High Quality Bio-Oil Production via Catalytic Pyrolysis of Pine Sawdust

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The objective of this study was to increase the selectivity of hydrocarbons in bio-oil by changing the degree of closure of the reactor. Using pine sawdust with a particle size of 0.5 to 0.8 mm as the pyrolysis material and HZSM-5 with a SiO_2/Al_2O_3 ratio of 60 as the catalyst, biomass catalytic pyrolysis experiments were carried out in a fixed bed reactor. The bio-oil compositions as a function of the closure time of the reactor and the catalyst-to-biomass weight ratios were investigated. The deactivation of the catalysts was also evaluated. The selectivity for the hydrocarbons obtained in the bio-oil was 18.99% at conditions of 550 °C reaction temperature and 20 wt.% HZSM-5 catalyst usage with no closure time. When the closure time of the fixed bed reactor was 1 h, the selectivity of the hydrocarbons reached 95.28%, and the heating value reached 32.5 MJ/kg; however, the organics yield in the liquid product was only 6.2%. This investigation verified that the quality of the bio-oil could be improved significantly through the closure of the reactor, which could be due to pyrolysis vapors that could be treated by the coupling effect between a high pressure and catalytic pyrolysis.

Keywords: Catalytic pyrolysis; Pine sawdust; HZSM-5; Reactor closure; Bio-oil

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INTRODUCTION

Biomass pyrolysis technology has attracted increasing attention because it can convert renewable lignocellulosic biomass into high-energy density liquid fuel with the potential to be used as a substitute for petroleum fuel (Dobele *et al.* 2007). Biomass pyrolysis is a process in which biomass undergoes decomposition rapidly at a moderate temperature to produce a liquid product called bio-oil. Crude bio-oil is dark brown, acidic, and thermally and chemically unstable, and it contains a large amount of oxygenated compounds with a low heating value. This is a drawback to its application; thus, it is essential to improve the quality of bio-oil to enable widespread utilization. Several approaches for upgrading bio-oil, such as reduced pressure distillation (Zheng and Wei 2011), reaction rectification (Xu *et al.* 2008), catalytic hydrogenation (Zhao *et al.* 2009), and catalytic pyrolysis (Lu *et al.* 2012) have been reported in the literature. Among these, catalytic pyrolysis is considered one of the most promising for large-scale applications because of its fast reaction rate and reliability; furthermore, it does not require additional facilities or processing steps.

Various types of catalysts, such as noble metals (Rh, Pd) supported by metal oxides or chars, transition metals (Ni, Co, Mo) supported by metal oxides, zinc oxide, magnesium oxide, aluminum oxide, and molecular sieves (ZSM-5, MCM-41, SBA-15) have been studied for their usefulness in the process of biomass catalytic pyrolysis

(Bridgwater 2012; Stefanidis *et al.* 2011; Bao *et al.* 2006; Mihalcik *et al.* 2011). The HZSM-5 catalyst has some advantages, such as sufficient acid sites and a specific pore structure; thus, it has been applied widely for catalytic deoxygenation in the petrochemical industry.

Due to the good catalytic performance of HZSM-5, it has also been studied extensively for bio-oil upgrading. Chen *et al.* (1986) verified that glucose and xylose could be converted to hydrocarbons by HZSM-5; however, the liquid yield decreased significantly. Thangalazhy *et al.* (2012) reported 25 wt% of carbon in the biomass as aromatic hydrocarbons from the catalytic pyrolysis of algae using HZSM-5. Adjaye and Bakhshi (1995a,b) reported that the weight ratio of hydrocarbons in the bio-oil reached up to 27%. They further verified that Brønsted acid sites played the key role in the deoxygenation reaction. Through increasing the quantity of the Brønsted acid sites to decrease the ratio of SiO_2/Al_2O_3, Foster *et al.* (2012) demonstrated that an increase in the quantity of the Brønsted acid sites favored hydrocarbon generation in bio-oil. However, catalysts with a SiO_2/Al_2O_3 ratio that was too low were deactivated rapidly due to severe coking. Therefore, HZSM-5 with a SiO_2/Al_2O_3 ratio of 30 to 60 was considered much more suitable for the catalytic deoxygenation of pyrolysis vapor.

One of the most popular bio-oil upgrading technologies is the bio-oil hydrogenation as described in Vispute *et al.* (2010). The characteristics of the technology include the usage of expensive metal catalysts, too much consumption of hydrogen, and relatively harsh reaction conditions; such factors have tended to prevent the industrial acceptance of the technology up to now. Researchers generally have focused on mixing biomass samples and the HZSM-5 catalyst in the reactor, or they had the pyrolysis vapor flow across the downstream catalyst bed directly (Li *et al.* 2008; Williams and Nugranad 2000). However, the pyrolysis vapor does not have enough residence time in the catalyst bed in the course of such a catalyst utilization method, which leads to lower hydrocarbon generation in the bio-oil. This upgraded bio-oil still cannot satisfy most applications based on such an insufficient catalytic pyrolysis.

In view of the issues just described, a new method to improve the quality of bio-oil is necessary for the development of biomass pyrolysis technology. It is worth bearing in mind that the quality of bio-oil may be much more important, although at the cost of reducing the quantity of bio-oil unavoidably. Pine sawdust was used as the pyrolysis material in this study due to the fact that Chinese Pine is the dominant species in coniferous forests of China (Ji *et al.* 2011). A goal of this study was to increase the selectivity of the hydrocarbons in bio-oil through closure of the reactor. By such an approach the pyrolysis vapors can be treated by the coupling effect between high pressure and catalysts in the closed reactor, which reaches the twin objectives of increasing the hydrocarbon selectivity and improving the bio-oil quality.

EXPERIMENTAL

Materials and Catalysts

The pine sawdust used in this investigation as a raw material was obtained from a local wood processing factory. Prior to use, the sample was dried at 105 °C in an oven up to a constant weight. Table 1 lists the characteristics of the sawdust.

The HZSM-5 catalyst in this study was commercially available and obtained from ZhuoYue Catalyst Co. (Shanghai, China). The catalytic materials were calcined at 500 °C for 4 h and stored in a desiccator before use. According to the technical information the manufacturer provided, the SiO_2/Al_2O_3 ratio of the HZSM-5 catalysts is 60 and the surface area is $\geqslant 330 m^2/g$. In a typical catalyst-regeneration experiment, the HZSM-5 catalyst mixed with chars was collected and calcined in a furnace at 500 °C in the presence of air for 6 h.

Table 1. Physicochemical Characteristics of Pine Wood Used in this Study

Analysis items	Values
Chemical composition (wt.%)	
Cellulose	40.9
Hemicellulose	30.4
Lignin	28.7
Proximate analysis (wt.%)	
Water	14.60
Combustibles	84.91
Ash	0.49
Ultimate analysis (wt.%)	
C	49.41
H	6.28
N	0.24
O	44.07

Apparatus and Experimental Parameters

As shown in Fig. 1, the catalytic pyrolysis system was composed of a 316 stainless steel, 3-cm-diameter, 40-cm-long reactor tube and a solid-tube furnace (Y-Feng Co., Shanghai, China). The furnace was equipped with a single set-point temperature controller for a maximum working temperature of up to 1200 °C. Before the experiments, turning the switches 4 and 5 on, N_2 was introduced into the reactor for 3 min to ensure an environment having an absence of oxygen. Then, the switch was turned off immediately. When the reaction temperature reached the desired value, the pine sawdust mixed with catalysts or silica sand for the catalytic and non-catalytic tests, respectively, was placed in the center of the tube and was supported by silica wool. The volatiles produced in the pyrolysis process entered into the downstream condensation system, which was composed of a vertically placed condenser and three 250-mL flasks dipped into an insulation box filled with glycol at a temperature of -20 °C. The condensable components in the volatiles were condensed and collected in the flask.

In an experiment with no closure time, switch 5 was kept on and the pyrolysis vapor left the reactor and flowed into the condenser. Each sample ran for 30 min to ensure that the entire pyrolysis vapor flowed through the cold flasks. In an experiment with reactor closure, switch 5 was kept off up to the set time and then was turned on slowly. The pyrolysis vapor flowed into the condenser, and the catalytic pyrolysis process ended after 30 min. After the experiments, the liquid collected in the flasks and the solid that remained in the reactor were quantified by weight. The gaseous product was quantified by the difference.

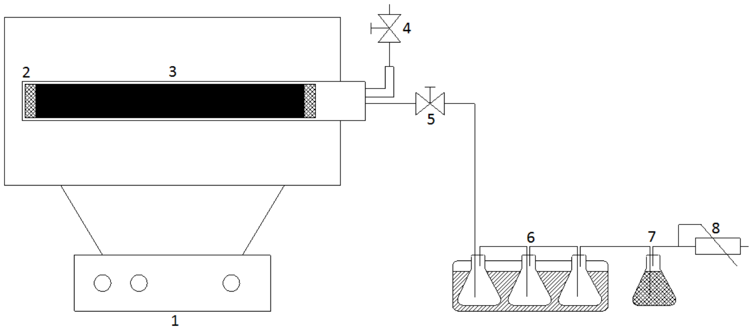

Fig. 1. Schematic diagram of experimental setup (1-furnace; 2-quartz wool; 3-pine sawdust mixed with quartz sand or HZSM-5 catalyst; 4, 5-switching valves; 6-a glycol solution bath; 7-filter; 8-soap flow meter)

Characterization

The water content of the bio-oil was determined by Karl-Fischer titration (Mettler Toledo Co., Sweden). The model number of the Karl Fischer titrator was KF-1. The calorific value of the bio-oil was determined using an Auto Adiabatic Bomb Calorimeter (Nasren Co., Shanghai, China). The chemical compositions of the bio-oil were analyzed using a GC/MS-QP2010 SE device (Shimadzu, Japan), and the compounds were detected using a Mass Selectivity (MS) detector equipped with a Rtx-5MS (30m × 0.25mm × 0.25μm) capillary column. The amount injected was 1 μL, and the split ratio was 25:1. Helium gas was employed as a carrier gas at a constant flow rate of 1.2 mL/min. The heating of the column started at 50 °C, where it was held for 5 min; then, the temperature was increased to 250 °C at a rate of 4 °C/min, at which point it was held for 5 min. The temperature of EI was 280 °C. The mass spectra obtained by GC-MS were interpreted based on an automatic library search (Wiley & NIST). Based upon such an analysis, the similarity of chemicals in the bio-oil by GC-MS detection lower than 78 was called "unidentified materials." The capillary column used in this study was not able to separate small organic chemicals, such as methanol, ethanol, formic acid, and acetic acid; thus, the change in small organic chemicals could not be analyzed in this study.

RESULTS AND DISCUSSION

The Influence of HZSM-5 Catalyst on the Distribution of Pyrolysis Products

Due to the finding that a higher proportion of liquid product (the bio-oil) can be obtained at a pyrolysis temperature of 550°C when using pine wood (Wang *et al.* 2009; Sun *et al.* 2011), the pyrolysis and catalytic pyrolysis of pine sawdust were carried out at a 550 °C reaction temperature in the fixed bed reactor, as shown in Table 2. As expected, the organics in the bio-oil decreased from 30.3 to 17.8 wt% and the water content increased from 19.2 to 24.6% when the pine sawdust was mixed with 20 wt% HZSM-5 catalyst as the pyrolysis material. Most of the organics reacted to hydrocarbons and water through deoxygenation; similar tendencies have been observed by other researchers (Wang *et al.* 2010; Mihalcik *et al.* 2011). With an increase in closure time from 0 to 1 h for 20 wt% HZSM-5 usage, organics in the bio-oil decreased sharply, from 17.8 to 6.2 wt%, and the water in the bio-oil increased from 24.6 to 30.3 wt%, which again shows that water is the main product of the deoxygenation reaction of pyrolysis vapor. Meanwhile, the gaseous product increased from 30.3 to 36.9 wt% and the solid char decreased slightly from 27.3 to 26.6 wt% with increasing closure time, which can be explained by the further decomposition of the solid fraction and secondary reactions of the liquid fraction of volatiles in the reactor.

With an increase in the quantity of HZSM-5 from 5 to 50 wt%, similar tendencies to the increase in the closure time were observed; the organics in the bio-oil decreased from 7.8 to 5.5 wt%, and the water content increased from 28.6 to 32.1 wt%. This indicated that longer closure time and more HZSM-5 may have a similar mechanism for the deoxygenation reaction of pyrolysis vapor. The heating value of the organics increased to 36.7 MJ/kg with 50 wt.% HZSM-5 with a 1-h closure time, a value that is similar to that of gasoline.

This study helps to open a new route to improve the quality of the bio-oil through the approach of closing the reactor. The 7.8 wt.% organics mainly consisted of hydrocarbons with the heating value of 29.3 MJ/kg on pine sawdust was obtained at the condition of 20wt.% HZSM-5 with 20 min closure time, and the organics were easily separated from the bio-oil. The quality of bio-oil was significantly higher than the bio-oil obtained from fast pyrolysis with the heating value of ~17 MJ/kg and with ~25% water that cannot readily be separated, as described in Bridgwater *et al.* (2012).

Table 2. Comparison of Bio-Oil Compositions between Pyrolysis and Catalytic Pyrolysis of Pine Sawdust (20 g pine sawdust, 550 °C reaction temperature)

Reaction Condition	Organics in bio-oil (wt.%)	Water in bio-oil (wt.%)	Gas yield (wt.%)	Char yield (wt.%)	*Heating value (MJ/kg)
The pyrolysis of pine sawdust	30.3	19.2	25.6	24.9	23.6
20 wt.% HZSM-5 with no closure time	17.8	24.6	30.3	27.3	26.3
20 wt.% HZSM-5 with 20 min closure time	7.8	28.4	36.3	27.5	29.3
20 wt.% HZSM-5 with 1 h closure time	6.2	30.3	36.9	26.6	32.5
5 wt.% HZSM-5 with 1 h closure time	9.3	27.6	35.9	27.2	27.7
50 wt.% HZSM-5 with 1 h closure time	5.5	31.0	37.1	26.4	36.7
50 wt.% used HZSM-5 with 1 h closure time	11.2	27.2	34.4	27.2	26.9
50 wt.% regenerated HZSM-5 with 1 h closure time	5.6	30.6	36.8	27	32.0

* Heating value = High heating value of organics in the bio-oil

Effect of HZSM-5 Catalyst on Bio-oil Composition

A comparison of the bio-oil composition between the pyrolysis and the catalytic pyrolysis of pine sawdust is shown in Table 3. The bio-oil from the pyrolysis of pine sawdust was extremely complicated and consisted of 2.26% alcohol, 6.65% aldehyde, 37.67% ketone, 5.07% ester, 5.05% furan, 33.3% phenol, and no hydrocarbons. Alonso *et al*. (2010) reported that the condensation reaction from aldehyde, ketone, and alcohol in the bio-oil led to large molecular chemical generation, which increased the viscosity of the bio-oil during the storage process. Bridgwater *et al.* (2011) reported that the key to improving the stability of the bio-oil was to reduce the content of aldehyde and ketone in the bio-oil. In this study, compared with pine sawdust pyrolysis, the selectivity of the aldehyde and ketone in the bio-oil decreased from 6.65% and 37.67% to 5.2% and 21.78%, respectively, when pine sawdust was mixed with 20 wt.% HZSM-5. The phenolic compounds increased slightly, from 33.3% to 35.62%; meanwhile, many hydrocarbons, such as toluene, p-xylene, and naphthalene, were also generated in the bio-oil. The increase in the phenolic compounds contributed to the competition between the decomposition of lignin and the catalytic pyrolysis of the phenolic compounds. When the lignin decomposition activity to produce phenols was higher, much more of the phenolic compound was generated in the bio-oil.

Table 3. Comparison of Bio-Oil Compositions between Pyrolysis and Catalytic Pyrolysis of Pine Sawdust (20 g pine sawdust, 550 °C, 20 wt.% HZSM-5 catalyst or quartz sand to pine sawdust, no reactor closure)

Organic products	Area %	
	Pine sawdust	20wt.% HZSM-5 used
Total of the alcohol		
Cyclopropylcarbinol	2.26	1.71
Total of the aldehyde		*5.2*
Heptanal	1.93	2.55
2-Butenal	0.92	0.48
Butanedial	3.21	1.11
2-Furancarboxaldehyde, 5-methyl-	0.59	1.06
Total of the ketone		
2-Propanone, 1-hydroxy-	21.32	8.34
2(5H)-Furanone	1.71	1.21
2[5H]-furanone, (S)-5-Hydroxymethyl-	0.5	0.46
2-Pentanone, 4-hydroxy-4-methyl-	0.38	-
3-Buten-2-one, 3-methyl-	0.45	0.7
2-Propanone, 1-(acetyloxy)-	0.84	-
1,2-Cyclopentanedione	2.39	2.21
2-Butanone, 3,3-dimethyl-	0.63	0.66
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.81	2.32
Ethanone, 1-(2-hydroxy-5-methylphenyl)-	4.85	3.99
2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	2.79	1.89
Total of the ester		
1,6-Heptadien-4-ol	0.99	0.57
Acetic acid, methyl ester	-	2.23
Propanoic acid, 2-oxo-, methyl ester	4.08	1.82
Total of the furan		
Furfural	4.37	4.17
6-Methoxy-3-methylbenzofuran	0.68	0.68
Total of the phenol		
Phenol	0.4	0.96
Phenol, 2-methyl-	0.51	0.84
Phenol, 3-methyl-	0.75	1.4
Phenol, 2-methoxy-	6.33	5.52
Phenol, 2-methoxy-4-methyl-	8.99	9.26
1,2-Benzenediol	1.88	2.94
1,2-Benzenediol, 3-methyl-	0.34	0.97
Phenol, 4-ethyl-2-methoxy-	3.64	4.02

Eugenol	1.21	1.16
Phenol, 2-methoxy-4-propyl-	0.68	1.53
Vanillin	0.5	0.97
Phenol, 2-methoxy-4-(1-propenyl)-	7.39	6.05
Total of the Acid		
Benzeneacetic acid, 4-hydroxy-3-methoxy-	0.66	0.81
Crotonic acid	0.55	
4-Pentenoic acid	0.62	-
Total of the hydrocarbon		
Toluene	-	4.24
p-Xylene	-	3.97
Naphthalene	-	4.73
Naphthalene, 1-methyl-	-	4.57
Naphthalene, 2,6-dimethyl-	-	1.48
Others		
Oxazolidine, 2,2-diethyl-3-methyl-	0.84	1.18
2-Cyclopenten-1-one, 2-methyl-	0.45	-
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	0.47	-
2-Furanmethanol	4.66	1.1

Effect of Closure Time on Bio-oil Composition

The effect of closure time of the reactor on the bio-oil composition was studied at 20 wt.% HZSM-5 usage and a 550 °C reaction temperature. As shown in Fig. 2a, compared with no closure time, the aldehyde and ester chemicals disappeared completely when the closure time was 20 min; the ketone and phenol chemicals decreased from 23.53% and 35.62% to 2.1% and 31.98%, respectively. As expected, a great quantity of hydrocarbon was produced in 1 h of closure time, and only traces of ketone, furan, and phenol chemicals were detected by the GC/MS in the bio-oil. This indicated that nearly all of the oxygenated compounds were converted to hydrocarbons, while the pyrolysis vapors had sufficient residence time in the HZSM-5 catalyst bed.

Figure 3a-c shows the spectrogram of the hydrocarbons in the GC/MS. With an increase in closure time, the variety of the hydrocarbons increased to 5, 27, and 31 sequentially, and the content of the hydrocarbons increased to 18.99, 62.62, and 95.28%, respectively. The distribution of the hydrocarbons is shown in Fig. 2b, of which the number of carbon atoms refers to all the hydrocarbons with the corresponding carbon atoms and heterocyclic refers to all the hydrocarbons with more than 10 carbon atoms. When the closure time was lower than 20 min, there were many hydrocarbons with C6-C9; their numbers decreased significantly as the closure time reached 60 min. Meanwhile, hydrocarbons with more than 10 carbon atoms increased greatly. This could be explained based on an assumption that most of the phenolic chemicals finished the deoxygenation reaction and converted the hydrocarbons with more than 10 carbon atoms with an increase in closure time. This also indicated that the phenolic compounds were mostly obtained from the pyrolysis of lignin, which required a much longer reaction time to become decomposed or deoxygenated, as described by Fahmi *et al.* (2008).

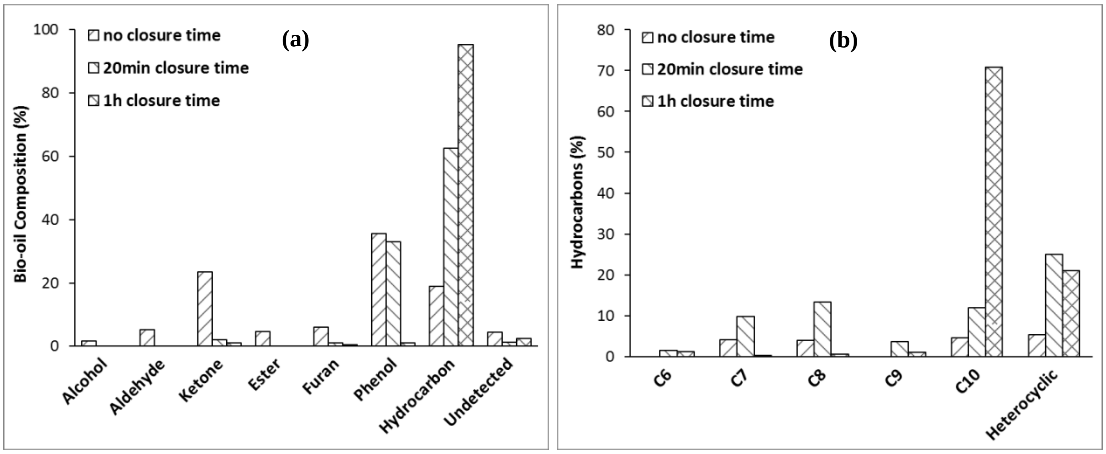

Fig. 2. The distribution of bio-oil composition (a) and hydrocarbon (b) as a function of the closure time of the reactor (550 °C, 20 wt.% HZSM-5 catalyst to pine sawdust)

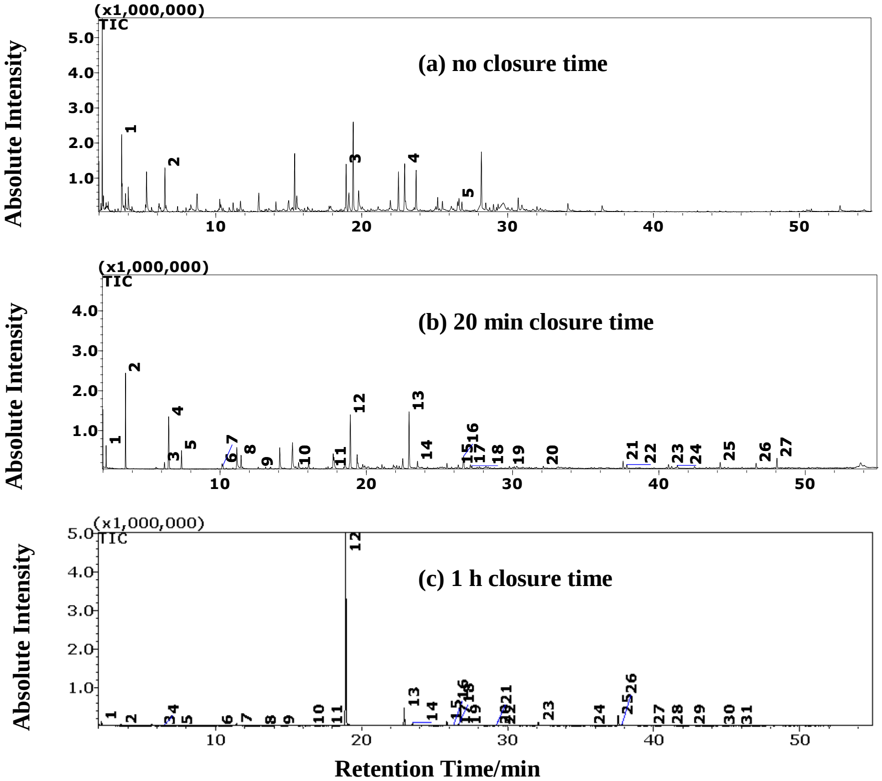

Fig. 3. GC/MS profile of bio-oil production via catalytic pyrolysis at 550 °C for 20% HZSM-5 catalyst to pine sawdust weight ratio

The reactor was closed in the process of pine sawdust pyrolysis so that the pyrolysis vapor would be stored in the reactor and build up to a certain pressure, which strongly favored the deoxygenation of the pyrolysis vapor. Meanwhile, the reactor closure also increased the vapor residence time. Both of these occurrences favored the deoxygenation reaction of the pyrolysis vapor in the HZSM-5 catalyst bed, which led to the production of many hydrocarbons. To improve the yield of bio-oil, the residence time of the pyrolysis vapor must be decreased. But as this occurs, the quality of the bio-oil is reduced; researchers have to find a balance point between the quality and the quantity of bio-oil. Therefore, the method proposed in this study has sparked a possibility to improve the quality of the bio-oil.

Effect of HZSM-5 on Bio-oil Composition

The effect of the amount of HZSM-5 on bio-oil composition was studied at 1 h of closure time of the reactor and 550 °C reaction temperature. As shown in Fig. 4a, the pine sawdust was mixed with 5 wt% HZSM-5; however, a certain amount of ketone and furan was detected in the bio-oil, and there were still many phenolic compounds, up to 29.8%. The content of the phenolic compounds in the bio-oil sharply decreased to 0.98% with 20 wt% HZSM-5 usage. When the percentage of HZSM-5 catalyst increased to 50 wt%, phenolic compounds were not detected, and traces of ketones and furans remained in the bio-oil. Therefore, Brønsted acid sites have a great effect on the catalytic deoxygenation of the oxygen compounds in the bio-oil.

The hydrocarbon distribution in the bio-oil as a function of the amount of HZSM-5 is shown in Fig. 4b. At HZSM-5 amounts of 5, 20, and 50 wt%, the selectivity of the hydrocarbons in the bio-oil reached 66.07, 95.28, and 97.82%, respectively. Thus, 20 wt% was considered an appropriate usage of HZSM-5 for bio-oil upgrading in this study. Compared with 5 wt% HZSM-5 usage, the selectivity of the hydrocarbons with carbon atoms ≥ 10 in the bio-oil was significantly higher with the 20 wt% HZSM-5 usage. Pyrolysis vapor was easier to decompose to smaller molecular hydrocarbons with sufficient Brønsted acid sites on the HZSM-5 catalyst by means of reactions such as cracking, decarboxylation, and decarbonylation. Similar results have been reported by Stefanidis *et al.* (2011).

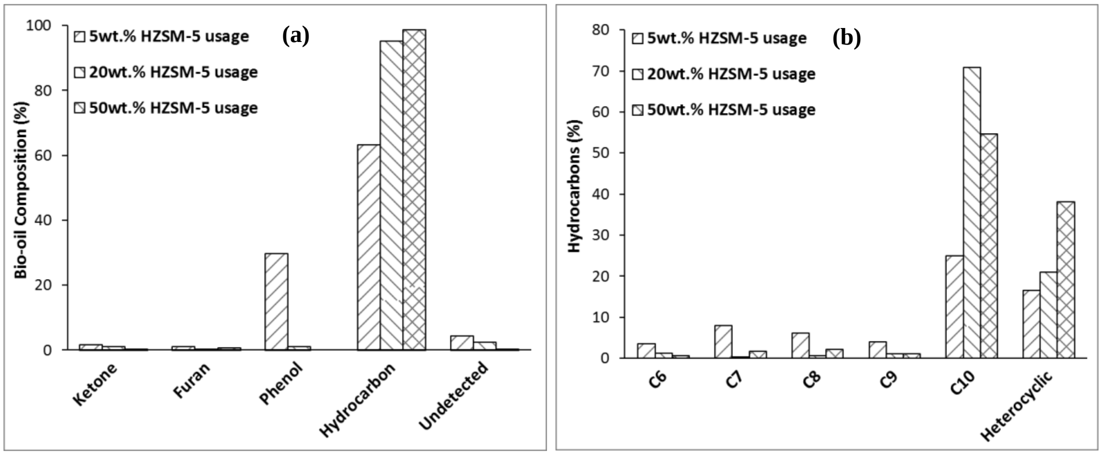

Fig. 4. The distribution of bio-oil composition (a) and hydrocarbon (b) as a function of the HZSM-5 catalyst to pine sawdust weight ratio (reaction conditions: 550 °C, 1 h closure time of the reactor)

Effect of Catalyst Regeneration on the Bio-oil Composition

To evaluate the deactivation of the used HZSM-5 catalyst, which was treated with a 1-h closure time at 550 °C in the former study, it was mixed with pine sawdust directly in the reactor. As shown in Fig. 5a, compared with the bio-oil obtained with the unused HZSM-5 catalyst, many ketone, furan, and phenol chemicals were detected by GC/MS. Meanwhile, the hydrocarbons decreased significantly, from 98.71% to 42.4%, indicating that the used HZSM-5 was deactivated sharply. The reasons for the HZSM-5 deactivation have been explained by various researchers. Vitolo *et al*. (2001) found that the quantities of Brønsted acid sites decreased significantly due to coking on the surface of the catalyst and that the activity of the catalyst was recovered by calcination at 500 °C for 4 h. Carlson *et al.* (2008) studied the pyrolysis of cellulose with HZSM-5 and found that the catalyst had severe coking due to its small pore size and strong acidity.

The selectivity of the phenolic compounds in the bio-oil with the used HZSM-5 reached 51.45%, which was higher than the 34.22% selectivity of the pyrolysis of pine sawdust. This may be because the deactivated HZSM-5 catalyst still has a high surface area, which is helpful for the pyrolysis of lignin to produce phenolic compounds. This result also demonstrated that phenol was hard to decompose on HZSM-5, in agreement with Gayubo *et al.* (2004). As shown in Fig. 5b, compared with the new HZSM-5 catalyst, the selectivity of C6-C9 hydrocarbons was higher and carbon atoms above 10 was decreased significantly in the bio-oil when used HZSM-5 was used as the catalyst.

This study included regeneration of the used HZSM-5 catalyst in a furnace at 500 °C in the presence of air for 6 h. The regenerated HZSM-5 was tested at 550 °C reaction temperature, 50 wt.% regenerated HZSM-5 usage for 1 h of closure time of the reactor. As Fig. 5 and Table 2 show, the yield of the organics, the compositions of the bio-oil obtained from the new HZSM-5, and the regenerated HZSM-5 were basically similar. The deactivated HZSM-5 could therefore be regenerated through the calcination. Park *et al.* (2010) reported that the activation of HZSM-5 catalyst used in the process of catalytic biomass pyrolysis was recovered through calcination at 500 °C for 12 h.

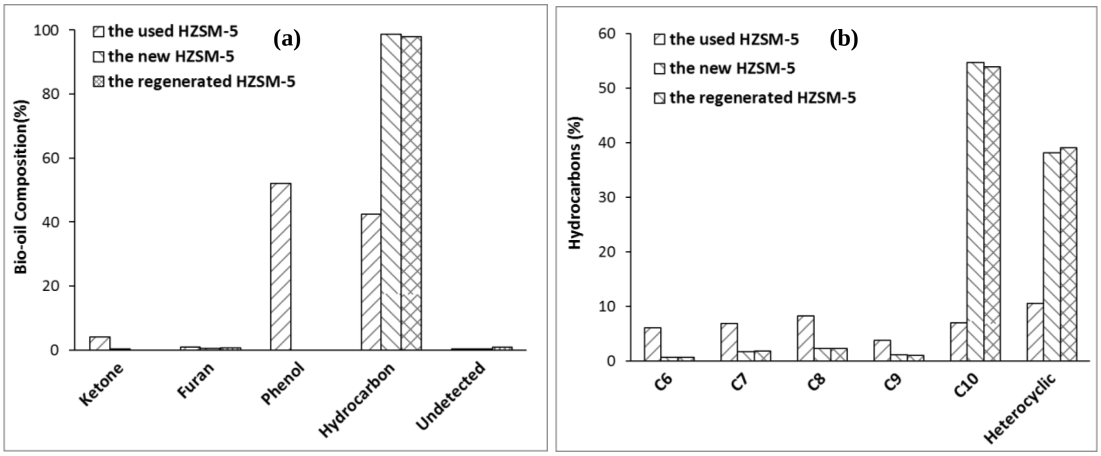

Fig. 5. The distribution of bio-oil composition (a) and hydrocarbon (b) for the new, used, and regenerated HZSM-5 (reaction conditions: 50 wt.% catalyst to pine sawdust, 550 °C, 1 h closure time)

CONCLUSIONS

1. The HZSM-5 catalyst exhibited suitability for the catalytic pyrolysis of pine sawdust. Several chemicals in the bio-oil, such as ketone and aldehyde, decreased significantly, and many hydrocarbons were generated.

2. The selectivity of the hydrocarbon in the bio-oil reached up to 95.28% at 550 °C reaction temperature, 20 wt% HZSM-5 catalyst usage, and 1 h of closure time. The yield of organics in the bio-oil was only 6.2%.

3. The heating value of the organics increased to 36.7 MJ/kg with 50 wt% HZSM-5 usage with 1 h of closure time, while the yield of organics in the bio-oil was only 5.5%.

4. The distribution of hydrocarbons in the bio-oil was affected by the quantities of the HZSM-5 catalyst and the closure time of the reactor. With an increase in the amount of HZSM-5 and closure time, the selectivity of the hydrocarbons with carbon atoms above 10 reached up to 70.87%.

5. The deactivated HZSM-5 catalyst was regenerated through calcination at 500 °C for 6 h, and the regenerated HZSM-5 exhibited a similar activity relative to the fresh catalyts.

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