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Characterisation of Biochar and Biooil Produced from Different Feedstocks

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Abstract: The objective of this study was to produce biochar and biooil from three different feedstocks and characterize their properties. Corn stover, big blue stem and praririe cord grass as feedstocks were usedf for this study. Ash content, moisture content, geometric mean diameter, true density, bulk density, porosity and heating value of produced biochar samples were studied. In addition, ash content, pH, density, viscosity, heating value of all the produced biooil samples were measured. Some significant differences in biochar and biooil properties as a function of different feedstocks, pyrolysis temperature, heating rate and feedstock particle size were found.
Key words: Corn stover, big blue stem, prairie cord grass, pyrolysis

INTRODUCTION

The diminishing stockpile of fossil fuels and the accompanying negative effects of their usage in terms of producing green house gases and shift in climate has also regenerate the interest in renewable energy sources (Bridgwater, 1995; Lehmann et al., 2006). Biochar and bioil are products of pyrolysis, which is carbon rich, with high heating value and relatively pollution free solid biofuel. The aim of this work is to produce and characterize biochar and bioil from different feedstocks (corn stover, big bluestem, and prairie cord grass) by conventional pyrolysis.

MATERIALS and METHOD

The pyrolysis was carried out in a reactor (mild steel 20 cm long, diameter of 10 cm) placed in an Isotemp programmable muffle furnace. Before heating, nitrogen was flushed in to the reactor for 10 min to remove air from the system. The heating rate was varied from 20-40°C/min. The temperature was maintained from 300 to 600˚C. Three different feedstocks namely corn stover (CS), big bluestem (BB), and prairie cord grass (PCG) were studied. Preliminarily corn stover was taken to evaluate the operating conditions, as consequence 4 mm particle size and 40°C/min has given the highest yield of biooil.

All the experiments were carried out in triplicates and the data collected was analyzed using SAS 9.2.

Biochar and biooil characterization procedures

Ash content of biochar: According to ASTM D3174-04 (2010), 1 g of biochar was heated at 750°C for 4 hours.

Moisture content of biochar: Two gram of biochar was kept on oven at 80°C for 24 h (Mausilili et al., 2010).

True density, bulk density and porosity of biochar: According to ASTM D6683 (2001), multivolume pyconometer (Model 1305, Micromatrics, Norcross, GA) was used for determination of these properties.

Geometrical mean diameter: According to ASAE S319.3 (2003), about 100 g of biochar was placed in a roto top with standard sieve and operated for 10 min.

Ash content of bio-oil: According to ASTM D 482-80 for petroleum products, 1 g of bio-oil heated at 750°C for 4 hours.

pH: The pH of the bio-oils was observed using a digital pH meter (Accumet model XL20, Fisher Scientific, Fair Lawn, NJ).

Heating value: The heating value was measured as calorimetric value by a Parr 1341 Oxygen Bomb Calorimeter (Parr Instrument Co., Moline, IL)

Density of biooil: A 15 ml glass beaker was filled with biooil, based on the weight and volume, the density was calculated.

Viscosity of biooil: According to ASTM D445, the viscosity was measured using cup and bob assembly in rheometer (ATS Rheosystems, Rheologica Instruments Inc, NJ) with approximately 15 mL of biooil.

RESULTS and DISCUSSION

The main effect of type of feedstock on biochar and biooil yield and their characteristics are tabulated in Table 1 and 2. Among three feedstocks the big blue stem had low biooil, high biochar yield, low pH and low density values compared to other two feedstocks. No significant difference in syngas and heating values were observed. Bio-oil yield from corn stover was in agreement with the yield reported from microwave assisted pyrolysis (MAP, 600-650°C) of corn stover pellets, whereas biochar yield was higher than MAP (Yang et al., 2010). A higher yield of bio-oil (60-66%) and lower yield of char (11.6-30.4%) and gas (9.6-24%) was reported by Zheng (2008) in fast pyrolysis when conducted at 480-540°C.

In general, as the pyrolysis temperature increases the biooil yield also increases and biochar yield decreases as shown in Table 3. Similar observation was reported for fast pyrolysis of corn stover by Zheng (2008), whereas Yang et al. (2010) and Figueioredo et al. (1989) reported an opposite trend in MAP of corn stover pellets and fast pyrolysis of holm-oak wood. The pH of biooil from different feedstocks were within the conventional bio-oil range of 2-3.8 because of organic acids mostly acetic and formic acids. The pH of biooil obtained from corn stover was in agreement with pH of biooil (3.2) produced from cron stover through fast pyrolysis [2008], whereas Yu et al [2007] reported a lower pH of 2.87 for the biooil produced from corn stover through MAP.

Table 1. Main effect of feedstock (FS) on product yields

FS	Biooil, %	Biochar, %	syngas, %
CS	35.1^{a}	28.6^{ab}	36.3^{a}
PCG	35.3^{a}	27.6^{b}	37.1^{a}
BB	34.1^{b}	29.7^{a}	36.2^{a}

Table 2. Main effect of feedstock (FS) on biooil properties

FS	Ph	Density kg/m^3	Ash, %
CS	3.4^{ab}	950^{a}	0.0684^{a}
PCG	3.5^{a}	920^{b}	0.0502^{c}
BB	3.4^{b}	910^{c}	0.0547^{b}

Among the feedstocks, corn stover biooil had a higher density when compared to other feedstocks. The density of the biooil from different feedstocks (Table 2-5) were less than water, which is easy to automize. This observation was in contrary to other corn stover pyrolysis through MAP (Yu et al., 2007) and fast pyrolysis (Zheng, 2008). Ash present in the bio-oil can cause erosion, corrosion, and gumming problems in the engine valves. According to Peacocke et al. (1994), when the ash content of bioil is higher than 0.1%, the problems become more serious. Considering this criteria, ash content of the biooil from different feedstocks were less than 0.1% and comparable with MAP of corn stover (Yu et al., 2007).

Table 3. Main effect of pyrolysis temperature on product yields and biooil properties

T, °C	Biooil, %	Biochar, %	Syngas, %	pH	Density, kg/m^3	Ash, %
300	30.1^{d}	42.5^{a}	27.4^{c}	3.0^{d}	940^{a}	0.0506^{d}
400	33.6^{c}	29.9^{b}	36.5^{b}	3.4^{c}	940^{a}	0.0588^{c}
500	36.1^{b}	23^{c}	39.1^{a}	3.6^{b}	930^{b}	0.0599^{b}
600	38.7^{a}	18.1^{d}	42.4^{a}	3.8^{a}	910^{c}	0.0648^{a}

Table 4. Main effect of heating rate (HR) on product yields and biooil properties

HR, °C/min	Biooil, %	Biochar, %	Syngas, %	pH	Density, kg/m^3
20	33.5^{b}	29.2^{a}	37.3^{a}	3.5^{a}	910^{b}
30	34.4^{ab}	29.6^{a}	35.9^{a}	3.4^{ab}	910^{b}
40	35.3^{b}	28.3^{a}	36.5^{a}	3.4^{b}	940^{a}

Table 5. Main effect of particle size (PS) on product yields and biooil properties

PS, mm	Biooil, %	Biochar, %	Syngas, %	pH	Density, kg/m^3
2	34.6^{a}	29.3^{a}	36.1^{b}	3.5^{a}	910^{b}
4	35.7^{a}	23.5^{b}	40.9^{a}	3.4^{a}	970^{a}
6	34.6^{a}	29.5^{a}	35.9^{b}	3.4^{a}	970^{a}
8	35.4^{a}	29.8^{a}	34.8^{b}	3.4^{a}	960^{a}

Different letter in each column indicates statistical difference at alpha = 0.05

In general, heating rate and particle size of the feedstock postively contributes for biooil yiled. However, in this study there was no significant differences in biooil yield due to heating rate and particle size. This obseravtion was in contrary to holm-oak wood pyrolysis reported by Figueioredo et al. (1989).

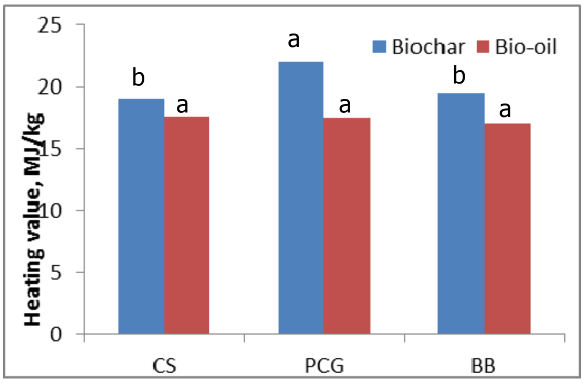

Figure 1. Mean heating value of biochar and biooil obtained from different feedstocks

The heating value of biooil from different feedstocks are shown in fig 1 and 2, which is about 17-18 MJ/kg. This is in agreement with MAP of corn stover (Yu et al., 2007) and other biooil from different feedstocks (15-19 MJ/kg). The heating value of these biooil is about 41% of the petroleuem fuels (42 MJ/kg), which shows that increased fuel flow is required to compensate the combustion.

Viscosity of bio-oil affects the operation of fuel injection equipment, particularly when the increase in the viscosity affects the fluidity of fuel at low temperatures. Power law describes the behavior well with consistency coefficient (k) about 0.998 and flow behavior index (n) of 0.002 to 0.004. The flow behavior indexes *n* less than 1 suggests that presence of the pseudoplastic behavior (shear thinning). Similar observation was also reported for biooils from different feedstocks such as corn cob, aspena and canola pellets (Karunanithy and Muthukumarappan, 2011).

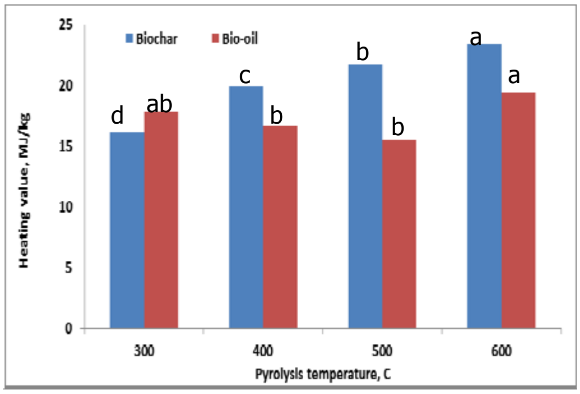

Figure 2. Effect of pyrolysis temperature on mean heating value of biochar and biooil

Biochar is carbon rich with high calorific value and can be used as solid fuel. The properties of biochar are important to decide on its final application such as soil conditioner, activated carbon, and remedial applications. Biochar properties are presented in Table 6 and 7. As noted from these tables, type of feedstock and pyrolysis temperature had a significant influence on the biochar properties. Among the feedstocks, biochar from corn stover had higher moisture content, ash content, and porosity than that of other two feedstocks. As the pyrolysis temperature increased the moisture content decreased and ash content increased. The highest pyrolysis temperature (600°C) resulted in a biochar with higher ash, bulk density and true density and GMD. The ash content of PCG was in agreement with various biochars reported by Ozçimen and Ersoy-Meriçboyu [2010]. The biochars of this study had a lower porosity than that of biochars (0.117-0.170) from different feedstocks (Ozçimen and Ersoy-Meriçboyu, 2010).

Among the feedstocks, PCG had a higher heating value than other two feedstocks. As expected, the heating value increased with pyrolysis temperature. The heating values were in agreement with biochar produced from different feedstocks reported by Ozçimen and Ersoy-Meriçboyu (2010).

Table 6. Main effect of different feedstocks on biochar properties

Feedstock	Moisture content, % wb	Ash content, %	GMD, mm	True density, kg/m^3	Bulk density, kg/m^3	Porosity	Heating value, MJ/kg
CS	4.54^a	34.8^a	0.42^{ab}	103.6^b	94.0^b	0.093^a	19.0^b
PCG	1.99^c	9.60^c	0.40^b	98.9^c	90.8^c	0.094^a	22.0^a
BB	2.24^b	26.3^b	0.44^a	107.6^a	98.2^a	0.087^b	19.5^b

Table 7. Main effect of pyrolysis temperature on biochar properties

Temperature, °C	Moisture content, %wb	Ash content, %	GMD, mm	True density, kg/m^3	Bulk density, kg/m^3	Porosity	Heating value, MJ/kg
300	3.68^a	20.8^d	0.47^a	94.2^c	85.5^d	0.093^{ab}	16.2^d
400	3.21^b	22.3^c	0.38^b	101.7^b	93.9^c	0.092^{ab}	19.9^c
500	2.65^c	24.4^b	0.37^b	107.8^a	97.8^b	0.093^a	21.7^b
600	2.20^d	26.8^a	0.45^a	109.8^a	100.1^a	0.088^b	23.3^a

CONCLUSIONS

This study showed that type of feedstock and pyrolysis temperature not only affect the yield of biooil and biochar but also the properties of biooil and biochar. Corn stover had a highest biooil yield and density. A highest biooil yield of 38.1% was recorded at a pyrolysis temperature of 600°C. The pH was comparable with literature values and ash content of the biooil was in the range of 0.4-0.6%, which is similar to other biooils. The heating value of the biooil and biochar was also omparbale to literatur values.

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