Slow Pyrolysis as a Promising Approach for Producing Biochar from Sunflower Straw

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Slow pyrolysis opened new channels for the highly efficient utilization of sunflower straw in salt-affected regions and obtained not only 28% to 40% biochar, but also 29% to 44% syngas and 29% to 31% bio-oil. Biochar yield decreased with increasing temperature, whereas syngas increased and bio-oil changed minimally. Both syngas and bio-oil had potential value as fuel. The biochar produced at 700 ºC had the highest pH, ash content, and water-soluble K^+ of 11.9, 212 g/kg, and 23.9 g/kg, respectively, and the lowest atomic ratios for H/C and O/C of 0.19 and 0.10, respectively. However, C, other minerals, surface area, and cation exchange capacity (CEC) of biochar reached a stable level at 500 ºC. Therefore, the differential characteristics of the biochar derived from sunflower straw might show potential value in removing pollutants and improving soil fertility at 500 ºC.

Keywords: Sunflower straw; Slow pyrolysis; Biochar; Syngas; Bio-oil

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INTRODUCTION

Sunflower (*Helianthus annuus* L.) is widely cultivated to produce cooking oil in the semi-arid and arid region of northern China due to its relatively high stress tolerance to salinity, alkalinity, and drought. More than 125 million tons of straw were produced in approximately 948,500 ha of land in 2014 (NBSPRC 2016). Currently, only a small amount is used as fuel, silage, or soil additive, but most sunflower straw is left in the field because of the shortage in effective measures for converting its biomass into valuable resources (Monlau *et al.* 2015; Nargotra *et al.* 2018).

Pyrolysis is one of the most common and convenient thermochemical conversion technologies to convert biomass into biochar, bio-oil, and syngas at a moderate temperature in the range of 300 to 700 °C (IBI 2015; Lehmann and Joseph 2015). Bio-oil and syngas can be used directly as fuel (Monlau *et al.* 2015). Biochar, with high carbon content, porous structure, huge specific surface area, and various functional groups, can be used directly as a fuel or an adsorption material, but most notably as a soil amendment (Buss *et al.* 2016; Weber and Quicker 2018). Increasing data have shown that biochar can also improve soil physicochemical and biological properties and ameliorate the contaminated soils with organic substances and heavy metals (Quilliam *et al.* 2013; Cao *et al.* 2016; Qian *et al.* 2016; Agegnehu *et al.* 2017). Meanwhile, biochar soil amendment can sequestrate carbon and reduce the emissions of greenhouse gases (Brassard *et al.* 2018; Zheng *et al.* 2018). Therefore, pyrolysis might be a feasible approach for achieving the highly efficient utilization of this discarded sunflower straw in the salt-affected areas (EBC 2018). However, the functions of pyrolysates largely depend on its properties that are strongly influenced by feedstocks and pyrolysis temperature (Tag *et al.* 2016). Hence, it is advisable to understand the properties of these pyrolysates before their promotion use.

Therefore, the authors hypothesize that (1) biochar from sunflower straw produced at high temperature (≥ 500 °C) might have more mineral nutrients and larger surface area, and thus have higher potential to be used as a soil conditioner to improve soil fertility and remove pollutants; and that (2) syngas and bio-oil can be used as a high quality of clean energy. Therefore, sunflower straw was pyrolyzed in a fixed-bed reactor at 300 °C, 500 °C, or 700 °C for 2 h in this study. The harvested syngas, bio-oil, and biochar were assayed for their compositions and characteristics. The objectives are (1) to investigate the changes of bio-products with pyrolysis temperature, (2) to understand the composition of syngas and bio-oil and then evaluate their potential values as fuel, and (3) to characterize biochar properties from physical and chemical aspects and further evaluate its potential value as a soil conditioner.

EXPERIMENTAL

Materials

Sunflower straw

Sunflower straw was collected from the saline soil in Hetao area of Inner Mongolia, China. The straw was air-dried and then chopped into pieces that were 2-cm-long. It had cellulose, hemicellulose, and lignin contents of 37.8%, 17.1%, and 12.3%, respectively. The contents of C, H, N, and water-soluble nutrients are shown in Table 1.

Pyrolysis device

The fixed bed pyrolysis system was comprised of a pyrolysis reactor, a bio-oil collector, a non-condensable gas discharge pipe, a condensing system, a thermal controller, and a data logger (Fig. 1). The pyrolysis reactor had an electric heater and a stainless-steel reactor equipped with five resistance wires in different heights and three thermocouples for monitoring the internal temperature. The gaseous products were cooled with the shell-and-tube heat exchange condensing tube. The condensable part, *i.e.*, bio-oil, entered the bio-oil collector while the non-condensable part was directly discharged.

Pyrolysis process

Approximately 100 g of the feedstock were placed into the pyrolysis reactor and then pyrolyzed for 2 h for each designated temperature of 300 °C, 500 °C, or 700 °C, with a heating rate of 10 °C/min, under a nitrogen flow rate of 1 L/min to keep an oxygen-free state. Three repetitions were performed under every designed temperature. The syngas was sampled every 30 min after reaching the designated temperatures with gas sampling bags. The mixed syngas samples were respectively marked as G300, G500, and G700, and measured for their compositions and relative contents by gas chromatography (Perkin Elmer AutoSystem XL, Waltham, MA, USA).

Table 1. Chemical Properties of Sunflower Straw and Its Biochars Produced at 300 °C, 500 °C, and 700 °C for 2 h in a Fixed Bed Slow Pyrolysis Reactor

Biochar	C	H	O	N	Ash	H/C	O/C	HV (MJ/kg)	pH	EC	WSN	WSP	WSOC	K^+	Na^+	Ca^{2+}	Mg^{2+}
	(g kg^{-1})									(mS/cm)	(g/kg)						
SF	440c	58a	422a	9b	70d	1.59a	0.72a	16.7c	6.3d	6.2c	0.32a	0.19a	12.5a	8.9d	0.55c	1.36a	30.0a
B300	578b	41b	220b	11a	150c	0.85b	0.29b	23.4b	8.9c	9.7b	0.08b	0.03b	10.7b	19.5b	0.95b	1.09a	23.2b
B500	667a	24c	122c	8c	179b	0.43c	0.14c	24.0a	10.4b	9.8b	0.04c	0.00c	1.2c	17.2c	1.05a	0.47b	6.2c
B700	680a	11d	87d	10a	212a	0.19d	0.10d	23.3b	11.9a	16.4a	0.04c	0.01c	0.7c	23.9a	1.03a	0.26b	0.8d

The different lowercase letters in the same column represent a significant difference at $p < 0.05$ among the feedstock and biochars.
SF: Sunflower straw; B300, B500, and B700: the biochar produced at 300 °C, 500 °C, and 700 °C, respectively;
HV: Heating value; EC: electrical conductivity; WSN: water soluble nitrogen; WSP: water soluble phosphorous; WSOC: water soluble organic carbon

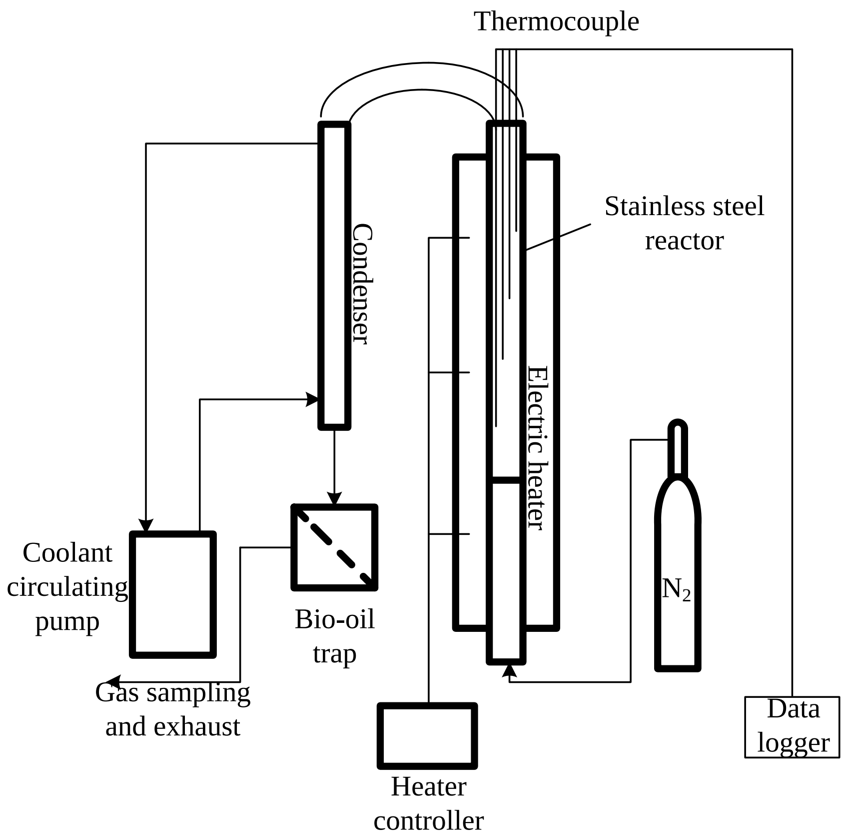

Fig. 1. Schematic structure of the biomass pyrolysis reactor

The lower heating value (LHV) was calculated from the measured gases according to Yue *et al.* (2016). The biochars (respectively marked as B300, B500, and B700) and bio-oils (respectively marked as O300, O500, and O700) were collected after cooling down to temperature near 0 °C in a glycol-based coolant, and were then measured for their masses, compositions, and physicochemical characteristics.

Methods

Biochar and feedstock assays

The ash of both the biochar and sunflower straw (the material was ground to pass through a 0.25 mm sieve) was determined according to the method of Bachmann *et al.* (2016). The contents of C, H, and N were determined by dry combustion using a vario EL III elemental analyzer (Elementar, Frankfurt, Germany). The oxygen was calculated by the difference of the other contents.

The water-soluble components in both biochar and feedstock were extracted with distilled water (1:10 ratio of solid to liquid) for 30 min. The pH value of the filtrate was determined by a glass electrode (Denver Instrument, Denver, CO, USA). The electrical conductivity (EC) was determined by a conductivity meter (Shanghai Inesa Scientific Instrument Co., Ltd., Shanghai, China).

The organic carbon (C) was determined by potassium dichromate volumetry and the nitrogen (N) content *via* the Kejeldal method. The phosphorus (P) was determined through molybdenum blue spectrophotometry. Both the K^+ and Na^+ were determined using flame photometry (Shanghai Inesa Scientific Instrument Co., Ltd., Shanghai, China), and lastly Ca^{2+} and Mg^{2+} were determined by EDTA titration.

An additional 10 g of biochars and feedstock (the material was ground to pass through a 0.25 mm sieve) were mixed with 100 mL of 1 M hydrochloric acid (HCl) to dissolve minerals and then washed with deionized water until the EC of the filtrate reduced to lower than 20 μS/cm. The acid-washed biochar was collected and then oven-dried at 105 °C overnight.

Scanning electron microscopy (SEM) was used to analyze the surface morphology of the biochar (S-3400N; Hitachi, Tokyo, Japan), and the pore size distribution and surface area were visualized *via* mercury intrusion porosimetry (Pore Master GT 60; Quantachrome Instruments, Boynton Beach, FL, USA), and its limit of detection (LOD) regarding pore size was between 0.003 and 400 μm. Fourier transform infrared (FTIR) spectrometry (Thermo Fisher Scientific, Waltham, MA, USA) was used to view the surface functional groups, and surface alkalinity and acidity were determined with Boehm titration. Cation exchange capacity (CEC), iodine adsorption capacity, and methylene blue adsorption capacity was measured according to the method of Yue *et al.* (2016).

Syngas analysis

The chemical composition and the content of the non-condensable gases were analyzed by a gas chromatograph with A and B double channels (PerkinElmer AutoSystem XL; PerkinElmer, Waltham MA, USA). Channel A was a programmed temperature split/splitless (PSS) capillary inlet with a DB-5 60 m × 0.25 mm × 0.25 μm capillary column, a shunting capacity of 30 mL/min under a nitrogen flow rate of 3 mL/min, and was connected to a hydrogen flame ionization detector (FID; PerkinElmer, Waltham MA, USA) to determine the content of CH_4, C_2H_6, C_2H_4, C_3H_8, and C_2H_2. Channel B was a packed (PKD) capillary inlet, with a DB-5 50 m × 0.32 mm × 1.00 μm capillary column, a high-purity helium flow rate of 35 mL/min, and was connected to a thermal conductivity detector (TCD; PerkinElmer, Waltham, MA, USA) to measure the content of H_2, CO, and CO_2.

Bio-oil analysis

The percentages of C, H, O, and N were performed using an elemental analyzer (EA3000; Leeman, Shanghai, China), and the heating value of bio-oil was estimated with the oxygen bomb calorimeter (Parr Instrument Co., Moline, IL, USA). Water content was measured with the MA-1A automatic fast Karl Fischer water meter (Shanghai, China).

Statistical analysis

All data were expressed as the mean of three replicates on an oven-dried basis. The significance difference ($p < 0.05$) of pyrolysis products prepared at different temperatures was compared by means of a one-way analysis of variance (ANOVA) with the SAS software package (SAS Institute Inc., version 8.1, Cary, NC, USA).

RESULTS AND DISCUSSION

Pyrolysis Products

Pyrolyzing sunflower straw at three temperatures yielded 28% to 40% biochar, 29% to 43% syngas, and 29% to 31% bio-oil. An increased pyrolysis temperature from 500 °C to 700 °C had no significant influence on bio-oil yield, but it reduced the biochar yield and enhanced the syngas volume. The pyrolysis of switchgrass and corn stover also obtained a similar result (Chen *et al.* 2016). The most remarkable changes in either biochar or syngas from 300 °C to 500 °C may be explained as the decomposition of hemicellulose and cellulose, respectively, in sunflower straw (Zornoza *et al.* 2016). High temperatures can induce secondary cracking reactions of organic compounds and solid product to form smaller, incondensable compounds and an increase of syngas production (Xie *et al.* 2014).

Chemical Properties of Biochar

Slow pyrolysis induced significant changes in the chemical properties of sunflower feedstock (Table 1). The parameters of C, ash, heating value, pH, EC, K^+, and Na^+ significantly increased 46%, 158%, 66%, 94%, 127%, and 84% on average, respectively, compared to the feedstock. In contrast, the H, O, water soluble components of C, N, P, Ca^{2+}, and Mg^{2+} significantly decreased 57%, 66%, 67%, 83%, 94%, 55%, and 23% on average, respectively (Table 1). Overall, most of these parameters changed minimally at temperatures above 500 °C, which might suggest that the pyrolysis reaction of sunflower straw came to a relatively stable status. Pyrolysis involves many reactions, such as dehydration, decarboxylation, dehydrogenation, condensation, carbonization, and polymerization, *etc.*, which may lead to the losses of H and O and consolidation of salts, as well as the relative accumulation of C and ash in biochar (Wu *et al.* 2012; Sadaka *et al.* 2014). In the present study, the atomic ratios of H/C and O/C decreased from 1.59 and 0.72 to 0.19 and 0.10, respectively. The lower H/C but higher C and O/C in the biochars derived from sunflower straw than in those derived from cereal crop straw may imply that the sunflower straw biochar has higher chemical stability, potential C sequestration capacity, and more negative charges, which might be due to its higher lignin content (Wu *et al.* 2012). The ash content and water-soluble K^+ in biochar from sunflower straw are similar to those of biochar from other straws (Rajkovich *et al.* 2012; MacDonald *et al.* 2014). However, compared to the biochars derived from wood feedstocks, such as hazelnut, oak, and pine, the obtained biochars in this study contained 3 times more K^+ and ash (Rajkovich *et al.* 2012). It is widely accepted that the biochar with high ash content and pH value has a high liming effect and a large reduction in Al^{3+} activity, and thus causes better improvement in acid soil fertility (MacDonald *et al.* 2014). The content of Mg^{2+} greatly decreased in the pyrolysis process probably due to the formation of insoluble compounds through solidification, but it was still higher than that obtained from wood materials (Singh *et al.* 2010; Rajkovich *et al.* 2012; Naeem *et al.* 2014). The rich minerals, such as K^+ and Mg^{2+}, in biochar ash can improve plant nutrition (Agegnehu *et al.* 2017).

Surface Morphology and Pore Structure

The SEM images showed that pyrolysis destroyed integral lignocellulose structure of sunflower feedstock (Fig. 2). The biochar surface (B300, B500, and B700) became smooth and formed cavities, likely due to the existence of vessels and volatilization of organic compounds in sieve tube. It was obvious that pyrolysis greatly reduced large pores but enhanced small pores (Fig. 2).

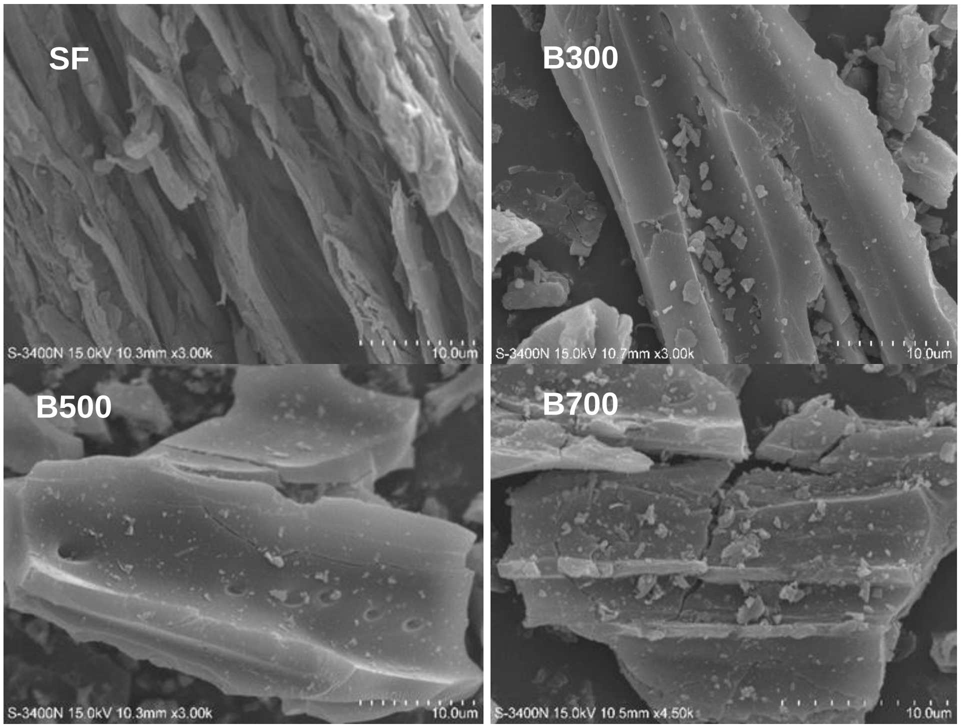

Fig. 2. SEM of sunflower straw and its biochars produced at 300 °C, 500 °C, and 700 °C for 2 h in a fixed bed slow pyrolysis reactor

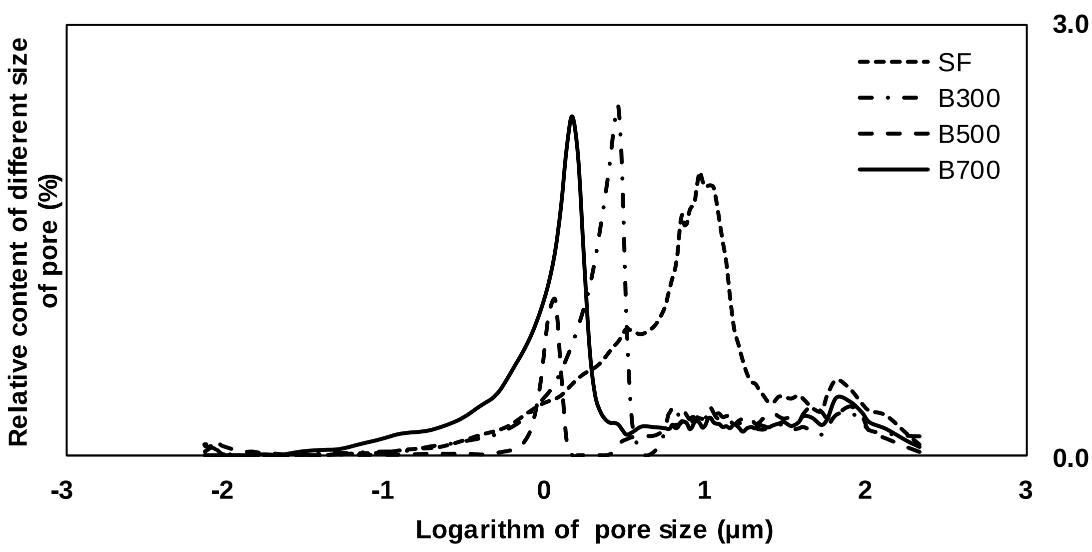

Fig. 3. Pore volume distribution of sunflower straw and its biochars produced at 300 °C, 500 °C, and 700 °C for 2 h in a fixed bed slow pyrolysis reactor

The small pores of 0.01 μm to 2 μm increased 22%, 20%, and 55% in B300, B500, and B700, respectively, compared to the feedstock in which the pores of 2 μm to 100 μm accounted for 80% of the total detected pore size (Fig. 3). Accordingly, the mode and mean pore diameters, as well as specific pore volume in biochars, decreased on average 81.6%, 47.0%, and 38.7%, respectively (Table 2). The surface area reached a maximum of 9.21 m^2/g in B500, and then decreased (Table 2). It was evident that the volatilization of organic matter in lignocellulose feedstock promoted the formation of small pore structure, which increased surface area of biochar accordingly. However, pyrolysis temperature that is too high, higher than 500 °C, certainly damages the porous structure and thus leads to the reduction of surface area (Fu *et al.* 2011; Fig.2). The huge surface area and well-developed pore structure of biochar enhances its adsorption capacity to water, ions, and pollutants (Tan *et al.* 2015; Mohamed *et al.* 2016). In addition, pores with small size can accommodate soil bacteria and fungi (Quilliam *et al.* 2013).

Table 2. Pore Structure Parameters of Sunflower Straw and Its Biochars Produced at 300 °C, 500 °C, and 700 °C for 2 h in a Fixed Bed Slow Pyrolysis Reactor

Biochar	Mode Pore Diameter (μm)	Mean Pore Diameter (μm)	Specific Pore Volume (cm^3/g)	Surface Area (m^2/g)
SF	9.45a	1.05a	1.63a	6.19c
B300	2.81b	0.80b	1.12c	5.60d
B500	1.10d	0.26d	0.59d	9.21a
B700	1.30c	0.61c	1.29b	8.53b

The different lowercase letters in the same column represent significant difference at $p < 0.05$ among feedstock and biochars

Surface Functional Groups

Sunflower straw contained 12 adsorption peaks in the FTIR spectrum, including the main functional groups such as -OH (3146 cm^{-1}), $-CH_2$ (2919 cm^{-1} and 897 cm^{-1}), fatty acid C=O (1740 cm^{-1}), aromatic C=C (1508 cm^{-1}), alkene C-H (1425 cm^{-1}), $-CH_3$ (1375 cm^{-1}), aromatic-NO_2- (1331 cm^{-1}), $(CH_3)_3C$- (1244 cm^{-1}), ester C-O-C (1053 cm^{-1}), and alkene C=C (897 cm^{-1}) (Fig. 4). Pyrolysis largely reduced the number of functional groups to 6, 2, and 1 in B300, B500, and B700, respectively, in which both the -OH and aromatic C=C were predominantly left behind. Meanwhile, the basic, acidic, and carboxyl groups significantly changed with pyrolysis temperature (Fig. 5). The content of basic groups increased linearly with increasing pyrolysis temperature from 0.04 mmol/g in feedstock (SF) to 0.33 mmol/g in B700. However, pyrolysis at 300 °C enhanced both the acid and carboxyl groups 60% and 39%, respectively. Increasing pyrolysis temperature to 700 °C reduced both acid and carboxyl groups to 0.36 mmol/g and 0.21 mmol/g, respectively, which was only 35% and 48%, respectively, of those of the feedstock.

Analogous to other feedstocks, the decarboxylation, dehydrogenation, and oxidation of lignocellulose in sunflower feedstock during pyrolysis contributed to the losses of carboxyl, carbonyl, and hydroxyl groups, as well as the enrichment of aromatic and basic groups (Xin *et al.* 2015; Peng *et al.* 2016). Sunflower straw biochar had similar hydroxyl, carboxyl, phenols, and aromatic C=C with corn stover biochar, and these functional groups may indue the biochar with specific adsorption of ions and organic compounds (Zhu *et al.* 2015).

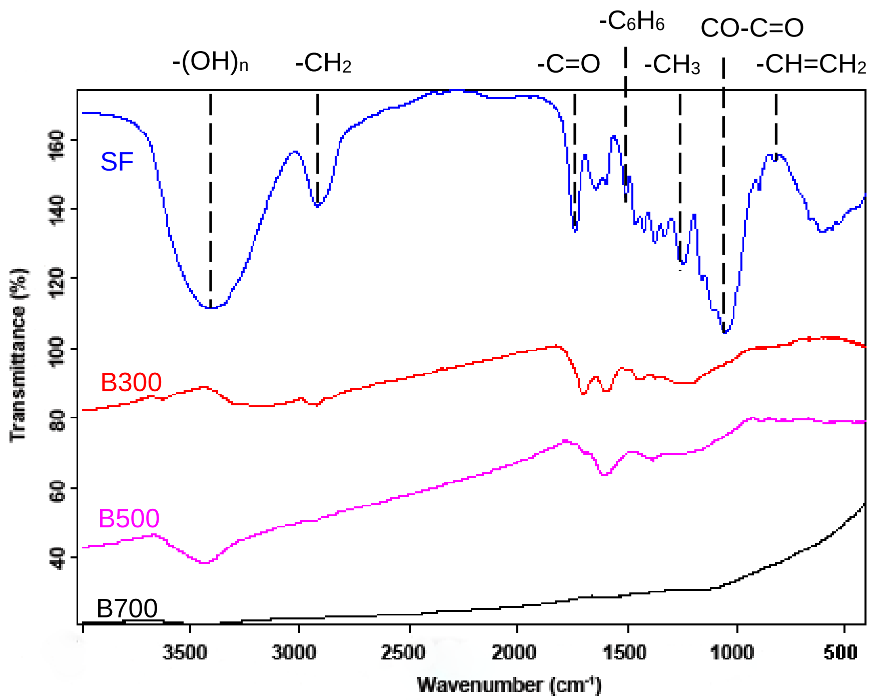

Fig. 4. FTIR of sunflower straw and the biochars produced at 300 °C, 500 °C, and 700 °C for 2 h in a fixed bed slow pyrolysis reactor

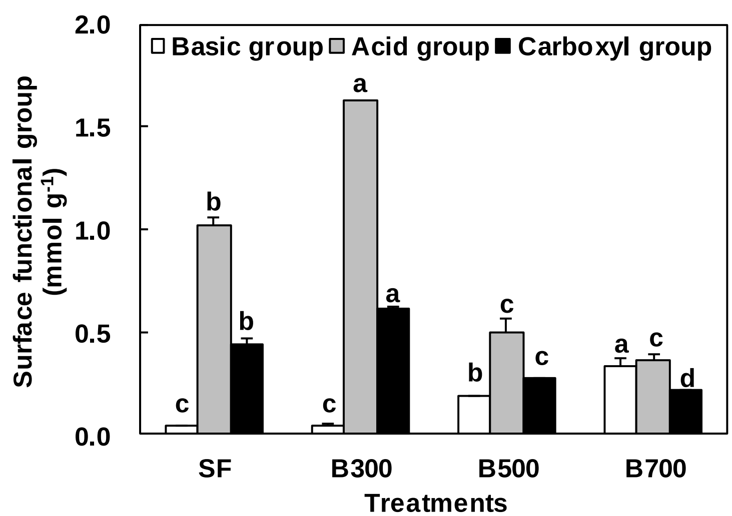

Fig. 5. The contents of basic, acid, and carboxyl groups determined by Boehm titration in sunflower straw and its biochars produced at 300 °C, 500 °C, and 700 °C for 2 h in a fixed bed slow pyrolysis reactor

Adsorption Capacity

Pyrolysis significantly influenced adsorption characters of sunflower straw (Table 3). The CEC of biochar increased 53% to 66%, compared to that of the feedstock, which indicated the newly-formed negative charge on the biochar surface during pyrolysis. The increasing CEC of biochar was not consistent with the changes of acid functional groups in Fig. 5, which was explained by the various contributions (*e.g.* Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) to CEC in biochar rather than only by acid groups measured through the Boehm titration method (Weber and Quicker 2018). The obtained sunflower straw biochar had much higher CEC than the biochars from corn straw, wheat straw, rice straw, and even hardwood, which might imply that sunflower straw biochar carried more negative charge (Rajkovich *et al.* 2012; Wu *et al.* 2012; Zhao *et al.* 2013). This biochar with high CEC as a soil amendment may effectively enhance soil CEC, reduce nutrient leaching, and thus improve nutrient use efficiency (Rajkovich *et al.* 2012).

Table 3. Cation Exchange Capacity (CEC) and Adsorption Capacities of Iodine and Methylene Blue in Sunflower Straw and its Biochars Produced at 300 °C, 500 °C, and 700 °C for 2 h in a Fixed Bed Slow Pyrolysis Reactor

Biochar	CEC	Iodine Adsorption	Methylene Blue Adsorption
	(cmol/kg)	(mg/g)	
SF	168b	237b	9.8a
B300	256a	332a	8.4a
B500	279a	190c	9.1a
B700	259a	166d	10.7a

The different lowercase letters in the same column represent significant difference at $p < 0.05$ among feedstock and biochars

The low pyrolysis temperature of 300 °C enhanced the iodine adsorption capacity 40%, while the high pyrolysis temperature it reduced 25% on average, compared to the feedstock. Methylene blue adsorption capacity was not significantly influenced by pyrolysis (Table 3). Similar results were obtained by Xiao *et al.* (2014), in which they reported that biochar had amphiphilic surfaces, dominant in a hydrophobic surface. Pyrolysis likely weakened the hydrophobicity of biochar due to the aromatization during pyrolysis (Zornoza *et al.* 2016). The amphiphilic natures of biochar allowed adsorbing polar and nonpolar substances such as herbicides, pesticides, PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), and others; and even reduced the bioavailability of these toxic materials. Therefore, biochar soil amendment is considered as a potential measure for remediating the lands contaminated by organic pollutants (Weber and Quicker 2018). Sunflower straw biochar had a higher methylene blue adsorption capacity than hardwood bark biochar, but a lower iodine adsorption capacity than bamboo biochar (Ye *et al.* 2015), which indicated that sunflower straw biochar had higher potential value as an adsorbent of polar organic contaminants.

Syngas and Bio-oil

Slowly-pyrolyzing sunflower straw in a fixed-bed reactor produced a significant volume of syngas. The syngas was mainly composed of H_2, CO, CO_2, and CH_4, among which 22% to 43% of the total concentration were combustible gases (Fig. 6). The relative proportions of the combustible gases, such as H_2, CO, and light hydrocarbons, increased with increasing pyrolysis temperature, while CO_2 decreased. Carbon dioxide might be reduced to CO at a high temperature (Beneroso *et al.* 2014). The LHVs of syngas increased from 2.8 MJ N/m^3 in G300, to 5.7 MJ N/m^3 in G500, and 6.0 MJ N/m^3 in G500. The syngas of sunflower straw had a lower LHV than those from crop straws of wheat, rice, corn, and from woodchips, which might be due to the high salt ions inhibiting the formation of combustible gases in sunflower feedstock (Wang *et al.* 2007; Dudyński *et al.* 2015). Pyrolysis of sunflower straw also released a notable amount of bio-oil. The bio-oils had 62% C, 30% O, 7% N, and 1% H (Table 4). The heating values of bio-oils were lower than that of crude oil (27.0 MJ/kg). Overall, pyrolysis temperature had little influence on these parameters. Similar results were reported by other researchers when they used corn stover, switch grass, and red cedar to produce bio-oils (Chen *et al.* 2016; Yang *et al.* 2016).

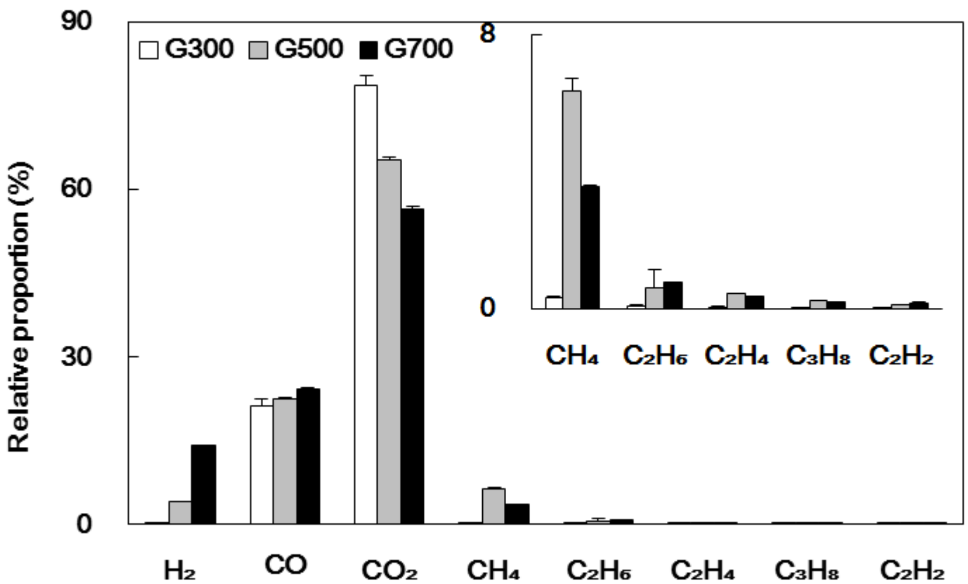

Fig. 6. The relative proportions of syngas derived from sunflower straw under 300 °C, 500 °C, and 700 °C for 2 h in a fixed bed slow pyrolysis reactor

Table 4. Element Composition and Heating Values of Bio-oil Derived from Sunflower Straw at 300 °C, 500 °C, and 700 °C for 2 h in a Fixed Bed Slow Pyrolysis Reactor

Bio-oil	C	H	O	N	Heating Value (MJ/kg)
	(g kg^{-1})				
O300	620a	12b	297b	72a	27.0a
O500	610b	18a	301a	71a	26.6b
O700	619a	12b	302a	68b	26.3b

The different lowercase letters in the same column represent significant difference at $p < 0.05$ among feedstock and biochars

CONCLUSIONS

1. Slow pyrolysis of sunflower straw in a fixed-bed reactor produced approximately 27% to 41% biochar, 29% to 44% syngas, and 29% to 31% bio-oil.
2. The differential characteristic of the biochar derived from sunflower straw showed the potential values in improving soil fertility and removing organic pollutants.
3. Overall, the suitable condition for producing biochar with sunflower straw to be used as a soil conditioner was 500 °C for 2 h in a fixed-bed slow pyrolysis reactor.

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