Reduction of the Variety of Phenolic Compounds in Bio-oil *via* the Catalytic Pyrolysis of Pine Sawdust

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The objective of this study was to evaluate phenolic compounds produced from the catalytic pyrolysis of pine sawdust by commercial catalysts. Eight types of commercial catalysts consisting of SiO_2, montmorillonite, α-Fe_2O_3, HZSM-5 (Si:Al = 25:1), ZnO, γ-Fe_2O_3, HZSM-5 (Si:Al = 50:1), and nano-HZSM-5 (Si:Al = 50:1) were screened in a fixed bed reactor at a reaction temperature of 500 °C and a vapor residence time of 3 s. All the tested commercial catalysts exhibited different catalytic performances for the adjustment of the composition of the bio-oil. HZSM-5 (Si:Al = 25:1) significantly increased hydrocarbon production in the bio-oil, which is helpful for improving its heating value. The different types of phenols were reduced significantly from 17 to 7 with nano-HZSM-5 (Si:Al = 50:1); however, the phenols content also decreased from 32.6% to 23.28% compared with non-catalytic pyrolysis. Meanwhile, the addition of nano-HZSM-5 (Si:Al = 50:1) to the raw material provided the highest amount of furans (up to 38.8%) among the tested commercial catalysts. The inexpensive ZnO and γ-Fe_2O_3 also were surprisingly effective for the reduction of the variety of phenolic compounds detected by GC/MS, reducing that number from 17 to 10.

Keywords: Phenolic; Commercial catalysts; Catalytic pyrolysis

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INTRODUCTION

Because of increasing concerns about the energy levels of fossil fuels, biomass pyrolysis technology has attracted more and more attention because it can convert renewable lignocellulosic biomass into high-energy density liquid fuel with the potential of substituting for petroleum fuel (Dobele *et al.* 2007). Biomass pyrolysis is a process in which biomass decomposes at moderate temperatures of about 500 °C and has short reaction times in the absence of oxygen to produce liquid products called bio-oil, along with solid chars and incondensable gases. Crude bio-oil is dark brown, acidic, thermally and chemically unstable, and contains high-value oxygenated compounds such as phenols, organic acids, and alcohols. For bio-oil products to be used in a wider variety of applications, it is usually upgraded physically, chemically, and catalytically. Among these processes, catalytic pyrolysis is considered as the most promising method because it produces chemicals and fuels compatible with the current petrochemical infrastructure (Dickerson and Soria 2013; Lu *et al.* 2012; Wang *et al.* 2013). Compared with crude bio-oil, upgraded bio-oil is much more stable, has a higher heating value, and its composition can be adjusted within limits depending on different catalysts (Bridgwater 2012).

Most of the organics in bio-oil are vital industrial chemical compounds primarily derived from petroleum. The separation and application of these chemicals from bio-oil has attracted increasing attention in recent years. Phenolic compounds in the bio-oil are important raw materials and additives in industry (Lin and Juang 2009; Hu *et al.* 2013). A number of researchers have tried to separate phenol from bio-oil as a substitute for petroleum-based phenol (Gonza´ *et al.* 2004; Boucher *et al.* 2000; Kang *et al.* 2011). However, because lignin is one of the most complicated aromatic chemicals in earth, its pyrolysis products contain a variety of phenolic compounds. The presence of dozens of phenolic compounds in the crude bio-oil not only increases the difficulty of separation, but also decreases the value of the separated phenolic product. Compared with petroleum-based phenol, the cost of separating phenol from bio-oil is still unbearable. Lu *et al.* (2010) tested CaO as a catalyst in a Py-GC/MS instrument, and the results showed that CaO was an effective catalyst for reducing the number of different phenols. Azuara *et al.* (2013) verified that γ-Al_2O_3 catalyst has a good effect for maximizing the levels of phenols.

In the present study, eight commercial catalysts consisting of SiO_2, montmorillonite, α-Fe_2O_3, HZSM-5 (Si:Al = 25:1), ZnO, γ-Fe_2O_3, HZSM-5 (Si:Al = 50:1), and nano-HZSM-5 (Si:Al = 50:1) in a fixed bed pyrolysis reactor was screened in order to find a highly effective and low-cost catalyst to reduce the number of different phenols in bio-oil and improve the value of the phenolic compounds separated from bio-oil. Experiments performed in a fixed bed reactor have been developed by several researchers (Putun *et al.* 2005; Adam *et al.* 2006; Luo *et al.* 2010; Wang *et al.* 2010) to screen the commercial catalysts. Traditional zeolites were used as a baseline to evaluate the catalytic performance of other catalysts.

EXPERIMENTAL

Materials and Catalysts

The pine sawdust used in this investigation as a raw material was obtained in China. Prior to use, the sample was dried at 105 °C in an oven for 24 h. Table 1 lists the characteristics of the sawdust. All the catalysts used in this study were commercially available. The catalytic materials were calcined at 500 °C for 4 h and stored in a desiccator before use.

Table 1. Physicochemical Characteristics of the Pine Wood Used in This Study

Analysis items	Values
Chemical composition (wt.%)	
Cellulose	40.8±1.3
Hemicellulose	30.1±1.9
Lignin	28.6±2.2
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 (by difference)

Apparatus and Experimental Parameters

As shown in Fig. 1, the catalytic pyrolysis system was composed of a 316 stainless steel, 1-in.-diameter, 24-in.-long reactor tube with a complete vacuum sealing assembly and a solid-tube furnace. The furnace was equipped with a single set-point temperature controller for a maximum working temperature of 1200 °C. As a carrier gas, N_2 with a flow rate of 1.2 L/min was introduced into the reactor to ensure the absence of oxygen during the experiments. 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 vertically supported by silica wool. When the reaction temperature reached the desired value, 9 g of pine sawdust mixed with 1.8 g of catalyst or silica sand was placed into the reactor. The volatiles produced in the pyrolysis process were swept out and entered the downstream condensation system, which was composed of three flasks dipped into an insulation box filled with ice. The condensable components in the volatiles were condensed and collected in the flasks. Table 1 shows the experimental parameters for catalytic pyrolysis.

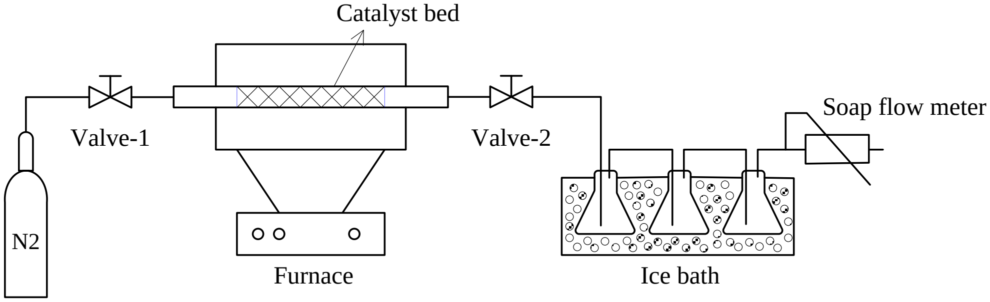

Fig. 1. Schematic diagram of experimental setup

In a typical experiment, each sample was run for 30 min to ensure that all of the pyrolysis vapor flowed through the cold flasks. 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 both quantified by weight. The gaseous product was quantified as the difference. Some earlier studies have also used the similar method (Putun *et al.* 2005; Adam *et al.* 2006) to screen the catalysts. The experimental parameters are shown in Table 2.

Table 2. Experimental Parameters of the Pyrolysis and Catalytic Pyrolysis of Pine Sawdust

Parameters	Pyrolysis/Catalytic pyrolysis
Biomass	Pine sawdust
Weight of biomass (g)	9
Pressure (atm)	1
Catalyst loading (wt.%)	-/20
Reaction temperature (°C)	500
N_2 flow rate (l/min)	1.2
Vapor residence time (s)	3

Characterization

The chemical composition of the bio-oil was analyzed using a GC/MS-QP2010 SE (Shimadzu, Japan) device, and compounds were detected using a Mass Selectivity (MS) detector equipped with an Rtx-5MS (30 m × 0.25 mm × 0.25 μm) 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).

RESULTS AND DISCUSSION

Influence of Commercial Catalysts on the Distribution of Pyrolysis Products

The pyrolysis and catalytic pyrolysis of pine sawdust were carried out at a reaction temperature of 500 °C and a pyrolysis vapor residence time of 3 s in a fixed bed reactor. The yields are shown in Fig. 2. As expected, the organics in the bio-oil varied with the different commercial catalysts used; the highest yield, of 33.1% bio-oil and 33.8% char, was obtained for the pyrolysis of the pure pine sawdust. Only 26.4% bio-oil was obtained with the γ -Fe_2O_3 catalyst, and 28.4% char was obtained with HZSM-5 (Si:Al = 25:1). The highest yield of gas (44.4%) was obtained with the ZnO catalyst. More biomass was converted to gas, which indicated that the solid char experienced further decomposition and secondary reactions of the liquid fraction of volatiles under the action of the catalysts in the reactor (Wang *et al* 2006). Meanwhile, the low effective liquid collection equipment could be another reason for the high content of gases. The differences among bio-oil, char, and gas generated using the commercial catalysts showed that different catalytic mechanisms occurred during the process of the catalytic pyrolysis of pine sawdust.

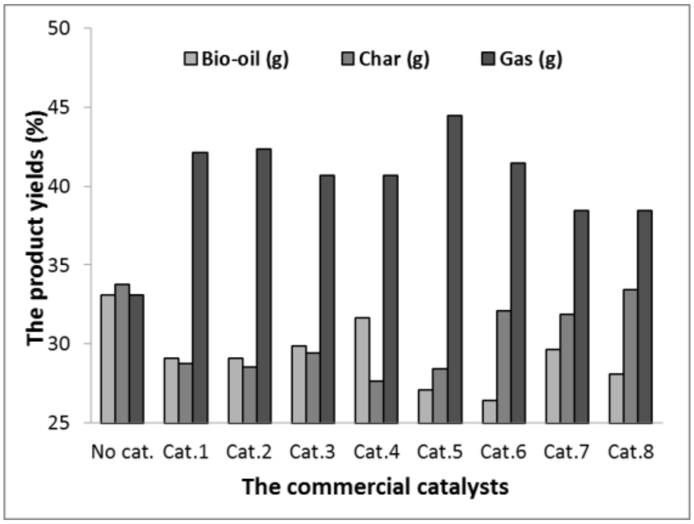

Fig. 2. The effect of catalysts on the product yields (9 g of pine sawdust, 500 °C, 20 wt.% catalyst addition). Cat. 1: SiO_2; Cat. 2: montmorillonoid; Cat. 3: α-Fe_2O_3; Cat. 4: HZSM-5 (Si:Al = 25:1); Cat. 5: ZnO; Cat. 6: γ-Fe_2O_3; Cat. 7: HZSM-5 (Si:Al = 50:1); Cat. 8: nano-HZSM-5 (Si:Al = 50:1))

Influence of Catalysts on Product Distribution of Bio-oil

Table 3 shows the difference in bio-oil composition for the tested catalysts. The identified compounds were classified into 9 groups: phenols, aldehydes, acids, esters, ketones, alcohols, furans, hydrocarbons, and others. Although the chromatographic peak area does not represent the actual content of the bio-oil, it is considered linear with its quantity (Lu *et al.* 2010). Compounds with high molecular weights that could not be analyzed by the GC-MS system were classified as others. Different catalysts were found to be important factors for product distribution and yield. Ketones and aldehydes are responsible for aging reactions in the bio-oil and greatly affect its quality (Lu *et al.* 2009; Zhao *et al.* 2010). High acid contents are corrosive and decrease the stability of the bio-oil (Huber *et al.* 2006). Esters in general reduce the heating value of the bio-oil. All of these compounds are thus considered undesirable when using bio-oil for energy production purposes.

The highest yield of the phenols was observed when using HZSM-5 (Si:Al = 25:1) as a catalyst, followed by HZSM-5 (Si:Al = 50:1). These yields were higher than those with other catalysts and non-catalytic pyrolysis, which indicated that a molecular sieve catalyst can significantly increase the phenolic composition of the bio-oil (Foster *et al.* 2012; Gopakumar *et al.* 2012). Stefanidis *et al.* (2011) obtained similar conclusions. In addition, it can be seen that the addition of nano-HZSM-5 (Si:Al = 50:1) to raw material provided the highest percentage of furans (up to 38.8%) among the tested commercial catalysts, which is attractive for further investigation on extracting furans from upgraded bio-oil.

Table 3. Comparison of Bio-oil Compositions between Pyrolysis and Catalytic Pyrolysis of Pine Sawdust (9 g of Pine Sawdust, 500 °C, 20 wt.% Catalyst Addition)

Parameters	Chemical Composition of Bio-oil (%)								
	No cat.	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7	Cat. 8
Phenols	32.6	25.6	27.7	24.7	35.6	23.2	26	33.1	23.3
Aldehyde	6.7	9.5	7.4	7.4	5.2	3.2	6.3	3.3	0.5
Acids	1.83	0	0	2.3	0.8	1.2	3.7	0.5	2.4
Esters	5.1	10.4	15.5	13.5	7.9	12.9	7.5	4.4	2.2
Ketones	37.7	27.8	23.4	26.9	21.8	24.4	27	28.9	18.3
Alcohol	2.4	0.7	0.9	1.5	1.7	6.5	0	0.4	0.2
Furans	11	15.2	12.8	10.2	4.9	11.9	13	9.8	38.8
Hydrocarbons	-	3.7	5.4	8.2	19	11.2	10.3	16.1	12.1
Other	8.4	7.1	6.9	5.3	3.1	5.5	6.2	3.5	2.2

Cat. 1: SiO_2; Cat. 2: montmorillonoid；Cat. 3: α-Fe_2O_3; Cat. 4: HZSM-5 (Si:Al = 25:1); Cat. 5: ZnO; Cat. 6: γ-Fe_2O_3; Cat. 7: HZSM-5 (Si:Al = 50:1); Cat. 8: nano-HZSM-5 (Si:Al=50:1)

Influence of Catalysts on the Phenolic Compounds of Bio-oil

The distribution of phenolic compounds in bio-oil is shown in Table 4. There were 17 phenolic compounds present in bio-oil obtained from the pyrolysis of pine sawdust. All the tested commercial catalysts were effective for the reduction of the number of different types of phenolic compounds, compared with non-catalytic pyrolysis. Significantly, the types of phenolic compounds decreased from 17 to 7 with nano-HZSM-5 (Si:Al = 50:1), and 40% of the phenolic compounds was 2-methoxyphenol, an important chemical compound used extensively in industrial applications. However, the contents of phenolic compounds also decreased from 32.6% to 23.28% compared with that obtained from non-catalytic pyrolysis. The number of different types of phenolic compounds decreased to 10 with catalytic pyrolysis using ZnO, γ-Fe_2O_3, or HZSM-5 (Si:Al = 50:1). Therefore, the nano-HZSM-5 catalyst was much more effective than these catalysts for reducing the variety of phenolic compounds in bio-oil. 2-Methoxyphenol, actually increased from 6.99% to 12.22% when using HZSM-5 (Si:Al = 50:1) as a catalyst. Among the tested catalysts, SiO_2, montmorillonite and α-Fe_2O_3 seemed to be mild catalysts, as most of phenolic compounds were unaltered. The commercial ZnO and γ-Fe_2O_3 are very cheap compared with HZSM-5 and nano-HZSM-5 catalyst, and they exhibited good catalytic performance. It is worth noting that γ-Fe_2O_3 showed high catalytic performance, but α-Fe_2O_3 is a mild catalyst, which indicated the different crystal structure of Fe_2O_3 exhibited completely different catalytic performance for the upgrading of bio-oil.

Table 4. Chemical Composition of Phenols in Bio-oil from Pyrolysis of Pine Sawdust (9 g of Pine Sawdust, 500 °C, 20 wt.% Catalyst Addition)

Name	Formula	Area Percentage								
		No Cat.	Cat. 1	Cat. 2	Cat. 3	Cat. 4	Cat. 5	Cat. 6	Cat. 7	Cat. 8
Phenol	$C_4H_6O_3$	1.7	2.45	1.79	2.75	0.96	2.27	3.29	3.57	2.78
Phenol, 2-methyl-	C_5H_8O	1.23	1.33	1.06	1.06	0.84	0.79	1.48	1.83	1.17
Phenol, 4-methyl-	$C_2H_2O_3$	0.82	1.05	0.72	0.91	-	-	1.09	1.16	1.74
Phenol, 3-methyl-	C_5H_6O	1.02	1.13	0.78	1.42	1.4	1.9	1.31	1.01	-
Phenol, 2-methoxy-	$C_5H_{10}O_2$	6.99	6.5	9.03	6.72	5.52	6.02	8.17	12.22	9.54
Phenol, 2,4-dimethyl-	$C_4H_6O_2$	0.4	0.36	0.24	-	-	-	-	-	0.33
Phenol, 3,4-dimethyl-, methyl-carbamate	$C_3H_6O_2$	0.36	-	0.26	-	-	-	0.27	0.62	-
Phenol, 2-methoxy-4-methyl-	$C_4H_8O_2$	8.74	6.94	8.96	7.4	9.26	7.19	7.81	8.65	6.4
1,2-Benzenediol	C_5H_8O	3.39	2.23	1.42	1.32	2.94	1.51	0.73	1.35	-
1,2-Benzenediol, 3-methyl-	$C_3H_7NO_2$	0.72	0.4	-	1.77	0.97	0.33	-	-	-
Phenol, 4-ethyl-2-methoxy-	$C_6H_{10}O_2$	2.35	1.43	1.87	-	4.02	1.51	1.42	1.77	1.32
1,2-Benzenediol, 4-methyl-	$C_5H_8O_2$	1.34	0.37	0.23	-	-	-	-	0.9	-
Phenol, 2-methoxy-4-(1-propenyl)-	$C_5H_4O_2$	0.71	0.28	0.24	0.51	6.05	0.5	-	-	-
Eugenol	$C_4H_2O_3$	0.57	0.32	0.3	-	1.16	-	-	-	-
Phenol, 2-methoxy-4-propyl-	$C_5H_4O_2$	1.46	0.69	0.59	1.14	1.53	1.2	0.38	-	-
Vanillin	$C_6H_{10}O$	0.34	-	-	0.5	0.97	-	-	-	-
2-Propanone, 1-(4-hydroxy-)-	$C_6H_{12}O_2$	0.75	-	-	0.33	-	-	-	-	-
Total of Phenolics		32.6	25.92	27.89	25.5	35.6	23.22	25.95	33.08	23.28

Cat. 1: SiO_2; Cat. 2: montmorillonite；Cat. 3: α-Fe_2O_3; Cat. 4: HZSM-5 (Si:Al = 25:1); Cat. 5: ZnO; Cat. 6: γ-Fe_2O_3; Cat. 7: HZSM-5 (Si:Al = 50:1); Cat. 8: nano-HZSM-5 (Si:Al = 50:1)

CONCLUSIONS

1. The HZSM-5 (Si:Al = 25:1) catalyst significantly increased hydrocarbon production in the bio-oil, which is helpful for improving the heating value of the bio-oil.

2. The number of different types of phenols was decreased significantly, from 17 to 7, with nano-HZSM-5 (Si:Al = 50:1); however, the contents of phenols also decreased from 32.6% to 23.28% compared with non-catalytic pyrolysis.

3. The addition of nano-HZSM-5 (Si:Al = 50:1) to the raw material produced the highest amount of furans (up to 38.8%) among the tested commercial catalysts, which is attractive for further investigation on extracting furans from upgraded bio-oil.
4. SiO_2, montmorillonite, and α-Fe_2O_3 seemed to be mild catalysts, as most of phenolic compounds were unaltered.

5. As a cheaper catalyst, the inexpensive ZnO and γ-Fe_2O_3 also were found to be surprisingly effective for the reduction of the variety of phenolic compounds which were detected by GC-MS, reducing the number from 17 to 10.

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