Improved Yields of High Value-added Ketones in Bio-oil from Biomass Fast Pyrolysis Employing ZnO-modified Magnesium Aluminum Spinel Catalyst

Di Yao, Dongmei Bi,* An Zhao, Jia Liu, Jing Liu, and Bozheng Li

Ketones are an important class of multi-purpose products used for the production of high value-added chemicals. Herein, a novel method for the generation of methylcyclopentenone and pyridone via the modification of a magnesium aluminum spinel catalyst is proposed. In this study, zinc oxide, magnesium aluminum spinel, and ZnO-loaded magnesium aluminum spinel were used as catalysts for the catalytic pyrolysis of rape straw, corn stalk, and camphorwood powder at different reaction temperatures. Experimental results showed that different experimental temperatures and catalyst types played a crucial role in the formation of methylcyclopentenone and pyridone. Catalytic pyrolysis of rape straw with ZnO-loaded magnesium aluminum spinel increased the yield of methylcyclopentenone by greater than 6-fold compared to the yield without the catalyst, and the catalytic pyrolysis of corn stover increased the production of pyridone to 12.4%. The increase was primarily attributed to the conversion of cellulose and hemicellulose to ketones promoted by the ZnO-loaded magnesium aluminum spinel. These findings demonstrated that ZnO-loaded magnesium aluminum spinel catalysts can provide a new approach for enhancing the yield of methylcyclopentenone and pyridone during biomass fast pyrolysis.

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Keywords: Biomass; Catalytic pyrolysis; Methylcyclopentenone; Pyridone; ZnO

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INTRODUCTION

Currently, fossil fuels are used in large quantities for energy use and chemical production cause serious environmental pollution, climate warming, and other problems. Thus, it has become a global consensus to actively seek clean and renewable alternative energy sources (Sun et al. 2021). Among them, biomass is an important renewable carbon source with carbon-neutral properties (Nian 2016; Koondhar et al. 2021). It has, therefore, become the focus of research and development for the next generation of new energy and green chemical systems (Zahed et al. 2021). The rapid pyrolysis of biomass is an effective method to realize the high-value utilization of biomass resources in high-quality bio-oil or biomass gas, as well as biochar and other products with important applications. In addition to being a liquid fuel, bio-oil contains a variety of high-value chemicals, including phenols (Alam et al. 2021), aldehydes (Cheng et al. 2019), and ketones (Shao et al. 2021a).

For example, methylcyclopentenone (MCP) is a safe food additive as well as a flavor and pharmaceutical intermediate (Tian et al. 2010). Moreover, methylcyclopentane, which is produced by MCP as an intermediate product, has a high octane number and can
be used as an additive for ethanol gasoline (Sacia et al. 2015). As early as 1976, Langin-Lanteri and Huet (1976) prepared MCPs via the oxidation of epoxy compounds under H$_2$O$_2$ alkaline conditions and hydrolysis with acid. In addition, Sacia et al. (2015) proposed the hydrolysis of 2,5-dimethylfuran to produce 2,5-hexanediol following by intramolecular aldol condensation over a basic catalyst to form MCP, but the results were not satisfactory. Duan et al. (2017) proposed the hydrogenation of 5-hydroxymethylfurfural to 1-hydroxy-2, 5-hexanediol (HHD) in water over a Pd/Nb$_2$O$_5$ catalyst, followed by the isomerization of HHD to MCP in the presence of a base. Existing MCP can achieve a wide source of low-cost raw materials in its production, but the environmental pollution caused by the use of toxic and hazardous substances in the production process still remains a difficult problem. In addition, pyridones are also a class of organic compounds with important biological activity and medicinal value (Stojanovic et al. 2020; Houshmandyar et al. 2021). Cyclic pyridones constitute a promising family of antimalarial compounds that have been shown to maintain excellent in vitro activity and in vivo efficacy in the Plasmodium jovic model and the humanized mouse model of Plasmodium falciparum (Felipe 2018). Öztürk et al. (2001) generated pyridone via the condensation of 4-pyrone and a primary amine. The raw materials for the preparation of pyridone are presently expensive, which increases the production cost of pyridone.

The fast pyrolysis technology of biomass can produce MCP, pyridone, and other ketones in one step via depolymerization and hydrogen bond breakage at high temperatures. However, the conventional rapid pyrolysis of biomass does not produce high-value chemical raw materials due to poor selective bond breaking and competition between the products, which results in complex components and low contents of single components in the bio-oil (Horne and Williams 1996; Hussain et al. 2013; Mourant et al. 2013). For this reason, the addition of suitable catalysts in the pyrolysis process combined with the regulation of the pyrolysis reaction conditions, in order to inhibit the generation of other products and to achieve the enrichment of high-value target products, have become the current focuses of research in biomass pyrolysis liquefaction technology.

There have been numerous studies on improving the quality of bio-oil by limiting the formation of oxygenated compounds, including carboxylic acids, in pyrolysis products through metal or metal-oxide catalysts. Among them, zinc, as a common transition metal, has been widely used for the selective catalytic pyrolysis of biomass. Eibner et al. (2015) found that zinc nitrate increased the yield of the biomass pyrolysis product 1-hydroxy-3,6-dioxabicyclo[3.2.1]octan-2-one, reduced the maximum pyrolysis rate of heterocellulose, increased the solid residue yield, and promoted the dehydration reaction of heterocellulose. ZnO is a relatively mild catalyst and has a lower effect on reducing the bio-oil yield compared to zinc chloride and zinc nitrate (Bulushev and Ross 2011; Nokkosmaki et al. 2000). In addition, the milder effect on the production of lignins and the increased stability of bio-oil, demonstrated ZnO was an effective catalyst for the pyrolysis of biomass to ketone chemicals (Lu et al. 2010). To improve the catalytic effect, the loaded metal catalysts can be used to obtain better catalytic performance with less active metal by the carrier effect. Magnesium aluminum spinel (MAS), whose primary component is MgAl$_2$O$_4$, has both acidic and basic active centers and possesses a rich pore structure, which has an impact on the strength, catalytic activity, and selectivity of biomass pyrolysis chemical enrichment (Qiu et al. 2007). Magnesium aluminum spinel acts as a carrier and has strong interactions with metal ions. Previous studies on MAS-loaded metal oxides and their catalytic pyrolysis in biomass, especially their selectivity for specific products in bio-oils, have been scarce. In this paper, with the research objective of obtaining additional
MCPs and pyridones in bio-oil, the authors used ZnO, MAS, and ZnO-loaded magnesium aluminum spinel (ZnO-MAS) for pyrolysis experiments on rape straw, corn stalk, and camphorwood powder. The effect of ZnO-MAS on the generation pattern of MCP and pyridone was investigated to provide a new method for the generation of MCP and pyridone. In addition, the used ZnO-MAS catalyst was used again for the catalytic reaction, and the results showed that the reacted catalyst retained some catalytic activity. This article will focus on the activity and reuse of the catalysts in the future.

EXPERIMENTAL

Materials
The biomass feedstock used in the experiment included rape straw, corn stalk (stalks and leaves), and camphorwood powder. The three kinds of raw materials that were collected were crushed, screened (at 40 mesh to 60 mesh), and then placed in a drying oven to dry at a temperature of 105 °C for 24 h to remove external moisture. The elemental and proximate analyses of the raw materials are shown in Table 1.

Table 1. Elemental and Proximate Analysis of the Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elemental Analysis (%)</th>
<th>Proximate Analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Rape straw</td>
<td>48.52 ± 1.5</td>
<td>5.74 ± 0.3</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>47.41 ± 1.2</td>
<td>5.78 ± 0.3</td>
</tr>
<tr>
<td>Camphorwood powder</td>
<td>53.16 ± 1.6</td>
<td>6.12 ± 0.4</td>
</tr>
</tbody>
</table>

Note: The samples are dry base and the O elements are calculated via the differential subtraction method.

The cellulose, hemicellulose, and lignin (three major fractions) contents of the rape straw, corn stalk, and camphorwood powder samples were determined using the Van Soest method (Soest 1963), and the measurements are shown in Table 2.

Table 2. Contents of the Three Components from the Different Test Materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Rape Straw (%)</th>
<th>Corn Stalk (%)</th>
<th>Camphorwood Powder (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>35.41 ± 1.00</td>
<td>32.54 ± 0.50</td>
<td>37.62 ± 0.35</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>17.84 ± 0.50</td>
<td>18.34 ± 0.40</td>
<td>12.65 ± 0.40</td>
</tr>
<tr>
<td>Lignin</td>
<td>21.64 ± 0.60</td>
<td>22.02 ± 0.60</td>
<td>34.74 ± 0.50</td>
</tr>
</tbody>
</table>
As shown in Tables 1 and 2, the lignin content of camphorwood powder was highest (34.7 wt%). Camphorwood powder, with a high lignin content, had the highest elemental carbon content (53.2 wt%) and the lowest elemental oxygen and ash content. Rape straw and corn stalk, which had a higher cellulose and hemicellulose content, possessed a higher oxygen content (45.2 wt% and 46.3 wt%, respectively), along with a lower volatile fraction.

**Catalyst Preparation**

*Preparation of magnesium aluminum spinel (MAS)*

Magnesium aluminum spinel was synthesized from alumina (greater than or equal to 98.5% purity) and magnesium oxide (greater than or equal to 96% purity) with an appropriate amount of high-grade magnesite (greater than 47% MgO) and other ingredients. These components were melted at a high temperature in an electric arc furnace and refined to produce the spinel clinker. Magnesium aluminum spinel is characterized by its high density and good color, its good thermal shock stability, and its high resistance to erosion. An electrofusion method using high-purity raw materials can control the content of impurities in the material. As a result, the content of MgO + Al₂O₃ could reach greater than 99%, and its grain development was good, possessing a dense texture and uniform structure.

*Preparation of ZnO-loaded magnesium aluminum spinel (ZnO-MAS)*

Magnesium-aluminum spinel and zinc acetate were mixed well at a 1 to 1 molar ratio and ultrasonically dispersed. Distilled water was added until the zinc acetate was saturated. The solution was then slowly stirred in a constant temperature stirrer at a temperature of 40 °C to evaporate and dry the solution. After being completely dried, the white solids obtained after drying were placed in a drying oven and dried at a temperature of 105 °C for 12 h. After further drying, the white powder was put into a muffle furnace at a temperature of 400 °C for 5 h. During heating, the zinc acetate will volatilize a large amount of acetic acid gas. Finally, the catalyst ZnO-MAS was obtained.

**Catalyst Characterizations**

Using the X-ray fluorescence principle, the percentage content of each element in the MAS and ZnO-MAS catalysts was measured via X-ray fluorescence spectrometry (XRF, type 9900). The appearance and morphology of the samples and catalysts were analyzed using a SIRON 200 scanning electron microscope with a magnification of 5000x to 100000x. Since the samples were not conductive, the samples needed to be gold sprayed before testing to make the imaging bright and clear. The specific surface area, pore volume, and pore size of the MAS and ZnO-MAS catalysts were measured via a BSD-PM series fully automatic specific surface and micropore analyzer.

**Catalytic Pyrolysis**

Fast pyrolysis of lignocellulosic biomass (rape straw, corn stalk, and camphorwood powder) was done in a horizontal tube furnace. The pyrolysis temperature was 400, 450, 500, 550, and 600 °C. The experiment consisted of a blank control, catalytic pyrolysis using ZnO, catalytic pyrolysis using MAS, and catalytic pyrolysis using MAS-ZnO. The mass ratio of biomass to catalyst was 1 to 1. Three replicate experiments were conducted for each group and the average was taken.
Prior to each pyrolysis, the reaction material was loaded into a quartz boat, the quartz boat was placed in the pending pyrolysis zone of the reactor, and air was removed for a period of time using nitrogen gas at a flow rate of 100 mL/min. As the reactor temperature reached the desired value (400 to 600 °C), the quartz boat containing the sample was pushed into the pyrolysis zone for 10 min. The bio-oil, biochar, and non-condensable biogas yields were calculated according to Eqs. 1 through 3, respectively,

\[ Y_{oil} = \frac{\text{Mass}_1 - \text{Mass}_2}{\text{Mass}} \]  
\[ Y_{char} = \frac{\text{Mass}_3 - \text{Mass}_4}{\text{Mass}} \]  
\[ Y_{gas} = 100\% - Y_{oil} - Y_{char} \]

where \( Y_{oil} \), \( Y_{char} \), and \( Y_{gas} \) represent the bio-oil, biochar, and non-condensable gas yield, respectively; \( \text{Mass} \) is the mass of the biomass before the reaction; \( \text{Mass}_1 \) is the mass of the cold trap after the reaction; \( \text{Mass}_2 \) is the mass of the cold trap before the reaction; \( \text{Mass}_3 \) is the mass of the quartz boat after the reaction; and \( \text{Mass}_4 \) is the mass of the quartz boat before the reaction.

The composition of the bio-oil was analyzed via the GC–MS system (Agilent, 6890–5973 N) equipped with a DB-1701 capillary column (60 m x 0.25 mm x 0.25 mm). The temperatures of the injector and Aux were set at 280 and 250 °C, respectively. The GC oven was heated from a temperature of 40 to 240 °C with a ramp of 5 °C/min, and then held at a temperature of 240 °C for 5 min. Split injection was performed at a split ratio of 60 to 1 using Helium (99.999 %) with a constant flow rate of 1 mL/min as the carrier-gas. The MS analysis was performed in EI mode with an ionization energy of 70 eV and a scanning range of \((m/z)\) 12 amu to 550 amu. The detailed chemical information corresponded to the chromatographic peaks were identified based on the NIST-MS 2.0 Library. The selectivity of the compounds were calculated via the peak area of the chromatographs.

**RESULTS AND DISCUSSION**

**Catalyst Characterization**

**X-ray fluorescence (XRF) spectroscopy**

Table 3 shows the XRF table of the MAS and ZnO-MAS catalysts. Since the vast majority of the metallic elements in MAS existed as oxide structures, the percentages of the elemental components detected by the XRF were converted to percentages of metal oxide components. It can be seen that the obtained magnesium aluminate spinel was primarily composed of MgO and Al₂O₃, and their component ratio was 23.4 to 74.1. The MAS samples also contained traces of other metal oxides, which were neglected over the course of the experiments due to their small content, i.e., less than 3% in total, and their expected negligible effect on biomass catalysis. After the ZnO impregnation loading MAS treatment, ZnO-MAS changed in the elemental components, and the ZnO content was considerably enhanced, which indicated a good impregnation loading effect.

**Scanning electron microscopy (SEM)**

Figure 1 shows the SEM images obtained for the MAS and ZnO-MAS samples at 5000x, 10000x, and 100000x magnification. It was observed in the MAS 5000x image that
the macroscopic magnesium aluminate spinel was formed in block form. In the MAS 100000x image, the electrofused magnesium aluminate spinel became a rod-like structure and interlocked and aggregated (a block-like structure, which was more stable).

**Table 3. Chemical Composition of Magnesium Aluminum Spinel (MAS) and ZnO-loaded Magnesium Aluminum Spinel (ZnO-MAS) (X-ray Fluorescence)**

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Content (%)</th>
<th>Element Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.401</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>23.4</td>
<td>12.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>74.1</td>
<td>32.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.516</td>
<td>0.321</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.0712</td>
<td>0.0309</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.0874</td>
<td>0.223</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0783</td>
<td>0.45</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.0617</td>
<td>0.0642</td>
</tr>
<tr>
<td>CaO</td>
<td>0.751</td>
<td>0.346</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.0385</td>
<td>0.0264</td>
</tr>
<tr>
<td>MnO</td>
<td>0.0213</td>
<td>0.0409</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.36</td>
<td>0.0204</td>
</tr>
<tr>
<td>NiO</td>
<td>0.0056</td>
<td>0.0093</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.0069</td>
<td>53.2</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>0.0121</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.0020</td>
<td>-</td>
</tr>
<tr>
<td>BaO</td>
<td>0.0212</td>
<td>-</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>0.0346</td>
</tr>
</tbody>
</table>
In the ZnO-MAS 100000x image, there were many fluffy substances on the surface of the spinel particles after loading the ZnO, and the small rod-like crystals of MAS were completely wrapped by ZnO. The effect of the MAS loaded with ZnO was obvious, which corresponded to the XRF results.

**Brunauer–Emmett–Teller (BET) analysis**

Table 4 shows the BET data of the magnesium aluminate spinel and magnesium aluminate spinel catalysts loaded with ZnO. It can be speculated that as the MAS was loaded with ZnO, the specific surface area decreased, while the pore size and pore volume increased. This may be due to the fact that the ZnO covered the surface of the MAS and plugged the smaller mesopores (Oseke et al. 2020; Jin et al. 2022). Miskolczi et al. (2017) demonstrated that the BET area of the catalyst decreases as the loaded metal content increases and that the plugging of the smaller pore size of the catalyst reflects good metal loading. The BET results were consistent with the results obtained from the XRF and SEM analysis, as show above.

**Table 4. Brunauer–Emmett–Teller (BET) Data for the Magnesium Aluminum Spinel (MAS) and ZnO-loaded Magnesium Aluminum Spinel (ZnO-MAS) Catalysts**

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS</td>
<td>10.2761</td>
<td>0.031245</td>
<td>12.3214</td>
</tr>
<tr>
<td>ZnO-MAS</td>
<td>7.6609</td>
<td>0.049634</td>
<td>22.3704</td>
</tr>
</tbody>
</table>

Bio-oil, bio-char, and bio-gas yields

The bio-oil, biochar, and non-condensable biogas yields from the pyrolysis, with rape straw, corn stalk, and camphorwood powder as the biomass feedstock, either without a catalyst or using ZnO, MAS, and ZnO-MAS as catalysts, are shown in Fig. 2.

Yields of pyrolysis products in blank

The bio-oil yields of the materials, i.e., rape straw, corn stalk, and camphorwood powder, firstly increased and then decreased as the pyrolysis temperature increased. The bio-oil yield of camphorwood powder was lower than the bio-oil yield of rape straw and corn stalk as the pyrolysis temperature decreased to 450 °C. The reason for the phenomenon was that the thermal stability of the lignins was high at a low temperature and the lignin content in camphorwood powder was high (Jiang et al. 2010). Therefore, the bio-oil yield of camphorwood powder was low. A high temperature could improve the thermal cracking of lignins. Therefore, the bio-oil yield of camphorwood powder reached 51.8% at a temperature of 500 °C. The bio-char yields of rape straw, corn stalk, and camphorwood powder decreased as the pyrolysis temperature increased. This is due to the large influence of the pyrolysis temperature on the coke yield (Demirbas 2004). The bio-char yield exhibited the following trend: rape straw was less than camphorwood powder, which was less than corn stalk. This was because lignins hinder the polymerization of levoglucan by cellulose, thus reducing biochar formation, while the cellulose-hemicellulose interactions had less effect on biochar formation and distribution (Kan et al. 2016). The bio-gas yields of rape straw, corn stalk, and camphorwood powder increased as the pyrolysis temperature was increased.
Yields of pyrolysis products in ZnO-catalytic pyrolysis

At a temperature of 400 to 550 °C, the bio-oil yields of the catalytic pyrolysis of rape straw, corn stalk, and camphorwood powder biomass decreased compared to the bio-oil yields from non-catalytic pyrolysis. The reason for this phenomenon was that the lignin in the biomass was not completely pyrolyzed at a low pyrolysis temperature, and the ZnO catalyst changed the pyrolysis reaction pathway of the lignins (Nokkosmaki et al. 2000). The pyrolysis temperature dominated over affecting the bio-oil yield compared to the catalyst. At a temperature of 400 °C, the bio-char yield from camphorwood powder reached the highest in the three materials (79.4 wt.%). This is because zinc oxide impedes the action of lignins on cellulose and alters the cleavage of cellulose and hemicellulose, resulting in elevated biochar yields (Wang et al. 2022). The bio-gas yields of rape straw and corn stalk increased during catalytic-pyrolysis compared to the bio-gas yields of the blank. The highest bio-gas yield was from rape straw at a temperature of 450 °C (38.4 wt.%). This was because the ZnO could improve the cracking of cellulose and hemicellulose into small molecule gas. This is consistent with the findings of Pütün (2010) and Zhou et al. (2013), i.e., that ZnO can reduce bio-oil oil yields while increasing gas and coke yields.

Yields of pyrolysis products in magnesium aluminum spinel (MAS)-catalytic pyrolysis

A comparison to the blank showed that the MAS catalyst made the high bio-oil yield shift to a low pyrolysis temperature. At a temperature of 400 to 550 °C, the bio-oil yields were lower in the MAS-catalytic pyrolysis than the bio-oil yields of the blank. When pyrolysis temperature increased to 500 °C, the bio-oil yield of camphor wood powder reached 52.9%. Therefore, the use of MAS catalysts had a catalytic effect on the bio-oil yield. A comparison to the blank showed that the bio-char decreased from the MAS-catalytic pyrolysis of the three materials, i.e., rape straw, corn stalk, and camphorwood powder. The bio-gas yield increased in the MAS-catalytic pyrolysis of the three materials, i.e., rape straw, corn stalk, and camphorwood powder, compared to the bio-gas yield in blank. The reason for this phenomenon was that the MAS catalyst could improve the conversion of the macromolecules in the biomass into aldehydes and ketones (Wang et al. 2017, 2022).

Yields of pyrolysis products in ZnO-loaded magnesium aluminum spinel (ZnO-MAS)-catalytic pyrolysis

As can be seen from Fig. 2, the ZnO-MAS catalyst can make the maximum bio-oil yield of biomass pyrolysis move to lower temperatures. This may be because of the catalytic effect of the element Mg. The element Mg combined with oxygen-containing functional groups to promote the decomposition of biomass at low temperatures by relatively weakening the bonds within the molecule. Hwang et al. (2015) also noted that magnesium considerably affects the decomposition of hemicellulose and the initial decomposition of cellulose, which in turn shifts the decomposition temperature range of biomass to a lower temperature. It can also be seen from Fig. 2 that the biochar yield obtained from rape straw and camphor wood powder under the catalytic effect of ZnO-MAS gradually decreased as the pyrolysis temperature increased. This may be due to the fact that Al₂O₃ and ZnO promote the process of devolatilization, which reduces the biochar yield, which is the same as the findings of Chen et al. (2019).
Effects of Different Catalysts on the Distribution of Ketones

Fig. 3. Ketones yields of the three feedstocks under different catalytic conditions

Fig. 4. Ketones species from different catalysts when the ketone yield was highest
As shown in Fig. 3, in the absence of a catalyst, cellulose, hemicellulose, and lignins can be pyrolyzed to produce ketones. Therefore, the ketones yield was relatively high. The relative content of the ketones was highest in the rape straw pyrolysis bio-oil throughout the experimental temperature interval; the minimum value of 20.1% at a temperature of 400 °C with rape straw was still close to the maximum value of the relative ketone content in the bio-oil from corn stalk and camphor wood pyrolysis. It can be seen that cellulose and hemicellulose were the primary causes of ketone production in bio-oil. Shao et al. (2021b) concluded that since bagasse contained more cellulose and hemicellulose in the same mass of biomass, it had the highest ketones yield in its pyrolysis products. The relative ketone content in the bio-oil obtained from rape straw and corn stalk reached respective maxima of 27.9% and 20.3% at a temperature of 550 °C. At a pyrolysis temperature of 600 °C, the relative ketone content in the pyrolyzed bio-oil from camphorwood powder reached a maximum value of 19.4%. It can be seen that the suitable pyrolysis temperature for ketones in biomass pyrolysis bio-oil is in the range of 550 °C to 600 °C.

As shown in Figs. 3 and 4, the addition of ZnO alone reduced the conversion of ketones from biomass. In the process of biomass pyrolysis, the addition of a ZnO catalyst may promote the depolymerization of cellulose and hemicellulose, which leads to a series of chemical changes, including the ring opening, bond breaking, and polymerization of levoglucan, reducing the ketones yield. When using MAS as the catalyst, at a pyrolysis temperature of 500 °C, the highest relative ketone content in bio-oil obtained from the catalytic pyrolysis of rape straw and corn stover was reached (19.2% and 13.4%, respectively). This may be because the Mg²⁺ in the MAS promoted the conversion of biomass pyrolysis products to ketones. During the ketonization reaction, the presence of magnesium promoted the conversion of small molecules, including alcohols and aldehydes, to carboxylic acids, which underwent ketonization reactions in the presence of a catalyst and were converted to the desired ketones (Gaertner et al. 2009; Wang et al. 2017). Therefore, the addition of magnesium promoted the production of specific ketones (Shimada et al. 2008). When catalytic pyrolysis was performed using ZnO-MAS, the ketone content was lower than without the catalyst. This indicated that ZnO-MAS had an inhibitory effect on the preparation of ketones. However, ZnO-MAS, as a catalyst, acted as a selector for the pyrolysis products of the three types of biomass, and the ketone species were substantially reduced. This may be due to the collective catalytic effect of Zn²⁺, Mg²⁺, and Al³⁺, which generate different intermediates and then specific substances in the presence of catalysts (Wang et al. 2022).

**Methylcyclopentenone (MCP) and Pyridone Yields**

As shown in Fig. 5, the MCP content in ketones was not high under catalyst-free conditions. The relative MCP content in the bio-oil obtained from rape straw was the highest among the three experimental feedstocks at different pyrolysis temperatures, with a highest relative content of 1.15% at a temperature of 550 °C. This may be because MCP was primarily produced from cellulose and hemicellulose. Shao et al. (2018) indicated that the primary products of lignin pyrolysis are phenolics.
The lignin content of camphor wood was the highest, so its products contained the least MCP. The relative pyridone content contained in the pyrolyzed bio-oil of all three experimental materials was low (less than 1%), and the relative pyridone content in rape straw and corn stalk were similar, while the relative pyridone content in the bio-oil of camphor wood was the lowest. In addition, the pyridone content did not considerably change as the pyrolysis temperature increased, which indicated that the amount of pyridones produced from cellulose and hemicellulose was more than the amount produced from lignin pyrolysis. Furthermore, pyridones are formed at lower pyrolysis temperatures and have a more stable structure.

In the catalytic action of zinc oxide, the relative MCP and pyridone contents in rape straw and corn stalk catalyzed pyrolysis bio-oil did not considerably change, while the relative MCP content in camphor wood catalyzed pyrolysis bio-oil increased and then decreased, reaching a maximum value of 3.59% at a temperature of 550 °C. The relative pyridone content in the catalytic pyrolysis of bio-oil with camphor powder was also greatly enhanced, and the highest relative content reached was 4.08% at a temperature of 550 °C. The catalytic effect of ZnO catalyst on camphor wood was more obvious compared to when no catalyst was used. This may be because the introduction of ZnO promoted the decomposition of lignins into small molecules, which facilitates the ketonization reaction of lignin to produce specific products (Zhou et al. 2013). Among the ketone pyrolysis products of camphor wood, MCP and pyridone were substantially reduced at a temperature of 600 °C, because the catalytic activity of zinc oxide is influenced by temperature. The changes in MCP and pyridone produced by the MAS-catalyzed pyrolysis of the three

Fig. 5. Relative MCP and pyridine content under different catalyst conditions
biomasses were not considerable. This indicated that the effect of MAS catalyzed alone on the targeted conversion of cellulose and hemicellulose was limited. However, the maximum increase in the relative pyridone content in the camphor-catalyzed pyrolysis bio-oil was 2.86% at lower pyrolysis temperatures. This was a 16-fold increase compared to the absence of a catalyst, which may be due to the considerable catalytic effect of MgO and Al₂O₃ on lignins. The optimum ketonization reaction temperature of camphor wood powder in the presence of MAS was 400 °C, compared to the optimum catalytic temperature of zinc oxide.

Under ZnO-MAS catalysis, the relative MCP content in the bio-oils obtained from the tested biomasses all continuously increased as the pyrolysis temperature increased, reaching maximum values of 7.44%, 4.51%, and 5.29% at a temperature of 600 °C, respectively. The catalytic effect of ZnO-MAS was considerable compared to the blank control, ZnO-catalyzed, and MAS-catalyzed groups. This may be due to the fact that ZnO, MgO, and Al₂O₃ are in a collaborative and competitive relationship with each other and contribute majorly to the production of specific ketones. Among them, the relative MCP content in rape straw catalytic pyrolysis bio-oil was the highest compared to corn stalk and camphorwood powder at different pyrolysis temperatures. This may be because rape straw catalyzed by ZnO-MAS first becomes intermediate products that can be converted into ketones, including acetic acid and acetaldehyde, and then undergoes a carbonylation reaction to produce MCP (Snell and Shanks 2013; Ding et al. 2021). It was interesting to note that the catalysis of ZnO-MAS resulted in a substantial increase in the pyridone yield from corn straw and rice husk compared to that catalyzed by ZnO and MAS alone, but not particularly for camphor powder. The possible reason for this is that ZnO-MAS has a large number of acidic and basic active sites (Orozco et al. 2017; Almutairi et al. 2018).

In general, ZnO-MAS catalyzed the generation of MCP and pyridone from corn straw, rape straw, and camphor wood flour very effectively. It is speculated that the mechanism of the pyrolysis reaction may be that ZnO-MAS catalyzed the dehydration, decomposition, ring opening, and isomerization of cellulose and hemicellulose into short-chain reactive intermediates, followed by C-O-C bond, C-C bond cleavage, and C=C bond and C=O bond formation to generate MCP and pyridone (Abella et al. 2007; Tao et al. 2013; Ding et al. 2021).

CONCLUSIONS

1. This work confirms that ZnO-MAS can be a possible method to enhance the yield of MCP and pyridone during the rapid pyrolysis of biomass. The relative MCP content produced by ZnO-MAS-catalyzed rape straw reached the highest value of 7.44% at a temperature of 600 °C. The relative pyridone content produced by ZnO-MAS-catalyzed pyrolysis of corn stover at a temperature of 400 °C reached 12.4%.

2. It was also found that the pyrolysis of cellulose and hemicellulose produced more pyridone than lignins. The separate catalysis by ZnO and MAS promoted the decomposition of lignins to small molecules, thus facilitating the ketonization reaction of the lignins. Overall, ZnO-MAS catalyzed the generation of MCP and pyridone from corn stover, rape straw, and camphor wood flour with remarkable effect.
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