Biochar of Corn Stover: Microwave-assisted Pyrolysis Condition Induced Changes in Surface Functional Groups and Characteristics

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Abstract: Biochar was prepared by microwave-assisted pyrolysis of corn stover at atmospheric pressure and different reaction temperatures and time. A central composite experimental design was used in the optimization of volatiles (bio-oil and syngas), biochar production, and the amount of carbon surface functional groups. Various types of oxygenated functional groups on the biochar were quantified by means of titrimetric techniques using a modified Boehm's method. The range of surface carbonyl groups amount was from 0.27 to 1.70 mmol/g carbon. The produced biochars were also characterized in terms of the elemental composition, BET surface area and chemical structure. The maximum surface area of the biochar was 45 m²/g. The result indicates that the surface functional groups of biochar were significantly influenced by the pyrolysis temperature and residence time. An adequate prediction model was developed to describe the development of carbon surface functional groups. Modification and characterization of biochar surface functional groups is a new way to improve or extend their catalytic application in biomass conversion and bio-oil upgrading.

Keywords: Biochar; Surface Functional Groups; Microwave; Pyrolysis; Corn Stover

1 Introduction

Biochar has been generated from a range of agricultural and organic materials. It is the intermediate solid residue, which can be formed by several thermochemical processes, including conventional carbonization, pyrolysis and gasification [1]. Biochar is a carbon-rich, fine-grained, porous substance, but it can also contain some oxygen and hydrogen. The lower heating value (LHV) of biochar is about 32 MJ/kg [2].

Pyrolysis of biomass is the major thermo-chemical decomposition process of organic compounds under inert condition with temperature ranging from 350 to 700 °C [3]. It is a well-known technology for the production of biofuels, syngas and value-added chemicals. With the development of biomass pyrolysis, increasing amount of biochar will be produced for applications. Most of the biochar exploitation mainly highlighted the benefit of using biochar in area of water treatment, soil amendment and further extending to the enhancement of environmental quality [4-6]. Recent studies showed that, the biochar could be developed and used as catalyst in biodiesel production [7], catalytic esterification [8], biomass hydrolysis and biogas reforming [8, 9], and bio-oil upgrading [10]. However, the potential value of the pyrolysis biochar used as carbon based catalyst is still in its infancy [11].

In pyrolysis, several studies already demonstrated that the quality and chemical composition of biochar are greatly influenced by the production parameters (principally heating rate,

temperature, residence time, particle size). In addition to that, the biomass feedstock also interacts with the rest of the variables in determining the properties of the produced biochar [12-14]. Sharma et al. [15] mentioned that the biochar from pectin and tobacco was governed more by pyrolysis conditions than the nature of the feedstock. Microwave pyrolysis is an energy and cost efficient way of converting biomass into higher value products. Compared 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 energy into heat, and transfer heat from the inside to the surface of biomass irradiation [16]. The microwave pyrolysis could somehow overcome heat transfer rate limitation which is suitable for the pyrolysis of large fragment materials [17]. Microwave heating is a very effective method for activating and modifying the surface chemistry of the biochar in the pyrolysis process [14, 18]. Therefore, it is possible to produce different types of biochar by altering the microwave pyrolysis conditions and select biochar with the best performance in catalysis, which is mainly dependent upon biochar properties.

The properties analysis for biochar shows that the biochar is porous and has a relatively high surface area [19], also a high mineral content. Many properties of biochar are significantly influenced by the chemisorption of oxygen onto the carbon surface. Oxygen in the surface oxides can be bound in the form of various surface organic functional groups. The surface functional groups are mainly derived from activation process, precursor, heat treatment and post chemical treatment. Some studies already demonstrated that the surface functional

groups anchored on/with carbon were found to be responsible for the variety in catalytic and physicochemical properties of the matter considered [20, 21]. Surface functional groups could be quantified by means of titrimetric techniques; the method was first proposed and established by Boehm [22].

The characteristics of biochar structure and the abundance of surface functional groups suggest that modification and characterization of biochar surface functional groups is a new way to improve or extend their practical application [23, 24]. Our previous research investigated the effects of biochar as a catalyst in biomass catalytic pyrolysis and bio-oil upgrading. The bio-oil chemical profile from catalytic pyrolysis and bio-oil upgrading over carbon catalyst was simplified to phenols and hydrocarbons [10]. These results indicated that corn stover derived biochar might be a cost-competitive catalyst in biomass conversion and bio-oil upgrading for fuels and chemicals production. However, the relationship between biochar properties and its potential to enhance the bio-oil quality is still unclear, and does not allow the establishment of the optimum pyrolysis conditions in order to produce a biochar with desired catalytic performance.

To our knowledge, there is no research to date on the production and surface functional groups analysis of biochar derived from microwave-assisted pyrolysis, and how to modify as well as characterize the surface functional groups by different pyrolysis conditions. Therefore, in this study, the biochar was prepared by microwave assisted pyrolysis of corn stover at atmospheric pressure and different pyrolysis reaction temperatures and residence time.

Various types of surface oxygenated functional groups on the biochar surface were quantified by means of titrimetric techniques using a modified Boehm's method [22, 25]. The chemical composition and surface functionality of both biomass feedstock and biochar were also investigated by means of Fourier transform infrared spectroscopy (FTIR).

The aim of the present study is to investigate the effect of microwave pyrolysis temperature, residence time and particle size on characteristics and chemical composition of the produced biochar from corn stover to develop prediction models for the amount of desired surface functional groups. This study is only an initial step, but further efforts are needed to perform carbon catalyst performance research in order to establish an appropriate pyrolysis process and condition for desired biochar functional groups.

2 Materials and Methods

2.1 Materials

Corn stover (collected from Brookings, South Dakota, USA) used in this experiment was dried in air at the room temperature. It was grinded mechanically by a Thomas-Wiley laboratory mill (Model No. 3375-E15, Thomas Scientific, USA) and sieved through a series of sieves in 5 different size (0.5mm, 1mm, 2mm, 3mm, and 4mm). Proximate analysis was performed for the raw material to analyze its chemical composition. Results are presented in Table 1.

2.2 Microwave pyrolysis of corn stover

Fig. 1 shows the schematic diagram of the microwave-assisted pyrolysis system. The microwave reactor was manufactured by Sineo Microwave Chemistry Technology Company (Shanghai, China). The microwave pyrolysis system consisted of the following components: a 700W, 2.45GHz microwave cavity, a 500mL 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 system was purged with nitrogen on a flow rate of 1000 mL/min for 30 min prior to microwave pyrolysis to create an oxygen free background. The temperature of biomass was measured by an infrared sensor through a dead end quartz tube which protruded to the center of the 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 temperature of cooling water in the condensers was about 5°C. During pyrolysis the heavier volatiles are condensed into liquids as bio-oil and the lighter volatiles escape as syngas. Biochar is left in the quartz flask. The weight of syngas product was calculated using the following equation:

$$\text{Weight of syngas} = \text{initial corn stover mass} - \text{bio-oil mass} - \text{biochar mass} \quad (1)$$

2.3 Experimental design

Central composite experimental design (CCD) was used in the optimization of volatiles (bio-oil and syngas) and biochar production. Reaction temperature (X_1 , °C), reaction residence time (X_2 , min) and particle size (X_3 , mm) were chosen as the independent variables and are shown in Table 2. Reaction residence time was recorded after the desired temperature was

reached. The amount of each titrable functional group was used as dependent variable. The reaction time was recorded after the desired temperature was reached. For statistical calculations, the variables X_i were coded as x_i according to Eq. 2:

$$x_i = (X_i - X_0)/\Delta X \quad (2)$$

where x_i is dimensionless, X_i is the real value of an independent variable, X_0 is real value of the independent variable at the center point, and ΔX is step change.

A 2^3 -factorial CCD, with 4 axial points ($\alpha=1.68$) and 6 replications at the center points ($n_0=6$) leading to a total number of 20 experiments, was employed (Table 2) for the optimization of the conditions of pyrolysis process. The second-degree polynomials (Eq. 3) were calculated with the statistical package (SAS Institute Inc., USA) to estimate the response of the dependent variable.

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{21}X_2X_1 + b_{31}X_3X_1 + b_{32}X_3X_2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (3)$$

where Y_i is predicted response, X_1 , X_2 and X_3 , are independent variables, b_0 is the offset term, b_1 and b_2 , b_3 are linear effects, b_{11} , b_{22} and b_{33} are squared effects, and b_{21} , b_{31} and b_{32} are interaction terms.

2.4 Total titrable surface functional groups analysis

The total negative surface charge was quantified by Boehm's method [25]. It involved suspending 0.5 g of carbon catalyst in 25 mL of a 0.1 N solution of sodium ethoxide, sodium hydroxide or hydrochloride acid. The samples were agitated by shaking in closed vessels for

24 h. After this time, the slurry was filtered and a 10 mL aliquot was added to 15 mL of 0.1 N HCl or NaOH (Sigma-Aldrich, 99.99%). The HCl or NaOH neutralized the unreacted base or acid and kept further reaction between atmospheric carbon dioxide and the various bases from occurring. The acidified solutions were bubbled with N₂ for 1 h to expel dissolved CO₂ from solution [26]. All samples were then back-titrated with 0.1N NaOH or HCl (Sigma-Aldrich, 99.99%), and the endpoints were potentiometrically determined using a pH meter (Oakton PC - 400). The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon. In all cases, results are expressed as mmol H⁺ equivalent/g carbon [27, 28]. All solutions were prepared with 18.2 MΩ water, and sodium ethoxide were made up with 100% ethanol. All titrations were carried out at room temperature (22 ± 3 °C).

2.5 Analysis of volatile products

The chemical compositions of the bio-oil were determined using an Agilent gas chromatography-mass spectrometer (GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was first maintained at 45 °C for 3 min and then increased at 10 °C /min to 300 °C and finally held isothermal for 10 min. The injector temperature was 280 °C and the injection 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. The NIST Mass Spectral libraries were used for the identification of the compounds found in the bio-oil.

The uncondensed gas released from our microwave catalytic pyrolysis apparatus was collected and analyzed using dual Channel Micro-GC (INFICON, 3000). The used Micro-GC contains two channels and the operating condition as are listed as follows: Channel A with molecular sieve 5A column (MS-5) was set at 95 °C for determination of H₂, CO and CH₄; Channel B with Porapak Q (PPQ) was set at 60 °C for checking the release property of CO₂, C₂H₄ and C₂H₆.

2.6 Characterization of biochar

The elemental analysis of biochar was performed at ALS Environmental laboratories (Tucson, AZ). Elemental analysis of the biochar products was performed according to ASTM D5373 and ASTM D 5291 standard test methods. Composition was determined according to ASTM D 3176. Empirical formula, H/C and O/C molar ratio were calculated from elemental composition.

The FT-IR spectra of raw biomass and produced biochar samples were obtained with an IR Prestige 21 spectrometer in the attenuated total reflection (ATR) mode (Shimadzu, Ge Crystal; software: IR Solution). The spectra were obtained at 8 cm⁻¹ resolution from 650 to 4500 cm⁻¹ using a combined 32 scans. All feedstock and biochar samples were analyzed without pretreatments.

Surface area measurements on corn stover biochar were obtained from nitrogen adsorption isotherms at 77 K using an automatic physisorption analyzer (Micromeritics TriStar II 3020).

Specific surface area were determined from adsorption isotherms using the Brunauer, Emmett, and Teller (BET) equation, applied in a relative pressure ranged from 0.05 to 0.30. To ensure the reproducibility and accuracy of analysis, repeated experiments were accomplished.

3 Results and discussion

3.1 Product yield and analysis

Previous research found that the pyrolysis products were influenced by different feedstocks, pyrolysis conditions, and heating methods [29, 30]. In this study the reaction temperature, residence time and biomass particle size were selected as independent variables to investigate the biochar yield and the further carbon surface functional groups. The detailed experimental design and yield distribution of products obtained at different microwave pyrolysis conditions were shown in Table 3.

The range of biochar yield varied from 23.4 to 26.5% with different pyrolysis conditions, bio-oil varied from 25.0 to 35.8%, and syngas varied from 39.1 to 50.2%. The maximum biochar yield was observed at 516°C and residence time of 15min with 2mm particle size corn stover, while the bio-oil yield was the lowest around 25.0%. As previous research also indicated the amount of biochar was influenced by the pyrolysis temperature. Low temperature result in more biochar; high temperatures result in less [31]. Similar phenomena were also reported in previous studies. Demirbas investigated the biochar yield from pyrolysis of agriculture residue, and they confirmed a high temperature and increasing heating rate resulting in a decrease biochar yield [13].

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217 The minimum biochar yield was observed at 600°C and residence time of 23.4 min with
218 2mm particle size corn stover, while the syngas yield was the highest around 50.2%. Similar
219 phenomenon can be observed in conventional pyrolysis, as a relatively low temperature over
220 an extended period time can maximize the char formation. Carbonization allows adequate
221 time for the condensable vapor to be converted into biochar and non-condensable syngas.

222

223 The volatiles from corn stover microwave pyrolysis were analyzed in our previous research
224 [10, 30]. The results implied that the condensed raw bio-oil was mainly composed of phenols,
225 guaiacols, aliphatic hydrocarbon, aromatic hydrocarbons, furan derivatives and some acids,
226 etc. These evolved compounds were related to the pyrolysis conditions. Decomposition of the
227 lignin found in biomass resulted in production of numerous phenolic compounds, which were
228 made up of phenol, methoxy phenols, diphenols, methyl phenols and ethyl phenols. Phenolic
229 compounds presented in the bio-oil were about 28% to 50% depending on the pyrolysis
230 conditions.

231

232 Non-condensable gases were also produced along with the bio-oil, as shown in Table 4. The
233 Micro-GC analysis results showed that the gas components mainly contains CO₂, CO, CH₄,
234 H₂, C₂H₆, C₂H₄, C₃H₆ and trace amounts of larger gaseous organics. Carbon dioxide present
235 the largest amount in both gases from run 2 and run 16, about 66.7 % and 58.5%, respectively.
236 The yield of hydrogen and methane was generally low but increased with temperature. These
237 results are in agreement with those reported in fast and slow pyrolysis reactors. In the

pyrolysis process, the heavier hydrocarbons are cracked, giving rise to lighter ones, methane and hydrogen at high temperatures.

3.2 Surface functional groups titration analysis

From the previous research, acidic and basic surface sites usually coexist. Basic surface character is found when a carbon surface cleaned at high temperature in vacuum, under an inert gas, or exposed to air and aqueous acid (or water) after cooling to room temperature. Besides, the concentration of basic sites decreases with increasing acidic character of the carbon surface [22].

It has been suggested that the basicity may be due to oxygen functional groups, and existence of pyrone-type structure on the edges of the polyaromatics. Microwave heating is a very effective method for modifying the surface chemistry of the carbon fibers with the production of pyrone group. When the carbonyl group and the ring oxygen of pyrone type structure are distributed on polycyclic aromatic, the base strength is even stronger than that of pyridine [32, 33]. Thus, the surface basicity of biochar produced by microwave pyrolysis can be explained.

Table 5 shows the detailed surface functional groups amount of biochar obtained at different microwave pyrolysis conditions. The surface functional groups data in Table 5 have been subtracted from each other in the following manner:

1. Total surface functional groups (NaOEt titn.) - Total surface functional charge (NaOH titn.) = Carbonyl groups amount (mmol/g carbon)

2. Total surface functional groups (HCl titn.) = Basic groups amount(mmol/g carbon)

The range of basic surface functional groups amount was found from 0.12 to 1.03 mmol/g carbon varied with different pyrolysis conditions. Carbonyl groups amount was from 0.27 to 1.70 mmol/g carbon. The maximum basic groups and carbonyl groups amount were both detected at 550°C and residence time of 10min with 1mm particle size corn stover.

3.3 Response surface analysis

3.3.1 Carbonyl functional groups

The most important physical factors that affected carbonyl groups production were the reaction time and reaction temperature. The suitable levels for these parameters were also determined using statistical CCD. The experimental design matrix is given in Tables 2 and 3. Experiments were performed using different combinations of the variables as per the CCD. Using the results of the experiments, the following second-order polynomial equation giving the amount carbonyl groups as a function of reaction temperature (X_1 , min) and reaction time (X_2 , °C) and particle size (X_3 , mm) were obtained:

$$Y_{\text{carbonyl groups}} = 26.06 - 0.041X_1 - 1.75X_2 + 0.0029X_2X_1 + 0.041X_3X_1 \quad (4)$$

According to the ANOVA results, It was found that the model terms corn stover size X_3 (P-value = 0.32) and X_1X_3 (P-value = 0.66) were insignificant (P-values > 0.05) when Equation 3 was used to fit the data. Equation 3 was reduced by using backward statistical analysis, and Equation 4 was obtained with its significant terms (P-value < 0.0001). The correlation

coefficients of determination, R^2 was 0.92 for carbonyl groups amount, implying that the reduced regression models can be used to explain the carbon surface functional groups generation, and the carbonyl groups amount variations were attributed to the independent variables of reaction time, reaction temperature, and their squared effects. Hence, these models can adequately represent the experimental data and can be used to predict the production of carbonyl groups amount for corn stover microwave pyrolysis processes.

Fig. 2 represents the response surface and contour line for the carbonyl groups amount. When temperature was over 600°C, the amount of carbonyl groups increased with the increase of the reaction temperature and decreased with residence time. When the temperature was below 600°C, the amount of carbonyl groups increased with the increase of the reaction temperature and residence time. The effect of particle size was found to be less significant on the carbonyl groups amount of biochar from corn stover pyrolysis.

Below 600°C, dehydration, decarboxylation and decarbonylation of biomass are the major reactions. Highly reactive sites were exposed on the carbon surface which had free-radical characteristics, when the surface oxides decomposed to CO₂ and CO on heating at high temperatures[32]. Above 600 °C, direct dehydrogenation and demethanation resulting in a large amount of aromatic and some oxygen functional groups. Meanwhile, microwave treatment also played a role in the process. The aforesaid modifications in the chemical structure of corn stover were related to changes of surface carbonyl groups amount in microwave pyrolysis to some extent.

3.3.2 Basic functional groups

Using the results of the experiments shown in Table 3, the following second-order polynomial equation giving the amount basic groups as a function of reaction temperature (X_1 , min), reaction time (X_2 , °C) and size (X_3 , mm) were obtained:

$$Y_{\text{basic groups}} = -200.12 + 0.68X_1 + 0.69X_2 + 5.27X_3 - 0.0067X_3X_1 - 0.0006X_1^2 - 0.0089X_2^2 - 0.29X_3^2 \quad (5)$$

According to the ANOVA results, it was found that the model terms X_2X_1 (P-value = 0.13) and X_2X_3 (P-value = 0.35) were insignificant (P-values > 0.05) when Equation 3 was used to fit the data. Equation 3 was reduced by using backward statistical analysis, and Equation 5 was obtained with its significant terms (P-value < 0.0001). The correlation coefficients of determination, R^2 was 0.91 for basic groups' amount, implying that the reduced quadratic regression models can be used to explain the carbon surface functional groups generation, and the basic groups' amount variations were attributed to the independent variables of reaction time, reaction temperature, and their squared effects. Hence, these models can adequately represent the experimental data and can be used to predict the production of basic groups' amount for corn stover microwave pyrolysis processes.

Fig. 3 represents the response surface and contour line for the basic group's amount. The amount of basic groups was found to be decreased with the increase of the reaction

temperature. A possible explanation is that the reduction in pyrone type ligands occurred in the microwave pyrolysis at a higher temperature, and the biochar became more carbonaceous.

3.4 Characteristics of Biochar

3.4.1 Elemental analysis

The elemental analysis values for biochar samples were given in Table 6. The results of the elemental analysis of biochar indicated that the temperature had a significant effect on the elemental composition of the corn stover biochar. Carbon (C) content generally increased, while hydrogen (H) and oxygen (O) content decreased with increasing temperatures. As the temperature increased, H/C and O/C atomic ratios decreased, indicating that the biochar became increasingly more aromatic and carbonaceous.

3.4.2 FTIR analysis

The FTIR method had been widely used to characterize the surface groups of different oxides, and also applied to various types of carbon and carbonaceous materials. Since FTIR transmission spectra had peaked shapes where the specific chemical bonds existed, it was possible to know which functionalities were created on the surface of biochar by comparing locations and depths of the peak lines [34, 35].

The FTIR spectra of both biomass feedstock and biochar obtained are useful to analyze the loss of lignocellulosic functional groups. As shown in Figure 4, compared to the raw corn stover spectra, the biochar spectra had a remarkable decrease in features associated with O-H

stretch ($3100\text{--}3600\text{ cm}^{-1}$), C=C stretching ($1600\text{--}1740\text{ cm}^{-1}$), C-O-C symmetric stretching (1030 cm^{-1}), and characteristics of cellulose and hemicellulose (pyranose rings and guaiacyl monomers). Concurrently, C-H bending for aromatic out-of plane deformation (790 , and 832 cm^{-1}) became apparent. The peak characteristics of carbonyl groups appear in 1660 to 1770 cm^{-1} , depending on the carbonyl groups whether or not are in conjunction with the aromatic ring [36]. Due to the disturbing effect on the electron density distribution, their relative intensity varies frequently when electronegative substituents are in the aromatic rings [37].

The assignment of the absorption bands was based on experience with molecular organic compounds. There is a loss of oxygen content in biochar compared to raw corn stover, implied by the loss of O-H ($3100\text{--}3600\text{ cm}^{-1}$) and the ratio of intensities for the C=O and C=C bands ($1500\text{--}1700\text{ cm}^{-1}$) to the shoulder ($1100\text{--}1200\text{ cm}^{-1}$) arising from aromatic (substituted) C-H deformations as well as the decrease in ratio of the C-O-C (1030 cm^{-1}) to the shoulder at $1100\text{--}1200\text{ cm}^{-1}$. These features could be explained by the dehydration of the cellulosic and ligneous components as well as an increase in degree of condensation over 400°C in the microwave pyrolysis [38]. Besides, an increasing drift in the baseline at high wavenumbers was found in the spectra after corn stover pyrolysis. Similar phenomena were also found in the literature study on maize stalk and pectin char [36, 37]. At high temperatures (over 600°C), the biochar was becoming more carbonized with an increasing aromatic carbon content. The loss the hydroxyl, aliphatic C-H, carbonyl and olefinic C=C groups from dehydration, decarbonylation, and decarboxylation reactions led to condensation and the growth of organic chemical structures which contained aromatic C=C bonds and ether

structures as oxygen functional groups [39]. This is also consistent with the shift to lower frequencies of the bands due to C=O and C=C vibration.

3.4.3 Surface properties analysis

Surface area, average pore volume; and pore size from produced biochar samples were analyzed by the N₂-adsorption/desorption automatic physisorption analyzer at 77 K, as shown in Table 7. The BET surface area of corn stover biochar from microwave pyrolysis was much lower than activated carbon with a maximum of 45 m²/g at 600 °C. The relatively low BET surface area and pore volume also suggests that either the biochar from corn stover are not typical microporous or that the pores within these biochar are extensively small and dead-ended, preventing the access of the adsorption gas. However, the BET surface area and pore volume of microwave pyrolysis biochar is still higher than most of the biochar prepared during biomass pyrolysis found in the previous studies [19, 36, 37]. Compared 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 energy into heat, and transfer heat from the inside to the surface of biomass irradiation. Microwave irradiation might be a good way for the modification of surface area and pore size distribution [18].

We also found that the higher temperature and retention time enhanced the pore structure of the microwave pyrolysis biochar. The BET surface area of corn stover biochar is less than 10 m²/g at temperature range from 500 to 550 °C. With increasing charring temperature,

devolatilization of bigger molecules occurred and size of the volatile molecules decreased gradually, while the release of smaller molecules would enhance the micropores in the sample giving rise to increase in the BET surface area. Those results were in accordance with Li et al. and Sharma, who reported the BET surface area and micropore volume an increased with the increase of temperature [15, 40].

4 Conclusions

This study investigated microwave pyrolysis of corn stover and demonstrated the influence of three main pyrolysis variables on the production and surface functionality of biochar. Two production models were satisfactorily developed to describe the total amount of surface carbonyl groups and basic groups respectively. The particle size was found to be a less significant parameter to the biochar surface functionality. The amount of basic groups was decreased with the increase of the reaction temperature. For carbonyl groups, the change of its amount was more complicated due to the biomass decomposition and vapour reforming reactions under different temperatures.

FTIR spectra indicate a loss of lignocellulosic functional groups from raw biomass feedstock to pyrolysis biochar. As the temperature increased, H/C and O/C atomic ratios decreased, which lead to a more aromatic and carbonaceous biochar. The maximum surface area of the biochar was 45 m²/g produced from microwave pyrolysis at 600 °C, which was much higher than that of corn stover biochar from traditional pyrolysis. Microwave assisted pyrolysis is a

potential way to produce higher surface area biochar. Indeed, modification and characterization of biochar surface functional groups could be a promising way to improve or extend their catalytic application.

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564

565 Table 1 Proximate analyses of initial raw feedstock

Characteristics		Corn stover
Proximate analysis (dry, wt.%)	Volatile Matter	74.46
	Fixed carbon	20.06
	Ash	5.48
Moisture (wt.%)		6.29
HHV (MJ/kg)		16.82

566

567 Table 2 Coded levels and experimental range of independent variables

Variables	Coded factor	Range and levels				
		-r(-1.68)	-1	0	1	+r(1.68)
Temperature(°C)	X_1	516	550	600	650	684.1
Time(min)	X_2	6.7	10	15	20	23.4
Particle Size(mm)	X_3	0.5	1	2	3	4

568

569

570 Table 3 Reaction conditions and product yield distribution

Run	Temperature (°C)	Time (min)	Particle size (mm)	Yield (%)		
				Biochar	Bio-oil	Syngas
1	516	15	2	26.5	25.0	48.6
2	550	10	1	25.0	30.5	44.4
3	550	10	3	25.7	32.6	41.7
4	550	20	1	25.1	31.6	43.4
5	550	20	3	25.3	31.3	43.4
6	600	6.7	2	23.8	26.5	49.7
7	600	15	0.5	24.0	33.8	42.2
8	600	15	2	25.7	32.3	42.0
9	600	15	2	26.2	33.2	40.6
10	600	15	2	26.2	32.4	41.4
11	600	15	2	26.1	32.8	41.1
12	600	15	2	26.2	32.9	40.9
13	600	15	2	26.1	33.2	40.7
14	600	15	4	25.5	35.1	39.4
15	600	23.4	2	23.4	26.4	50.2
16	650	10	1	25.2	35.8	39.1
17	650	10	3	25.1	32.1	42.9
18	650	20	1	24.6	32.7	42.6
19	650	20	3	24.6	30.3	45.1
20	684.1	15	2	24.0	29.9	46.1

571

572

573 Table 4. Major components of non-condensable gases from microwave pyrolysis of corn
 574 stover at different conditions

Retention time (min)	Components	Formula	Amount (vol %)	
			Run 2	Run 16 [*]
24.5	Hydrogen	H ₂	19.4	24.8
71.4	Methane	CH ₄	3.7	4.9
108.0	Carbon Monoxide	CO	4.9	5.9
19.1	Carbon Dioxide	CO ₂	66.7	58.5
62.4	Ethylene	C ₂ H ₄	2.6	2.8
99.2	Ethane	C ₂ H ₆	1.3	1.1
105.8	Propene	C ₃ H ₆	1.2	1.6

575 ^{*} Run 2: 550 °C and 10 min; Run 16: 650 °C and 10 min

576 Table 5 Summary of carbon surface functional groups results

Batch	Particle size (mm)	Temperature (°C)	Time (min)	Surface functional groups (mmol/g carbon)	
				Basic groups	Carbonyl groups
A	1	650	10	0.47	1.03
	1	550	10	1.03	1.70
	1	650	20	0.11	0.99
	1	550	20	0.51	0.27
B	2	600	15	0.73	0.98
	2	516	15	0.18	0.35
	2	600	6.7	0.52	0.44
	2	600	23.4	0.48	0.72
C	3	650	20	0.48	0.51
	3	550	10	0.48	0.90
	3	550	20	0.50	0.34
	3	650	10	0.37	0.38

577

578 Table 6. Elemental analysis (dry basis) of the pyrolysis biochar derived from corn stover.

Characteristics		Biochar-550°C	Biochar-650°C
Elemental analysis (wt.%)	C	68.01	81.47
	H	1.84	0.72
	N	0.74	0.69
	O	5.94	4.38
	S	0.05	0.04
O/C molar ratio		0.12	0.07
H/C molar ratio		0.32	0.11
Ash (wt.%)		23.42	12.70

579

580 **Table 7 Porous properties of the typical pyrolysis biochars derived from corn stover.**

Run	Conditions	BET surface area (m ² /g)	Average pore volume (cm ³ /g)	Average pore width (nm)
3	550°C, 10min	9.1	0.009	14.7
5	550°C, 20min	18.3	0.011	8.7
15	600°C, 15min	45	0.021	6.6

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

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Fig.2 The response surface and contour line of carbonyl groups amount as a function of reaction time(X_1 , min), temperature(X_2 , °C) and particle size(X_3 , mm): (a) X_1 X_2 , (b) X_1 X_3 , (c) X_2 X_3 ,

(a)

(b)

592

(c)

Fig.3 The response surface and contour line of basic groups amount as a function of reaction time(X_1 , min), temperature(X_2 , °C) and particle size(X_3 , mm): (a) X_1 X_2 , (b) X_1 X_3 , (c) X_2 X_3 ,

(a)

(b)

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(c)

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601 Fig.4 FT-IR spectra of the raw corn stover and biochar derived from microwave pyrolysis

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