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THERMOCHEMICAL VALORISATION OF WASTE: PYROLYTIC CONVERSION OF HORSE STABLE RESIDUE INTO BIOCHAR

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ABSTRACT

In this study, horse stable waste (horse manure, peat and wood sawdust) was processed under pyrolytic conditions. The chemical and physical properties of biochar obtained from different mixtures of horse stable residues were compared. All measurements followed an experimental design using a mixture model. This approach allowed the properties of any combination of ingredients to be predicted and the influence of each component on the final value to be estimated, with very good agreement between predicted and observed values. The results of the analysis of pH, polycyclic aromatic hydrocarbons (PAH), specific surface area (SSA) and CHNSO (carbon, hydrogen, nitrogen, sulphur and oxygen) showed that all possible combinations of materials can be used as soil amendments, since: an alkaline pH (>7) prevents soil acidification and a concentration of PAH below the limit (ΣPAH<12mg/kg) does not pose a risk to human health. A high SSA value (>180 m^2/g) and a different particle size distribution (PSD) provide habitat for microorganisms, increase water retention capacity and reduce greenhouse gas (GHG) emissions from the soil.

1. INTRODUCTION

Livestock waste is a valuable and important resource. Animal manure is commonly used in agriculture as an organic soil improver due to its high nutrient content (phosphorus, nitrogen and potassium). However, this type of residue has some serious drawbacks: manure leaks during storage and disposal can negatively impact soil and water quality and cause environmental problems (US Environmental Protection Agency, 2017). Its decomposition, when stored or managed in lagoons or storage tanks, produces enormous amounts of greenhouse gases. Uncomposted horse manure has been shown to immobilise nitrogen in the soil, affecting crop growth. In addition, the use of horse manure as a soil amendment poses the problem of weed seeds that can germinate after composting. It is estimated that 700 000-800 000 m^3 of this material is produced annually in Finland (Nikama et al., 2015), most of which is incinerated as waste, leading to significant CO_2 emission problems.

Horse bedding in Finland generally consists of a mixture of wood and peat, which provides a good balance between manure adsorption and animal well-being.

Peat consists of partially decomposed organic material, where decomposition by plants or animals is inhibited by acidic and anaerobic conditions (Syifa Rinaldi et al., 2019). In contrast to other countries and organisations, Finland classifies peat as a "slowly renewable biomass fuel" and allows its combustion for heat and electricity production (Finnish Ministry of Trade and Industry (KTM), 2000). The consequences of this process mainly concern CO_2 emissions, as its combustion produces 106 gCO2/MJ (more than coal), and the extraction of peat from peatlands negates its natural carbon sink effect. In fact, peat naturally binds and stores the carbon dioxide produced during its formation (Hagberg et al., 2008). Wood is one of Finland's most important natural resources and has wide range of industrial applications, from the sawmills to pulp and paper. Of greater interest is its combustion with manure and peat. Wood is often added to manure and peat fuels to improve the LHV and reduce carbon dioxide emissions (Hagberg et al., 2008). In general, there are more valuable options for valorisation of these residues than pure incineration. These include anaerobic digestion and gasification, which produce biogas that can be used directly for heating and electricity generation. Another option would be to use these materials as a feedstock to produce biochar through a slow pyrolysis treatment. This innovative technology is very promising due to its social, economic and environmental benefits: low operating costs at small and large scales (atmospheric pressure conditions and moderate temperatures),

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sustainable waste management and useful applications of the product (Adánez-Rubio et al. 2021), (Li et al. 2021). Biochar is defined as a solid material produced by the thermochemical conversion of biomass in an oxygen-free or low-oxygen environment; in principle, the carbon sequestered in biochar by pyrolysis must remain in this form for a long time (land use). In contrast, the use of charcoal as a fuel or carbon source for chemicals involves CO_2 emissions (Schmidt et al., 2021). Biochar has great potential to sequester greenhouse gases and could play an important role in waste management in the near future. This potential can be summarised in the following points:

- Long-term sequestration of Carbon due to its stability;
- Cogeneration of primary energy during the pyrolysis process. Use of this primary energy in industry, thereby reducing emissions;
- Reduction of nitrous oxide and methane emissions resulting from biomass decomposition;
- Reducing the use of landfills, thereby reducing greenhouse gas emissions;
- Improvement of areas arable lands;
- Reducing the energy used to transport waste over long distances;

  (Gunarathne et al., 2019), (Li et al. 2021), (Liu et al., 2014), (Schmidt et al., 2021).

The aim of this paper is to provide indicators for better use of agricultural and industrial residues through the use of a thermochemical conversion process.

In summary, the first part of this paper is dedicated to the physical and chemical characterisation of biochar products obtained by slow pyrolysis treatment of horse stable wastes (horse manure, peat and wood sawdust). In the second part, a Mixture model for residues (which are inseparably bounded after pyrolysis) is established to predict the reaction for each empirically producible combination of components and to estimate the influence of each component in combination with the others. The Mixture model is a powerful tool for combining several data-generating processes into a single model. Finally, the quality of the biochar and its potential use as a soil amendment are assessed, considering the soil protection thresholds set by European legislation.

2. MATERIALS AND METHODS

2.1 Biochar production

2.1.1 Horse stable residues

In this study, stable waste consisting of horse manure, peat and wood sawdust, was used to produce biochar. All these wastes were collected directly from the Espoo Riding School near Helsinki. The peat used is a commercial peat produced in Estonia called "BALTIC PEAT" with an organic matter content of at least 90%, a pH of 3,5-4,5 and a degree of humidification of H2-H6 (all data are taken from the product label). The wood sawdust is a commercial product called "POLKKYpets" produced by the company "Poelkky Oy" (Finland) from Finnish pine and spruce sawdust.

2.1.2 Samples preparation

It was found that the moisture content of manure and peat as delivered is much higher than that of sawdust, almost 53% for peat and as much as 68% for manure. Since the aim of this work is to characterise a mixture of these three elements, it can be assumed that this mixture is subjected to an industrial-scale drying process before pyrolysis. Therefore, to make all values comparable, the initial moisture content of peat and manure was reduced by drying. Specifically, freshly collected horse manure was stored at room temperature with forced ventilation for seven days, while peat was dried in a ventilated oven at 40°C for almost 18 hours. Wood chips MC: 7,6%, manure MC: 7,1%, peat MC: 8,8%. All the original biomass was ground (2-5 mm). This procedure allowed the homogenisation of both pure materials, as peat consists of different elements, and mixed materials. Seven diverse types of samples were prepared and characterised. Table 1 shows the composition of each sample, and all productions were conducted in triplicate for statistical reasons.

2.1.3 Experimental setup

Pyrolysis of all samples was performed in a quartz tube furnace (NBD-O1200, Nobody Material Science and Technology CO., LTD, China). The experimental setup and photographs are shown in Figure 1. Oxygen-free conditions were achieved by a nitrogen flow of 10 mL/min controlled by a flowmeter, and nearly 2 g of samples per crucible were processed. In their previous work (Caro et al., 2021), Caro et al. found optimal values for the process parameters for manure, namely a heating rate of 10°C/min, a HHT (highest heating temperature) of 600°C and a residence time of 2 h. These values were also taken as the minimum optimal values for this work, as the focus of the study is on the mixing of the three materials. The synthesis gases produced during pyrolysis were condensed using a water cooling system. The operating scheme of the furnace is shown in Figure 1(C).

2.2 Biochar characterisation

2.2.1 TGA analysis

Thermogravimetric analysis (TGA) was carried out on both the original biomass and the biochar samples obtained. A TGA Q500 TA instrument (USA) was used for this

TABLE 1: List of all the samples used to produce biochar, with each specific original biomass composition.

Sample	Horsemanure	Peat	Wood
	[%]	[%]	[%]
Manure	100	0	0
Peat	0	100	0
Wood	0	0	100
MPW (manure-Peat-Wood)	33,33	33,33	33,33
MP (Manure-peat)	50	50	0
MW (Manure-wood)	50	0	50
PW (peat-wood)	0	50	50

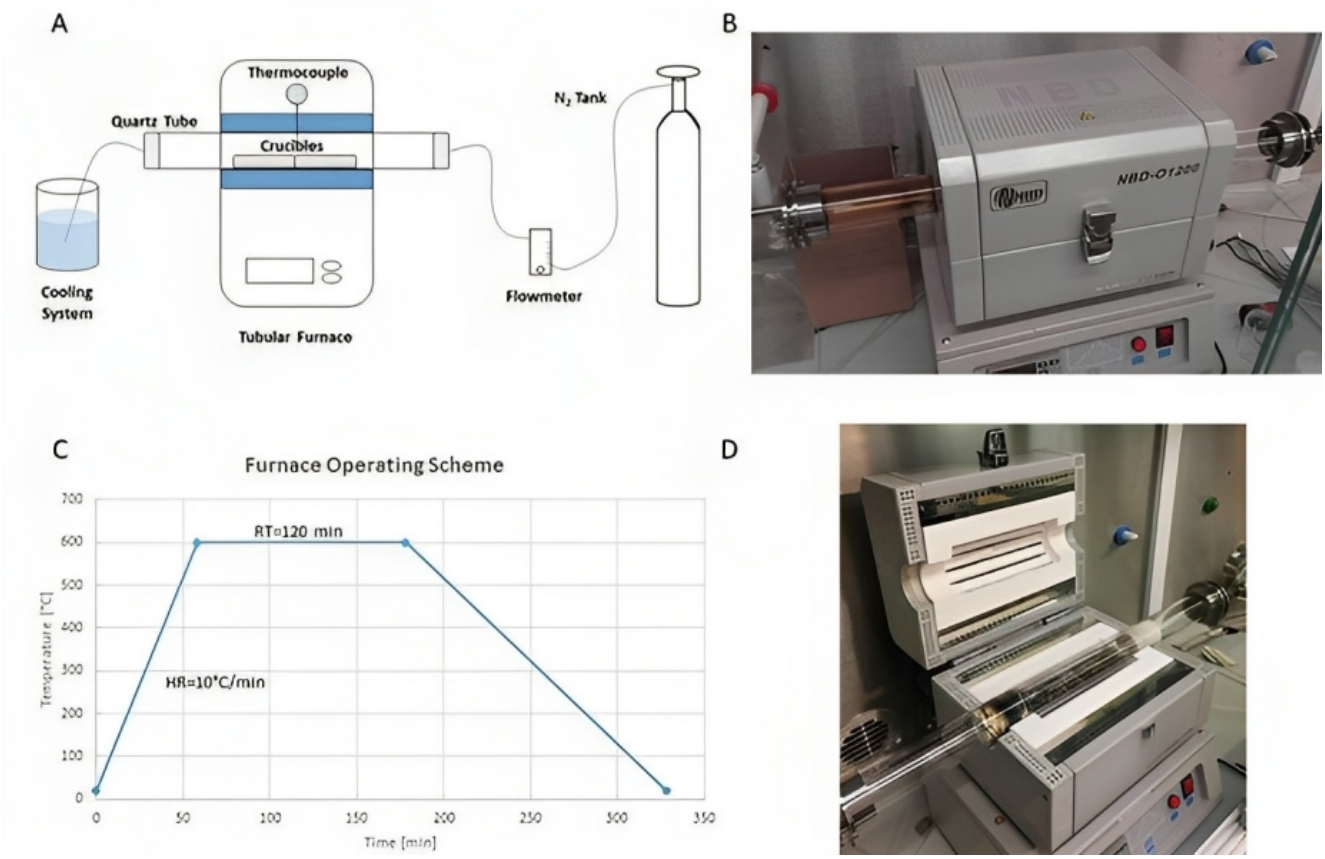


FIGURE 1: Experimental setup scheme (A), furnace operating scheme (C), closed furnace picture (B) and open furnace picture (D).

analysis. The test method used consisted of heating the sample in an inert environment (provided by a nitrogen flow of 60 NmL/min) from 20°C to 900°C at a heating rate of 10°C/min and a final isothermal combustion at 900°C with pure oxygen for 5 minutes.

2.2.2 Proximate analysis

Proximate analyses were performed on both the original biomass and the biochar produced. As for the biomass, all analyses were performed according to the ASTM standard. For moisture content (MC), ASTM E1756-08 was followed (ASTM, Standard Test Method for Determination of Total Solids in Biomass, 2006). Ash content was determined according to ASTM E1755-01 (ASTM, Standard Test Method for Ash in Biomass, 2015). The volatile matter (VM) content was determined according to ASTM E872-82 (ASTM, Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels, 2013). Finally, the fixed carbon (FC) content was determined as the difference between 100 and the sum of the other contents. On the other hand, the proximate analysis for biochar samples was performed according to the EBC (European Biochar Certificate) analysis methods (Schmidt et al., 2021). These methods are similar to the previous ones, with only minor differences in the target temperatures. 2.2.3 CHNSO analysis

The carbon, hydrogen, nitrogen, sulphur and oxygen contents of the biochar were determined using a Perkin Elmer CHNS/O 2400 series analyser II (dry combustion method). In particular, the C, H, N and S contents were measured directly with the instrument, while O was calculated as the difference between 100 and the sum of the other contents and ash according to the EBC guideline (Schmidt et al., 2021), as the sample is assumed to consist essentially of these elements. For statistical reasons, this analysis was performed for the mixture model in triplicate for the MPW mixture, in duplicate for the pure materials (M, P, W) and in single for the MP, MW and PW mixtures (see section 4).

2.2.3 SSA Analysis

Specific surface area (SSA), pore volume and pore size of all biochar produced were determined by Bruner-Emmett-Teller analysis (using Tristar II -Micrometrics, USA, with covered liquid nitrogen tank). The Barrett-Joyner-Halenda (BJH) method was used to estimate pore size distribution based on pore volume. Micropore volume and surface area were determined using the T-plot method These results were compared with the total pore volume and SSA determined using the Brunauer-Emmett-Teller (BET) equation. The contribution of micropores and meso-macropores was expressed as a percentage. All methods used are in accordance with standard procedures for porous materials (Phuong et al., 2016).

2.2.4 PAH Analysis

PAH analysis was performed on the same number of samples as for CHNSO analysis. The sample (approximately 0,5 g dry weight) was weighed into an extraction thimble

and extracted with 50 mL of analytical grade toluene for two hours (reflux method). Finally, the extract was concentrated to 10 mL by evaporation under reduced pressure. The PAHs in the extract were analysed using a gas chromatograph and mass spectrometer (Agilent GC 7890A and 5975C Inert MSD). An internal standard was used to quantify the PAH concentrations. The column was an HP 5MS (30 m x 0,25 mm x 0,25 µm). The temperature programme 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 temperatures applied were as follows: Transfer line: 280°C; MSD: 150°C; injector: 250°C. The injection volume was 1,0 µL and the carrier gas flow (helium) was 1,5 mL/min (International Organisation for Standardisation 18287:2006, 2006).

2.2.5 pH Analysis

The pH of all samples, both the original biomass and the produced biochar, was determined using the same procedure proposed in the EBC analytical methods (Schmidt et al., 2021). A 25 mL volume of 0,01 M $CaCl_2$ solution was prepared and added to a 5 mL volume of the sample in a glass vessel. The solution was stirred for 1 hour to obtain a homogeneous suspension. After this treatment, the pH was measured using an Orion 2 Star pH meter (Thermofisher Scientific, USA).

3. RESULTS AND DISCUSSION

3.1 Feedstock physical and chemical properties

In Table 2 the physical and chemical properties of the raw materials are shown.

In terms of volatile content, the highest value is attributed to wood with 87,4%, followed by manure and peat (77,2% and 74,8% respectively). As shown in Table 2, the ash content of the biomass varies considerably depending on the species. As expected, the ash content of wood is almost zero, while the ash content of manure is the highest (7,4%), which is due to the high mineral content. The content of fixed carbon ranges from 12,3% to 23,8%. All the data obtained are in good agreement with the TGA results (Figure 2 and Figure 3).

3.2 TGA Analysis results

As reported by (Hernandez-Mena et al., 2014) and (Katesa et al., 2013) in their analyses, cellulose, hemicellulose and lignin behave quite differently under thermal decomposition. According to (Hernandez-Mena et al., 2014), the degradation temperature of cellulose and hemicellulose is 200-360°C and 360-600°C for lignin; (Katesa et al., 2013) report a range of 250-350°C for cellulose and hemicellulose and 350-750°C for lignin.

In Figure 2, the TGA curves for all materials show the highest mass loss up to 350°C, about 55% for manure and peat and even more for wood. These results agree well with the structural composition of these materials where, for example, the sum of cellulose and hemicellulose is almost 58% for manure (Caro et al., 2021) and on average 65-75% for wood (Pettersen, 1984). Furthermore, the graph shows that a constant mass is only reached at a temperature of 550°C, i.e. complete lignin degradation. Since higher lignin content leads to higher biochar yields as described in (Lehmann et al., 2009), peat and manure are expected to give the highest yields, followed by wood. Considering the data from the TGA curves in Figure 2, a first mass loss in a temperature range between 30-150°C is due to water evaporation, which is consistent with the literature from (Hernandez-Mena et al., 2014) and (Katesa et al., 2013). The second and largest, which occurs in the 200-550°C range, is mainly related to the release of volatiles (CO_2 and CH_4). Finally, from 600°C to 900°C, the last mass loss reflects the content of fixed carbon and ash (García et al., 2013). As can be easily seen, the amount of VM produced from biomass is directly related to the content of cellulose and hemicellulose (partly also lignin), while the fixed carbon is mainly due to lignin. The TGA of wood has the highest slope, followed by manure and peat, so a higher value of volatiles is expected in this material. On the other hand, peat and manure show higher weight losses at 900°C (about 30%). Wood shows a mass loss of almost 20% at 600°C, which increases to 10 and 15% for manure and peat respectively. As a result, the biochar yield is expected to be higher from peat, followed by manure and wood.

Figure 3 shows that all curves follow a similar trend of thermal degradation trend up to 500°C. After that, there is a clear difference between the curves, resulting in a higher mass loss for wood biochar (almost 25% in the range 500-900°C) compared to peat and manure. In particular, peat biochar shows the lowest total weight loss, less than 10%; this is closely related to the original mineral content of the feedstock.

3.3 Physical and chemical properties of the raw materials and their biochar

Table 3 provides an overview of the physical and chemical properties of the biochar. As expected, the yields vary depending on the feedstock. In particular, it is again shown that biochar produced from manure has higher values than that obtained from agricultural residues. In fact, the yield of wood is 21% higher, while that of horse manure is 10% higher.

Regarding the properties of the biochar, the volatile matter content decreases significantly, while the ash and

TABLE 2: Results of physical and chemical properties of raw materials.

Material	Sample	Ash	VM	FC	C	H	N	S	O	H/C	O/C	pH
		[%db]	[%db]	[%db]	[%]	[%]	[%]	[%]	[%]	-	-	-
Biomass	Manure	7,4	77,2	15,4	47,3	6,1	1,7	0,8	36,1	0,13	0,76	6,9
	Wood	0,2	87,4	12,3	50,0	6,0	1,0	1,0	42,0	0,12	0,84	4,3
	Peat	1,4	74,8	23,8	56,0	5,0	1,0	1,0	37,0	0,09	0,66	3,1

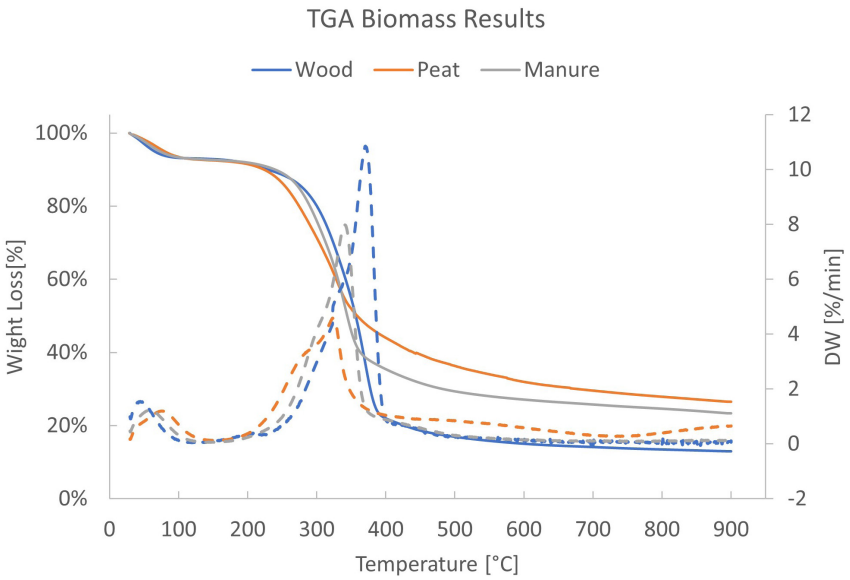


FIGURE 2: TGA (solid line) and DTG (dash line) curves of the three different biomass.

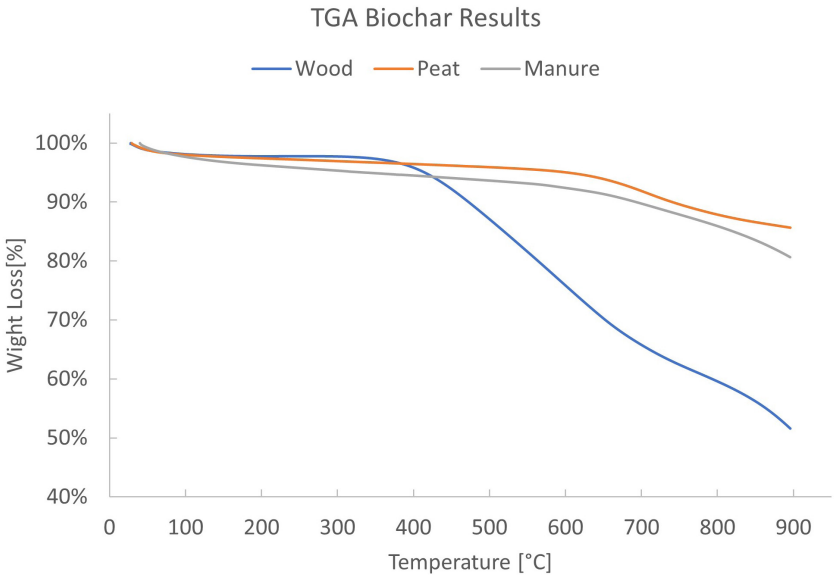


FIGURE 3: TGA of wood, peat and manure biochar.

fixed carbon content show an opposite trend. As with the original biomass, manure biochar has the highest ash content at almost 22%, while wood has the highest VM value. The carbon content varies between 68% (manure) and 90% (peat and wood). The carbon content increases significantly, by almost 30%, when the biomass is pyrolysed. This increase is accompanied by a decrease in the H and O content, a phenomenon well confirmed in the literature by the works of (Jindo et al., 2014), (Bayan, 2012) and (Lee et al., 2013). On the other hand, the correlation between nitrogen in the initial biomass and its variation during pyrolysis is not well understood, in this case showing different tendencies depending on the feedstock. As for the sulphur content, its proportion in horse manure decreases after pyrolysis, which is common for manure-based biochar, where it is more sensitive to mass loss in the vapour phase. It is suggested that part of the sulphur contained in the volatile organic compounds is lost at 350°C and the remaining is more resistant to bond breakage in accordance with the work of (Cantrell et al., 2012). Mixtures of pure elements show an average value weighted by mass composition. The reduction of these two ratios after pyrolysis is the result of dehydration and decarboxylation reactions (Jindo et al., 2014). In general, a low O/C ratio corresponds to low polarity and a hydrophilic surface, while the higher the degree of aromatisation and charring, the lower the H/C ratio, resulting in extremely stable structure formation (Gai et al., 2014). Peat and wood biochar (0,08) show better stability than manure (0,31), especially their location in the low H/C - higher O/C range can be attributed to the fact that ash

TABLE 3: Results of physical and chemical properties of biochar.

Material	Sample	Ash	VM	FC	C	H	N	S	O	H/C	O/C	Yield	SSA	PV	PS	pH
		[%db]	[%db]	[%db]	[%]	[%]	[%]	[%]	[%]	-	-	[%]	[m²/g]	[cm³/g]	[nm]	-
Biochar	Manure	21,8	6,1	72,1	68,2	1,7	2	0,2	20,9	0,02	0,31	29,0 ± 0,002	45 ± 6,9	0,03 ± 0,003	2,9 ± 0,14	10,1 ± 0,02
	Wood	1,4	22,3	76,3	89,8	2,1	0,6	0,2	6,9	0,02	0,08	19,4 ± 0,009	351,3 ± 5,17	0,19 ± 0,006	2,2 ± 0,09	7,6 ±0,04
	Peat	3,1	4,1	92,8	87,3	2,5	1,7	0,4	6,7	0,03	0,08	27,6± 0,04	307,1 ± 10,85	0,18 ± 0,001	2,3 ± 0,08	7,4 ± 0,03
	MPW	16,3 ± 0,2	-	-	80,1 ± 0,02	2,1 ± 0,00076	1,7 ± 0,001	0,2 ± 0,001	12,9 ± 0,02	0,03 ± 0,005	0,16 ± 0,03	27± 0,014	227,8 ± 4,15	0,13 ± 0,003	2,2 ± 0,02	8,8 ± 0,01
	MP	13,1	-	-	74,4	2,1	1,5	0,2	17,3	0,03	0,23	30,6± 0,002	197,2 ± 4,43	0,11 ± 0,001	2,3 ± 0,08	9,2 ± 0,03
	MW	13,6	-	-	78,3	2,2	1,4	0,2	14,2	0,03	0,18	25,6± 0,001	180,8 ± 15,37	0,1 ± 0,008	2,2 ± 0,02	9,3 ± 0,02
	PW	2,9	-	-	78,6	2,2	1,2	0,2	16,9	0,03	0,21	26,5 ± 0,005	313,5 ± 8,85	0,17 ± 0,0016	2,2 ± 0,04	7,5 ± 0,06

minerals change their composition by melting and sintering during pyrolysis, as shown in (Xin et al., 2014). As far as the BET analysis is concerned, the average SSA value for all the biochars studied varies between 45-350 m^2/g. This value was measured according to the multipoint surface model for materials with large variations in pore size. Considering that biochar has a complex structure in which all types of pores coexist, this measurement should be representative, as the single-point measurement at p/ps = 0,299, which has higher values in all analyses performed, overestimates this value (Bachmann et al., 2016). As expected, wood biochar has the highest SSA value and manure the lowest. These results are in good agreement with the literature (Caro et al., 2021), (Singh et al., 2010) and (Cantrell et al., 2012). The biochar produced from the mixed materials has high SSA values of over 150 m2/g.

Figure 4 shows how the PSD value varies depending on the feedstock. In particular, manure biochar has the highest proportion of macropores at almost 20%, while peat and wood have a higher proportion of micropores. The high proportion of micropores is also reflected in the proportion of total area and volume (Figure 5-6). The figures for the PSD and area fractions are in good agreement with previous studies, while the volume fractions show a higher proportion of micropores (Phuong et al., 2016). Furthermore, (Ioannidou et al., 2007) found that lignin develops macropores while cellulose favours the formation of micropores, which is in perfect agreement with the results obtained.

3.4 AH (polycyclic aromatic hydrocarbons) Analysis results

In Table 4, total PAH concentrations range from 4 to 9,1 mg/kg. All determined values are well below the EBC limit of 12 mg/kg, so that all biochar can be applied to the soil (Schmidt et al., 2021). Biochar mixtures do not behave as a mass-weighted value. In fact, PAH levels are higher than expected in all the mixtures studied, especially when peat is present. The explanation for this phenomenon is not fully understood and needs further investigation. A possible correlation between the SSA of biochar and the pore size distribution and/or the functional surface group with the PAH concentrations could provide an explanation. In general, all these values are expected to be higher than those

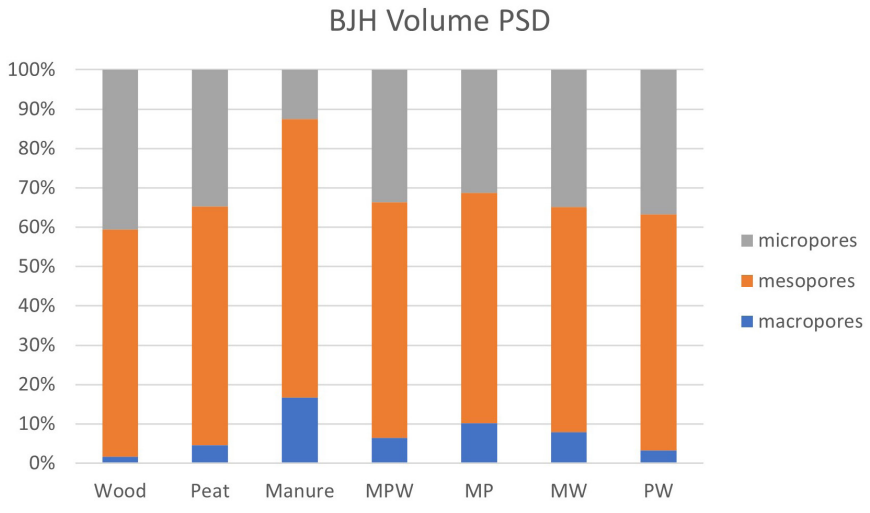


FIGURE 4: Particle size distribution of all studied biochar derived using BJH model for pore volume.

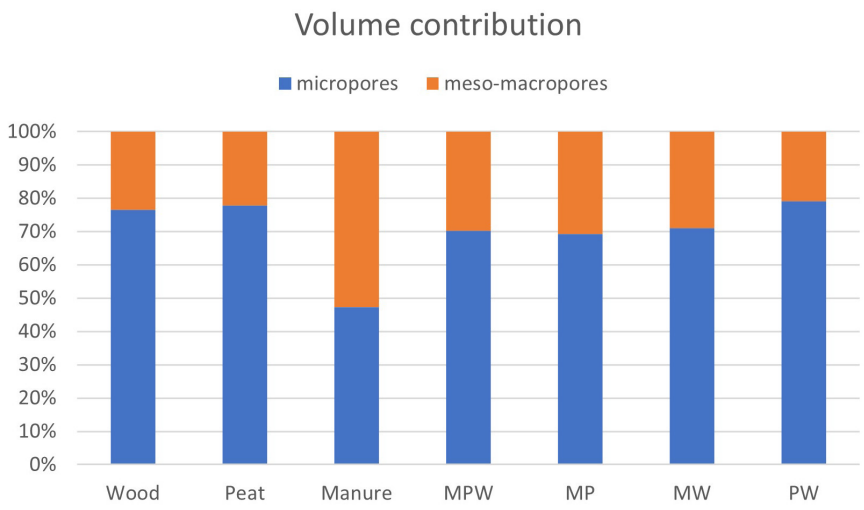


FIGURE 5: Contribution of micro, meso and macropores volume in the total pore volume for all studied biochars according to BET and t-plot data.

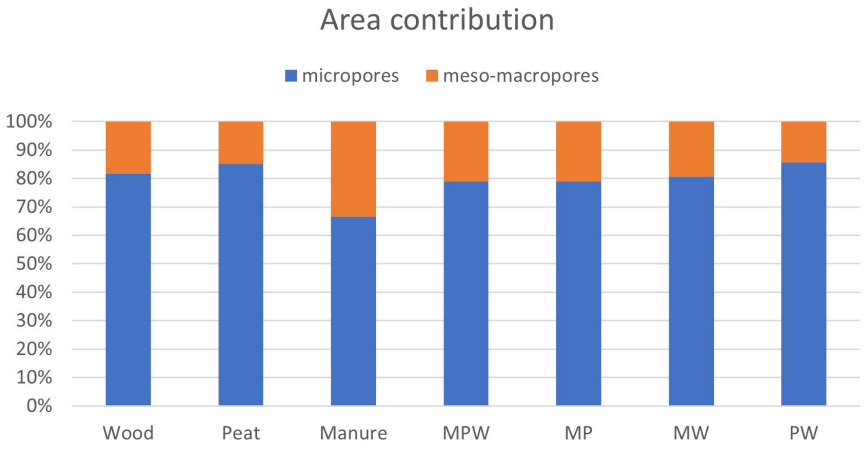


FIGURE 6: Contribution of micro-, meso- and macrospores volume in the total pore area in total SSA for all studied biochars according to BET and t-plot data.

obtained from the analysis of the same biochar produced on an industrial scale. This is due to the small size of the quartz tube, which does not allow perfect evaporation of the gaseous PAHs deposited on the biochar after condensation. Furthermore, Table 4 shows that naphthalene is the most abundant compound; this result is in good agreement with the literature (Bachmann et al., 2016).

4. EXPERIMENTAL DESIGN USING MIXTURE MODEL

4.1 Model implementation

According to the Scheffé-type model and the number of components q=3 (wood, peat and horse manure), a total run of 7 design points was chosen, as shown in Figure 7. As can be seen, there are no upper or lower limits for the proportions of the three components in this experimental range, except for the only external condition that they must sum to one (Eriksson et al., 1998). In fact, points P1-3-5 represent the pure mixture elements, while points 2-4 and 6 represent the binary mixture (second degree centroids), which has two non-zero components with equal values. Points P7 represent ternary mixtures, which contain all components in equal proportions.

For the analysis of yield, pH and BET, all experiments were performed in triplicate. For the remaining experiments, only P7 was performed in triplicate, while the second degree centroids were performed in single and the pure ones in duplicate. This choice is consistent with performing as few measurements as possible to still obtain a correct statistical result in the model. All the results obtained were analysed using the MODDE software. Thus, an analysis of the effects of each term of the special cubic equation (see Equation 1) was conducted in order to neglect the irrelevant terms.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 \quad (1)$$

Always using MODDE, an ANOVA analysis was performed to estimate the model likelihood of regression and lack of fit. Finally, the β-coefficients were determined and the predicted values of each trait were plotted.

TABLE 4: List of both single PAH compound concentrations expressed in ng/g and both total PAH concentration expressed in mg/kg according to EBC standards. (1: LOD= 10-50 ng/g and 2: LOD= 50-100 ng/g.).

Sample	Wood	Peat	Manure	MPW	MW	MP	PW
PAH Compound	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**	**[ng/g]**
Naphthalene[1]	3 371	5 464	5 625	6 772	5 383	5 069	5 989
Asenaphtylene[1]	62	60	48	40	40	100	LOD
Asenaphtene[1]	94	96	LOD	78	LOD	86	LOD
Fluorene[1]	49	LOD	LOD	LOD	LOD	70	LOD
Phenanthrene[1]	161	115	808	419	102	462	303
Anthracene[1]	110	96	174	197	76	222	61
Fluoranthene[1]	34	50	66	172	72	158	42
Pyrene[1]	19	49	35	124	44	120	LOD
Benz(a)antracene[1]	73	88	74	214	98	194	842
Chrysene[1]	40	40	61	194	68	170	LOD
Benzo(b)fluoranthene[2]	LOD	LOD	92	261	48	239	LOD
Benzo(k)fluorantene[2]	LOD	LOD	62	141	LOD	157	LOD
Benzo(a)pyrene[2]	LOD	LOD	79	174	75	172	LOD
Benzo(ghi)perylene[2]	LOD	LOD	LOD	94	LOD	116	LOD
Dibenz(ah)antracene[2]	LOD	LOD	LOD	58	LOD	LOD	LOD
Indeno(1,2,3-cd)pyrene[2]	LOD	LOD	LOD	89	LOD	110	LOD
ΣPAHS [mg/kg]	4,0	6,1	7,1	9,1	6,0	7,4	7,2

4.2 Model Results and Discussion

The predicted values of the main biochar properties resulting from the Scheffé mixture model are shown in Figure 8. Regarding the plots (A-B-C-D-E-F), almost all properties show a linear dependence on pure mixtures (βi > > βij), only one quadratic term over three was found to be non-negligible for each property compared to the others. The only exception is PAH, where the βij coefficients have a higher value, showing that interactions between all components are relevant and should not be neglected.

Main variables of ANOVA statistical analysis are shown in Table 5. In the table:

n represents the number of observations considered for the model

$R^2 = {SS_{reg}}/{SS_{tot}}$ represents the goodness of fit

$SS_{reg} = \sum(\hat{y}_i - \bar{y})^2$ regression sum of squares explained by the model

$SS_{tot} = \sum(y_i - \bar{y})^2$ total sum of squares

$R^2_{adj} = 1 - \frac{{SS_{reg}}/{(n-p)}}{{SS_{tot}}/{(n-1)}}$ represents the adjusted goodness of fit

The quality of the generated models can be seen in both Figure 8 and Table 5, where a good agreement between predicted and observed value (R^2 close to one) can be observed for almost all characteristics. Furthermore, almost all models are statistically good, as the regression probability is close to zero (regression < 0,005). Only for the properties SSA and Yields the fit is insufficient as the p-value is close to zero. This SSA value is mainly due to the inherent properties of the machine BET.

TABLE 5: Relevant ANOVA statistic values for each modelled property.

Property	n	R^2	R^2_{adj}	$p_{regression}$	$p_{lack\text{-}of\text{-}fit}$
C	11	0,945	0,932	<0,005	0,147
H	11	0,924	0,891	<0,005	0,523
S	10	0,889	0,852	<0,005	0,116
pH	19	0,944	0,928	<0,005	0,182
SSA	19	0,993	0,992	<0,005	0,008
Yield	19	0,94	0,856	<0,005	0,026
PAH	11	0,800	0,600	0,077	0,230

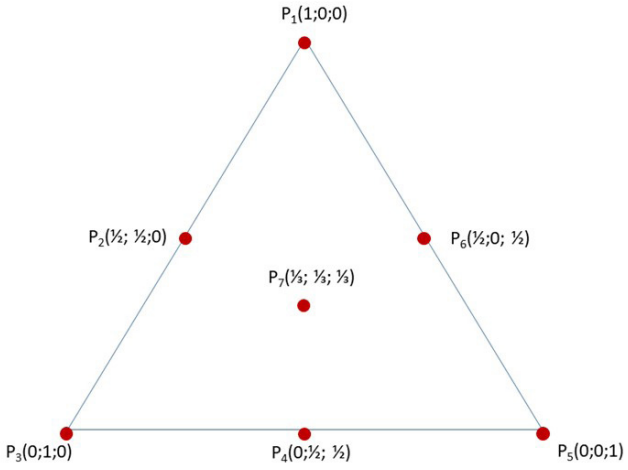
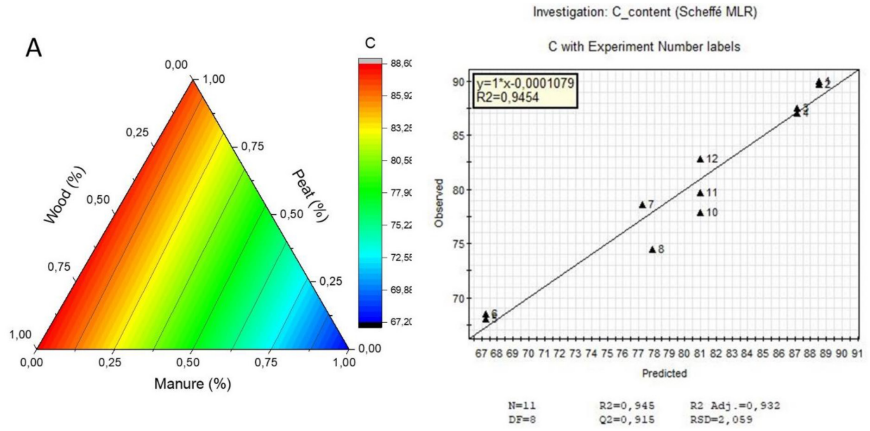
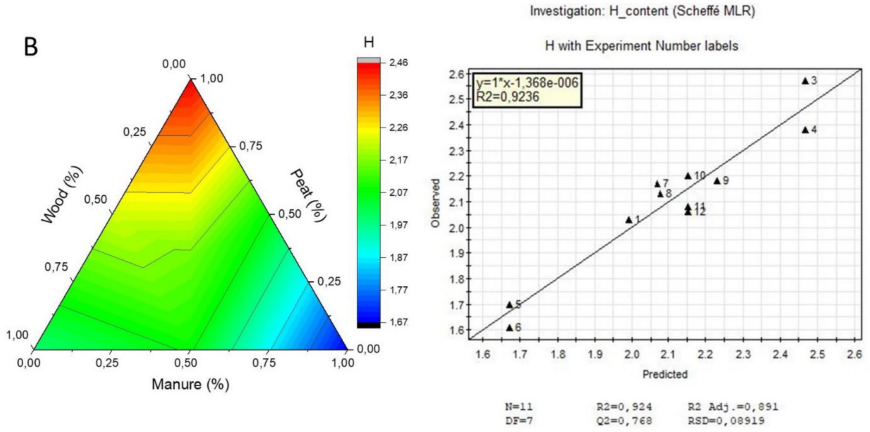
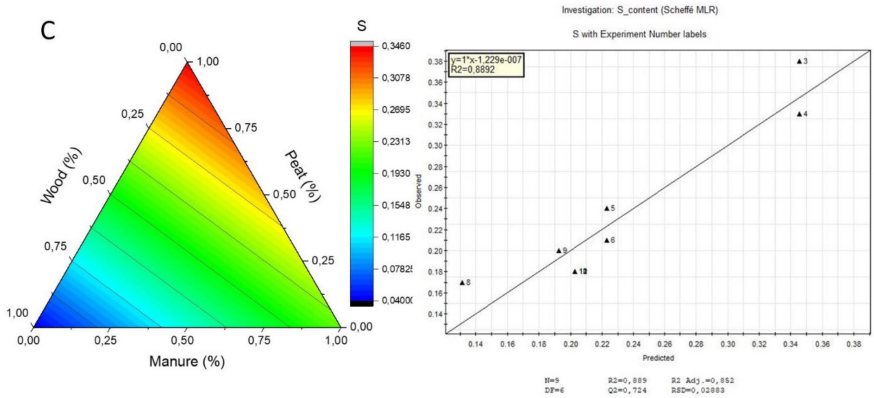
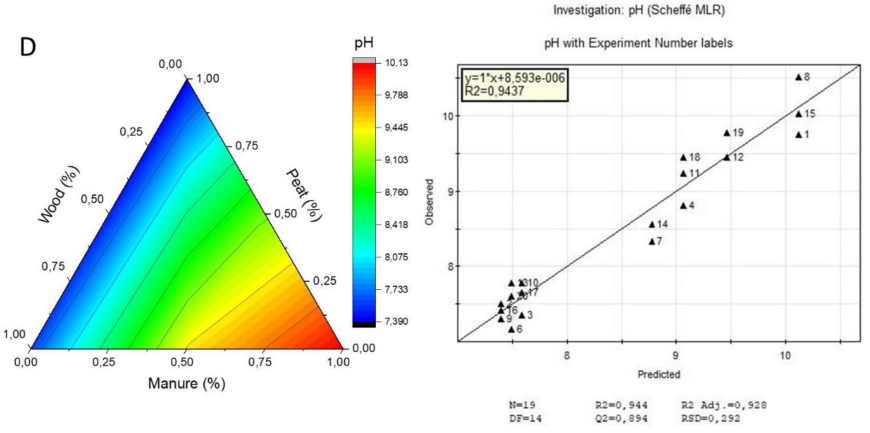


FIGURE 7: Representation of the selected design points for the mixture model.


A
C
Wood (%)
Peat (%)
Manure (%)
Investigation: C_content (Scheffé MLR)
C with Experiment Number labels
y=1*x-0,0001079
R2=0,9454
Observed
Predicted
N=11
DF=8
R2=0,945
Q2=0,915
R2 Adj.=0,932
RSD=2,059


B
H
Wood (%)
Peat (%)
Manure (%)
Investigation: H_content (Scheffé MLR)
H with Experiment Number labels
y=1*x-1,368e-006
R2=0,9236
Observed
Predicted
N=11
DF=7
R2=0,924
Q2=0,768
R2 Adj.=0,891
RSD=0,08919


C
S
Wood (%)
Peat (%)
Manure (%)
Investigation: S_content (Scheffé MLR)
S with Experiment Number labels
y=1*x-1,229e-007
R2=0,8892
Observed
Predicted
N=9
DF=6
R2=0,889
Q2=0,724
R2 Adj.=0,852
RSD=0,02883


D
pH
Wood (%)
Peat (%)
Manure (%)
Investigation: pH (Scheffé MLR)
pH with Experiment Number labels
y=1*x+8,593e-006
R2=0,9437
Observed
Predicted
N=19
DF=14
R2=0,944
Q2=0,894
R2 Adj.=0,928
RSD=0,292

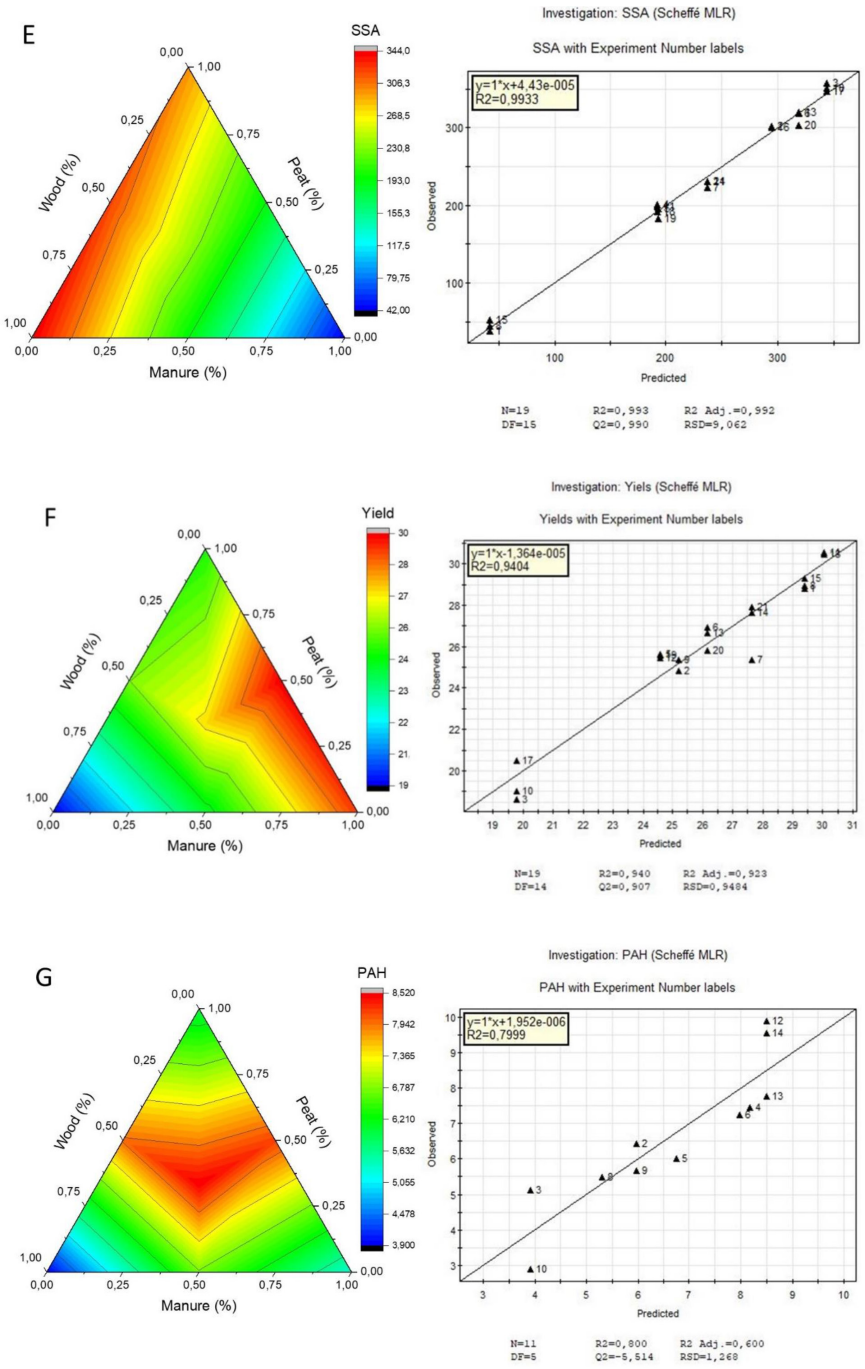


FIGURE 8: Contour plot of predicted values (left) and plot of measured values versus predicted values (right) (Values for C, H, S, and yield are in [%], while SSA [m^2/g], PAH [mg/kg], and pH are pure numbers).

The only property for which no mixture model was found is PAH, as it has the lowest coefficient of determination (0,8) and is statistically poor (regression = 0,077). In fact, the behaviour of PAH is not fully understood. In order to find some possible correlations between PAH and all the other properties studied, a correlation matrix was created using MODDE. The results of this analysis are shown in Figure 9, where PAH has a weak negative correlation with SSA (-0,37) and PV (-0,40) and a weak positive correlation with manure (0,32). It was assumed that SSA and PV or the surface functional groups are the most likely properties to explain the behaviour of PAH. The principal component analysis (PCA) also did not explain the trend of PAH very well. However, this may indicate that variables with a strong influence on PAH are not present in the data set studied. These results suggest that more in-depth studies of the PAH formation mechanism and interaction with porous materials are needed.

5. CONCLUSIONS

A range of detailed information was provided to verify the quality of the produced biochar and its applicability.

The results of proximate and CHNSO analysis show that the biochar produced has less variation in elemental composition compared to the original biomass. In particular, the carbon content of all products is greater than 50%, allowing the char produced to be classified as 'biochar' in accordance with the main voluntary biochar product standards (EBC, Biochar Quality Mandate (BQM) and International Biochar Initiative Standard (IBI-BS). Greater variation in specific values depending on the choice of feedstock was found in the analysis of pH, PAH and BET. In particular, the results of the BET analysis show that woody and peaty biochar have higher SSA values, namely more than 181 m^2/g in each sample where at least one of the two substances is present. In addition, manure biochar has a higher percentage of macropores, resulting in a lower SSA value (only 45 m^2/g). pH results show how pyrolytic conversion increases this value enormously, as all biochar produced is classified as alkaline. The PAH analysis shows that all the biochar can be applied to the soil as its value is below the threshold of 12 mg/kg according to the EBC criteria (Schmidt et al, 2021). The results of the pH, PAH and BET analyses indicate that biochar can be used as a soil amendment: a high pH can prevent the problem of soil acidification, a PAH concentration below the limit does not pose a risk to human health, and a high SSA and PSD variation provides habitat for microorganisms and reduces GHG emissions in the soil. The shape of the original feedstock is retained after the pyrolysis process. This is not the case for volume, which is significantly reduced. This reduction is particularly evident in the case of woody materials, where the volume of biochar is halved compared to the biomass. This phenomenon has positive implications for waste disposal. The application of the mixture model to the experimental data showed how mixtures subjected to pyrolysis behave as physically bounded materials. Using this approach, it was possible to predict the response of key properties for any combination of constituents and calculate the influence of each component on the final value, with very good agreement between estimated and observed values. This could also be useful on an industrial scale to predict what the final biochar will look like, or to adjust the properties of the final product to a good approximation. This result suggests that this type of approach could also be applied to other types of organic residues. The only exception was the PAH content. It was found that this property does not behave as a function of the mixture components, as the concentrations in mixtures are higher than in pure materials. Further analysis and studies are needed to gain a better understanding of the behaviour of the PAH content and the mechanisms of its formation. Research on the pyrolysis of mixed organic materials can serve as a basis for future studies in the field of organic waste recycling and disposal. For instance, the disposal of municipal and agricultural effluents. These materials are difficult to pyrolyse due to their high moisture content and low carbon content, but when mixed with other biomass can produce reusable products for the agricultural and industrial sectors.

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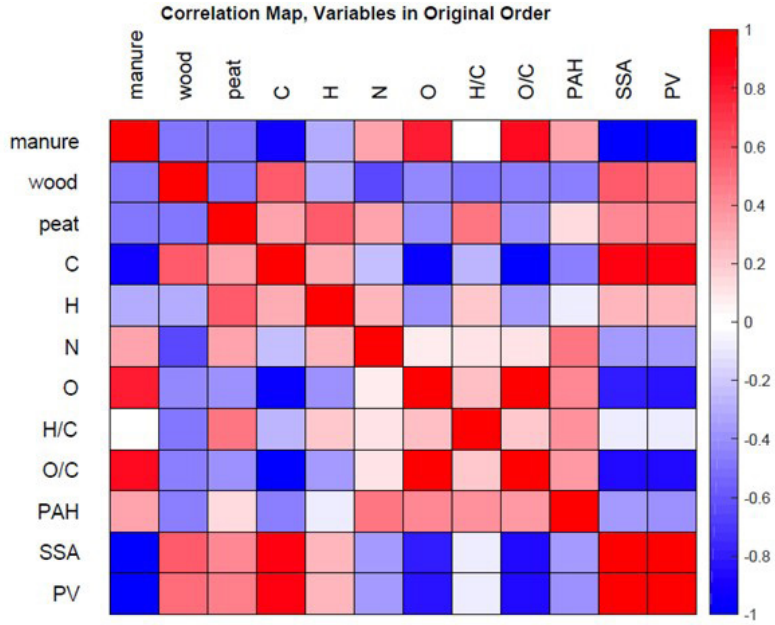

FIGURE 9: Correlation matrix among all investigated biochar properties.

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