

Characterization of energy carriers obtained from the pyrolysis of white ash, switchgrass and corn stover – Biochar, syngas and bio-oil

Tianju Chen^{a,b,c}, Ronghou Liu^{a,b,*}, Norman R. Scott^{a,**}

^a Department of Biological and Environmental Engineering, Cornell University, Riley-Robb Hall, Ithaca, NY 14853, USA

^b Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

^c Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Qingdao 266101, PR China

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ABSTRACT

The pyrolysis of three representative sources of biomass, namely, white ash, switchgrass and corn stover were investigated using a fixed-bed reactor to observe and compare the characterizations of three energy carriers, biochar, syngas and bio-oil. The characteristics of biochar were determined by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffractometer (XRD) and Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS), Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GC-MS). The results showed that the carbon content of biochar increased with the increase of pyrolysis temperature. More than 52 wt.% of the carbon was captured in the biochar. The infrared spectra of char samples illustrated that various bands in the spectra were identified, corresponding to stretches -NH-, aliphatic stretches -CH-, stretches conjugate -C=C-, -CH₃ and stretches -C-O-. The surface morphology of biomass sample changed after pyrolysis and carbon fiber can be formed at the temperature of 500 °C. The content of combustible gas CH₄, H₂ and CO was changed from 50% to 70%. The GC-MS analysis of bio-oil showed that most of the chemical compounds detected were phenolic ones. This study provides a useful reference for energy carriers from the pyrolysis of biomass.

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1. Introduction

The Earth's environment is threatened by an increase of CO₂ in the atmosphere that can be attributed to the rapid consumption of fossil fuels during human development. Increasing anthropogenic CO₂ emission and global warming have challenged the world to find new and better ways to meet the world's increasing needs for energy while reducing greenhouse gases [1]. Biomass was once an important source of energy for humankind and it is starting to play the role again [2] because biomass is a clean, cost-effective, CO₂ neutral and low sulfur content renewable material which can be used for heat and fuel production [3].

Pyrolysis is a thermochemical conversion process, in which the feedstock is heated in the absence of air. Three kinds of energy carriers including biochar, bio-oil and syngas are produced from biomass pyrolysis process [4]. There are two kinds of pyrolysis: fast pyrolysis and slow pyrolysis. The main production is bio-oil from the fast pyrolysis. Properties and chemical composition of bio-oil are distinct from petroleum fuel. In general terms, with its relatively high content of water

and oxygen, bio-oil is acidic and not stable when heating, and its heating value lower than petroleum. Bio-oil is easy to transport, making biomass a dominant choice for the replacement of fossil fuels [5]. Its use as fuel in boilers and engines has been tested [6,7]. The content of the syngas is primarily CO, H₂, CH₄ and CO₂ which can be used as the heat source in a recycling fluidized-bed reactor [8]. Biochar is like charcoal and is the solid component created by pyrolysis of biomass. It is proposed as a source for carbon sequestration via carbon capture and storage. Thus, biochar has the potential to help mitigate climate change, via carbon sequestration. It can be used as a soil amendment, and has, also, attracted attention due to its ability for long term improvements of soil physical and chemical properties, with potentially important beneficial effects on soil biota [9]. Specifically, biochar may improve water infiltration, soil water retention, ion exchange capacity [10], pH [11,12], and improve N use efficiency. The substantial changes in bulk soil properties and biochar particles have shown to influence soil biological processes with significant implications for soil biogeochemistry [13]. Biochar can be used as an activated carbon when its pore structure and surface area are appropriate [14]. In addition, biochar can act as a soil conditioner enhancing plant growth, and more importantly, retain nutrients and provide other benefits such as improvement of soil physical and biological properties [15–21].

Furthermore, biochar is carbon-rich (typically more than 60% carbon) solid, which is mainly composed of aromatic hydrocarbons, simple

* Correspondence to: R. Liu, Department of Biological and Environmental Engineering, Cornell University, Riley-Robb Hall, Ithaca, NY 14853, USA.

** Corresponding author.

E-mail addresses: liurhou@sjtu.edu.cn (R. Liu), nrs5@cornell.edu (N.R. Scott).

substance carbon, or carbon with graphene structure [18]. It exhibits better biology stability and thermo-stability than precursor biomass. Also, biochar has a higher energy density and is therefore regarded as better fuel than the precursor raw biomass. It could be used as a solid fuel in boilers where bagasse or other biomass is presently burned [19–21]. Abdullah et al. [19] investigated the significant differences in the fuel quality and ash properties of biochars produced from the slow pyrolysis of various mallee biomass components (leaf, wood and bark) at five temperatures. The results show that biochars of all mallee biomass have better fuel qualities, such as lower moisture content, better grind ability, and higher energy density than the original biomass material [19]. Cao et al. [22] also reported that dairy manure can be efficiently converted into a biochar material with potential to serve as an amendment for remediation and agronomic purposes. The existing literature has primarily focused on the characterizations of biochar while syngas and bio-oil are useful energy carriers. The carrier gas was also used in previous studies, which can obviously decrease the content of combustible gases such as CO, H₂ and CH₄. Up to date, the existing literature has only focused on the characterizations of biochar or bio-oil. With respect to studies of two or more energy carriers, Mahinpey et al. [23] examined the influence of pyrolysis pressure on product yield from wheat straw pyrolysis. Uzun et al. [21] studied the characteristic and quantities of bio-oil and biochar from the pyrolysis of tea waste. However, comprehensive investigations of three energy carriers are rather lacking. This research addresses the areas of comprehensive investigations of bio-oil, biochar and syngas obtained from slow pyrolysis of biomass.

In previous research, the kinetic analysis of biomass pyrolysis [24,25] and the characterizations of biochar, syngas and bio-oil were investigated [26,27]. The main objective of this research was to investigate the characteristics of biochar, syngas and bio-oil from slow pyrolysis of white ash wood, switchgrass and corn stover at the temperature range from 300°C to 500°C. The slow pyrolysis of biomass was conducted in a fixed bed reactor. The characteristics of biochar, syngas and bio-oil can provide a useful reference for energy carriers from the pyrolysis of biomass.

2. Methods

2.1. Materials

In this experimental study, three kinds of biomass were used: white ash chips (a wood material, Telenet company, New York), switchgrass (a grass, from Cornell University farm) and corn stover (a crop waste material, from Cornell University farm). White ash samples were cut to about 1.5 cm² in size, 3 mm thick and corn stover was cut to 5–7 cm in length. Switchgrass remained untreated with an approximate length of 30 cm. The proximate and ultimate analyses of the three types of feedstocks are listed in Table 1. Volatile matter and ash content were determined using a slightly modified ASTM method (D-1762-84) involving measurement of weight loss following combustion of about 10 g biomass in a ceramic crucible at 900°C for 7 min and 750°C for 6 h, respectively. Fixed carbon was determined by mass balance following C analysis of the nonvolatile residue. The feedstock was put into an oven to outgas the water content at the temperature of 105°C for 12 h before experiments.

2.2. Experimental apparatus and procedure

A fully controlled, slow pyrolysis reactor system was specifically designed and used for slow pyrolysis experiments. The schematic diagram of the system is shown in Fig. 1. It can be seen that the reactor system includes reaction section, condenser unit, filter, gas flow meter, gas collection and gas analysis. The reactor was made of stainless steel with a thermocouple and an auto temperature controller to control reaction temperature. The reactor (height = 490 mm, inner diameter = 310 mm) is heated by an electric tubular furnace. About 1.0 kg of feedstock can be put into the reactor. In this work, the temperature was heated from room temperature to the set temperature (300°C, 400°C, or 500°C) with a heating rate of 10°C min^{−1}, and held at set temperature for 120 min. There was no carrier gas used in the pyrolysis process. With the increase of the temperature, the production of the hot vapors caused the pressure inside the reactor to increase. A soapy-water solution was used to test the tightness of the reactor. Pyrolysis gases are condensed through a condenser system where cold water was used to condense the vapors to room temperature. Liquid production was collected in a liquid receiver. Corn cob was used to filter the vapors. After the filter, the gas volume is measured by a wet gas flow meter (QW CROM, Lim. Co, Germany, QK 2000) and collected in a gas bag. Very little tar was condensed in the gas bag, so there was no special purification needed for the syngas in our experiment. Syngas of 50 L (sometimes 25 L) was collected in each gas bag. The composition of the gas was determined by a gas chromatography (GC).

2.3. Analysis methods

The thermal stability of the biomass was investigated by Thermogravimetric (TG) analysis. The characterizations of biochar including elemental analysis, ash content, the pH value and heating value were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffractometer (XRD) and Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS). The chemical composition of the liquid condensate was investigated by Gas Chromatography Mass Spectrometry (GC-MS).

2.3.1. TG analysis

The experiments were performed using a TG analyzer (TA Instruments, Q500, USA) at the temperature of 300°C, 400°C and 500°C, operating at the heating rate of 10°C min^{−1}. Samples were kept at the reaction temperature for 1 h. A thin layer of the sample (ca. 10 mg) was distributed evenly in a ceramic crucible. During heating, mass and temperature of the sample were simultaneously and continuously recorded. In the pyrolysis experiments, N₂ of ultra-high purity was passed through the TGA at a constant flow rate of 100 mL min^{−1} to provide the inert gas environment and to sweep away the volatiles released.

2.3.2. Elemental analysis

The elemental content of the pyrolysis oils and biochar was determined by a Model 240C Perkin-Elmer Elemental Analyzer. In the method, c Carbon, hydrogen and nitrogen were simultaneously determined as gaseous products (carbon dioxide, water vapor and nitrogen). The oxygen content was calculated by difference.

Table 1
The proximate and ultimate analyses of feedstocks.

Proximate analysis	Elemental analysis		
	White ash	Switch-grass	Corn stover
Moisture (wt.%)	10.54 ± 0.07	7.82 ± 0.17	9.18 ± 0.14
Volatiles (wt.%)	75.83 ± 0.68	72.04 ± 0.23	74.76 ± 0.46
Fixed carbon (wt.%)	13.22 ± 0.68	15.46 ± 0.23	12.66 ± 0.48
Ash (wt.%)	0.41 ± 0.05	4.68 ± 0.03	3.40 ± 0.42
	White ash	Switch-grass	Corn stover
C (wt.%)	47.45	47.50	49.58
H (wt.%)	6.53	5.57	8.61
N (wt.%)	0.43	0.65	0.38
O ^a (wt.%)	45.59	45.28	41.43

^a By difference.

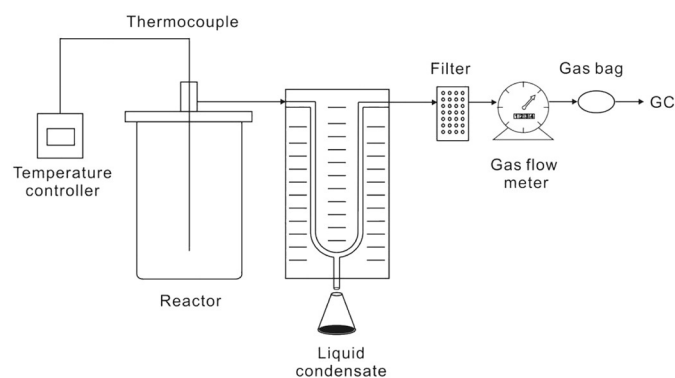


Fig. 1. The schematic diagram of the system.

2.3.3. pH value

The pH of biochar was determined in a mixture of 5 g biochar and 20 mL de-ionized water following 1 h equilibrium. The pH level was measured with a hand-held meter (Oakton pH 6, Vernon Hills, IL).

2.3.4. Heating value

The heating value of biochar was determined using an oxygen bomb calorimeter (Parr 6300, USA) according to ASTM D 5468-95. A thin layer of the biochar sample (ca. 1 g) was distributed evenly in the oxygen

bomb calorimeter. The pressure of the oxygen was kept at 450 Psi for 1 min.

2.3.5. FT-IR

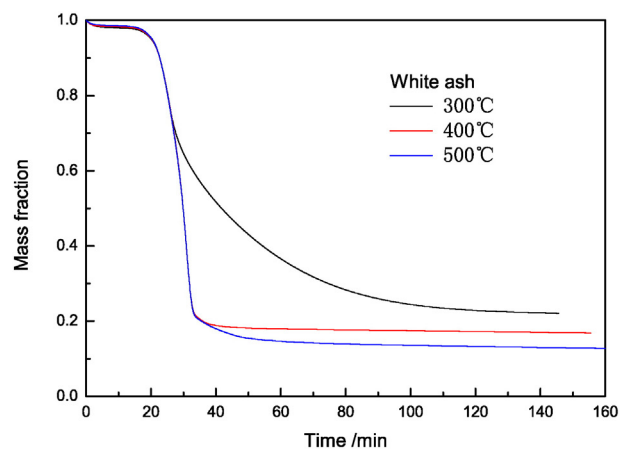
The biochar was mixed with KBr powder which had been dried at 105°C at a ratio of 3 mg biochar: 1000 mg KBr for all biochar samples. The biochar-powder mixture was then re-ground in a mortar and pestle to ensure homogeneity and was stored in a desiccator. Pellets were created using 150–250 mg of powder in a pellet press at 10 MPa of pressure. Two pellets were created for each biochar. Using a Mattson Model 5020 FT-IR Spectrometer (Madison, WI) at wave numbers from 400 to 4000 cm^{-1} , each sample was scanned 100 times, with a resolution of 4 cm^{-1} , subtracting a blank value obtained from a pure KBr pellet.

2.3.6. XRD

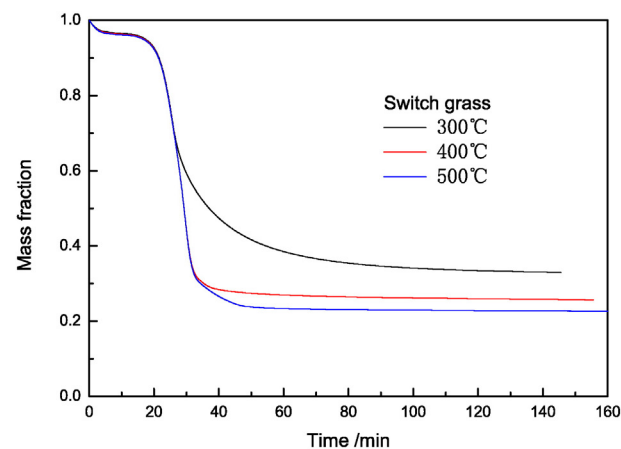
XRD analysis was carried out to identify crystallographic structure in the biochar samples using a computer-controlled X-ray diffractometer (Bruker: D8 Advance, Germany) equipped with a stepping motor and graphite crystal monochromator.

2.3.7. SEM-EDS

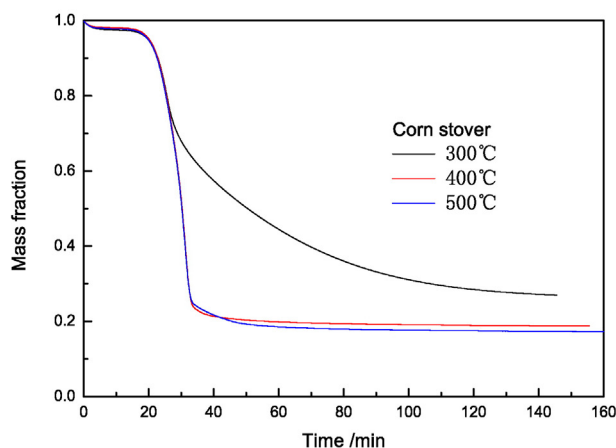
The morphology of the white ash particles and white ash biochars was characterized using SEM-EDS. The samples were coated with gold to achieve good visibility of the images. Images were taken at 15 kV with a JSM-6360 model SEM-EDS.



(a)



(b)



(c)

Fig. 2. Thermogravimetric analyses for the feedstocks under different temperatures: (a) white ash, (b) switch grass, (c) corn stover.

Table 2

The effect of the temperature on the product yields and the characteristics of biochar from the biomass pyrolysis.

Biomass	Temperature/°C	Biochar yield/wt. %	Bio-oil yield/wt. %	Gas volume/L	C	H	N	O ^b	Biochar carbon yield/wt. % ^a	ash	pH value	Heating value/MJ/kg
White ash	300	39.20	43.33	153.7	77.82	3.42	0.54	15.58	64.29	2.64	7.16 ± 0.05	30.9
	400	31.04	40.65	179.7	87.6	2.50	0.56	6.27	57.30	3.07	7.23 ± 0.12	32.4
	500	27.68	38.05	225.2	90.19	1.50	0.49	4.05	52.61	3.77	7.91 ± 0.10	33.5
Switch grass	300	39.58	31.6	175.5	76.06	3.87	0.66	10.74	63.38	8.67	8.22 ± 0.10	28.9
	400	36.72	28.5	205.0	80.77	3.02	0.64	5.27	62.44	10.3	8.42 ± 0.06	30.2
	500	29.34	27.5	271.3	86.33	1.90	0.59	0.54	53.32	10.64	8.6 ± 0.10	31.5
Corn stover	300	41.72	31.03	175.5	69.91	4.04	0.94	13.42	58.83	11.69	7.31 ± 0.01	28
	400	35.44	30.7	213.0	74.78	3.15	1.05	6.18	53.45	14.84	7.79 ± 0.11	28.8
	500	33.50	26.73	239.7	78.11	2.11	0.92	3.77	52.78	15.09	8.1 ± 0.15	30.5

^a The C weight of the biochar from 1 kg biomass was equal to the product of the biochar yield and its C content. The ratio of the C weight of each biochar for the C content of 1 kg feedstock is equal to biochar carbon yield.

^b By difference.

2.3.8. Gas analysis

Gas analysis was carried out using a Gas Chromatograph (GOW-MAC Instrument Company, Series 580) equipped with thermal conductivity detector (TCD). Standard gases were used for calibration, and argon was used as the carrier gas. The ultra-high purity gases were used as the standard gases.

2.3.9. GC–MS analysis

Although bio-oil cannot be completely analyzed by GC–MS only, because it contains some large molecules as well as some undistillable matter that cannot be investigated by this technique only, it is still

widely used to identify most compounds of bio-oils from the pyrolysis of biomass. The GC–MS system consists of a gas chromatograph coupled to a quadrupole mass spectrometer (GC–MS QP 2010, Shimadzu) using a capillary column (30 m × 0.25 mm i.d.; film thickness, 0.25 μm). Electron ionization (EI) was used with an ion source temperature of 230°C and interface temperature of 280°C, with EI spectra obtained at 70 eV. In EI, the instrument was used in SCAN mode initially to confirm the identity of the compounds and then in SIM (selected ion monitoring) mode for quantitative analysis. The GC system was equipped with a split/splitless inlet. The injector temperature was 250°C. A LEAP Technologies autosampler with a 10 μL syringe was used for injections of

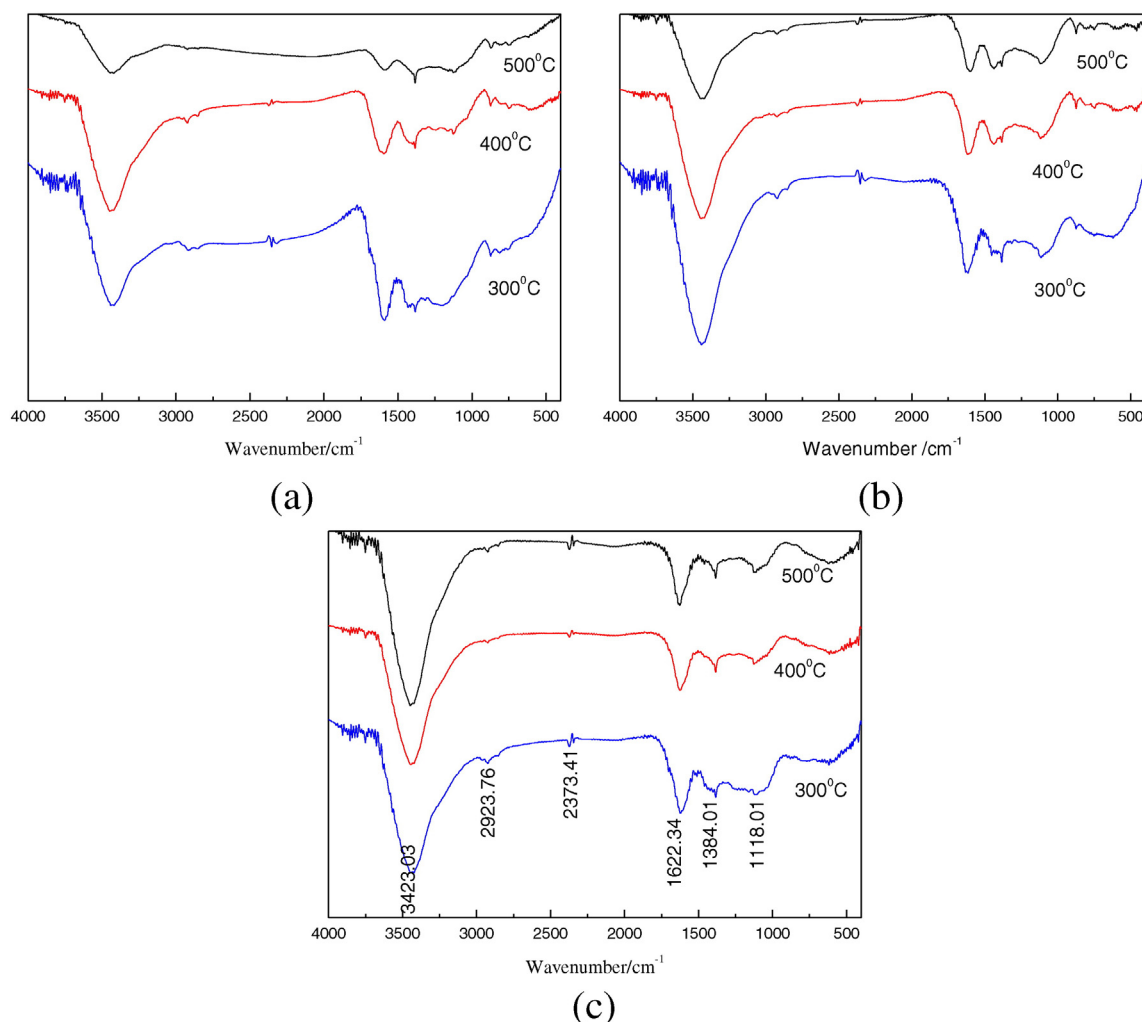


Fig. 3. FT-IR spectra of bio-char: (a) white ash, (b) switch grass, (c) corn stover.

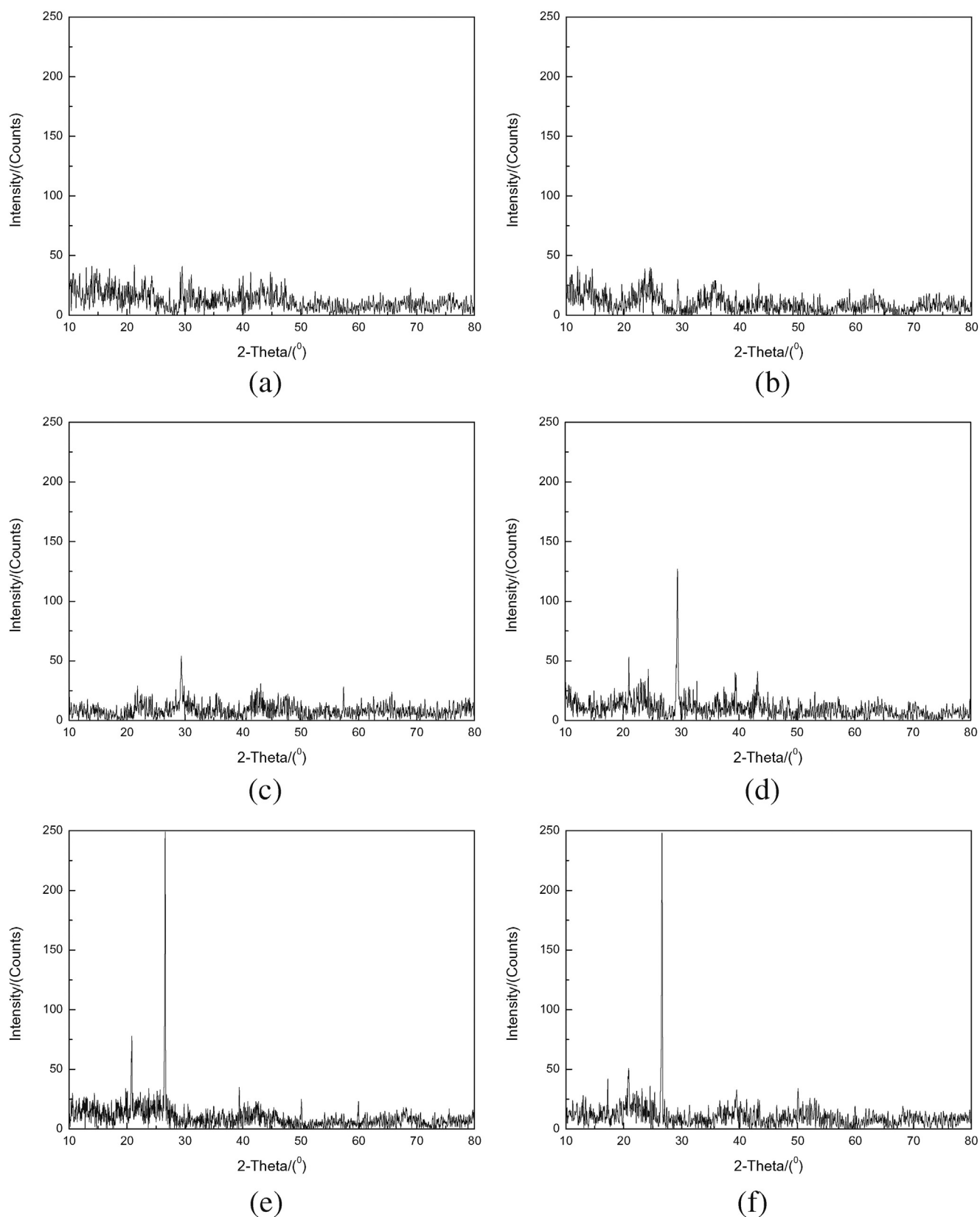


Fig. 4. XRD patterns of the biochar: (a) white ash biochar at 300 °C, (b) white ash biochar at 500 °C, (c) switch grass biochar at 300 °C, (d) switch grass biochar at 500 °C, (e) corn stover biochar at 300 °C, (f) corn stover biochar at 500 °C.

1 μL at a rate of 10 $\mu\text{L s}^{-1}$. The carrier gas was helium (UHP) at a constant flow of 1.0 mL min^{-1} . The oven temperature program had an initial temperature of 60 °C held for 2.0 min, rising by 8 °C min^{-1} to 300 °C,

which was held for 10.0 min with a total run time of 35.0 min. This temperature program was selected to provide adequate separation of most of the compounds of interest.

3. Results and discussion

3.1. Pyrolysis behavior and its mass balance

3.1.1. TG analysis of biomass

In Fig. 2(a), it can be seen that the weight loss of white ash increased with the increase of pyrolysis temperature. The weight loss continued to decrease when the temperature reached 300°C. However, at temperatures of 400°C and 500°C, the weight loss is small. In Fig. 2(b and c), it can be seen that switchgrass and corn stover had the same trend as white ash because the biomass material was typically composed of

cellulose, hemicellulose and lignin. Basak et al. [21] reported that hemicellulose began to thermally decompose at 150°C–350°C, and cellulose degradation appeared between 275°C and 350°C. However, lignin degradation took place at 200°C–700°C. For these results, temperatures were raised to the selected temperature at a heating rate of 10°C min⁻¹ and held for 1 h. After 1 h of heating, the furnace was turned off and the sample was cooled to room temperature.

3.1.2. Mass balance of biomass pyrolysis

Biochar, bio-oil and syngas are produced from slow pyrolysis of biomass. The biochar is a black solid material. The bio-oil is a dark brown

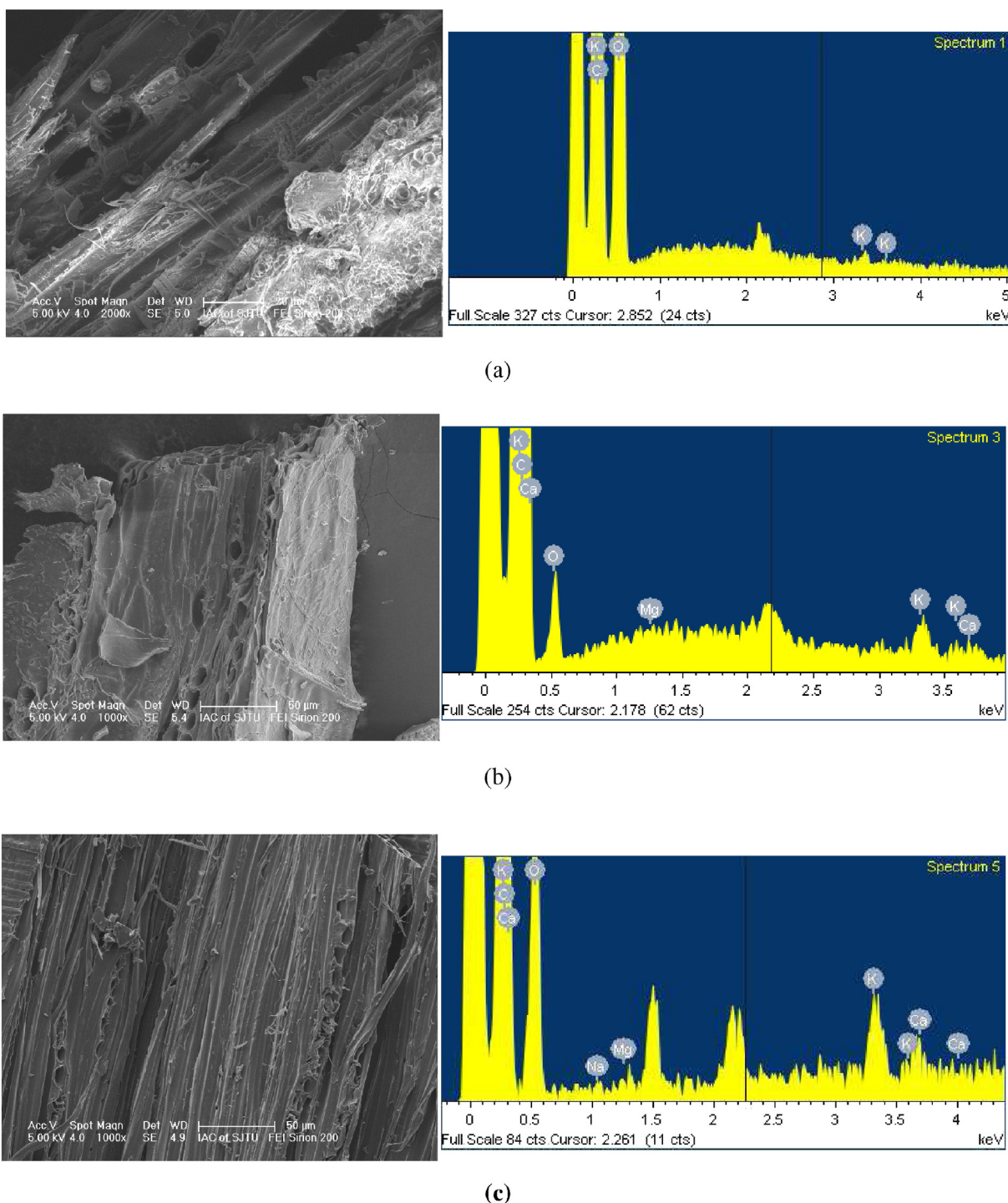
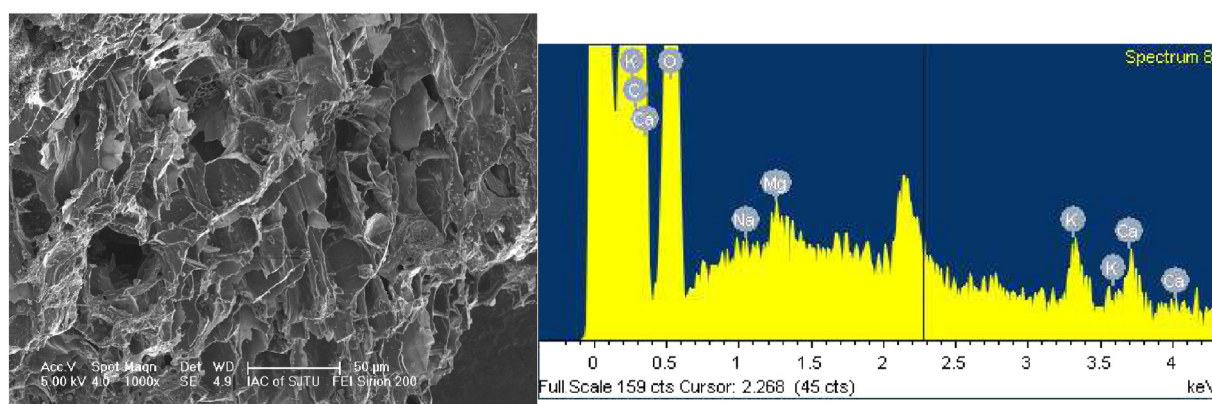
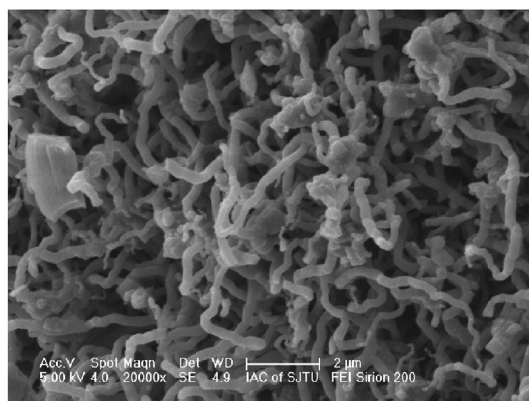


Fig. 5. SEM-EDS analysis: (a) white ash, (b) biochar at 300 °C, (c) biochar at 400 °C, (d) biochar at 500 °C, (e) carbon fiber from biochar at 500 °C.



(d)



(e)

Fig. 5 (continued).

liquid which can be combusted. There are large quantities of CO, CH₄ and H₂ (the combustible gas contents can be 60%) in the syngas. The effect of temperature on the product yield from the biomass pyrolysis is shown in Table 2. In Table 2, it can be seen that for the three kinds of biomass, the biochar and bio-oil yields decreased with the increase of pyrolysis temperature. However, more syngas was produced at higher temperatures (the combustible gas contents were about 40–60%). Corn stover had the highest biochar yield of 41.72% at 300°C and a lower yield of 33.50% at 500°C, while white ash had the lowest yield of 39.20% at 300°C, compared to 27.68% at 500°C. Biochar derived from corn stover had a higher ash content (about 10 wt.%), with increased pyrolysis temperature.

3.2. Characteristic of biochar

3.2.1. Elemental analysis

The effect of temperature on the elemental analyses and the ash content of biochar is shown in Table 2. In Table 2, it can be seen that for all three biochars, the hydrogen and oxygen content decreased with the increase of pyrolysis temperature, and carbon and ash content increased with the increase of temperature. The carbon content of the biochar from the white ash was higher than that from the switch grass and corn stover. The carbon content was 90.2% for the biochar from white ash at the temperature of 500°C. Because biochar has a stable structure, it has the potential to help mitigate climate change, via carbon sequestration. Table 2 also showed that carbon sequestration rates decreased with the increase of the temperature, and more than 52% of the carbon was captured in biochar. Secondary decomposition of the biochar took place at higher temperature, and more CO, CH₄, CO₂ and chemical

compounds containing carbon were produced. That is why the carbon sequestration rate decreased at high temperature.

3.2.2. pH value

In Table 2, it can be seen that the biochar is alkaline. The pH value increased with the increase of pyrolysis temperature. The switch grass biochar has a higher pH value than the corn stover and white ash, with a pH value of 8.5 at 500°C. These results indicate that biochar has potential as an amendment to neutralize soil acidity [22]. The alkali metals of Na, K, Ca and Mg were detected in biochar in our previous study [26]. Although more volatiles were released with the increase of pyrolysis temperature, the alkali metals were difficult to volatile in the biomass pyrolysis process. Therefore, the contents of alkali metals in the biochar increased with the increasing pyrolysis temperature. The switchgrass had the highest ash content. The content of alkali metals in the biochar from switchgrass was higher than from white ash and corn stover and is why the switchgrass biochar had the highest pH value.

3.2.3. Heating value

It can be seen in Table 2 that the heating value increased with the increase of the reaction temperature. The heating value is determined by the carbon content and white ash biochar has the highest carbon content. Thus, it has a higher heating value than switch grass and corn stover biochar with a heating value of 33.0 MJ kg⁻¹ at 500°C. It has been reported that converting biomass to biochar would lead to a substantial increase in fuel mass energy density from ~10 MJ kg⁻¹ of green biomass to ~28 MJ kg⁻¹ for biochar [19,20].

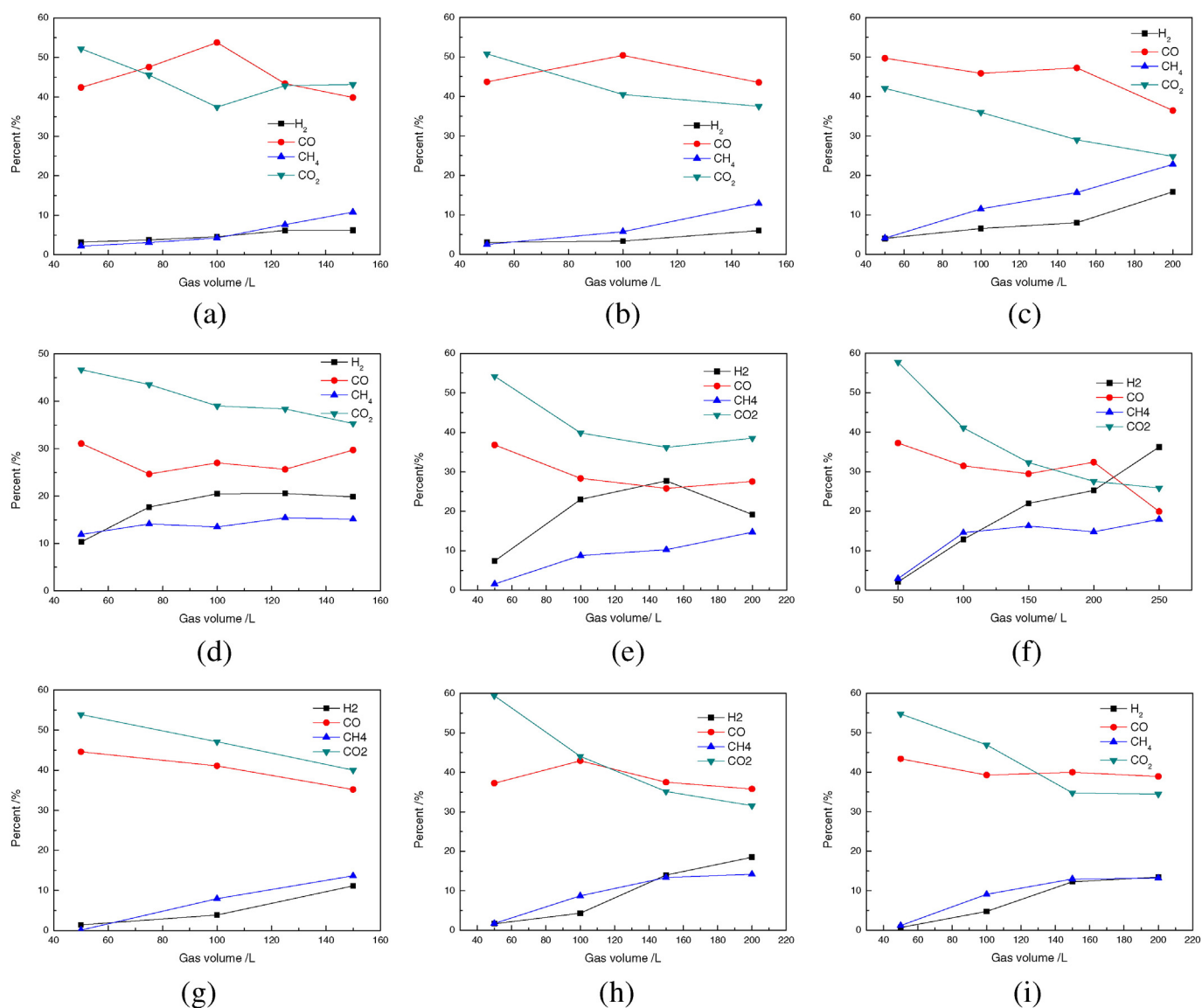


Fig. 6. The content of syngas: (a) white ash at 300 °C, (b) white ash at 400 °C, (c) white ash at 500 °C, (d) switch grass at 300 °C, (e) switch grass at 400 °C, (f) switch grass at 500 °C, (g) corn stover at 300 °C, (h) corn stover at 400 °C, (i) corn stover at 500 °C.

3.2.4. FT-IR

In the pyrolysis process, the biomass feedstocks cannot be pyrolyzed completely. The results of elemental analysis of the biochar showed that there is a large amount of carbon, hydrogen and oxygen in the biochar. Thus, there must be a lot of chemical bonds in biochar. Fourier-transform infrared (FT-IR) spectroscopy represents an advanced version of the more traditional infrared (IR) spectroscopy method. FT-IR is primarily used for the structural determination of organic (carbon-based) molecules. FT-IR has also been used to describe characteristic bonds of biochar [28]. FT-IR spectra of biochar: (a) white ash, (b) switch grass and (c) corn stover are shown in Fig. 3. In Fig. 3 it can be seen that the infrared spectra of biochar samples illustrates various bands in the spectra, corresponding to stretches N—H (3423 cm^{-1}), aliphatic stretches C—H (2923 cm^{-1}), stretches conjugate C=C (1622 cm^{-1}), $-\text{CH}_3$ (1384 cm^{-1}) and stretches C—O (1118 cm^{-1}) [27]. The broad bands at 3423 cm^{-1} were attributed to the hydroxyl groups (O—H) due to the water content in the nine biochars. The presence of water in the biochars could be from absorption of moisture by the biochars or KBr during pellets preparation [29]. For the nine biochars, all of them have the same chemical bonds. That is because the

biomass material consists of cellulose, hemicellulose and lignin which have a large amount of C, H and O [24]. It can also be seen that the strength of all chemical bonds was enhanced with the decrease of the temperature, which was also confirmed by Lee et al. [28]. Secondary decomposition of the biochar took place at higher temperatures, which led to the strength of all chemical bonds being weaker. All the bands in the bio-char can be found except the C—C bond. In general, ether- and ester-linkages can be cleaved via pyrolysis. The C—C bond has the longest bond length ($154 \times 10^{-12}\text{ m}$) and has the lowest bond energy (332 kJmol^{-1}). This kind of chemical bonds is easier to cleave at high temperature [27].

3.2.5. XRD analysis

In order to know the crystalline compounds in the biochar samples, XRD detection was used and the results are shown in Fig. 4. It can be seen that all the biochar samples had a strong peak at 28° that was identified as C (C_{12} and C_{60}), which was in agreement with Wu et al. [30] that there existed crystalline C in different biochar samples. The XRD spectra is stronger at 500°C than at 300°C . That is because carbon content of the biochar is very high at higher temperature. More crystalline C

Table 3

The effect of temperature on components of bio-oil from white ash wood pyrolysis and their relative mass contents detected by GC–MS.

Peak number	Main identified compounds	RTA (min)	Mol. mass	Qualitative ion, mass-to charge ratio (m/z)	Temperature (°C)		
					300	400	500
1	Pyruvic acid	2.2	88	18,58,59			0.73
2	Oxiranemethanol, acetate	2.7	116	18,42,73	10.57		12.11
3	1-Hydroxy-2-pentanone	3.37	102	18,32,58	0.55		0.81
4	Furfural	3.55	96	18,43,71	10.15	14.97	12.35
5	Furfuryl alcohol	3.85	98	18,43,58		11.11	7.17
6	N-propyl-acetamide	4.31	101	18,28,32	0.90		0.68
7	4-Amino-furazan-3-ol	4.55	101	18,28,32			1.46
8	Butyrolactone	4.79	86	18,44,86	8.15	8.10	6.58
9	5-Methyl-2(5H)-furanone	5.21	98	18,28,44	0.49		3.35
10	Phenol	6.07	94	18,28,44	2.96	4.60	4.14
11	Propanoic acid, 2-methyl-,anhydride	6.52	158	18,69,102	2.25		
12	Corylon	6.93	112	18,28,44	4.34	4.78	3.56
13	2-Methyl-phenol	7.45	108	18,28,85	2.85		
14	4-Methyl-phenol	7.84	108	28,43,108	3.90		
15	2-Methoxy-phenol	8.15	124	18,44,57	4.90	5.56	3.52
16	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	8.69	126	28,38,97	0.90		
17	2,5-Dimethyl-phenol	9.23	122	18,44,57	2.01	1.88	
18	2,3-Dimethyl-phenol	9.6	122	18,28,44	0.83		
19	4-Methoxy-3-methyl-phenol	9.82	138	18,28,44	1.33		
20	Metacetamol	10.17	151	18,44,64	8.36	11.70	8.11
21	4-Methoxy-1,2-benzenediol	11.3	140	18,44,124	2.87	7.11	7.92
22	4-Ethyl-2-methoxy-phenol	11.62	152	18,44,97	4.66		
23	3,4-Dimethoxy-phenol	12.84	154	18,44,107	9.13	8.65	5.97
24	2,5-Dimethyl-1,4-benzenediol	13.38	138	18,44,58	0.63	0.90	
25	4-Methoxy-3-[methoxymethyl]phenol	14.4	168	18,44,58	4.70	3.69	3.32
26	D-allose	14.94	180	29,73,98	5.68	11.46	10.19
27	1-Methyl-2-[2,3,5-trimethoxyphenyl]ethylamine	15.66	225	18,28,44	3.89	3.44	4.88
28	3,4,5-Trimethoxy-N-methyl-benzethanamine	17.51	225	18,28,32	0.88		
29	4-Allyl-2,6-dimethoxy-phenol	18.2	194	18,44,105	0.95		
30	1-[2,4,6-Trihydroxyphenyl],2-pentanone	19.14	210	18,44,78	1.17	2.06	3.17

was formed at 500°C. The XRD spectra of the biochar showed several peaks, including the peak at 21°, 40° and 51°. These results indicated that there were some mineral crystals such as MgO and CaCO₃ in the biochar [22]. The existence of alkali metals (Na, K, Ca and Mg) in the biochar was reported in our previous work [26,27].

3.2.6. SEM-EDS analysis

Fig. 5 shows the SEM-EDS analysis of white ash wood and the biochar from white ash. These visual images suggested that the raw material is made of solid cells with slits, which seemed to continue inside the particle. It was clear from these images that the surface morphology of

Table 4

The effect of temperature on components of bio-oil from switch grass pyrolysis and their relative mass contents detected by GC–MS.

Peak number	Main identified compounds	RTA (min)	Mol. mass	Qualitative ion, mass-to charge ratio (m/z)	Temperature(°C)		
					300	400	500
1	Oxiranemethanol, acetate	2.7	116	18,42,73	12.08	0.72	10.33
2	Furfural	3.55	96	18,43,71	16.28	22.96	14.93
3	Furfuryl alcohol	3.85	98	18,43,58	11.57	9.20	9.52
4	N-propyl-acetamide	4.31	101	18,28,32	0.74		
5	Butyrolactone	4.79	86	18,44,86	8.52	13.04	9.04
6	5-Methyl-2-furaldehyde	5.74	110	18,28,44	4.90	5.68	4.31
7	Phenol	6.07	94	18,28,44	7.99	9.26	4.99
8	Corylon	6.93	112	18,28,44	4.41	5.90	4.90
9	4-Methyl-phenol	7.84	108	28,43,108			4.03
10	2-Methoxy-phenol	8.15	124	18,44,57	4.53	6.58	4.81
11	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	8.69	126	28,38,97		1.20	0.88
12	2,5-Dimethyl-phenol	9.23	122	18,44,57			1.62
13	2,3-Dimethyl-phenol	9.6	122	18,28,44	1.04		
14	4-Methoxy-3-methyl-phenol	9.82	138	18,28,44		0.95	
15	Metacetamol	10.17	151	18,44,64	7.29	1.10	9.40
16	Anhydro-dOmannosan	10.64	162	28,41,97	1.62	1.81	1.32
17	4-Methoxy-1,2-benzenediol	11.3	140	18,44,124	5.13	7.04	5.84
18	4-Methyl-1,2-benzenediol	11.77	124	28,44,97		2.23	1.76
19	3,4-Dimethoxy-phenol	12.84	154	18,44,107	4.99		
20	2,5-Dimethyl-1,4-benzenediol	13.38	138	18,44,58	0.44	0.94	0.59
21	4-Hydroxy-benzeneethanol	14.01	138	28,44,123			0.61
22	4-Methoxy-3-[methoxymethyl]phenol	14.4	168	18,44,58	1.76	2.77	2.48
23	D-allose	14.94	180	29,73,98	4.80	5.27	7.98
24	1-Methyl-2-[2,3,5-trimethoxyphenyl]ethylamine	15.66	225	18,28,44	1.38	2.82	
25	1-[2,4,6-Trihydroxyphenyl],2-pentanone	19.14	210	18,44,78	0.53	0.52	0.66

Table 5

The effect of temperature on components of bio-oil from corn stover pyrolysis and their relative mass contents detected by GC–MS.

Peak number	Main identified compounds	RTA (min)	Mol. mass	Qualitative ion, mass-to charge ratio (m/z)	Temperature (°C)		
					300	400	500
1	Oxiranemethanol acetate	2.7	116	18,42,73	10.74	7.76	11.04
2	Furfural	3.55	96	18,43,71	15.52	10.81	13.66
3	Furfuryl alcohol	3.85	98	18,43,58	10.27	7.20	9.12
4	N-propyl-acetamide	4.31	101	18,28,32			0.24
5	Butyrolactone	4.79	86	18,44,86	8.22	5.17	8.07
6	5-Methyl-2-furaldehyde	5.74	110	18,28,44	4.42	3.16	4.21
7	Phenol	6.07	94	18,28,44	9.21	6.81	8.65
8	Corylon	6.93	112	18,28,44	3.64	3.19	3.85
9	4-Methyl-phenol	7.84	108	28,43,108	6.62	5.49	0.59
10	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	8.69	126	28,38,97		0.91	0.82
11	2,5-Dimethyl-phenol	9.23	122	18,44,57	1.81		
12	2,3-Dimethyl-phenol	9.6	122	18,28,44		2.40	2.36
13	Metacetamol	10.17	151	18,44,64	7.57	10.21	8.55
14	Anhydro-dOmannosan	10.64	162	28,41,97		5.76	2.18
15	4-Methoxy-1,2-benzenediol	11.3	140	18,44,124	5.22	6.85	7.43
16	4-Methyl-1,2-benzenediol	11.77	124	28,44,97			1.86
17	3,4-Dimethoxy-phenol	12.84	154	18,44,107	4.23	4.96	4.25
18	2,5-Dimethyl-1,4-benzenediol	13.38	138	18,44,58	0.97	1.60	0.94
19	4-Methoxy-3-[methoxymethyl]phenol	14.4	168	18,44,58	1.50	2.15	1.37
20	D-allose	14.94	180	29,73,98	9.46	14.90	10.66
21	4-Allyl-2,6-dimethoxy-phenol	18.2	194	29,73,58	0.20		
22	1-[2,4,6-Trihydroxyphenyl]-2-pentanone	19.14	210	18,44,78	0.37	0.66	0.17

white ash particles changed after pyrolysis, and became thinner and shrunken. The softening of the solid matrix was caused by the heat. The thermal decomposition and the melting of some compounds can break the chemical bonds of the original material. In Fig. 5(e), it can be seen that there were some carbon fibers at the surface of the biochar at 500°C. The ideal biochar structure developed at high treatment temperature (HTT) can be divided into three processes: (a) increased proportion of aromatic C, a highly disordered amorphous mass, (b) growing sheets of conjugated aromatic carbon, turbostratically arranged; and (c) structure becoming graphitic in the third dimension with order. It is known that at 500°C, the chemical bonds break, and some small molecular compounds are volatilized. These results are attributed to a high carbon content of 90.2% for white ash biochar at 500°C. Under this condition, the chemical bonds would rebuild. That is why carbon fibers formed at the surface of the biochar at 500°C. There are some alkali metal oxides in the biomass which were difficult to volatilize, thus leading them to be enriched in the biochar. The EDS method provides a rapid qualitative, or with adequate standards, semi-quantitative analysis of elemental composition with a sampling depth of 1–2 µm [31]. In this experiment, the alkali metals of Na, K, Ca and Mg were tested. In Fig. 5(a, b, c and d), it can be seen that, the alkali metal content increased with the increase of the temperature.

3.3. Gas analysis

The syngas from pyrolysis of biomass is useful if the CO, H₂ and CH₄ contents are high. The literature [27] has reported that syngas can be used as a heat source in a recycling fluidized-bed reactor. In this experiment, the syngas was collected every 50 L (sometimes 25 L), and the fraction of CO, H₂ and CH₄ and CO₂ was measured by GC. The composition of syngas from all three biomass is shown in Fig. 6 at three temperatures. In Fig. 6(a–i) it can be seen that the main content of the syngas was CH₄, H₂, CO and CO₂. The content of the combustible gases was more than 50% (v/v). The content of CO and CO₂ decreased with time, while the contents of H₂ and CH₄ increased with time. Because there was no carrier gas in this system, the content of combustible gas ranged from 50% to 70% in syngas. The syngas can easily be combusted and its combustion flame is large. In addition, the CO and H₂ in the syngas are valuable feedstocks in the synthesis process of liquid fuel. Li et al. [31,

27] reported the Cu–La₂O₃–ZrO₂/γ-Al₂O₃ hybrid catalysts in a one-step synthesis of dimethyl ether from syngas.

3.4. GC–MS analysis of bio-oil

GC–MS analysis was carried out to identify the compounds in bio-oils from the pyrolysis of biomass. The effect of temperature on components of bio-oil from white ash, switchgrass and corn stover pyrolysis and their relative mass contents detected by GC–MS are shown in Tables 3, 4 and 5, respectively. The compounds were ordered according to their retention times. The mol content of the chemical compounds is determined by comparing the peak areas and the relative abundance in terms of area percentage. It can be seen in Tables 3–5 that 30, 25 and 22 kinds of chemical compounds were detected from white ash, switchgrass and corn stover bio-oils, respectively. It has been reported that bio-oils produced from different types of biomass samples under similar conditions have similar composition [5]. Table 3 shows that the white ash bio-oils (300°C, 400°C and 500°C) had a large amount of compounds including furfural (relative mol contents were 10.15%, 14.97%, 12.35%, respectively), Butyrolactone (relative mol contents were 8.15%, 8.10%, 6.58%, respectively), metacetamol (relative mol contents were 8.36%, 11.70%, 8.11%, respectively) and D-allose (relative mol contents were 5.68%, 11.46%, 10.19%, respectively). Table 4 shows that the switchgrass bio-oils (at 300°C, 400°C and 500°C) had large amounts of compounds including furfural (relative mol contents were 16.28%, 22.96%, 14.93%, respectively), Furfuryl alcohol (relative mol contents were 11.57%, 9.20%, 9.52%, respectively) and Butyrolactone (relative mol contents were 8.52%, 13.04%, 9.04%, respectively). Table 5 shows that the corn stover bio-oils (at 300°C, 400°C and 500°C) have large amounts of compounds oxiranemethanol acetate (relative mol contents were 10.74%, 7.76%, 11.04%, respectively), furfural (relative mol contents were 16.28%, 22.96%, 14.93%, respectively), Furfuryl alcohol (relative mol contents were 11.57%, 9.20%, 9.52%, respectively) and D-allose (relative mol contents were 9.46%, 14.90%, 10.66%, respectively). Thus, bio-oil is a complex mixture with a lot of a chemical compounds. Furfural, D-allose and phenolic compounds are the main chemical compounds in the bio-oil for the three kinds of biomass. Similar results were reported in our previous research [23,32] and the work of Mahinpey [5]. Properties and chemical composition of bio-oil are

distinct from petroleum fuel because of its relatively high content of water and solids, acidity and instability when heated [26]. These disadvantages limit the use of bio-oil. In the slow pyrolysis process, the water content of the bio-oil is high. The bio-oil is a good feedstock for steam reforming for hydrogen production [33].

4. Conclusion

The characteristics of biochar, syngas and bio-oil created from the pyrolysis of white ash, switchgrass and corn stover at the temperatures of 300, 400 and 500°C were investigated. The biochar yields ranged from 27% to 42% and more than 52% of the carbon was captured in biochar. The ash content, pH value and heating value of biochar increased with the increase of the pyrolysis temperature. The biochar from pyrolysis of switchgrass had the highest pH value (8.6 at the reaction temperature of 500°C). The biochar from pyrolysis of white ash had the highest heating value (33.5 MJ kg⁻¹ at the reaction temperature of 500°C). Various bands of stretches –NH–, aliphatic stretches CH, stretches conjugate –C=C–, –CH₃ and stretches –C–O– were detected in the biochar. The carbon fibers formed at the temperature of 500°C showed that the structure of the biochar became graphitic in the third dimension at higher temperatures. The switchgrass feedstock can produce more combustible gases than those of white ash and corn stover. The content of the combustible gases (CH₄, H₂ and CO) ranged from 50% to 70% in the syngas. Furfural, D-allose and phenolic compounds are the main chemical compounds in the bio-oil for the three kinds of biomass. The biochar, syngas and bio-oil are better heat carriers than the raw biomass feedstock. Application of the three heat carriers is recommended for further study.

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