

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.

DOI: 10.15376/biores.17.3.4656-4672

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

Contact information: School of Agricultural Engineering and Food Science, Shandong University of Technology, Zibo 255000 China; *Corresponding author: dongmei070719@163.com

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 H₂O₂ alkaline conditions and hydrolysis with acid. In addition, Sacia *et al.* (2015) proposed the hydrolysis of 2,5-dimethylfuran to produce 2,5-hexanedione followed 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-hexanedione (HHD) in water over a Pd/Nb₂O₅ 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 jovis* 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 MgAl₂O₄, 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

Samples	Elemental Analysis (%)						Proximate Analysis (%)		
	C	H	O	N	C/H	C/O	Fixed Carbon	Volatiles	Ash
Rape straw	48.52 ±1.5	5.74 ± 0.3	45.23	0.51 ± 0.02	8.4 5	1.07	15.27 ± 0.45	79.18 ± 3.1	5.55 ± 0.91
Corn stalk	47.41 ± 1.2	5.78 ± 0.3	46.37	0.44 ± 0.01	8.2 1	1.02	12.26 ± 1.1	80.59 ± 2.5	7.15 ± 0.85
Camphorwood powder	53.16 ± 1.6	6.12 ± 0.4	40.34	0.38 ± 0.01	8.6 9	1.32	13.35 ± 1.5	86.14 ± 1.8	0.51 ± 0.15

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

Samples	Rape Straw (%)	Corn Stalk (%)	Camphorwood Powder (%)
Cellulose	35.41 ± 1.00	32.54 ± 0.50	37.62 ± 0.35
Hemicellulose	17.84 ± 0.50	18.34 ± 0.40	12.65 ± 0.40
Lignin	21.64 ± 0.60	22.02 ± 0.60	34.74 ± 0.50

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,

$$Y_{oil} = \frac{Mass_1 - Mass_2}{Mass} \quad (1)$$

$$Y_{char} = \frac{Mass_3 - Mass_4}{Mass} \quad (2)$$

$$Y_{gas} = 100\% - Y_{oil} - Y_{char} \quad (3)$$

where Y_{oil} , Y_{char} , and Y_{gas} represent the bio-oil, biochar, and non-condensable gas yield, respectively; $Mass$ is the mass of the biomass before the reaction; $Mass_1$ is the mass of the cold trap after the reaction; $Mass_2$ is the mass of the cold trap before the reaction; $Mass_3$ is the mass of the quartz boat after the reaction; and $Mass_4$ 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)

Chemical Composition	Content (%)		Element Spectrum
	MAS	ZnO-MAS	
Na ₂ O	0.401	-	Na-KA
MgO	23.4	12.2	Mg-KA
Al ₂ O ₃	74.1	32.8	Al-KA
SiO ₂	0.516	0.321	Si-KA
P ₂ O ₅	0.0712	0.0309	P-KA
SO ₃	0.0874	0.223	S-KA
Cl	0.0783	0.45	Cl-KA
K ₂ O	0.0617	0.0642	K-KA
CaO	0.751	0.346	Ca-KA
Cr ₂ O ₃	0.0385	0.0264	Cr-KA
MnO	0.0213	0.0409	Mn-KA
Fe ₂ O ₃	0.36	0.0204	Fe-KA
NiO	0.0056	0.0093	Ni-KA
ZnO	0.0069	53.2	Zn-KA
Ga ₂ O ₃	0.0121	-	Ga-KA
ZrO ₂	0.0020	-	Zr-KA
BaO	0.0212	-	Ba-KA
PbO	-	0.0346	Pb-KA

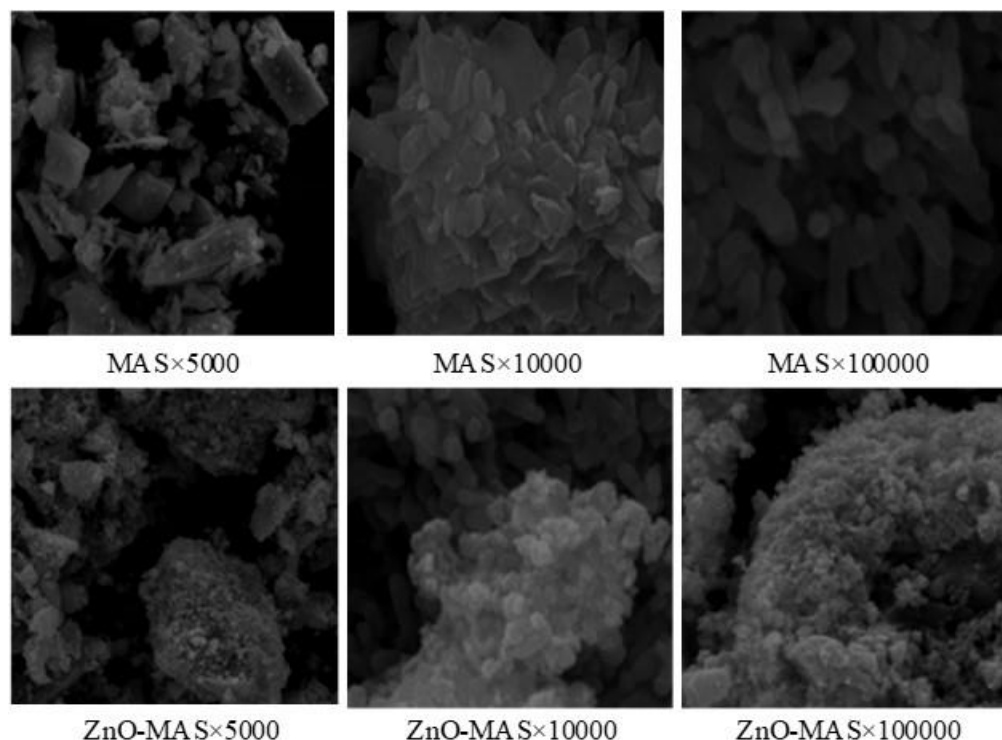


Fig. 1. Micrographs of the ZnO-MAS catalyst

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

Samples	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
MAS	10.2761	0.031245	12.3214
ZnO-MAS	7.6609	0.049634	22.3704

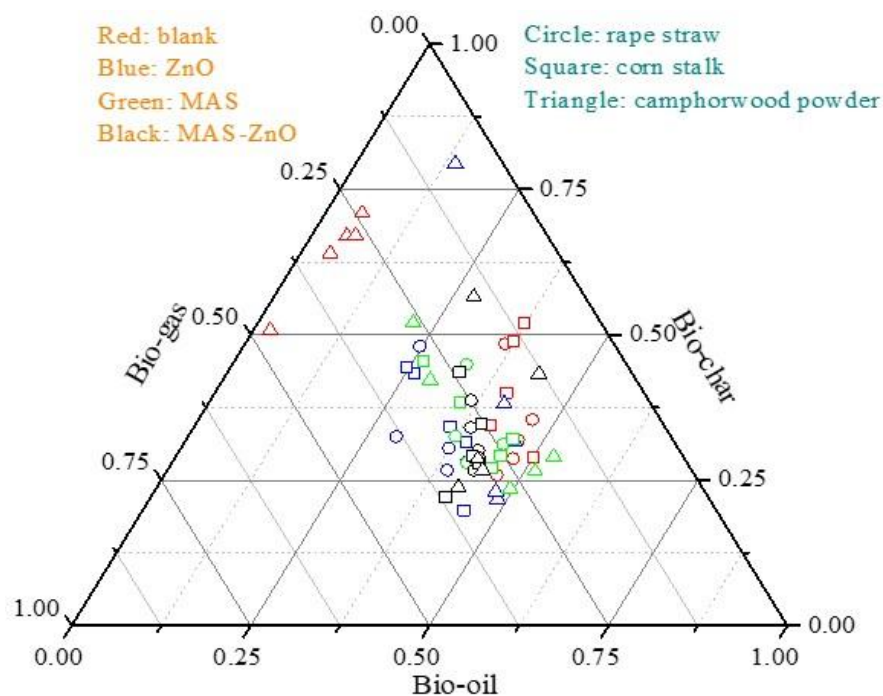


Fig. 2. Bio-oil, bio-char, and non-condensable biogas yields

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 450 °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

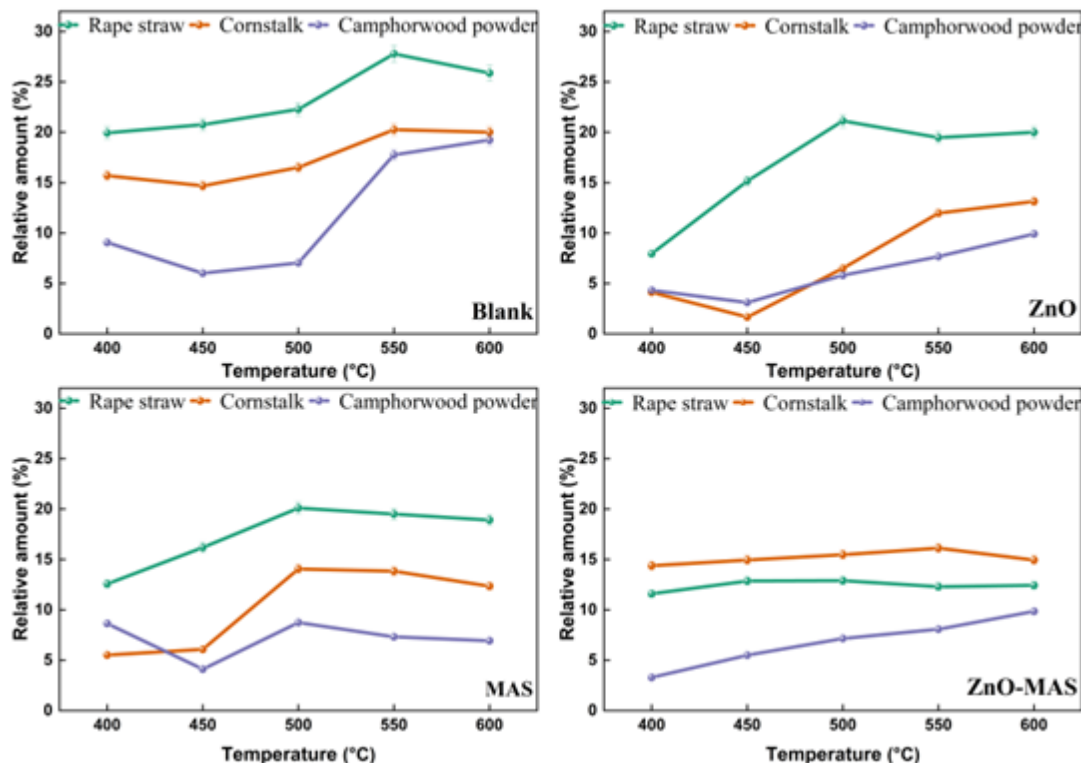


Fig. 3. Ketones yields of the three feedstocks under different catalytic conditions

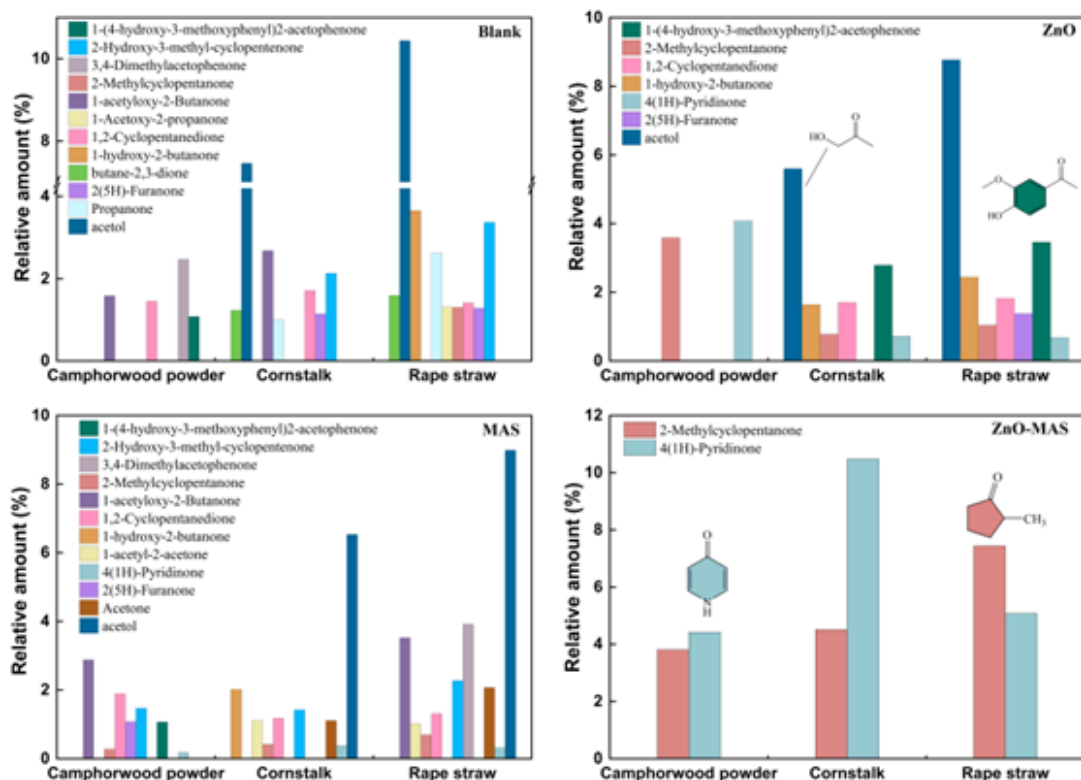


Fig. 4. Ketones species from different catalysts when the ketone yield was highest

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 Mg^{2+} 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 Zn^{2+} , Mg^{2+} , and Al^{3+} , 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.

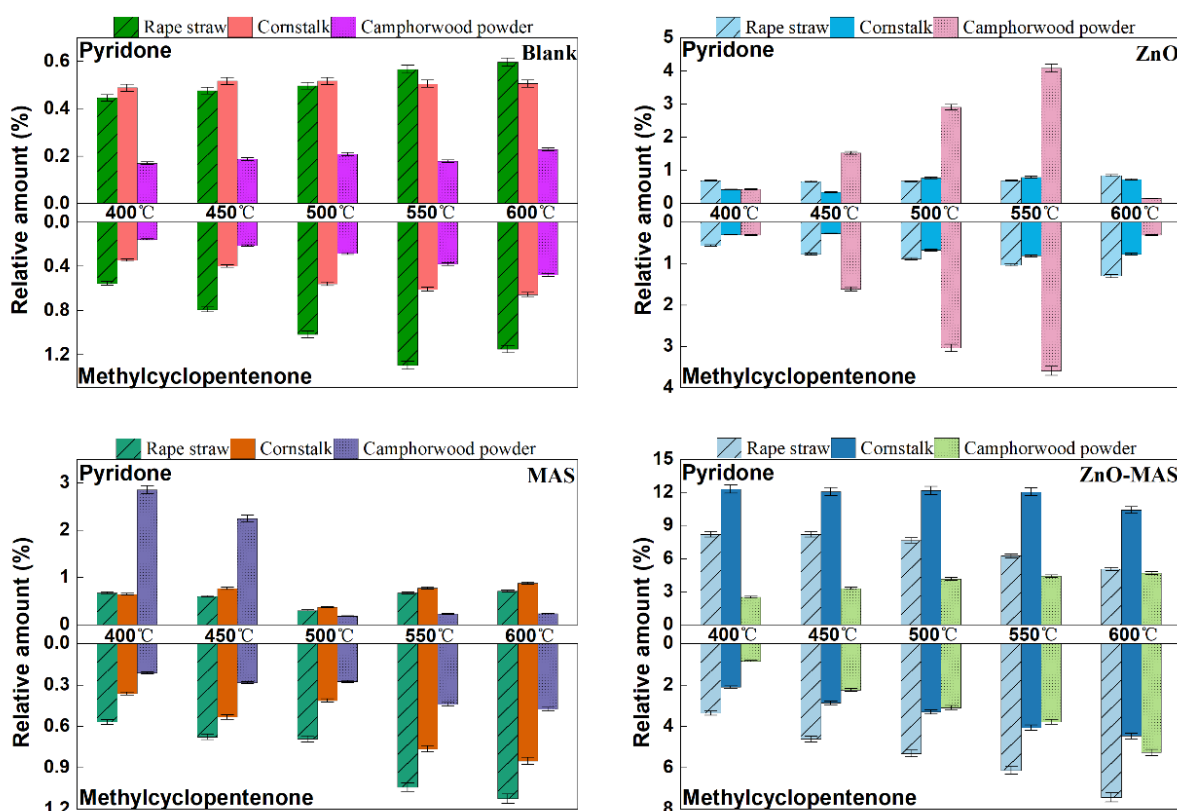


Fig. 5. Relative MCP and pyridine content under different catalyst conditions

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

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.

ACKNOWLEDGEMENTS

The research was sponsored by the National Natural Science Foundation of China (Grant No. 52176193), the Shandong Provincial Natural Science Foundation, China (Grant No. ZR2020ME184), the National Key Research and Development Program of China (Grant No. 2019YFD1100602), and the SDUT & Zhoucun City Integration Development Project (Grant No. 2020ZCXCZH09).

REFERENCES CITED

- Abella, L., Nanbu, S., and Fukuda, K. (2007). "A theoretical study on levoglucosan pyrolysis reactions yielding aldehydes and a ketone in biomass," *Memoirs of Faculty of Engineering, Kyushu University* 67(2), 68-69.
- Alam, M. A., Muhammad, G., Khan, M. N., Mofijur, M., Lv, Y., Xiong, W., and Xu, J. (2021). "Choline chloride-based deep eutectic solvents as green extractants for the isolation of phenolic compounds from biomass," *Journal of Cleaner Production* 309, 1-13. DOI: 10.1016/j.jclepro.2021.127445
- Almutairi, S. T., Kozhevnikova, E. F., and Kozhevnikov, I. V. (2018). "Ketonisation of acetic acid on metal oxides: Catalyst activity, stability and mechanistic insights," *Applied Catalysis A: General* 565, 135-145. DOI: 10.1016/j.apcata.2018.08.008
- Bulushev, D. A., and Ross, J. R. H. (2011). "Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review," *Catalysis Today* 171(1), 1-13. DOI: 10.1016/j.cattod.2011.02.005
- Chen, X., Chen, Y., Yang, H., Wang, X., Che, Q., Chen, W., and Chen, H. (2019). "Catalytic fast pyrolysis of biomass: Selective deoxygenation to balance the quality and yield of bio-oil," *Bioresource Technology* 273, 153-158. DOI: 10.1016/j.biortech.2018.11.008
- Cheng, S., Shu, J., Xia, H., Wang, S., Zhang, L., Peng, J., Li, C., Jiang, X., and Zhang, Q. (2019). "Pyrolysis of Crofton weed for the production of aldehyde rich bio-oil and combustible matter rich bio-gas," *Applied Thermal Engineering* 148, 1164-1170. DOI: 10.1016/j.applthermaleng.2018.12.009
- Demirbas, A. (2004). "Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues," *Journal of Analytical and Applied Pyrolysis* 72(2), 243-248. DOI: 10.1016/j.jaap.2004.07.003
- Ding, K., Zhou, H., Wan, Y., Huang, Y., Zhang, Y., Hu, X., Zhang, H., and Zhang, S. (2021). "Ketonization of xylose over CeO₂ to produce mono-functional ketones," *Fuel Processing Technology* 211, 1-6. DOI: 10.1016/j.fuproc.2020.106585
- Duan, Y., Zheng, M., Li, D., Deng, D., Ma, L.-F., and Yang, Y. (2017). "Conversion of HMF to methyl cyclopentenolone using Pd/Nb₂O₅ and Ca–Al catalysts via a two-step procedure," *Green Chemistry* 19(21), 5103-5113. DOI: 10.1039/C7GC02310C
- Eibner, S., Broust, F., Blin, J., and Julbe, A. (2015). "Catalytic effect of metal nitrate salts during pyrolysis of impregnated biomass," *Journal of Analytical and Applied Pyrolysis* 113, 143-152. DOI: 10.1016/j.jaap.2014.11.024
- Felipe, M. P. (2018). *Design, Synthesis and Biological Evaluation of Novel 4 (1H)-Pyridones as Antimalarial Inhibitors of Plasmodium falciparum Cytochrome bc1*, Ph.D. Dissertation, Autonomous University of Madrid, Madrid, Spain.
- Gaertner, C. A., Serrano-Ruiz, J. C., Braden, D. J., and Dumesic, J. A. (2009). "Catalytic

- coupling of carboxylic acids by ketonization as a processing step in biomass conversion,” *Journal of Catalysis* 266(1), 71-78. DOI: 10.1016/j.jcat.2009.05.015
- Horne, P. A., and Williams, P. T. (1996). “Influence of temperature on the products from the flash pyrolysis of biomass,” *Fuel* 75(9), 1051-1059. DOI: 10.1016/0016-2361(96)00081-6
- Houshmandyar, S., Eggleston, I. M., and Bolhuis, A. (2021). “Biofilm-specific uptake of a 4-pyridone-based iron chelator by *Pseudomonas aeruginosa*,” *BioMetals* 34(2), 315-328. DOI: 10.1007/s10534-020-00281-x
- Hussain, Z., Khan, K. M., Khan, A., Ullah, S., Karim, A., and Perveen, S. (2013). “The conversion of biomass into liquid hydrocarbon fuel by two step pyrolysis using cement as catalyst,” *Journal of Analytical and Applied Pyrolysis* 101, 90-95. DOI: 10.1016/j.jaap.2013.02.007
- Hwang, H., Oh, S., Choi, I.-G., and Choi, J.W. (2015). “Catalytic effects of magnesium on the characteristics of fast pyrolysis products – Bio-oil, bio-char, and non-condensed pyrolytic gas fractions,” *Journal of Analytical and Applied Pyrolysis* 113, 27-34. DOI: 10.1016/j.jaap.2014.09.028
- Jiang, G., Nowakowski, D. J., and Bridgwater, A. V. (2010). “Effect of the temperature on the composition of lignin pyrolysis products,” *Energy & Fuels* 24(8), 4470-4475. DOI: 10.1021/ef100363c
- Jin, T., Wang, H., Peng, J., Wu, Y., Huang, Z., Tian, X., and Ding, M. (2022). “Catalytic pyrolysis of lignin with metal-modified HZSM-5 as catalysts for monocyclic aromatic hydrocarbons production,” *Fuel Processing Technology* 230, 107201 . DOI: 10.1016/j.fuproc.2022.107201
- Kan, T., Strezov, V., and Evans, T. J. (2016). “Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters,” *Renewable and Sustainable Energy Reviews* 57, 1126-1140. DOI: 10.1016/j.rser.2015.12.185
- Koondhar, M. A., Tan, Z., Alam, G. M., Khan, Z. A., Wang, L., and Kong, R. (2021). “Bioenergy consumption, carbon emissions, and agricultural bioeconomic growth: A systematic approach to carbon neutrality in China,” *Journal of Environmental Management* 296, 113242. DOI: 10.1016/j.jenvman.2021.113242
- Langin-Lanteri, M. T., and Huet, J. (1976). “Rearrangement of cyclic α , β -epoxyketones in aqueous acid,” *Synthesis* 1976(8), 541-543. DOI: 10.1055/s-1976-24116
- Lu, Q., Zhang, Z.-F., Dong, C.-Q., and Zhu, X.-F. (2010). “Catalytic upgrading of biomass fast pyrolysis vapors with nano metal oxides: An analytical Py-GC/MS study,” *Energies* 3(11), 1805-1820. DOI: 10.3390/en3111805
- Miskolczi, N., Juzsakova, T., and Sója, J. (2017). “Preparation and application of metal loaded ZSM-5 and γ -zeolite catalysts for thermo-catalytic pyrolysis of real end of life vehicle plastics waste,” *Journal of the Energy Institute* 92(1), 118-127. DOI: 10.1016/j.joei.2017.10.017
- Mourant, D., Lievens, C., Gunawan, R., Wang, Y., Hu, X., Wu, L., Syed-Hassan, S. S. A., and Li, C.-Z. (2013). “Effects of temperature on the yields and properties of bio-oil from the fast pyrolysis of mallee bark,” *Fuel* 108, 400-408. DOI: 10.1016/j.fuel.2012.12.018
- Nian, V. (2016). “The carbon neutrality of electricity generation from woody biomass and coal, a critical comparative evaluation,” *Applied Energy* 179, 1069-1080. DOI: 10.1016/j.apenergy.2016.07.004
- Nokkosmäki, M. I., Kuoppala, E. T., Leppämäki, E. A., and Krause, A. O. I. (2000). “Catalytic conversion of biomass pyrolysis vapours with zinc oxide,” *J. Analytical*

- and *Applied Pyrolysis* 55(1), 119-131. DOI: 10.1016/S0165-2370(99)00071-6
- Orozco, L. M., Renz, M., and Corma, A. (2017). "Cerium oxide as a catalyst for the ketonization of aldehydes: Mechanistic insights and a convenient way to alkanes without the consumption of external hydrogen," *Green Chemistry* 19(6), 1555-1569. DOI: 10.1039/C6GC03511F
- Oseke, G. G., Atta, A. Y., Mukhtar, B., Jibril, B. Y., and Aderemi, B. O. (2020). "Highly selective and stable Zn-Fe/ZSM-5 catalyst for aromatization of propane," *Applied Petrochemical Research* 10(2), 55-65. DOI: 10.1007/s13203-020-00245-9
- Öztürk, G., Erol, D. D., Uzbay, T., and Aytemir, M.D. (2001). "Synthesis of 4 (1H)-pyridinone derivatives and investigation of analgesic and antiinflammatory activities," *Il Farmaco* 56(4), 251-256. DOI: 10.1016/S0014-827X(01)01083-7
- Pütün, E. (2010). "Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst," *Energy* 35(7), 2761-2766. DOI: 10.1016/j.energy.2010.02.024
- Qiu, Y., Chen, J., and Zhang, J. (2007). "Effects of MgO promoter on properties of Ni/Al₂O₃ catalysts for partial oxidation of methane to syngas," *Frontiers of Chemical Engineering in China* 1(2), 167-171. DOI: 10.1007/s11705-007-0031-7
- Sacia, E. R., Deaner, M. H., Louie, Y. L., and Bell, A. T. (2015). "Synthesis of biomass-derived methylcyclopentane as a gasoline additive via aldol condensation/hydrodeoxygenation of 2, 5-hexanedione," *Green Chemistry* 17(4), 2393-2397. DOI: 10.1039/C4GC02292K
- Shao, S., Zhang, H., Xiao, R., Li, X., and Cai, Y. (2018). "Controlled regeneration of ZSM-5 catalysts in the combined oxygen and steam atmosphere used for catalytic pyrolysis of biomass-derivates," *Energy Conversion and Management* 155, 175-181. DOI: 10.1016/j.enconman.2017.10.062
- Shao, S., Hu, X., Dong, W., Li, X., Zhang, H., Xiao, R., and Cai, Y. (2021a). "Integrated C-C coupling/hydrogenation of ketones derived from biomass pyrolysis for aviation fuel over Ni/Mg-Al-O/AC bifunctional catalysts," *Journal of Cleaner Production* 282, 1-33. DOI: 10.1016/j.jclepro.2020.124331
- Shao, S., Liu, C., Xiang, X., Li, X., Zhang, H., Xiao, R., and Cai, Y. (2021b). "In situ catalytic fast pyrolysis over CeO₂ catalyst: Impact of biomass source, pyrolysis temperature and metal ion," *Renewable Energy* 177, 1372-1381. DOI: 10.1016/j.renene.2021.06.054
- Shimada, N., Kawamoto, H., and Saka, S. (2008). "Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis," *Journal of Analytical and Applied Pyrolysis* 81(1), 80-87. DOI: 10.1016/j.jaap.2007.09.005
- Snell, R. W., and Shanks, B. H. (2013). "Insights into the ceria-catalyzed ketonization reaction for biofuels applications," *ACS Catalysis* 3(4), 783-789. DOI: 10.1021/cs400003n
- Soest, P. J. V. (1963). "Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determination of fiber and lignin," *Journal of Association of Official Agricultural Chemists* 46(5), 829-835. DOI: 10.1093/jaoac/46.5.829
- Stojanović, M., Bugarski, S., and Baranac-Stojanović, M. (2020). "Synthesis of 2, 3-dihydro-4-pyridones and 4-pyridones by the cyclization reaction of ester-tethered enaminones," *J. Organic Chem.* 85(21), 13495-13507. DOI: 10.1021/acs.joc.0c01537
- Sun, H., Feng, D., Sun, S., Zhao, Y., Zhang, L., Chang, G., Guo, Q., Wu, J., and Qin, Y. (2021). "Thermal evolution of gas-liquid-solid products and migration regulation of C/H/O elements during biomass pyrolysis," *Journal of Analytical and Applied*

- Pyrolysis* 156, 1-10. DOI: 10.1016/j.jaap.2021.105128
- Tao, H., Xie, X., Tang, C., and Tian, W. (2013). "Mechanism of ketones formation from cellulose liquefaction in sub-and supercritical ethanol," *Journal of Fuel Chemistry and Technology* 41(1), 60-66. DOI: 10.1016/S1872-5813(13)60010-9
- Tian, J., Li, D., Zhai, F., Wang, X., and Li, R. (2010). "Synthesis and biological evaluation of cyclopenten-1-one Mannich base oxovanadium compound," *Medicinal Chemistry Research* 19(9), 1162-1173. DOI: 10.1007/s00044-009-9260-2
- Wang, J., Zhang, B., Zhong, Z., Ding, K., Deng, A., Min, M., Chen, P., and Ruan, R. (2017). "Catalytic fast co-pyrolysis of bamboo residual and waste lubricating oil over an ex-situ dual catalytic beds of MgO and HZSM-5: Analytical PY-GC/MS study," *Energy Conver. Management* 139, 222-231. DOI: 10.1016/j.enconman.2017.02.047
- Wang, W., Lemaire, R., Bensakhria, A., and Luart, D. (2022). "Review on the catalytic effects of alkali and alkaline earth metals (AAEMs) including sodium, potassium, calcium and magnesium on the pyrolysis of lignocellulosic biomass and on the co-pyrolysis of coal with biomass," *Journal of Analytical and Applied Pyrolysis* 163, 1-33. DOI: 10.1016/j.jaap.2022.105479
- Zahed, M. A., Movahed, E., Khodayari, A., Zanganeh, S., and Badamaki, M. (2021). "Biotechnology for carbon capture and fixation: Critical review and future directions," *Journal of Environmental Management* 293, article no. 112830. DOI: 10.1016/j.jenvman.2021.112830
- Zhou, L., Yang, H., Wu, H., Wang, M., and Cheng, D. (2013). "Catalytic pyrolysis of rice husk by mixing with zinc oxide: Characterization of bio-oil and its rheological behavior," *Fuel Processing Technology* 106, 385-391. DOI: 10.1016/j.fuproc.2012.09.003

Article submitted: April 12, 2022; Peer review completed: June 11, 2022; Revised version received and accepted: June 17, 2022; Published: June 21, 2022.
DOI: 10.15376/biores.17.3.4656-4672