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Bio-based phenols and fuel production from catalytic microwave pyrolysis of lignin by activated carbons

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HIGHLIGHTS

- Catalytic microwave pyrolysis of lignin from activated carbon was investigated.
- 45% of phenol, 78% of total phenolics, and 15.3% of hydrocarbons were achieved.
- The heating value of lignin-derived biochars was significantly higher than lignin.
- The thermal degradation and reaction mechanism were analyzed.

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ABSTRACT

The aim of this study is to explore catalytic microwave pyrolysis of lignin for renewable phenols and fuels using activated carbon (AC) as a catalyst. A central composite experimental design (CCD) was used to optimize the reaction condition. The effects of reaction temperature and weight hourly space velocity (WHSV, h^{-1}) on product yields were investigated. GC/MS analysis showed that the main chemical compounds of bio-oils were phenols, guaiacols, hydrocarbons and esters, most of which were ranged from 71% to 87% of the bio-oils depending on different reaction conditions. Bio-oils with high concentrations of phenol (45% in the bio-oil) were obtained. The calorific value analysis revealed that the high heating values (HHV) of the lignin-derived biochars were from 20.4 to 24.5 MJ/kg in comparison with raw lignin (19 MJ/kg). The reaction mechanism of this process was analyzed.

1. Introduction

The rapid depletion of fossil fuels is leading to the global energy crisis; as a result, the cost of crude oil is increasing eventually. Additionally, the negative side effect led by burning of fossil fuels, such global warming and the formation of acid rain, is becoming one of the biggest challenges in human history. Therefore, considerable researches are focusing on developing alternatives for fossil fuels in the past two decades. As the major feedstock of second generation biofuels, an increasing attention has been paid to converting lignocellulosic biomass into liquid fuels and value-added chemicals.

Lignin is the second abundant component in lignocellulosic biomass following cellulose; it comprises about 23–33 wt.% and 16–25 wt.% of the mass in softwoods and hardwoods, respectively (Mohan et al., 2006), and contributes about 40% of energy content in lignocellulosic biomass (Holladay et al., 2007). Lignin is composed of three phenylpropenyl units: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. From the thermal behavior view of point, lignin is the most heat-resistant component among the major components of lignocellulosic biomass. As a result, more residual char was produced during lignin pyrolysis than pyrolysis of lignocellulosic biomass. Phenols are produced through the cleavage of ether (mainly α or β-o-4 bonds) and C—C linkages during pyrolysis of lignin (Chen et al., 2001; Mohan et al., 2006). Lignin sources are becoming more abundant with the development of lignocelluloses-to-ethanol industry (Pandey and Kim, 2010). Besides, it is well-known that lignin is the main by-product of conventional pulp and paper industry. However, the main use of lignin is as a low-grade energy source in combustion and has not received much attention until recently (Huber et al., 2006). Holladay et al. (2007) evaluated the potential of making use of lignin for value-added chemicals from biorefinery lignin; they pointed out that the overall revenue will be improved from \$12 to \$35 billion if the lignin is used for purposes, such as chemicals

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and transportation fuels, other than low-grade energy source for power. And the market value implies that the products potentially derived from lignin such as phenols (phenol: \$0.55–\$0.65/1b; substituted phenols: \$0.7–\$2.00 1b) are attractive (Holladay et al., 2007).

The characteristics of chemical structure and the abundance of lignin suggest that it has great potential to be used as value-added chemical feedstock such as phenol, benzene, toluene and xylene. Holladay et al. (2007) mentioned that lignin is the only renewable source of the aromatics. Phenolic compounds are workhorses in the chemical industry such as synthesis of phenol formaldehyde resin and plastics (Kleinert and Barth, 2008; Pandey and Kim, 2010). The low molecular weight of products resulted from high degree of depolymerization suggests that pyrolysis may be useful for the controlled molecular weight reduction of lignin (Holladay et al., 2007).

Pyrolysis of biomass is a thermal decomposition process of organic compounds in the absence of oxygen to obtain char, syngas, and bio-oil. Pyrolysis has been widely used for production of liquid fuels and value-added chemicals (Mohan et al., 2006; Bu et al., 2012; Chen et al., 2001). Microwave pyrolysis is a process that transfers heat 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 (Fernandez et al., 2011; Luque et al., 2012; Hu et al., 2012). Recent studies on microwave pyrolysis of biomass include the conversion of wood (Bu et al., 2012; Salem and Ani, 2012; Wang et al., 2012), sewage sludge (Mendez et al., 2004; Dominguez et al., 2008) and microalgae (Du et al., 2011; Hu et al., 2012).

Recently, a multitude of researches focused on pyrolysis of lignin (Wild et al., 2012; Brebu and Vasile, 2010; Luo et al., 2012). And some attempts aim to displace phenol in the phenol formaldehyde resin synthesis (Xu and Leitch, 2010; Wang et al., 2009; Cheng et al., 2010). However, so far there are only few reported investigations on microwave-assisted pyrolysis of lignin for value-added chemicals and fuels (Chan and Krieger, 1981).

Therefore, the aim of the present study is to make use of lignin as a model compound for renewable phenols and fuel production by catalytic microwave pyrolysis, which will shed light on the reaction pathway of microwave pyrolysis of lignocellulosic biomass and application of lignin. The effects of reaction temperature and weight hourly space velocity (WHSV, h^{-1}) on product yield were investigated and models to predict the product yields were established as well. The chemical compositions of the resulting bio-oils were characterized by GC/MS analysis and the heating value of the bio-char was determined. The reaction mechanism of catalytic lignin pyrolysis was analyzed.

2. Methods

2.1. Materials

The alkali lignin (CAS number 8068-05-1) was purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA). The lignin was used as received. GAC 830 PLUS, an activated carbon (AC) with high purity produced by steam activation of selected grades of coal was purchased from Norit Americas Inc. (Marshall, TX, USA). Sodium ethoxide (Catalog No. AC16859-5000), sodium hydroxide and methyl red indicator (Catalog No. S25435) were purchased from Fisher Scientific Corporation (Pittsburgh, PA, USA).

2.2. Microwave pyrolysis of lignin

Fig. 1 shows the schematic diagram of the microwave-assisted pyrolysis system. The microwave pyrolysis system mainly consisted of several components: a 1000 W, 2.45 GHz microwave cavity, an 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 lignin 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. The weight of syngas product was calculated using the following equation:

$$\text{Weight of syngas} = \text{initial lignin mass} - \text{biooil mass} - \text{biochar mass} \tag{1}$$

2.3. Experimental design

A central composite experimental design (CCD) was employed to optimize the process conditions and product yields distribution. The reaction temperature (X_1, °C) and weight hourly space velocity, WHSV (X_2, h^{-1}), were selected as independent variables. The weight of lignin feed was 20 g, and activated carbon mass was in the range of 31.8–88.2 g. The product yields of bio-oils, gas, and biochar were chosen as dependent variables. The reaction time was recorded after the desired temperature was reached. For statistical calculations, the variables X_i are coded as x_i according to Eq. (2):

$$x_i = (X_i - X_0/\Delta X) \tag{2}$$

where X_i is the coded value of an independent variable, X_i is a real value, X_0 is a central value of the independent variable, and $X_0/\Delta X$ is the step change. A 2^2-factorial CCD, with 4 axial points $\left(\alpha = \sqrt{2}\right)$ and 3 replications at the center points leading to a total number of 11 experiments was employed to optimize the reaction conditions. The second degree polynomials (Eq. (3)) were calculated with the SAS statistical package (SAS Institute Inc., USA) to estimate the response of the dependent variables:

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{21}X_2X_1 + b_{22}X_2^2 \tag{3}$$

where Y_i is predicted response, X_1, X_2 are independent variables, and b_0, b_1, b_2, b_{11}, b_{22} and b_{21} are regression coefficients.

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. Compounds were identified by comparing the spectral data with that in the NIST Mass Spectral library.

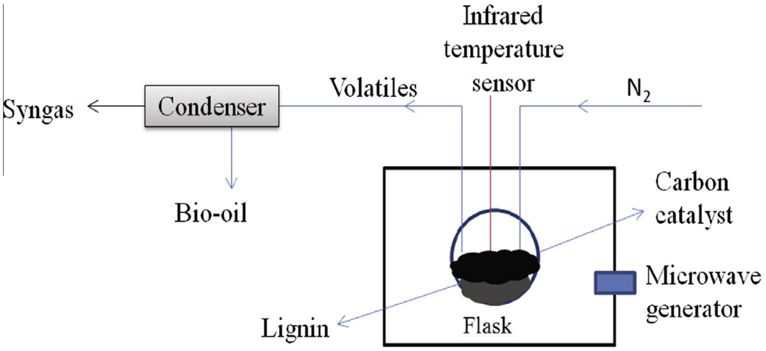

Fig. 1. The schematic diagram of lab scale microwave-assisted pyrolysis system.

2.5. Heating value determination

The heating value of the biochar was analyzed using a Parr adiabatic calorimeter according to ANSI/ASTM D2015-77 and determined by the Poultry Lab at the University of Arkansas.

2.6. Determination of titrationable surface functional groups

Various types of oxygen containing group on the carbon surface could be quantified by Boethm's method. It involved suspending 0.5 g of carbon catalyst in 25 mL of a 0.1 N solution of sodium ethoxide, sodium hydroxide or sodium bicarbonate. The samples were agitated by shaking in closed vessels for 24 h. After that, the slurry was filtered and a 10 mL aliquot was added to 15 mL of 0.1 N HCl. The HCl neutralized the unreacted base and kept further reaction between atmospheric carbon dioxide and the various bases from occurring. The acidified solutions where bubbled with N_2 for 1 h to expel dissolved CO_2 from solution. All samples were then back-titrated with 0.1 N NaOH, and the endpoints were potentiometrically determined using a pH meter (Oakton PC – 400). All titrations were carried out at room temperature (22 ± 3 °C).

3. Results and discussion

3.1. Response surface analysis

Previous research found that the reaction temperature and WHSV had a significant influence on products yield distribution during microwave pyrolysis of biomass using activated carbon as a catalyst (Bu et al., 2011, 2012). Therefore, in the present study, reaction temperature and WHSV were selected as independent variables to investigate the product yield distribution during catalytic pyrolysis of lignin.

The detailed experimental design and yield distribution of products obtained at different reaction conditions were shown in Table 1. Linear model equations for bio-oil (Eq. (4)), gas (Eq. (5)), and biochar (Eq. (6)) as a function of reaction temperature (X_1, °C) and WHSV (X_2, h^{-1}) were obtained using the results of the experiments:

$$Y_{\text{bio-oil}} = 19.27 + 0.026X_1 - 6.89X_2 - 0.018X_1X_2 + 0.000026X_1^2 + 3.18X_2^2 \quad (4)$$

$$Y_{\text{gas}} = -1.38 + 0.068X_1 + 2.57X_2 \quad (5)$$

$$Y_{\text{biochar}} = 82.62 - 0.084X_1 + 0.42X_2 \quad (6)$$

Table 1
Experimental design and yield distribution.

Run	Temperature (°C)	WHSV (h^{-1})	Bio-oil (%)	Gas (%)	Biochar (%)
L-1	350	1.70	18.50	26.85	54.65
L-2	550	2.18	20.25	38.10	41.65
L-3	350	0.82	22.95	20.60	56.45
L-4	550	0.97	26.65	25.15	48.20
L-5	309	1.12	19.80	24.95	55.25
L-6	591	1.72	23.25	45.50	31.25
L-7	450	2.62	19.07	36.38	44.55
L-8	450	0.88	41.48	10.27	48.25
L-9	450	1.38	22.10	33.00	44.90
L-10	450	1.38	21.80	33.45	44.75
L-11	450	1.38	21.25	34.10	44.65
L-12	450	–	15.46	55.10	29.44

Note: Retention time was 8 min; L-1 to L-11 was conducted with catalyst addition; L-12 was the control; WHSV $= \frac{\text{feed mass rate}}{\text{catalyst mass}}$; statistical standard deviation for product yield at center points: bio-oil (21.72 ± 0.43%), gas (33.52 ± 0.55%), and biochar (44.77 ± 0.13%).

The model for yield prediction was reduced by using backward statistical analysis, and parameters were sequentially removed based on the coefficient's *P*-value until all remaining were significant (*P*-value < 0.05). According to the ANOVA results, the *P* values (*P*-value = 0.0073, 0.0008, 0.0005) were all less than 0.05, suggesting that these equations were significant to describe the yield of bio-oil, gas and biochar. The coefficient of determination (R^2) for Eq. (4) was 0.98, indicating that the second order regression model represents well the relationships among the independent variables for bio-oil production. The coefficient of determination (R^2) for Eq. (5) was 0.91, meaning that the model can be used to predict the gas yield from microwave pyrolysis of lignin. The *P* value for model term X_1 was significant (*P*-value = 0.0012 < α = 0.05) when Eq. (5) was used to fit the data for gas, suggesting that the temperature had significant influence on gas yield. The coefficient of determination (R^2) for Eq. (6) was 0.92, indicating that the model was suitable to fit the data for biochar. The model terms X_1 (*P*-value = 0.0003) was significant (*P*-value < 0.05), indicating that the temperature had significant influence on biochar yield during catalytic microwave pyrolysis with activated carbon catalyst.

Fig. 2 represents the response surface and contour line for the product yields. The yield of bi-oils was increased with the increase of the reaction temperature and decreased with WHSV. The bio-oil yield was ranged from 18.5 to 41.48 wt.% of lignin, and the maximum yield of bio-oil (41.48 wt.%) was obtained at the reaction temperature of 450 °C and WHSV of 0.88 h^{-1}. The gas yield was found to be increased with the increase of temperature, which was in the range of 10.27–45.5 wt.% of lignin. The maximum gas yield was observed at 591 °C and WHSV of 1.72 h^{-1}. It was observed that the biochar yield was decreased with the increase of temperature, which varied from 31.25 to 56.45 wt.% of lignin, and the lowest biochar yield was obtained at 591 °C and WHSV of 1.72 h^{-1}. Similar phenomenon about the effects of reaction temperature on product (bio-oil, gas and biochar) yield was

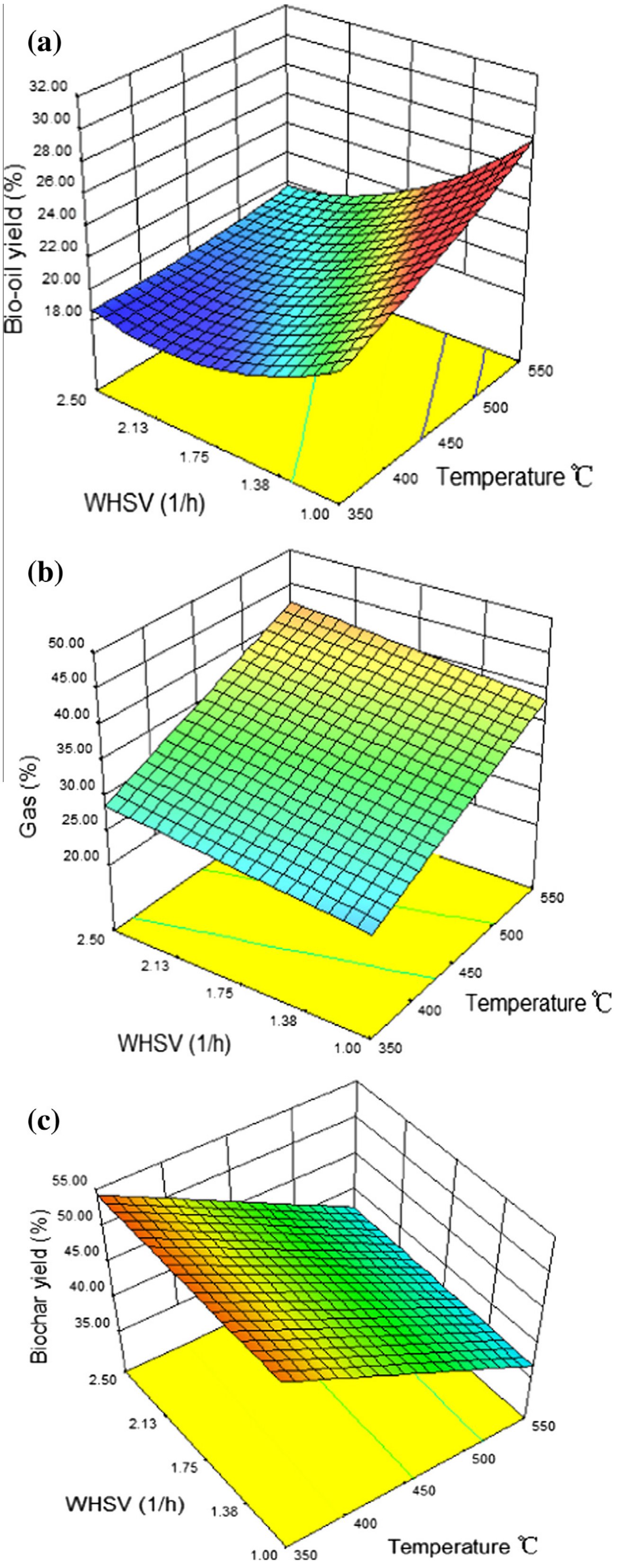

Fig. 2. The response surface and contour line of product yields as a function of reaction temperature and WHSV: (a) bio-oil, (b) gas, and (c) biochar.

observed by other studies during pyrolysis of lignin (Cho et al., 2012; Sharma et al., 2004).

3.2. GC/MS analysis of the bio-oils

In order to further understand the chemical reaction of lignin pyrolysis, the obtained bio-oils were analyzed by GC/MS. The water content of most obtained bio-oils was in the range of 20–31% of bio-oils, water content was derived from both the moisture of raw lignin and the subsequent dehydration reaction during lignin pyrolysis. The typical compositions of bio-oils include aldehydes, ketones, sugars, carboxylic acids, esters, phenolics, guaiacols, hydrocarbons, furan derivatives, and some unclassified composition. The chemical composition of bio-oils by GC/MS analysis was categorized according to the differences of functional groups as shown in Fig. 3, it was observed that the main chemical compounds of the bio-oils from catalytic microwave pyrolysis of lignin were phenols, guaiacols, hydrocarbons and esters; the amount of these compounds were in the range of 71–87% of bio-oils for most of the bio-oils depending on different reaction conditions. In comparison with the bio-oils obtained by conventional pyrolysis of lignin which were mainly comprised of guaiacols (Maldhure and Ekhe, 2013; Nowakowski et al., 2010), the amounts of phenols, hydrocarbons and esters in bio-oils derived from catalytic microwave pyrolysis of lignin were significantly increased. Results showed that high amount (~78% of bio-oils) of phenolics (phenols and guaiacols) were observed for run L-2 and L-7 which was conducted at 550 °C and WHSV of 2.18 h^{-1}, and 450 °C and WHSV of 2.62 h^{-1}, respectively. The maximum amount of phenol (45% of the bio-oil) was obtained at 550 °C and WHSV of 2.18 h^{-1} as shown in the experimental run L-2.

Besides, one phenomenon had attracted our attention is that the concentrations of hydrocarbons and esters in the bio-oils from lignin pyrolysis increased significantly comparing with other reports about lignin pyrolysis (Maldhure and Ekhe, 2013; Nowakowski et al., 2010). The high amount of hydrocarbons was observed in L-3 and L-9 which produced 15.29% and 13.81% of hydrocarbons in bio-oils, respectively. It was observed that the produced hydrocarbons were mainly comprised of undecane which is a straight chain aliphatic hydrocarbon of gasoline composition. Most of the detected esters were straight chain fatty esters, such as dodecanoic acid, methyl ester; hexadecanoic acid, methyl ester; octadecanoic acid, methyl ester; and methyl tetradecanoate. These long chain esters are significant compositions of biodiesel. Therefore, the high amount of hydrocarbons and esters can be used as transportation fuel after separation or as chemical feedstock for chemical industry.

3.3. Heating value analysis for bio-char

The high heating value (HHV) of lignin-derived biochar obtained at different reaction conditions was ranged from 20.4 to 24.5 MJ/kg in comparison with raw lignin (19 MJ/kg). The highest HHV (24.5 MJ/kg) of the produced biochar was obtained at the reaction condition: temperature 350 °C and WHSV of 0.82 h^{-1}, which was about 24% increases compared with that of the origin lignin. The lowest HHV was 20.4 MJ/kg for biochar obtained at 591 °C, WHSV of 1.72 h^{-1}; this may be explained by the excessive pyrolysis of lignin at higher temperatures as activated carbon was acted as a microwave absorber which resulted in ball lighting and plasma phenomena and the pyrolysis of the fixed carbon of biochar (Salema and Ani, 2012). The high heating value analysis and the high yield of lignin-derived char by pyrolysis indicated that the obtained biochar has the potential to be used as a fuel source.

3.4. Mechanism analysis of lignin decomposition

The main phenolic compounds as shown in Table 2 revealed that the phenol contents in the lignin-derived bio-oils by catalytic

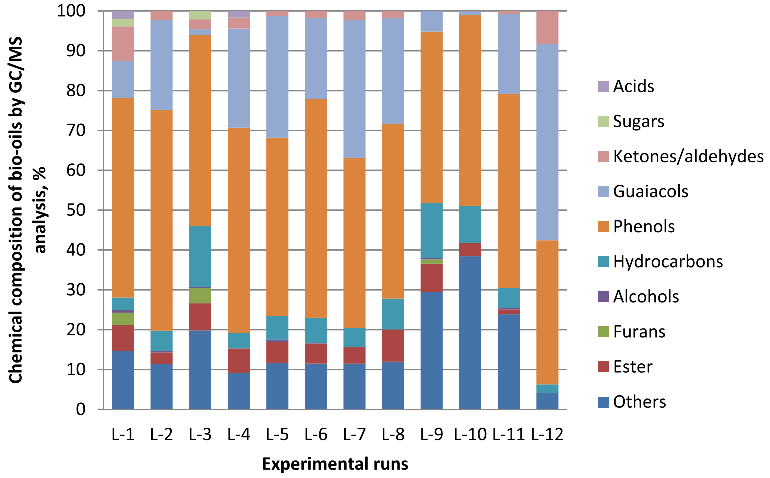

Fig. 3. Chemical compositions by GC/MS analysis for bio-oils obtained under different reaction conditions.

Table 2
Main phenols compounds by GC/MS analysis of bio-oils from lignin pyrolysis.

	GC/MS area % of major phenols						
Run	Phenol	O-cresol	M-cresol	P-cresol	Guaiacol	Creosol	Vanillin
L-1	42.9	2.4	1.4	3.1	2.6	1.7	0.6
L-2	45.0	7.5	2.8	–	18.0	0.9	0.7
L-3	22.2	1.2	4.7	–	1.2	2.5	0.3
L-4	36.9	1.9	4.9	–	0.9	–	–
L-5	32.2	2.1	–	4.6	1.0	–	–
L-6	28.5	5.0	–	7.6	19.0	2.7	0.9
L-7	30.8	2.7	–	8.0	26.0	6.1	0.6
L-8	20.8	0.8	1.1	–	6.2	1.4	1.4
L-9	41.2	0.9	0.6	–	5.2	–	–
L-10	43.3	3.2	–	–	0.9	–	–
L-11	34.7	9.0	5.1	17.0	0.8	–	–
L-12	12.8	4.4	11.3	0.6	22.0	8.3	4.2

pyrolysis were increased significantly with the decrease of guaiacols content comparing with the control (run L-12). This phenomenon might be illuminated by guaiacols (GUA) conversion by the effect of gases (such as H_2, CO) and various endothermic reforming reactions (Bu et al., 2013) occurring at high temperatures which might be led by the formation of hot spots due to microwave heating. Consequently, the degree of deoxygenation during lignin decomposition reaction was promoted.

In order to further understand the reaction mechanism of using AC as a catalyst in this process, individual surface polar/acidic oxygen functional groups (TOFG) were analyzed. Modified Boehm's TOGF analysis confirmed functional groups of carboxyl, carboxylic anhydride, and carbonyl groups in the activated carbon catalysts (Boehm, 1994). When a superheated (200–500 °C) water from pyrolysis entered activated carbon, carboxylic anhydride (0.85 mmol/g activated carbon) was reacted with water to generate carboxylic acids which become proton (H^+) donors and acid catalyst. It was observed that the amount of carbonyl group on the activated carbon used for lignin pyrolysis increased to 0.095 mmol/g activated carbon after carbon catalysis which was not observed on raw activated carbon. The increase in carbonyl groups can be correlated with a reduction of oxygenated bio-oils. The surface carbonyl density might affect the kinetics of a variety of reduction–oxidation processes at carbon surface (Chen et al., 1995).

The protonation reaction of the carbonyl oxygen can be promoted by the acids in bio-oils. Mechanistically, the carbonyl oxygen is protonated first because it is the most nucleophilic site (Peter et al., 2007). Some of the electron density on oxygen that was available for donation to the carbonyl carbon is taken up by the new O—H bond. The net effect of protonation is thus to weaken the carbon oxygen π bond. Protonation of the carbonyl makes the carbonyl carbon a stronger electrophile. This means it will react more quickly with whatever nucleophiles might be present in bio-oil; in our case, the methoxide ($O\text{-}CH_3$) which is an electron rich species donates electrons to electron-poor carbon. Thus $O\text{-}CH_3$ homolysis for guaiacols conversions is catalyzed by activated carbon catalyst. The protonation mechanism is reversible. The electrons on the newly formed O^- atom can collapse back down to reform the carbonyl and kick off a good leaving group. The only good leaving group is CH_3O^-. The high concentrations of phenols were then generated by the reaction of $O\text{-}CH_3$ homolysis where the guaiacols were stabilized as phenols with saturated alkyl- or hydrogen from other reforming reactions in this process (Bu et al., 2012, 2013). The increase in carbonyl groups on the surface of the carbon catalyst indicated that the oxidation level of a carbon increased while the reduction of bio-oils was confirmed by guaiacol conversions to phenol and phenolics.

4. Conclusions

Catalytic microwave pyrolysis of lignin using AC as a catalyst was investigated. The main chemical compounds of bio-oils were phenols, guaiacols, hydrocarbons and esters (71–87% of bio-oils). The optimized condition for maximizing amount of phenol and phenolics was at 550 °C and WHSV of 2.18 h^{-1}. The highest HHV of biochar from lignin pyrolysis was about 24% increase comparing with that of the origin lignin. The increase of carbonyl groups in ACs by TOFG analysis suggested that the deoxygenation of bio-oils can be achieved which explained the reaction mechanism of carbon catalysis of lignin.

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