-Rs sample generally decreased after $\text{Al}_2\text{O}_3$ addition. $\text{Al}_2\text{O}_3$ and potassium phosphates showed synergistic effects in the regulation of the type of ketones and were suitable for the production of ketone-rich bio-oil, which is an important precursor for the preparation of power or jet fuel [65, 66].

**Acids**

Figure 10 shows the contents of acids. The contents of total acids decreased after $\text{Al}_2\text{O}_3$ addition alone. The yields of acetic acid decreased from 4.67 to 2.55% at $R = 0$ to 1.5. The contents of acids co-catalyzed by $\text{Al}_2\text{O}_3$ and potassium phosphates decreased compared with those catalyzed by potassium phosphates alone. For 30% K2-Rs and 30% K3-Rs samples, the contents of acids could decrease to nearly 0 after $\text{Al}_2\text{O}_3$ addition. For 50% K2-Rs and 30% K3-Rs samples, the contents of acetic acid could decrease to 0 after $\text{Al}_2\text{O}_3$ addition. The lowest contents of acids and acetic acid (LCA) were in general lower than the values reported in the literatures for biomass catalytic pyrolysis using CaO/$\text{Al}_2\text{O}_3$ and potassium phosphates alone or in combination [44, 49, 50, 56]. $\text{Al}_2\text{O}_3$ and potassium phosphates were suitable for the production of acid-low bio-oil.

**Aldehydes**

Figure 11 shows the contents of aldehydes. The contents of total aldehydes increased after $\text{Al}_2\text{O}_3$ addition alone. The contents of total and most aldehydes from most samples co-catalyzed by $\text{Al}_2\text{O}_3$ and potassium phosphates generally decreased compared with those catalyzed by potassium phosphates alone. The yields of hydroxy-acetaldehyde from 30 and 50% K1-Rs samples and 30% K2-Rs samples could decrease to 0 after $\text{Al}_2\text{O}_3$ addition.

**Furans**

Figure 12 shows the contents of furans. The relative contents of total furans decreased after $\text{Al}_2\text{O}_3$ addition alone. The yields of furfural increased a lot from 2.55 to 4.88% at $R = 0$ to 1.5. The contents of total furans and furfural from most samples except 50% K2-Rs sample and 30% and 50% K3-Rs samples co-catalyzed by $\text{Al}_2\text{O}_3$ and potassium phosphates increased compared with those catalyzed by potassium phosphates alone in general. The yields of furfural from 50% K2-Rs sample and 30% and 50% K3-Rs samples could decrease to 0 after $\text{Al}_2\text{O}_3$ addition. The yields of 2,3-dihydro-benzofuran from all samples decreased after $\text{Al}_2\text{O}_3$ addition. $\text{Al}_2\text{O}_3$ and potassium phosphates showed synergistic effects in the decrease of furans and the regulation of the type of furans.

**Levoglucosan (LG)**

Figure 13 shows the contents of LG. The relative contents of LG decrease after high amount of $\text{Al}_2\text{O}_3$ addition [69–71]. The contents of LG co-catalyzed by $\text{Al}_2\text{O}_3$ and potassium phosphates decreased generally compared with those catalyzed by potassium phosphates alone. The contents of LG from most samples except for 10% and 30% K1-Rs samples could decrease to 0 after $\text{Al}_2\text{O}_3$ addition.
Conclusions

This paper studied the synergistic effects of CaO or Al₂O₃ and three potassium phosphates (i.e., KH₂PO₄, K₂HPO₄·3H₂O, and K₃PO₄·3H₂O) in the rice straw pyrolysis through Py-GC/MS experiments, which can provide a basis for the production of valuable bio-oil in the pyrolysis of biomass with the joint catalysis of CaO/Al₂O₃ and potassium phosphates and the further studies of the synergistic effects of metallic oxides and potassium phosphates. The conclusions are as follows:

1. Potassium phosphates alone increased the yields of total phenols. The promotion effects decreased in the order of K₃PO₄·3H₂O > K₂HPO₄·3H₂O > KH₂PO₄. The formation of ketones was promoted by K₃PO₄·3H₂O and K₂HPO₄·3H₂O alone, while inhibited by KH₂PO₄. K₃PO₄·3H₂O alone significantly reduced acids. Potassium phosphates alone also reduced aldehydes, furans, and LG.

2. After CaO addition alone, the contents of phenol, p-cresol, and 3-methyl-phenol increased and those of 2-methyl-1,3-benzenediol decreased markedly. The yields of ketones increased significantly, furans increased a little, and those of acids and aldehydes decreased.

3. After catalyzed by Al₂O₃ alone, the contents of total phenols, acids, and aldehydes, and 4-ethyl-2-methoxy

Fig. 11 Aldehydes in the products of rice straw pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates. a Aldehydes. b Hydroxy-acetaldehyde. c Succinaldehyde. d Pentanal
phenol, 3-methoxy-1,2-benzenediol and 2-methyl-1,3-benzenediol, and acid decreased and those of total ketones and furans increased.

(4) After co-catalyzed by CaO/Al$_2$O$_3$ and potassium phosphates, the total contents of phenols, aldehydes, acids, and LG from most samples decreased and those of ketones increased compared with those catalyzed by potassium phosphates alone. CaO/Al$_2$O$_3$ and potassium phosphates showed synergistic effects in the regulation of the type or content of phenols, ketones, aldehydes, etc. Dehydration reactions, etc. were further promoted under the co-catalysis of the two catalysts, and some phenols could be converted to benzene products, etc.

(5) CaO/Al$_2$O$_3$ and potassium phosphates together were suitable for the production of ketone-rich and acid-low bio-oil, which was an important precursor for the preparation of power or jet fuel. The highest contents of ketones (HCK) reached 56.65% and 56.02% in the pyrolysis of K$_3$PO$_4$·3H$_2$O impregnated rice straw with CaO or Al$_2$O$_3$, respectively. The lowest contents of acids and acetic acid (LCA) were nearly or equal to 0, respectively. HCK and LCA were respectively significantly higher and lower than the values reported in the literatures for biomass catalytic pyrolysis using CaO/Al$_2$O$_3$ and potassium phosphates alone or in combination. For 50% K$_3$PO$_4$·3H$_2$O impregnated sample, the
yields of furans reduced sharply after CaO addition. The contents of total furans and furfural from most samples except 50% K₂HPO₄·3H₂O sample and 30% and 50% K₃PO₄·3H₂O impregnated samples co-catalyzed by Al₂O₃ and potassium phosphates increased compared with those catalyzed by potassium phosphates alone.

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**Declarations**

**Conflict of Interest** The authors declare no competing interests.

**References**

1. Proskurina S, Sikkema R, Heinimö J, Vakkilainen E (2016) Five years left--how are the EU member states contributing to the 20% target for EU’s renewable energy consumption; the role of woody biomass. Biomass Bioenergy 95:64–77. https://doi.org/10.1016/j.biombioe.2016.09.016
2. Wang S, Zhao S, Uzoejina BB et al (2020) A state-of-the-art review on dual purpose seaweeds utilization for wastewater treatment and crude bio-oil production. Energy Convers Manag 222:113253. https://doi.org/10.1016/j.enconman.2020.113253
3. Chen W, Li K, Chen Z et al (2021) A new insight into chemical reactions between biomass and alkaline additives during pyrolysis process. Proc Combust Inst 38:3881–3890. https://doi.org/10.1016/j.proci.2020.06.023
4. Soh M, Chew JJ, Liu S, Sunarso J (2019) Comprehensive kinetic study on the pyrolysis and combustion behaviours of five oil palm biomass by thermogravimetric-mass spectrometry (TG-MS) analyses. Bioenergy Res 12:370–387. https://doi.org/10.1007/S12155-019-00974-9/FIGURES/5
5. Anupam K, Swaroop V, Deepika et al (2015) Turning Leucaena leucocephala bark to biochar for soil application via statistical modelling and optimization technique. Ecol Eng 82:26–39. https://doi.org/10.1016/j.ecoleng.2015.04.078
6. Barati B, Zeng K, Baeyens J et al (2021) Recent progress in genetically modified microalgae for enhanced carbon dioxide sequestration. Biomass Bioenergy 145:105927. https://doi.org/10.1016/J.BIOMBBIO.2020.105927
7. Cao B, Yuan J, Jiang D et al (2021) Seaweed-derived biochar with multiple active sites as a heterogeneous catalyst for converting macroalgae into acid-free biooil containing abundant ester and sugar substances. Fuel 285:119164. https://doi.org/10.1016/j.fuel.2020.119164
8. Lakshmikandan M, Murugesan AG, Wang S et al (2020) Sustainable biomass production under CO2 conditions and effective wet microalgae lipid extraction for biodiesel production. J Clean Prod 247:119398. https://doi.org/10.1016/J.JCLEPRO.2019.119398
9. Xia M, Chen W, Wu J et al (2021) Organic salt-assisted pyrolysis for preparation of porous carbon from cellulose, hemicellulose and lignin: new insight from structure evolution. Fuel 291:120185. https://doi.org/10.1016/j.fuel.2021.120185
10. Hu C, Zhang H, Wu S, Xiao R (2020) Molecular shape selectivity of HZSM-5 in catalytic conversion of biomass pyrolysis vapors: the effective pore size. Energy Convers Manage 210:112678. https://doi.org/10.1016/j.enconman.2020.112678
11. Chang SH (2019) (2019) Rice husk and its pretreatments for bio-oil production via fast pyrolysis: a review. BioEnergy Res 131(13):23–42. https://doi.org/10.1016/J.BIOFUEL.2020.125118
12. Wang X, Zhai M, Guo H et al (2021) High-temperature pyrolysis of biomass pellets: the effect of ash melting on the structure of the char residue. Fuel 285:119084. https://doi.org/10.1016/j.fuel.2020.119084
13. Wang S, Zhao S, Cheng X et al (2021) Study on two-step hydrothermal liquefaction of macroalgae for improving bio-oil. Bioresour Technol 319:124176. https://doi.org/10.1016/J.BIOREJ.2020.124176
14. Lakshmikandan M, Wang S, Murugesan AG et al (2021) Co-cultivation of Streptomyces and microagal cells as an efficient system for biodiesel production and biofloculation formation. Bioresour Technol 332:125118. https://doi.org/10.1016/J.BIOREJ.2021.125118
15. Xu S, Cao B, Uzoejina BB et al (2020) Synergistic effects of catalytic co-pyrolysis of macroalgae with waste plastics. Process Saf Environ Prot 137:34–48. https://doi.org/10.1016/J.PSEPP.2020.02.001
16. Fu Q, Argyropoulos DS, Tilotta DC, Lucia LA (2008) Understanding the pyrolysis of CCA-treated wood: part II. Effect of phosphoric acid. J Anal Appl Pyrolysis 82:140–144. https://doi.org/10.1016/J.JAAP.2008.02.007
17. Wang S, Karthicneyan V, Sivakumar E, Lakshmikandan M (2020) Experimental investigation on pumpkin seed oil methyl ester blend in diesel engine with various injection pressure, injection timing and compression ratio. Fuel 264:116868. https://doi.org/10.1016/j.fuel.2019.116868
18. Wei M, Marrakechi F, Yuan C et al (2022) Adsorption modeling, thermodynamics, and DFT simulation of tetracycline onto mesoporous and high-surface-area NaOH-activated macroalgae carbon. J Hazard Mater 425: 127887. https://doi.org/10.1016/j.jhazmat.2021.127887
19. Chen W, Gong M, Li K et al (2020) Insight into KOH activation mechanism during biomass pyrolysis: chemical reactions between O-containing groups and KOH. Appl Energy 278:115730. https://doi.org/10.1016/j.apenergy.2020.115730

20. Gândara Terrazo RI, Escobedo Bretado BC, Nájera Luna JA et al (2016) Kinetic study of the pyrolysis of Pinus cooperi and Quercus sideroxyba to obtain bio-oil and a thermodynamic analysis for hydrogen production. Int J Hydrogen Energy 41:23238–23246. https://doi.org/10.1016/j.ijhydene.2016.09.156

21. Viswanathan K, Wang S (2021) Experimental investigation on the application of preheated fish oil ethyl ester as a fuel in diesel engine. Fuel 285:119244. https://doi.org/10.1016/J.FUEL.2020.119244

22. Zhang ZB, Lu Q, Ye XN et al (2015) Production of phenolic-rich bio-oil from catalytic fast pyrolysis of biomass using magnetic solid base catalyst. Energy Convers Manag 106:1309–1317. https://doi.org/10.1016/J.ENERCON.2015.10.063

23. Reckamp JM, Garrido RA, Satrio JA (2014) Selective pyrolysis of paper mill sludge by using pretreatment processes to enhance the quality of bio-oil and biochar products. Biomass Bioenergy 71:235–244. https://doi.org/10.1016/J.BIOMBIOE.2014.10.003

24. Chen Y, Fang Y, Yang H et al (2019) Effect of volatiles interaction during pyrolysis of cellulose, hemicellulose, and lignin at different temperatures. Fuel 248:1–7. https://doi.org/10.1016/j.fuel.2019.03.070

25. Yuan C, Wang S, Cao B et al (2019) Optimization of hydrothermal co-liquefaction of seaweeds with lignocellulosic biomass: merging 2nd and 3rd generation feedstocks for enhanced bio-oil production. Energy 173:413–422. https://doi.org/10.1016/j.energy.2019.02.091

26. Ryu HW, Kim DH, Jae J et al (2020) Recent advances in catalytic co-pyrolysis of biomass and plastic waste for the production of petroleum-like hydrocarbons. Bioresearch Technol 310:124373. https://doi.org/10.1016/J.BIORENT.2020.123473

27. Wang S, Hu S, Shang H et al (2020) Study on the co-operative effect of kitchen wastewater for harvest and enhanced pyrolysis of microalgae. Bioresearch Technol 317:123983. https://doi.org/10.1016/J.BIORENT.2020.123983

28. Sun Z, Toan S, Chen S et al (2017) Biomass pyrolysis-gasification over Zr promoted CaO-HZSM-5 catalysts for hydrogen and bio-oil co-production with CO2 capture. Int J Hydrogen Energy 42:16031–16044. https://doi.org/10.1016/j.ijhydene.2017.05.067

29. Yuan C, El-Fatah Abomohra A, Wang S et al (2021) High-grade biofuel production from catalytic pyrolysis of waste clay oil using modified activated seaweed carbon-based catalyst. J Clean Prod 313:127928. https://doi.org/10.1016/J.JCLEPRO.2021.127928

30. Saracoğlu E, Uzun BB, Apaydin-Varol E (2017) Upgrading of fast pyrolysis bio-oil over Fe promoted ZSM-5 catalyst to enhance the formation of phenolic compounds. Int J Hydrogen Energy 42:21476–21486. https://doi.org/10.1016/j.ijhydene.2017.07.001

31. Qin W, Luo L, Chen S et al (2021) Efficient strategy of utilizing alkaline liquid waste boosting biomass chemical looping gasification to produce hydrogen. Fuel Process Technol 217:106818. https://doi.org/10.1016/J.FUPROCP.2021.106818

32. He Y, Zhu L, Luo Y et al (2021) Selective upgrading of biomass pyrolysis oil into renewable p-xylene with multifunctional M/SiO2/HZSM-5 catalyst. Fuel Process Technol 213:106674. https://doi.org/10.1016/J.FUPROCP.2020.106674

33. Matamba T, Tahmasebi A, Rish SK, Yu J (2021) Understanding the enhanced production of poly-aromatic hydrocarbons during the pyrolysis of lignocellulosic biomass components under pressurized entrained-flow conditions. Fuel Process Technol 213:106645. https://doi.org/10.1016/J.FUPROCP.2020.106645

34. Lu Q, Zhang ZB, Yang XC et al (2013) Catalytic fast pyrolysis of biomass impregnated with K3PO4 to produce phenolic compounds: analytical Py-GC/MS study. J Anal Appl Pyrolysis 104:139–145. https://doi.org/10.1016/J.JAAP.2013.08.011

35. Zhang ZX, Li K, Ma SW et al (2019) Fast pyrolysis of biomass catalyzed by magnetic solid base catalyst in a hydrogen atmosphere for selective production of phenol. Ind Crops Prod 137:495–500. https://doi.org/10.1016/J.INDCROP.2019.05.066

36. Ye XN, Lu Q, Wang X et al (2017) Catalytic fast pyrolysis of cellulose and biomass to selectively produce levoglucosanone using activated carbon catalyst. ACS Sustain Chem Eng 5:10815–10825. https://doi.org/10.1021/ACSUSCHEMENG.7B02762

37. Shao S, Zhang H, Xiao R et al (2013) Comparison of catalytic characteristics of biomass derivedates with different structures over ZSM-5. Bioenergy Res 6:1173–1182. https://doi.org/10.1007/S12155-013-9303-X/FIGURES/12

38. Gupta J, Papadikis K, Konyshova EY et al (2021) CaO catalyst for multi-route conversion of oakwood biomass to value-added chemicals and fuel precursors in fast pyrolysis. Appl Catal B Environ 285:119858. https://doi.org/10.1016/J.APCAB.2020.119858

39. Li Y, Shaheen SM, Rinklebe J et al (2021) Pyrolysis of Aesculus chinensis Bunge Seed with Fe2O3/ NiO as nanocatalysts for the production of bio-oil material. J Hazard Mater 416:126012. https://doi.org/10.1016/J.JHAZMAT.2021.126012

40. Hu B, Xie WL, Wu Y et al (2021) Mechanism study on the formation of furfural during zinc chloride-catalyzed pyrolysis of xylene. Fuel 295:120656. https://doi.org/10.1016/J.FUEL.2021.120656

41. Lu Q, Li W, Zhang X et al (2020) Experimental study on catalytic pyrolysis of biomass over a Ni/Ca-promoted Fe catalyst. Fuel 263:116690. https://doi.org/10.1016/J.FUEL.2019.116690

42. Chen X, Che Q, Li S et al (2019) Recent developments in lignocellulosic biomass catalytic fast pyrolysis: strategies for the optimization of bio-oil quality and yield. Fuel Process Technol 196:106180. https://doi.org/10.1016/J.FUPROCP.2019.106180

43. Chen X, Li S, Liu Z et al (2019) Pyrolysis characteristics of lignocellulosic biomass components in the presence of CaO. Bioresearch Technol 287:121493. https://doi.org/10.1016/J.BIORENT.2019.121493

44. Chen X, Chen Y, Yang H et al (2019) Catalytic fast pyrolysis of biomass: selective deoxygenation to balance the quality and yield of bio-oil. Bioresearch Technol 273:153–158. https://doi.org/10.1016/J.BIORENT.2018.11.008

45. Lin Y, Zhang C, Zhang M, Zhang J (2010) Deoxygenation of bio-oil during pyrolysis of biomass in the presence of CaO in a fluidized-bed reactor. Energy Fuels 24:5686–5695. https://doi.org/10.1021/ef1009605

46. Zhang C, Lin Y, Zhang M, Zhang J (2015) Experimental study of CaO facilitated cellulose pyrolysis in a drop tube pyrolyzer. Energy Sources, Part A Recover Util Environ Eff 37:2662–2670. https://doi.org/10.1080/15567036.2012.721055

47. Veses A, Aznar M, Martinez I et al (2014) Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. Bioresearch Technol 162:250–258. https://doi.org/10.1016/J.BIORENT.2013.03.146

48. Mahadevan R, Shaky S, Neupane S, Adhikari S (2015) Physical and chemical properties and accelerated aging test of bio-oil produced from in situ catalytic pyrolysis in a bench-scale fluidized-bed reactor. Energy Fuels 29:841–848. https://doi.org/10.1021/ef502353m

49. Zhang ZB (2016) Research on catalytic fast pyrolysis of biomass to produce value-added chemicals. North China Electric Power University, Beijing, China

50. Zhang ZB, Lu Q, Ye XN et al (2014) Selective production of phenolic-rich bio-oil from catalytic fast pyrolysis of biomass:
51. Lu Q, Zhang ZB, Yang XC et al (2013) Catalytic fast pyrolysis of biomass impregnated with K3PO4 to produce phenolic compounds: analytical Py-GC/MS study. J Anal Appl Pyrolysis 104:139–145. https://doi.org/10.1016/j.jaap.2013.08.011

52. Li K, Zhu C, Zhang L, Zhu X (2016) Study on pyrolysis characteristics of lignocellulosic biomass impregnated with ammonia source. University of Science and Technology of China, Hefei, China

53. Lin Y, Zhu L, Wang H et al (2019) Thermogravimetric and mass spectrometry analyses of cellulose pyrolysis under the synergistic effect of CaO and K2HPO4·3H2O. Energy Sources, Part A Recover Util Environ Eff 42:10–16. https://doi.org/10.1080/1556036.2019.1587049

54. Chen F, Yao J, Lin Y et al (2020) Thermogravimetric mass spectrometry of lignin pyrolysis under the co-action of CaO and K2HPO4·3H2O. BioResources 15:3356–3367

55. Lin Y, Zhang C, Zhu L et al (2021) Experimental study on pyrolysis of camphor wood catalyzed by CaO-calced phosphate mixture. Fuel 288:119642. https://doi.org/10.1016/J.FUEL.2020.119642

56. Wang Z, Dang D, Lin W, Song W (2017) Catalytic pyrolysis of corn straw fermentation residue for producing alkyl phenols. Renew Energy 109:287–294. https://doi.org/10.1016/j.renene.2017.03.060

57. Wang T, Tang L, Feng X et al (2022) Influence of organic binders on the pyrolysis performance of rice straw pellets. J Anal Appl Pyrolysis 161:105366. https://doi.org/10.1016/j.jaap.2021.105366

58. Cen K, Zhuang X, Gan Z et al (2021) Effect of the combined pretreatment of leaching and torrefaction on the production of bio-aromatics from rice straw via the shape selective catalytic fast pyrolysis. Energy Rep 7:732–739. https://doi.org/10.1016/j.egyr.2021.01.031

59. Cao Z, Niu J, Gu Y et al (2020) Catalytic pyrolysis of rice straw: screening of various metal salts, metal basic oxide, acidic metal oxide and zeolite catalyst on products yield and characterization. J Clean Prod 269:122079. https://doi.org/10.1016/j.jclepro.2020.122079

60. Ma Y, Li H, Yang H, et al (2021) Effects of solid acid and base catalysts on pyrolysis of rice straw and wheat straw biomass for hydrocarbon production. J Energy Inst. https://doi.org/10.1016/j.joei.2021.08.010

61. Zhang Z, Dong C, Ye X et al (2014) Preparation of levoglucosenone by catalytic pyrolysis of cellulose over solid phosphoric acid. Huagong Xuebao/CIESC J 65:912–920. https://doi.org/10.3969/j.issn.0043-1157.2014.03.021

62. Zhang ZB, Lu Q, Ye XN et al (2015) Selective production of levoglucosenone from catalytic fast pyrolysis of biomass mechanically mixed with solid phosphoric acid catalysts. Bioenergy Res 8:1263–1274. https://doi.org/10.1007/s12155-015-9581-6

63. Ma SW, Zhang G, Li H, et al (2020) Catalytic fast pyrolysis of walnut shell with K/Al catalyst for the production of phenolic-rich bio-oil. Biomass Convers Biorefinery 1–12. https://doi.org/10.1007/s13399-020-00799-7

64. Geng J, Wang WL, Yu YX et al (2017) Adding nickel formate in alkali lignin to increase contents of alkylphenols and aromatics during fast pyrolysis. Bioresour Technol 227:1–6. https://doi.org/10.1016/j.biortech.2016.11.036

65. Mansur D, Yoshikawa T, Norinaga K et al (2013) Production of ketones from pyrolygineous acid of woody biomass pyrolysis over an iron-oxide catalyst. Fuel 103:130–134. https://doi.org/10.1016/j.fuel.2011.04.003

66. Shao S, Liu C, Xiang X et al (2021) In situ catalytic fast pyrolysis over CeO2 catalyst: impact of biomass source, pyrolysis temperature and metal ion. Renew Energy 177:1372–1381. https://doi.org/10.1016/j.renene.2021.06.054

67. Dobele G, Dizhbite T, Rossinskaja G et al (2003) Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis: a promising method for obtaining 1,6-anhydro saccharides in high yields. J Anal Appl Pyrolysis 68–69:197–211. https://doi.org/10.1016/S0165-2370(03)00063-9

68. Téllez JF, Silva MP, Simister R et al (2021) Fast pyrolysis of rice husk under vacuum conditions to produce levoglucosan. J Anal Appl Pyrolysis 156:105105. https://doi.org/10.1016/j.jaap.2021.105105

69. Kuzhiyil N, Dalluge D, Bai X et al (2012) Pyrolytic sugars from corn straw fermentation residue for producing alkyl phenols. Energy Rep 8:1263–1274. https://doi.org/10.1007/s12155-015-9581-6

70. Patwardhan PR, Satrio JA, Brown RC, Shanks BH (2010) Influence of inorganic salts on the primary pyrolysis products of cellulosic biomass. Chemsuschem 5:2228–2236. https://doi.org/10.1002/cssc.20100341

71. Zheng A, Zhao Z, Huang Z et al (2015) Overcoming biomass recalcitrance for enhancing sugar production from fast pyrolysis of biomass by microwave pretreatment in glycerol. Green Chem 17:1167–1175. https://doi.org/10.1039/c4gc01724b

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