Renewable phenols production by catalytic microwave pyrolysis of Douglas fir sawdust pellets with activated carbon catalysts

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HIGHLIGHTS

- Conducted biomass catalytic microwave pyrolysis with activated carbon as catalyst.
- Achieved high concentration of phenols (about 74%) in bio-oil.
- The first report using wood based activated carbon for phenols production.

ARTICLE INFO

ABSTRACT

The effects of different activated carbon (AC) catalysts based on various carbon sources on products yield and chemical compositions of upgraded pyrolysis oils were investigated using microwave pyrolysis of Douglas fir sawdust pellets. Results showed that high amounts of phenols were obtained (74.61% and 74.77% in the upgraded bio-oils by DARCO MRX (wood based) and DARCO 830 (lignite coal based) activated carbons, respectively). The catalysts recycling test of the selected catalysts indicated that the carbon catalysts can be reused for at least 3–4 times and produced high concentrations of phenol and phenolic compounds. The chemical reaction mechanism for phenolics production during microwave pyrolysis of biomass was analyzed.

1. Introduction

The dramatic rise of oil prices around the world has promoted the desire of reducing dependence on crude oil by developing alternatives for fossil fuels. More significantly, developing renewable and clean energy is further promoted by the desire of reducing the detriments caused by burning fossil fuels, such as the global warming and air pollution. Biomass has been identified as one of the most significant renewable resources on the earth to be converted to liquid fuel and has recently received considerable attentions when people seek for supplement of fossil fuels (Rocha et al., 1996; Tang et al., 2009; Isahak et al., 2012). Biomass is mainly composed of cellulose, hemicellulose and lignin. In general, there are two major methods for biomass conversion to fuels and chemicals: biochemical method and thermochemical processes which involve pyrolysis, liquefaction, and gasification (Huber et al., 2006; Yaman, 2004; Mohan et al., 2006). Pyrolysis of biomass is a thermal decomposition process of organic compounds in the absence of oxygen to obtain biochar, syngas, and bio-oil. Pyrolysis has been

widely used for production of liquid fuels and value-added chemicals (Yaman, 2004; Mohan et al., 2006; Bu et al., 2012; Chen et al., 2001), for example, aromatic chemicals from lignin pyrolysis bio-oil (Holladay et al., 2007), levoglucosan from pyrolytic product of cellulose, and furfural from pyrolysis of cellulose and hemicellulose (Zhu and Lu, 2010; Wild et al., 2009). Potential value-added chemicals from pyrolysis of biomass include phenolics for resins and foams, levoglucosenon for polymers, and aromatic hydrocarbons for fuels and solvents (Bu et al., 2012; Maher and Bressler, 2007; Czernik and Bridgwater, 2004).

It is known that more than 90% of phenols used for phenol–formaldehyde resin are from petroleum-derived phenols (Xu and Leitch, 2010). Therefore, with the depletion of fossil fuels and high cost of crude oils, an increasing interest has been recently directed to make use of biomass-derived phenolics as partial substitute for phenolic resin synthesis (Xu et al., 2010; Yi et al., 2012). Conversion of biomass into bio-oil and extraction phenol from bio-oils and partial replacement of petroleum phenols for resin synthesis have been developed through pyrolysis and liquefaction (Czernik and Bridgwater, 2004; Wang et al., 2009). However, there are only few researches on making phenolic rich bio-oils from pyrolysis of biomass (Bu et al., 2012; Wang et al., 2012; Salema and Ani,

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2012a,b). Lei and his colleagues at Washington State University have focused on production of phenolic rich bio-oil through catalytic microwave pyrolysis of biomass-derived feedstock (Bu et al., 2012).

The particle size was found to have significant impacts on the products yield during conventional pyrolysis of biomass (Sensoz et al., 2000) which requires size reduction due to the low heat transfer of large biomass particles. Fine particles are required for conventional pyrolysis but size reduction increases the capital cost and requires high energy input. Microwave pyrolysis is a process that heat transfers occur from the inside to the surface of biomass by microwave irradiation. Comparing with conventional pyrolysis, the advantages of microwave pyrolysis include fast and selective heating, energy efficiency and cost effectiveness since both energy and capital cost for size reduction and drying are not required for microwave pyrolysis, but required for conventional pyrolysis processes (Luque et al., 2012; Hu et al., 2012). However, the heat uniformity and process scaling-up are the main challenges of microwave pyrolysis in comparison with conventional pyrolysis (Luque et al., 2012). Recent studies in the field of microwave pyrolysis include the conversion of wood (Bu et al., 2012; Salema and Ani, 2012a,b; Wang et al., 2012), sewage sludge (Mendez et al., 2004), corn stover (Lei et al., 2009), microalgae (Hu et al., 2012) and waste automotive engine oil (Lam et al., 2012) into biofuels and value-added chemicals.

The previous study (Bu et al., 2012) showed that a bituminous coal based activated carbon as a catalyst has significant influence on products yield and chemical compositions of the phenolic rich bio-oil during microwave pyrolysis of biomass. This was also observed by Salema and Ani (2012a). In this study, activated carbons based on different carbon sources were used as catalysts. The objective of this study was to investigate the effects of different carbon source catalysts on products yield and the chemical composition of bio-oils from microwave pyrolysis of Douglas fir sawdust pellets. The catalysts recycling test were conducted and the chemical reaction mechanism of this process was analyzed.

2. Materials and methods

2.1. Materials

Douglas fir sawdust pellet (7 mm in diameter and 15 mm in length) was used as biomass feedstock as received (Bear Mountain Forest Products Inc., USA). Acid-washed granular activated carbon samples with high purity produced by steam activation, GAC 830 PLUS, DARCO 830, GCA 1240 PLUS and DARCO MRX, were kindly provided by Norit Americas Inc. (Marshall, TX, USA). Table 1 shows the characteristics of different granular activated carbons used in this study which were summarized from the technical datasheet of the supplier.

2.2. Microwave pyrolysis apparatus

A schematic diagram of the microwave pyrolysis system is shown in Fig. 1. The microwave pyrolysis system mainly consisted of several components: a 1000 W, 2.45 GHz microwave cavity, an
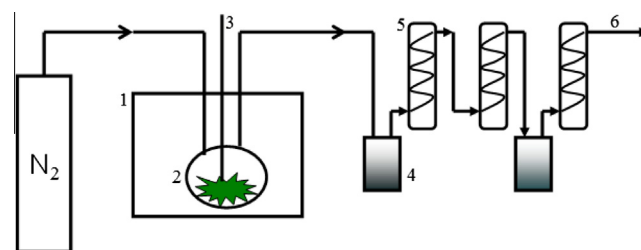

Fig. 1. The schematic diagram of lab scale microwave-assisted pyrolysis system: (1) Microwave cavity; (2) quartz reactor; (3) Infrared temperature sensor; (4) Condensable liquid (bio-oil); (5) Condensers; (6) Non-condensable syngas.
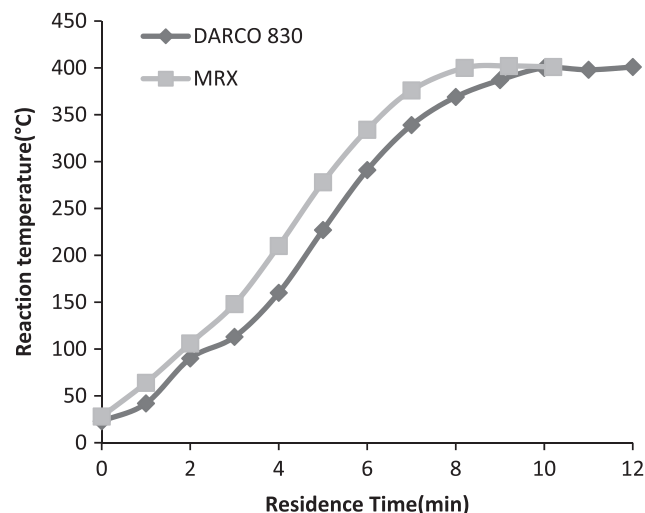

Fig. 2. Plot of residence time vs. reaction temperature during microwave pyrolysis of Douglas fir pellet using DARCO 830 and MRX catalysts.

infrared temperature sensor for temperature measurement, a 500 mL quartz flask inside the microwave oven which loaded the biomass, and a product cooling and collection system where the condensable liquid (bio-oil) was collected. The temperature of cooling water in condensers was about 5 °C. The microwave reactor was manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). A constant microwave power setting (700 W) was used. The reaction temperature of biomass was monitored by an infrared sensor through a closed end quartz tube which was penetrated to the central of the reaction flask. 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. The system was purged with nitrogen on a flow rate of 1000 mL/min for 15 min prior to pyrolysis reaction to maintain an oxygen-free environment.

2.3. Experimental procedure

In previous studies (Bu et al., 2011, 2012), the reaction temperature and ratio of catalyst to biomass were found to have

Table 1
Characteristics of AC used in this study.

AC types	Carbon source	Properties			
		Apparent density (g/mL)	Total pore volume (mL/g)	Surface area (m²/g)	Particle size (mesh)
GCA 1240 PLUS	Coconut shell	0.49	–	–	12–40
GAC 830 PLUS	Bituminous coal	0.51	–	–	8–40
DARCO MRX	Wood	–	0.95	650	10–30
DARCO 830	Lignite coal	0.39	0.95	650	8–30

Table 2
Yield distribution of catalytic microwave pyrolysis of Doulgas fir pellet using different catalysts.

AC types	Yield (%)			
	Bio-oil	Syngas	Biochar	Volatile
GCA 1240 PLUS	33.2	44.8	22	78
GAC 830 PLUS	31	44.6	24.4	75.6
DARCO MRX	26.5	52.67	20.83	79.17
DARCO 830	28.97	47.53	23.5	76.5
No AC	45.2	11.8	43	57

Fig. 3. Chemical composition of bio-oils produced from different AC catalysts by GC–MS analysis.

a significant influence on products yield distribution during microwave pyrolysis of biomass using activated carbon as a catalyst. The optimized reaction temperature and ratio of catalyst to biomass was 400 °C and 3:1, respectively. Therefore, the reaction conditions of this study were set at the ratio of catalyst to biomass (Douglas fir sawdust pellet) 3:1 with a fixed total loading of 120 g, reaction temperature of 400 °C, and reaction time of 8 min. The selected catalysts (DARCO 830 and MRX) were reused for repeat catalysis runs at the same reaction conditions without any treatment for catalyst recycling tests. Fig. 2 shows the relationship between residence time and reaction temperature during microwave pyrolysis of Douglas fir pellet. It can be seen that a constant heating power (700 W) gave stage heating rates of 30 °C/min, 40 °C/min before the first three minutes for Darco 830 and MRX, respectively, and about 60 °C/min for both catalysts between 3 and 7 min. It took
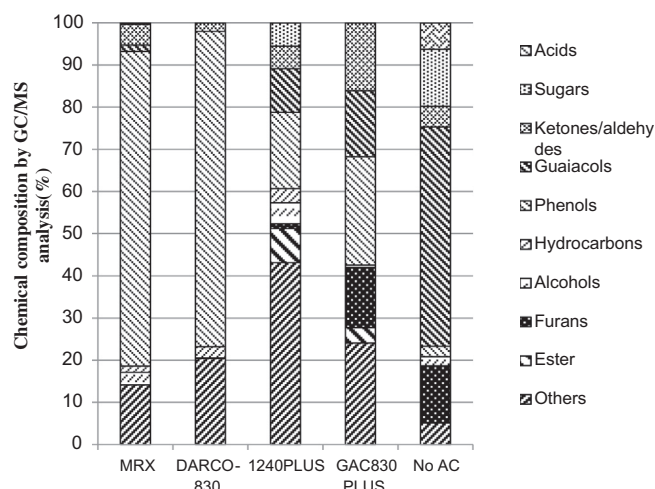
about 9 min to reach the desired temperature. During pyrolysis the heavier volatiles were condensed into liquids as bio-oils and the lighter volatiles escaped as syngases at the end of the condensers where they were either burned or collected for analysis. Char

Table 3
Main chemical compounds of bio-oils from microwave pyrolysis of biomass using different catalysts.

Categories	Compounds name	Retention time (min)	DARCO830 (% in area)	MRX (% in area)	GAC830 (% in area)	No AC (% in area)
Phenols	Phenol	13.68	42.52	30.35	12.84	0.68
	Phenol,2-methyl-	16	5.89	9.13	3.11	0.97
	Phenol,3-methyl-	15.82/16.3	0.22	–	–	–
	Phenol,4-methyl-	16.7	21.51	22.95	6.54	–
	Phenol,2,3/4/5/6-dimethyl-	19.1/19.9	2.24	6.18	2.17	0.89
	Phenol,3,4/5-dimethyl-	19.6/20.4	2.61	3.26		
	Phenol, 2/3/4-ethyl-	18.6/18.7	–	–	1.08	–
	Total		74.77	71.87	25.74	2.54
Guaiacols	Phenol, 2-methoxy-	17.2/17.3	–	0.71	7.98	5.32
	Phenol, 2-methoxy-4-methyl-	20.3/20.5	–	–	4.13	14.03
	Phenol, 2-methoxy-4-propyl-	25.3/25.4	–	0.14	–	–
	Phenol, 4-ethyl-2-methoxy-	22.9/23.0	–	0.48	1.89	4.98
	1,2-Benzenediol	17	–	–	1.65	3.67
	Phenol, 2-methoxy-4-propyl-	27.5	–	–	–	2.8
	Phenol, 2-methoxy-3-(2-propenyl)-	14.4	–	–	–	1.51
	Phenol, 2-methoxy-4-(1-propenyl)-	14.9	–	–	–	1.35
	1,2-Benzenediol, 3/4-methyl-	12.8	–	–	–	2.93
	Vanillin	15.1	–	–	–	1.51
	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	15.5	–	–	–	7.75
	2-Methoxy-4-vinylphenol	13.6				2.93
	Total		–	1.33	15.65	48.78
Furans	Furan, tetrahydro-2,5-dimethoxy-	6.6	–	–		1.07
	Furfural	8.7	–	–	14.24	2.83
	Total		–	–	14.24	3.9
Ketones/aldehydes	2-Cyclopenten-1-one	8.7/8.85	1.28	1.97	–	–
	2-Cyclopenten-1-one, 2-methyl-	11.0/11.23	0.47	0.63	1.82	0.29
	2-Cyclopenten-1-one, 3-methyl-	13.3	0.27	–	1.52	2.38
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	15.2	–	–	3.45	–
	2-Cyclopenten-1-one, 2,3-dimethyl-	15.64	–	–	0.51	–
	2-Cyclopenten-1-one, 3,4,4-trimethyl-	16.4	–	–	0.8	–
	Ethanone, 1-(2-furanyl)-	11.3/11.4	–	–	1.66	1.33
	2-Furancarboxaldehyde, 5-methyl-	13.0/13.1		0.43	7.09	1.64
	Maltol	10.7	–	–	–	1.15
	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	16	–	–	–	1.79
	Benzaldehyde, 3-hydroxy-4-methoxy-	15.1	–	–	–	1.78
	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	12.4	–	–	–	3.98
	Total		2.02	3.03	16.85	10.36
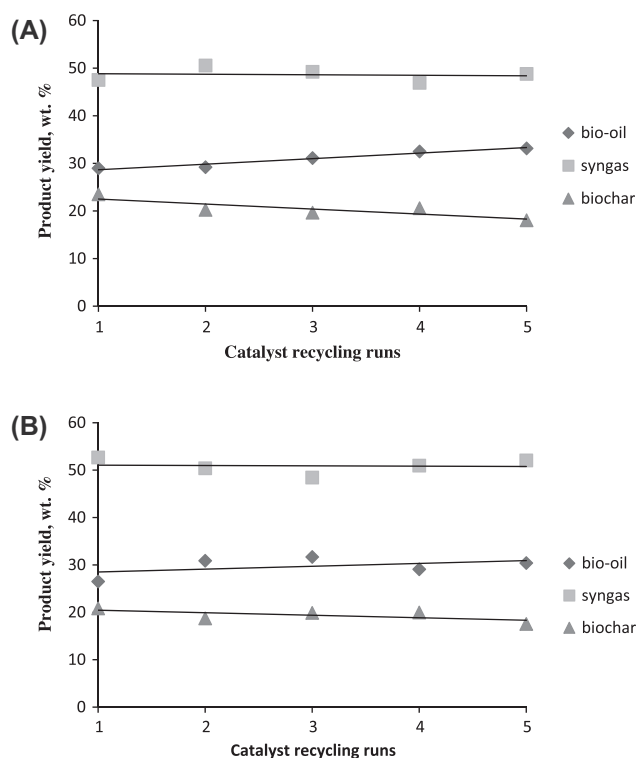
Fig. 4. Effects of catalyst reuse on products yield: (A) DARCO 830 and (B) MRX.

Fig. 5. Effects of catalyst recycling on chemical composition of bio-oils: (A) DARCO 830 and (B) MRX.

was left in the quartz flask. The weight of syngas product was calculated using the following equation:

$$\text{Weight of syngas} = \text{initial wood pellet mass} - \text{biooil mass} - \text{biochar mass} \quad (1)$$

2.4. GC–MS analysis of bio-oils

The liquid product was bio-crude oil collected after pyrolysis and condensation of volatile products. The chemical composition of bio-oils was determined with an Agilent gas chromatography–mass spectrometer (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was programmed to heat to 40 °C for 0.5 min followed by heating to 300 °C at a rate of 10 °C/min. The injection sample size was 1 μL. The flow rate of the carrier gas (helium) was 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector (Lei et al., 2009). Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library.

2.5. GC analysis of gas

A Carle 400 gas chromatograph (GC) (Chandler Engineering, Broken Arrow, OK, USA) with a thermal conductivity detector was used to determine the chemical composition of syngases.

3. Results and discussion

3.1. Effects of different catalysts on products yield

The obtained products (bio-oil, syngas and char) yield with and without carbon catalysts were shown in Table 2. The bio-oil yield with activated carbon addition were from 26.50 to 33.20 wt.% of biomass. The highest yield of bio-oils was obtained from GCA
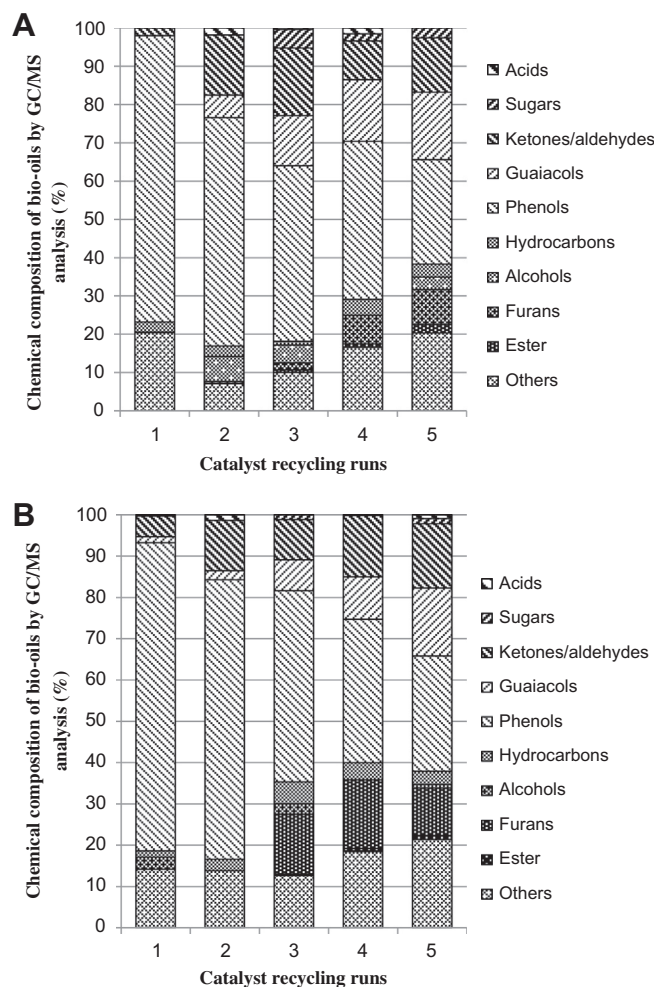
1240 PLUS. However, the yield of bio-oil without AC addition was obviously higher (45.20 wt.% of biomass) than those with AC additions. The syngas yield with AC as a catalyst was in the range of 44.60–52.67 wt.% of biomass, which were much higher than that without AC additions (11.80 wt.% of biomass). Similar phenomenon was also observed by others (Fernandez et al., 2009; Salema and Ani, 2012a,b; Hu et al., 2012). This should have a close relationship with activated carbon as a catalyst during microwave heating, which may be explained by the competing reaction or heterogeneous gas–solid reaction between the formation of liquids and gases. As a good microwave absorber, AC had a much higher temperature than the surrounding solids and gases during microwave heating (Jones et al., 2002); besides, the formation of hot spots due to microwave heating resulted in much higher temperature of solid than the average temperature measured (Fernandez et al., 2009). As a result, the high temperature promotes the secondary cracking of bio-oils and catalytic cracking of biomass (Fernandez et al., 2009; Hu et al., 2012).

It was observed that the char yields with AC addition (20.83–24.40 wt.% of biomass) were significantly lower than that without AC addition (43.00 wt.% of biomass), which means that the volatile yields (75.60–79.17 wt.% of biomass) using AC as a catalyst were increased comparing to the volatile yield (57.00 wt.% of biomass) without AC addition as shown in Table 2. This may be explained by the catalytic cracking of biomass due to high temperature of microwave heating using AC as a catalyst and a microwave

absorber (Fernandez et al., 2009; Fernandez et al., 2010; Omar et al., 2010; Hu et al., 2012).

3.2. GC–MS analysis of the bio-oil

Bio-oil is typically comprised of aldehydes, ketones, sugars, carboxylic acids, esters, phenolics, guaiacols, hydrocarbons, furan derivatives, and some unclassified compounds (Mortensen et al., 2011; Mohan et al., 2006). The chemical composition of bio-oils by GC–MS analysis was categorized according to their different functional groups as shown in Fig. 3, which indicates that the chemical composition of bio-oils was influenced by the addition of AC as a catalyst. The GC–MS spectra showed that the phenols content was 74.61% and 74.77%, in the upgraded bio-oils for MRX and DARCO 830, respectively, and the corresponding guaiacols content was 1.50% and 0%. However, phenols and guaiacols from the control without AC addition were 2.54% and 51.98% in the raw bio-oil, respectively. Therefore, the results revealed that the addition of AC as a catalyst had significant influence on the phenols and guaiacols content of bio-oils though the yield of bio-oils was decreased from 45% (non-catalytic) to about 26.50–33.20 wt.% of biomass from microwave pyrolysis with catalyst additions. It was observed that the main components of phenols were phenol, 2-methyl-phenol (o-cresol), 4-methyl-phenol (p-cresol), 2,4-di-methyl-phenol and 3,4-dimethyl-phenol. A maximum phenol yield of 42.52% was obtained for the upgraded bio-oil produced with the addition of MRX (wood based AC). The amount of phenol in the bio-oil was 30.35% from pyrolysis with DARCO 830 (lignite coal based AC) as a catalyst. The 4-methyl-phenol (p-cresol) content was 22.95% and 21.51% in the upgraded bio-oils with additions of MRX and DARCO 830, respectively. The results of main chemical compounds of bio-oils from catalytic microwave pyrolysis of biomass were shown in Table 3. Results revealed that the addition of different ACs had significant influence on the chemical composition of the produced bio-oils. As a result, MRX and DARCO 830 were selected for catalyst recycling tests in this study.

3.3. Catalyst recycling test

In order to further understand the lifetime and economic feasibility of the catalysts, DARCO 830 and MRX were selected to conduct catalyst recycling test. The selected catalysts were reused for 5 catalysis runs at the same reaction conditions (reaction temperature 400 °C, ratio of catalyst to biomass 3:1, reaction time 8 min) without any treatment.

3.3.1. Effects of catalyst recycling on products yield

Fig. 4(A) shows the effects of DARCO 830 recycling on products (bio-oil, char and syngas) yield distribution. It was observed that the liquid yield had an increasing trend with the catalyst reuse time. A linear model was obtained as shown in Fig. 4(A). The coefficient of determination (R^2) for this model was 0.95, suggesting that the model accurately predicted the liquid yield for recycling tests of microwave pyrolysis of biomass using DARCO 830 as a catalyst. The yield of char which were from 18.5 to 23.5 wt.% of biomass had a decreasing trend with the increase of runs as shown in Fig. 4(A). The similar phenomenon was observed for MRX catalyst as shown in Fig. 4(B) for the effects of catalytic recycling on bio-oils and char yield. This phenomenon may be explained by coking formation which had negative impacts on the secondary cracking of bio-oils. Results showed that the influence of catalyst recycling on syngas yield was not obvious.

3.3.2. Effects of recycled catalysts on chemical compositions of bio-oils

To further understand the chemical reaction of this process and the effects of catalyst recycling on the chemical composition of the

bio-oils, GC/MS was used to characterize the bio-oil as shown in Fig. 5. It can be seen from Fig. 5(A) that there is a decreasing trend for phenols content from 74.77% to 27.25% in the upgraded bio-oils for DARCO 830. An increasing trend (0–17.65% of bio-oils) of guaiacols was observed with the increase of catalyst recycling runs. Fig. 6(A) illustrates the effects of catalyst recycling on the amount of phenols and guaiacols for DARCO 830. Two linear models for predicting the amount variances of phenols and guaiacols were obtained as shown in Fig. 6(A). The coefficient of determination (R^2) for these two models was 0.98 and 0.94, respectively, implying these linear models are suitable to predict the amount of phenols and guaiacols during the recycling test of catalytic microwave pyrolysis of Douglas fir sawdust pellet using DARCO 830 as a catalyst. Fig. 5(B) shows the effects of catalyst recycling on chemical composition of the upgraded bio-oils for MRX. Similar trends for the amount of phenols and guaiacols with DARCO 830 were observed. The phenols content was reduced from 74.61% to 27.85% in the bio-oils after 5 recycling runs, and the guaiacols were increased from 1.5% to 16.48% in the bio-oils after 5 runs. Two linear models for predicting the amount variances of phenols and guaiacols with recycling runs were established as shown in Fig. 6(B) for MRX catalysts. The coefficient of determination (R^2) for these two models was 0.97 and 0.95, respectively, indicating these linear models accurately predict the variances of the amount of phenols and guaiacols during the recycling test of catalytic microwave pyrolysis of Douglas fir pellet using MRX as a catalyst. However, the amount of phenolic compounds were about 57% and 54% in the upgraded bio-oils for DARCO 830 used for 4 runs and MRX used for 3 runs, respectively. Therefore, the high concentration of phenolic compounds indicated that the selected AC catalysts can be reused for

(A) $y = -11.16x + 83.03$, $R^2 = 0.98$; $y = 4.54x - 3.08$, $R^2 = 0.94$

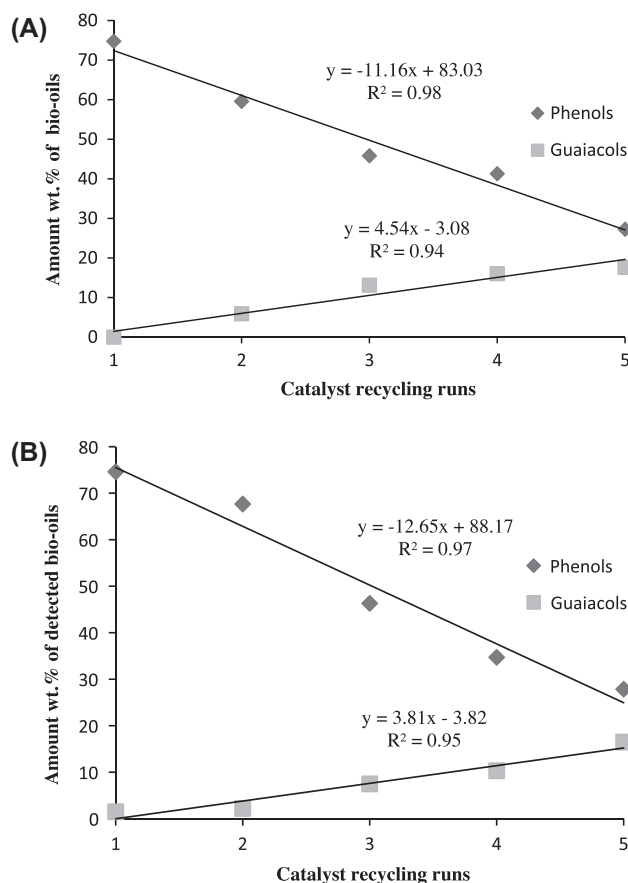(B) $y = -12.65x + 88.17$, $R^2 = 0.97$; $y = 3.81x - 3.82$, $R^2 = 0.95$

Fig. 6. Effects of catalyst recycling on amount of phenolics in the obtained bio-oils: (A) DARCO 830 and (B) MRX.

at least 3–4 times without any treatment for production of phenolic rich bio-oils during microwave-assisted pyrolysis of biomass.

GC/MS results implied that the concentration of furans and ketones/aldehydes presented in upgraded bio-oils increased obviously with the increase of recycling runs. The main chemical compounds of bio-oils were shown in Table 4 for catalyst recycling tests of catalytic microwave pyrolysis of biomass. The amount of furans was increased from 0% to 9.16%, after catalyst recycling runs for DARCO 830, while furans were increased from 0% to 16.59% for MRX. The concentration of ketones/aldehydes in bio-oils using DARCO 830 as a catalyst was increased from 2.02% to 17.66%, while ketones/aldehydes were increased from 4.96% to 15.52% for the bio-oils using MRX as a catalyst.

3.4. Reaction mechanism analysis

Pyrolyis oil can be separated into two fractions according to water solubility: the water-soluble fraction and water-insoluble fraction (Ni et al., 2006). The major components (hemicelluloses, cellulose, and lignin) of biomass decompose at different temperature ranges. In general, the decomposition of cellulose and hemicellulose occurs at low temperatures (200–400 °C) (Yang et al., 2007) and results in water-soluble fraction (small molecular compounds such as acid, ketones, aldehydes, sugars and furans). Lignin is the most heat-resistant component among the major components of lignocellulosic biomass, and it is typically decomposed in the temperature range of 280–500 °C, which generates the water-insoluble fraction (lignin-derived guaiacols and phenolics).

In the past two decades, a number of researches focused on production of H_2 by steam reforming of the water-soluble fraction of pyrolysis oil and made use of it for upgrading of lignin-derived guaiacols and phenolics (Wang et al., 1997; Marquevich et al., 1999; Marker et al., 2005). Endothermic reforming reaction occurs at high temperatures. The pyrolysis temperature in this study might not be high enough to promote the endothermic reforming reaction. However, as a good microwave absorber, the temperature
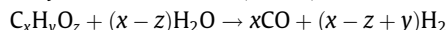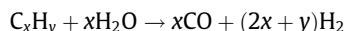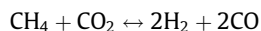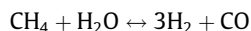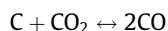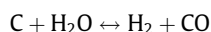
Table 4
Main chemical compounds of bio-oils from catalytic microwave pyrolysis of biomass at different catalyst recycles.

Categories	Compounds name	Retention time (min)	Yield (% in area)									
			D-1	D-2	D-3	D-4	D-5	M-1	M-2	M-3	M-4	M-5
Phenols	Phenol	13.68	42.52	22.35	18.5	9.62	6.98	30.4	21.5	17.7	12.8	9.2
	Phenol,2-methyl-	16	5.89	9.29	6.15	7.45	–	9.13	8.35	6.72	–	–
	Phenol,3-methyl-	15.82/16.3	0.22	–	–	12.6	10.3	–	–	0.27	12.7	–
	Phenol,4-methyl-	16.7	21.51	18.49	14	0.36	–	23	21.3	15.1	–	11
	Phenol,2,3/4/6-dimethyl-	19.1/19.9	4.73	3.12	0.75	5.25	2.68	6.18	0.67	3.43	–	0.7
	Phenol,3,4/5-dimethyl-	19.6/20.4	3.46	0	2.98	5.39	0.66	3.26	2.31	2.9	0.67	5.8
	Phenol, 2/3-ethyl-	18.6/18.7	–	0.26	2.88	4.26	3.86	–	5.08	2.68	–	0.3
	Phenol, 2/4-ethyl-2/3/4/6-methyl-	22.3	–	0.62	–	2.71	1.67	0.8	1.31	0.46	0.96	0.3
	Phenol, 2,4,6-trimethyl-	20.8/22.7	–	0.26	–	0.42	0.7	–	0.65	–	0.65	–
	Total		74.77	54.39	45.2	48.1	26.8	72.7	61.2	49.2	27.8	–
Guaiacols	Phenol, 2–methoxy-	17.2/17.3	–	2.82	2.8	3.09	2.79	0.71	1.74	2.09	3	3
	Phenol, 2-methoxy-4-methyl-	20.3/20.5	–	2.52	–	6.56	6.74	–	–	3.34	4.35	5.8
	Phenol, 2-methoxy-4-propyl-	25.3/25.4	–	–	–	1.8	1.6	0.14	–	0.45	–	1.5
	Phenol, 4-ethyl-2-methoxy-	22.9/23.0	–	0.35	6.18	3.35	3.19	0.48	0.47	1.28	1.96	3
	1,2-Benzenediol, 3/4-methyl-	22.2/23	–	–	2.33	0.18	1.84	–	–	0.32	–	–
	Total		0	5.69	11.3	15	16.2	1.33	2.21	7.48	9.31	13
Furans	Furan, 2,5-dimethyl-	8.2/8.4	–	0.37	–	–	–	–	–	–	–	–
	Furan, 2-ethyl-	9.97	–	0.21	–	–	–	–	–	–	–	–
	5-(Hydroxymethyl)-2-(dimethoxymethyl) furan	23.2	–	–	0.24	–	–	–	–	–	–	–
	Furfural	8.7	–	–	–	4.23	6.18	–	–	11.8	11.2	7.6
	Benzofuran	14.2	–	–	–	0.56	0.7	–	–	–	–	0.7
	Benzofuran, 2-methyl-	17.8	–	–	–	0.44	0.49	–	–	–	0.46	0.5
	Total		–	0.58	0.24	5.23	7.37	–	–	11.8	11.7	8.8
Hydrocarbons	2/3-Hexene, (E)-	7.53	0.16	–	–	–	–	–	0.77	–	–	–
	Cyclopentane, ethylidene-	13.28	0.44	–	–	–	–	–	–	–	–	–
	Undecane	17.4/17.53	2.06	0.61	0.65	2.19	1.44	1.35	0.64	4.22	2.89	1.8
	Bicyclo[3.3.1]nonane	16.8	–	–	0.44	–	–	–	–	–	–	–
	Naphthalene, 1/2-methyl-	24	–	–	0.12	0.98	0.9	–	0.44	0.43	0.77	0.8
	Biphenyl	25.7	–	–	–	0.47	–	–	–	–	0.18	0.5
	Naphthalene, 2,6/7-dimethyl-	26.9	–	–	–	0.25	0.19	–	–	0.11	0.23	–
	2,4-Hexadiene, 2,3/5-dimethyl-	12.3	–	–	–	–	–	–	0.45	–	-	–
	4-Pentenal, 2-methylene-	14.2	–	–	–	–	–	–	–	0.36	–	–
	Total		2.66	0.61	1.21	3.89	2.53	1.35	2.32	5.12	4.07	3.1
Ketones/aldehydes	2-Cyclopenten-1-one	8.7/8.85	1.28	6.99	6.15	–	–	1.97	5.07	–	–	–
	2-Cyclopenten-1-one, 2-methyl-	11.0/11.23	0.47	2.13	1.31	1.23	1.27	0.63	1.36	1.58	1.75	1.4
	2-Cyclopenten-1-one, 3-methyl-	13.3	0.27	1.09	–	–	1.04	–	1.14	–	–	1.1
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	15.2	–	0.32	–	1.27	–	–	0.13	–	1.01	–
	2-Cyclopenten-1-one, 3,4-dimethyl-	14.17	–	0.34	–	0.17	0.31	–	0.27	–	0.22	0.4
	2-Cyclopenten-1-one, 2,3-dimethyl-	15.64	–	1.42	–	0.96	0.96	–	0.14	0.83	1.3	1.2
	Ethanone, 1–(2-furanyl)-	11.3/11.4	–	1.22	–	–	–	–	0.81	–	–	–
	2-Furancarboxaldehyde, 5-methyl-	13.0/13.1	–	1.75	–	–	2.22	0.43	1.18	2.77	4.41	2.4
	2-Propanone, 1-hydroxy-	4.3/4.4	–	–	1.25	4.12	3.5	–	–	2.62	2.97	3.6
	Cyclopentanone	7.4	–	–	0.9	–	1.63	–	–	–	1.73	1.7
	Butyrolactone	11.2	–	–	2.37	1.53	2.32	–	–	1.87	2.01	2.4
	2-Furancarboxaldehyde, 5-methyl-	13	–	–	1.55	2.47	–	–	–	–	–	–
	2-Propanone, 1-(acetyloxy)-	9.7	–	–	–	0.77	0.91	–	–	–	1.19	1
	1,2-Ethanediol	5.6	–	–	–	–	–	–	–	1.9	–	–
	Total		2.02	15.26	13.5	12.5	14.2	3.03	10.1	11.6	16.6	15

Note: D-1, D-2, D-3, D-4, D-5 represents DARCO 830 catalyst recylcing run, respectively; M-1, M-2, M-3, M-4, M-5 represents MRX catalyst recylcing run, respectively.

of AC is much higher than the surrounding solids and gases during microwave heating; the formation of hot spots due to microwave heating will result in much higher temperature of solid than the average temperature measured (Fernandez et al., 2009). Consequently, the gases generated by reforming reaction participated in the lignin decomposition reaction, which promotes the degree of deoxygenation. Phenols were generated after a series of reactions such as decarboxylation and dehydration. This was confirmed by the GC/MS analysis of the chemical composition of bio-oils, which showed that the main compositions of the upgraded bio-oils were phenols such as phenol and cresol; the concentrations of the small molecular compounds, such as acid, furans, sugars, ketones and aldehydes, were decreased significantly comparing with the raw pyrolysis oils such as those from fluidized bed and Vortex pyrolysis (Wang et al., 1997). Fig. 1 in supplementary data shows a reaction pathway for catalytic microwave pyrolysis of biomass.

GC analysis showed that the major gas components are H_2, CH_4, CO, CO_2 and some low molecular hydrocarbons, suggesting that the endothermic reforming reactions might play a significant role during microwave heating (Fernandez et al., 2009; Fernandez et al., 2010; Lam et al., 2012; Hu et al., 2012):

$$C + H_2O \leftrightarrow H_2 + CO$$
$$C + CO_2 \leftrightarrow 2CO$$
$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$
$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$
$$C_xH_y + xH_2O \rightarrow xCO + (2x + y)H_2$$
$$C_xH_yO_z + (x - z)H_2O \rightarrow xCO + (x - z + y)H_2$$

represents the water-soluble fractions of pyrolysis oil.

4. Conclusion

This study investigated production of renewable phenols from biomass-derived feedstock by catalytic microwave pyrolysis with different activated carbon catalysts. The high concentrations of phenols, 74.61% and 74.77% of the bio-oils were obtained from MRX and DARCO 830 catalysts, respectively. Catalyst recycling test showed that the selected catalysts (MRX and DARCO 830) can be reused at least 3–4 times with high concentration (~55% of the bio-oils) of phenolic compounds. Further study to investigate catalyst regeneration and kinetics study will shed light on better understanding the reaction mechanism of this study.

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