Effects of pyrolysis parameters on the yield and properties of biochar from pelletized sunflower husk

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Abstract. Pyrolysis of biomass residues from agriculture and food processing industry allows production of biochars with diverse physical and chemical properties for a wide range of applications in agriculture and environmental protection. Biochars produced from pelletized sunflower husks through slow pyrolysis in the range of temperatures (480–580°C) showed total carbon of 70.53%–81.96%, total nitrogen of 1.2%, alkaline pH (9.37–10.32), low surface area (0.93–2.91 m^2 g^{-1}) and porosity of 13.23–15.43%. Higher pyrolysis temperatures resulted in lower biochar yields. With the increase in temperature the content of organic matter, nitrogen, Ca and Mg decreased whereas the increase in temperature resulted in higher contents of total carbon and phosphorus. Produced biochars showed potential for agricultural applications.

1 Introduction

Thermal conversion of biomass through pyrolysis allows production of materials that can be used for a wide range of applications that provide solutions to the most pressing environmental problems [1–9]. However, the properties of biochars will determine the type of application and the efficiency of the processes involved. The literature provides a great number of studies on different types of biochars used as sorbents for removal of various organic and inorganic contaminants, soil amendments and fertilizers, supplementary materials for composting and anaerobic digestion, additives for remediation of contaminated soil, etc. [10–14]. The most recent applications include using biochar as a potential hydroponic growth substrate [15], a biochar composite membrane or a wood polymer composite [16, 17], a green roof substrate [18] or a microbial carrier [19]. The most important properties of biochars include chemical composition, porosity and surface area, pH, and also surface functional groups. These properties can be "designed" by modifying the process of pyrolysis through temperature, heating and retention times

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[20–22] and also by modifying the properties of substrates for biochar production (physically or chemically). Depending on the properties of biochar substrates, the increase in pyrolysis temperature can result in the increase in surface area [23] and carbon content [24] in the obtained biochars. Biochar can be produced from a wide range of substrates including agricultural residues such as sunflower husk [25]. However, the literature provides only few studies on converting pelletized sunflower husk into biochar and the effects of different pyrolysis parameters on the selected properties of the produced biochars.

The overall goal of this study was to analyse the effects of pyrolysis parameters (i.e. temperature, heating and retention times) on the yield and selected properties of biochars produced from pelletized sunflower husk.

2 Materials and methods

2.1 Pelletized sunflower husk

Pelletized sunflower husk (PSH) was used to produce biochar. The shape of the investigated pellets was typical for biomass pellets [26, 27], i.e. cylindrical elongated and regular with the diameter of 8 mm and the length from 5 to 25 mm. The moisture (MC) and organic matter (OM) content of PSH was of 7.44% and 89.33% (d.b.), respectively. Selected properties of pelletized sunflower husk are presented in Table 1.

Table 1. Selected properties of pelletized sunflower husk (PSH).

	DM, %	OM, % (d.b.)	pH	C_{tot}, g kg^{-1}	N, g kg^{-1}
PSH	92.56	89.33	5.70	474.65	7.94

2.2 Pyrolysis parameters

Pelletized sunflower husk was pyrolysed in a continuous pyrolysis reactor (PRW-S100x780/11, max. temperature up to 1100°C, under nitrogen atmosphere of 5 dm^3 m^{-1}) under different conditions of temperature, heating and retention times (Table 2). The real temperature inside of the reactor was measured by a thermocouple.

Table 2. Pyrolysis parameters (temperature, heating time, retention time) used in this study.

Parameters	Values											
Temperature, °C	480				530				580			
Heating time, min	65		120		65		120		65		120	
Retention time, min	10	60	10	60	10	60	10	60	10	60	10	60

Pelletized sunflower husk (100 g) was placed in the reactor and heated with the temperature of 480°C, 530°C and 580°C (assumed values) at different heating times (65 and 120 minutes) and retention times (10 and 60 minutes). After the completion of the process the samples were left in the reactor until they reached room temperature. The temperatures measured by a thermocouple during pyrolysis were lower than the values assumed at the beginning of the process (Table 3).

Table 3. Temperatures during pyrolysis measured by a thermocouple.

Pyrolysis parameters (temperature, heating time, retention time)	480 65 10	530 65 10	580 65 10	480 120 10	530 120 10	580 120 10	480 120 60	530 120 60	580 120 60	480 65 60	530 65 60	580 65 60
Temperatures measured during the process, °C	426	480	537	444	496	550	463	514	564	461	513	564

2.3 Physicochemical and physical analyses

Biochars obtained from pyrolysis of pelletized sunflower husk were analysed for moisture content (by oven drying in 105°C), organic matter (by incineration in a muffle furnace at 550°C for 5 h), total carbon (by MultiN/C, Analytkjena, in 4 replications), pH (1:10 v/v, in 2 replications), Kjeldahl nitrogen, and selected elements (by ICP-OES Thermo Elemental IRIS INTREPID II XSP DUO, in 3 replications). Porosity and surface area were determined with the mercury intrusion porosimeter (PoroMaster 33). In addition, density and particle size of the produced biochars were analysed and biochar surface was analysed with scanning microscopy (SU3500 Hitachi).

3 Results and discussion

3.1 Pyrolysis efficiency, moisture and organic matter contents

The efficiency of pyrolysis, i.e. the yield of conversion of pelletized sunflower husk (Fig. 1) into biochar depended on temperature and retention time (Table 4).

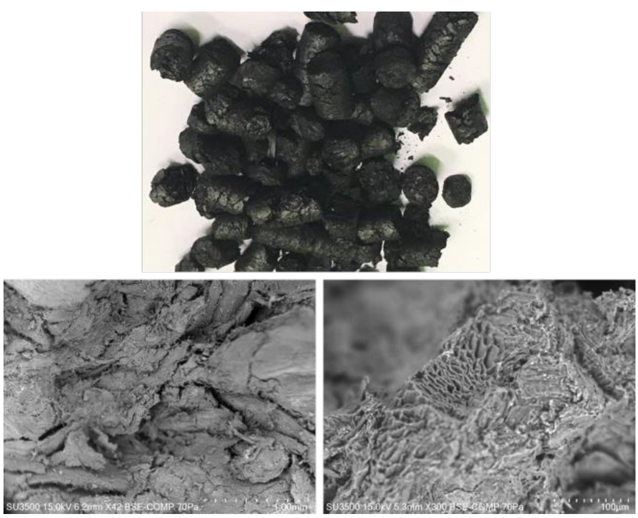

Fig 1. Biochar produced from pelletized sunflower husk (magnified by 42 and 300 times).

The biochar yield was in the range of 30.04–36.23% of the initial substrate weight and decreased with the increase in temperature at the same heating and retention times. This is in line with other studies that demonstrated that the biochar yield depends on pyrolysis temperature and retention time [28–31]. For example, biochar yield obtained from pyrolysis of pelletized sunflower at 400°C decreased from 36.17% to 33.19% at 500°C [27].

Table 4. Pyrolysis parameters (temperature, heating time, retention time) used in this study.

Pyrolysis parameters	Biochar yield, % (d.b. of PSH)	Average yield, %	Moisture content, %	Organic matter content, %
480/65/10	35.63 ± 0.24	32.68	2.69 ± 0.42	88.21 ± 0.73
530/65/10	32.03 ± 0.10		3.24 ± 0.90	87.23 ± 1.09
580/65/10	30.39 ± 0.28		3.31 ± 0.51	86.19 ± 0.88
480/120/10	36.23 ± 0.39	33.74	2.30 ± 0.87	88.77 ± 1.20
530/120/10	33.46 ± 0.36		2.81 ± 0.99	87.92 ± 1.43
580/120/10	31.54 ± 0.22		2.53 ± 0.72	87.48 ± 1.23
480/120/60	33.91 ± 0.13	32.49	3.48 ± 0.44	86.60 ± 0.87
530/120/60	31.96 ± 0.04		3.20 ± 0.59	86.54 ± 0.52
580/120/60	31.60 ± 0.33		3.55 ± 0.24	85.87 ± 0.56
480/65/60	33.42 ± 0.69	31.59	2.94 ± 0.54	87.68 ± 0.78
530/65/60	31.31 ± 0.62		3.61 ± 0.47	86.24 ± 0.47
580/65/60	30.04 ± 0.04		3.18 ± 0.22	86.18 ± 0.07

The retention time of 60 min resulted in slightly lower biochar yield when compared to time of 10 min. Also, heating time had an effect on the biochar yield. Longer heating times (120 min) resulted in higher average biochar yield. The content of organic matter decreased with the increase in temperature which was reported in other studies [27].

3.2 Total carbon, total nitrogen, selected elements and pH

The total carbon content of biochars produced at different pyrolysis parameters ranged from 70.53% to 81.96% (Table 5), as higher temperatures result in higher carbonization. Heating time of 65 min led to higher contents of total carbon at the retention time of 60 min (79.43%) as compared to 10 min (75.29%). The heating time of 120 min and the retention time of 60 min resulted in higher carbon contents in biochars (78.99%) than in biochars obtained at the same heating time but at the retention time of 10 min (78.71%).

Table 5. Total carbon, total nitrogen and pH of produced biochars.

Pyrolysis parameters	C_{tot}, %	C_{tot} (average), %	N_{tot}, %	pH
480/65/10	70.53 ± 0.72	75.29	1.25 ± 0.02	9.89 ± 0.03
530/65/10	75.27 ± 0.37		1.22 ± 0.05	10.09 ± 0.03
580/65/10	80.06 ± 1.23		1.21 ± 0.06	9.57 ± 0.03
480/120/10	77.35 ± 0.97	78.71	1.29 ± 0.04	9.90 ± 0.14
530/120/10	79.02 ± 0.61		1.28 ± 0.04	9.91 ± 0.07
580/120/10	79.74 ± 0.89		1.22 ± 0.04	9.53 ± 0.03
480/120/60	77.28 ± 0.54	78.99	1.42 ± 0.06	10.03 ± 0.03
530/120/60	79.53 ± 0.99		1.27 ± 0.03	9.53 ± 0.03
580/120/60	80.18 ± 0.98		1.22 ± 0.06	9.37 ± 0.03
480/65/60	77.63 ± 0.32	79.43	1.27 ± 0.03	10.32 ± 0.07
530/65/60	78.70 ± 0.69		1.24 ± 0.07	9.83 ± 0.07
580/65/60	81.96 ± 0.42		1.17 ± 0.05	9.47 ± 0.07

The content of nitrogen decreased with the increase in temperature due to conversion of nitrogen compounds into gaseous substances. The heating and retention times did not have an effect of the nitrogen content. The content of total carbon and nitrogen depends on the properties of biochar substrates. For example, biochars obtained from sewage sludge and cattle manure showed the carbon content of 20% and 42% (525°C) and nitrogen content of 0.94% and 1.8%, respectively [32]. The pH values of the obtained biochars ranged from 9.37–10.32. The alkaline character was mostly due to the presence of Ca^{2+}, Mg^{2+}, Na, K (Table 6). No significant differences in pH values with the increase in temperature were observed. However, significant differences in pH values were observed in biochars pyrolysed at 300°C (pH 9.5) and at 600°C (pH 11.5) [33]. The analysis of water biochar extracts showed increased concentration of phosphorous with the increased temperatures (Table 6). The phosphorous concentrations were very low which could result from transformation of phosphorous into less water soluble forms during pyrolysis. Similar results were obtained by other researchers [33]. The concentration of Ca and Mg decreased with the increase in temperature. Higher pyrolysis temperatures could result in lower water solubility of these forms.

Table 6. The content of selected elements in water extracts from produced biochars.

Pyrolysis parameters	Ca, g kg^{-1}	Mg, g kg^{-1}	Na, g kg^{-1}	P, g kg^{-1}	K, g kg^{-1}	B, g kg^{-1}	Fe, g kg^{-1}
480/65/10	0.522	0.472	0.015	0.006	0	0.016	0.006
530/65/10	0.243	0.441	0.012	0.004	0	0.021	0.003
580/65/10	0.331	0.189	0.012	0.045	0	0.020	0.003
480/120/10	0.773	0.617	0.012	0.004	0	0.015	0.002
530/120/10	0.298	0.322	0.013	0.004	0	0.019	0.004
580/120/10	0.233	0.150	0.012	0.086	0	0.017	0.002
480/120/60	0.513	0.382	0.013	0.006	0	0.020	0.002
530/120/60	0.355	0.185	0.009	0.026	0	0.019	0.003
580/120/60	0.202	0.143	0.014	0.120	0	0.015	0.001
480/65/60	0.376	0.384	0.014	0.003	0	0.017	0.001
530/65/60	0.301	0.191	0.008	0.018	0	0.016	0.001
580/65/60	0.218	0.118	0.012	0.082	0	0.010	0.003

3.3 Surface area and porosity

The surface area of the obtained biochars was low and ranged from 0.93 to 2.91 m^2 g^{-1} and was not affected by temperature (Table 7). Surface area of biochars depends on the properties of substrates, including mechanical pretreatment of substrates (such as pelletizing). Similar results were reported in other studies [28]. It was observed that biochars with low surface area showed potentials towards application as sorbents for nonferrous metals [28]. Porosity of the obtained biochars ranged from 13.23–15.43%. The results showed that the retention and heating times can affect biochar porosity. The particle size of the investigated biochars ranged from 0.29–1.99 mm. Higher temperature and shorter heating and retention time (up to 105–500°C s^{-1}) resulted in finer particles of biochar (50–2000 μm) [20]. Slower pyrolysis results in coarser particles of biochars [21].

Table 7. Porosity, surface area and density of produced biochars.

Pyrolysis parameters	Open porosity, %	Surface area, $m^2 g^{-1}$	Density, $g cm^{-3}$
480/65/10	13.56	1.32	1.67
480/65/60	13.23	1.22	1.22
480/120/10	14.43	1.64	0.92
480/120/60	15.43	1.76	0.76

4 Conclusions

Pyrolysis parameters, i.e. temperature, heating and retention times determined the biochar yield and properties. Higher temperatures resulted in lower biochar yield whereas longer heating times resulted in higher biochar yield. Higher retention times caused decrease in the biochar yield. With the increase in temperature organic matter, nitrogen, Ca and Mg in biochars decreased whereas the total carbon and phosphorus increased. Produced biochars were of alkaline. Low surface area of the obtained biochars does not limit their application as sorbents (e.g. for nonferrous metals). The produced biochars were the source of calcium, iron, boron, magnesium and phosphorus – these elements are crucial for plant growth. The investigated biochars demonstrated required properties for application in agriculture or protection of the environment.

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