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Thermochemical valorisation of waste: Pyrolytic conversion of horse manure

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ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Pyrolysis Biochar Horse manure Waste disposal	The efficient and sustainable disposal of waste represents one of the major challenges for the human beings in the next future. The thermochemical conversion of livestock manure to biochar has received much interest thanks to its greenhouse gases extenuation and amendment power. In this study, horse manure was processed under pyrolytic condition at different temperatures, heating rate and residence times. In the first phase, a set of preliminary analysis aimed to assess the physical and chemical properties of the horse manure were carried out. Analogously, after the pyrolysis, the biochar was analysed both from the chemical and physical point of view. The results showed that the major impact on biochar yield (average -32%), pH (average $+ 40\%$), SSA (average $27.8 \text{ m}^2/\text{g}$), PAH content, C (average $+ 37.4\%$) H (average -53.1%) N (average -15.5%) S (average -65.9%) O (average -37%) content was due to the HHT (highest heating temperature). Residence time (RT) and heating rate (HR) do not display a noticeable trend for most of the parameters. This analysis permitted to assess a range of pyrolysis parameters to treat this kind of biomass: 600°C (HHT), 10°C/min (HR) and 2h (RT) , in order to comply with EBC (European Biochar Certification) standard.

1. Introduction

Animal manure, due to its richness in nutrients such as phosphorous, nitrogen and potassium was used generally as organic fertilizer in agriculture. This kind of fertilizer, however, produces also some serious drawbacks: manure leakage from the storage and disposal could have a negative impact on soil and water quality causing environmental concerns (EPA, 2017). Its degradation, when stored or managed in lagoons or holding tanks, produces large quantities of GHG. Besides, not composted horse litter was proven to cause N immobilization in soil, arming the growth of crops. Further, the use of horse manure, focus of this essay, as a fertilizer, poses also the problem of weed seeds that remain vigorous even after composting. It was estimated that 700,000-800,000 m³ of such material is produced annually in Finland according to (Nikama, 2014) and the majority of it is incinerated as waste, even though such mixtures are actually rich in nutrients like phosphorus and potassium. Its incineration has severe problems as this emits lots of CO₂. In addition, it is subject to a strict regulation: Directive 2000/76/EC on the Incineration of Waste. The parameters of operation, emission and monitoring are severe and make this solution uneconomic. Anaerobic digestion is a valuable option to valorise agriculture waste and manure. Producing biogas for internal combustion engines to generate electricity, or directly using it for cooking or heating, we have the possibility to cut the use of fossil fuels. Per contra, some type of relatively dry manure, like horse manure, poses the question on the possibility to use it in alternative process, converting it to more valuable by-products. The scope of this study is to prove that the thermochemical conversion of horse manure through slow pyrolysis could represent a valuable and environomical alternative to the mere incineration. Entailing an enormous cut of GHG emissions and producing an innovative, even though exploited in ancient times, soil amendment. Moreover, the optimal thermodynamic parameters (HHT, HR and RT) were studied according to the physical and chemical characterisation of the biochar.

2. Material and methods

2.1. Manure characterisation

2.1.1. Horse manure characterisation

The "as received" moisture content of manure was 68%. It can be

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Fig. 1. Experimental setup scheme (A), furnace operating scheme (C), closed furnace picture (B) and open furnace picture (D).

assumed that, in industrial scale, the material will undergo a drying process before being pyrolyzed. Horse manure was left for 7 d at ambient temperature and forced ventilation. The original biomasses were grinded (2–5 mm). This process helped the homogenization.

2.1.2. Proximate analysis

Proximate analysis was carried out following the reference ASTM standard. Precisely ASTM E1756-08 was followed for moisture content (MC) (ASTM, Standard Test Method for Determination of Total Solids in Biomass, 2006). Ash content, instead, was assessed following ASTM E1755-01 (ASTM, Standard Test Method for Ash in Biomass, 2015). Volatile matter content (VM) was evaluated as indicated in ASTM E872-82 (ASTM, Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels, 2013). Lastly, fixed carbon content (FC) was obtained as the difference between 100 and the sum of the other contents.

2.1.3. Extractives

Following the standard SCAN-CM 49:03 (Scandinavian Pulp Paper and Board Testing Committee, 2003) the acetone extractives of the manure performed. The samples, of about 7 g, faced an extraction with 250 mL of acetone for 6 h.

Concerning the carbohydrates measurement, the dry matter of the extracted manure was transferred into a test tube, mixed with 3 mL of 72% H₂SO₄ and then incubated in a water bath (30 °C \pm 3 °C) for 60 min, carefully mixing every 5 min. Deionized water was added into the test tube and from that, all the content was transferred in a Duran bottle. From this point the Duran bottle was transferred in autoclave (Systec DE-23, Germany) and hydrolysed at 121 °C for 2 h. Thereafter, once cooled down at room temperature, the sample was diluted and filtered through a 0.2 µm filter to an auto sampler vial. Through the HPAEC

analysis, the sugar composition of the hydrolysates solution was stated. The concentration of sugars was calculated comparing the corresponding monomeric sugars. Through the UV–vis spectrophotometer (Shimadzu), dissolved acid-soluble lignin content was obtained. The measure was performed at 240 nm wavelength. Deionized water was used as blank. The aliquot was diluted to make the absorbance lie in the range of 0.7–1.0. For calculating the Insoluble Klason lignin, the solid residue of the hydrolysis was dried overnight at 105 $^{\circ}$ C until a constant weigh was achieved and then cooled down in a desiccator. Finally the residue was weighed.

2.1.4. TGA

Thermo-gravimetric analysis (TGA) was carried out for both original biomass and obtained biochar samples. For this analysis a TA instrument named TGA Q500 (USA) was adopted. The used testing method pathway was: heating the sample in inert environment (guaranteed by a 60 NmL/ min flow of nitrogen) from 20 °C up to 900 °C with HRs of 5–10 °C/min and a final 5 min-long isothermal combustion at 900 °C with pure oxygen.

2.1.5. CHNSO analysis

Carbon, hydrogen, nitrogen, Sulphur and oxygen contents of biochar were determined by means of a Perkin Elmer CHNS/O 2400 series II analyser (dry combustion method). In particular C, H, N and S contents were directly measured by the device, while O is calculated as the difference between 100 and the sum of the other contents and ash, following EBC guideline (Schmidt et al., 2021). This is due to the assumption that the sample is essentially consisted by these elements.

2.1.6. pH

The pH level for all samples, both original biomass and produced

Table 1

Proximate analysis and composition data of manure.

Sample	Proximate Analysis		Composition				
	VM	ASH	FC	MC	VM	ASH	FC
Manure	[% _{db}] 77.2	[% _{db}] 7.4	[% _{db}] 15.4	[%] 7.1	[%] 72.1	[%] 6.9	[%] 13.9

thimble and extracted (reflux method) with 50 mL of analytical grade toluene for 2 h. Finally, the extract was concentrated to 10 mL under gentle nitrogen evaporation. PAHs in the extract were analysed by gas chromatograph – mass spectrometer (Agilent GC 7890A and 5975C Inert MSD). Internal standard was applied in quantification of PAH concentrations. The column was an HP 5MS (30 m \times 0.25 mm x 0.25 µm). Temperature program was as follows: 90 °C (0.5 min), 20 °C/min to 250 °C; 5 °C/min to 275 °C; 20 °C/min to 320 °C (5 min). The following



Fig. 2. Horse manure TGA - 5 °C/min - 10 °C/min.

Table 9

 Table 2

 Chemical composition and carbohydrates composition of horse manure.

Content in %, based on dry amount of material	
Carbohydrates	49.42
- Arabinose	1.88
- Rhamnose	0.00
- Galactose	0.75
- Glucose	28.85
- Xylose	17.47
- Mannose	0.46
Extractives	2.98
Ash	7.06
Lignin	28.81
- Acid insoluble	27.19
- Acid soluble	1.62
Total	88.27
Unidentified	11.73

biochar, was determined following the same procedure, suggested by EBC analytical methods (Schmidt et al., 2021). So, a 25 mL volume of 0.01 M CaCl2 solution was prepared and added to a 5 mL volume of sample in a glass vessel. In order to obtain a homogeneous suspension, the solution was stirred for 1 h. After this treatment, the pH level was measured by means of the Orion 2 Star (Thermofisher scientific, USA) pH-meter.

2.1.7. PAH (polycyclic aromatic hydrocarbons)

The sample (ca. 0.5 g of dry weight) was weighed into an extraction

temperatures were applied: transfer line 280 °C; MSD 150 °C; injector 250 °C. Injection volume was 1.0 μL , and carrier gas (helium) flow 1.5 mL/min.

2.1.8. Specific surface area

Specific surface area, pore volume and pore size of all the produced biochar were determined by means of Bruner-Emmett-Teller analysis (using Tristar II-Micrometrics, USA device).

able 5				
Biochar vi	eld according to	o HHT, Heating	g rate and reside	nce time.

N°	HHT [°C]	Residence Time [h]	Heating rate [°C/min]	Yield [%]
1	350	2	10	40.7
2	350	4	10	36.6
3	350	8	10	36.3
4	450	2	10	31.3
5	450	4	10	29.7
6	450	8	10	29.8
7	550	2	10	28.4
8	550	4	10	28.6
9	550	8	10	27.7
10	350	2	5	38.8
11	350	4	5	37.0
12	350	8	5	35.4
13	450	2	5	30.8
14	450	4	5	30.2
15	450	8	5	29.1
16	550	2	5	28.9
17	550	4	5	28.8
18	550	8	5	28.5



Fig. 3. Biochar pH according to HHT, Heating rate and residence time. Grey dot = 5 °C/min, blue dot = 10 °C/min. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4	
PAH concentrations	(ng/g).

All the adsorption isotherm measurements were carried out at liquid-N temperature (77 K) by increasing nitrogen relative pressure from 0 to 0.99 bar? Tested material were dried for 30 min at 105 °C under constant nitrogen flow. Test sample mass (M_s [g]) was calculated as:

 $M_s = \frac{10}{SSA_{exp}}$ where SSA_{exp} is the expected specific surface value, expressed in m²/g. All the obtained data were processed by means of the BET equation in order to determine pores total volume and SSA:

 $\frac{1}{[VA(\frac{PD}{P}-1)]}=\frac{C-1}{VMC}*\frac{P}{P0}+\frac{1}{VMC}$ (Brunauer et al., 1938) where,

P is partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), [Pa].P0 is saturated pressure of adsorbate gas [Pa]. VA is volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 \times 105 Pa)], [mL]. VM is volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, [mL]. C is dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

PAH compound	T 350 °C 5 °C/min	T 350 °C 10 °C/min	T 450 °C 5 °C/min	T 450 °C 10 °C/min	T 550 °C 5 °C/min	T 550 °C 10 °C/min
	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]	[ng/g]
Naphthalene (1)	13,087	9962	11,369	14,417	12,061	11,828
Asenaphtylene (1)	<lod< td=""><td><lod< td=""><td>33</td><td>53</td><td>45</td><td>42</td></lod<></td></lod<>	<lod< td=""><td>33</td><td>53</td><td>45</td><td>42</td></lod<>	33	53	45	42
Asenaphtene (1)	84	108	45	86	143	44
fluorene (1)	<lod< td=""><td>62</td><td>55</td><td>65</td><td>61</td><td><lod< td=""></lod<></td></lod<>	62	55	65	61	<lod< td=""></lod<>
Phenanthrene (1)	161	202	209	166	78	105
Anthracene (1)	102	107	31	141	34	43
Fluoranthene (1)	47	207	66	50	29	36
pyrene (1)	25	153	99	44	18	34
benzo(a)anthracene (1)	105	446	178	183	176	126
Chrysene (1)	92	431	118	300	82	56
benzo(b)fluoranthene (2)	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
benzo(k)fluoranthene (2)	<lod< td=""><td>667</td><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	667	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
benzo(a)pyrene (2)	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
benzo(ghi)perylene (2)	<lod< td=""><td>1165</td><td><lod< td=""><td>719</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	1165	<lod< td=""><td>719</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	719	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
dibenzo(ah)anthracene	<lod< td=""><td><lod< td=""><td><lod< td=""><td>275</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>275</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>275</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	275	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
(2)						
indeno(1,2,3-cd)pyrene (2)	1336	1001	<lod< td=""><td>645</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	645	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Sum Σ	15,040	14,511	12,203	17,144	12,726	12,313

(1)The LODs (S/N = 3) are in the range of 10–50 ng/g.

(2)The LODs (S/N = 3) are in the range of 50–100 ng/g.

Table 5
BET analysis values.

Sample	HHT [°C]	Residence time [h]	Heating rate [°C/min]	SSA [m ² /g]	Pore volume [cm ³ /g]	Pore size [nm]
1	350	2	10	5.360	0.009	6.620
2	350	4	10	3.600	0.009	10.073
3	350	8	10	4.090	0.009	8.890
4	450	2	10	6.770	0.014	8.200
5	450	4	10	9.830	0.017	6.910
6	450	8	10	8.729	0.016	7.389
7	550	2	10	63.229	0.058	3.681
8	550	4	10	55.534	0.039	3.590
9	550	8	10	57.950	0.050	3.519
10	350	2	5	6.167	0.011	7.667
11	350	4	5	6.210	0.011	7.133
12	350	8	5	6.740	0.013	7.970
13	450	2	5	4.415	0.008	7.763
14	450	4	5	4.206	0.009	8.796
15	450	8	5	7.037	0.013	7.749
16	550	2	5	62.987	0.034	2.738
17	550	4	5	52.955	0.032	2.869
18	550	8	5	61.376	0.044	2.890

Table 6

CHNSO content of biochar and horse manure.

Sample	Carbon [%]	Hydrogen [%]	Nitrogen [%]	Sulphur [%]	Oxygen [%]	O/C	H/C
BC - 350 - 5 °C/min	61.52	3.89	2.02	0.33	25.85	0.42	0.06
BC - 450 - 5 °C/min	65.69	2.92	1.88	0.28	22.85	0.35	0.04
BC - 550 - 5 °C/min	67.57	2.21	1.76	0.29	21.77	0.32	0.03
BC - 350 - 10 °C/min	61.36	4.24	2.15	0.34	24.02	0.39	0.07
BC - 450 - 10 °C/min	64.24	3.05	1.95	0.31	22.57	0.35	0.05
BC - 550 - 10 °C/min	66.26	2.25	1.84	0.22	21.53	0.32	0.03
Horse manure	47.30	6.14	1.68	0.82	36.16	0.76	0.13

2.2. Biochar production

2.2.1. Pyrolysis setup

Pyrolysis of all the samples was carried out in a quartz tube furnace (NBD-O1200, Nobody Material Science and Technology CO., LTD, China). Experimental setup scheme and photos are shown in Fig. 1. Anaerobic conditions were obtained by means of a 10 mL/min nitrogen flow, controlled by a flowmeter, and almost 2 g of sample per crucible were processed Synthesis gasses produced during pyrolysis were condensed by means of a cooling system and all the treatments took place in a laminar flow suction hood with maximum aspiration level. The operating scheme of the furnace, at 600 °C - 10 °C/min - 2h of residence time taken as example, is shown in Fig. 1C.

3. Results and discussion

3.1. Horse manure composition

3.1.1. Proximate analysis

Proximate analysis results of original biomass are shown in Table 1.

3.1.2. Extractives

The next Table 2 summarizes the overall chemical composition and carbohydrates composition of horse manure.

3.1.3. TGA analysis

As reported in their analysis, (Hernandez-Mena, 2014) and (Katesa and Tangsathitkulchai, 2013), cellulose, hemicellulose and lignin behave in a completely different way under thermal decomposition. According to (Hernandez-Mena, 2014), the degradation temperature of cellulose and hemicellulose are 200–360 °C, for lignin 360–600 °C (Katesa and Tangsathitkulchai, 2013); reported a range of 250–350 °C for cellulose and hemicellulose and 350–750 °C for lignin.

In Fig. 2 the degradation curve and its derivative are shown according to the TGA analysis.

The first mass loss (between 50 and 150 °C) is imputable to the residual moisture content and to the evaporation of some extractive compounds. The second mass loss takes place from about 200 to 350 °C; here the hemicellulose and cellulose are degraded. Where the maximum of DTG curve represents the cellulose complete degradation. Lignin degradation requires a longer and higher temperature range, how it can be seen from the graph, it lasts until 550 °C, this is in accordance with the literature (Sjöström, 1993) (Hernandez-Mena, 2014) where similar range of degradation temperature where obtained. Moreover, it can be noticed that increasing the rump rate from 5 °C/min to 10 °C/min, for equal temperature, the biochar yield increases. This is clearer around 350 °C.

These results are consistent with the cellulose, hemicellulose and lignin content of horse manure found in the extractives analysis. At 350 °C, both cellulose and hemicellulose are degraded; in fact, TGA report presents a mass loss of about 55% around that temperature (not considering the remaining moisture content), that is coherent with the sum of cellulose and hemicellulose content in horse manure. Same for Lignin.

3.2. Biochar characterisation

3.2.1. Biochar yield

In the following Table 3 the production yield of biochar according to heating rate and residence time are shown.

From the results, it can be discerned that the major factor influencing the biochar yield is HHT. There is a clear hop between the yields issued from different residence HHT. This find accordance with the analysis of (Shafizadeh, 1982) and (Bulmău et al., 2010).

The residence time seems to have a slight influence on the yield; this can be observed quite clearly when the HHT is 350 °C, consistently with literature (Bulmău et al., 2010). The more the HHT increases the less residence time appears to influence the yield. At 550 °C residence time appears not have influence at all. This finds accordance with the study of (Ronsse et al., 2012) where several species are pyrolyzed at different HHT and residence times. It can be seen that a clear hop appears only when the HHT is 300 °C, on the other hand at 450, 600 and 750 °C this difference markedly diminished. Especially with straw, material assimilable with horse manure (Ronsse et al., 2012). Similar results were obtained in the study of (Sadakaet al., 2014). Concerning the heating rate, the difference in yield of the biochar produced at 5 °C/min and 10 °C/min does not follow a clear trend. Besides, the biochar yield produced at different temperatures finds accordance with the results obtained through the TGA analysis (Fig. 2).

3.2.2. pH

The horse manure presented a pH equal to 7.3. How it can be observed from Fig. 3 the pH of the pyrolyzed material faced a noticeable increment, ranging from 9.1 to 11.3. The biochar issued at 550 °C presents the highest pH. The pH increases averagely with the HHT increase. This is consistent with the previous study of (Jindo et al., 2014), where a broad physical and chemical characterisation of biochars from different biomass was carried out.

On the other hands, residence time and heating rate seem not to have a discernible impact. These results find accordance with the work done by (Crombie et al., 2014).

Table 7a

Optimized biochar characterisation - yield.

YIELD		
[%wb]	[% _{db}]	[% _{daf}]
29	31	34

Table 7b

Optimized biochar characterisation – elemental analysis.

Elemental Analysis						
C [%]	H [%]	N [%]	S [%]	O [%]	H/C	0/C
68.23 pH 10.1	1.66	2.00	0.23	20.90	0.02	0.31

PAH COMPOUND [ng/g]								
NAPHTHALENE ^a	ASENAPH	TYLENE ^a ASENAP	HTENE ^a FLUOREI	NE ^a PHEN	ANTHRENE ^a A	ANTHRACENE ^a F	'LUORANTHENE ^a	YRENE^a
135	<lod< td=""><td>89</td><td><pre><pre>CIOD</pre></pre></td><td>282</td><td>1</td><td>.69 1</td><td>54</td><td>7</td></lod<>	89	<pre><pre>CIOD</pre></pre>	282	1	.69 1	54	7
aThe LODs $(S/N = 3)$) are in the rang	te of 10–50 ng/g.						
bThe LODs $(S/N = 3)$) are in the rang	ge of 50−100 ng/g.						
PAH COMPOUND [ng/g]								
BENZ(A)ANTRACENE ^a	CHRYSENE^a	BENZO(B)FLUORANTHENE ^b	BENZO(K)FLUORANTENE ^b	BENZO(A)PYRENE ^b	BENZO(GHI)PERYLENE ^b	DIBENZ(AH)ANTRACENE ^b	INDENO(1,2,3-CD)PYRENE ^b	ΣPAHS
<tod< td=""><td>326</td><td><tod< td=""><td>247</td><td><lod< td=""><td>340</td><td><tod< td=""><td>183</td><td>2010</td></tod<></td></lod<></td></tod<></td></tod<>	326	<tod< td=""><td>247</td><td><lod< td=""><td>340</td><td><tod< td=""><td>183</td><td>2010</td></tod<></td></lod<></td></tod<>	247	<lod< td=""><td>340</td><td><tod< td=""><td>183</td><td>2010</td></tod<></td></lod<>	340	<tod< td=""><td>183</td><td>2010</td></tod<>	183	2010

Optimized biochar characterisation – PAH compounds

Table 7c

Table 7d

Optimized biochar characterisation – SSA, bore volumes, bo	ore siz	ıze
--	---------	-----

SSA		PORE VOLUME	PORE SIZE	
Mv [M ² /G]	Err [m ² /g]	Mv [cm ³ /g]	Mv [nm]	
44.96	± 1.29	0.03	2.92	

3.2.3. PAH

In the following Table 4 the PAH concentrations (ng/g) are reported. Naphthalene represents the most abundant PAH in the biochar. This finds accordance with the interlaboratory study from (Bachmann et al., 2016). PAH total amount decreases when the pyrolysis temperature increases from 350 °C to 550 °C. The influence of the heating rate is not delineative. According to the EBC, the PAH threshold, equal to the sum of the EPA's 16 main pollutants, must be under 12,000 ng/g DM for basic grade (Schmidt et al., 2021). The obtained biochar is close to this parameter only when it reaches the highest HHT.

3.2.4. SSA

The results of the BET analysis according to the various temperatures and residence times are listed in Table 5.

Between 350 °C and 450 °C the surface area spans between 3.6 and 8.7 m²/g for both the heating rates, but there is not a clear trend variating according to temperature and heating rate. On the other hands, a big hop can be ascertained when the HHT increases to 550 °C. The same trend can be noticed for the pore volume. Although an indiscernible variation can be spotted Between 350 °C and 450 °C (at different residence times and heating rates) a clear increase occurs at 550 °C. A reverse trend results if the pore size is considered; it remains in the same spectrum of parameters at 350 °C and 450 °C (at different residence times and heating rates), decreasing when the HHT reaches 550 °C. According to the results, RT and HR do not show a relevant influence.

3.2.5. CHNSO analysis

Here following (Table 6) the results are shown (see Table 7).

Carbon content increases with the increase in temperature, while hydrogen, nitrogen, sulphur and oxygen presents an opposite trend. Consequently, both O/C and H/C ratios decrease when the HHT increases.

3.3. Parameters improvement

In light of the first series of analysis, the obtained biochar cannot comply with EBC standard (Schmidt et al., 2021) relatively to the PAH content. Besides, it can be stated from the results that HR and RT did not show a relevant influence on the biochar characteristics. In order to improve the quality and optimize the process (reduced RT and higher HR) the pyrolysis condition were set at: 600°C (HHT), 10 °C/min (HR) and 2h (RT).

3.3.1. Optimized biochar characterisation

In the following tables the characteristic of the new biochar were listed.

Following the temperature increase, it can be clearly seen that the sum of the PAH compounds strongly decreased. The biochar obtained largely comply with EBC standard (Schmidt et al., 2021).

4. Conclusions

The results showed that the major impact on biochar yield, pH, BET, PAH content, CHNSO content was due to the HHT. Concerning RT and HR, they do not display a relevant trend for most of the parameters. RT seems to have a slight influence on the yield, but this is limited, consistently with literature, at 350 °C of HHT. This modest influence fades away at 450 °C and 550 °C. The PAH level overcomes the "Basic

Grade" limits of the EBC, making it not spreadable for agriculture purposes.

After the improvement and optimisation of the thermodynamic parameters, the PAH content decreased considerably, making the biochar fulfilling the "Premium Grade" limits of the EBC corresponding to the level defined by the strict Swiss Chemical Risk Reduction Act (Schmidt et al., 2021).

In light of the results, it can be stated that the thermochemical conversion of horse manure could represent an environomical option to valorise this kind of waste. Through the pyrolysis of this feedstock, the environmental barriers deriving from its incineration and loss of efficiency could be overcome. Carbonisation of biomass residues is a valuable carbon capture method, Fawzy S. et al. (Fawzy S., 2021) estimated a potential sequestration of 0.3–2 Gt CO₂ year–1 by 2050 through production, use and storage of biochar. When the biochar is used as soil amendment it become a perfect example of circular economy (EBC, 2020).

Moreover, biochar could be seen also as a valuable product able to encourage and push the rural economy, offering a new stream of revenue.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- ASTM, 2006. Standard Test Method for Determination of Total Solids in Biomass. ASTM International. W, Conshohocken, PA: US.
- ASTM, 2013. Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels. ASTM International, W, Conshohocken, PA: US.
- ASTM, 2015. Standard Test Method for Ash in Biomass. ASTM International, W, Conshohocken, PA: US.

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Bachmann, H.J., Bucheli, T.D., Dieguez-Alonso, A., Fabbri, K.D., Schmidt, H., Ulbricht, A., Becker, R., Buscaroli, A., Buerge, D., Cross, A., Dickinson, D., Enders, A., Esteves, V.I., Evangelou, M.W.H., Fellet, G., Friedrich, K., Guerrero, G.G., Glaser, B., Zehetner, F., 2016. Toward the standardization of biochar analysis: the COST action TD1107 interlaboratory comparison. Journal of Agricultural and Food Chemistry, American Chemical Society 64, 513–527.

- Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309–319.
- Bulmau, C., Marculescu, C., Badea, A., Apostol, T., 2010. Pyrolysis parameters influencing the bio-char generation from wooden biomass. U.P.B. Sci. Bull., Series C 72, 29–38.
- Crombie, K., Mašek, O., Cross, A., Sohi, S., 2014. Biochar synergies and trade-offs between soil enhancing properties and C sequestration potential. GCB Bioenergy 7 (5), 1161–1175.
- EBC, 2020. Certification of the Carbon Sink Potential of Biochar. Ithaka Institute, Arbaz: Switzerland. Version 2.1E of 1st February 2021. http://European-biochar.org.
- EPA, 2017. National Water Quality Inventory:. Report to Congress EPA 841-R-16-011 Environmental Protection Agency, Washington, DC: U.S.
- Fawzy, S., Osman, A., Yang, H., Doran, J., Rooney, D., 2021. Industrial biochar systems for atmospheric carbon removal: a review. Environmental Chemistry Letters. https://doi.org/10.1007/s10311-021-01210-1.
- Hernandez-Mena, L.E., 2014. Slow pyrolysis of bamboo biomass: analysis of biochar properties. Chemical Engineering Transactions 37, 115–120.
- Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M.A., Sonoki, T., 2014. Physical and chemical characterization of biochars derived from different agricultural residues. Biogeosciences 11, 6613–6621.
- Katesa, J., Tangsathitkulchai, C., 2013. Effect of carbonisation temperature on properties of char and activated carbon from coconut shell. Suranaree J. Sci. Technol 20 (4), 270–278.
- Nikama, J.K.-K., 2014. The role of bedding material in recycling the nutrients of horse manure. *Equi-meeting infrastructures horses and equestrian facilities*. Le Lion d'Angers: France.
- Ronsse, F., Van Hecke, S., Dickinson, D., Prins, W., 2012. Production and characterization of slow pyrolysis biochar: influence of feedstock type and pyrolysis conditions. GCB Bioenergy 5 (2), 104–115.
- Sadaka, S., Sharara, M., Ashworth, A., Keyser, P., Allen, F., Wright, A., 2014. Characterization of biochar from switchgrass carbonization. Energies 7 (2), 548–567.
- Scandinavian Pulp Paper and Board Testing Committee, 2003. Content of acetonesoluble matter. SCAN-CM 49:03. Stockholm: Sweden.
- Schmidt, H.P., Bucheli, T., Kammann, C., Glaser, B., Abiven, S., Leifeld, J., 2021. European Biochar Certificate - Guidelines for a Sustainable Production of Biochar. European Biochar Foundation (EBC).
- Shafizadeh, F., 1982. Introduction to pyrolysis of biomass. J. Anal. Appl. Pyrol. 3, 283–305.
- Sjöström, E., 1993. Wood Chemistry: Fundamentals and Applications, second ed. Academic Press, San Diego, US.