

Characterization of Thermo-Chemical Degradation and Pyrolysis Properties for Three Kinds of Biomass Residues

Xiao Liu, Wen Hua, and Shubin Wu*

This study investigated the thermo-chemical degradation and fast pyrolysis of watermelon seed shells (WSS), pumpkin seed shells (PSS), and sunflower seed shells (SSS). The raw materials and pyrolysis products were analyzed. The results showed that the carbon content (52.96%), hydrogen content (7.38%) and higher heating value (HHV) (23.88 MJ/kg) of PSS were highest, and the bio-oil from the PSS pyrolysis had high amounts of phenolic compounds. For SSS, the content of holocellulose (83.47 wt.%) was the highest, but the lignin content (13.62 wt.%) was lower than the other samples. The gas yield from the SSS pyrolysis was the largest and the bio-oil content of acids (acetic acid 36.53%) and ketones (1-hydroxy-2-propanone 9.90%) were higher. For WSS, the yield of the biochar was 39.14 wt.%. Additionally, the raw materials' structures were similar. The thermal decomposition process of all seed shells had three stages, *i.e.* dehydration, active pyrolysis, and passive pyrolysis. In all three kinds of bio-oil, the components were mainly guaiacol-type and phenol-type. The guaiacol-type in the bio-oils from PSS (43.78%) and WSS (32.33%) were higher than in the bio-oil from SSS.

Keywords: Pyrolytic product; Seed shells; Thermal decomposition characteristic; Fast pyrolysis

Contact information: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, Guangdong 510640, PR China; * Corresponding author: shubinwu@scut.edu.cn

INTRODUCTION

Sunflower, pumpkin, and watermelon seeds are consumed by humans as snacks after salting and roasting. China, a big consumer of melon seeds, is the main producer of these edible seeds in the world. In China, the planting areas of sunflowers, seed-used pumpkins, and watermelons are about 1.34, 4.33, and 0.3 million hm², respectively (NBSC 2013). Sunflowers are part of the Compositae family, while watermelon and pumpkins are part of the Cucurbitaceae family. Sunflower, pumpkin, and watermelon seeds and seed shells are produced in considerable amounts and a large amount of seed shells of sunflower, pumpkin, and watermelon can be generated from the cooking oil process. But only a small portion of the seed shells is utilized for animal fodder. Most seed shells are burned off, which leads to air pollution. This phenomenon does not arouse much public attention. However, seed shells are typical lignocellulosic biomass, and also such feedstock compositions in terms of extractives, cellulose, hemicellulose and lignin content can be different depending on what kinds of oil extraction method are used to generate such byproducts. They have the potential for use in biofuels, biomaterials, and biochemical production. If used properly, seed shells may be turned from “waste” into “wealth”. Thus, it is necessary to explore potential uses for seeds and seed shells.

There has been some research on the uses of seed shells. For example, sunflower seed shells (SSS) contain a lot of pentosan, which can be used to extract the important industrial solvent furfural and ethanol (Telli-Okur and Eken-Saraçoğlu 2008). SSS also have very high amounts of chlorogenic acid, which has medicinal uses (Duan and Wang 2006; Gao and Dou 2009). Biocarbon production from sunflower seeds produce oil as a “waste” by-product that can be used to manufacture biodiesel fuel (Antal *et al.* 2007; Rai *et al.* 2015).

To meet the requirements of the economic conditions and environmental protection, production of energy from seed shells *via* pyrolysis was considered as a potential thermochemical conversion method. Pyrolysis can also help to avoid problems caused by waste disposal. There have been many studies on the application of melon seeds and pyrolysis characteristics of SSS (Cancalon 1971; Demirbaş 2006; Raclavská *et al.* 2011; Rai *et al.* 2015). The pyrolysis of SSS provides an option for thermal upgrading to higher calorific value fuels through the separation and purification to high grade energy (Zabaniotou *et al.* 2008). The by-products and wastes of pumpkin seed shells (PSS) and watermelon seed shells (WSS) may have the same or different pyrolysis uses as SSS. Unfortunately, the pyrolysis characteristics of PSS and WSS are rarely reported.

This work characterized the properties of pyrolysis products from WSS, SSS, and PSS. In this study, the elemental and component analysis of these samples was performed. The structure of the samples was analyzed by Fourier transform infrared spectroscopy (FT-IR). Furthermore, the thermal decomposition characteristics of samples were examined by thermogravimetric (TG) analysis, and the static tubular furnace was used to study the pyrolysis of samples. To explore the distribution of pyrolysis products and the composition of biochar and bio-oil, a gas chromatograph (GC), FT-IR, elemental analyzer, and gas chromatograph/mass spectrometer (GC/MS) were used. This research may help to reveal potential applications of these seed shells.

EXPERIMENTAL

Materials

Samples and preparation for the analysis procedure

WSS, PSS, and SSS were collected from Zhenglin Food Co., LTD of Lan Zhou. After cleaning with clear water, the samples were air-dried, ground, and oven-dried at 105 °C for 6 h. The dried samples were crushed by a micro mill (DWF-100A, China) and milled in a porcelain ball jar at a rotational speed of 36 rpm. The particle size of the samples was kept between 40- and 60-mesh size.

Properties of materials analysis methods

Elemental analysis (C, H, N, and S) of WSS, PSS, and SSS was determined by an elemental analyzer (Vario EL, Elementar, Germany). The holocellulose, lignin, and ash content of the three raw materials were determined as specified in the Chinese standards (GB/T 2677.10 (1995), GB/T 2677.8 (1994), GB/T 2677.3 (1993)). The extractives content was measured by benzene-ethanol extraction.

To explore the functional groups of these materials, WSS, PSS, and SSS were analyzed with FT-IR (Nexus Thermo Nicolet, USA) using the KBr pellet technique in the range 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} .

Thermochemical Methods

Thermal analysis with TGA

Thermogravimetric analysis (TGA) of the three samples was performed on a TGA instrument (Q500TGA, TA Instruments, New Castle, USA) thermal analysis system. High purity nitrogen (99.99%) was used as the carrier gas with a continuous flow rate of 40 mL/min in the thermogravimetric analyzer. Approximately 9 mg of each sample was distributed in a platinum crucible. Samples were heated from room temperature to 700 °C at a rate of 20 °C/min.

Pyrolysis in the static tubular furnace

The fast pyrolysis experiment was carried out with a self-made small static tube furnace (Lou and Wu 2011). With a U-pipe as the carrier, the three samples were separately pushed into the center of the furnace and pyrolyzed in an N₂ atmosphere at 600 °C, which was selected by consulting various reports (Wu *et al.* 2009; Chen *et al.* 2014). Static tubular furnace was heated from room temperature to 600 °C at a rate of 10 °C/s. In this pyrolysis system, under atmospheric pressure, nitrogen (flow rate of 200 mL/min) was used as the carrier gas and the shielding gas. A chromel/alumel thermocouple was embedded in the tube in the furnace to measure the temperature. The released gas was collected by an ice-water condenser. The condensed liquid product, bio-oil, was absorbed in the condenser. The solid product, biochar, was cooled under N₂ atmosphere and collected for FT-IR and elemental analysis.

Analytical Methods

Gas analysis

Qualitative and quantitative analysis of volatiles produced during pyrolysis were performed by a GC-7890 II with a TCD detector, a double-column system, GDX104 reagents, and a 5A molecular sieve packed column (TECHCOMP, Shanghai, China). The analysis was carried out with a mixed standard gas as an external standard. The gas was composed of H₂ (8.93%), O₂ (1.07%), N₂ (71.94%), CH₄ (2.04%), CO (9.71%), CO₂ (1.09%), C₂H₂ (3.22%), C₂H₄ (0.98%), and C₂H₆ (1.02%). The GC testing conditions were an injector temperature of 50 °C, a TCD temperature of 100 °C, and a TCD current of 70 mA (Lv *et al.* 2013).

Biochar analysis

Elemental analysis (C, H, N, and S) of biochar was performed on the previously described elemental analyzer. The infrared spectra of biochar were analyzed on a FT-IR. The samples were analyzed with the KBr pellet technique. The spectra were scanned ranging from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Bio-oil analysis

The bio-oil solution was first dehydrated and then filtered with Millipore filters to eliminate ash residue. The solution was then analyzed by a GC-7890A coupled with a 5975C MS and a DB-5MS column (30 m × 0.25 mm × 0.25 μm) (Agilent Technologies, Santa Clara, USA). High purity helium was used as the carrier gas, and the flow rate was 1.00 mL/min. The temperature program was as follows: initial column temperature of 50 °C for 3 min, increase to 120 °C at a rate of 8 °C/min, increase to 250 °C at a rate of 6 °C/min, and a final hold at 250 °C for 5 min. The injector, gasification chamber, and detector temperatures were all set at 250 °C. The sample size was 1.0 μL, and the split ratio

was 5:1. The MS was set at an ionizing voltage of 70 eV, and the scan range was varied from 30 to 500 amu. Data processing was performed using Perkin Elmer NIST Spectral Version 08.

RESULTS AND DISCUSSION

Element and Component Analysis

Element analysis

The C and H content in PSS (52.96%, 7.38%) were higher than in WSS (46.78%, 6.43%) and SSS (46.95%, 6.46%) (Table 1). The O content in PSS (32.45%) was considerably lower than in WSS and SSS (41.68%, 43.66%). This was attributed to the differences in feedstock components (Xiao *et al.* 2001). The distribution of C, H, and O indicated that PSS contained more lignin, while WSS and SSS contained more carbohydrates. The component analysis (Table 2) supported these conclusions. In regards to the H/C ratio among the three kinds of seed shells, PSS had the highest, and all of three had higher values than corn stalk (1.55). The high H/C ratios helped to produce high-quality bio-oil (Lv *et al.* 2013). Meanwhile, the HHV of all three samples was higher than rice straw and corn stalk, especially PSS, which was the highest at 23.88 MJ/kg. The high HHV values may have caused an increase in the calorific value and improvement in the quality of bio-oil during pyrolysis (Lou and Wu 2011; Liu *et al.* 2014).

Table 1. Elemental Analysis of Sunflower Seed Shells (SSS), Pumpkin Seed Shells (PSS), and Watermelon Seed Shells (WSS)

Samples ^a	Elemental Contents (%)					O/C ^c	H/C	HHV ^d (MJ/kg)
	C	H	O ^b	N	S			
SSS	46.95	6.46	43.66	0.73	0	0.70	1.65	19.24
PSS	52.96	7.38	32.45	4.19	0	0.46	1.67	23.88
WSS	46.78	6.43	41.68	1.06	0.03	0.67	1.65	19.38

^a oven-dried, ^b Determined by difference, ^c atomic ratio, ^d calculated from Dulong formula (Ferdinand *et al.* 2012)

Table 2. Component Analysis of Sunflower Seed Shells (SSS), Pumpkin Seed Shells (PSS), and Watermelon Seed Shells (WSS)

Samples	Extractives (wt.%)	Holocellulose (wt.%)	Lignin (wt.%)	Ash (wt.%)
SSS	0.84 ± 0.72	83.47 ± 2.89	13.62 ± 1.12	2.19 ± 0.15
PSS	2.87 ± 0.41	60.36 ± 2.24	33.86 ± 1.63	2.97 ± 0.28
WSS	3.64 ± 0.55	64.58 ± 1.95	29.22 ± 1.48	3.74 ± 0.43

Component analysis

The components of WSS, PSS, and SSS are shown in Table 2. The holocellulose content of SSS (83.47 wt.%) was noticeably higher than in the other two samples (WSS

64.58 wt.%, PSS 60.36 wt.%). The lignin of SSS, WSS, and PSS were 13.62 wt.%, 29.22 wt.%, and 33.86 wt.%, respectively. Thus, SSS may contain high amounts of carbohydrates. The three samples contained a low content of extract, which was below 4 wt.% for all three seed shell types. A previous study indicated that the extract mainly consists of pigments, phenolics, and inorganic salt (Demirbaş 2006). Additionally, compared with rice straw, the relative content of ash of these samples was low. This may help to alleviate the problem of corrosion and scaling during the biomass pyrolysis process. The different components of these three seed shells may have an important influence on the thermal degradation behaviors and pyrolysis characteristics.

Structure Analysis

The FT-IR spectra of the raw materials are shown in Fig. 1. The respective functional groups and assignment to lignocellulose fractions are summarized in Table 3. A strong hydrogen bonded (O-H) stretching absorption was observed at 3422 cm^{-1} . The signal at 2860 cm^{-1} represented the C-H_x symmetric stretching. The absorption intensity of PSS was relatively stronger than that of WSS and SSS, suggesting that it contained more alkylated compounds. The peak at approximately 1730 cm^{-1} was attributed to the C=O in unconjugated carbonyls stretching and water-soluble lignin absorption. The intensities of WSS and PSS were stronger than SSS. One possible explanation is that the absorption intensity (C=O in unconjugated carbonyls stretching) of wood lignin is more observable than that of non-wood lignin, and the chemical structure of WSS and PSS is similar to that of coniferous wood (Hua *et al.* 2016). The infrared bands of WSS and PSS at 1512 cm^{-1} (assigned to the aromatic skeletal in lignin) were stronger than SSS. This result further illustrated that the WSS and PSS were enriched with lignin. The peaks at 1161 , 1060 , and 899 cm^{-1} were characteristic absorption peaks of carbohydrate comprising C-O-C connection bridge, C-O stretch in hemicellulose and cellulose, and C-H deformation in cellulose, respectively.

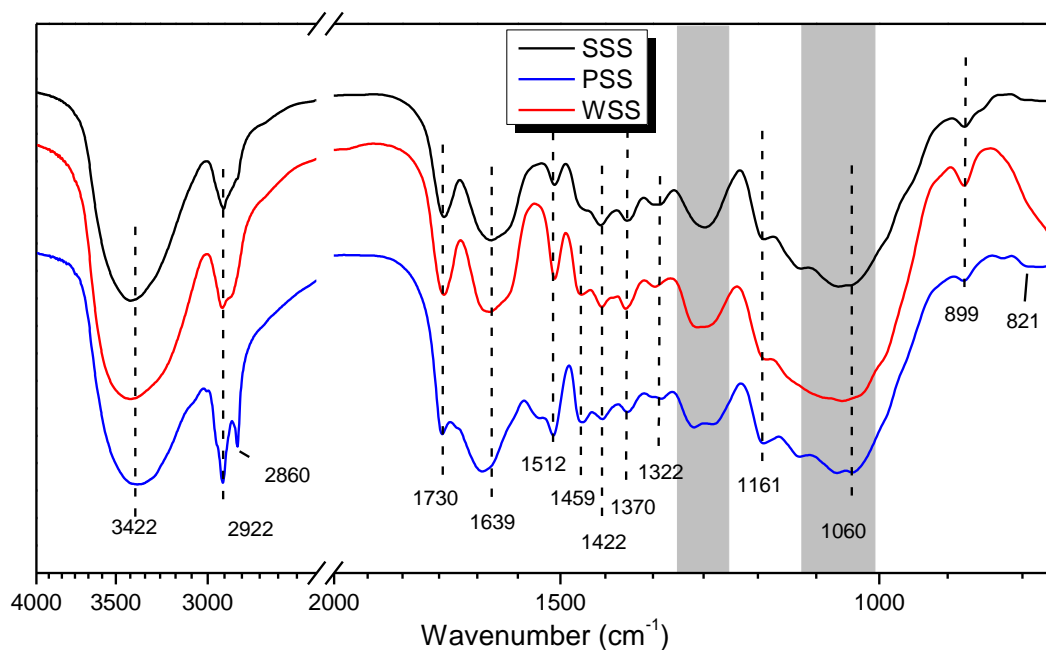


Fig. 1. Comparison of FT-IR spectra of sunflower seed shells (SSS), pumpkin seed shells (PSS), and watermelon seed shells (WSS)

Table 3. Characteristic Bands of Absorbance in FT-IR Spectra, Respective Functional Groups, and Assignment to Lignocellulose Fractions

Wavenumber (cm ⁻¹)	Functional group	Assignment
3422	O-H stretching vibration	
2922	C-Hx asymmetric stretching	Aliphatic
2860	C-Hx symmetric stretching	Alkyl
1730	unconjugated C=O in xylan	Hemicellulose
1639	C=O stretching conjugated to the aromatic ring	Lignin
1512	aromatic skeletal vibrations	Lignin
1459	C-H deformation in methyl groups	Lignin
1422	C-H bending vibration in methyl groups	Lignin
1370	C-H deformation	Cellulose and Hemicellulose
1322	C-H vibration in cellulose and C _i -O vibration in syringyl derivatives	Cellulose and Lignin
1247	syringyl rings and C-O stretch in lignin and xylan	Hemicellulose and Lignin
1161	C-O-C stretching	Cellulose and Hemicellulose
1060	C-O stretching and C-O deformation	Cellulose and Hemicellulose
899	Glucose ring stretch, C-H deformation	Cellulose
821	C-H deformation in guaiacum rings	Lignin

Thermal Decomposition Characteristics

Figure 2 shows mass loss (TG) and mass loss rate (DTG) curves of WSS, PSS, and SSS, with a heating rate of 20 °C/min. The thermal decomposition process could be divided into three distinct stages. The first stage was dehydration, which took place before 200 °C. The second stage was the active pyrolysis stage, which also can be called the stage of devolatilization from 200 to 400 °C. In this stage, substantial organic materials including cellulose, hemicelluloses, and lignin macromolecules were depolymerized, and various volatiles were released. Above 400 °C was the third stage. This stage also called passive pyrolysis stage. In this final stage, the lignin and residues slowly decomposed and carbonized (Yang *et al.* 2007).

Compared to SSS, decomposition of PSS and WSS occurred at lower temperatures. The DTG curves depicted a shoulder peak around 230 °C (WSS) and 240 °C (PSS) in the thermal degradation process. This was probably due to the different chemical structures and composition of the three feedstocks. WSS and PSS may contain more hemicellulose, which is generally degraded in the low temperature zone (Lv *et al.* 2013). Additionally, the lignin structure of branched chain aliphatic hydroxyl cleavage may also contribute to the appearance of the shoulder. The maximum devolatilization rate temperature of PSS was the largest. This can probably be attributed to the fact that the lignin content of PSS was higher than the other two samples. PSS had a 27.98% yield of charred residue, which was slightly higher than SSS (21.77%) and WSS (17.98%). This was also due to the high lignin content of PSS. Generally, lignin is a top contributor of charred residue in the three components of biomass. Excluding lignin, the charcoal residue may be due to the presence of inorganic mineral contents (Patwardhan *et al.* 2010; Ramirez-Corredores 2013).

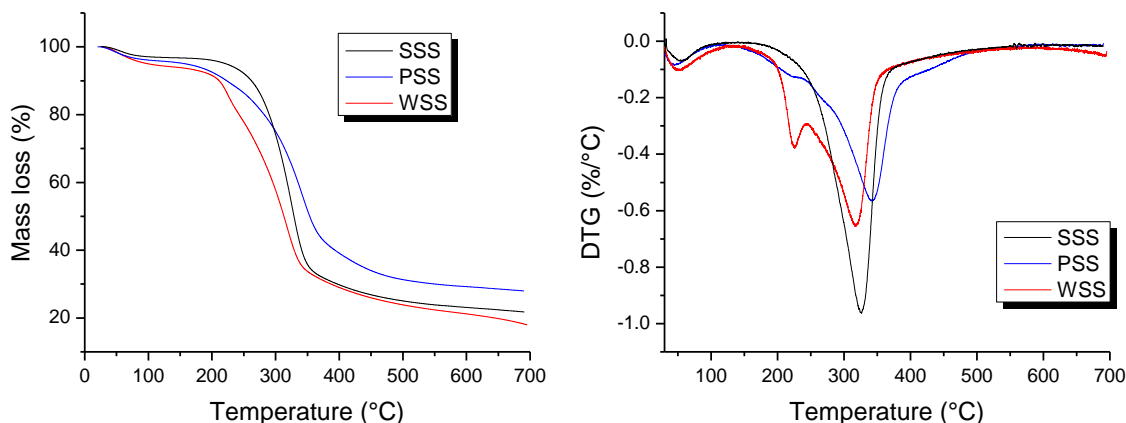


Fig. 2. TG and DTG curves of sunflower seed shells (SSS), pumpkin seed shells (PSS), and watermelon seed shells (WSS), with a heating rate of 20 °C/min⁻¹

Table 4. Yield of Bio-Oil, Biochar, and Gas from Pyrolysis Characterized by Gas Chromatograph (GC)

Samples	Biochar (wt.%)	Gas (wt.%)	Bio-oil (wt.%)
SSS	20.75	14.39	64.84
PSS	26.74	10.99	62.25
WSS	39.14	9.32	51.54

Table 5. Composition and Yields of Gases from Sunflower Seed Shells (SSS), Pumpkin Seed Shells (PSS), and Watermelon Seed Shells (WSS) (mg/g)

Composition	SSS	PSS	WSS
H ₂	0.37	0.39	0.19
CH ₄	4.67	6.15	3.40
CO	33.25	17.39	21.98
CO ₂	105.68	86.02	67.60
C ₂ H ₄	1.08	1.03	2.79
C ₂ H ₆	0.68	0	0

Tubular Furnace Pyrolysis of SSS, PSS, and WSS

Gas analysis

The pyrolysis experiment of the three samples was carried out at 600 °C with a tubular furnace. The yield of the pyrolytic products biochar, gas, and bio-oil is shown in Table 4. The composition of gases and their yields are presented in Table 5. The three major components were CO₂, CO, and CH₄. For SSS, gaseous products accounted for 14.39 wt.% of pyrolytic products, which was larger than for PSS (10.99 wt.%) and WSS (9.32 wt.%). In the gaseous products from SSS, CO₂ and CO had the largest amounts at 105.68 mg/g and 33.25 mg/g, respectively. The amount of CO₂ might be due to the higher content of carbonyl and carboxyl groups in the hemicellulose structure, as CO₂ was mainly formed by the cracking and reforming of C-O and COOH. The high yield of CO is due to the higher C-O-C and C-O content from the cellulose (Lv *et al.* 2013). These yield distributions

corresponded with the high holocellulose content of SSS. Thus, using the gaseous products from SSS pyrolysis as a new source of energy fuel is a good prospect for development, but more intensive study is needed (Yang *et al.* 2007).

Table 6. Elemental Analysis of Biochar from Sunflower Seed Shells (SSS), Pumpkin Seed Shells (PSS), and Watermelon Seed Shells (WSS)

Samples ^a	Elemental Contents (%)					O/C ^c	H/C	HHV ^d (MJ/kg)
	C	H	O ^b	N	S			
SSS-Char	74.20	3.45	17.65	2.43	0.08	0.18	0.56	28.33
PSS-Char	65.41	3.73	21.10	6.69	0.10	0.24	0.68	25.45
WSS-Char	35.46	1.89	56.44	2.38	0.09	1.19	0.64	8.57

^a oven-dried, ^b Determined by difference, ^c atomic ratio, ^d calculated from Dulong formula (Ferdinand *et al.* 2012)

Biochar analysis

Table 4 shows the yields of pyrolysis residue. For WSS, the yield of biochar was 39.14 wt.%, which was a larger portion than the others (PSS 26.75 wt.%, SSS 20.75 wt.%). In general, due to biomass thermal cracking, the biochar is derived from the fast pyrolysis of lignin. The char yield of cellulose and hemicellulose in biomass from fast pyrolysis is lower than from lignin decomposition. Guaiacol and its intermediate in the fast pyrolysis process are very easy to coke (Wang *et al.* 2009). Therefore, the biochar yield of WSS and PSS in the process of fast pyrolysis would be higher, and this was confirmed by the component and structure analysis. The elemental composition of the biochar is presented in Table 6. The higher carbon content of biochar in SSS and PSS meant less residual organics in the biochar. The high quantity of different compounds in the bio-oil (Table 7) supported these results. This effect also explains why SSS and PSS had less ash content. Compared with SSS and PSS, the carbon content of biochar in WSS was noticeably lower and the O/C ratio was higher. These results may reflect that WSS contain more ash and metallic oxide (Raclavská *et al.* 2011).

To investigate the alterations of functional groups, the biochar produced from tubular furnace pyrolysis was analyzed by FT-IR (Fig. 3). Compared with the FT-IR spectra of samples, O-H stretching absorption at 3450 cm⁻¹ still existed. However, peaks around 2900 cm⁻¹ almost disappeared. This suggested that alkylated compounds disappeared due to pyrolysis. Peaks in the 1000 to 1600 cm⁻¹ range were weaker and fewer than in the FT-IR spectra of samples. Typical signals of aromatic skeletal vibrations at peaks 1420 cm⁻¹ and 1580 cm⁻¹ still persisted. This illustrated that the aromaticity of biochar still existed, which may have a positive influence on biochar analysis and use of seed shells.

Bio-oil analysis

The bio-oil derived from the three samples pyrolysis at 600 °C was analyzed with a GC/MS. The bio-oil components are summarized and classified in Table 7. The bio-oil consisted of typical pyrolytic products, including furans, acids, ketones, and phenolic compounds.

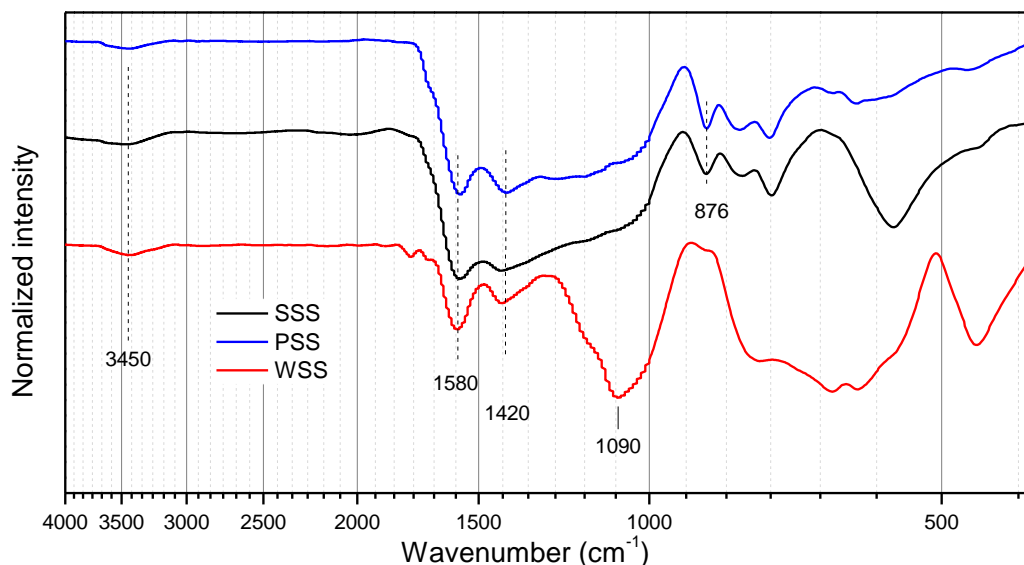


Fig. 3. Peak assignments for the FT-IR spectra of fast pyrolysis biochar from sunflower seed shells (SSS), pumpkin seed shells (PSS), and watermelon seed shells (WSS)

For the bio-oil of SSS, acids and ketones were the main components, at 39.28% and 20.02%, respectively. The amounts of acetic acid (36.53%) and 1-hydroxy-2-propanone (9.90%) were higher than in the bio-oil from WSS and PSS. They were generally from the decomposition of cellulose and hemicellulose, especially the cleavage of acetyl groups and uronic acid side chains in cellulose and hemicellulose. Glycosides and C-C keys disconnect to form various furans and ketones (Peng and Wu 2011; Liang *et al.* 2015). These component distributions corresponded with the high holocellulose content of SSS.

Compared with the bio-oil of SSS and WSS, the bio-oil of PSS had lower amounts of acids and higher amounts of phenolic compounds, which were associated with the high lignin content of PSS. The structure primarily consisted of phenyl propane units, which contain a large number of aromatic compounds with various functional groups. Phenolic compounds from the bio-oil could be divided into guaiacol-type (G), syringol-type (S), and phenol-type (H). For the bio-oil of PSS, 2-methoxy-phenol (10.73%) and 2-methoxy-4-vinylphenol (9.39%) were the predominant G-types. The most common S-type was 2,6-dimethoxy-phenol (1.86%) and the most predominate H-type was 4-methyl-phenol (8.25%). In the three kinds of bio-oil, the components were mostly G- and H-type phenols. In particular, the G-type in the bio-oil from PSS (43.78%) and WSS (32.33%) were higher than in the bio-oil from SSS. This was probably due to their basic structures, which were mainly composed of guaiacyl propane. Furthermore, the common types of interunit linkage in lignin are α -O-4, β -O-4, and 4-O-5 bonds, which could easily produce guaiacol in the lignin degradation process (Hua *et al.* 2016). Moreover, nitrogen compounds (pyrrole 1.67%, acetamide 1.19%) were identified in the bio-oil from PSS.

For the WSS bio-oil, the percentages of phenolic compounds, acids, and ketones were 43.37%, 20.52%, and 15.56%, respectively. Compared with the PSS bio-oil, the phenolic compounds of the WSS bio-oil were lower. This was mainly attributed to the higher lignin content of PSS. The percentages of 2-methoxy-4-vinylphenol and 2-methoxy-4-(1-propenyl)-(Z)-phenol were 9.39% and 7.98%, respectively for the bio-oil from PSS. The amounts of acids and ketones in the WSS bio-oil were lower than in the SSS bio-oil. This corresponded with the low holocellulose content of WSS. Moreover, furans derived

from the WSS pyrolysis reached 9.28% (furfural 3.39%, 2-furanmethanol 4.14%). The products of some compounds can be used in the chemical industry or as pharmaceutical intermediates and some of them have very high economic values. For example, acetic acid can be used in organic synthesis. Furfural is the preparation of a variety of medicines and industrial products of raw materials. Phenols and other aromatic compounds are also commonly used chemical raw materials. Based on the pyrolysis characteristics of the three kinds of raw material and their generated products, biomass pyrolysis technology can be used to produce high-value compounds. Further research into biomass renewable energy applications is of vital importance.

Table 7. Components Identification of Bio-Oil Collected from Sunflower Seed Shells (SSS), Pumpkin Seed Shells (PSS), and Watermelon Seed Shells (WSS) Pyrolysis at 600 °C

Groups	Compounds	Formula	Area Percentage		
			WSS	PSS	SSS
Alcohols	2-methyl-Cyclopentanol	C ₆ H ₁₂ O	0.26	—	—
	Cyclopentanol	C ₅ H ₁₀ O	0.41	—	—
	3-Ethoxy-1,2-propanediol	C ₅ H ₁₂ O ₃	0.81	—	0.57
	2-Cyclohexen-1-ol	C ₆ H ₁₀ O	1.00	—	—
	Cyclopropyl carbinol	C ₄ H ₈ O	3.83	—	3.10
total			6.31		3.68
Aldehydes	3-hydroxy-Butanal	C ₄ H ₈ O ₂	0.12	1.01	—
	Butanedial	C ₄ H ₆ O ₂	0.72	—	—
	3-hydroxy-Butanal	C ₄ H ₈ O ₂	—	—	0.58
total			0.84	1.01	0.58
Furans	Furfural	C ₅ H ₄ O ₂	3.39	—	3.96
	2-Furanmethanol	C ₅ H ₆ O ₂	4.14	1.27	1.40
	2(5H)-Furanone	C ₄ H ₄ O ₂	1.76	1.33	1.19
total			9.28	2.60	6.55
Acids	3-hydroxy-Butanoic acid	C ₄ H ₈ O ₃	0.59	—	0.28
	Acetic acid	C ₂ H ₄ O ₂	18.28	13.77	36.53
	Propanoic acid	C ₃ H ₆ O ₂	1.65	1.47	1.82
	4-hydroxy-Butanoic acid	C ₄ H ₈ O ₃	—	—	0.64
	Hexanoic acid	C ₆ H ₁₂ O ₂	—	1.90	—
	Octanoic Acid	C ₈ H ₁₆ O ₂	—	1.10	—
total			20.52	18.23	39.28
Ketones	4-sec-Butoxy-2-butanone	C ₈ H ₁₆ O ₂	0.41	—	0.31
	2-Pentanone	C ₅ H ₁₀ O	0.75	—	—
	1-hydroxy-2-Propanone	C ₃ H ₆ O ₂	7.37	2.55	9.90
	2-Cyclopenten-1-one	C ₅ H ₆ O	0.89	—	0.99
	2-methyl-2-Cyclopenten-1-one	C ₆ H ₈ O	—	—	0.27
	1-Hydroxy-2-butanone	C ₄ H ₈ O ₂	—	—	0.61
	1-(acetyloxy)-2-Propanone	C ₅ H ₈ O ₃	—	—	1.63
	1,2-Cyclopentanedione	C ₅ H ₆ O ₂	4.24	—	2.70
	3-methyl-1,2-Cyclopentanedione	C ₆ H ₈ O ₂	1.50	2.54	2.94
	3-ethyl-2-hydroxy-2-Cyclopenten-1-one	C ₇ H ₁₀ O ₂	0.40	0.57	0.67
total			15.56	5.65	20.02

Groups	Compounds	Formula	Area Percentage		
			WSS	PSS	SSS
Esters	2-Hydroxyacetic acid ethyl ester	C ₄ H ₈ O ₃	1.55	—	0.70
	Methyl hydroxyacetate	C ₃ H ₆ O ₃	0.96	—	—
	Propyl butyrate	C ₇ H ₁₄ O ₂	—	—	1.35
total			2.52		2.05
Phenols G ^a	Phenol	C ₆ H ₆ O	2.65	7.52	1.91
	2-methoxy-Phenol	C ₇ H ₈ O ₂	4.77	10.73	5.03
	2-methoxy-4-methyl-Phenol	C ₈ H ₁₀ O ₂	4.04	7.15	1.95
	4-ethyl-2-methoxy-Phenol	C ₉ H ₁₂ O ₂	2.19	3.58	1.47
	2-methoxy-4-propyl-Phenol	C ₁₀ H ₁₄ O ₂	—	1.16	—
	2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	6.44	9.39	3.79
	2-methoxy-5-(1-propenyl)-(E)-Phenol	C ₁₀ H ₁₂ O ₂	1.11	2.53	0.53
	2-methoxy-4-(1-propenyl)-(E)-Phenol	C ₁₀ H ₁₂ O ₂	1.14	1.26	0.63
	2-methoxy-4-(1-propenyl)-(Z)-Phenol	C ₁₀ H ₁₂ O ₂	7.98	7.98	3.14
	3-Hydroxy-4-methoxybenzoic acid	C ₈ H ₈ O ₄	1.66	—	0.88
	3-hydroxy-4-methoxy-Benzaldehyde	C ₈ H ₈ O ₃	0.63	—	—
	1-(4-hydroxy-3-methoxyphenyl)-Ethanone	C ₉ H ₁₀ O ₃	1.09	—	—
	1-(4-hydroxy-3-methoxyphenyl)-2-Propanone	C ₁₀ H ₁₂ O ₃	1.28	—	—
	4-hydroxy-3-methoxy-Benzeneacetic a	C ₉ H ₁₀ O ₄	—	—	1.59
	total			32.33	43.78
S ^b	2,6-dimethoxy-Phenol	C ₈ H ₁₀ O ₃	1.89	1.86	2.15
	2,6-dimethoxy-4-(2-propenyl)-Phenol	C ₁₁ H ₁₄ O ₃	1.22	1.00	0.98
total			3.12	2.86	3.14
H ^c	2-methyl-Phenol	C ₇ H ₈ O	0.98	1.70	1.95
	3-methyl-Phenol	C ₇ H ₈ O	0.73	1.07	0.55
	4-methyl-Phenol	C ₇ H ₈ O	1.25	8.25	0.72
	4-ethyl-Phenol	C ₈ H ₁₀ O	0.41	1.34	—
	3-tert-Butyl-4-hydroxyanisole	C ₁₁ H ₁₆ O ₂	1.91	0.49	1.31
total			5.28	12.85	4.54
total			43.37	67.01	28.58
Others	p-Dioxane-2,3-diol	C ₅ H ₁₂ O ₃	0.93	0.87	—
	Pyrrrole	C ₄ H ₅ N	—	1.67	—
	Acetamide	C ₂ H ₅ NO	—	1.19	—
	4(1H)-Pyridone	C ₅ H ₅ NO	—	0.95	—
	2-(Ethenyloxy)propane	C ₅ H ₁₀ O	0.68	—	—
	d-Mannose	C ₆ H ₁₂ O ₆	—	0.81	—
total			1.61	5.50	

G^a guaiacol-type compounds, S^b syringol-type compounds, H^c phenol-type compounds
Area Percentage: the ratio of the area of a single peak to the whole area of total ion-current (TIC) spectrogram.

CONCLUSIONS

1. For PSS, the C and H content (52.96%, 7.38%) and its HHV (23.88 MJ/kg) were the highest among the three kinds of seed shells. For SSS, the content of holocellulose (83.47 wt.%) was higher, but the content of lignin (13.62 wt.%) was lower than for the others. For the FT-IR of these seed shells, the raw material structures were similar.
2. The thermal decomposition process of all seed shells can be divided into the three thermal degradation stages of dehydration, active pyrolysis, and passive pyrolysis. The yield of solid residue was 17.98% for WSS, 27.98% for PSS, and 21.77% for SSS.
3. The amount of gas from the SSS pyrolysis and the yield of the biochar from WSS were the largest among the three samples. The bio-oil from the PSS pyrolysis had high phenolic compounds. However, the content of acids (acetic acid 36.53%) and ketones (1-hydroxy-2-propanone 9.90%) in the bio-oil from SSS were higher than in the others. In the bio-oil from all three kinds of seed shells, the pyrolysis products were mainly guaiacol-type and phenol-type. The guaiacol-type in the bio-oil from PSS (43.78%) and WSS (32.33%) were higher than in the bio-oil from SSS.

ACKNOWLEDGEMENTS

This work was supported by the National Major Fundamental Research Program of China (973 programs, NO.2013CB228101)

REFERENCES CITED

- Antal, M. J., Wade, S. R., and Nunoura, T. (2007). "Biocarbon production from Hungarian sunflower shells," *J. Anal. Appl. Pyrol.* 79(1-2), 86-90. DOI: 10.1016/j.jaap.2006.09.005
- National Bureau of Statistics of China (NBSC) (2013). "China statistical yearbook 2013," (<http://www.stats.gov.cn/tjsj/ndsj/2013/indexce.htm>), Accessed June 28, 2016.
- Cancelon, P. (1971). "Chemical composition of sunflower seed hulls," *J. Am. Oil Chem. Soc.* 48(10), 629-632. DOI: 10.1007/BF02544577
- Chen, Q., Yang, R., Zhao, B., Li, Y., Wang, S., Wu, H., Zhuo, Y., and Chen, C. (2014). "Investigation of heat of biomass pyrolysis and secondary reactions by simultaneous thermogravimetry and differential scanning calorimetry," *Fuel* 134, 467-476. DOI: 10.1016/j.fuel.2014.05.092
- Demirbaş, A. (2006). "Effect of temperature on pyrolysis products from four nut shells," *J. Anal. Appl. Pyrol.* 76(1-2), 285-289. DOI: 10.1016/j.jaap.2005.12.012
- Duan, L., and Wang, X. (2006). "Extraction and antibiotic effect of chlorogenic acid from sunflower shell mea," *Journal of Southwest Agricultural University* 28(1), 124-126.
- Ferdinand, F. W., Steene, L. V. D., Blaise, K. K., and Siaka, T. (2012). "Prediction of pyrolysis oils higher heating value with gas chromatography-mass spectrometry," *Fuel* 96(1), 141-145. DOI: 10.1016/j.fuel.2012.01.007
- Gao, Q., and Dou, X. (2009). "Microwave-assisted extraction of chlorogenic acid from sunflower seed kernel," *China Oils and Fats* 34(6), 68-69.

- GB/T 2677.3 (1993). "Fibrous raw material - Determination of ash," Standardization Administration of China, Beijing, China.
- GB/T 2677.8 (1994). "Fibrous raw material - Determination of acid-insoluble lignin," Standardization Administration of China, Beijing, China.
- GB/T 2677.10 (1995). "Fibrous material - Determination of holocellulose," Standardization Administration of China, Beijing, China.
- Hua, W., Liu, C., Wu, S., and Li, X. (2016). "Analysis of structural units and their influence on thermal degradation of alkali lignins," *BioResources* 11(1), 1959-1970. DOI: 10.15376/biores.11.1.1959-1970
- Liang, J., Lin, Y., Wu, S., Liu, C., Lei, M., and Zeng, C. (2015). "Enhancing the quality of bio-oil and selectivity of phenols compounds from pyrolysis of anaerobic digested rice straw," *Bioresource Technol.* 181, 220-223. DOI: 10.1016/j.biortech.2015.01.056
- Liu, C., Wang, H., Karim, A. M., Sun, J., and Wang, Y. (2014). "Catalytic fast pyrolysis of lignocellulosic biomass," *Chem. Soc. Rev.* 43(22), 7594-7623. DOI: 10.1039/c3cs60414d
- Lou, R., and Wu, S. (2011). "Products properties from fast pyrolysis of enzymatic/mild acidolysis lignin," *Appl. Energ.* 88(1), 316-322. DOI: 10.1016/j.apenergy.2010.06.028
- Lv, G., Wu, S., Yang, G., Chen, J., Lui, Y., and Kong, F. (2013). "Comparative study of pyrolysis behaviors of corn stalk and its three components," *J. Anal. Appl. Pyro.* 104, 185-193. DOI: 10.1016/j.jaap.2013.08.005
- Patwardhan, P. R., Satrio, J. A., Brown, R. C., and Shanks, B. H. (2010). "Influence of inorganic salts on the primary pyrolysis products of cellulose," *Bioresource Technol.* 101(12), 4646-4655. DOI: 10.1016/j.biortech.2010.01.112
- Peng, Y., and Wu, S. (2011). "Fast pyrolysis characteristics of sugarcane bagasse hemicellulose," *Cell. Chem. Technol.* 45(9-10), 605-612.
- Raclavská, H., Juchelková, D., Roubicek, V., and Matýsek, D. (2011). "Energy utilisation of biowaste – Sunflower-seed hulls for co-firing with coal," *Fuel Process. Technol.* 92(1), 13-20. DOI: 10.1016/j.fuproc.2010.03.006
- Rai, A., Mohanty, B., and Bhargava, R. (2015). "Modeling and response surface analysis of supercritical extraction of watermelon seed oil using carbon dioxide," *Sep. Purif. Technol.* 141, 354-365. DOI: 10.1016/j.seppur.2014.12.016
- Ramirez-Corredores, M. M. (2013). "Pathways and mechanisms of fast pyrolysis: Impact on catalyst research," in: *The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals*, K. Triantafyllidis, A. Lappas, and M. Stöcker (eds.), Elsevier, Amsterdam, Netherlands, pp. 161-216. DOI: 10.1016/B978-0-444-56330-9.00006-1
- Telli-Okur, M., and Eken-Saraçoğlu, N. (2008). "Fermentation of sunflower seed hull hydrolysate to ethanol by *Pichia stipitis*," *Bioresource Technol.* 99(7), 2162-2169. DOI: 10.1016/j.biortech.2007.05.036
- Wang, S., Wang, K., Liu, Q., Gu, Y., Luo, Z., Cen, K., and Fransson, T. (2009). "Comparison of the pyrolysis behavior of lignins from different tree species," *Biotechnol. Adv.* 27(5), 562-567. DOI: 10.1016/j.biotechadv.2009.04.010
- Wu, Y., Zhao, Z., Li, H., and He, F. (2009). "Low temperature pyrolysis characteristics of major components of biomass," *Journal of Fuel Chemistry and Technology* 37(4), 427-432. DOI: 10.1016/S1872-5813(10)60002-3

- Xiao, B., Sun, X. F., and Sun, R. (2001). "Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw," *Polym. Degrad. Stabil.* 74(2), 307-319. DOI: 10.1016/S0141-3910(01)00163-X
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12–13), 1781-1788. DOI: 10.1016/j.fuel.2006.12.013
- Zabaniotou, A. A., Kantarelis, E. K., and Theodoropoulos, D. C. (2008). "Sunflower shells utilization for energetic purposes in an integrated approach of energy crops: Laboratory study pyrolysis and kinetics," *Bioresour. Technol.* 99(8), 3174-3181. DOI: 10.1016/j.biortech.2007.05.060

Article submitted: June 14, 2016; Peer review completed: August 13, 2016; Revised version received and accepted: August 20, 2016; Published: August 30, 2016.
DOI: 10.15376/biores.11.4.8806-8819