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Production of phenols and biofuels by catalytic microwave pyrolysis of lignocellulosic biomass

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ABSTRACT

Catalytic microwave pyrolysis of biomass using activated carbon (AC) was investigated to determine the effects of pyrolytic conditions on the yields of phenol and phenolics. Bio-oils with high concentrations of phenol (38.9%) and phenolics (66.9%) were obtained. These levels were higher than those obtained by pyrolysis without AC addition and were closely related to the decomposition of lignin. A high concentration of esters (42.2% in the upgraded bio-oil) was obtained in the presence of Zn powder as catalyst and formic acid/ethanol as reaction medium. Most of the esters identified by GC–MS were long chain fatty acid esters. The high content of phenols and esters obtained in this study can be used as partial replacement of petroleum fuels after separation of oxygenates or as feedstock for organic syntheses in the chemical industry after purification.

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1. Introduction

Pyrolysis of biomass is a thermal decomposition process of organic compounds in the absence of oxygen to obtain char, syngas and bio-oil. Bio-oil is considered an alternative to petroleum-based sources for a wide range of solvents, fuels and chemicals and other products (Bu et al., 2011; Yaman, 2004). Bio-oil can be used to make liquid transportation fuels by upgrading through deoxygenation of oxygen-containing bio crude oil. Potential bio-based 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 which is a significant industrial feed found in myriad industrial products is produced mainly from fossil fuels. Phenolic resins are typically cross-linked polymeric resins, and because phenol price and availability are linked to that of petroleum, industrial products using phenol as feed such as phenol–formaldehyde or phenolic resins are relatively expensive. Attempts have been made to substitute petroleum-based phenol in phenolic resins with cost-effective phenols derived from lignocellulosic materials (Pakdel et al., 2009; Effendi et al., 2008), however, none of these techniques are believed to allow complete substitutions without negative impacts on quality. Therefore, in order to reach the goal of a price competitive renewable resin, further research is required to meet

these challenges of lowering renewable resin cost and satisfying quality requirement (Effendi et al., 2008; Roy et al., 2000).

Fast pyrolysis oil from lignocellulosic materials is known to contain a complex mixture of phenolic compounds which are the products primarily derived from the lignin fractionation of the biomass. Lignins are much more thermally stable than cellulose and hemicellulose during biomass pyrolysis (Bridgwater, 1999). The compounds obtained from decomposition of lignin have become one of the biggest challenges during upgrading of bio-oils. Although a number of studies have been conducted on the preparation of phenolic resin such as phenol–formaldehyde using phenolic rich pyrolysis oil as partial substitution of petroleum-based phenol (Pakdel et al., 2009; Effendi et al., 2008), few studies were done on how to make phenolic rich bio-oil (Wang et al., 2009; Chum et al., 1989).

In contrast to 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 field into heat (Sobhy and Chaouki, 2010). Some studies on pyrolysis have used microwaves as heating resource to prepare biomass pyrolysis oils (Huang et al., 2008; Lei et al., 2009).

In the present study, the preparation of phenolic rich pyrolysis oils by microwave-assisted pyrolysis of biomass was investigated at different reaction temperatures, retention times, and ratios of catalyst to feedstock. Activated carbon (GAC 830 PLUS) was used as catalyst for phenolic rich pyrolysis oil production via microwave-induced pyrolysis. A reaction mechanism was proposed and

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analyzed. In addition, Zn powder was used for the first time as a catalyst with formic acid as a hydrogen donor and ethanol as reaction medium. The chemical composition of bio-oil obtained in this study was analyzed using gas chromatography–mass spectrometry (GC–MS).

2. Methods

2.1. Materials

Douglas fir (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, GAC 830 PLUS, with high purity produced by steam activation of selected grades of coal was purchased from Norit Americas Inc. (Marshall, TX, USA). Anhydrous ethanol and formic acid were purchased from Fisher Scientific (Pittsburgh, PA, USA). Zn powder was purchased from Alfa Aesar (Ward Hill, MA, USA).

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 retention time were varied with a fixed microwave power input of 700 W. This power setting gave a constant heating rate of about 60 K min⁻¹. The temperature was measured by an infrared temperature sensor attached to the 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. During pyrolysis the heavier volatiles were condensed into liquids as bio-oils and the lighter volatiles escaped as syn-gases at the end of the condensers where they were either burned or collected for analysis. Char was left in the quartz flask. The weight of syn-gas product was calculated using the following equation:

$$\text{Weight of syn-gas} = \text{initial wood pellet mass} - \text{bio-oil mass} - \text{biochar mass}$$

Detailed procedures of microwave pyrolysis process were described in Lei et al. (2009, 2011).

2.3. Bio-oil upgrading

A closed reaction system with a stirred stainless steel batch reactor of the 4570 HP/HT type and a 4848 Reactor Controller from Parr Instrument company (Moline, IL, USA) (with a 1.8-L vessel) was used. Formic acid and ethanol were used as a reaction medium; the ratio of formic acid to ethanol and Zn powder to bio-oil was 1:1 and 5:1, respectively. The heating temperature was from room temperature to 230 °C with an approximate heating rate of 5 °C/min. Once the desired heating temperature was reached, the reaction was kept at that temperature for different amounts of time. After the reaction, the reactor was cooled to room temperature in a refrigerated water bath. The ethanol was evaporated from the reaction mixture using a rotary evaporator at 60 °C (225 rpm). After evaporation the upgraded oil was separated by simple decanting because there was a phase separation.

2.4. GC–MS analysis of liquid (bio-oil) product

The liquid product was bio crude oil collected after pyrolysis and condensates 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 (Dominguez et al., 2003; Samanya et al., 2010).

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 gases.

3. Results and discussion

The product yield distributions obtained under different reaction conditions are shown in Table 1. Most of the liquids had yields from 25 to 38% wt. of feedstock; however, the gas yields were much higher than those obtained by microwave pyrolysis of Douglas fir without AC addition (12% wt. of feedstock) (Table 1). The high yields (~75%) of volatiles (including condensable liquid and non-condensable gas components) implied a close relationship between yields and using AC as a catalyst. The AC functioned as a microwave receptor and also a catalyst (Fidalgo et al., 2008; Menendez et al., 2010). The product distribution favored syn-gas and bio-oil production, and these might have resulted from self-gasification by “microplasmas” (Menendez et al., 2007). This phenomenon concurred with the conclusion by Omar et al. (2010) that utilizing microwave absorbers facilitate heating during pyrolysis of biomass as heat is transferred by a conductive and convective mechanism from absorber to biomass.

3.1. Effects of process conditions

3.1.1. Effects of temperature on product distribution

The effects of temperatures on product distribution with a constant ratio (2:3) of catalyst to biomass are shown in Fig. 1A. Gas

Table 1
Reaction conditions and product yield distribution.

#	Temperature (K)	Ratio of AC to Douglas fir	Time (min)	Liquid yield (%)	Gas yield (%)	Volatiles (%)
1	589	3:1	8	12.5	43.0	55.5
2	623	2:1	4	20.3	46.5	66.8
3	623	2:1	12	48.1	40.5	88.6
4	623	4:1	4	26.97	42.97	69.9
5	623	4:1	12	25.78	46.18	72.0
6	673	No AC	8	45.2	11.8	57.0
7	673	1.32:1	8	30.2	34.8	65
8	673	2:1	8	26.1	42.1	68.2
9	673	3:1	1.27	30.7	48.8	79.5
10	673	3:1	4	30.7	48.1	78.8
11	673	3:1	8	31.0	44.6	75.6
12	673	3:1	12	36.2	50.0	86.2
13	673	3:1	14.73	22.8	53.8	76.6
14	673	4:1	8	38.3	50.4	88.7
15	673	4.68:1	8	24.6	51.7	76.3
16	723	2:1	4	35.1	54.0	89.1
17	723	2:1	12	29.3	56.5	85.7
18	723	4:1	4	23.1	53.9	77
19	723	4:1	12	27.8	54.5	82.2
20	757	3:1	8	26.4	57.5	83.9

yields were from 36.8 to 46.6% wt. of biomass and were obviously higher than that 12% obtained by microwave-assisted pyrolysis without AC addition (Table 1). The liquid yields increased from 32.3% (589 K) to 38.8% (673 K), but decreased to 36.2% at higher temperature such as 757 K. More biomass was converted to gas at high temperature, which was consistent with literature reports (Wu et al., 2008). The solid yield decreased significantly from 30.9% to 18.9% as the temperature increased from 589 to 757 K.

Therefore, 673 K was selected as the optimum temperature in this study.

3.1.2. Effects of catalyst to biomass ratio on product distribution

The relationship between product distribution and catalyst to biomass ratio is given in Fig. 1B. 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 lower

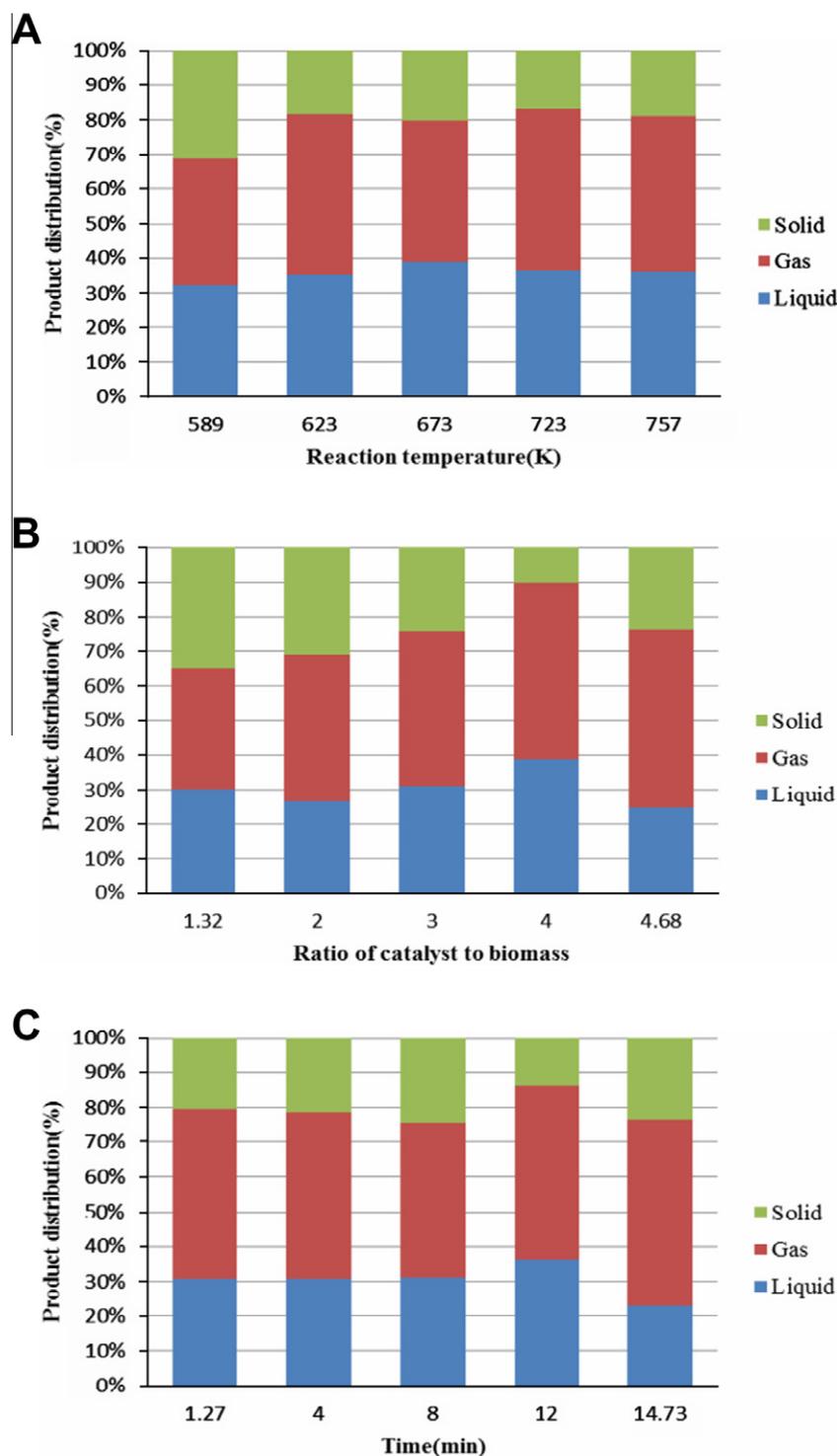


Fig. 1. Effects of reaction conditions on the products distribution: (A) yields vs. temperature (reaction condition: a constant ratio of catalyst to biomass (2/3) and retention time 8 min); (B) yields vs. ratio of catalyst to Douglas fir (reaction conditions: reaction temperature 673 K and reaction time 8 min); (C) yields vs. retention time (reaction condition: reaction temperature 673 K and ratio of catalyst to biomass 3:1).

catalyst to biomass ratios (<2), and a steady increase of liquid yields from 26 to 38% wt. of biomass was observed when the ratio increased from 2 to 4. There was a decreasing trend for liquid yields when the ratio increased continuously from 4 to 4.68; however, when the ratio increased from 3 to 4, both the liquid yield and volatile yield were maximized and the solid yield was minimized. 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 ($p < 0.05$) from 35% to 10%. The catalyst can be reused at least two times with good stability and conversion efficiency. The phenols content was 25.68 and 26.73% wt. of bio-oil for AC used first time (673 K, 3:1, 8 min) and second time (673 K, 3:1, 14 min), respectively; this should have close relationship with the microwave regeneration of activated carbon (Chang et al., 2010; Ania et al., 2005).

3.1.3. Effects of retention time on product distribution

The maximum liquid and volatile yields were realized when the reaction time was 12 min; however, the effects of retention time on product distribution were not as significant as reaction temperatures and ratios of catalyst to biomass (Fig. 1C).

3.2. GC–MS analysis of the bio-oil

The chemical composition of typical bio-oil products are shown in Fig. 2. Fig. 1 in Supplementary data is the GC/MS profile for bio-oils with maximum phenol and phenolics obtained under different pyrolysis conditions. Although tremendous research has been carried out on the mechanism of thermal degradation of biomass, catalyzed biomass decomposition from microwave-assisted pyrolysis has not yet been well-studied. However, catalytic biomass decomposition has great potential for further development of upgrading and refining bio crude oil in order to produce quality and cost-competitive substitutes of petroleum fuels. Bio-oil was mainly comprised of phenols, aliphatic hydrocarbons, aromatic

hydrocarbons, furan derivatives, and some acids phenols and guaiacols were about 28–40% in bio-oils depending on the reaction conditions, and included phenol, methyl phenol, ethyl phenols and methoxy phenols (Lei et al., 2009). The GC–MS spectra showed that the phenolics content reached 66.89% in the bio-oils with the addition of activated carbon (GAC 830 PLUS) at temperatures from 589 to 623 K with different catalyst to biomass ratios and reaction times, the amount of phenol in bio-oils reached 39.0%. A maximum yield of phenols (66.89% in the bio-oil) was obtained at 589 K, with a catalyst to biomass ratio of 3:1 and a reaction time of 8 min. High concentrations of phenol, 2-methyl phenol and 4-methyl phenol were obtained from microwave pyrolysis of lignocellulosic biomass at temperatures of 589 K and 623 K with different catalyst to biomass ratios and retention time as shown in Fig. 1 in Supplementary data. However, with a further increase in pyrolysis temperatures such as 757 K and ratios of catalyst to biomass such as 4:7, the production of phenol and phenolics were not favored. Similar trends were previously shown by Vasalos et al. (1988). GC–MS results indicated that the concentration of esters presented in bio-oils obtained with AC addition as a catalyst was significantly higher ($p < 0.05$) than that in bio-oils without catalyst. Fig. 2 shows that the ester concentrations reached 9.6% and 11.5% with retention times of 4 and 12 min, respectively at the same reaction temperature of 623 K and a catalyst to biomass ratio of 4:1.

The yield of the main liquid products, such as phenols, esters, furfural and its derivatives, varied with pyrolysis temperatures and ratios 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 could have significant economic benefits for the chemical industry which uses, example, phenols for the synthesis of PF resin and medicines (Esfendi et al., 2008; Yu et al., 2007).

3.3. Mechanism analysis

Table 2 reveals the yield distribution of the major products in the bio-oil, which indicated that the product selectivity was

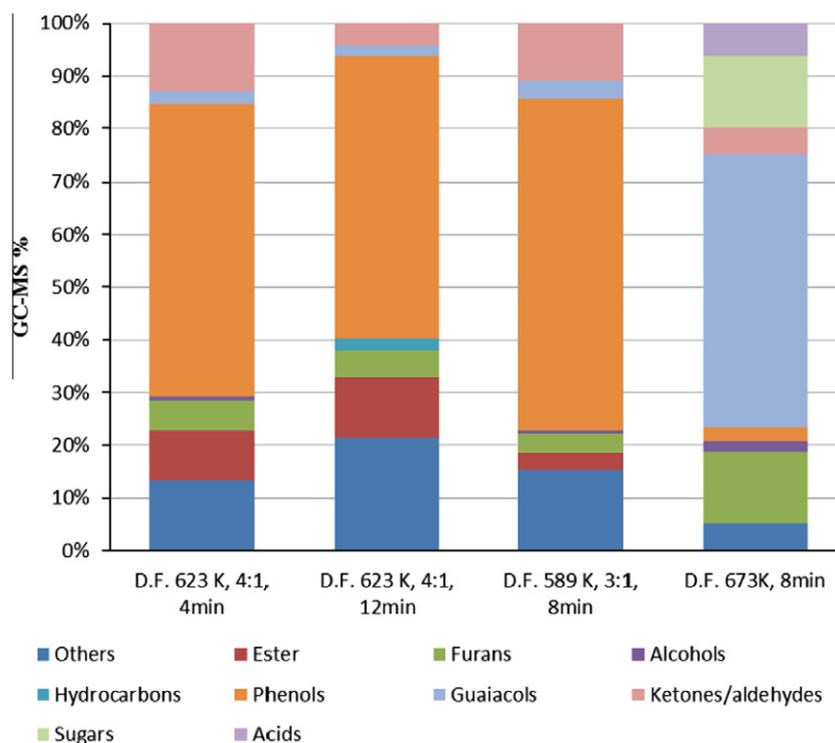


Fig. 2. Chemical composition of bio-oil with maximum phenolics from microwave pyrolysis of lignocellulosic material at different conditions.

Table 2GC/MS analysis of major products of bio-oils from microwave pyrolysis of biomass at different conditions.^a

Reaction conditions	#	Phenol (area %)	Phenolics (area %)	Guaiacols (area %)
With AC addition	Run1	37.72	55.31	2.42
	Run2	34.16	53.54	2.06
	Run3	38.98	66.89	3.48
Without AC addition	Run6	0.68	2.54	51.98

^a Run1: 623 K, 4:1 and 4 min; run2: 623 K, 4:1 and 12 min; run3: 589 K, 3:1 and 8 min; run6: 673 K, 8 min. (Phenolics include phenol and the alkyl substituent products of phenol.)

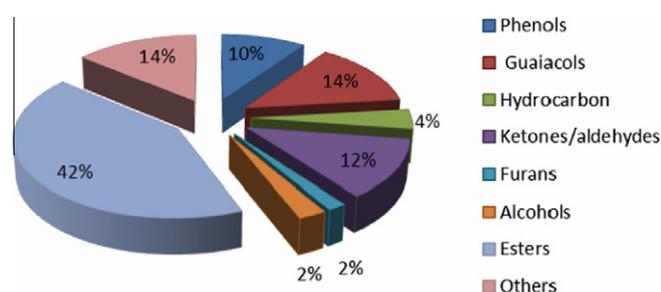


Fig. 3. Upgraded bio-oil using Zn powder, 230 °C, 1 h, ratio of Zn to bio-oil 5:1, formic acid to ethanol 1:1 (120 ml loading).

affected by adding AC during microwave-assisted pyrolysis. It can be seen that the phenol content of bio-oils produced with AC addition (34–39% in the bio-oils) were obviously higher than those without AC addition (less than 1% in the bio-oil).

Furthermore, the guaiacols were almost completely replaced by phenolics (the phenol was about 60% in the phenolics) with AC addition. The phenol content in bio-oils was significantly increased ($p < 0.05$) with AC addition while the guaiacol content of the bio-oils was significantly decreased from 52% (without AC) to 2–3.5% (with AC addition). The results implied that the addition of AC affected the mechanism of thermal decomposition. This may be explained by the interaction mechanism for lignin-cellulose pyrolysis proposed by Hosoya et al. (2009) who concluded that cellulose was effective in reducing secondary char formation from lignin and improving the formation of lignin-derived products. This mechanism may be used to illustrate the high volatile yield and low char formation as activated carbon functioned as a microwave absorber which facilitated heating in biomass pyrolysis. The high concentrations of phenolics were probably generated by the three radical reaction of O–CH homolysis where cellulose-derived volatiles and lignin-derived products function as H-donations and H-acceptors, respectively. As a result, the guaiacols were stabilized as phenolics with saturated alkyl- or H-donation from other products (Hosoya et al., 2009). GC analysis showed that the major gas components are hydrogen, methane, CO, CO₂ and some low molecular hydrocarbons. The methane contents increased compared with those from microwave pyrolysis of biomass without AC addition. This increased methane content is consistent with the radical reaction of O–CH₃ homolysis of guaiacols.

3.4. Bio crude oil upgrading using formic acid–alcohol as a reaction medium

The chemical composition analysis of upgraded oil using Zn powder as a catalyst and formic acid–alcohol as a reaction medium by GC–MS is shown in Table 2 (Supplementary table). Fig. 3 shows the distribution of some chemical compounds of the upgraded

bio-oil. Many of the components identified were long chain fatty acid esters, including 11.04% of hexadecanoic acid, methyl ester, 2.37% of hexadecanoic acid, ethyl ester, 9.74% of 8-octadecenoic acid, methyl ester, 2.33% of octadecanoic acid, methyl ester and 2.18% of ethyl oleate. There were 85.15% of the long chain fatty acid esters (≥ 10 carbon atom) in the identified esters. In order to make quality competitive biofuels, further study will have to focus on exploring optimum reaction conditions using Zn powder as catalyst and formic acid–ethanol as a reaction medium.

4. Conclusions

This study investigated microwave catalytic pyrolysis of biomass with activated carbon as a catalyst. The increase in phenol and phenol derivatives was closely related to the decomposition of lignin in the presence of AC. A high concentration of long chain fatty acid esters was obtained in the presence of Zn powder as a catalyst and formic acid–ethanol as a reaction medium. The high content of esters and phenols obtained in this study suggests that the described process could be used to generate fossil fuel substitutes after separation of oxygenates or feedstock for the chemical industry.

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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.2011.12.125.

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