Experimental Study On Pyrolysis of Rice Straw Catalyzed By CaO/Al₂O₃-Phosphate Mixture

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Abstract

This paper studied the synergistic effects of CaO or Al₂O₃ and three potassium phosphates (e.g., KH₂PO₄, K₂HPO₄·3H₂O and K₃PO₄·3H₂O) in the rice stalk pyrolysis through pyrolysis-gas chromatography-mass spectrometer (Py-GC/MS) experiments. The results show that after co-catalyzed by CaO/Al₂O₃ and potassium phosphates, the total contents of phenols, aldehydes, acids, LG from most samples decrease and those of ketones increase compared with those catalyzed by potassium phosphates alone. CaO/Al₂O₃ and potassium phosphates show synergistic effects in the regulation of the types or contents of phenols, ketones, aldehydes, etc. and are suitable for the production of ketone-rich bio-oil. Dehydration reactions, etc. are further promoted under the co-catalysis of the two catalysts, and some phenols can be converted to benzene products, etc. The contents of acetic acid can decrease to 0. For 50% K₃PO₄·3H₂O impregnated sample, the yields of furans reduce sharply after CaO addition. For most impregnated samples except 50% K₂HPO₄·3H₂O sample and 30%, 50% K₃PO₄·3H₂O, the contents of total furans and furfural increase after Al₂O₃ addition.

1 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[1–6]. Biomass has the advantages of renewability, low cost, abundant reserves and carbon neutrality, providing about 10% of global energy consumption [7–10]. 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 [11–14]. However, the primary pyrolysis bio-oil has many harmful properties, such as high oxygen content, acidity, viscosity, and low heating value [13, 15–19]. The use of catalysts within the pyrolysis process, known as catalytic pyrolysis, can decrease the oxygen content selectively convert biomass into high-value-added chemicals or high-quality bio-oil. It has attracted the attention of many researchers[20–23]. The commonly used catalysts are metal oxide catalysts, metal salt catalysts, molecular sieve catalysts, etc.

Metal oxide catalyst has large pore structure and good catalytic characteristics, and mainly includes: calcium oxide (CaO), alumina (Al₂O₃), nickel oxide (NiO), iron oxide (Fe₂O₃), magnesium oxide (MgO), zinc oxide (ZnO), etc. Lu et al. [24] used Py-GC/MS to study the effects of metal oxides, such as CaO, Fe₂O₃, NiO, MgO, TiO₂ and ZnO, on the polar pyrolysis process. The results showed that CaO significantly reduced the content of acids, phenols and anhydrosugar, and increased the content of cyclopentane ketone and hydrocarbon products. Fe₂O₃, NiO, MgO and TiO₂ can reduce the content of linear aldehyde and increase the content of ketone product. ZnO slightly changed the product contents with mild catalytic effect. Chen et al. [25, 26] studied the effects of 11 heterogeneous catalysts (CaO, Al₂O₃, NiO, Fe₂O₃, MgO, CuO, ZnO, ZrO₂, TiO₂, HZSM-5 and MCM-41) on the biomass pyrolysis characteristics, and found that CaO, Al₂O₃ and NiO could effectively reduce the oxygen content of bio-oil and improve the quality of bio-oil. Lin et al. [27, 28] found that by the co-pyrolysis of biomass and CaO, the oxygen content of bio-oil

decreased, the yield of organic components in the pyrolysis products decreased, and the water content increased. Wang et al. [29, 30] proved that CaO could inhibit the generation of acid substances in the corn cob pyrolysis products. Veses et al. [31] studied the pyrolysis characteristics of pine with CaO and found that CaO decreased the oxygen content and increased the calorific value of bio-oil during the catalytic process. Acids, furans, 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. [32] studied the influence of CaO, MgO and ZSM-5 in the biomass pyrolysis process. It was found that after CaO addition, acids decreased, the contents of furan and ketone products increased. MgO is a mild catalyst with only a slight change in the quality of the bio-oil. ZSM-5 has no significant effect on the acid content of the bio-oil.

Phosphate can provide lots of acidic sites or active sites and plays a great catalytic role in the process of pyrolysis. Zhang, et al. [33, 34] used Py-GC/MS to study the catalytic pyrolysis of poplar wood by phosphates and found that K_3PO_4 , K_2HPO_4 and KH_2PO_4 promoted the generation of phenolic products. And the selectivity of phenolic products from high to low were K_3PO_4 , K_2HPO_4 and KH_2PO_4 . Lu et al. [35] found that K_3PO_4 inhibited the devolatilization of cellulose to form organic volatiles, while promoted the decomposition of lignin to generate phenolic compounds. Li Kai [36] found that loading K_3PO_4 on the surface of rice husk was beneficial to reduce the reaction activation energy of rice husk pyrolysis and change the pyrolysis transformation path of rice husk. Wang et al. [37] found that the alkyl phenol yield in bio-oil significantly increased to about 50% during the catalytic process of corn straw with KH_2PO_4 supported by activated alumina.

Both metallic oxides and potassium phosphates` are useful catalysts in the biomass pyrolysis. In our previous studies, CaO and phosphates showed synergistic effects in the pyrolysis of camphor wood. CaO and calcined $K_3PO_4 \cdot 3H_2O$ together reduced the relative contents of 3-methoxy-2,5,6-trimethylphenol, 3-methoxy-1,2-benzenediol significantly, while enhanced those of isoeugenol, trans-isoeugenol, and furfural. CaO and calcined $K_2HPO_4 \cdot 3H_2O$ together increased the relative contents of phenols and cyclopentanones. It can be assumed that metallic oxides and potassium phosphates would show some beneficial synergistic effects in the biomass pyrolysis process. Besides, Rice stalks from agricultural crops are often disposed as waste. Catalytic pyrolysis, which convert rice stalk into high-valuable bio-oil or chemicals, is an important technical means for rice stalk utilization. A lot of researches have been done on the catalytic pyrolysis of rice stalk. In this paper, Py-GC/MS was utilized to study the fast pyrolysis of rice stalk with the co-catalysis of two metallic oxides (e.g., CaO, Al_2O_3) and three types of potassium phosphates, (e.g., KH_2PO_4 , $K_2HPO_4 \cdot 3H_2O$ and $K_3PO_4 \cdot 3H_2O$).

Besides, potassium phosphate can be added to biomass by direct mixing and impregnation. In impregnation process, potassium phosphate can penetrate into the pores of biomass particles, disperse evenly, contact with biomass fully, and the catalytic cracking reaction is more intense. Lu et al. 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 this paper, 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.

In this paper, the distributions of pyrolysis products were analyzed and the synergistic effects of CaO or Al₂O₃ and three potassium phosphates (e.g., KH₂PO₄, K₂HPO₄·3H₂O and K₃PO₄·3H₂O) in the rice stalk pyrolysis were investigated, 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.

2 Experimental

2.1 Experimental materials and preparation

The biomass used in the research was rice stalk purchased from Jiaxing City, Zhejiang Province. First, the rice stalks were crushed by a shredder, and then were screened through standard sample screening. Rice stalks with particle size of 160-200 mesh (0.075-0.1mm) were selected for this experiment. Before each experiment, the biomass was dried in a drying oven at 105°C for 12h. The proximate and elemental analysis of the rice stalk are shown in Table 1.

Table 1
Analysis of rice stalk composition

specimen	proximate analysis(wt.%)				elemental analysis(wt.%)				
	M	A	V	FC	C	H	O	N	S
rice straw	10.02	9.03	61.27	19.68	41.05	6.54	50.95	1.31	0.15

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 4h. 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, according to the impregnation ratio, a certain amount of potassium phosphates was weighed and put into distilled water, then 2g of camphor wood was added and stirred by magnetic stirrers for 12h in order to ensure sufficient contact with the solution. Finally, the mixed sample was placed in a drying oven for 12h at 120 °C and sealed for use. Three main impregnation ratios were selected: 10%, 30% and 50%. Calcined CaO, Al₂O₃ were mechanically mixed with rice stalk 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 1mg.

2.2 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. 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.

3 Results And Analysis

In this study, rice straw, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ were represented by Rs, K1, K2 and K3, respectively. Rice straw sample with 30 wt% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation was represented as 30% K3-Rs, and other samples were expressed according to this method.

3.1 Co-catalytic pyrolysis by CaO and potassium phosphates

As illustrated above, calcined CaO was mechanically mixed with rice stalk samples impregnated with KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, 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, and a few others. The contents were represented by the relative peak areas.

(1) Phenols

Fig. 1(a) shows the relative yields of total phenols and Fig. 1(b)-(j) shows the relative yields of different phenols produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. R is the mass ratio of CaO to impregnated biomass. The total content of phenols from Rs sample is 16.63%. For the Rs samples, the total yields of phenols slightly decrease and then increase with the increase of CaO addition ratios. The relative yields of 2-methoxy-4-vinylphenol, mequinol are high in the Rs sample pyrolysis. The relative yields of phenol, p-cresol and 3-methyl-phenol increase and those of 2-methyl-1,3-benzenediol decrease markedly after CaO addition. When R is greater than or equal to 1, 2-methyl-1, 3-benzenediol could not be detected.

It can be seen that except with 10% KH_2PO_4 addition (10%K1-RS), the total yields of phenols increase, indicating that potassium phosphates alone can promote the generation of phenols, which is in accordance with Zhang et al.'s studies [34, 38, 39]. With 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation only, the total yields of phenols content reached the highest value of 27.69%. Under most impregnation ratios, the

catalytic effect for the rising value of the yields of phenols are in the descending order of $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, KH_2PO_4 , and the values increase with the increase of impregnation amount [40]. The contents of 4-ethyl-2-methoxy phenol, phenol and p-cresol all increase after potassium phosphate impregnation only. After 50% KH_2PO_4 impregnation only, the relative yield of 2-methoxy-4-vinylphenol increases from 3.14% to 4.19%, with the highest value in phenols, and that of 4-ethyl-2-methoxy phenol increases from 0.72% to 2.55%. After 50% $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ impregnation only, the yield of 2, 6-dimethoxy phenol increases from 1.21% to 1.77% and that of phenol increases from 1.05% to 2.17%. After 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation only, the yield of mequinol increases from 2.18% to 3.94%, and that of 3-methyl-phenol increases from 0.61% to 1.89%. Some phenols are inhibited by potassium phosphates. After 30%, 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation only, the yields of 3-methoxy-1, 2-phenylenediol and 2-methyl-1, 3-phenylenediol decrease to 0. This is because potassium phosphate can further promote the deoxidation, demethylation, demethoxylation reactions, etc., and also promote the removal of alkyl side chains on benzene ring in some phenols [41].

On the whole, the total contents of phenols co-catalyzed by CaO and potassium phosphates decrease compared with those catalyzed by potassium phosphates alone. The total contents of phenols decrease obviously from 27.69% to 17.57% with the increase of R when co-catalyzed by CaO and 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. This is because CaO can further catalyzes dehydration reactions, etc. to convert phenols to form benzene products, etc. Some phenols from some impregnated samples are 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, p-cresol and 3-methyl-phenol from the pyrolysis of K2-Rs. Some phenols from some impregnated samples are inhibited after CaO addition on the whole, such as 2-methoxy-4-vinylphenol, 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, 2-methyl-1,3-benzenediol from the pyrolysis of 50% K3-Rs, 50% K2-Rs and most impregnated samples, respectively can even be reduced to 0 after CaO addition. The yields of some phenols from some impregnated samples reach the highest value at certain R, such as phenol from 30% K1-Rs, 10% K2-Rs, 30% K3-Rs samples at $R=0.5$, 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 show some synergistic effects in the regulation of the type of phenols.

(2) Ketones

Fig. 2(a) shows the relative yields of total ketones and Fig. 2(b)-(g) shows the relative yields of different ketones produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. A lot of ketones are derived from the ring-opening reaction of cellulose, and acids are partially converted into ketones under catalytic pyrolysis [42]. The yields of ketones show the highest value, with 34.47% in the products in the pure rice stalk pyrolysis, indicating that rice stalk is suitable for prepare 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 can be seen from Figure 3(b)-(f) that the relative contents of most

ketones except 1,2-cyclopentanedione increase after CaO addition only. The yields of 1-hydroxy-2-acetone show the highest value in the ketones, with 10.86% from pure rice stalk pyrolysis and maximum content 13.05% at R=1.

$K_3PO_4 \cdot 3H_2O$ and $K_2HPO_4 \cdot 3H_2O$ alone promote the formation of ketones, while KH_2PO_4 inhibits the formation of ketones. This is because $K_2HPO_4 \cdot 3H_2O$ and $K_3PO_4 \cdot 3H_2O$ are alkaline, while KH_2PO_4 is acidic. Alkaline environment is conducive to the production of ketone products. After KH_2PO_4 impregnation alone, the yields of 1-hydroxy-2-acetone and 2-hydroxy-3-methyl-2-cyclopentene-1-one decrease, the yield of 1-acetyloxy-2-propanone decrease and the yields of acetone and 1,2-cyclopentanedione don't change much.

High impregnation amount of $K_2HPO_4 \cdot 3H_2O$ reduces the contents of 1-hydroxy-2-acetone, 1, 2-cyclopentanedione. $K_2HPO_4 \cdot 3H_2O$ increases the content of 2-hydroxy-3-methyl-2-cyclopentene-1-one, but has little effect on 1-acetyloxy-2-propanone. After 50% $K_3PO_4 \cdot 3H_2O$ impregnation only, the yields of 2-hydroxy-3-methyl-2-cyclopentene-1-one increase from 1.48% to 2.35% and those of 1, 2-cyclopentanedione, 1-acetyloxy-2-propanone decrease to 0. After 10% $K_3PO_4 \cdot 3H_2O$ impregnation only, the yields of 1-hydroxy-2-acetone increase from 10.86% to 13.3%, while those of 1-hydroxy-2-acetone decrease with high $K_3PO_4 \cdot 3H_2O$ impregnation amount.

On the whole, the total contents of ketones co-catalyzed by CaO and potassium phosphates further increase compared with those catalyzed by potassium phosphates alone. From R=0 to R=1.5, the yields of ketones increase from 44.62% to the highest value 56.65% from the pyrolysis of 10% K3-Rs. CaO and potassium phosphates show some synergistic effects in the regulation of the type of ketones and are suitable for the production of ketone-rich bio-oil.

(3) Acids

Fig. 3(a) shows the relative yields of total acids and Fig. 3(b) shows the relative yields of acid produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $K_2HPO_4 \cdot 3H_2O$, and $K_3PO_4 \cdot 3H_2O$. It can be seen from Figure 3(a) that CaO alone significantly reduce 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 Equations (1) and (2).

Acids mainly contain acetic acid. As shown in Fig. 4(b), CaO alone significantly reduce the total content of acid products from 4.67–2.33% at R=0 to R=1.5.

$K_3PO_4 \cdot 3H_2O$ alone significantly reduce acids. After 50% $K_3PO_4 \cdot 3H_2O$ impregnation, the yields of acids decrease to 2.39% and those of acetic acid decrease to 0. Except for 10% and 30% KH_2PO_4 addition

alone, the contents of acetic acid decrease after potassium phosphates addition alone.

The total contents of acids from the pyrolysis of rice stalk co-catalyzed by CaO and potassium phosphates further decrease significantly compared with those catalyzed by potassium phosphates alone. Except for 10% and 50% K1-Rs, the contents of acetic acid can decrease to 0 after CaO addition. CaO and potassium phosphates together show strong synergistic effects in decreasing acids, which is in accordance to our previous findings.

(4) Aldehydes

Fig. 4(a) shows the relative yields of total aldehydes and Fig. 4(b)-(d) shows the relative yields of different aldehydes produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen from Figure that CaO alone reduce 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 decrease after CaO addition alone.

Potassium phosphates alone reduce aldehydes, the higher the impregnation amount, the more the reduction of aldehyde content. $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ shows the highest reduction effects. 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ alone reduce the yield of total aldehydes to 1.36%. Hydroxy-acetaldehyde and succinaldehyde decrease to 0 after 30%, 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and 50% $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ impregnation alone. Pentanal decrease to 0 after 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation alone.

On the whole, the total contents of aldehydes co-catalyzed by CaO and potassium phosphates from most samples decrease compared with those catalyzed by potassium phosphates alone. Other samples have fluctuated content of total aldehydes. The decrease is also because CaO can further catalyzes dehydration and deoxidation reactions. The yields of pentanal from the pyrolysis of 30%, 50% K1-Rs and 10%K2-Rs further increase after CaO addition on the whole.

Some aldehydes from some impregnated samples are inhibited after CaO addition on the whole, such as hydroxy-acetaldehyde from the pyrolysis of most samples, hydroxy-acetaldehyde from the pyrolysis of 10%, 30% K2-Rs and 10% K3-Rs, pentanal from the pyrolysis of 30% K3-Rs. Some aldehydes from some impregnated samples show fluctuated trends with the increase of R. CaO and potassium phosphates show some synergistic effects in the regulation of the type of aldehydes.

(5) Furans

Fig. 5 shows the relative yields of total furans produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that CaO alone increase the total content of furans. This is because CaO promotes the depolymerization, ring opening and dehydration of xylan and 4-O-methylglucuronic acid units, etc. 50% KH_2PO_4 alone increase the yields of total furans to 9.52% from 5.31% in the pyrolysis products of pure rice stalk. For 50% K3-Rs sample, the yields of furans reduce sharply after CaO addition.

(6) Levoglucosan (LG)

Levoglucosan (LG) is an important product in the biomass pyrolysis. Fig. 6 shows the relative yields of Levoglucosan (LG) produced from the catalytic pyrolysis of rice stalk with CaO, KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. CaO alone changes the yields of LG a little.

On the whole, most potassium phosphates alone reduce LG [43]. $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ shows the highest promotion effects. This is because alkaline environment induced by $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ is harmful for the production of ketone products [44]. 30%, 50% KH_2PO_4 impregnation increase the yields of LG.

On the whole, the contents of LG co-catalyzed by CaO and potassium phosphates decrease compared with those catalyzed by potassium phosphates or CaO alone. For 50% K2-Rs and all the K3-Rs samples, they can decrease to 0 after CaO addition.

3.2 Co-catalytic pyrolysis by Al_2O_3 and potassium phosphates

(1) Phenols

Fig. 7(a) shows the relative yields of total phenols and Fig. 7(b)-(j) shows the relative yields of different phenols produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that the relative contents of total phenols, 4-ethyl-2-methoxy phenol, 3-methoxy-1,2-benzenediol and 2-methyl-1, 3-benzenediol decrease after Al_2O_3 addition alone.

On the whole, the contents of most phenols co-catalyzed by Al_2O_3 and potassium phosphates decrease compared with those catalyzed by potassium phosphates alone. For certain samples, three small phenols, i.e., phenol, p-cresol, 3-methyl-phenol can reach its highest value at certain R, such as phenol at $R=1, 1.5, 1.5, 0.5$ for 30%, 50% K1-Rs samples and 10%, 50%K2-Rs samples, respectively. For 50% impregnation samples, the yields of total phenols decrease maximumly from 27.69–8.17% at $R=0$ to 1.5. The yields of 2-methyl-1,3-benzenediol from all the samples decrease to 0 after Al_2O_3 addition. The yields of 3-methoxy-1,2-benzenediol from 30%, 50% K2-Rs samples decrease to 0 after high CaO addition amounts. Al_2O_3 and potassium phosphates show some synergistic effects in the regulation of the type of phenols.

(3) Ketones

Fig. 8(a) shows the relative yields of total phenols and Fig. 8(b)-(f) shows the relative yields of different phenols produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that the relative contents of total ketones increase a lot after Al_2O_3 addition alone.

The contents of ketones co-catalyzed by Al_2O_3 and potassium phosphates increase a lot further compared with those catalyzed by potassium phosphates alone. The yields of ketones reach the maximum value 56.02% at 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnation and $R=0.5$. On the whole, the yields of 1-hydroxy-2-propanone from 10% K1-Rs sample, 30%, 50%K2 samples and all K3-Rs samples, 1,2-cyclopentanedione from 30%, 50% K2-Rs samples and 10%, 30% K3-Rs samples, 1-acetyloxy-2-propanone from 50% K2-Rs sample decrease after Al_2O_3 addition. Al_2O_3 and potassium phosphates show some synergistic effects in the regulation of the type of ketones and are suitable for the production of ketone-rich bio-oil.

(3) Acids

Fig. 9(a) shows the relative yields of total acids and Fig. 8(b) shows the relative yields of acetic acid produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that the relative contents of total acids decrease after Al_2O_3 addition alone. The yields of acetic acid decrease from 4.67% to 2.55% at $R=0$ to 1.5.

The contents of acids co-catalyzed by Al_2O_3 and potassium phosphates decrease compared with those catalyzed by potassium phosphates alone. For 50% K2-Rs and 30% K3-Rs samples, the yields of acetic acid can decrease to 0 after Al_2O_3 addition.

(4) Aldehydes

Fig. 10(a) shows the relative yields of total aldehydes and Fig. 8(b)-(d) shows the relative yields of different aldehydes produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that the relative contents of total aldehydes increase after Al_2O_3 addition alone.

On the whole, the contents of total and most aldehydes from most samples co-catalyzed by Al_2O_3 and potassium phosphates decrease compared with those catalyzed by potassium phosphates alone. The yields of hydroxy-acetaldehyde from 30%, 50% K1-Rs samples and 30%K2-Rs samples can decrease to 0 after Al_2O_3 addition.

(5) Furans

Fig. 11(a) shows the relative yields of total furans and Fig. 11(b)-(c) shows the relative yields of different furans produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. It can be seen that the relative contents of total furans decrease after Al_2O_3 addition alone. The yields of furfural increase a lot from 2.55% to 4.88% at $R=0$ to 1.5.

On the whole, the contents of total furans and furfural from most samples except 50% K2-Rs sample and 30%, 50%K3-Rs samples co-catalyzed by Al_2O_3 and potassium phosphates increase compared with those catalyzed by potassium phosphates alone. The yields of furfural from 50% K2-Rs sample and 30%,

50%K3-Rs samples can decrease to 0 after Al_2O_3 addition. The yields of 2,3-dihydro-benzofuran from all samples decrease after Al_2O_3 addition. Al_2O_3 and potassium phosphates show some synergistic effects in the decrease of furans and the regulation of the type of furans.

(6) Levoglucosan (LG)

Fig. 12 shows the relative yields of LG produced from the catalytic pyrolysis of rice stalk with Al_2O_3 , KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$. The relative contents of LG decrease after high amount of Al_2O_3 addition [45–47].

On the whole, the contents of LG co-catalyzed by Al_2O_3 and potassium phosphates decrease compared with those catalyzed by potassium phosphates alone. The contents of LG from most samples except for 10%, 30% K1-Rs samples can decrease to 0 after Al_2O_3 addition.

4 Conclusions

This paper studied the synergistic effects of CaO or Al_2O_3 and three potassium phosphates (e.g., KH_2PO_4 , $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$) in the rice stalk pyrolysis through Py-GC/MS experiments. The conclusions are as follows:

(1) Potassium phosphates alone can increase the yields of total phenols. The promotion effects decrease in the order of $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O} > \text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O} > \text{KH}_2\text{PO}_4$. $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ alone promote the formation of ketones, while KH_2PO_4 inhibits the generation of ketones. $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ alone significantly reduce acids. Potassium phosphates alone also reduce aldehydes, furans and LG.

(2) After CaO addition alone, the relative yields of phenol, p-cresol and 3-methyl-phenol increase and those of 2-methyl-1,3-benzenediol decrease markedly. The yields of ketones increase significantly, furans increase a little, and those of acids, aldehydes decrease.

(3) After catalyzed by Al_2O_3 alone, the relative contents of total phenols, acids, and aldehydes, and 4-ethyl-2-methoxy phenol, 3-methoxy-1,2-benzenediol and 2-methyl-1, 3-benzenediol, acid, etc. decrease and those of total ketones and furans increase.

(4) After co-catalyzed by $\text{CaO}/\text{Al}_2\text{O}_3$ and potassium phosphates, the total contents of phenols, aldehydes, acids, LG from most samples decrease and those of ketones increase compared with those catalyzed by potassium phosphates alone. $\text{CaO}/\text{Al}_2\text{O}_3$ and potassium phosphates show synergistic effects in the regulation of the type or content of phenols, ketones, aldehydes, etc. and are suitable for the production of ketone-rich bio-oil. Dehydration reactions, etc. are further promoted under the co-catalysis of the two catalysts, and some phenols can be converted to benzene products, etc. The contents of acetic acid can decrease to 0.

(5) For 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnated sample, the yields of furans reduce sharply after CaO addition. The contents of total furans and furfural from most samples except 50% $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ sample and 30%, 50% $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ impregnated samples co-catalyzed by Al_2O_3 and potassium phosphates increase compared with those catalyzed by potassium phosphates alone.

Declarations

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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Figures

Figure 1

Phenols in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

Figure 2

Ketones in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

(a) Acids

(b) Acetic acid

Figure 3

Acids in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

(a) Aldehydes

(b) Hydroxy-acetaldehyde

(c) Succindialdehyde

(d) Pentanal

Figure 4

Aldehydes in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

Figure 5

Furans in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

Levoglucosan (LG)

Figure 6

LG in the products of rice stalk pyrolysis co-catalyzed by CaO and potassium phosphates

Figure 7

Phenols in the products of rice stalk pyrolysis co-catalyzed by Al_2O_3 and potassium phosphates

(a) Ketones

(b) 1-Hydroxy-2-propanone

(c) 1,2-Cyclopentanedione

(d) 2-Hydroxy-3-methyl-2-cyclopenten-1-one

(e) 1-(acetyloxy)-2-Propanone

(f) 2-Butanone

Figure 8

Ketones in the products of rice stalk pyrolysis co-catalyzed by Al_2O_3 and potassium phosphates

(a) Acids

(b) Acetic acid

Figure 9

Acids in the products of rice stalk pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates

(a) Aldehydes

(b) Hydroxy-acetaldehyde

(c) Succindialdehyde

(d) Pentanal

Figure 10

Aldehydes in the products of rice stalk pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates

(a) Furans

(b) Furfural

(c) 2,3-Dihydro-benzofuran

Figure 11

Furans in the products of rice stalk pyrolysis co-catalyzed by Al₂O₃ and potassium phosphates

Levogluconan (LG)

Figure 12

LG in the products of rice stalk pyrolysis co-catalyzed by Al_2O_3 and potassium phosphates