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The effects of mineral salt catalysts on selectivity of phenolic compounds in bio-oil during microwave pyrolysis of peanut shell

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Abstract−Catalytic microwave pyrolysis of peanut shell (PT) using Fe_3O_4, Na_2CO_3, NaOH, and KOH for production of phenolic-rich bio-oil was investigated. The effects of catalyst type, pyrolysis temperature, and biomass/catalyst ratio on product distribution and composition were studied. Among four catalysts tested, Na_2CO_3 significantly increased the selectivity of phenolic compounds in bio-oil during microwave pyrolysis. The highest phenolics concentration of 57.36% (area) was obtained at 500 °C and PT : Na_2CO_3 ratio of 8 : 1. The catalytic effect to produce phenolic compounds among all the catalysts tested can be summarized in the order $Na_2CO_3 > Fe_3O_4 > KOH > NaOH$. Using KOH and NaOH as catalyst resulted in formation of bio-oil with enhanced higher heating value (HHV) and lower oxygen content, indicating that these catalysts enhanced the deoxygenation of bio-oil. The scanning-electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis of char particles showed the melting of magnetite and vaporization-condensation of mineral salt catalysts on char particle, which was attributed to extremely high local temperatures during microwave heating.

Keywords: Biomass, Catalytic Pyrolysis, Microwave Irradiation, Phenolic Compounds, Alkali Catalysts

INTRODUCTION

The increased global energy demand and environmental issues with fossil fuels such as coal has made the replacement of fossil fuels with environmentally friendly energy sources crucial. Biomass accounts for around 14% of global energy sources [1]. It is the only renewable source to be converted into liquid fuel and fine chemicals [2,3] and is known as the only renewable energy source for replacement of fossil fuels (coal, petroleum, natural gas) in production of these commodities [4]. Biomass-based chemicals such as phenolics for resins, levoglucosan and levoglucosenon for polymers, and aromatic hydrocarbons for fuels have been investigated [5]. Biological processes (digestion, fermentation, etc.) require long time to produce specialty products. As an alternative, thermochemical conversion processes such as fast pyrolysis can be applied for production of biomass-based products. A more fundamental understanding of chemical depolymerization of biomass is necessary to achieve higher efficiency and higher selectivity of fine chemicals in bio-oil [6]. A number of studies have reported on the production of value-added products such as bio-fuel, bio-oil, bio-char and hydrogen from biomass feedstock [7-10].

The bio-oil produced during biomass pyrolysis has a complex composition and is usually unstable [11]. Currently, bio-oil from pyrolysis cannot be used directly due to high oxygen content, corrosive nature, and relative instability. Thus, before bio-oils can be used as fuels or source of fine chemicals, they need to be upgraded (typically via cracking and/or hydrotreating) [12,13]. As an alternative, one-step in-situ upgrading is possible, where appropriate catalysts are incorporated directly into the pyrolysis process. Incorporation of catalyst improves the quality of bio-oil and makes downstream upgrading less-complicated [3].

Microwave pyrolysis has been used to enhance pyrolysis and improve the efficiency of biomass conversion [1,14,15]. The addition of inorganic additives such as metal oxides, salts, and acids to lignocellulosic biomass as microwave receptors and catalysts has been reported [11,16-18]. Microwave pyrolysis of different types of biomass has also been reported in the literature [19-21]. However, most studies focused on increasing the bio-oil yield, and the major issue has been the selectivity of chemical compounds in the pyrolysis bio-oil. To decrease the cost and complications of purification methods, the selectivity of fine chemicals needs to be increased in bio-oil by using catalyst.

As building blocks of new synthetic bio-plastics, phenol-formaldehyde resins or epoxy- or polyurethane materials, phenols have wide applications in the chemical industry. Bio-oil with high phenolics content can be directly applied to synthesis of phenolic resins [22]. Thangalazhy-Gopakumar used fixed-bed reactor for pyrolysis of palm oil sludge at 550 °C and reported that bio-oil was mainly composed of pyridine, pyrrole, phenol, indole and their ethyl and methyl derivatives [9]. Zhou et al. reported the phenolics yield of 17.2 wt% for Alcell lignin and 15.5 wt% for Asian lignin at 600 °C [23]. Abdul Aziz et al. [24] studied the fluidized-bed pyrolysis of palm kernel shell and obtained a bio-oil yield of 44-56 wt%. The highest concentration of phenol in bio-oil reached 31% (area) at

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289 °C. Bu et al. studied the microwave pyrolysis of Douglas fir in the presence of activated carbon at 400 °C and reported high concentration of phenolics (75% (area)) in bio-oil [25]. Peng et al. [17] studied the catalytic pyrolysis of lignin in fixed-bed reactor using NaOH and KOH as catalyst and obtained a phenols rich bio-oil (80% in liquid). Lu et al. [26] studied the pyrolysis of poplar wood biomass using K_3PO_4 as catalyst, and reported that the concentration of phenolic compounds reached 60% (area).

This study was focused on increasing the selectivity of phenolic compounds in bio-oil through catalytic microwave pyrolysis of peanut shell by using mineral salts such as Fe_3O_4, Na_2CO_3, NaOH, and KOH as microwave receptor and catalyst. The chemical structure and morphology of chars were also analyzed by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). This study aims to provide fundamental understanding of thermo-chemical conversion of agricultural waste to value-added chemicals through catalytic microwave pyrolysis.

EXPERIMENTAL SECTION

1. Materials

Peanut shell (PT) from North China was used in this study. As-received biomass sample was crushed and sieved to particle size of 150-300 μm. To remove the moisture in sample prior to pyrolysis, biomass samples were dried in a vacuum oven at 105 °C for 12 h. The proximate and ultimate analyses of the sample are given in Table 1. Analytical grade magnetite (Fe_3O_4) (Sinopharm Chemical Reagent Co., Ltd.), sodium carbonate (Na_2CO_3) (Sinopharm Chemical Reagent Co., Ltd.), potassium hydroxide (KOH) (Sinopharm Chemical Reagent Co., Ltd.), and sodium hydroxide (NaOH) (Tianjin Yongda Chemical Reagent Co., Ltd.) were used as microwave receptor and catalyst in microwave pyrolysis experiments.

2. Microwave-induced Pyrolysis Experiments

Pyrolysis experiments were carried out in a specially designed quartz reactor (with an internal diameter of 5 cm and volume of about 549.78 cm^3), which was heated in a microwave oven (Tangshan Microwave Thermal Instrument CO. Ltd., China) with maximum power output of 2,000 W and frequency of 2.45 GHz (Fig. 1). Approximately 8 g biomass was evenly blended with microwave receptor (Fe_3O_4, Na_2CO_3, NaOH, and KOH) at the mass ratios of 8 : 1 and 8 : 0.5. Prior to each run, the reactor was purged with high purity nitrogen gas (99.96%) at 400 ml/min flow rate for 30 min to achieve an inert atmosphere. Pyrolysis runs were carried out at final temperatures of 400 and 500 °C. The volatiles produced during pyrolysis were purged out of the reactor using nitrogen with a flow rate of 400 ml/min. Pyrolysis runs were 50 min. This reaction time was chosen based on the preliminary experiments to ensure the pyrolysis reactions were completed. The temperature of sample was measured continuously at 2 s intervals by a thermocouple inserted into the sample. After the sample bed reached the desired temperature, the microwave oven equipped with automatic temperature/power control system used a minimum power to maintain the desired temperatures. The pyrolysis runs were repeated at least twice to ensure the reproducibility of the experimental results.

Table 1. Proximate and ultimate analyses of peanut shell sample

Sample	Peanut shell (PT)
Moisture content (wt%, ad)	8.03
Volatile matter (wt%, ad)	58.39
Ash (wt%, ad)	11.3
Fixed carbon (wt%, ad)	22.28
C (wt%, daf)	37.87
H (wt%, daf)	5.18
N (wt%, daf)	1.57
S (wt%, daf)	0.14
O^* (wt%, daf)	55.24
H/C	0.14
O/C	1.46

ad: air dried; daf: dry ash free

*By difference

After pyrolysis, biomass char and solid catalyst particles were separated by sieving based on the difference in their particle size. The yields of solid and liquid products were measured by directly weighing each fraction and the gas yield was calculated by difference. The yields of pyrolysis products were calculated from the following equations [27]:

$$Y_{char} = \frac{M_{char}}{M_0} \times 100 \tag{1}$$

$$Y_{bio\text{-}oil} = \frac{M_{bio\text{-}oil}}{M_0} \times 100 \tag{2}$$

$$Y_{gas} = 100 - [Y_{char} + Y_{bio\text{-}oil}] \tag{3}$$

where Y_{char}, $Y_{bio\text{-}oil}$, Y_{gas} are the yields of char, bio-oil, and gas in percentage, respectively. M_{char} is the mass of char (g), $M_{bio\text{-}oil}$ is the mass of bio-oil (g), and M_0 is the initial mass of biomass sample (g).

3. Recovery and Characterization of Bio-oil

The volatile matter released during biomass pyrolysis was passed through four consecutive tar condensers containing dichloromethane (Sinopharm Chemical Reagent Co., Ltd.) placed in an ice-water bath. The organic bio-oil fraction dissolved in dichloromethane was separated by distillation and then analyzed by gas chromatography-mass spectrometry (GC-MS, Thermo Scientific ISQ). The GC-MS was equipped with a capillary column coated with TR-5MS (cross-link 5% Phenyl (equiv.) Polysilphenylene-siloxane, 30 m length, 0.25 mm inner diameter, 0.25 lm film thickness) and a quadrupole analyzer operating in electron impact (70 eV) mode. The oven was heated at 10 °C/min from 40 to 100 °C, and then at a rate of 15 °C/min from 100 to 280 °C, and held at 280 °C for 15 min. The data were acquired and processed using the Chemstation software. The compounds were identified by comparing their mass spectra to spectral data in the instrument database. A semi-quantitative analysis was made to compare the distribution of the compounds in different oils. The relative proportions of compounds in the pyrolysis oils were calculated using the areas (%) from the total ion chromatogram peak area. Elemental analysis of bio-oils involved using a Euro Vector Euro EA elemental analyzer.

4. Characterization of Pyrolysis Chars

Changes in the chemical structure of biomass were studied by

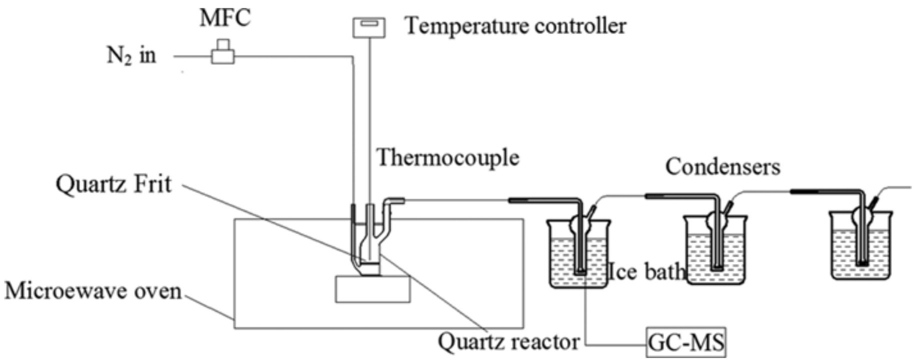

Fig. 1. Schematic diagram of microwave pyrolysis experimental setup.

FTIR. Infrared spectra of raw biomass and pyrolysis chars were obtained with a Thermo Fisher Nicolet IS5 mid-FTIR spectrometer. KBr pellets were prepared by grinding around 1 mg sample with 100 mg KBr. The IR spectrum of pure KBr pellet without the addition of any sample was obtained as a reference spectrum. The bands in the infrared spectra were assigned according to the literature [28,29]. The surface morphology of chars from catalytic microwave pyrolysis of PT was analyzed by using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS, ZEISS Sigma HD).

RESULTS AND DISCUSSION

1. Temperature Profiles of the Sample Bed

Fig. 2 shows the temperature profile of PT and its blends with Fe_3O_4, Na_2CO_3, NaOH, and KOH at final temperatures of 400 and 500 °C and biomass : catalyst ratio of 8 : 1. When no microwave receptor was used, the maximum temperature of the PT sample reached around 140 °C and no pyrolysis took place. Only some water vapor condensation on the tubing was observed. Thus, PT is not a good microwave absorber and to achieve pyrolysis temperatures (400 and 500 °C), the addition of a microwave receptor is necessary. All four additives (Fe_3O_4, Na_2CO_3, NaOH, and KOH) showed great ability to absorb microwave. When mineral salt catalysts were used, a very fast heating rate was achieved and final pyrolysis temperatures were reached in less than 4 min (Fig. 2). Once the desired temperature was reached, a relatively stable temperature was observed due to the controlled heating of microwave oven. During microwave heating, plasma arc formation was observed, which resulted in a rapid increase in bed temperature. The formation of a plasma arc, which also been reported in the literature [20,30], is due to excitement in the electron and ion exchange as a result of biomass and microwave irradiation interaction [30]. The fluctuations observed in sample temperature can be attributed to the formation of plasma arcs.

The heating mechanism of microwave has an important effect on the secondary pyrolysis reactions. During microwave heating, the temperature of sample bed is higher than the surroundings inside the reactor [31]. Therefore, after leaving the sample bed, volatiles move from high temperature region to lower temperature regions, leading to minimized secondary pyrolysis reactions. Thus, the yield and composition of bio-oil under microwave heating mainly depends upon the primary pyrolysis reactions and catalytic effect of microwave receptors.

2. Product Distribution

It has been reported that the nature of the microwave receptor

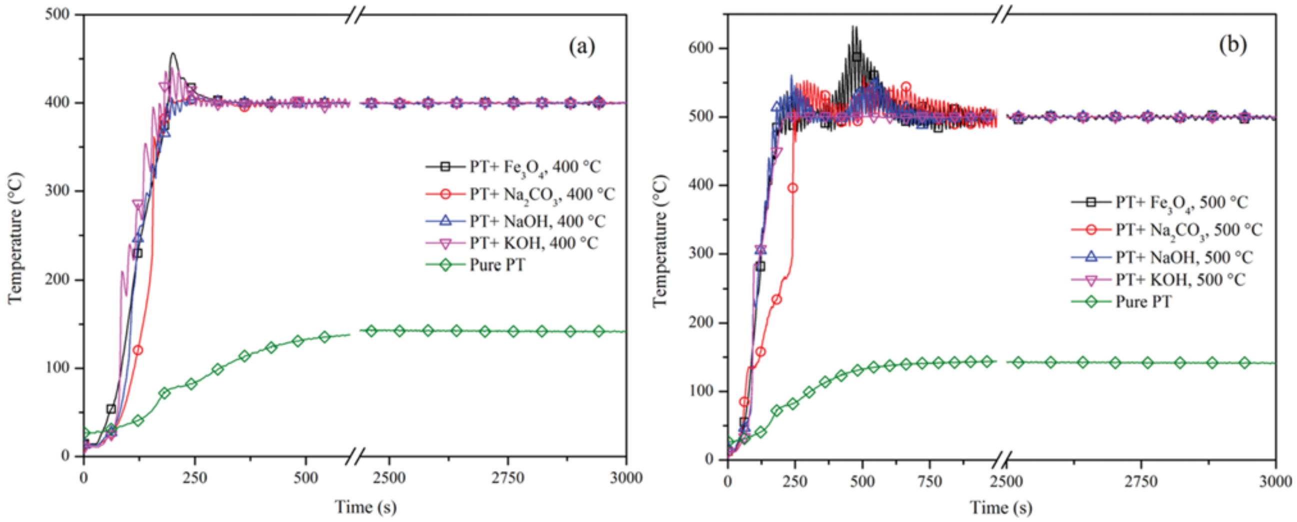

Fig. 2. Temperature profiles of PT sample during microwave pyrolysis using Fe_3O_4, Na_2CO_3, NaOH, and KOH as catalyst at biomass : catalyst ratio of 8 : 1 and different final temperatures: (a) 400 °C; (b) 500 °C.

Table 2. Yields of pyrolysis products during microwave pyrolysis of peanut shell using Fe_3O_4, Na_2CO_3, NaOH, and KOH as microwave receptor

Sample	Temperature (°C)	Char (wt%)	Bio-oil (wt%)	Water in bio-oil (wt%)	Gas (wt%)
PT : Fe_3O_4=8 : 1	400	50.88±0.57	21.76±0.71	28.48±3.08	27.36±0.31
	500	37.99±0.81	17.00±1.26	24.13±1.51	45.01±0.45
PT : Fe_3O_4=8 : 0.5	500	38.95±0.86	16.82±1.24	27.77±4.67	44.23±0.38
PT : Na_2CO_3=8 : 1	400	53.75±1.23	17.00±1.53	18.07±1.35	29.25±2.76
	500	41.46±2.45	24.03±1.36	21.31±2.40	34.51±1.09
PT : Na_2CO_3=8 : 0.5	500	41.55±1.22	20.24±0.95	19.64±1.32	38.21±0.26
PT : NaOH=8 : 1	400	54.63±2.38	15.00±0.47	35.84±2.48	30.37±1.91
	500	42.75±3.03	16.50±0.44	18.56±2.58	40.75±2.59
PT : NaOH=8 : 0.5	500	47.48±1.16	18.77±0.71	20.87±2.62	33.75±0.45
PT : KOH=8 : 1	400	69.25±0.62	11.58±1.00	9.67±0.28	19.17±0.38
	500	38.88±2.90	17.39±0.91	17.55±0.42	43.73±1.99
PT : KOH=8 : 0.5	500	43.00±2.20	13.80±0.68	12.44±0.81	43.20±1.52

may affect product distribution during biomass conversion under microwave irradiation [32]. The product yields (bio-oil, char, and non-condensable gases) from microwave pyrolysis of PT as a function of temperature and biomass to microwave receptor ratio are shown in Table 2. As seen, increasing the pyrolysis temperature from 400 °C to 500 °C resulted in an increase in bio-oil yield for all the mineral salt catalysts tested, except for Fe_3O_4, where the maximum bio-oil yield was observed at 400 °C. Fe_3O_4 and Na_2CO_3 seemed to favor the bio-oil formation. The yield of bio-oil ranged between 11.58 to 24.03 wt%. The highest bio-oil yield of 24.03± 1.36 was obtained at 500 °C and using Na_2CO_3 as catalyst at ratio of PT : Na_2CO_3=8 : 1. The char yield decreased with increasing pyrolysis temperature for all the catalysts tested. Higher content of catalyst in the blends generally increased the weight loss and favored the formation of bio-oil, as seen in Table 2. The yield of bio-oil when NaOH was used as catalyst with an 8 : 1 biomass : catalyst ratio, was lower than that of 8 : 0.5 ratio. This can be attributed to strong basicity of NaOH, which resulted in cracking of larger molecules to form non-condensable gases. Higher pyrolysis temperatures increased the yield of non-condensable gases, which was in agreement with the literature results [33,34]. The water content in bio-oils obtained from PT ranged between 9.67±0.28 and 35.84±2.48 wt%.

3. Bio-oil Characterization

Fig. 3 shows the chemical composition of bio-oils derived from microwave pyrolysis of PT as a function of pyrolysis temperature, biomass to catalyst ratio, and the type of catalyst. No bio-oil was obtained from pyrolysis of pure PT under microwave since the sample temperature did not reach the desired pyrolysis tempera-

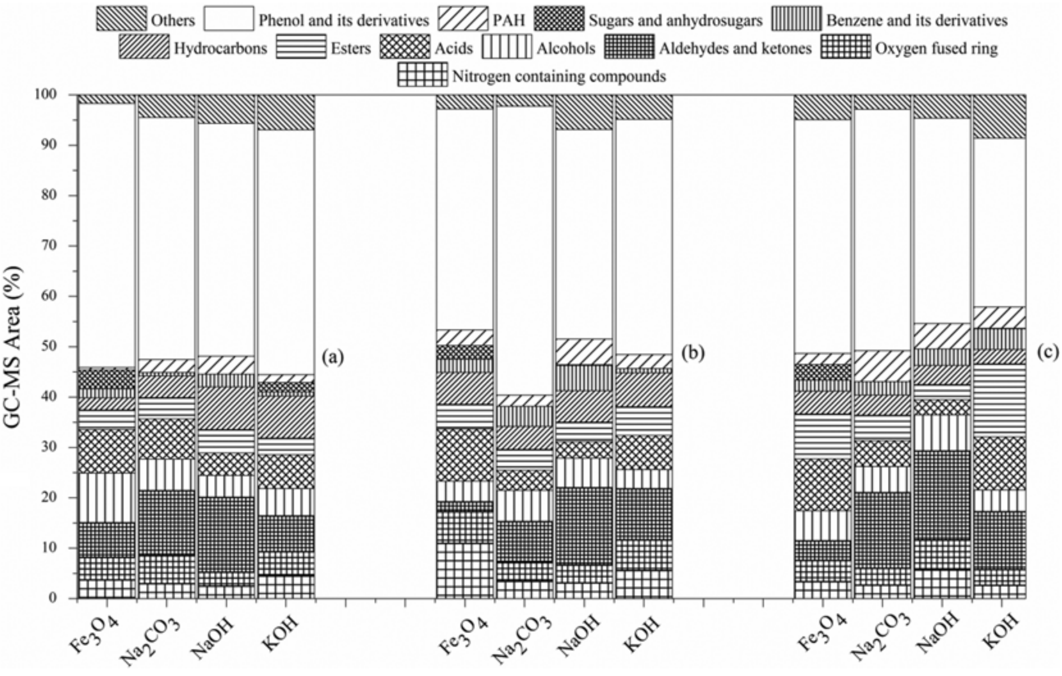

Fig. 3. Chemical composition of the bio-oil from microwave pyrolysis of PT in the presence of Fe_3O_4, Na_2CO_3, NaOH, and KOH: (a) 400 °C, PT : catalyst=8 : 1; (b) 500 °C, PT : catalyst=8 : 1; and (c) 500 °C, PT : catalyst=8 : 0.5.

tures in the absence of microwave receptor. The detected chemical compounds were grouped in eleven groups: phenols, Polycyclic aromatic hydrocarbons (PAHs), sugar and anhydrosugars, benzene and its derivatives, hydrocarbons (mostly consisting of long-chain hydrocarbons with short side branches (CH_3-CH_2-, CH_3-, CH_2=), such as 2,6,10,15-Tetramethylheptadecane, 2-Methylnonadecane, 7-n-Hexyleicosane, 3-Ethyl-5-(2′-ethylbutyl)octadecane, (7Z)-7-Hexadecene, 2-Methyleicosane, (4Z)-2-Methyl-4-tetradecene, etc.), esters, acids, alcohols, aldehydes, oxygen fused rings, and nitrogen containing compounds. Main chemical compounds identified in the bio-oil from microwave pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as microwave receptor at 8 : 1 ratio are given in Table 3. Since phenol and its derivatives were the main chemical compounds in bio-oil derived from PT, bio-oils were highly phenolic chemically. The phenolic compounds consisted of phenol, Phenol, 3-methyl-, Phenol, 2-methoxy-, Phenol, 3-ethyl-, Phenol, 4-ethyl-2-methoxy-, Phenol, 2-methoxy-4-propyl-, and Phenol, 2-methoxy-4-(1-propenyl)-. Apart from phenolic compounds, small amounts of Cyclopropyl carbinol, 3,4-Dimethoxytoluene, and 1,2-Cyclopentanedione, 3-methyl- were also detected in the bio-oil. It can be seen in Table 3 that Fe_3O_4 and Na_2CO_3 facilitated the formation of methxoy-phenols, while more alkyl-phenols were formed with the alkali hydroxide catalysts. Similar results were reported by Peng et al. [17]. Alkaline additives decreased the yields of aldoketones (such as vanillin), which can be attributed to promotion of decarboxylation or decarbonylation reactions. The deoxygenation and decarbonylation from methoxy-phenols by OH^- resulted in high contents of alkyl-phenols in bio-oils obtained in the presence of NaOH and KOH.

From Fig. 3, NaOH favored the formation of PAHs in bio-oils. The concentration of benzene and its derivatives also increased when KOH and NaOH were used as catalyst during microwave pyrolysis and reached 5.02 and 4.09% (area) at 500 °C, respectively. NaOH, Na_2CO_3, and KOH promoted the formation of aldehydes and ketones. The concentration of aldehydes and ketones reached 17.7 (500 °C, PT : NaOH=8 : 0.5), 15.02 (500 °C, PT: Na_2CO_3=8 : 05), and 11.47 (500 °C, Pt : KOH=8 : 1) in case of NaOH, Na_2CO_3, and KOH, respectively. In presence of Fe_3O_4, the concentration of acids

Table 3. Main chemical compounds identified in the bio-oil obtained during the microwave pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as microwave receptor at 8 : 1 ratio

Compounds name	Residence time (min)	GC-MS peak area (%)			
		Fe_3O_4 (400 °C)	Na_2CO_3 (500 °C)	NaOH (400 °C)	KOH (400 °C)
2-Cyclopenten-1-one	3.26	-	1.36	1.80	
Phenol	4.81	-	2.46	4.12	2.25
Phosphonic acid,(p-hydroxyphenyl)-	4.81	1.88	-	-	-
2-Norbornanone	5.03	-	-	-	1.03
1,2-Cyclopentanedione,3-methyl-	5.50	2.67	5.50	-	-
2-Cyclopenten-1-one,2,3-dimethyl-	5.68	-	1.33	1.89	2.16
Phenol, 2-methyl-	5.97	1.09	-	-	-
Phenol, 3-methyl-	6.41	3.12	5.68	7.19	7.25
Phenol, 2-methoxy- (Guaiacol)	6.62	9.08	9.05	6.01	7.71
Cyclopropyl carbinol	6.95	5.78	3.70	-	-
Phenol, 2,4-dimethyl-	7.74	0.51	-	3.20	-
Phenol, 2,6-dimethyl-	7.74	0.6	1.86	-	-
Phenol, 2,3-dimethyl-	7.78	-	-	1.87	2.89
Phenol, 4-ethyl-	8.07	-	-	2.77	1.89
Phenol, 3-ethyl-	8.08	2.5	1.20	-	2.08
Phenol, 2,3-dimethyl-	8.26	-	1.45	0.95	0.98
2-Methoxy-5-methylphenol	8.48	-	4.85	-	-
Creosol	8.49	3.95	-	2.28	3.58
1H-Indene, 1-methylene-	8.55	-	-	1.18	-
1,4:3,6-Dianhydro-à-d-glucopyranose	9.06	2.86	-	-	1.52
3,4-Dimethoxytoluene	9.25	1.27	1.09	-	-
Phenol,2-ethyl-6-methyl-	9.27	-	0.60	2.32	2.48
Phenol,4-ethyl-2-methoxy-	9.89	3.58	3.41	2.51	3.83
2-Methoxy-4-vinylphenol	10.52	7.63	6.88	3.82	4.52
Phenol,2-methoxy-4-propyl-	11.24	0.74	1.08	0.65	1.37
Phenol,2-methoxy-4-(1-propenyl)-	11.88	11.06	8.58	5.41	6.21
Phenol,2,6-dimethoxy-4-(2-propenyl)-	15.61	1.03	1.11	0.58	0.55
n-Hexadecanoic acid	18.19	2.28	-	-	-
Octadecane,3-ethyl-5-(2-ethylbutyl)-	22.02	-	1.14	-	-

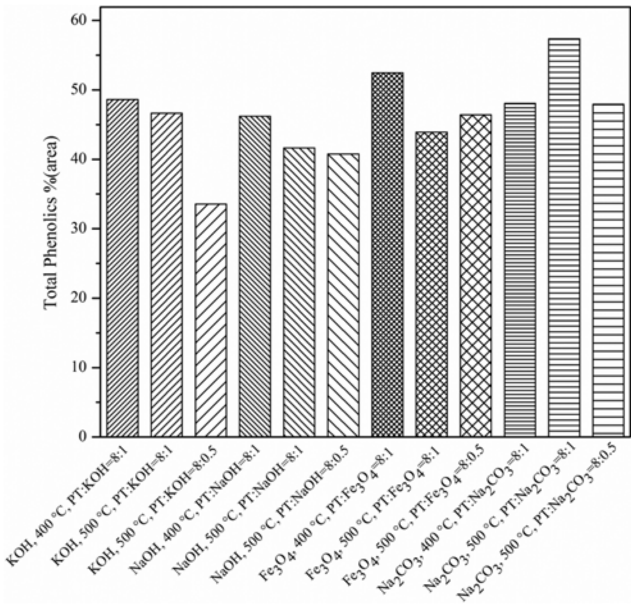

Fig. 4. Total phenolic compounds in bio-oil obtained from catalytic pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as catalyst at different experimental conditions.

increased in bio-oil and reached 10.35% (area) at 500 °C. Fe_3O_4 also increased the concentration of alcohols and hydrocarbons in bio-oil.

Fig. 4 shows the total phenolics content in bio-oil as a function of catalyst type, pyrolysis temperatures, and PT : catalyst ratio. As seen, the concentration of phenolic compounds in bio-oil obtained from PT ranged between 33.56-57.36% (area). The highest phenolics concentration of 57.36% (area) was obtained when PT was blended with Na_2CO_3 at 8 : 1 ratio and pyrolyzed at 500 °C. The highest concentration of phenolics in bio-oil using Fe_3O_4, KOH, and NaOH was 52.47, 48.62, and 46.2% (area), respectively, at PT : catalyst ratio of 8 : 1 and 400 °C. Bio-oil rich in phenolic compounds is of great interest and is an alternative to petroleum-derived phenols [35].

As mentioned, bio-oils obtained during catalytic microwave pyrolysis are complex mixtures of compounds consisting of a wide range of chemical groups (up to 50 chemical compounds in some cases). Therefore, obtaining the weight percentages of chemical compounds in bio-oil through calibration standards is extremely difficult and time consuming. However, in this study the bio-oil samples were subjected to calibration in GC-MS for the two most common phenolic compounds in bio-oil samples: phenol and guaiacol. The calibrated values for phenol and guaiacol were obtained for bio-oil samples and are shown in Table 4 in mg/g basis. The phenol and guaiacol contents in bio-oil obtained from catalytic pyrolysis of PT in different experimental conditions were in the range of 0-1.19 and 0.19-0.38 mg/g bio-oil, respectively.

The main characteristics of bio-oil obtained from microwave pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as catalyst are shown in Table 5. The higher heating value (HHV) of bio-oil was 31.33, 30.44, 32.02, and 33.49 MJ/kg when Fe_3O_4, Na_2CO_3, NaOH, and KOH were used as catalyst. These values were higher than those reported in the literature [36,37]. The oils produced by microwave heating have been reported to be less polar and contain less sulfur than those obtained by conventional pyrolysis [16]. As seen from Table 5, bio-oil obtained from catalytic pyrolysis using NaOH and KOH had higher carbon and lower oxygen content compared to those of Fe_3O_4 and Na_2CO_3, indicating that NaOH and KOH enhanced the deoxygenation of bio-oil, resulting in higher heating value. The positive effect of NaOH and KOH on deoxygenation of phenolic compounds with methoxyl group(s) has been reported in the literature [17].

Table 4. Concentration (mg/g bio-oil) of phenol and guaiacol in the bio-oil obtained during the catalytic microwave pyrolysis of PT

Sample	Temperature (°C)	Phenol	Guaiacol
PT : Fe_3O_4=8 : 1	400	0.54	0.29
PT : Fe_3O_4=8 : 0.5	500	0.52	0.21
PT : Fe_3O_4=8 : 1	500	ND	0.19
PT : Na_2CO_3=8 : 1	400	0.65	0.26
PT : Na_2CO_3=8 : 0.5	500	0.74	0.28
PT : Na_2CO_3=8 : 1	500	0.53	0.23
PT : NaOH=8 : 1	400	0.64	0.24
PT : NaOH=8 : 0.5	500	1.16	0.38
PT : NaOH=8 : 1	500	0.74	0.28
PT : KOH=8 : 1	400	0.54	0.23
PT : KOH=8 : 0.5	500	0.64	0.24
PT : KOH=8 : 1	500	0.56	0.24

Table 5. Comparison of the compositions of bio-oil from microwave pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as microwave receptor at PT : catalyst = 8 : 1

Items	Fe_3O_4 (400 °C)	Na_2CO_3 (500 °C)	NaOH (400 °C)	KOH (400 °C)
Elemental analysis (wt%)				
C	67.89	67.03	69.36	70.97
H	8.29	7.85	8.18	8.77
N	3.56	4.36	4.95	4.54
S	ND	ND	0.24	0.36
O[a]	20.26	20.76	17.27	15.36
HHV (MJ/kg)	31.33	30.44	32.02	33.49
Solid content (wt%)	0.1	0.1	0.1	0.1
Ash content (wt%)	<0.1	<0.1	<0.1	<0.1

[a]Calculated by difference; ND: Not detectable

4. Chemical Structure Changes in Pyrolysis Chars

The IR spectra of PT sample and its chars from microwave pyrolysis at different temperatures and in the presence of four catalysts (Fe_3O_4, Na_2CO_3, NaOH, and KOH) are shown in Fig. 5. The position and assignments of bands in the IR spectra of the samples are listed in Table 6. Significant changes were observed in chemical structure of char samples compared to raw biomass, especially at 500 °C. These changes occurred mostly in 3,700-3,000 cm^{-1} (-OH), 3,000-2,800 cm^{-1} (C-H), 1,740-1,030 cm^{-1} (C=O, C=C, O-CH_3, C-O), and 900-400 cm^{-1} (C-H and C-C) regions in PT chars. The peak intensity of all the functional groups decreased after pyrolysis at

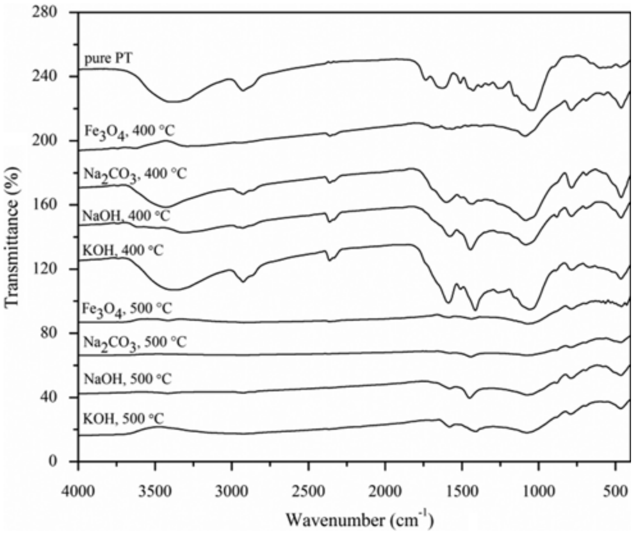

Fig. 5. FTIR spectra of raw PT and its chars obtained from catalytic microwave pyrolysis at 400 and 500 °C.

400 and 500 °C, which was attributed to the release of volatiles during pyrolysis [27]. Decomposition of these groups leads to formation of bio-oil and light gases [29,38]. The intensity of the peak in 3,700-3,000 cm^{-1} region (OH groups) decreased significantly after pyrolysis at 500 °C, indicating the decomposition and release of phenolic or alcoholic groups and water during pyrolysis [27]. The peaks in 3,000-2,800 cm^{-1} region corresponded to alkyl and aliphatic hydrogen groups. The intensity of these peaks decreased after pyrolysis under microwave irradiation, indicating that the methyl groups were removed from the substituted aromatic rings. The peaks in 1,740-1,720 and 1,580-1,480 cm^{-1} regions corresponded to aromatic rings. The decomposition of these groups at 500 °C indicated a decrease in the oxygen containing groups (C=O, C-O, O-CH_3). The decomposition of C-O groups resulted in formation of CO_2 [39], while the O-CH_3 group mainly contributed to formation of CH_4 [29]. Intensity of peaks in 900-750 cm^{-1} (C-H) region decreased after pyrolysis, suggesting the changes in aromatic hydrogen structures and indicating that fused rings were formed at 500 °C.

5. Morphology of Chars

The SEM images of chars from catalytic microwave pyrolysis of PT using Fe_3O_4 and NaOH as catalyst are shown in Fig. 6. Melting morphology of iron can be seen on biomass char samples (Fig. 6(a)), even though the bed temperature was in the range of 500-600 °C. The melting of iron is the result of extremely high temperatures experienced by iron oxide catalyst and the formation of hot spots

Table 6. The assignment of main functional groups in biomass and char samples

Wavenumber (cm^{-1})	Functional groups	Compounds
3,700-3,000	OH stretching	Phenols alcohols and water
3000-2,900	C-H_n stretching	Akyl,aliphatic
1,740-1,730	COOH	Carboxyl acids
1,700-1,550	C=O stretching	Ketone and Carbonyl
1,580-1,480	C=C stretching	Aromatic skeletal
1,460-1,420	O-CH_3	Methoxyl-O-CH_3
1,400-1,370	OH bending	Acid
1,250-1,230	C-O-C stretching	Aryl-alkyl ether linkage
1,050-1,030	C-O stretching and deformation	C-OH(ethanol)
900-750	C-H	Aromatic hydrogen
750-400	C-C stretching	

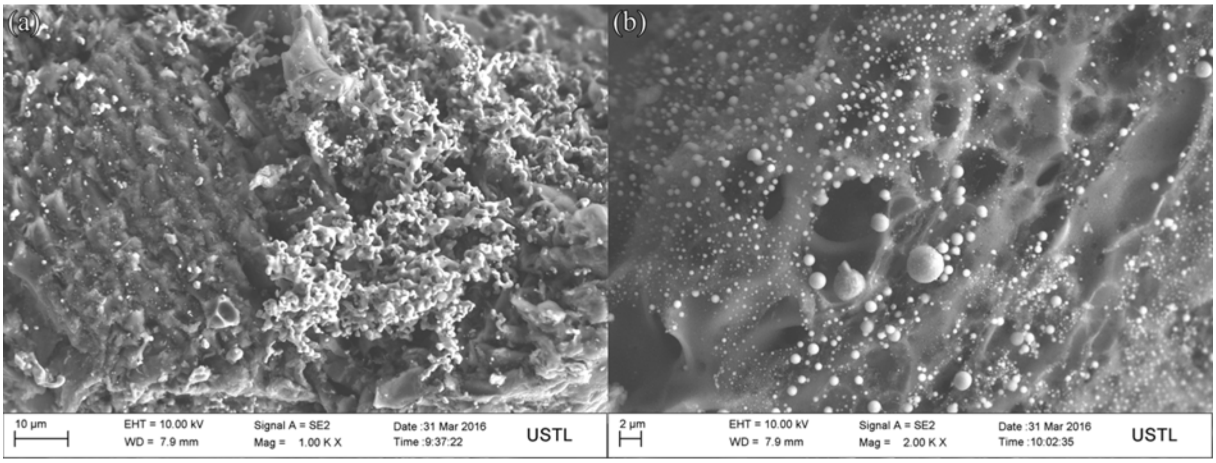

Fig. 6. SEM images of PT char after catalytic microwave pyrolysis at 500 °C using different catalysts: (a) Fe_3O_4; and (b) NaOH.

during microwave heating of biomass char, which is a superior microwave absorber. In the case of NaOH (Fig. 6(b)), the deposition of vaporized mineral particles on char surface was observed.

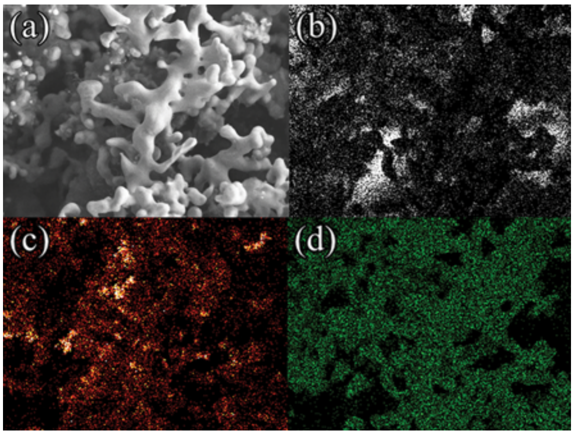

Fig. 7. SEM images of iron oxide on PT char: (a) morphology; (b) elemental mapping of carbon; (c) elemental mapping of oxygen; (d) elemental mapping of iron.

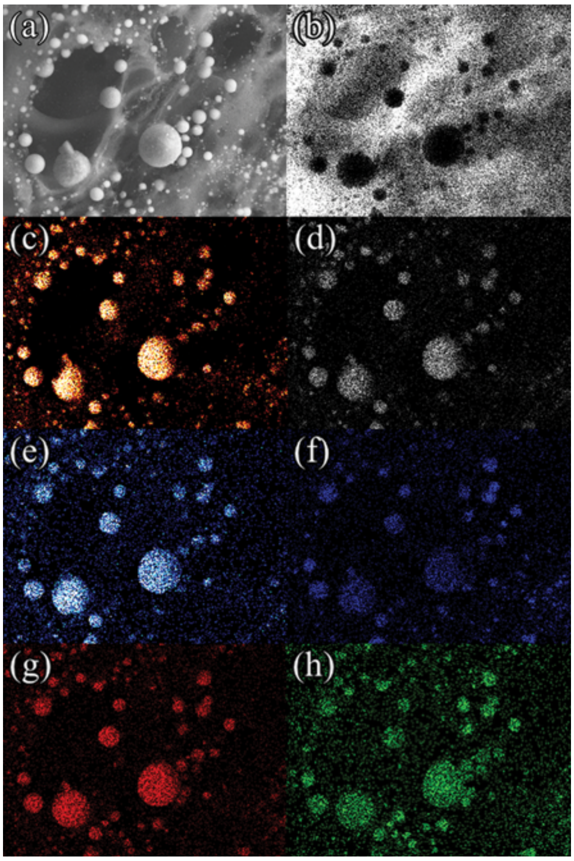

Fig. 8. SEM images of PT char from catalytic pyrolysis using NaOH: (a) morphology; (b) elemental mapping of carbon; (c) elemental mapping of oxygen; (d) elemental mapping of sodium; (e) elemental mapping of magnesium; (f) elemental mapping of aluminum; (g) elemental mapping of silicon; (h) elemental mapping of calcium.

In our previous study [34,35], the formation of carbon nanotubes during microwave pyrolysis was observed when activated carbon was used as catalyst. However, in this study and in presence of mineral salt catalysts, no evidence of nanotubes formation was observed, which implies that the formation of nanotubes on biochar particles requires a special condition, which has not been fully understood.

To better understand the structure and characteristics of PT char particles, EDS analysis was carried out on chars from microwave pyrolysis when Fe_3O_4 and NaOH were used as catalyst. The elemental mapping of carbon, oxygen, and iron in Fig. 7 showed that the melted minerals were closely associated with oxygen and iron. As mentioned, the melting of iron oxide on char particles was probably due to the high local temperatures experienced by iron oxide particles as a result of microwave heating. The morphology and elemental mapping of PT char from microwave pyrolysis in the presence of NaOH is shown in Fig. 8. The spherical particles on char surface were closely associated with oxygen, sodium, magnesium, aluminum, silicon, and calcium. The formation of complex oxides of Na/Mg/Al/Si/Ca/O indicated the vaporization and subsequent condensation and deposition on the char particle surface. These elements may originate from the catalysts particles or the mineral matter in biomass sample.

CONCLUSION

Bio-oils obtained from catalytic microwave pyrolysis of PT using Fe_3O_4, Na_2CO_3, NaOH, and KOH as catalyst were highly phenolic. Na_2CO_3 significantly increased the selectivity of phenolic compounds in bio-oil, and phenolic content reached 57.36% (area) at 500 °C.

Bio-oil obtained from catalytic pyrolysis using KOH and NaOH showed lower oxygen content and higher HHV, indicating that these catalysts enhanced the deoxygenation of bio-oil during microwave pyrolysis.

The SEM-EDS analysis of char particles indicated the melting of iron oxide and vaporization and condensation of mineral salt additives on char particle surface because of extremely high local temperatures and formation of hot spots during microwave heating of biomass char.

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