

Pyrolysis of wheat and barley straw

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Abstract: Pyrolysing agricultural crop residues and other biomass constitutes a newer method of transforming often difficult, waste materials into a novel type of soil amendment/additive. Simultaneously, this process also makes it possible to exploit part of the energy released in the agricultural production. Biochar, viewed as the solid product of biomass pyrolysis, is a remarkable, porous material, rich in carbon. Two agricultural crop residues, such as wheat and barley straw, were selected for the experimental studies. The results indicate that the practical temperature for the production of biochar from the two explored materials occurs in the vicinity of 600 °C. Starting at this temperature, the biochar produced complies safely with the principal European Biochar Certificate standards (EBC 2012). Thus, for the wheat straw and barley straw – originated char, the content of the carbon amounts to 67.2 and 67.0 mass %, the atomic ratio H : C is as large as 0.032 and 0.026, and the specific surface area amounts to 217 and 201 m²·g⁻¹, respectively.

Keywords: carbonization; thermolysis; biomass; biochar; crop residue

In general, pyrolysis (also known as thermolysis) is viewed as series of highly endothermic physical and chemical processes occurring when an organic substance (e.g., coal or biomass) is exposed to temperatures of 200–900 °C in an oxygen-starving environment.

During such an operation, the original complex molecules are breaking apart into simpler units. In this way, pyrolysis produces a number of light gases (e.g., H₂, H₂O, CO, CO₂ and hydrocarbons), liquid (tar/oil), and a porous solid residue/char predominantly containing carbon. As is evident, the

products distribution can vary very widely and is affected by a number of factors such as the sort and form of the precursor/feedstock and the operating conditions of the reaction (s).

A char that originated from a biomass and/or intended for use in agriculture is usually termed a biochar. Because of its favourable porous structure and large active surface area, the biochar is increasingly employed as an effective sorbent for air and water pollutants, a catalyst for upgrading syngas and as a means for soil conditioning (Trakal et al. 2014).

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Aside from carbon sequestering, the biochar also shows a strong potential to ameliorate the physical texture of the soil, to facilitate nutrient accessibility and support growth of the needed microbial strains in the soil. Moreover, the biochar is capable of accumulating a considerable amount of moisture within its porous structure. Further application fields such as hydrogen storage or fuel cells are envisaged in the near future.

The outstanding technical and practical features of a biochar are inherently related to its physicochemical characteristic including, e.g., the pore volume, the extent and activity of the surface area, and the pore size distribution. Contemporary experience indicates that the origin/sort of the precursor/feedstock, the temperature of the reaction, the heating rate, and the residence time of the solids are the most important factors affecting the textural properties of the biochar.

The biochar quality is assessed on the basis of its functionality (e.g., in the soil). Its important characteristics are the mass yield on the feedstock, the water holding capacity, its high carbon content, and chemical stability. These qualities are influenced by the type of pyrolysis reactor, the pyrolysis temperature, the residence time, the heating rate of the material, and the type of biomass feedstock (Pohořelý et al. 2017). The biochar yield and the carbon content in the biochar decrease with the increasing pyrolysis temperature. The water retention (related to the nutrition retention) increases with the pyrolysis temperature until a critical point. The decomposition and volatility of the organic matter either naturally present in the feedstock or formed during the pyrolysis process are heavily affected by the pyrolysis temperature. Overall, the biochar quality increases with the residence time in the reactor hot-zone.

There are two main sources of biochar: woody and straw biomass. A woody biomass gives higher biochar yields compared to those of a straw biomass. Such a biochar is more stable, contains more carbon and less nitrogen, and has a higher specific surface area. Nevertheless, the straw biomass is an easily accessible feedstock for pyrolysis and, therefore, is the main interest of this study.

Several studies on wheat and barley straw pyrolysis were made in the past. They focused mainly on the mass yields (Di Blasi et al. 1999; Wang et al. 2011; Burhenne et al. 2013; Crombie et al. 2013; Ronsse et al. 2013; Wang et al. 2013; Yang et al. 2014; Tinwala et al. 2015; Aqsha et al. 2017; Bis-

was et al. 2017; Farooq et al. 2018; He et al. 2018; Jazini et al. 2018), the proximate analysis (Ghaly et al. 1993; Wang et al. 2011; Kloss et al. 2012; Crombie et al. 2013; Ronsse et al. 2013; Wang et al. 2013; Yang et al. 2014; Tinwala et al. 2015; He et al. 2018; Jazini et al. 2018) and the ultimate analysis (Ghaly et al. 1993; Di Blasi et al. 1999; Chun et al. 2004; Kloss et al. 2012; Crombie et al. 2013; Ronsse et al. 2013; Wang et al. 2013; Yang et al. 2014; Aqsha et al. 2017; He et al. 2018; Jazini et al. 2018). Some of the authors also studied the higher and lower heating values of the products of pyrolysis (Ghaly et al. 1993; Di Blasi et al. 1999; Wang et al. 2011; Ronsse et al. 2013; Yang et al. 2014; Tinwala et al. 2015), the surface of the solid product (Chun et al. 2004; Min et al. 2011; Kloss et al. 2012; Ronsse et al. 2013; Wang et al. 2013; Jazini et al. 2018;), and the pore volume (Min et al. 2011; Hartman et al. 2013; Jazini et al. 2018; Hartman et al. 2019). Other qualities were also analysed: e.g., the pH (Kloss et al. 2012; Ronsse et al. 2013; Wang et al. 2013; Jazini et al. 2018), the electrical conductivity (Kloss et al. 2012), and the cation exchange capacity (Kloss et al. 2012; Wang et al. 2013).

However, all of the pyrolysis experiments were conducted under widely different conditions (e.g., diverse types of furnaces and different residence times) which results in inconsistent data. Furthermore, the analytical techniques used to determine the biochar characteristics are varied, too. All these circumstances make a comparison difficult and it is hard to come to unambiguous conclusions. A typical example of such differences can be the values of the specific surface area of the biochar shown in Table 1, which is influenced, for example, by the type of feedstock, pyrolysis temperature, and analytical method.

The results of the elemental analysis and ash content in the biochar given by several researchers are compared in Table 2. As can be seen, the carbon content depends on the pyrolysis temperature and varies between 49.5 and 75 mass %.

The target of this work was to explore the effect of the pyrolysis temperature on the mass and energy balance of the process, the composition of the pyrolysis gas, and the physicochemical properties of the actual biochar. Two common, agricultural materials – wheat and barley straw – are investigated and compared. An effort was made to provide the consistent data needed for the design and operation of larger pyrolysis units.

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Table 1. The specific surface area of the biochars produced at the different temperatures and residence times

Authors	Feedstock	Temperature (°C)	Residence time (h)	Specific surface area BET (m ² ·g ⁻¹)
Wang et al. 2013	WS	500	4	2.48
	WS	500	8	51.50
	WS	500	16	68.50
	WS	700	4	319.00
	WS	700	8	378.00
	WS	700	16	421.00
Chun et al. 2004	WS	300	6	116.00
	WS	400	6	189.00
	WS	500	6	309.00
	WS	600	6	438.00
	WS	700	6	363.00
Jazini et al. 2018	BS	300	1	1.30
	BS	400	1	2.13
	BS	500	1	1.43
Kloss et al. 2012	WS	400	5	4.80
	WS	460	5	2.80
	WS	525	5	14.20
Ronsse et al. 2013	WS	450	1	16.00
	WS	600	1	22.00

WS – wheat straw; BS – barley straw

Table 2. Ultimate analysis and ash content of the biochars produced at the different temperatures and residence times on a dry basis

Authors	Feedstock	Temp (°C)	Res. time (h)	C (mass%)	H (mass%)	N (mass%)	S (mass%)	O (mass%)	Ash (mass%)
Aqsha et al. 2017	WS	500	1	67.87	3.0	3.0	0.6		
	BS	500	1	72.61	3.1	1.7	0.6		
Wang et al. 2011	WS	500	4	49.8		0.5			14.5
	WS	500	8	52.3		0.4			17.4
	WS	500	16	53.6		0.4			22.2
	WS	700	4	52.6		0.3			17.9
	WS	700	8	49.5		0.2			18.6
	WS	700	16	51.3		0.4			28.9
Crombie et al. 2013	WS	350	1	63.2	4.9	1.5		19.6	10.9
	WS	450	1	68.5	4.4	1.1		8.3	17.6
	WS	550	1	69.0	2.9	0.6		7.5	20.0
	WS	650	1	74.7	2.9	1.2		0.0	21.3
Jazini et al. 2018	BS	300	1	56.1	2.2	0.7	0.1	30.0	11.1
	BS	400	1	57.0	2.1	0.9	0.1	28.8	11.3
	BS	500	1	66.5	1.4	0.8	0.1	19.1	12.2
Kloss et al. 2012	WS	400	5	65.7	4.1	1.1			9.7
	WS	460	5	72.4	3.2	1.1			12.0
	WS	525	5	74.4	2.8	1.0			12.7
Yang et al. 2014	BS	450	0,5	74.8	3.5	0.1		8.5	13.1
Di Blassi et al. 1999	WS	577	–	64.3	2.4	0.5	0.3	14.3	
Ronsse et al. 2013	WS	300	1	61.6	4.0				19.1
	WS	450	1	66.6	2.7				22.9
	WS	600	1	68.2	1.6				24.5
	WS	750	1	69.5	0.9				25.8
Ghaly et al. 1993	WS	700	–	54.2	1.4	0.9	0.1	5.0	38.5

WS – wheat straw; BS – barley straw

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MATERIAL AND METHODS

Feedstock. Pelletised wheat and barley straw biomass was used as the feedstock materials. As is shown in Table 3, the wheat and barley straw pellets exhibited similar properties. The presented results correspond to the previous research on the straw pyrolysis, e.g., (Ghaly et al. 1993; Wilén et al. 1996).

Table 3. The proximate analysis, ultimate analysis, and calorific values of the pelletised wheat straw (WS) and barley straw (BS)

	Feedstock	
	WS	BS
Water content	8.40	8.60
Ash	6.00	6.30
Volatiles	62.40	62.10
Fixed Carbon	23.30	23.10
Higher heating value	15.60	15.60
Lower heating value	13.40	13.30
C	42.36	42.44
H	5.27	5.25
N	1.12	1.18
O	36.88	36.30
S _{total}	< 0.1	< 0.1

Experimental setup. Wheat straw (WS) pellets were pyrolyzed in a quartz, fixed-bed reactor at 400, 500, 600, 700, and 800 °C, barley straw (BS) pellets were pyrolyzed only at 500 and 600 °C. The pyrolysis apparatus scheme is displayed in Figure 1; helium was introduced to the bottom of the reactor at a flow rate of 150 cm³·min⁻¹ as a carrier inert gas. The reactor (2) was placed into a hot furnace (1), preheated to the pyrolysis temperature and the experiment ended when the release of the primary pyrolysis products (gas and condensate) ceased which occurred after approximately 90 minutes of exposure. Subsequently, the reactor was removed from the furnace and cooled under an oxygen-free atmosphere. The exhaust of the primary pyrolysis products from the reactor was secured. The primary pyrolysis products (diluted by the carrier gas - helium) flowed through three impingers (3–5), cooled in ice baths to collect all the condensable vapours, then passed through a porous filter (6) and, finally, the permanent gases were collected in Tedlar bags (7).

Thermal analysis. The thermogravimetric analyses were performed in SDT Q600 (TA Instruments,

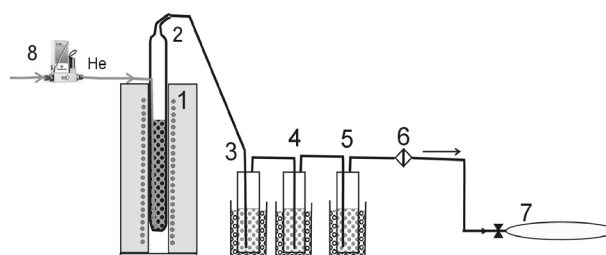


Figure 1. The pyrolysis apparatus schematic

1 – the furnace; 2 – the reactor; 3–5 – the impingers; 6 the porous filter; 7 – the tedlar bags.

USA) horizontal thermo-balance scales for understanding the biochar behaviour and determining the volatile matter, fixed carbon, and ash content. Approximately 4.5 ± 0.5 mg of each sample was heated from room temperature to 105 °C in a high purity N₂ atmosphere with a flow rate of 100 cm³·min⁻¹, followed by an isothermal period for 10 min to determine the moisture content. After this period, the sample was heated to 900 °C at a heating rate of 80 °C·min⁻¹ to determine the volatile matter content (Elder 1983; Saldarriaga et al. 2015; Velázquez-Martí et al. 2018). The atmosphere was then replaced with air at a flow rate of 25 cm³·min⁻¹. The sample was left to burn for 20 min, all the samples were measured under the same conditions.

Analytical methods. The mass of the biochar and the condensable products were obtained by measuring the weights of the apparatus components before and after the experiments. The water content (W) was determined by the standard ČSN EN 15414- 3:2011. The sample mass used for the analysis was as large as 10 g to secure better reproducibility. The ash content (A) was established according to the standard ČSN EN 15403:2011 at the temperature of 550 °C. The volatile content was measured on the basis of the standard ČSN EN 15148:2010–2016 at 900 °C. The higher heating value (HHV) was determined according to the standard ČSN EN 15400:2011 by means of an IKA C 2000 calorimeter and the lower heating value (LHV) was calculated according to the same standard. A Flash EA 1112 (Thermo Fisher Scientific, USA) elemental analyser in the CHNS-O configuration was used for the determination of the carbon, nitrogen, hydrogen, and sulphur content. The oxygen content was calculated by the difference with regard to the ash and chlorine content. The gaseous products from the Tedlar bags were analysed on a GC HP6890 (Hewlett-Packard, USA)

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instrument with two independent channels for the permanent gas analysis (TCD) and the hydrocarbon analysis (FID). A gas chromatograph (Agilent 7890 A, USA) combined with a sulphur chemiluminescence detector (Agilent 355, USA), (GC-SCD) was used for the determination of the sulphurous compounds. The specific surface area, S_{BET} , was evaluated from the nitrogen adsorption isotherm in the range of the relative pressure corresponding to $p/p_0 = 0.05\text{--}0.25$ using the standard BrunauerEmmettTeller (BET) procedure. On digesting the sample by means of an HNO_3/HCl mixture for 1 hour at $200\text{ }^\circ\text{C}$ in a high pressure, microwave oven (CEM Mars 5, USA), the digestant was analysed for heavy metals by the method of atomic emission spectroscopy in compliance with ČSN EN ISO 11885:1999–2009. The pH values were measured in the aqueous solutions prepared according to the Czech/European standard ČSN EN 12457-2:2003. The polyaromatic hydrocarbons were determined according to ČSN P CEN/TS 16181:2014–2018.

RESULTS AND DISCUSSION

Thermal analysis. The following two figures, Figures 2 and 3, present the measured curves from the fast Thermogravimetric analysis (TGA) measurements of the solid pyrolysis residues produced at $400\text{--}800\text{ }^\circ\text{C}$ and an exposure of 90 minutes. The initial loss of the mass represents the moisture content of the measured samples. The further weight loss during the heating period corresponds to the release of the volatile matter. The inert gas was then replaced with air, which caused the combustion of the fixed carbon and allowed the quantification of the unburned matter.

The water content of the samples ranged from 4.0% for WS600 to 5.0% for WS500 and BS500, which are usual values for the conditions in the laboratory where the samples were stored. All the samples have a considerable volatile matter content, which is typical of a biochar. It ranges from 11.0% for WS800 to 27.7% for WS400. The volatile matter contents are consistent with the preparation of the samples. The samples exposed to higher temperatures during the preparation have a volatile matter content lower than those exposed to the lower temperatures. The fixed carbon contents were from 58.8% for WS400 to 69.0% for WS700; the ash content ranged from 13.5% for WS400 to 20.7% for BS600.

Mass and energy balance. The results of the mass and energy balance based on weighing are shown in

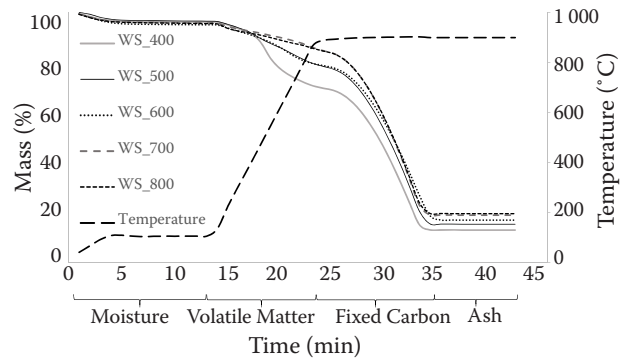


Figure 2. The TGA curves of the WS biochar samples produced at $400\text{--}800\text{ }^\circ\text{C}$ and an exposure time of 90 min

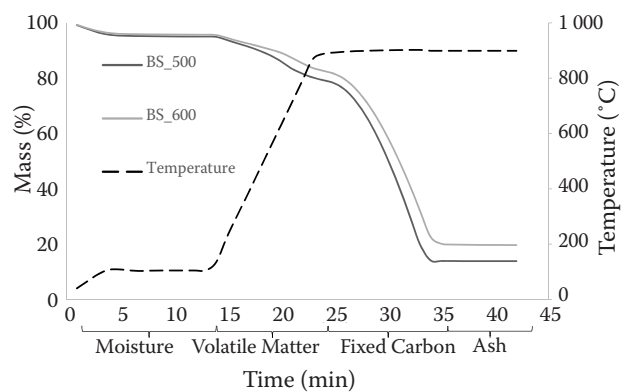


Figure 3. The TGA curves of the BS biochar samples produced at 500 and $600\text{ }^\circ\text{C}$ and an exposure time of 90 min

Table 4. The values are presented for the solid char, the producer gas, and the liquid (consisting of an organic and an aqueous phase) products. The mass of the gaseous products was calculated from its measured volume and the determined composition.

The biochar yield decreases with an increasing temperature from 32.9% at $400\text{ }^\circ\text{C}$ to 24.3% at $800\text{ }^\circ\text{C}$ for the wheat straw biomass, mainly in favour of the gas production. Moreover, the gas composition also changed significantly with the temperature. Such a trend corresponds to the literature findings (Wang et al. 2011; Ronsse et al. 2013; Wang et al. 2013; Aqsha et al. 2017; Biswas et al. 2017; Jazini et al. 2018). The liquid yield rises slightly with the temperature. The pyrolysis of the barley straw shows very similar results. The liquid yield is slightly higher (by approx. 2–2.5%) at the same temperatures at the expense of the lower biochar yield. The amount of gas and its composition were similar for the two feedstocks. The total sum of all the pyrolysis products ranges between 97.3 and 99.4%. Considering the experiment scale, it appears to be in very good agreement.

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Table 4. The mass and energy balance of the pyrolysis products

Feedstock	WS	WS	WS	WS	WS	BS	BS
Temperature (°C)	400	500	600	700	800	500	600
Mass of sample (g)	60.5	50.8	60.0	57.0	54.2	57.3	54.0
Yield (mass %)							
Char	32.9	29.9	28.9	25.4	24.3	27.9	25.8
Liquid	49.9	49.0	49.1	51.3	52.0	52.6	52.5
Gas (measured)	15.6	18.4	19.7	22.1	22.4	19.0	19.9
Sum	98.3	97.3	97.8	98.9	98.6	99.4	98.2
The thermochemical characteristics of the pyrolysis products							
Gas production (m ³ ·t ⁻¹)	91.8	115.9	133.0	171.2	177.8	120.6	137.4
Gas HHV (MJ·m ⁻³)	7.6	10.0	10.9	12.5	12.7	11.0	11.7
Char HHV (MJ·kg ⁻¹)	25.4	25.1	24.6	25.5	25.6	25.5	25.9
Liquid HHV (MJ·kg ⁻¹)	12.8	12.5	11.8	11.8	12.6	12.8	11.3
Energy yield (kJ)							
Char	8 354	7 497	7 118	6 492	6 208	7 110	6 683
Liquid	6 374	6 108	5 809	6 033	6 525	6 716	5 935.0
Gas	6 95	1 156	1 454	2 136	2 248	1 321	1 614.0
Sum	15 424	14 762	14 381	14 660	14 981	15 147	14 231.0
Energy yield (%)							
Char	53.5	48.0	45.6	41.5	39.7	45.7	43.0
Liquid	40.8	39.1	37.2	38.6	41.8	43.2	38.2
Gas	4.5	7.4	9.3	13.7	14.4	8.5	10.4
Sum	98.7	94.5	92.0	93.8	95.9	97.4	91.5

WS – wheat straw; BS – barley straw; HHV – higher heating value

The calorific values are given because the energy balance is needed for the technological design of the pyrolysis plants. The energy yield of the gaseous products was calculated from the measured gas volumes and their composition. The energy yield of the char and the liquid products was calculated from the higher heating value and their mass yield.

The energy yield in the solid pyrolysis product from the wheat straw pellets decreases with an increasing temperature from 53.4% at 400 °C to 39.7% at 800 °C. On the contrary, the energy content in the gas increases with the temperature from 4.5% to 14.4% at 800 °C. A significant amount of chemical energy is bound to the liquid products. A great variation in the values was observed due to the different analytic methods and certain characteristics of the liquid. The overall sum of the chemical energy bound to the pyrolysis products ranges between 91 and 98 % of the energy contained in the original material.

Pyrolysis gas composition. The average gas composition and gas production per tonne of pellets at

different temperatures is shown in Table 5. In general, the gas production increased with the pyrolysis temperature. Aerosols formed at higher temperatures that got into the Tedlar bags, despite of the efficient cooling device, where they settled on the bags' surface. This phenomenon can explain why the sum of the pyrolysis product in Table 4 is under 100%. To minimise it, frits were used during the experiments at higher temperatures.

Sulphur balance in the gaseous phase.

As can be seen in Table 6, the largest portion of sulphur present in the gaseous phase occurs in the form H₂S and CH₃SH. It is important to determine the contents of the main sulphur compounds for the design of the pyrolysis plant due to the sulphurous emissions and the possible corrosion of the pyrolysis device. The results indicate that the sulphur compounds are already released at 400 °C, even though the amount of other gaseous products is minimal. The total sulphur content in the raw feedstock is very low, which results in only small amounts of sulphur compounds in the gaseous products.

Table 5. The average contents of the gaseous products

Feedstock	WS	WS	WS	WS	WS	BS	BS
Temperature (°C)	400	500	600	700	800	500	600
Mass of sample (g)	60.5	50.79	59.98	56.98	54.15	57.34	54.03
Gas production (m ³ ·t ⁻¹)	91.83	115.86	133.02	171.19	177.78	120.58	137.42
The contents of the gaseous product (%)							
CO ₂	61.26	55.7	50.59	41.01	39.46	53.92	48.17
H ₂	0.182	3.97	9.36	18.91	20.98	3.83	10.35
CO	33.05	29.02	27.6	25.94	25.53	29.14	27.31
CH ₄	2.73	7.62	8.59	10.42	10.28	8.68	10.13
N ₂	0.0005	0.039	0.098	0.079	0.066	0.068	0.047
Ethane	0.811	1.385	1.413	1.356	1.312	1.675	1.511
Ethylene	0.4	0.56	0.576	0.61	0.659	0.685	0.621
Ethyne	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001
Propane	0.235	0.315	0.322	0.292	0.281	0.382	0.336
Propene	0.311	0.381	0.397	0.404	0.419	0.48	0.425
Butanes	0.067	0.077	0.079	0.068	0.064	0.094	0.081
Pentanes	0.012	0.016	0.017	0.014	0.013	0.02	0.017
Hexanes	–	–	–	0.001	0.001	–	0.0004
Butene isomers	0.309	0.25	0.275	0.247	0.243	0.358	0.303
1,3-butadiene	0.021	0.02	0.024	0.038	0.05	0.025	0.029
Propyne	0.024	0.022	0.022	0.022	0.022	0.028	0.024
But-1-en-3-yne	0.013	0.013	0.014	0.011	0.011	0.017	0.014
1,3-Cyclopentadiene	0.001	0.053	0.001	0.001	0.001	0.001	0.001
Benzene	0.009	0.092	0.029	0.091	0.077	0.111	0.105
Toluene	0.008	0.026	0.05	0.045	0.048	0.032	0.057
Sulphur compounds	0.133	0.131	0.149	0.114	0.119	0.107	0.145
Other	0.423	0.311	0.395	0.342	0.355	0.337	0.316
HHV (MJ·m ⁻³) *	7.57	9.98	10.93	12.48	12.65	10.95	11.74
LHV (MJ·m ⁻³) *	7.27	9.32	10.19	11.5	11.64	10.28	10.92

*Calorific values – calculated at the reference temperature of 15 °C; WS – wheat straw; BS – barley straw; HHV – higher heating value; LHV – lower heating value

Biochar composition. The basic biochar properties are shown in Table 7. As can be seen, the bulk density of the pellets decreases considerably because of the pyrolysis. The diameters of the biomass particles before entering the process were 10.6–10.8 mm for the WS pellets and 10.2 to 10.4 mm for the BS pellets. The product diameters ranged between 7.8 and 9.2 mm after the pyrolysis and no temperature dependence was found. The measurements were repeated 30 times for each sample. It is of interest to note that the mass loss caused by the pyrolysis is practically the same for the both feedstocks and amounts to approx. 57%.

The ash content increased with the temperature from 6.5 mass %, in the original sample, to

23.6 mass % at 800 °C simultaneously with the carbon content, which led to an increase in HHV^{daf}. Such an increasing tendency of the ash and carbon content can be also approximately seen in the literature shown in Table 2. The higher heating value of the WS biochar was the same for all the temperatures, fluctuating from 25.5 to 26.0 MJ·kg⁻¹. Similar results were obtained with the BS biochar; the values from the literature also exhibit such a trend. As is known, the declaration of the bulk density, ash and volatile matter content is a prerequisite to obtain a European Biochar Certificate.

The specific surface area increased rapidly with the increasing temperature from 3 m²·g⁻¹ at 400 °C to 351 m²·g⁻¹ at 800°C. The EBC standard states

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Table 6. The content of the sulphur compounds in the gaseous products for the different temperatures

Feedstock	WS	WS	WS	WS	WS	BS	BS
Temperature (°C)	400	500	600	700	800	500	600
Gas production (m ³ ·t ⁻¹)	91.83	115.86	133.02	171.19	177.78	120.58	137.42
The content of the gaseous products (mg·m⁻³)							
H ₂ S	297.9	601.9	1311.7	593.6	787.1	270.7	1207.6
COS	80.2	85.1	57.9	43.5	39.8	50.5	42.8
CH ₃ SH	961.9	1,063.8	1,144.7	497.4	496.0	735.7	812.2
CS ₂	4.7	2.3	3.1	1.0	0.9	4.2	1.0
Other	404.8	139.6	144.5	78.4	80.1	240.1	95.4
Total	1 749.0	1 893.0	2 662.0	1 214.0	14 04.0	1 301.0	2 159.0
Yield (g·t⁻¹)							
H ₂ S	27.4	69.7	174.5	101.6	139.9	32.6	165.9
COS	7.4	9.9	7.7	7.4	7.1	6.1	5.9
CH ₃ SH	88.3	123.3	152.3	85.1	88.2	88.7	111.6
CS ₂	0.4	0.3	0.4	0.2	0.2	0.5	0.1
Other	37.2	16.2	19.2	13.4	14.2	29.0	13.1
Total	161.0	219.0	354.0	208.0	250.0	157.0	297.0

WS – wheat straw; BS – barley straw

that the biochar should have the surface area larger than 150 m²·g⁻¹. The carbon content is higher than 50 mass % for both the feedstocks, which safely meets the requirements of the EBC standard. The high stability of the biochar is indicated by a low H : C atomic ratio which amounts to approx. 0.03; the maximum allowed by the EBC standards is as large as 0.7. This suggests that the probability of the biochar to persist in the soil for decades (or possibly a century) is very high. The literature shows similar results, with the maximum H : C ratio of approx. 0.07 for the lower temperatures around 350 °C. The pH values of the aqueous leachate do not seem to be affected by the temperatures of 400–800 °C, which is in agreement with the literature (Kloss et al. 2012). However, the pH values reported in (Ronsse et al. 2013; Wang et al. 2013; Jazini et al. 2018) increase with the temperature of the pyrolysis.

Due to the characteristic features of the pyrolysis procedure (operated at a medium to high temperature), the polyaromatic hydrocarbons (PAH) values are low, mostly less than 0.5 mg·kg⁻¹. The EBC standard limits for PAHs are 4 and 12 mg·kg⁻¹, and the ÚKZÚZ limit is as large as 20 mg·kg⁻¹. The content of the polyaromatic hydrocarbons is generally very low and safely meets the requirements given by both the EBC and the ÚKZÚZ standards according to Regulation 474/2000 of the Czech Ministry of Agriculture.

CONCLUSIONS

This study was aimed at exploring the effect of the pyrolysis temperature on the mass and energy balance, the composition of the pyrolysis gas, and the pertinent properties of the biochar produced in a fixed bed reactor. The results indicate that the practical temperature for the materials explored (pelletised WS and BS) is a temperature of 600 °C. The quality of the char produced at such a temperature complies very well with the main European Biochar Certificate (EBC) standards, i.e., the carbon content is larger than 50 mass %, the atomic ratio H : C ≤ 0.7 (WS – 0.032 and BS – 0.026), and the specific surface area is greater than 150 m²·g⁻¹ (WS – 217 and BS – 201 m²·g⁻¹). The pH measured in the aqueous suspensions amounted to an approximate value of 10 and was practically independent of the pyrolysis temperature in the range 400–800 °C. As to the heavy metals and the PAH, the produced biochars comply with both the EBC and the national standards. In accordance with the Central Institute for Supervising and Testing in Agriculture (ÚKZÚZ), the biochar is classified as a supporting soil material. The content of the PAH in all the biochars was less than 0.5 mg·kg⁻¹ and the content of the heavy metals was deeply below the limits.

Table 7. The selected characteristics of the biochar for the different pyrolysis temperatures and EBC and ÚKZÚZ standards

Feedstock	WS	WS	WS	WS	WS	WS	WS	BS	BS	BS	EBC standard	ÚKZÚZ
Pyrolysis temperature (°C)	–	400.0	500	600	700	800	–	500	600	–	Basic	–
Bulk density (kg·m ⁻³)	470.0	206.0	203.0	204.0	202.0	203.0	510.0	248.0	222.0	–	premium	–
Ash content (%)	6.5	18.0	20.5	20.4	23.1	23.6	6.8	20.5	22.7	–	declaration	–
Volatiles (%)	68.1	24.6	14.7	13.5	7.7	7.1	67.9	15.2	10.6	–	–	–
Specific surface area (m ² ·g ⁻¹)	–	3.0	60.0	217.0	280.0	351.0	–	55.0	201.0	–	preferably < 150	–
HHV (MJ·kg ⁻¹)	17.1	25.4	25.1	25.9	25.5	25.6	17.0	25.5	25.9	–	–	–
HHV ^{daf} (MJ·kg ⁻¹)	18.2	31.0	31.5	32.5	33.2	33.5	18.3	32.1	33.4	–	–	–
Carbon content (%)	46.2	63.0	65.4	67.2	70.1	69.5	46.4	64.7	67.0	–	≥ 50%	–
Hydrogen content (%)	5.8	3.4	2.3	2.2	1.1	0.8	5.7	2.3	1.8	–	–	–
Nitrogen content (%)	1.2	0.8	0.7	0.6	0.5	0.4	1.3	0.6	0.5	–	–	–
Sulphur content (%)	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	–	–	–
H : C ratio	0.13	0.05	0.04	0.03	0.02	0.01	0.12	0.04	0.03	–	< 0.7	–
pH	–	10.1	10.2	10.2	10.4	10.1	–	10.5	10.4	–	declaration	–
As (mg·kg ⁻¹)	–	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	–	< LOQ	< LOQ	–	–	20
Ca (g·kg ⁻¹)	–	13	16	16	17	17	–	15	16	–	declaration	–
Cd (mg·kg ⁻¹)	–	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	–	< LOQ	< LOQ	–	1.5	1
Cr (mg·kg ⁻¹)	–	2	2	2	2	6	–	2	2	–	90	80
Cu (mg·kg ⁻¹)	–	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	–	< LOQ	< LOQ	–	100	100
Hg (mg·kg ⁻¹)	–	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	–	< 0.1	< 0.1	–	1	1
K (g·kg ⁻¹)	–	23.0	31.0	31	36	37	–	27	30	–	declaration	–
Mg (g·kg ⁻¹)	–	2.9	3.6	3.5	3.6	3.5	–	3.4	3.7	–	declaration	–
Ni (mg·kg ⁻¹)	–	1.1	1.6	0.8	0.9	1.0	–	1.1	1.2	–	50	30
P (g·kg ⁻¹)	–	1.7	2.4	2.1	2.2	2.4	–	2.1	2.1	–	declaration	–
Pb (mg·kg ⁻¹)	–	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	–	< LOQ	< LOQ	–	150	120
Zn (mg·kg ⁻¹)	–	12.0	< LOQ	< LOQ	< LOQ	< LOQ	–	< LOQ	< LOQ	–	400	400
PAH (mg·kg ⁻¹)	–	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	–	< 0.5	< 0.5	–	12	4

LOQ – the limit of quantification; WS – wheat straw; BS – barley straw; EBC – European Biochar Certificate; ÚKZÚZ – Central Institute for Supervising and Testing in Agriculture; HHV – higher heating value; ^{daf} – dry ash free

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