Effects of Torrefaction Pretreatment and Mg-Al Modified HZSM-5 Catalysts on Components Distribution in Bio-Oils from Camphorwood Pyrolysis

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Torrefaction pretreatment conducted at a low temperature is an important technique for refining the bio-oil and improving the production of some chemicals in the bio-oil (*e.g.* aromatic hydrocarbons). In this work, the effects of torrefaction temperature and catalysts on the yields of pyrolysis products and components distribution in the bio-oils were analyzed. The weak acid sites shifted to higher temperature as the HZSM-5 was modified by Mg^{2+} or Al^{3+}. The catalytic pyrolysis from camphorwood was done at pyrolysis of 450 °C and torrefaction temperature of 200 °C. The catalysts remarkably influenced the yields of bio-oil and components distribution. The catalysts increased the production of phenols. The content of phenols in the resulting bio-oil exhibited the following trend: HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5. In addition, the content of 2,6-dimethoxyphenol was the highest among all phenol components (5.58%). The production of aldehydes was remarkably improved by the Al_2O_3-modified HZSM-5, resulting in a maximum content of 8.21%. Thus the torrefaction temperature and catalysts would refine the bio-oil (such as the acid value decreased) and significantly improve the contents of components (such as D-allose, 2,6-dimethoxy-4-(2-propeny)-phenol, 1,2,4-trimethoxybenzene, and 2,6-dimethoxyphenol). The results provide a theoretical basis for the resource recovery of biomass.

Keywords: Biomass; Torrefaction; Mg-Al modified; HZSM-5; Bio-oil

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INTRODUCTION

Since the industrial revolution, the production of chemicals has relied on fossil feedstock. However, for environmental protection, increasing attention has been placed on utilizing sustainable and abundant biomass for fuels and high-value chemicals. Biomass can be converted into a variety of chemicals by thermochemical technologies, and less secondary pollutants will be produced during this process (Sheldon 2014; Sharma *et al*. 2015; Kabir and Hameed 2017). By utilizing thermochemical technologies for the production of chemicals in an ideal manner, zero emission standards and energy security could both be achieved. With the ongoing energy crisis and accompanying environmental issues plaguing countries around the world, there has been an interest in using biomass to develop clean fuels and chemicals, because it is the only sustainable source of carbon to meet the energy, chemical, and material needs of society (Cai *et al*. 2014; Sommerhuber *et al*. 2015).

Catalytic pyrolysis is a process that efficiently utilizes resources to convert biomass into high-quality bio-oil, bio-gas, and bio-char under anaerobic or hypoxic conditions at a high temperature (Bender *et al*. 2018; Bi *et al*. 2019). The incorporation of catalysts could decrease the pyrolysis temperature and increase the production of target chemicals (Hassan *et al.* 2016; Kan *et al.* 2016; Yildiz *et al.* 2016). Therefore, high-efficiency catalysts could enhance selectivity of pyrolysis products and reduce energy consumption (Zhang *et al.* 2015; Schultz *et al.* 2017).

However, biomass contains a relatively high content of oxygen compared with fossil fuels (Masnadi *et al.* 2014), which leads to poor bio-oil traits, including a high-water content and high acidity (Prabu *et al.* 2017). Torrefaction pretreatment of biomass at low temperatures is effective in reducing the acidity and oxygen content of bio-oil and increasing the calorific value of bio-oil. Medic *et al.* (2012) torrefied corn straw on a fixed bed at 200 °C, 250 °C, and 300 °C. The O/C ratio decreased from 1.11 to 0.60, and the energy density increased by 19% as corn straw was torrefied (Medic *et al.* 2012). Chen *et al*. (2018) pyrolyzed rubber chips at torrefaction temperatures of 200 °C, 250 °C, and 300 °C. The content of oxygenated acids and aldehydes in bio-oil decreased, and the bio-oil yield decreased when the torrefaction temperature increased (Chen *et al.* 2018). Chen *et al*. (2015) pyrolyzed cotton stalks on a fixed bed at torrefaction temperatures of 220 °C, 250 °C, and 280 °C, respectively. The H/C ratio of pyrolysis production increased after cotton stalks were torrefied. The content of CH_4 and H_2 in the bio-gas noticeably increased (Chen *et al.* 2015). Above all, the yield of bio-oil decreased, the content of acid in the bio-oil decreased, and the content of phenols increased as the torrefaction temperature increased. Therefore, torrefaction affected the cracking process of the three biomass components (cellulose, hemicelluloses, and lignin) and the distribution of components in the bio-oil.

HZSM-5 zeolite has been incorporated in previous studies due to its numerous advantages, including its ability to decrease the oxygen and acidity of bio-oil, its ability to improve the stability and quality of bio-oil, and its selectivity towards cracking, isomerization, and aromatization reactions. HZSM-5 zeolite was used to pyrolyze *Pinus taeda* at 500 °C (Hilten *et al*. 2013). The content of organic acids and aldehydes in bio-oil noticeably decreased, while the content of L-glucose increased. Beech was pyrolyzed in a tandem microreactor at 400 °C, 500 °C, and 600 °C. The content of L-glucose, acetic acid, aldehydes, ketones, and phenols in bio-oil was higher than that in non-catalytic bio-oil. The content of oxygenated hydrocarbons and aromatic compounds increased with increasing addition of HZSM-5. Moreover, the aromatic compounds increased with the increase of HZSM-5 zeolite loading (Karagöz *et al.* 2016). HZSM-5 catalyzed the pyrolysis of pine, cellulose, and lignin. The formation of aromatic compounds was promoted, and the formation of coke was inhibited (Mullen and Boateng 2015; Xue *et al.* 2018).

Using MgO as the catalyst to pyrolyze cotton stalks on a fixed bed at 550 °C and the mass ratio of MgO to cotton stalks of 2:1, Zeng *et al.* (2018) showed that the yield of bio-char decreased from 48.21% to 22.05% when the torrefaction temperature was raised from 200 °C to 350 °C. Therefore, MgO could greatly reduce the yield of bio-char. The addition of Al^{3+} during the pyrolysis of wheat straw could promote the decarboxylation reaction of macromolecular organics, causing a reduction of oxygen content in the pyrolysis products (Pütün 2010; Navarro *et al.* 2018).

At present, research on the effects of torrefaction or catalysts have only analyzed impacts associated with the bio-oil yield and distribution of components in bio-oil (Zhang *et al.* 2013; Chagas *et al.* 2016; Du *et al.* 2016). In this paper, the effects of torrefaction and catalysts on biomass pyrolysis were investigated. MgO and Al_2O_3-modified HZSM-5 zeolites were introduced in the pyrolysis of torrefaction camphorwood. Subsequently, the yield of bio-oil, bio-gas, and bio-char along with the distribution of components in the bio-oil were all investigated. The results of this paper could provide basic data for the bio-oil upgrading, and the production of high-value chemicals using biomass.

EXPERIMENTAL

Materials

Camphorwood is an abundant resource harvested in the southern part of the world and China. Camphorwood is used as an urban street tree because its ability to absorb smoke, dust, and noxious gas. It is a commonly employed wood in the construction and furniture industry because of its hard texture and ability to repel insects. There is a lot of waste generated, including leaves, branches, roots, and sawdust, during the utilization of camphorwood. Therefore, camphorwood was employed as the pyrolysis material in this study. The diameter of particles was 40 to 60 mesh. The camphorwood was dried in a thermostatic air bio-power driven drying oven for 12 h at 105 °C.

Torrefaction of Camphorwood

Torrefaction removes free water and bound water from the biomass. This could lead to a reduction of moisture and oxygen content. After torrefaction, the content of water and volatiles in biomass decreases, and the content of fixed carbon increases (Wang *et al.* 2017). The content of H and O in camphorwood decreases, while the content of C increases with increased torrefaction temperature (Zheng *et al.* 2018). Torrefaction promotes the depolymerization of cellulose, hemicellulose, and lignin in biomass, which causes an increase of bio-oil yield and subsequent refinement of bio-oil (Zhang *et al.* 2018).

Torrefaction of camphorwood is conducted in a torrefaction box (Kejing, GSL-1700X-VT; Hefei Ke Jing Materials Technology Co., Ltd, Hefei, China). The heating rate was 10 °C/min, and the holding time was 30 min. The torrefaction temperature of camphorwood was 200 °C, 250 °C, or 300 °C. To avoid the burning of camphorwood, nitrogen was passed through the torrefaction box with a flow rate of 100 mL/min.

The industrial and elemental analyses of camphorwood are shown in Table 1. Volatile matter exhibited the highest content within camphorwood, followed by fixed carbon and moisture content. Almost no ash was detected. Therefore, most of the pyrolysis of camphorwood was gas, including condensable gas and non-condensable gas. The condensable gas was condensed into the bio-oil. The contents of C and O were high, but the contents of N and S were low. The main components of bio-oil obtained by pyrolysis of camphorwood were C, H, and O compounds. Moreover, the hydrogen content was low, the oxygen content was high, and the calorific value of bio-oil was low. Therefore, decreasing the oxygen content and increasing the hydrogen content were the key factors for improving the quality of bio-oil. The three biomass components were detected by two-step acid hydrolysis. The monosaccharides obtained from biomass hydrolysis were detected by high performance liquid chromatography (HPLC) with a refractive index detector (Waters 2698, New York, USA). The three biomass components of camphorwood are shown in Table 1. The elemental analysis results demonstrated that the content of C, H, and O were the main elements in camphorwood, with values amounting to 46.58 wt%, 5.07 wt%, and 46.93 wt%, respectively. The content of C increased with the increase of torrefaction temperature. The content of H peaked when the torrefaction temperature was 200 °C. The content of O decreased with the increase of torrefaction temperature. The volatiles content was the highest in camphorwood at torrefaction temperature of 200 °C. The camphorwood was enriched with fixed carbon as the torrefaction temperature increased. The content of cellulose decreased with the increase of torrefaction temperature. The content of hemicelluloses was the highest at a torrefaction temperature of 200 °C, and the lowest content was observed at a torrefaction temperature of 300 °C. The content of lignin increased with the increase of torrefaction temperature.

Table 1. Proximate and Elemental Analysis of Camphorwood

	Original Camphorwood	Torrefaction Temperature (°C)		
		200	250	300
Element (wt%)				
C_{ad}	46.58	51.24	55.41	60.67
H_{ad}	6.07	6.44	6.36	4.25
N_{ad}	0.36	0.65	0.65	0.73
O_{ad}	46.99	41.67	37.58	34.35
Composition (wt%)				
M_{ad}	5.60	0.00	0.00	0.00
A_{ad}	1.00	4.06	4.66	3.02
V_{ad}	78.97	80.67	77.60	68.16
FC_{ad}	14.43	15.27	17.74	28.82
Three biomass components (wt%)				
Cellulose	49.11	47.01	45.62	24.04
Hemicellulose	12.16	14.90	12.41	0.40
Lignin	23.28	27.05	33.91	75.63

Note: M_{ad}, A_{ad}, V_{ad}, and FC_{ad} represented moisture, ash, volatiles, and fixed carbon on an air-dried basis, respectively. C_{ad}, H_{ad}, N_{ad}, S_{ad}, and O_{ad} represented carbon, hydrogen, nitrogen, sulfur, and oxygen in the air drying base, respectively.

Catalysts

HZSM-5 zeolite was used as the catalyst, which had a ratio of silicon to aluminum of 38 and a specific surface area of 320 m^2/g. The catalyst was calcined in a tube furnace at 600 °C for 1 h before pyrolysis. The mass ratio of HZSM-5 to MgO (or Al_2O_3) was 1:1, and the concentration of impregnated solution was 0.5 mol/L.

The metal oxide was loaded on the HZSM-5 zeolite. Subsequently, the surface acid site activity was reduced, and the microporous structure of molecular sieve was adjusted, thereby improving the catalytic shape-selective performance of HZSM-5 zeolite (Trubetskaya *et al.* 2018). The common method for loading metal oxides on HZSM-5 zeolite is through ion exchange or an impregnation method (Chen *et al.* 2017). An impregnation method was employed in this paper.

The preparation steps of metal oxide-modified HZSM-5 were as follows: the mixture of HZSM-5 and $MgCl_2$ (or $AlCl_3$) solution was stirred in a WH240-plus constant temperature magnetic heating stirrer (Efson Biotechnology Co., Ltd., China) at 25 °C for 6 h. Then, the mixture was filtered with a water recirculation vacuum pump. The filtered HZSM-5 was dried at 110 °C for 4 h. Finally, the metal oxide-modified HZSM-5 was calcined at 500 °C for 3 h, and the heating rate was 50 °C/h. In addition, the chemical reaction of $MgCl_2$ (or $AlCl_3$) during the calcination was $MgCl_2 \rightarrow MgO + Cl_2$ ($2AlCl_3 \rightarrow Al_2O_3 + 3\ Cl_2$).

Pyrolysis of Camphorwood

The pyrolysis of camphorwood was carried out in a horizontal tube furnace in a nitrogen atmosphere with a N_2 flow rate of 40 mL/min. The heating rate of horizontal tube furnace was 15 to 20 °C/min, and the pyrolysis residence time was 2 min. The experiment consisted of three parts: the direct pyrolysis of camphorwood, pyrolysis using the torrefaction camphorwood, and *in situ* pyrolysis of camphorwood and catalyst. The pyrolysis temperature was 400 °C, 450 °C, 500 °C, 550 °C, or 600 °C. The mass ratio of camphorwood to catalyst was 1:1.

The quartz reaction tube was placed in a horizontal tube furnace and heated. To avoid the production of ash from the camphorwood, a flow of nitrogen was introduced to create a hypoxic environment. To enhance the condensation effect of pyrolysis gas, two-stage condensation was adopted, as shown in Fig. 3. The bio-oil was extracted with absolute ethanol (analytical grade). The yields of bio-oil ($Y_{bio\text{-}oil}$), bio-gas ($Y_{bio\text{-}gas}$), and bio-char ($Y_{bio\text{-}char}$) were analyzed as shown in Eqs. 1, 2, and 3, respectively,

$$Y_{bio-oil} = \frac{m_{bio-oil}}{m_{biomass}} \tag{1}$$

$$Y_{bio-gas} = \frac{m_{biomass} - m_{bio-oil} - m_{bio-char}}{m_{biomass}} \tag{2}$$

$$Y_{bio-char} = 1 - Y_{bio-oil} - Y_{bio-gas} \tag{3}$$

where $m_{bio\text{-}oil}$, $m_{biomass}$, and $m_{bio\text{-}char}$ were the mass of bio-oil, g, the mass of camphorwood, g, and the mass of bio-char, g, respectively.

The bio-oil components were analyzed by gas chromatography-mass spectrometry (GC-MS; Model 5972N, Agilent, Santa Clara, USA). The pyrolysis components with a relative content greater than 1% were selected for analysis. The heating rate was 5 °C/min. The carrier gas was He (> 99.99%). The flow rate was 5 mL/min. The split ratio was 30:1. The ion source temperature was 240 °C. The interface temperature was 250 °C.

RESULTS AND DISCUSSION

Characterization of Catalysts

The SEM images presents the catalysts of MgO-modified HZSM-5 (Fig.1a) and Al_2O_3-modified HZSM-5 (Fig.1b). The loading quantities of Mg and Al are listed in Table 2, and they were detected by ICP-MS (Inductively Coupled Plasma Mass Spectrometry, USA, 7500ce). The contents of Mg and Al in HZSM-5 were 13.1 and 51.8 mg/kg. The content of Mg increased up to 3200 mg/kg as the HZSM-5 was modified by the MgO. Meanwhile, the content of Al increased up to 13580 mg/kg as the HZSM-5 was modified by the Al_2O_3. So, the Mg and Al were successfully loaded on the surface of HZSM-5. The acidic properties of HZSM-5, MgO-modified HZSM-5, and Al_2O_3-modified HZSM-5 were studied by the TPD (Temperature Programmed Desorption, USA, AutochemII 2920), as shown in Fig. 1c. Experimental conditions: The mass of sample was 50 mg (20-30 mesh). The carrier gas was He and the purge time of He was 40 min at 400 ℃. The NH_3 would be absorbed with a flow rate of 50 cm^3/min of a mixed gas (NH_3-He) as the temperature decreased to 110 ℃. The temperature increased up to 150 ℃ when the NH_3 reached the saturation state. He was used as a purge for 30 min in order to remove the physically adsorbed NH_3. Then the temperature increased up to 600 ℃ with a heating rate of 10 ℃/min. Two peaks were detected in the TPD spectrum of HZSM-5. The desorption peak at 233 ℃ was attributed to the weak acid sites and the desorption peak at 362.5 ℃ was attributed to the strong acid sites. In addition, the weak acid sites shifted to the higher temperature as HZSM-5 was modified with Mg^{2+} or Al^{3+}. The strong acid sites shifted to higher temperature as HZSM-5 was modified by Mg^{2+}. Meanwhile, the strong acid sites shifted to lower temperature as HZSM-5 was modified with Al^{3+}.

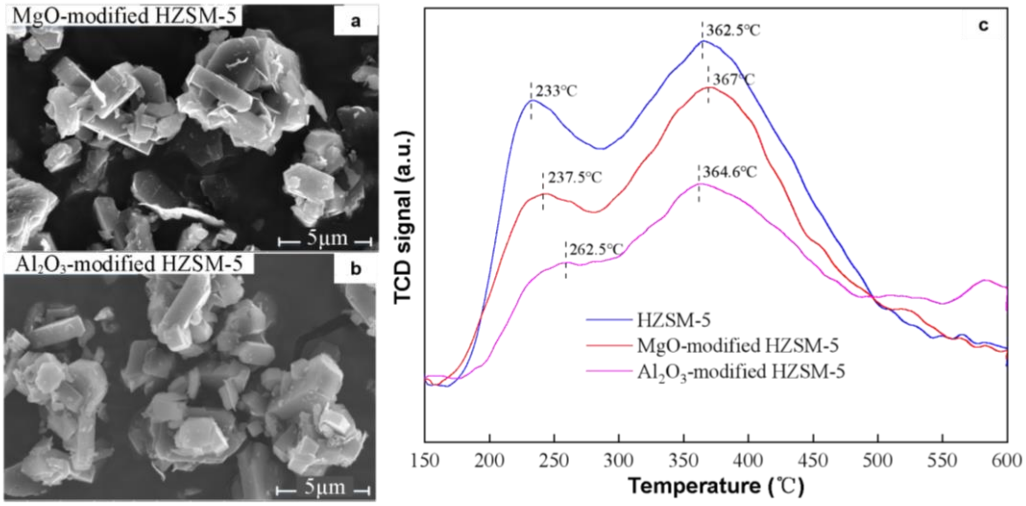

Fig. 1. SEM of MgO-modified HZSM-5 (a) and Al_2O_3-modified HZSM-5 (b); NH_3-TPD curve (C)

Table 2. Catalyst Content of Mg and Al

	HZSM-5	MgO-modified HZSM-5	Al_2O_3-modified HZSM-5
Mg (mg/kg)	13.07 ± 0.47	3204.22 ± 67	6.94 ± 0.04
Al (mg/kg)	51.79 ± 5	15.48 ± 1.42	13578.6 ± 58

Products of Pyrolysis from Camphorwood

The yields of bio-oil, bio-gas, and bio-char from camphorwood are shown in Fig. 2a. The yield of bio-oil first increased then decreased with the increase of pyrolysis temperature. The yields of bio-oil were 45.3% and 45.4% at 450 and 500 °C, respectively. Therefore, the biomass was more completely degraded at 450 and 500 °C than other pyrolysis temperatures. When the pyrolysis temperature was lower than 450 °C, the pyrolysis of camphorwood was incomplete, resulting in the production of tar and bio-char. The yield of bio-char was the highest at 400 °C. When the camphorwood was directly pyrolyzed, the difference between bio-oil yields was not significant at 450 and 500 °C. In order to obtain a greater content of high-value chemicals, a higher yield of bio-oil is desired. However, a high pyrolysis temperature also leads to an increase in the energy consumption and incurs a greater economic cost. Thus, the optimal pyrolysis temperature was judged to be 450 °C for camphorwood.

Figure 2b shows the yield of bio-oil, bio-gas, and bio-char from camphorwood at torrefaction temperatures of 200 °C, 250 °C, and 300 °C. The pyrolysis temperature for this condition was 450 °C. The yield of bio-oil deceased with increasing torrefaction temperature because the mass of camphorwood decreased and the bio-char yield increased after torrefaction pretreatment. The content of ash decreased after torrefaction, as demonstrated in Table 1. When the torrefaction temperature was increased from 250 °C to 300 °C, the yield of bio-oil markedly decreased from 44.4% to 27.4% (decreased by 38.3%). The waste sawdust was pyrolyzed after it was torrefied (Yoo and Choi 2016). When the torrefaction temperature was higher than 280 °C, the yield of bio-oil markedly deceased. The reason for this phenomenon was that most of cellulose and hemicellulose in the biomass were decomposed when the torrefaction temperature was higher than 280 °C. Compared with direct pyrolysis, the bio-oil yield at a torrefaction temperature of 200 °C was higher. But at torrefaction temperatures of 250 °C and 300 °C, the bio-oil yields were lower than that of direct pyrolysis. This could be attributed to the fact that the cellulose and hemicellulose in the biomass were decomposed when the torrefaction temperature was higher than 250 °C. In order to obtain a high bio-oil yield and high-quality bio-oil, the optimal torrefaction temperature of camphorwood pyrolysis was 200 °C.

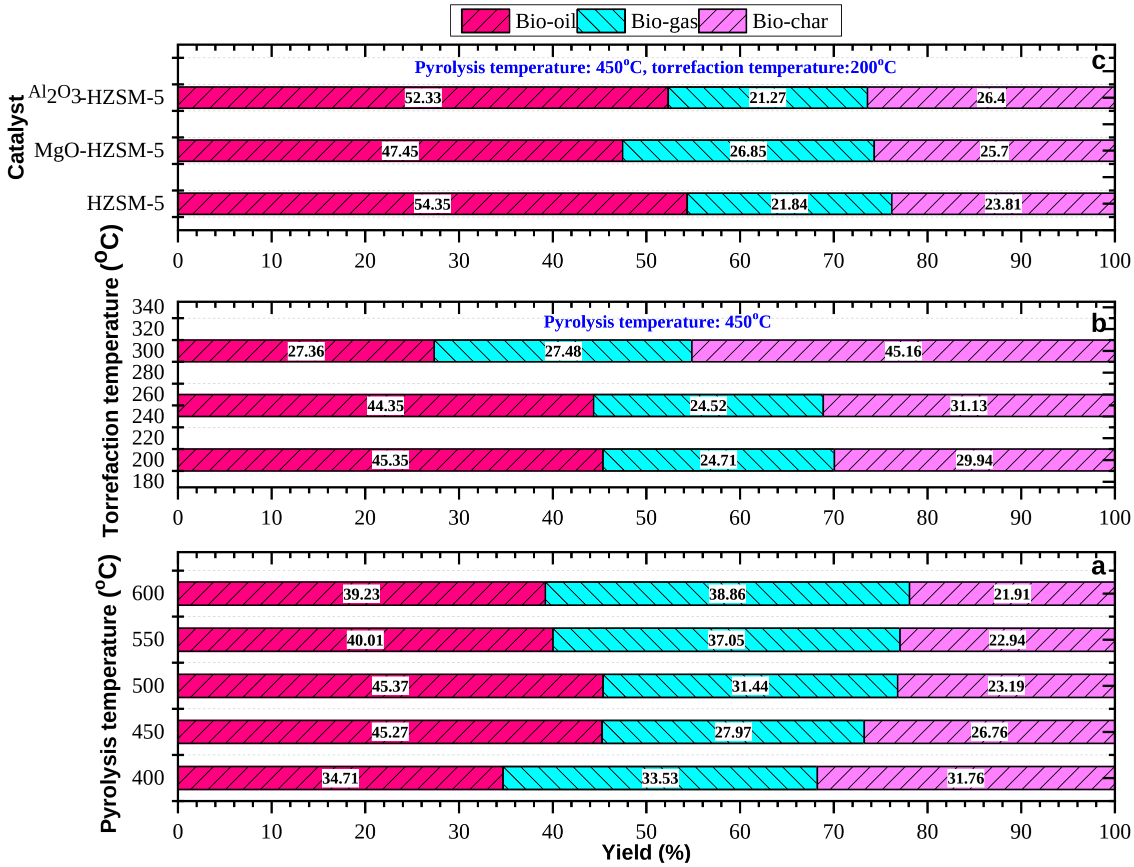

Fig. 2. Yields of bio-oil, bio-gas and bio-char at different pyrolysis temperatures (a), at different torrefaction temperatures (b), using different catalysts (c)

Figure 2c represents the yields of bio-oil, bio-gas, and bio-char resulting from catalytic pyrolysis. The pyrolysis temperature and torrefaction temperature were 450 °C and 200 °C, respectively. The catalysts were HZSM-5, MgO-modified HZSM-5, and Al_2O_3-modified HZSM-5. The yields of catalytic bio-oil were higher than the yields resulting from bio-oil derived from direct pyrolysis and torrefaction pyrolysis. HZSM-5 could improve the yields of bio-oil in comparison to bio-oil derived from MgO-modified HZSM-5 and Al_2O_3-modified HZSM-5. The rate of increase of bio-oil yield was more prominent than these of bio-gas and bio-char when the catalysts were used. The reason for this phenomenon was that the incorporation of catalysts could significantly inhibit the secondary decomposition of bio-oil. The bio-gas yield achieved the highest value for direct pyrolysis (28.0%), and the bio-gas yield achieved the lowest value for Al_2O_3-modified HZSM-5 catalytic pyrolysis (21.3%). The yields of bio-char decreased during catalytic pyrolysis. The bio-char yield followed the trend: HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5.

Distribution in Bio-oil from Camphorwood

Figure 3 shows components in the bio-oil derived from camphorwood. The pyrolysis temperature was 450 °C. The torrefaction temperature was 200 °C. The catalysts were HZSM-5, MgO-modified HZSM-5, and Al_2O_3-modified HZSM-5, respectively. The bio-oil contained various high-value chemicals, such as phenols, aldehydes, sugars, ketones, hydrocarbons, alcohols, and lipids. The content of phenols in bio-oil was the highest among all the chemical components. The content of phenols was the highest at pyrolysis temperature of 450 °C and torrefaction temperature of 200 °C, leading to a content of 31.5%. The torrefaction pretreatment and catalysts could all increase the production of aldehydes. The content of sugars reached the highest using HZSM-5 as the catalyst, 10.4%. The Al_2O_3-modified HZSM improved the content of ketones. The content of lipids was lower than the other six compounds, and the content of lipids was highest at high temperatures (4.27%).

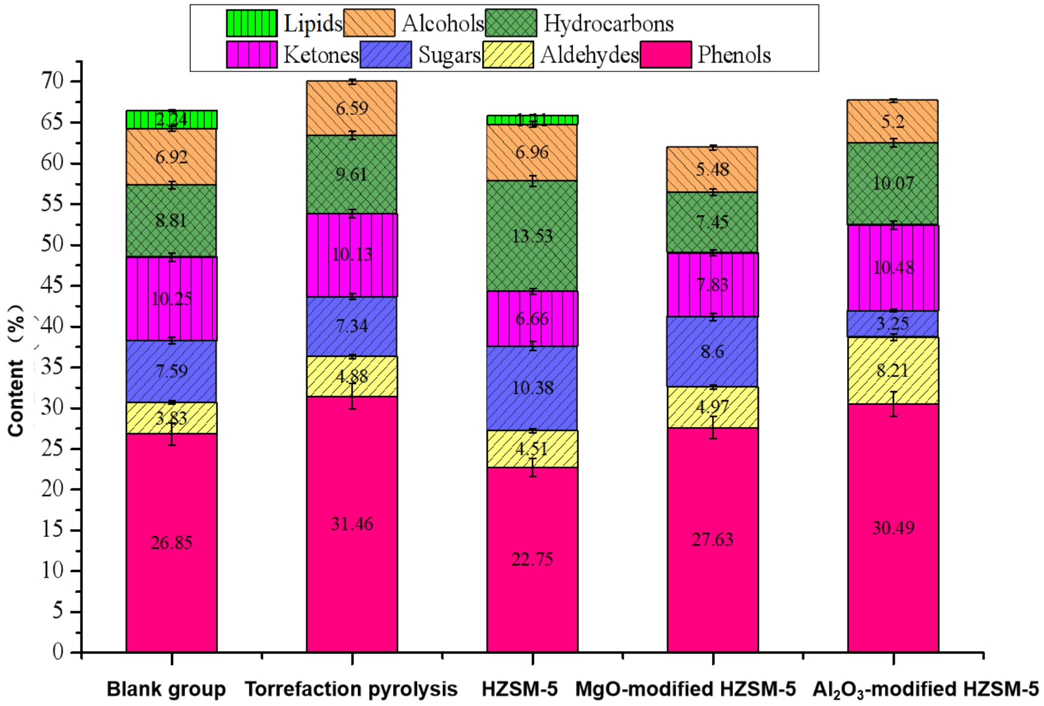

Fig. 3. Distribution of bio-oil using different catalysts

The phenols content followed the trend: HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5. However, the content of phenols was lower than that resulting from torrefaction pyrolysis. The production of phenols was remarkably improved because of torrefaction pretreatment. The phenols were produced by the deoxygenation of lignin derivatives. When camphorwood was torrefied, the content of lignin increased, resulting in an increase in the content of phenols. The production of aldehydes was markedly increased by the incorporation of Al_2O_3-modified HZSM-5 catalyst. The phenol content in this trial was 8.21%. The sugar content achieved the highest value when HZSM-5 was employed as the catalyst. The content of ketones was the highest when Al_2O_3-modified HZSM-5 was utilized as the catalyst. HZSM-5 could degrade lignin-derived oxygenates which improved the production of hydrocarbons. Therefore, the content of hydrocarbons was the highest when HZSM-5 was the catalyst. The content of alcohols was the highest when HZSM-5 was the catalyst, and it was the lowest when Al_2O_3-modified HZSM-5 was the catalyst. The content of lipids was 2.24% and 1.11% for direct pyrolysis and catalytic pyrolysis with HZSM-5 utilized as the catalyst, respectively. In addition, the torrefaction temperature was 200 °C and the catalysts were HZSM-5, MgO-modified HZSM-5, and Al_2O_3-modified HZSM-5. The results show that the categories of phenol, aldehyde, sugar, ketone and alcohol increased because of torrefaction pretreatment or use of catalyst. In addition, the contents of phenols (*e. g*. 2-methoxy- phenol, 2-methoxy-4-(1-propenyl)-phenol, and 2,6-dimethoxy-4-(2-propenyl)-phenol) increased. The production of 1,2,4-trimethoxybenzene and 1,2,3-trimethoxybenzene were increased after camphorwood was torrefied. The reason for this phenomenon was that the content of lignin increased because of torrefaction pretreatment. The cracking of lignin derivatives could result in the formation of polycyclic aromatic hydrocarbons, *e. g*., 1,2,4-trimethoxybenzene and 1,2,3-trimethoxybenzene. The contents of desaspidinol and (2’,3’,4’)-4-dihydro-6-methyl-2-(3,4-dimethoxyphenyl)-3-2H-1-benzopyran-3,4-diol were 1.53% and 3.73%, respectively. These compounds were classified as diols. Lignin could improve the formation of diols, as demonstrated in a previous study (Wang *et al.* 2018).

The content of D-allose was the highest in bio-oil when HZSM-5 was the catalyst (10.38%). However, D-allose decreased to trace in bio-oil when MgO-modified HZSM-5 and Al_2O_3-modified HZSM-5 were the catalysts. The production of 3-furaldehyde was significantly improved by MgO-modified HZSM-5 and Al_2O_3-modified HZSM-5, and their contents were 2.45% and 4.19%, respectively. The order of selectivity of aliphatic ketones, including 1,2-cyclopentanedione and 2-hydroxy-3-methyl-2-cyclopenten-1-one, was HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5. The order of selectivity of aromatic ketones, such as (1S)- 7,7-trimethyl-bicyclo[2.2.1]heptan-2-one, was HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5. Categories of phenols in catalytic bio-oil increased compared with the type of phenols derived from direct pyrolysis and torrefaction pyrolysis. However, the content of phenols did not markedly change. The selectivity of MgO-modified HZSM-5 for phenols was higher than HZSM-5 and Al_2O_3-modified HZSM-5. The selectivity of MgO-modified HZSM-5 for 1,6-anhydro-á-D-glucopyranose (levoglucosan) was higher than Al_2O_3-modified HZSM-5. The content of acids was lower when HZSM-5 was the catalyst.

In summary, the order impact of different parameters on the bio-oil yield followed the trend: HZSM-5 > Al_2O_3-modified HZSM-5 > MgO-modified HZSM-5 > torrefaction pyrolysis > direct pyrolysis. The content of phenols was the highest when camphorwood was torrefied at 200 °C. The types of phenols increased markedly in catalytic bio-oil. In addition, the content of phenols was higher when Al_2O_3-modified HZSM-5 was the catalyst. The productions of aldehydes, sugars, hydrocarbons and alcohols were enhanced for catalytic pyrolysis. The contents of ketones decreased when HZSM-5 and MgO-modified HZSM-5 were the catalysts.

CONCLUSIONS

1. When the pyrolysis temperature was 450 °C, the yield of bio-oil was the highest. The contents of phenols and ketones in bio-oil were highest at 450 °C, amounting to values of 26.8% and 10.2%, respectively. The highest content of hydrocarbons was 8.81% at 450 °C. The main components of aldehydes included 3-furaldehyde and syringaldehyde, 2.81% and 1.02%, respectively.
2. When the torrefaction temperature was 200 °C, the yield of bio-oil from camphorwood was highest and it was 45.4%. The types of phenols increased, and the phenols content

increased up to 4.6%. The sugars content at a torrefaction temperature of 200 ℃ increased two-fold compared with that at a torrefaction temperature of 300 ℃. The production of hydrocarbons was improved, and its content increased from 8.8% to 9.6%.

3. The type of phenols in catalytic bio-oil increased compared with that in direct pyrolysis bio-oil and the torrefaction pyrolysis bio-oil. The production of aldehydes was markedly improved by the Al_2O_3-modified HZSM-5, and its content was 8.2%. The content of sugars achieved the highest value when the HZSM-5 was the catalyst. The content of ketones was the highest when Al_2O_3-modified HZSM-5 was the catalyst. The order of selectivity of aliphatic ketones, including 1,2-Cyclopentanedione and 2-hydroxy-3-methyl-2- cyclopenten-1-one, was HZSM-5 < MgO-modified HZSM-5 < Al_2O_3-modified HZSM-5.

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