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Short Communication

Phenol and phenolics from lignocellulosic biomass by catalytic microwave pyrolysis

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ABSTRACT

Catalytic microwave pyrolysis of biomass using activated carbon was investigated to determine the effects of pyrolytic conditions on the yields of phenol and phenolics. The high concentrations of phenol (38.9%) and phenolics (66.9%) were obtained at the temperature of 589 K, catalyst-to-biomass ratio of 3:1 and retention time of 8 min. The increase of phenol and its derivatives compared to pyrolysis without catalysts has a close relationship with the decomposition of lignin under the performance of activated carbon. The concentration of esters was also increased using activated carbon as a catalyst. The high content of phenols obtained in this study can be used either directly as fuel after upgrading or as feedstock of bio-based phenols for chemical industry.

1. Introduction

As the only renewable resource to be converted to liquid fuel, biomass has been realized as one of the most significant sustainable replacements for petroleum based fuels (Tang et al., 2009). Currently, bio-oil derived from biomass pyrolysis has drawn increasing attention as an alternative source to fuels and chemicals. The biomass pyrolysis can produce about 40% of liquid oil, with the potential to substitute petroleum-based oil (Tang et al., 2009; Peng et al., 2008; Xu et al., 2010a,b; Adjaye and Bakhshi, 1995). Bio-oil can be used as a liquid fuel or for the production of chemicals and high grade transportation fuels by upgrading and hydrodeoxygenation techniques. Potential renewable chemicals from bio-oil include phenolics and cyclic ketones for resins and solvents, levoglucosan and levoglucosenon for polymers and aromatic hydrocarbons for fuels and solvents (Elliot, 2004; Maher and Bressler, 2007).

Phenol and its derivatives are vital industrial chemical compounds found in myriad industrial products mainly produced from petroleum. Phenolic resins are typically cross-linked polymeric resins made from petroleum based phenol and its derivatives. Industrial products using phenol as feed such as phenol–formaldehyde and phenolic resins are relatively expensive as phenol price and its availability are linked to and determined by petroleum. Recently, a large number of attempts have been done to make substitution of the petroleum-based phenol in phenolic resins with cost-effective phenols derived from lignocellulosic materials, however, these techniques with low concentrations of biomass derived phenols are believed to have negative impacts on its effectiveness compared to commercial formulations based on petroleum derived phenol. Therefore, in order to reach the goal for a price competitive renewable resin, further research is required to meet these challenges to lower renewable resin costs and satisfy quality requirements (Effendi et al., 2008).

The fast pyrolysis oil from lignocellulosic materials contains a complex mixture of phenolic compounds which are the products primarily derived from lignin. Although a number of researches have been conducted on the preparation of phenolic resin such as phenol–formaldehyde using phenolic-riched pyrolysis oil as partial substitution of petroleum-based phenol, few works were done on how to make phenolics-enriched bio-oils.

In contrast with conventional heating mechanisms, where energy is first converted to heat then transferred along temperature gradients from the surface to the core of the material, microwaves induce heat at the molecular level by direct conversion of the electromagnetic energy into heat (Sobhy and Chaouki, 2010). Recently, some studies on pyrolysis started to use microwaves as heating resource to prepare biomass pyrolysis oil (Huang et al., 2008; Lei et al., 2009).

The objective of this study is to investigate the production of biomass derived phenol and phenolics by catalytic microwave pyrolysis of biomass under distinct reaction conditions, including the reaction temperature, retention time, and the ratio of catalyst

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to feedstock. An activated carbon (GAC 830 PLUS) was first used as a catalyst for phenol and phenolics production via microwave-induced pyrolysis.

2. Methods

2.1. Materials

Douglas fir (7 mm in diameter and 15 mm in length) was used as biomass feedstock which was purchased from Washington State, USA. The commercial activated carbon (GAC 830 PLUS) was purchased from Norit Americas Inc. GAC 830 PLUS is an acid washed granular activated carbon with high purity produced by steam activation from selected grades of coal. The chemical compositions of pyrolysis oil produced with and without using activated carbon were analyzed by a GC–MS.

2.2. Experimental procedure

A central composite experimental design (CCD) was employed in the catalytic microwave pyrolysis process (Table 1).The ratio of activated carbon (GAC 830 PLUS) to biomass (Douglas Fir) was varied from 1.32 to 4.86 but with a fixed total loading of 120 g. The reaction temperature and reaction retention time were varied with a fixed power input of 700 W. This power setting gave a constant heating rate of about 60 K min^{-1} before desired temperatures. The temperature was measured by an infrared temperature measurement attached to microwave reactor manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). After reaching desired reaction temperatures, the microwave reactor equipped with automatic temperature/power control used a minimum power (e.g. 0–100 W) to maintain the desired reaction temperatures. Detailed procedures of microwave pyrolysis and GC/MS (GC: Agilent 7890A; MS: Agilent 5975C) analysis were described in Lei et al. (2009, 2011).

3. Results and discussion

The product yield distributions from different reaction conditions were shown in Table 1. It can be seen that the liquid yields in this study were from 6.8 to 48.1 wt.% of biomass. But most of the observed results indicated that liquid yields were from 25% to 35%. High yields of gas and volatile were obtained. The gas yields were higher than 50% for most of the experiments and the volatile yields were higher than 75%. The volatile and liquid yields were in the range of conventional methods which indicated a close relationship between yields and using activated carbon as a catalyst, but detailed catalytic mechanism still needs to be explored in the future.

Table 1
Reaction conditions and experimental results.

#	T(K)	*t* (min)	Ratio	Liquid yield (%)	Gas yield (%)	Volatile (%)
1	723	4	2:1	35.1	54.0	89.1
2	723	12	2:1	29.3	56.5	85.7
3	623	12	2:1	48.1	40.5	88.6
4	623	4	2:1	20.3	46.5	66.8
5	673	8	2:1	26.1	42.1	88.2
6	623	12	4:1	6.8	66.2	73.0
7	723	12	4:1	27.8	54.5	82.2
8	623	4	4:1	17.5	57.1	74.6
9	723	4	4:1	23.1	53.9	77.0
10	673	8	4:1	38.3	50.4	88.7
11	757	8	3:1	26.4	57.5	83.9
12	589	8	3:1	12.5	43.0	53.4
13	673	8	4.68:1	24.6	51.7	76.3
14	673	8	1.32:1	30.2	34.8	65.0
15	673	8	3:1	31.0	44.6	75.6
16	673	14.73	3:1	22.8	53.8	76.6
17	673	1.27	3:1	30.7	48.8	79.5
18	673	4	3:1	30.7	48.1	78.8
19	673	12	3:1	36.2	50.0	86.2
20	673	15	–	50.2	13.1	63.3

Biomass pyrolysis was performed at different reaction temperatures with a heating rate of 60 K min^{-1}. Results indicated that the reaction temperature had significant effects on the yields of volatile and liquid. The liquid yield increased with the temperature from 589 to 673 K, but decreased at higher temperature such as 757 K. More biomass was converted to gas at high temperature, which was consistent with literature report (Wu et al., 2008). The solid yield decreased significantly from 30.9% to 18.9% as the temperature increased from 589 to 757 K.

The ratio of catalyst to biomass was observed as an important factor for product distribution and yield. A slight decrease in liquid yield was observed at the lower ratios of catalyst to biomass (<2), and a steady increase of liquid yields was observed when the ratio increased from 2 to 4. The ratios of catalyst to biomass from 3 to 4 were considered the optimum conditions for maximum yields of volatile and liquid gas yields increased from 35% to 52% when the ratio increased from 1.32 to 4 while the solid yield decreased significantly from 35% to 10%. After the catalytic pyrolysis, the catalyst was separated and reused at the same pyrolysis conditions. Results indicated that the catalyst can be reused two times with good stability and conversion efficiency. Further study on catalyst lifetime and regeneration will be investigated.

The maximum liquid and volatile yields were realized when the reaction time was 12 min. However, it can be seen from results that the effects of retention time on products distribution is not as significant as reaction temperature and catalyst to biomass ratio.

In order to further understand the chemical reactions and conditions to maximize phenolics content in bio-oil, the chemical compositions of bio-oil from activated carbon (GAC 830 PLUS) as a catalyst were identified and quantified by a GC/MS. The bio-oil samples were prepared from catalytic pyrolysis of Douglas fir by microwave heating from 589 to 673 K with different reaction time and amount of catalyst. The chemical compositions of bio-oil without using catalyst at 673 K and 15 min and 120 g biomass loading (#20 in Table 1) were also measured by the GC/MS. The results of the composition of typical bio-oil products were shown in Table 2.

Although extensive research has been carried out on the mechanism of thermal degradation of biomass, catalyzed biomass decomposition has not been well-studied. However, catalytic biomass decomposition does provide great potential for further development of upgrading and refining of bio-oil in order to produce high quality and cost competitive substitute for petroleum fuels. Bio-oil was mainly composed of phenols, aliphatic hydrocarbons, aromatic hydrocarbons, furan derivatives, and some acid, etc. Phenols in bio-oil include phenol, methyl phenol, ethyl phenols and methoxy phenols (Lei et al., 2009). The results indicated that phenol content presented in bio-oil from microwave-assisted pyrolysis of Douglas fir without catalyst was 0.91%, and the phenols were 31.7%. This result was in good agreement with previous literatures (Lei et al., 2009; Yang et al., 2010). The GC–MS spectra showed that the phenolics were increased to 66.9%, with the addition of activated carbon (GAC 830 PLUS) at temperatures from 589 to 623 K with different catalyst-biomass ratios and reaction time, and the amount of phenol was significantly increased to 39.0%.

Phenolics are produced from decomposition of lignin. A maximum yield of phenolics (66.9 wt.%) was obtained at the temperature of 589 K, with a catalyst to biomass ratio of 3:1 and reaction time of 8 min. High concentrations of phenol, 2-methyl phenol and 4-methyl phenol were produced from biomass pyrolysis at

Table 2
Chemical composition of bio-oil from microwave pyrolysis of biomass at different conditions[a].

Number	Retention time	Name	Formula	Area percentage %			
				Run1	Run2	Run3	Run4
1	3.15/3.171/3.192/3.203	Butanoic acid, methyl ester	$C_5H_{10}O_2$	8.69	10.68	0.64	2.50
2	4.108	1-Pentene, 2-methoxy-	$C_6H_{12}O$	ND	ND	ND	0.60
3	4.876	Acetic acid, hydroxy, methyl ester	$C_3H_6O_3$	ND	ND	0.95	ND
4	4.897	2-Hexene	C_6H_{12}	ND	2.21	ND	ND
5	5.896/5.907/5.97	Furfural	$C_5H_4O_2$	4.64	5.00	14.24	3.68
6	6.654/6.664	3,3-Dimethoxy-2-butanone	$C_6H_{12}O_3$	2.57	3.16	1.54	1.21
7	7.895/7.917	2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	2.85	ND	1.82	2.33
8	8.043/8.053/8.064	Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	1.53	ND	1.66	1.49
9	8.821	Butyrolactone	$C_4H_6O_2$	0.90	ND	ND	ND
10	8.874	2(5H)-Furanone	$C_4H_4O_2$	1.90	ND	ND	ND
11	8.895/8.916	Butane, 1,1,3-trimethoxy-	$C_7H_{16}O_3$	ND	1.10	ND	0.85
13	9.095	3-Furanmethanol	$C_5H_6O_2$	ND	ND	1.22	ND
15	9.632/9.642/9.684	2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	1.46	ND	7.09	2.11
16	10.442/10.484/10.494/10.568/10.6	Phenol	C_6H_6O	37.72	34.16	12.84	38.98
17	10.726	2-Cyclopenten-1-one, 2,3-dimethyl-	$C_7H_{10}O$	ND	ND	0.51	ND
18	10.789	Pentanoic acid, 4-oxo-, methyl ester	$C_6H_{10}O_3$	ND	ND	0.77	ND
19	11.967	2-Acetyl-5-methylfuran	$C_7H_8O_2$	0.94	ND	ND	ND
20	11.968	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	ND	ND	3.45	ND
21	11.967	2H-Pyran-2-one, 4,6-dimethyl-	$C_7H_8O_2$	ND	ND	ND	1.26
22	12.062	Norbornan-7-one	$C_7H_{10}O$	1.79	ND	ND	ND
23	12.073	4-Octyne	C_8H_{14}	ND	2.36	ND	ND
24	12.136	2-Cyclopenten-1-one, 2,3-dimethyl-	$C_7H_{10}O$	ND	ND	ND	1.04
25	12.494/12.525	Phenol, 2-methyl-	C_7H_8O	4.22	ND	3.11	5.89
26	12.494/13.156/13.167/13.188/13.209	Phenol, 4-methyl-	C_7H_8O	11.02	16.00	6.5	14.52
27	12.904/12.914	Butanedioic acid, methyl-, dimethyl ester	$C_7H_{12}O_4$	0.91	0.85	1.27	0.82
28	13.514/13.525/13.535/13.546	Phenol, 2-methoxy-	$C_7H_8O_2$	2.42	1.32	7.98	2.88
29	15.008/15.019	Salicyl alcohol	$C_7H_8O_2$	0.89	ND	ND	0.62
30	15.271	Phenol, 2,5-dimethyl-	$C_8H_{10}O$	1.73	ND	ND	ND
31	15.282	Phenol, 2,4-dimethyl-	$C_8H_{10}O$	ND	ND	2.17	1.81
32	15.292	Phenol, 3,5-dimethyl-	$C_8H_{10}O$	ND	1.94	ND	ND
33	15.882/15.85	Phenol, 4-ethyl-	$C_8H_{10}O$	0.62	0.71	1.08	0.72
34	16.587/16.597	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	ND	0.74	4.13	0.60
35	16.881/17.039	1,2-Benzenediol	$C_6H_6O_2$	ND	ND	1.65	0.87
36	19.007/19.038	Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	ND	0.73	1.89	ND

[a] Run 1, 623 K, 4:1 and 4 min; Run 2, 623 K, 4:1 and 12 min; Run 3, 673 K, 3:1 and 8 min; Run 4, 589 K, 3:1 and 8 min; ND, Not detectable.

temperatures of 589 and 623 K with different catalyst to biomass ratios and retention time. At high pyrolysis temperatures such as 757 K and high ratios of catalyst to biomass such as 4.7, the production of phenol and phenolics were not favored. This result is in good agreement with previous work done by Vasalos et al. (1988).

The concentration of esters presented in bio-oil prepared by using activated carbon as the catalyst was significantly higher than that in bio-oil without catalyst. The esters were 9.6% and 11.5% with retention time of 4 and 12 min, respectively at the same reaction temperature of 623 K and catalyst to biomass ratio of 4:1.

The yield of the main liquid products, such as phenol, phenolics, esters, furfural and its derivatives, was affected by both pyrolysis temperature and ratio of catalyst to biomass. High concentrations of mono-aromatic compounds such as phenol, 2-methyl phenol and 4-methyl phenol were observed. These high value compounds or their derivatives play critical roles in chemical industry, for example, phenols are significant synthetic materials in organic chemistry such as synthesis of PF resin, medicines and so forth. In this study, the feasibility of obtaining bio-oils with high concentration of phenols and other mono-aromatic compounds show the great potential of making use of bio-oils as sources of chemical industry (Dominguez et al., 2003;Yu et al., 2007). In conclusion, the roles of activated carbon (GAC 830) used in this study not only improve the yield of phenols but also enrich the kinds of esters that were expected in bio-oil upgrading.

4. Conclusions

This study investigated microwave pyrolysis of biomass under the performance of activated carbon and determined the effects of pyrolytic conditions on the yields of product distributions and phenols. The highest concentration of phenols in bio-oils was 66.9 wt.% (including 38.9% of phenol). Both the reaction temperature and the amount of activated carbon added played vital roles in the product distributions and phenolics concentrations. The high content of phenols obtained in this study can be used either directly as fuel after upgrading or as feedstock for chemical industry such as organic synthesis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2011.04.025.

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