

Effects of ZnCl₂ on the Distribution of Aldehydes and Ketones in Bio-oils from Catalytic Pyrolysis of Different Biomass

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Bio-oil can serve as an alternative fuel source or resource to extract high value-added chemicals. This paper focuses on the effect of six types of biomass (rape straw, corn straw, walnut shell, chestnut shell, camphor wood, and pine wood) and ZnCl₂ catalyst on the bio-oil yield and chemicals in the bio-oil, including aldehydes, ketones, and four high-value chemicals (1-hydroxy-2-butanone, propionaldehyde, 5-HMF, 2(5H)-furanon). The results showed that the yields of bio-oil decreased when the ZnCl₂ was the catalyst. The ZnCl₂ promoted the production of aldehydes and ketones. The higher contents of aldehydes and ketones were obtained from camphor and pine wood, at 58.9 wt% and 42.0 wt%, respectively. The ZnCl₂ catalyst exhibited an active influence on the production of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanon. Compared with the non-catalytic pyrolysis, the content of 1-hydroxy-2-butanone and 2(5H)-furanone in bio-oil increased by 936% and 612%, respectively. The contents of propionaldehyde and 5-HMF in catalytic bio-oil were the highest from rape straw and increased by 193% and 86%, respectively.

Keywords: Pyrolysis; Biomass; ZnCl₂; Aldehydes; Ketones; High-value chemicals

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INTRODUCTION

Currently, fossil energy is the primary energy resource in the world (Knaggs *et al.* 2015). However, it will inevitably be depleted due to its continual uses. In addition, the combustion and usage of fossil fuels results in the emission of noxious greenhouse gases, including CO₂, NO_x, and sulfides (Sovacool *et al.* 2016; Zhou and Feng 2017). In contrast, biomass is a promising alternative to fossil fuel because of its renewable and carbon-neutral nature. Biomass can be used as a feedstock to produce various environmentally friendly materials, such as bio-asphalt (Zezelew *et al.* 2013), hydrophobic agents (Penmetsa and Steele 2012), and adsorbents (Li *et al.* 2017). Many preceding studies have focused on bio-oil through the incorporation of biomass pyrolysis technology (Wang *et al.* 2015). Bio-oil can be used as an engine fuel (Chwist *et al.* 2017), environmentally friendly binder (Hernando *et al.* 2019; Zabelkin *et al.* 2019), and organic chemical resource (Sharma *et al.* 2015). The utilization of biomass could lessen the extent of the greenhouse effect and reduce the presence of acid rain (Kan *et al.* 2012; Günther *et al.* 2015; Krivtcova *et al.* 2015).

Organic chemicals in bio-oil produced from biomass can reduce the cost of

traditional chemicals and enhance the development of green environmentally friendly synthesis methods (Arevalo-Gallegos *et al.* 2017). High value-added chemicals (1-hydroxy-2-butanone, propionaldehyde, 5-hydroxymethylfurfural (5-HMF), and 2 (5H)-furanone) that are extracted from bio-oil can be mainly used as adhesives, food additives (Laino *et al.* 2012), preservatives (Magdalena *et al.* 2018), fine chemicals (Li *et al.* 2013), and fuel additives (Climent *et al.* 2014). The production of these chemicals requires expensive catalysts and strict reaction conditions of traditional methods, which would increase the production cost (Shen *et al.* 2015; Wang *et al.* 2019; Ye *et al.* 2019). Catalytic pyrolysis of biomass is a new technology for producing high value-added chemicals, in which the bio-oil can be used as the substrate. The chemical categories in bio-oil from catalytic pyrolysis mainly are sugars, acids, aldehydes, ketones, phenols, and lipids (Kabir and Hameed 2017; Bi *et al.* 2019). It has many advantages, such as gentle conversion conditions, low energy and cost inputs, higher yield, and selectivity of high-value chemicals.

Many high-value chemicals can be produced from biomass. For example, 1-hydroxy-2-butanone (\$111/g, purity: 98%, 2019) is an important intermediate for synthesizing the anti-tuberculosis drug ethambutol. Paine *et al.* (2008) showed that levoglucosan was mainly produced from pyrolysis of cellulose. Zheng *et al.* (2016) and Lédé (2012) studied the mechanism of cellulose pyrolysis and found that 1-hydroxy-2-butanone was mainly formed by the dehydration and decarboxylation of cellulose. Propionaldehyde (\$19/g, purity: 97%, 2019) is widely used as a raw material for synthetic resins, rubber promoters, *etc.* Propionaldehyde can be produced through the cracking/dehydration of light oxides during the pyrolysis of biomass (Brech *et al.* 2016). 5-HMF (\$34/g, purity: 97%, 2019) and its secondary derivatives, which are excellent substitutes for petroleum fuels, were important intermediates for synthesizing liquid alkanes (Ito *et al.* 2016). 5-HMF can be used as a raw material for medicine and pesticides. 5-HMF has been mainly formed from the cracking, acetal, and dehydration reaction of cellulose and hemicellulose (Bai *et al.* 2014). 2(5H)-furanone (\$18/g, purity: 98%, 2019) has high biological activities; hence, it is widely used for antibacterial, anti-inflammatory, antiviral, and anti-cancer applications. In addition, 2(5H)-furanone has been shown to be a suitable starting point to synthesize medicinal and industrial products in recent years (Li *et al.* 2016; Rossi *et al.* 2017).

Ketones are also a high-value chemical in bio-oil. Lazzari *et al.* (2016) found that the highest yield of chemicals in bio-oil were mainly in the form of ketones (34 wt%), which were obtained from the pyrolysis of mango residues. 2(5H)-Furanone accounted for the highest proportion of ketone content (9.4 wt%) in the bio-oil. Based on this finding, various catalysts have been found to play significant roles on the bio-oil yield and high-value chemicals content (Li *et al.* 2018; Hemando *et al.* 2019; Liu *et al.* 2019). $ZnCl_2$ is an inexpensive and abundant type of catalyst. It has been shown that the pyrolysis of poplar, corn cob, and cellulose can be enhanced by $ZnCl_2$ at a lower temperature (Lu *et al.* 2011). This is because the cracking of holocellulose and the depolymerization of lignin are promoted, while the activation energy of impregnated wood is decreased by $ZnCl_2$ (Néstor *et al.* 2016). Hence, it seems that $ZnCl_2$ could be an effective catalyst to promote the cracking of cellulose and hemicellulose into high-value chemicals.

In this study, $ZnCl_2$ was used as the catalyst during the pyrolysis process of biomass. Six types of biomass (rape straw, corn straw, walnut shell, chestnut shell, camphor wood, and pine wood) were used as feedstock. The main purposes of this study were to investigate the effects of $ZnCl_2$ catalyst on the yield of bio-oil and the content of

high-value chemicals (1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone) from pyrolysis of various biomass feedstock. This study, which aimed to analyze pyrolysis oil containing high-value chemicals, can be of great importance for improving the utilized value of biomass and exploring alternatives to fossil fuels.

EXPERIMENTAL

Materials

The raw materials used in this work were obtained from different regions in China. Specifically, rapeseed straw was harvested from Suzhou City (China), corn straw and pine were harvested from Zibo City (China), chestnut shell was harvested from Qingzhou City (China), and camphor wood was harvested from Shangrao City (China). All materials were pre-dried, pulverized, and screened before utilization. The particle size ranged from 0.22 to 0.38 mm. The main components of the six biomasses (cellulose, hemicellulose, and lignin) were determined by the Van Soest measurement method (Rutkowski, 2011). The elemental analysis of biomass was performed using an elemental analyzer (EA3000; EuroVector, Milan, Italy). The proximate analysis of biomass was conducted in a muffle furnace (SX2-2.5-12; Jintanliangyou, Changchou, China). The content of the components is shown in Fig. 1. The elemental analysis and proximate analysis results of samples are shown in Table 1.

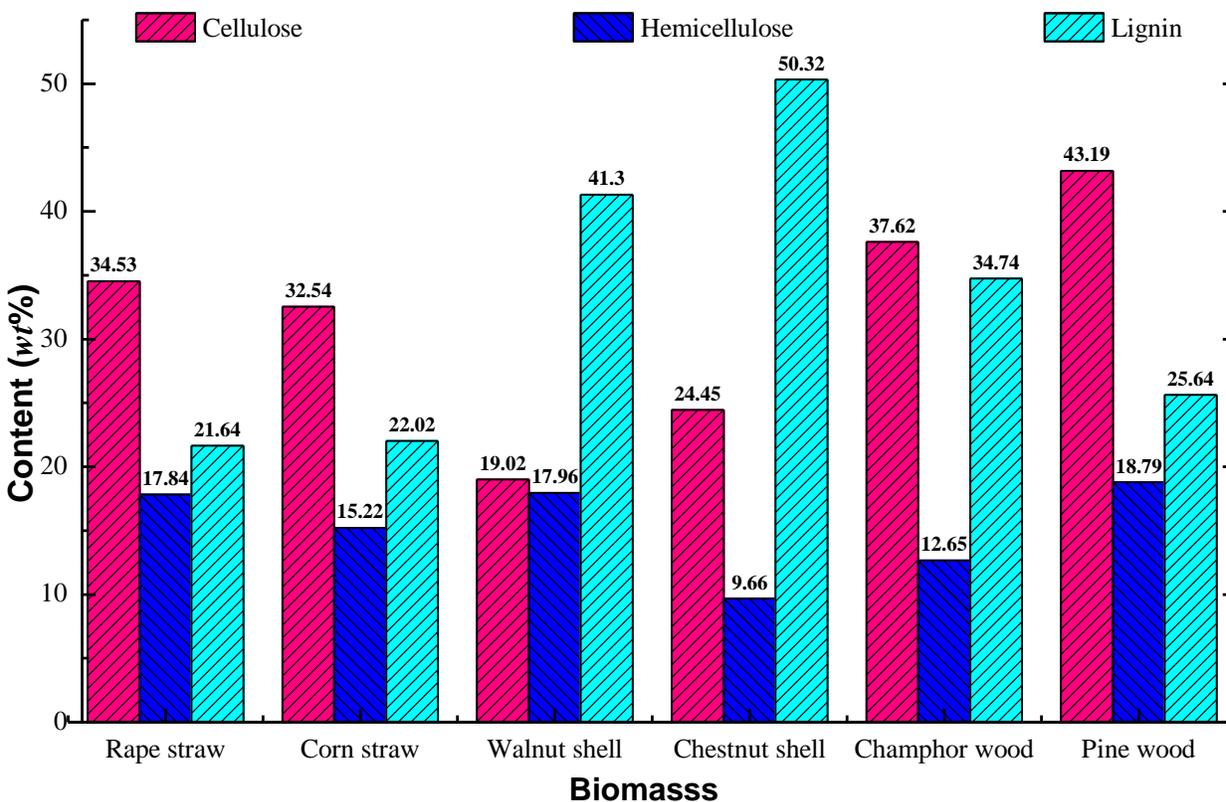


Fig. 1. Cellulose, hemicellulose, and lignin content for different types of biomass

Table 1. Proximate Analysis and Elemental Analysis Results of the Materials

Material	Elemental Analysis (%)			Proximate Analysis (%)		
	C	H	O	Fixed Carbon	Volatiles	Ash
Rape straw	48.52	5.74	45.74	15.27	79.18	5.55
Corn straw	47.46	5.78	46.76	12.26	80.59	7.15
Walnut shell	48.23	5.72	46.05	18.39	81.21	0.4
Chestnut shell	48.10	5.82	46.08	28.08	70.84	1.08
Camphor wood	53.16	6.12	40.72	13.35	86.14	0.51
Pine wood	50.16	5.77	44.07	17.06	80.07	2.87

Experimental Methods

The pyrolysis equipment used in this study was a SKZ-4-B constant temperature horizontal tube furnace reactor. Figure 2 shows the schematic diagram of the reactor. The reactor consisted of a pyrolyzer and a condensing device. Prior to conducting experiments, nitrogen gas was introduced for a period of time to ensure an oxygen-limited environment. Non-catalytic pyrolysis and catalytic pyrolysis were conducted on the reactor. As for catalytic pyrolysis, $ZnCl_2$ was chosen as catalyst, and it was mixed with raw materials at the mass ratio of 1:1. Once the temperature of the furnace reached 500 °C, the biomass was quickly placed into the reactor. During the pyrolysis, the raw materials were placed in a porcelain boat, which was then covered by quartz wool with a thickness of 0.5 mm. The $ZnCl_2$ catalyst was then placed on the quartz wool to ensure the catalytic influenced the pyrolysis process. The flow rate of nitrogen was set at a rate of 60 L/h. The retention time was 5 min because the reaction finished within 1 s. After the pyrolysis experiments completed, the gas product was condensed by a condenser at -10 °C, and bio-oil was subsequently collected. The residue solid was bio-char. The catalysts can be effectively separated from raw materials using the quartz wool with good gas permeability. The catalyst can remain catalytic activity and be used for reusing after regeneration.

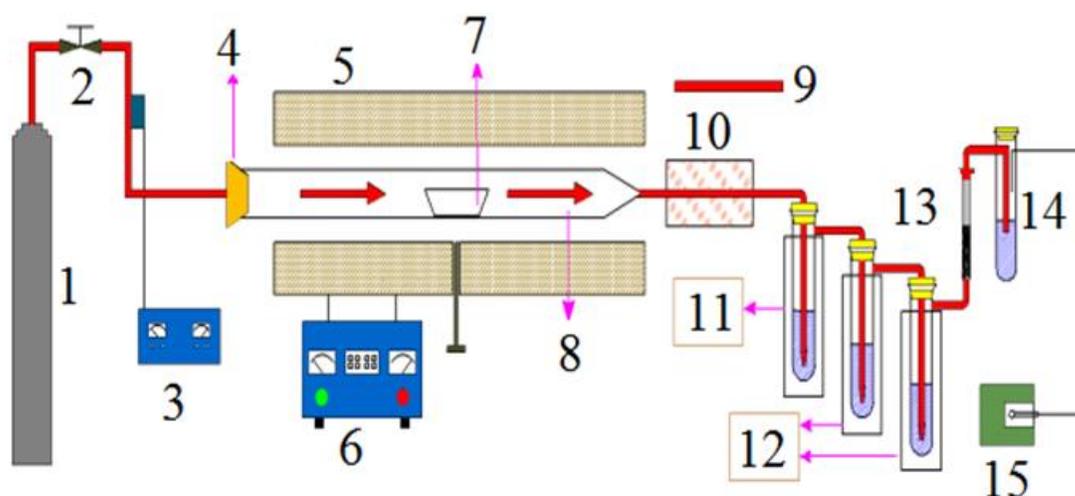


Fig. 2. Schematic diagram of the biomass pyrolysis horizontal tube furnace reaction: 1. N_2 bottle; 2. Valve; 3. Mass flow meter; 4. Rubber plug; 5. Horizontal tube furnace; 6. Control box; 7. Porcelain boat; 8. High temperature resistant quartz tube; 9. Rubber tube; 10. Insulated rock wool; 11. First stage condensation; 12. Cold trap; 13. Low temperature thermostat; 14. Gas drying device; 15. Air bag

Products of Pyrolysis

The yields of products can be calculated by the followed equations.

$$\text{Bio-oil yield: } Y_{oil}: Y_{oil} = \frac{M_{oil}}{M} \times 100\% \quad (1)$$

where M_{oil} and M represent the weights (g) of bio-oil and biomass.

$$\text{Bio-char yield, } Y_{char}: Y_{char} = \frac{M_{char}}{M} \times 100\% \quad (2)$$

where M_{char} and M represent the weights (g) of bio-char and biomass.

$$\text{Bio-gas yield, } Y_{gas}: Y_{gas} = 100 - Y_{oil} - Y_{char} \quad (3)$$

Two typical ketones (1-hydroxy-2-butanone and 2(5H)-furanone) and two typical aldehydes (propionaldehyde and 5-HMF) were selected to analyze. The content of chemicals in bio-oil was determined by gas chromatography-mass spectrometry (GC-MS), (5972N; Agilent, Santa Clara, CA, USA) equipped with a Rtx-5 capillary column (30 m × 0.25 mm × 0.25 μm). The carrier gas was He with high purity (>99.99%). The split ratio was 30:1, the injection volume was 0.2 μL. and the gasification temperature was 280 °C. The temperature procedure was set to increase from room temperature to 240 °C with a heating rate of 5 °C/min, and then held for 5 min. The ionization mode was EI. The electron bombardment energy was 70 eV. The temperature of ion source and the interface were set at 240 °C and 250 °C, respectively.

RESULTS AND DISCUSSION

Products Yields and Distribution

The yields of bio-oil, bio-gas, and bio-char with or without ZnCl₂ catalyst are shown in Fig. 3. The highest bio-oil yield was from camphor wood (45.8 wt%), while the lowest bio-oil was from chestnut shell (35.5 wt%). Compared with that, lower yields (44.1 wt% and 42.5 wt%) were obtained by pine wood and rape straw, respectively. The varied yields produced from the raw materials could be impacted by the varied content of components (Qu *et al.* 2011; Wang *et al.* 2016). In this case, walnut shell had a higher bio-oil yield (42.4 wt%) than those of corn straw (40.8 wt%) and chestnut shell (35.5 wt%), which was because walnut shell had a higher content of vegetable oil that was mainly converted into bio-oil. The highest volatiles were obtained in camphor wood (Table 1), which might be the cause for the higher yield of biochar. In the control groups, the highest bio-char yield (38.8 wt%) was obtained from camphor wood.

The bio-oil and bio-char yields from catalytic pyrolysis are depicted in Fig. 3. The highest bio-oil yield was from corn straw (40.4 wt%), while the lowest bio-oil was from camphor wood (32.5 wt%). These results showed that bio-oil yields from catalytic pyrolysis were definitely lower than that from non-catalytic pyrolysis. It can be concluded that the ZnCl₂ catalyst exhibited a negative impact on the yields of bio-oil. The bio-oil yields of camphor wood and pine wood noticeably decreased 29.0% and 14.6%, respectively, which was attributed to the fact that the conversion of cellulose and hemicellulose into small gas molecules was promoted, while the decomposition of lignin was inhibited (Stefanidis *et al.* 2014). The results were consistent with a previous study from Hu *et al.* (2017) who used ZnCl₂ as catalyst during pyrolysis of corn straw lignin and

found that the production of bio-oil was inhibited, while that of bio-char and bio-gas was promoted. The bio-oil yields of camphor wood and pine wood were higher compared to that of rape straw, corn straw, walnut shell, and chestnut shell. As shown in Fig. 1, the contents of cellulose and lignin in camphor wood and pine wood were higher than those in rape straw, corn straw, walnut shell, and chestnut shell. Hence, higher content of cellulose and lignin resulted in greater reduction in bio-oil yield. Meanwhile, there was no noticeable influence of $ZnCl_2$ catalyst on corn straw-derived bio-oil yield, which only decreased 1.03 wt%. However, the $ZnCl_2$ catalyst showed a positive effect on the production of bio-char. To be specific, the increase of bio-char yields from camphor wood and pine wood were relatively lower than that from chestnut shell, corn straw, walnut shell, and rape straw.

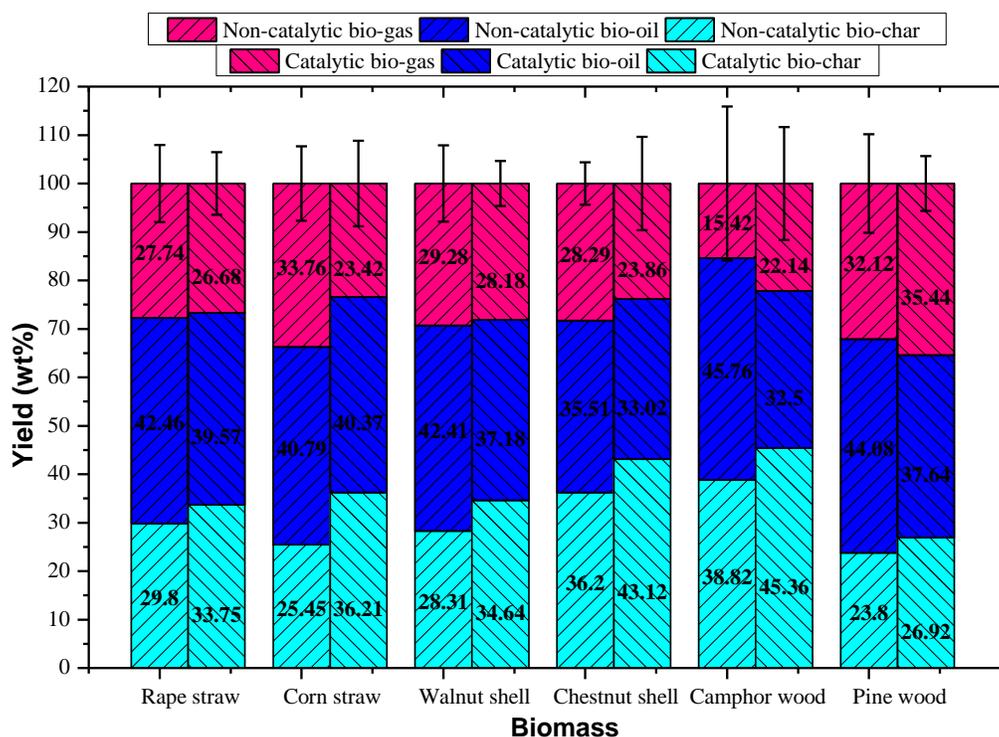


Fig. 3. Pyrolysis products yields from six types of biomass

Content of Aldehydes and Ketones in Bio-oil

The content of aldehydes and ketones in bio-oils is shown in Fig. 4. For non-catalytic pyrolysis of six types of biomass, the content of aldehydes and ketones in bio-oil from rape straw and corn straw was 29.7 wt% and 24.1 wt%, respectively. This was because the two biomass feedstocks had higher content of holocellulose (cellulose and hemicellulose) that were the main resources of aldehydes and ketones. During the process of pyrolysis, aldehydes and ketones can be converted from the cracking of cellulose and hemicellulose (Zhang *et al.* 2018). When the $ZnCl_2$ catalyst was added, the contents of aldehydes and ketones in the catalytic bio-oil of six types of biomass increased. Specifically, a higher content was obtained from camphor wood and pine wood (58.9 wt% and 42.0 wt%), which was mainly caused by the promotion of the $ZnCl_2$ catalyst in the interaction of lignin with cellulose. Hence, camphor wood and pine wood would be the optimum feedstock to produce aldehydes and ketones when applying $ZnCl_2$ catalyst during the process of pyrolysis.

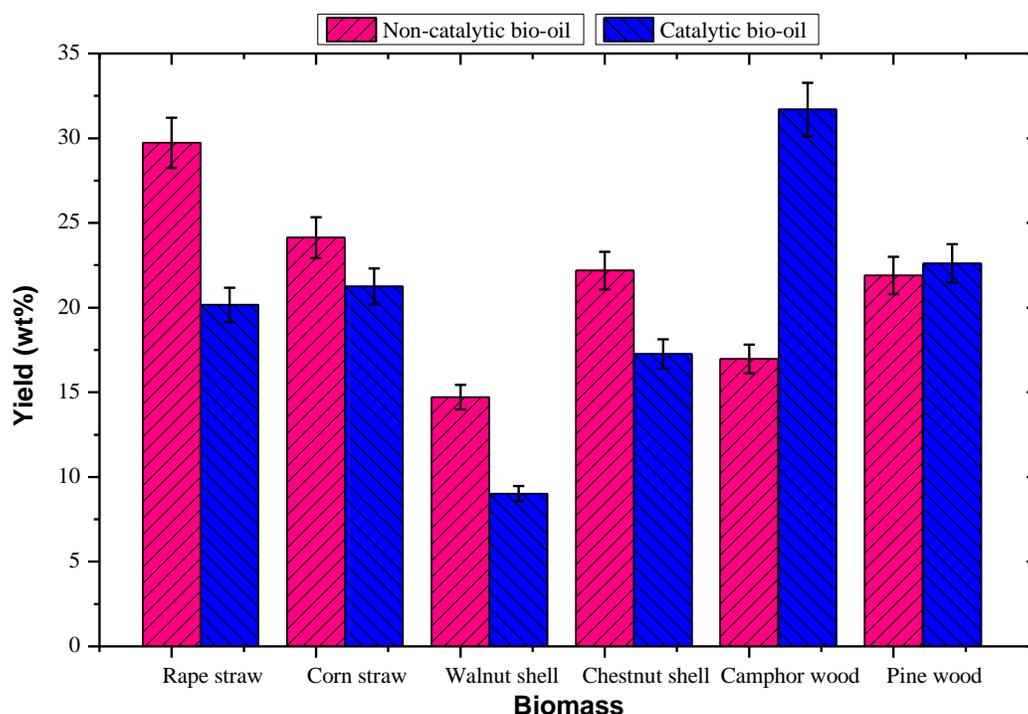


Fig. 4. Contents of aldehydes and ketones in the bio-oil obtained from six types of biomass under non-catalytic pyrolysis and catalytic pyrolysis

High-value Chemicals in Bio-oil

There are many kinds of high-value chemicals in the bio-oil. In this paper, 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone were selected for analysis. These chemicals were selected because they had a high market value and they had a relatively high concentration in the bio-oil. Therefore, the influence of the biomass and ZnCl_2 catalyst on the content of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone was analyzed. The influence of different biomass types and ZnCl_2 catalyst on the content of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone is displayed in Fig. 5. The results showed that the content of 1-hydroxy-2-butanone were higher than propionaldehyde, 5-HMF and 2(5H)-furanone. In the non-catalytic bio-oil, the contents of 1-hydroxy-2-butanone, 5-HMF, and 2(5H)-furanone from chestnut shell were the highest. The content of propionaldehyde derived from rape straw was the highest. The content of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone from six types of biomass increased after the ZnCl_2 was used as catalyst. In the catalytic bio-oil, the contents of 1-hydroxy-2-butanone and 2(5H)-furanone were the highest when derived from chestnut shell. Compared with the non-catalytic pyrolysis, the contents of 1-hydroxy-2-butanone and 2(5H)-furanone in bio-oil increased 936% and 612%, respectively. The contents of propionaldehyde and 5-HMF were the highest when derived from rape straw. Compared with the non-catalytic pyrolysis, the contents of propionaldehyde and 5-HMF in bio-oil increased 6.9% and 194%, respectively. In catalytic bio-oil, the content of 1-hydroxy-2-butanone was higher than the other three types of chemicals from six types of biomass.

The ZnCl_2 catalyst played important roles on the content of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone. With the effects of the catalyst, the content

of 1-hydroxy-2-butanone in bio-oil from camphor wood increased from 4.46 wt% to 46.22 wt%, the content of 5-HMF in bio-oil from corn straw increased from 0.22 wt% to 1.53 wt%, the content of propionaldehyde in bio-oil from camphor wood increased from 0.22 wt% to 1.08 wt%, and the content of 2(5H)-furanone in bio-oil from camphor wood increased from 1.25 wt% to 3.52 wt%. However, the content of 5-HMF from pine wood did not remarkably change. The production of 1-hydroxy-2-butanone and 2(5H)-furanone from rape straw, camphor wood, and pine wood was drastically promoted by the catalyst. The content of 1-hydroxy-2-butanone from rape straw, camphor wood, and pine wood increased by 774%, 1040%, and 661%, respectively. The content of 1-hydroxy-2-butanone from rape straw, camphor wood, and pine wood increased by 350%, 715%, and 282%, respectively. The contents of cellulose in camphor wood, rape straw, and pine wood were higher than that in corn straw, chestnut shell, and walnut shell. The productions of 1-hydroxy-2-butanone and 2(5H)-furanone were derived from the cracking of cellulose during the pyrolysis process (Stefanidis *et al.* 2014). In addition, the contents of 1-hydroxy-2-butanone, 5-HMF, and 2(5H)-furanone in non-catalytic bio-oil were higher compared to the catalytic bio-oil. The result was mainly caused by the effect of $ZnCl_2$ catalyst on lignin conversion, in which the conversions of 1-hydroxy-2-butanone, 5-HMF, and 2(5H)-furanone were inhibited.

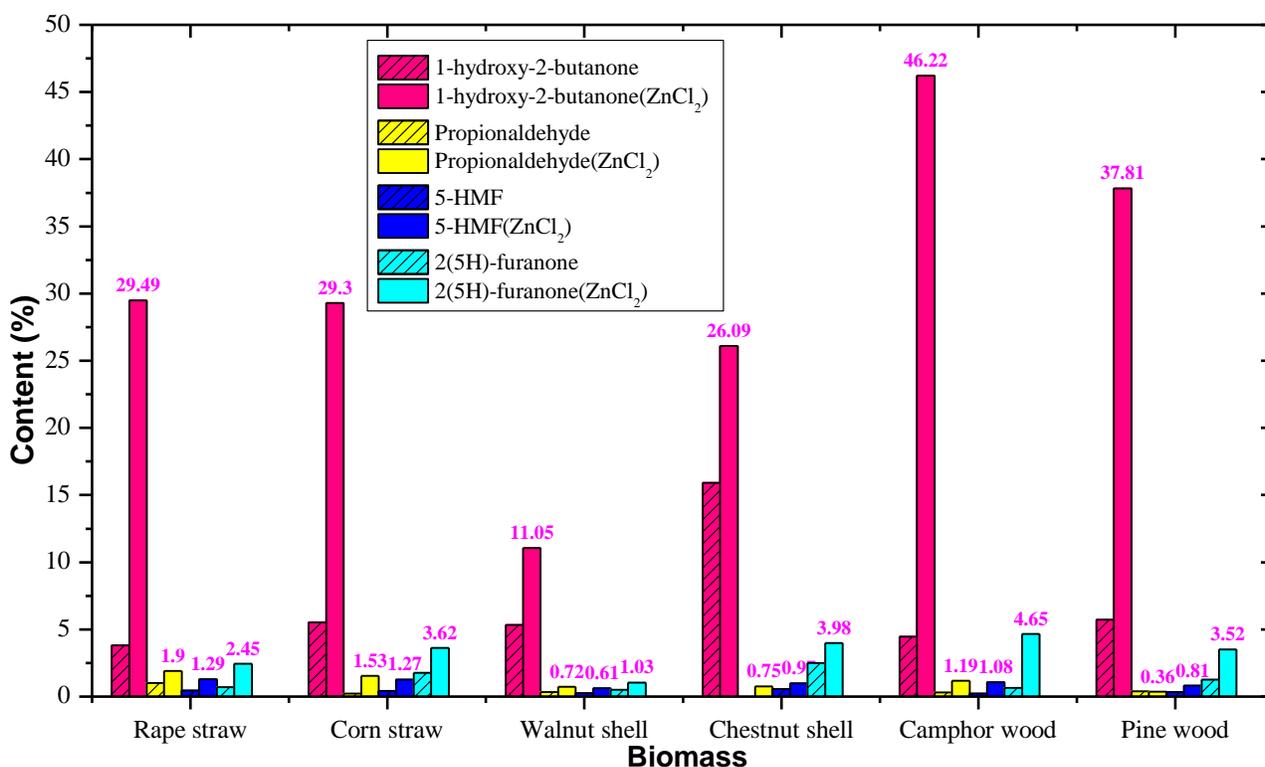


Fig. 5. Contents of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone in non-catalytic and catalytic bio-oils

From the above results, it can be concluded that the contents of high-value chemicals were remarkably affected by the inclusion of a $ZnCl_2$ catalyst during the pyrolysis of the six type of biomass (rape straw, corn straw, walnut shell, chestnut shell, camphor wood, and pine wood). The $ZnCl_2$ catalyst had a negative effect on the yields of bio-oil from six types of biomass. Therefore, it is of great importance to use different types

of biomass as feedstock to produce high-value chemicals, which is helpful for the industrial production of chemical compounds from renewable biomass and to realize high-value utilization of biomass.

CONCLUSIONS

1. The influence of biomass and ZnCl_2 catalyst on the yields of bio-oil was analyzed. The highest bio-oil yield was from camphor wood (45.8 wt%), while the lowest bio-oil was from chestnut shell (35.5 wt%). Additionally, the highest non-catalytic bio-char yield was from camphor wood because of its highest content of volatiles. The ZnCl_2 catalyst exhibited negative roles on the yields of bio-oils. The bio-oil yields of camphor wood and pine wood were remarkably decreased by 29.0% and 14.6%, respectively. In comparison with the bio-oil yields of camphor wood and pine wood, the yields of rape straw, corn straw, walnut shell, and chestnut shell were higher due to their lower content of cellulose and lignin. The ZnCl_2 catalyst exhibited active roles on the yields of bio-char. The increases of bio-char yields from camphor wood and pine wood were lower than that from chestnut shell, corn straw, walnut shell, and rape straw.
2. The influence of biomass and ZnCl_2 catalyst on the contents of aldehydes and ketones in bio-oils was analyzed. The contents of aldehydes and ketones in non-catalytic bio-oils from biomass with higher contents of holocellulose (rape straw and corn straw) were higher. The contents of aldehydes and ketones in the catalytic bio-oil of six types of biomass increased.
3. The influence of biomass and ZnCl_2 catalyst on the contents of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone was analyzed. In the non-catalytic and catalytic bio-oil, the contents of 1-hydroxy-2-butanone, 5-HMF, and 2(5H)-furanone from chestnut shell were the highest. The contents of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone were increased because of ZnCl_2 . So the ZnCl_2 catalyst played noticeable roles on the content of 1-hydroxy-2-butanone, propionaldehyde, 5-HMF, and 2(5H)-furanone. In the catalytic bio-oil, the contents of 1-hydroxy-2-butanone and 2(5H)-furanone were the highest from chestnut shell. Compared with the non-catalytic pyrolysis, the content of 1-hydroxy-2-butanone and 2(5H)-furanone in bio-oil increased 936 % and 612 %, respectively. The contents of propionaldehyde and 5-HMF were the highest from rape straw. Compared with the non-catalytic pyrolysis, the content of propionaldehyde and 5-HMF in bio-oil increased 6.86 % and 194 %, respectively.

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