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ORIGINAL PAPER

Features of Biochar Produced Under Different Pyrolysis Conditions and their Possible Significance for Soil Fertility

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Abstract
Agricultural activities generate a significant amount of by-products, which significantly contribute to various environmental issues. These environmental issues include the formation of pests and diseases in the stored areas, water pollution caused by pesticides, and air pollution from incineration. To promote sustainable agriculture, biochar is produced from these agricultural wastes to improve soil fertility parameters and enhance crops productivity. The aim of this study was to investigate physicochemical properties of biochar obtained from various agricultural wastes and assess their significance for agricultural and environmental applications. The expert consisted of a total of 45 pyrolysis experiments with three different temperatures (300, 400 and 500 °C), three different heating rates (5, 10 and 20 °C/min.) and five types of biomasses (wheat straw, tomato, carnation, banana and vineyard pruning). The analyses were performed on the biomass samples: moisture, ash, volatile matter, fixed carbon, cellulose, hemicelluloses, lignin and extractive contents. For biochar samples, biochar yield, biochar image analysis, elemental C, H, N, S and cation exchange capacity (CEC), electrical conductivity (EC) and pH properties were analyzed. As the pyrolysis temperature and heating rate increased, a more distinct biochar was formed. The increase in pyrolysis temperature and heating rate decreased biochar H and N content. The increase in heating rate was effective in increasing biochar CEC value. This study proposes that agricultural wastes with a lignocellulosic structure can be evaluated by pyrolysis. Furthermore, the properties of biochar pyrolyzed at 500 °C and a heating rate of 20 °C/min have the potential to improve soil fertility.

Keywords Agricultural waste · Biochar · Biomass · Carbon · Soil conditioner

1 Introduction

With an increase in the global population, the demand for food worldwide has multiplied exponentially. Currently, the total land area worldwide is about 13 Gha (1Gha = 109 ha), and approximately 1.5 Gha of this area is used to grow arable crops (Tripathi et al. 2016). However, this situation has led to a surge in production, consumption and, subsequently, the amount of generated waste. More than 400 million tons of food, yards, and green waste were sent to landfills or dumped haphazardly (Kaza et al. 2018). Biodegradable waste is one of the main sources of environmental pollution risks (Sauve and Van Acker 2020).

Türkiye is a country known for its intensive agricultural activities. With a wide range of diverse crops cultivated and significant amounts of agricultural waste are generated. It has been estimated that 5.2 Mt of waste biomass have been generated from horticultural activities in Türkiye (Başçetinçelik et al. 2005).

According to the calculations, an average of 80–100 t ha^{-1} of wet biomass or 25–30 t ha^{-1} of dry biomass is obtained from on a medium yielding piece of land in Türkiye with an average of annual precipitation around 250 mm.

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The incineration of agricultural wastes, which is an important source of biomass in the world, their storage in piles around greenhouses, lead to the production of pests and diseases (Suárez-Estrella et al., 2007). Moreover, the presence of pesticides in these wastes and being a source of greenhouse gases pose a potential environmental hazard (Parra et al. 2008). Inadequate or faulty organic waste management can affect soil and water pollution, as well as global warming through the release of greenhouse gases into the atmosphere. Research indicates that biochar has bioavailability and intervention potential to mitigate climate change and improve soil fertility, while also addressing environmental pollutants (Kavitha et al. 2018). Elsewhere, the disposal of organic waste leads to a significant loss of natural resources such as organic matter, nutrients and energy (Stahel 2016). However, it is crucial to consider the risk of food safety breaches associated with raw materials. The effects of uncontrolled risks can be deadly for businesses as well as consumers. Therefore, certificatory that includes good agricultural practices is given great importance all over the world (Daniel and Petra 2013).

Biomass can be defined as the total mass of living organisms within a species or community of various species at a given time. It can be categorized based on various parameters, such as organic, inorganic, and liquid (Vassilev et al. 2010), or primary, secondary and tertiary biomass (Vassilev et al. 2013). Waste biomass commonly used for biochar production includes animal residues, agricultural waste, forest waste, food waste, municipal waste solids, and wastewater (Cantrell et al. 2012).

Biochar is defined as a black solid material with a high carbon content resulting from the thermal treatment of organic materials (Qian et al. 2015). Today, a wide variety of biological resources (food wastes, sewage sludge, post-harvest residues in plant production, etc.) are used to minimize the cost of biochar to be produced (Xiong et al., 2021). However, it is known that the cost of biochar production is influenced by numerous factors, making it highly variable. According to Thengane et al. (2020), the breakeven point in biochar production cost is €310 t^{-1}. However, Keske et al. (2020), have reported that the lowest achievable cost for biochar production in mobile units is 423 € t^{-1}. It is reported that the cost calculations vary considerably based on the effect of biochar obtained from different biological wastes on soil properties, and fermentation residues have been found to offer the lowest cost per increase in soil properties (Maroušek and Trakal., 2022). According to a study conducted by Stehel et al. (2020), the reported cost of biochar production is less than €30 per ton. Fibirova and Petera (2013) have identified three highly profitable areas in biochar production, namely wastewater treatment, revenue generation from waste treatment, and special fertilizer production. However, Vochozka et al. (2016) have reported that the price of biochar derived from biowaste is 40–70% lower compared to biochar obtained from wood. Biochar, which can be obtained either separately or through the co-pyrolysis of biomass, serves various purposes in environmental and agricultural applications. It acts as an adsorbent in water treatment, while also functioning as a soil conditioner and/or soil improvement material. Biochar provides a unique opportunity to improve soil fertility, nutrient-use efficiency for plant production and renewable materials in a sustainable way (Kamarudin et al. 2022). Many studies report that the unique physical and chemical properties of biochar have made it a promising material for soil improvement, wastewater treatment, carbon sequestration, energy storage and fertilization (Maroušek and Trakal 2022). Biochar, a highly stable C-rich material, has been proposed as a soil amendment, since it improves soil physicochemical properties (Jatav et al. 2021). Biochar also provides great opportunities to turn the Green Revolution into sustainable agroecosystem practice. Since biomasses containing lignin in their structure are not easily fermented and cannot be separated sufficiently by biochemical conversion methods, they can be converted into biofuels and useful chemicals at high rates by applying thermo chemical conversion methods (Williams et al. 2003). Lignocellulosic residues formed after harvest in horticulture and clean wastes from domestic, commercial and industrial processes are considered suitable as potential raw materials for pyrolysis (Sohi et al. 2015).

The pyrolysis process varies depending on the heating rate to which the biomass is exposed. It can be divided into two main groups: slow pyrolysis (traditional) and fast pyrolysis (Bridgwater 2012). Slow pyrolysis involves the production of biochar after a long pyrolysis period at low temperatures (300–700 °C) (Demirbaş and Arin, 2002). On the other hand, fast pyrolysis is the preferred method as it achieves maximum bio-oil yield through high heating rates and short heating times. In this process, the residence time of the vapors produced is kept low in the reactor (Ronsse 2016). Fast pyrolysis is characterized by high heating rates (410–200 °C s^{-1}) and short pyrolysis times, typically less than 2 s, although it can range from 0.5 to 10 s (Demirbas and Arin, 2002). While higher biochar yields are obtained from biomass through slow pyrolysis, whereas fast pyrolysis and gasification methods yield higher amounts of liquid and gaseous products, respectively. It was reported that the amount of biochar decreased with the increase in the heating rate (Karaosmanoglu et al., 2000), and at higher pyrolysis temperatures, the surface area generally increases (Uchimiya et al. 2011). In biochar production, the physical and chemical properties of the resulting biochar, such as composition, particle size, and pore size distribution, are greatly influenced by the properties of the biomass and the conditions of pyrolysis (Verheijen et al. 2009). For example, with the increase in pyrolysis temperature, the pH and EC value of biochar also increase (Kończak et al. 2019). The quality of the obtained biochar material depends on its high adsorbing capacity, high cation exchange capacity and low concentrations of mobile materials (such as tar, resin) (Glaser et al. 2002). Biochar has a wide surface area and a pore network (Mukherjee et al. 2011). Due to its large specific surface area and pore structure, biochar possesses a specific adsorption effect on plant nutrition and water in the soil (Han et al. 2020). This means that biochar is a productive material for improving soil properties and improving overall soil quality. With its active surface area and porous structure, biochar offers several positive effects, including increased nutrient retention in the soil (Liang et al. 2006), retaining more water at field capacity (Laird et al. 2010) and reduced soil bulk density (Oguntunde et al. 2008). The decrease of the soil bulk density increases soil porosity and soil aeration and may have a positive effect on root and microbial respiration (Basso 2012).

We hypothesized that biochar parameters would significantly change depending on temperature and heating rate and pH and CEC properties of biochar would depend on temperature. Besides, EC of biochar would depend on the type of biomass and that together with its other properties, it would provide significant improvements in soil fertility. The knowledge of physicochemical properties of biochar obtained from agricultural wastes may be contributes to the better management of agricultural practices and environmentally friendly utilization of agricultural wastes within the scope of waste management for European Union (EU) harmonization acquis.

2 Materials and Methods

2.1 Biomass Preparation

All biomasses (tomato, wheat straw, banana, clove and vineyard pruning) used in biochar production in this study were obtained from greenhouse and field production areas in the Mediterranean Region (Antalya, Turkey). These biomasses are the stem and leaf residues of carnation, tomato and banana produced under greenhouse conditions, as well as vineyard pruning residues after grape harvest and wheat straw residues after wheat harvest produced under field conditions. The collected wastes were dried in the laboratory under controlled air conditions, then ground in a mill and sieved using a Rotary sieve shaker to achieve a particle size of 1–1.5 mm. These sieved biomass samples were subsequently utilized in the pyrolysis analysis.

2.2 Pyrolysis Experiments

Biochar production experiments were carried out using the specially designed pyrolysis system (drop-tube reactor) given in Fig.S1. The system consisted of a quartz glass reactor measuring 110 cm in length and 2.5 cm in diameter, with approximately 10 to 15 cm of glass wool placed inside. The furnace was divided into two sections, one for the biomass bed (heated zone 1) and the other for the catalyst bed (heated zone 2). To begin the experiment, a 40 g sample of biomass was placed into the reactor in heated zone 1, and the reactor was securely attached to the system using bolts. Prior to starting the experiment, nitrogen gas heated to 150 °C was introduced into the system to remove any oxygen present inside the reactor. This step was carried out approximately 5 min before the experiment commenced.

During the pyrolysis process, the nitrogen gas was heated to 150 °C to prevent any sudden temperature changes or turbulence when it encountered the high temperature environment (300–500 °C) inside the reactor. High purity nitrogen gas (N2) was used as the entraining gas to carry the pyrolysis vapor formed during the experiments. The amount and speed of nitrogen gas delivered to the system was carefully controlled and measured using a mass flow controller. Then, the furnace was set to the desired temperature (300, 400, 500 °C) that reaches at the defined duration, therefore, three different heating rates (5, 10, 20 °C min^{-1}) and were used as an experimental parameter. The thermo-couple and carrier gas flow amount, which indicates the temperature of the reactor, was monitored by a control panel with digital display. Pyrolysis vapor formed during the experiment was condensed by using condenser system to obtain bio-oil, but non-condensable gases were given to the atmosphere through the gas outlet. After the experiment was completed, the temperature of the furnace was adjusted to room temperature, and the system was waiting for cooling. After the experiment, the solid product (biochar) remaining in the reactor was directly weighed and the biochar yield was calculated. The parameters of the processes used in the pyrolysis experiments are given in Table 1.

3 3. Biomass Analysis

Moisture determination of biomass samples was carried out according to ASTM D3173(2003) principles and moisture content was calculated with the equation given below.

$$\text{Moisture}(\%) = [(W2 - W3)]/[(W2 - W1)] \times 100 \qquad (1)$$

Table 1 Parameters of processes used in pyrolysis experiments

Biomass type	Biomass particle size	Pyrolysis temperature	Heating rate	Number of experiments
	(mm)	(ºC)	(ºC/min.)	
Tomato	1–1.5.5	300–400-500	5–10-20	9
Vineyard pruning	1–1.5.5	300–400-500	5–10-20	9
Banana	1–1.5.5	300–400-500	5–10-20	9
Carnation	1–1.5.5	300–400-500	5–10-20	9
Wheat straw	1–1.5.5	300–400-500	5–10-20	9
Total number of experiments				45

where, *W1* is the weight of the crucible, *W2* is the initial weight of the crucible + sample, and *W3* is the weight of the crucible + sample after the oven.

Ash contents of biomasses were analyzed according to ASTM D3174(2002) principles and calculated according to the equation given below.

$$\mathrm{Ash}(\%) = [(\mathrm{W3} - \mathrm{W1})/[(\mathrm{W2} - \mathrm{W1})] \times 100 \quad (2)$$

where, *W1* is the weight of the crucible, *W2* is the initial weight of the crucible + sample, and *W3* is the weight of the crucible + sample after the oven.

Volatile matter contents of biomass were determined according to ASTM D3175(2007) principles and calculated according to the equations given below.

$$Weightloss(\%) = [(W2 - W3)]/[(W2 - W1)] \times 100 \quad (3)$$

$$Volatile\ matter\ loss(\%) = Weight\ loss(\%) - Moisture(\%) \quad (4)$$

where, *W1* is the weight of the crucible, *W2* is the initial weight of the crucible + sample, and *W3* is the weight of the crucible + the sample after the oven.

Fixed carbon amount of biomass was determined according to ASTM E 872 (1982) principles and calculated according to the equation given below.

$$Fixed\ carbon\ (\%) = 100 - (Moisture + Ash + Volatile\ matter) \quad (5)$$

Extractive substance content of biomass was determined according to ASTM D1107(1996) principles and the amount of extractive substance was calculated according to the equation given below.

$$Extractive\ subs\tan ce\ (\%) = [(M0 - M1)]/(M0) \times 100 \quad (6)$$

where, *M0* is the initial weight of the sample and *M1* is the weight of the sample after extraction.

Lignin contents of biomass samples were determined according to ASTM D1106(1996) principles and acid-insoluble lignin (AIL) amount of biomass was calculated according to the equation given below.

$$\mathrm{AIL}\ (\%) = [(\mathrm{W3} - \mathrm{W2})]/[(\mathrm{W1})\ \times\ (\mathrm{SCS})/100] \times 100 \quad (7)$$

where, *W1* is the initial weight of the sample, *W2* is the weight of the crucible + the sample, *W3* is the initial weight of the crucible; *SCS* is the % solids content of the sample.

$$\mathrm{Cellulose}(\%) = [(\mathrm{W3} - \mathrm{W1})]/[(\mathrm{W1}) \times (\mathrm{SCS}/100)] \times 100 \quad (8)$$

Cellulose and hemicelluloses analysis of biomass samples were determined according to Kurschner and Hoffer (1969) method and cellulose content of biomass was calculated according to the equation given below. where, *W1* is the initial weight of the sample, *W2* is the weight of the crucible + the sample, *W3* is the initial weight of the crucible; *SCS* is the % solids content of the sample.

The hemicelluloses content of the biomass samples was calculated with the following formula.

$$\%Hemicellulose = \%Holocellulose - \%\alpha - Cellulose \quad (9)$$

3.1 Biochar Analysis

In the study, some predicted analyzes were made on biochars obtained from the pyrolysis of 5 different (TB: Tomato biochar; VPB: Vineyard pruning biochar; CB: Carnation biochar; BB: Banana biochar; WSB: Wheat straw biochar) agricultural wastes. LEO Evo 40 model Scanning Electron Microscope (SEM) was used to determine the structural characteristics of the biochar samples. After placing the biochar samples in the SEM imaging device, images were obtained at different magnifications based on the gray level difference using a secondary electron detector with an acceleration voltage of 20 keV under high vacuum. Carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) contents of biochars were determined using CHNS-932 (LECO) Elemental Analyzer. The pH and EC values were determined in a 1:2.5 ratio biochar-water mixture by Jackson (1967), and the cation exchange capacity (CEC) was determined according to the extraction method with 1 N NH_4OAc (Ross and Ketterings 2011).

The equation given below was used to calculate the biochar yield.

$$Biocharyield\ (\%) = [W\ (g)/W0\ (g)] \times 100 \quad (10)$$

where, *W* is the mass of the biochar resulting from pyrolysis and *W0* is the mass of the pre-pyrolysis biomass sample.

3.2 Statistical Analysis

Descriptive statistics are presented as mean and standard deviation values. Normality assumption was checked with Shapiro Wilk Test. One-way Analysis of Variance (ANOVA) was used to analyze the difference between the numerical data of more than two groups when the data fit the normal distribution. In significant cases, pairwise comparisons were made with Duncan's Test. Analyses were performed with SAS 9.4 proc glm procedure. $P < 0.05$ was considered statistically significant.

4 Results and Discussion

4.1 Physicochemical Properties of Biomasses

Some analytical results performed on biomass obtained from different agricultural wastes used in the research are given in Table 2. The moisture content of the biomasses varies between 4 and 7%, the highest moisture content was ~7% in carnation, and the lowest moisture content was ~5% in wheat straw. It is stated that the moisture value of <10% is the generally accepted limit value for the thermo–chemical conversion processes of biomasses (Braga et al. 2014). In terms of ash content, the biomass with the highest ash content was banana with ~13%, and the lowest (~4%) was vineyard pruning waste. This value obtained is less than the value (9%) found by Rosas et al. (2015). On the other hand, it is seen that the results obtained in our study show parallelism with values of the ash content of banana biomass consisting of peel, leaves and stems some researchers determined by (Kabenge et al. 2018). In the study, it was determined that vineyard pruning waste had the highest volatile matter content (~72%) among all other biomasses. On the other hand, the lowest (~66%) volatile matter value in the study belongs to tomato biomass (Table 2). Rosas et al. (2015) found the volatile matter content in the vineyard residues to be ~71% in a similar study.

The fixed carbon content of tomato, vineyard pruning, carnation, banana and wheat straw biomasses were determined as ~17%, ~19%, ~13%, ~15% and ~15%, respectively (Table 2). According to these results, vineyard pruning biomass has the highest fixed carbon value. This value we found is slightly different from the fixed carbon values found in tomatoes by Rosas et al. (2015).

In terms of cellulose and hemicelluloses contents, wheat straw is the biomass with the highest cellulose (~47%) and the lowest hemicelluloses content (~19%). On the other hand, banana has the highest hemicelluloses (~41%) and the lowest cellulose (~31%) content (Table 2). It was determined that the highest value (~27%) in terms of lignin content belonged to vineyard pruning waste and the lowest lignin content belonged to tomato and carnation.

The lowest extractive substance value was obtained in vineyard pruning waste with a value of ~5%, while the highest extractive substance content was obtained in carnation with a value of ~17% (Table 2). It is seen that the hemicelluloses value of the banana biomass obtained in the study is like the banana hemicelluloses value (~41%) reported by Kabenge et al. (2018). Analytical results given in Table 2 accord with the ranges given for the main components of some agricultural wastes in the studies carried out by (Kan et al. 2016).

4.2 Physicochemical Properties of Biochars

The analytical data of the yield of five different biochar obtained at different pyrolysis temperatures and heating rates are given in Table 3. Considering all pyrolysis temperature levels, heating rates and residence time it was determined that the highest biochar yield was obtained from carnation biomass, and the lowest biochar yield was obtained from wheat straw biomass. The highest biochar yield was obtained from vineyard pruning waste biomass at VPB_{500-20}. On the other hand, the lowest biochar yield was obtained from the banana biomass at BB_{300-5} in 60 min residence time. In addition, biochar yield increased especially with the increase in pyrolysis temperature and heating rate

Table 2 Analytical results of biomasses before pyrolysis experiments

Biomass	Moisture (%)	Ash (%)	Volatile matter (%)	Fixed carbon (%)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Extractive substance (%)
Tomato	5.15c	12.52b	65.57d	16.76b	35.26d	40.66a	11.56d	14.07b
Vineyard pruning	5.52b	4.08e	71.83a	18.57a	39.07c	29.44c	27.41a	5.30e
Carnation	6.82a	10.51d	69.78b	12.89e	40.87b	37.04b	11.58d	16.81a
Banana	5.24c	13.12a	66.54c	15.09d	31.16e	40.77a	14.94c	12.06c
Wheat Straw	4.52d	10.89c	69.12b	15.47c	46.80a	18.92d	23.39b	5.94d
Er.Mean Sq	±0.005	±0.004	±0.201	±0.033	±0.063	±0.089	±0.024	±0.004
Significance	***	***	***	***	***	***	***	***

Duncan test $P < 0.05$, $n = 3$

The differences between values not shown with the same letter are significant at *** $P < 0.001$

Table 3 Yield of Biochar obtained from biomass via pyrolysis at different temperature, heating rate, residence time, and physicochemical analysis results of Biochars

Biochar	Residence time (Min.)	Biochar yield (%)	C (%)	H (%)	*N* (%)	S (%)	pH (1:2.5)	EC (dS m^{-1})	CEC (cmol kg^{-1})
TB_{300-5}	60	36.63	50.26	3.816	2.179	0.398	7.52	4.90	6.71
TB_{400-5}	80	43.91	46.20	2.885	1.996	0.203	8.75	5.23	7.23
TB_{500-5}	100	43.40	44.93	1.689	1.648	0.597	10.47	5.20	7.34
TB_{300-10}	30	51.65	48.68	3.190	1.650	0.199	8.52	5.62	6.71
TB_{400-10}	40	48.94	39.60	2.721	1.615	0.492	9.09	5.52	7.09
TB_{500-10}	50	53.58	51.61	1.912	1.585	0.311	10.58	5.26	7.38
TB_{300-20}	15	51.09	45.48	3.278	1.607	0.311	8.40	5.78	7.35
TB_{400-20}	20	54.78	42.48	2.927	1.597	0.275	9.38	5.11	7.37
TB_{500-20}	25	58.63	44.21	1.976	1.208	0.494	10.48	5.08	7.38
Mean		49.17**b**	45.93**e**	2.71**e**	1.67**c**	0.364**a**	9.24**a**	5.30**a**	7.17**b**
VPB_{300-5}	60	31.45	56.69	4.946	0.842	0.102	5.53	0.53	1.52
VPB_{400-5}	80	43.24	72.24	3.662	1.193	0.010	6.54	0.54	1.72
VPB_{500-5}	100	35.67	67.32	2.908	1.163	0.095	9.05	0.23	1.60
VPB_{300-10}	30	40.33	52.76	4.590	1.313	0.048	5.68	0.52	1.58
VPB_{400-10}	40	45.20	72.52	3.676	1.034	0.040	7.15	0.70	2.09
VPB_{500-10}	50	49.72	69.85	2.683	0.989	0.134	8.48	0.46	1.61
VPB_{300-20}	15	49.58	55.34	4.737	1.296	-	6.35	0.75	1.94
VPB_{400-20}	20	49.27	62.04	3.734	1.259	0.123	7.68	0.91	2.32
VPB_{500-20}	25	60.07	70.19	2.597	0.844	0.049	9.30	0.26	1.57
Mean		44.94**c**	64.32**a**	3.72**a**	1.10**d**	0.066**e**	7.30**e**	0.54**e**	1.77**d**
CB_{300-5}	60	59.08	51.29	4.479	3.576	0.060	8.36	3.57	8.93
CB_{400-5}	80	45.65	47.57	3.742	3.954	0.194	8.42	3.17	8.51
CB_{500-5}	100	47.78	56.01	2.507	3.235	0.274	9.84	2.64	8.34
CB_{300-10}	30	48.14	49.47	4.048	3.010	0.106	8.81	3.93	10.05
CB_{400-10}	40	50.97	54.81	3.258	3.083	0.138	8.54	2.90	8.65
CB_{500-10}	50	59.48	49.24	2.325	2.874	0.155	9.98	3.04	8.64
CB_{300-20}	15	50.88	49.84	3.697	2.959	0.343	9.11	3.84	10.54
CB_{400-20}	20	59.04	53.18	3.142	2.826	0.161	8.87	2.98	8.72
CB_{500-20}	25	59.02	54.64	2.763	2.943	0.110	9.96	3.05	8.85
Mean		53.33**a**	51.45**c**	3.32**c**	3.16**a**	0.171**c**	9.09**b**	3.23**b**	9.02**a**
BB_{300-5}	60	26.38	46.39	4.132	2.127	0.190	6.33	2.60	1.53
BB_{400-5}	80	31.15	49.03	3.225	1.883	0.094	8.29	3.27	1.56
BB_{500-5}	100	38.93	49.92	2.289	1.859	0.117	10.35	2.63	1.75
BB_{300-10}	30	41.38	46.14	3.971	1.761	0.127	6.54	2.86	1.83
BB_{400-10}	40	44.28	51.27	3.380	2.210	0.103	8.52	3.32	1.80
BB_{500-10}	50	44.36	51.98	2.395	1.956	0.088	10.47	2.54	1.98
BB_{300-20}	15	44.70	48.46	3.844	1.870	0.071	6.72	3.10	1.51
BB_{400-20}	20	53.56	50.88	3.417	2.560	0.238	9.00	2.79	2.07
BB_{500-20}	25	54.54	51.85	2.196	1.837	0.085	10.47	2.56	2.06
Mean		42.14**d**	49.54**d**	3.20**d**	2.00**b**	0.123**d**	8.52**c**	2.85**c**	1.78**c**
WSB_{300-5}	60	27.95	55.68	4.407	0.811	0.122	6.14	1.02	1.39
WSB_{400-5}	80	32.86	52.62	3.348	0.705	0.242	7.05	1.21	1.52
WSB_{500-5}	100	34.97	54.05	2.544	0.629	0.108	9.52	1.21	1.54
WSB_{300-10}	30	33.57	49.01	4.506	0.985	0.125	6.22	1.08	1.32
WSB_{400-10}	40	30.87	58.21	3.309	0.781	0.396	7.05	1.14	1.57
WSB_{500-10}	50	38.15	55.33	2.479	0.562	0.154	9.57	1.16	1.54
WSB_{300-20}	15	41.02	58.01	4.246	0.855	0.199	6.18	1.20	1.41
WSB_{400-20}	20	47.65	60.53	3.257	0.775	0.158	7.42	1.19	1.53
WSB_{500-20}	25	30.71	61.36	2.511	0.616	0.210	9.69	1.29	1.50
Mean		35.30**e**	56.09**b**	3.40**b**	0.74**e**	0.190**b**	7.64**d**	1.16**d**	1.47**e**
Significance		***	***	***	***	***	***	***	***

Duncan test, $P<0.05$. $n=3$

The differences between values not shown with the same letter are significant at *** $P<0.001$. *TB* Tomato Biochar, *VPB* Vineyard Pruning Biochar, *CB* Carnation Biochar, *BB* Banana Biochar, *WSB* Wheat Straw Biochar

(Fig. 1a-b). This result may be since the vineyard pruning waste contains the highest lignin and lowest extractive matter. Among the biomasses, wheat straw has the highest cellulose content, which may have affected the result. Thus, it can be said that biomass with high lignin content was more effective in biochar yield. As a matter, it is stated that valorization of lignocellulosic waste through biological means is inefficient, and these wastes are ideal feedstocks for biochar production (Gustavo Adolfo et al. 2022). It has been observed that the increase in biochar yield, especially with the increase in temperature, heating rate and residence time, is not consistent when compared with many scientific data on this subject. This situation reveals that more studies on biomass and pyrolysis parameters should be carried out. As a matter of fact, a study with similar biomass and pyrolysis conditions (14–22% fixed carbon, pyrolysis temperature of 350–750 °C and heating rate of 5–10 °C/min) reported that fixed carbon and pyrolysis temperature had a negative effect on biochar yield while heating rate had a positive effect (Mariyam et al., 2024). Intani et al. (2016) reported that biochar yields were negatively correlated with temperature, and the heating rate had a slight effect on the biochar yield during the pyrolysis of maize residues.

On the other hand, it was reported that an increase in flow rate of purging gas such as nitrogen had no significant effect on the biochar yield (Demiral et al. 2012). When some research results are considered, it is understood that there are still uncertainties in the effectiveness of pyrolysis parameters on biochar yield. Therefore, more research is needed on laboratory scale pyrolysis, especially regarding the biomasses used in the research.

Biomass type, biochar production method and pyrolysis are effective on the physicochemical and biological properties of biochar. At high pyrolysis temperatures, the carbon content of the biochar increases and after 400 to 450 °C biochar with high thermal stability are produced (Sun et al. 2014). In the pyrolysis process, while the lignin content of the biomass is the main component responsible for the formation of biochar, cellulose and hemicelluloses mostly contribute to the formation of volatile compounds (Maia et al. 2011).

The ratios of C, H, O, N and S compounds of the materials are determined by ultimate analysis in the literature. These analyzes reveal the ratios of the elements in the substance and provide the opportunity to compare the raw materials to determine the heating values of the raw materials. Physicochemical analysis results of the biochars obtained from agricultural wastes in our study are given in Table 3.

According to the results, with the increase of pyrolysis temperature and heating rate, the carbon (C) contents of some biochars increased and some decreased. Considering all pyrolysis temperature levels and heating rates it was determined that the highest C content was obtained from vineyard pruning biomass, and the lowest biochar yield was obtained from tomato biomass. While the C content of biochar increased with the increase in pyrolysis temperature, the highest increase was realized at 20 °C/min when the heating rate was considered (Fig. 1c-d). In addition, the highest C content was obtained in VPB_{400-10} with 72.52% values.

Considering all pyrolysis temperature levels and heating rates it was determined that the highest H content was obtained from vineyard pruning biomass, and the lowest H content was obtained from tomato biomass. H content of the biochars clearly decreased with the increase in the pyrolysis temperature and heating rate (Fig. 1e-f). The highest decrease was observed in TB_{500-5} with the values of 1.68% (Table 3). Chen et al. 2016 reported that the H/C ratios in experimentally produced biochar at different pyrolysis temperature values decreased with increasing temperature. The researchers stated that this result is due to the conversion of unsaturated carbons in sugars and carbohydrates of biomass, which are difficult to hydrolyze and decompose by microorganisms, to a relatively stable C with higher aromaticity and saturation in biochar.

Considering all pyrolysis parameters, the highest N content was obtained in carnation biochar, and the lowest N content was obtained in wheat straw biochar. The minimum N content was obtained in the WSB_{500-10} with a value of 0.562% (Table 3). In addition, the increase in heating rate caused a net decrease in the N content of biochar. The highest biochar N content was obtained at 400 C pyrolysis temperature (Fig. 1g-h).

Under all pyrolysis parameters, the highest S content was obtained in tomato biochar, and the lowest S content was obtained in vineyard pruning biochar. The maximum S content was 0.597% in TB_{500-5} and the minimum S content was 0.010% in VPB_{400-5}. No S was detected in VPB_{300-20} (Table 3). On the other hand, the increase in pyrolysis temperature caused an increase in the sulfur (S) content of biochar. In the effect of heating rate, the highest biochar S content was obtained at 20 °C min^{-1}. (Fig. 2a-b). Dhyani and Bhaskar (2018) have been reported that according to the ultimate analysis results of the biochars obtained from the pyrolysis of 29 different agricultural wastes the C, H, N and S contents of biochars ranged between 41 and 90%, 0–5%, 0.17–16% and 0–2%, respectively.

Soil pH, which is an expression of soil acidity, is one of the most important soil fertility parameters. The best ideal soil pH in plant production is 6.5–7.5. At high or low pH levels, the availability of some nutrients in the soil increases, while others decrease, and accordingly, different problems are encountered in plant production (Neina 2019). The bioavailability of phosphorus decreases at high or low pH.

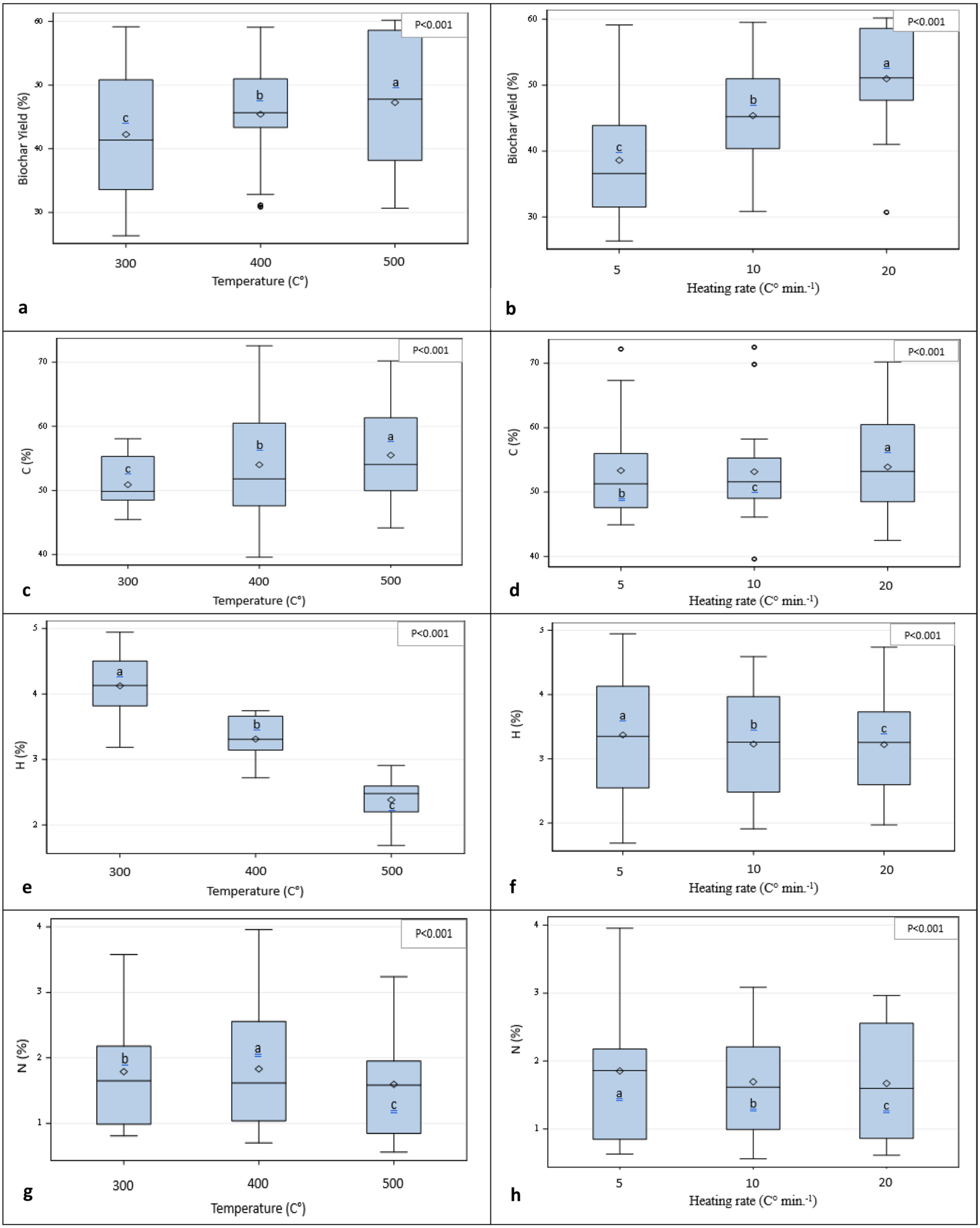

Fig. 1 Effects of pyrolysis parameters on biochar properties. a-b: Biochar yield, c-d: Carbon (C) content, e-f: Hydrogen (H) content, g-h: Nitrogen (N) content Duncan test, $P<0.05$. $n=3$. The differences between values not shown with the same letter are significant

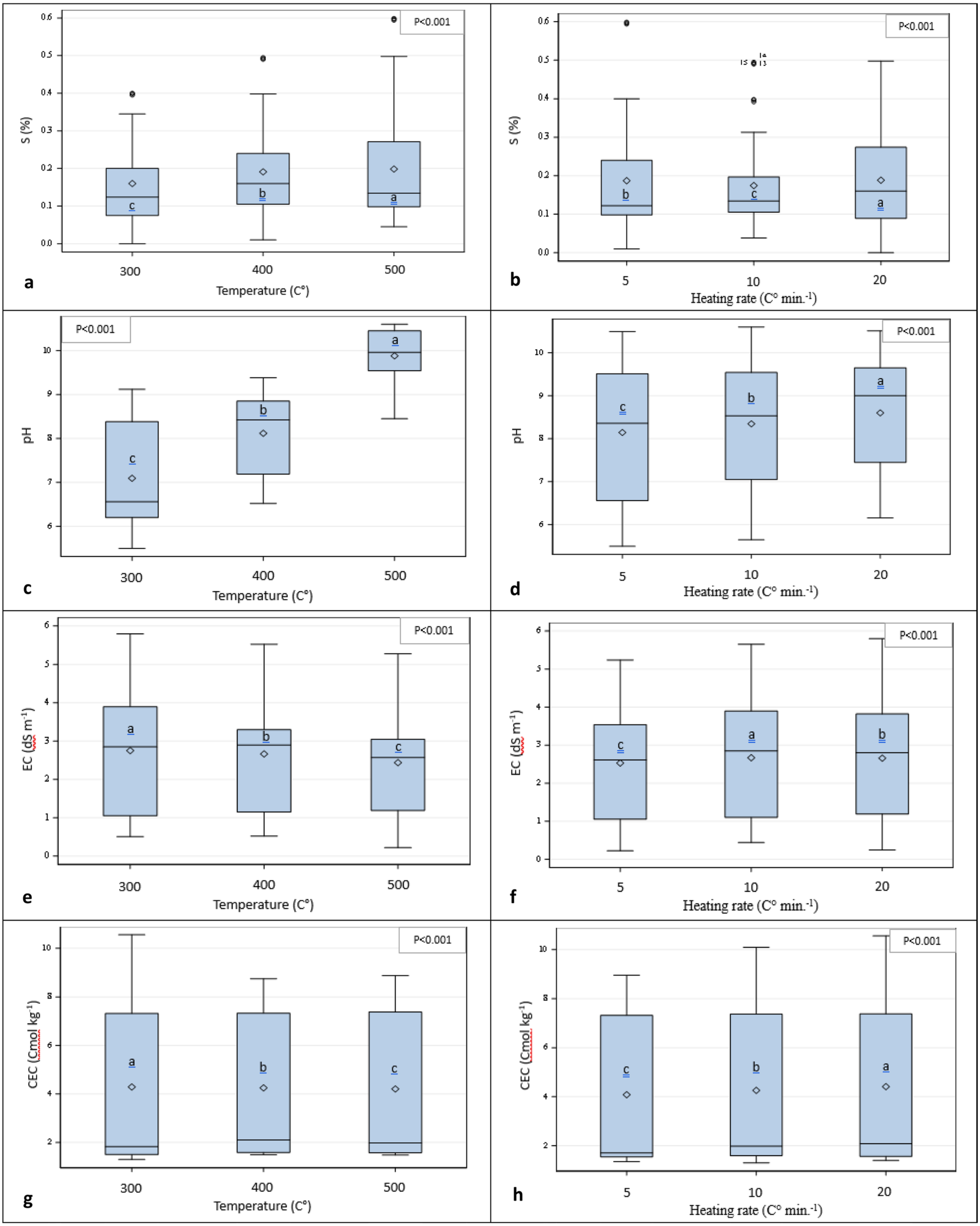

Fig. 2 Effects of pyrolysis parameters on biochar properties, a-b: Sulfur (S) content, c-d: Acidity and alkalinity (pH) level, e-f: Electrical conductivity (EC) level and g-h: Cation exchange capacity (CEC) Duncan test, $P<0.05$. $n=3$. The differences between values not shown with the same letter are significant

Phosphorus forms strong bonds with Al3 + and Fe3 + ions in acid soils (Tian et al. 2016) and with Ca + 2 ions in alkaline soils (Preisner et al. 2020), thereby significantly reducing its agricultural chemical efficiency. In addition, Stávkova and Maroušek (2021) reported that biochar captures the most valuable P for plant nutrition, mostly in the form of calcium phosphate (CaP), providing sufficient evidence to meet the P requirement at the lowest possible cost and increase the agronomic value of P in plant nutrition.

The changes in pH of biochars obtained from different biomasses at different pyrolysis temperatures and heating rates are given in Table 3. Considering all pyrolysis parameters, the highest pH value was obtained in tomato biochar, and the lowest pH value in vineyard pruning biochar. According to the data the pH values of biochars increased with an increase in the heating rate, especially the increase in the pyrolysis temperature (Fig. 2c-d). Differences in pH show significant variability depending on the biomass difference and pyrolysis parameters. pH value of biochars obtained from tomato wastes reached pH 10 at the highest pyrolysis temperature (500 °C) and heating rate (20 min). The use of this high pH biochar on alkaline soils rich in lime may cause significant problems in terms of plant nutrition. Thus, the use of biochar in agricultural soils with high lime content (Aluviyal-Calcaric fluvisol; Red Mediterranean-Chromic luvisol; and Red Brown Mediterranean-Haplic luvisol), which is widely distributed in the region where the study was conducted, may pose a risk in terms of high pH. However, it may be more suitable for use as a remedial material in acidic soils or other low pH growing media (such as peat). Several researchers suggested that biochars could be used to replace lime application (Prasad et al. 2018).

The pH of biochar is an important property for agriculture in terms of applications such as soil remediation. Increasing pH in biochar is a direct consequence of increasing alkalinity and for pyrolysis temperatures above 500 °C, the maximum achievable pH is usually in the range 10–12 (Weber and Quicker 2018). Soil pH has increased in most studies reporting effects of biochar additions on soil pH (Brockhoff et al. 2010). Crude biomass is typically slightly acidic or slightly basic, with pH values generally ranging from 5 to 7.5. The increase in the pH values of biochar is generally directly proportional to the increase in the degree of carbonization (Quicker et al. 2016). The pyrolysis temperature is the most important factor on the pH values of biochars. In addition, the pH value of biochar increases with the increase in heating time. However, this effect becomes significant only in the first 5–10 min of carbonization (Conti et al. 2014). This is an indication that most of the acidic reacting functional groups are released in the early stages of the carbonization process. The effect of heating rate on pH is generally evaluated limited and small in terms of practical (Angın, 2013).

Electrical conductivity (EC) is an indicator of salinity and is an important property to be determined before the application of organic resources to soils. The ideal soil EC value in plant production is 2–4 dS m^{-1}. Many plants are adversely affected above this value. In addition, soils with an EC value above 4 dS m^{-1} are considered saline soils (Qadir et al. 2007). In our study, the EC values of the obtained biochars ranged between 0.23 and 5.62 dS m^{-1}. In all pyrolysis parameters, the highest EC value was obtained in tomato biochar, and the lowest EC value in vineyard pruning biochar (Table 3). The increase in pyrolysis temperature level caused a decrease in biochar EC value. The effect of heating rate was irregular, and the highest EC value was determined at a heating rate of 10 °C min^{-1}. (Fig. 2e-f). According to the results obtained, the higher EC values of biochars belonging to tomato, carnation and banana biomass may be since these plants were grown under intensive fertilization programs, especially in greenhouse production. It is stated that the EC level of biochar may be increase due to the pyrolysis temperature level and the amount of inorganic ash of the biochar (De Luca et al. 2015). This difference in biochar conductivity may be also likely related to the sand/soil contained in the wastes during physical collection (Rehrah et al. 2014). Soil EC is an index used to identify site-specific management zones as it is highly correlated with crop yield (Li et al. 2008). The importance of soil EC in crop production is related to the number of ions present in the plant root zone. Crops have their own optimal EC value, and this depends on environmental conditions. High EC increases the osmotic pressure of the soil environment, making it difficult for the plant to absorb water and nutrients. Very low EC levels in the soil limit plant growth due to nutrient deficiency, while very high EC levels inhibit plant growth due to salinity stress (Ding et al. 2018). There are many risks in agricultural production and sustainability, and the management of these risks is very important (Prokopchuk et al. 2018). On the other hand, there are many factors that can negatively affect the fertility levels of soil, and one of them is the increase in soil EC level. Considering the EC values of the biochars, it is seen that biochars obtained from wastes other than tomatoes may not contain any risk in terms of soil fertility and plant production. Biochar obtained from tomato and carnation wastes with high EC levels (5.23–5.30 dS m^{-1}) may be increase the osmotic pressure of the soil, causing a decrease in soil water availability and thus a negative effect on plant water consumption.

Cation exchange capacity (CEC) is the number of exchangeable cations (e.g. Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, and NH_4^{+}) a material can hold (Lee et al. 2010). This property is a result of the attractiveness of the cations on the negative surfaces of the material and is used to reveal the fertility status of the soils. Therefore, CEC is directly related to the surface structure and surface area of the material with functional groups that provide surface charge. Biochar, which has a higher CEC value, has a higher effect on soil fertility. As a matter of fact, depending on the high CEC value, more plant nutrients will be retained in the soil, thereby increasing soil productivity. It is generally, the CEC values of biochars depend on the nature of their origin biomass. It is stated that biochars obtained from lignocellulosic agricultural materials have higher CEC values than biochars obtained from urban solid wastes, and the high carbon and low ash content of agricultural wastes are effective in this result. On the other hand, some researchers stated that the effect of pyrolysis temperature on the CEC is quite small (Inés et al. 2018).

In our study, the CEC values of biochars ranged between 1.32 and 10.54 cmol kg^{-1}. In all pyrolysis parameters, the highest CEC value was obtained in carnation biochar, and the lowest CEC value in wheat straw biochar (Table 3). Considering the data for all biomasses, the increase in pyrolysis temperature caused a decrease in biochar CEC values and the increase in heating rate caused an increase in CEC values (Fig. 2g-h). The high CEC level of biochar obtained from carnation and tomato wastes shows that they can be the two most important additives in improving the fertility capacity of the soil. Carnation biochar, which has a lower EC and higher CEC level than tomato biochar, can be more effective in terms of soil fertility. In addition, as well as improving soil fertility, obtained biochars with high CEC values can contribute to the prevention of atmospheric and environmental pollution, thanks to the retention of carbon, heavy metals and pesticides in the soil (McCarl et al. 2009). It has been reported that carbon dioxide and methane emissions were decreased with biochar-amended soil, and these can be attributed to carbon sequestration (Ibrahim et al. 2017). Cation exchange capacity which is an important property of biochars for remediation of metal-contaminated soils (Kavitha et al. 2018).

The effectiveness of biochar in agricultural environments is controlled by various factors such as pyrolysis conditions, feedstock, soil type and biotic interactions (Kavitha et al. 2018). The use of biochar in agriculture or non-agriculture offers many market opportunities. The extent to which these markets can be developed depends on many factors related to the cost of biochar production relative to existing alternatives, as well as the properties and relative effectiveness of biochar for its intended use. For example, biochar contains Ca and Mg, which can significantly increase soil pH, providing significant financial benefits by saving on liming (Sheng and Zhu 2018). On the other hand, the black color of biochar allows the soil to warm up more quickly, resulting in early crop production. In this way, more profit will be obtained by saving on the use of pesticides (Bamminger et al. 2016). In addition, it is reported that biochar can be economically viable if the market price of biochar is low enough to allow the farmer to make a profit (Galinato et al. 2011). Contrary to all these, some studies have reported that biochar causes a decrease in the thermal diffusivity of the soil, in worm and/or fungus growth, and root biomass of some plants (Zhao et al. 2016). Furthermore, weed problems have been reported with biochar applications (Safaei Khorram et al. 2018) and the ability of biochar to absorb pollutants is selective (Denyes et al. 2016).

4.3 SEM Analysis

The size, shape and structure of biochar are an important measure in terms of biochar morphology. This property is usually obtained as a reflection of the biochar surface area and differs according to the pyrolysis temperature and the type of biomass. SEM images of biochars obtained by pyrolysis in our study are given in Figs. 3 and 4.

SEM images show that large structural differences occur in biochar morphology. It was observed that with the increase in pyrolysis temperature and heating rate, more net geometric shapes and pores were formed in biochar obtained from tomato, carnation and vine pruning wastes (Fig. 3).

In the biochar obtained from vineyard pruning wastes, it was observed that many net pores with honeycomb or rib-like form were formed with the increase in pyrolysis temperature level and heating rate. On the other hand, in some image analyzes, it was observed that the structures turned rib-like with the increase in pyrolysis temperature and heating rate, and the presence of various honeycomb formations observed in these structures (Fig. 3e). Rod-like porous structures were formed in carnation biochar (Fig. 3ı). In addition, point openings were formed in the structure of some pores and polyp (bubbly)-like structures were observed on the inner surfaces of the pores (Fig. 3g). Lehmann et al. (2011) stated that in SEM images of biochars obtained from the pyrolysis of biomasses with low lignin content and high volatile matter content, formations with tarry edges or surfaces occur and formations in the form of sediment are observed on these surfaces. As a matter of fact, similar formations were observed in SEM images of biochars obtained from tomato and carnation biomass, which had these criteria in our study.

In biochar obtained from banana waste, the presence of filamentous structures in the main pores is striking (Fig. 4a). It has been determined that these formations occur at low heating rate and pyrolysis temperature values, and at high heating rate and pyrolysis temperature levels, the porous structures formed have more regular and clear geometric shapes (Fig. 4b). Indeed, Fu et al. (2009) reported that the

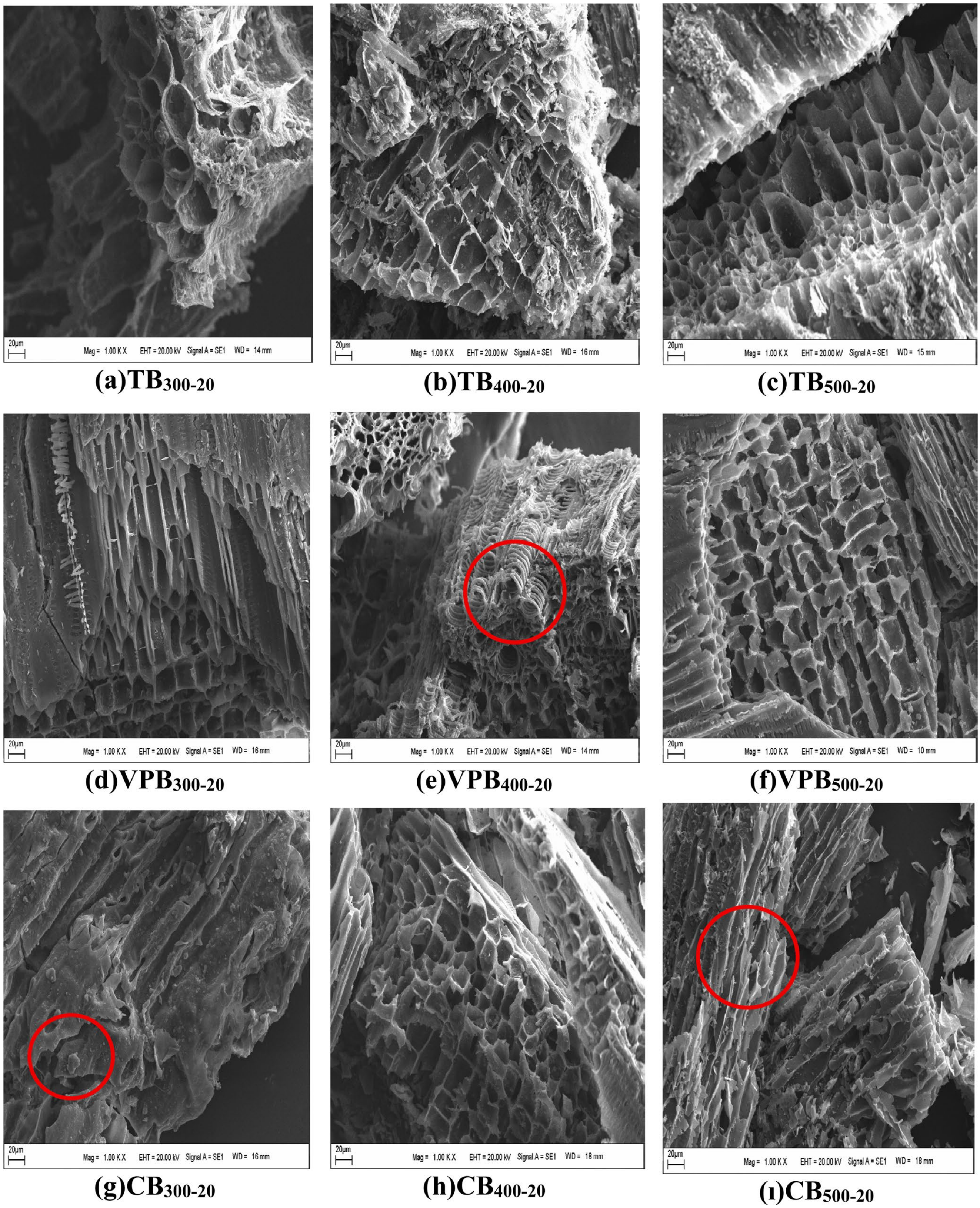

Fig. 3 Differences in the pore structure of tomato (TB), vine pruning (VPB), and carnation (CB) biochar depending on changes in pyrolysis parameters as observed under a scanning electron microscope (SEM). (e) Honeycomb or Rib-like structure in VPB_{400-20}; (g) Polyp (bubbly)-like structures in CB_{300-20} and (ı) Rod-like structure in CB_{500-20} (The different structural forms in biochars are shown within the circle)

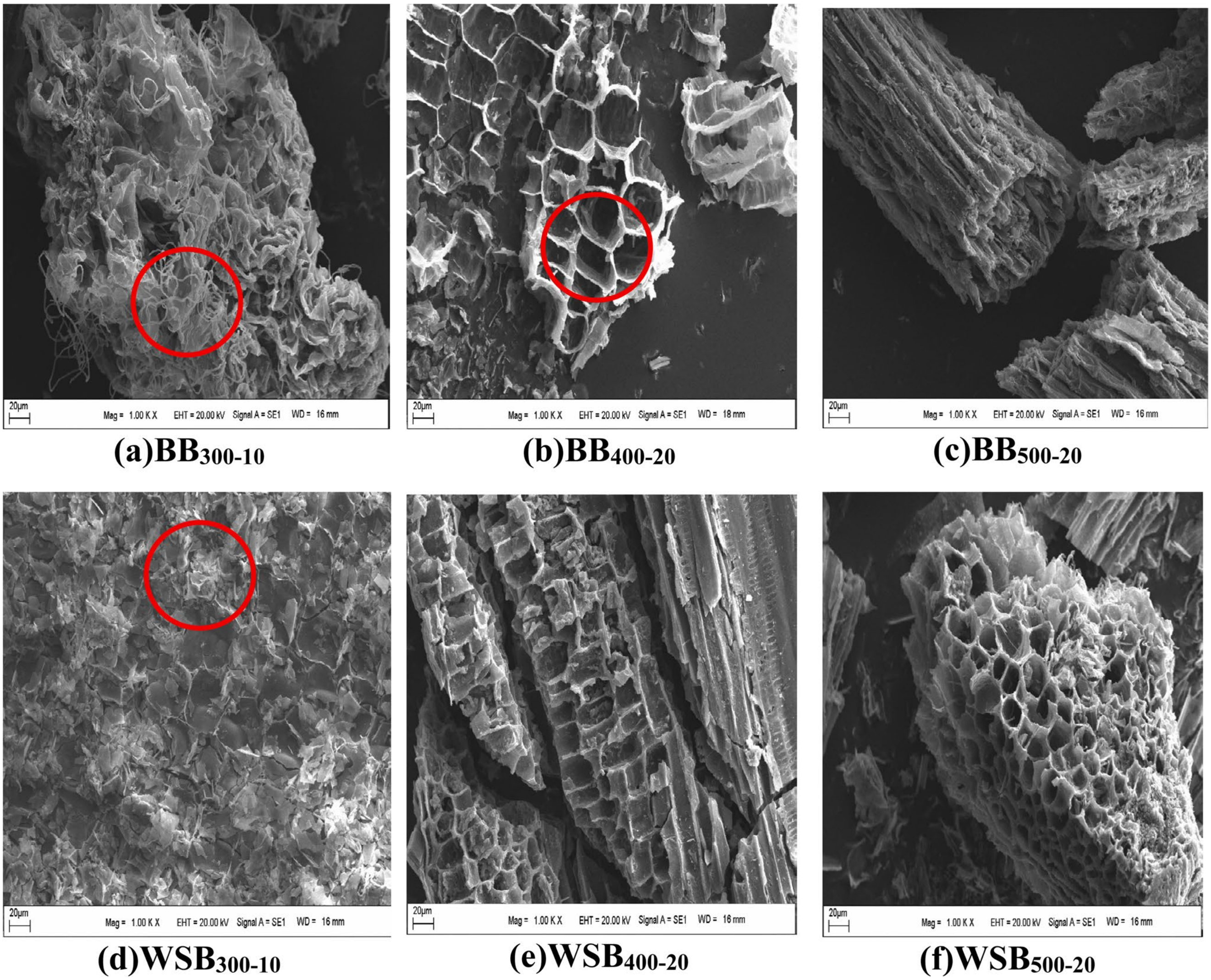

Fig. 4 Differences in the pore structure of banana (BB) and wheat straw (WSB) biochar depending on changes in pyrolysis parameters as observed under a scanning electron microscope (SEM). (a) Filamentous structures in $BB_{300\text{-}10}$; (b) Regular and clear geometric structure in $BB_{400\text{-}20}$; (d) Brittle and unclear pore structure in $WSB_{300\text{-}10}$ (The different structural forms in biochars are shown within the circle)

thermal degradation of chemical bonds and the melting of some compounds can break the chemical bonds, and the structural structure of the original materials can become a larger pore structure. In also some studies on this subject, it has been reported that high pore numbers are obtained in biochars obtained at high pyrolysis temperature values (Suman and Gautam 2017). In wheat straw biochar, it was determined that a brittle and unclear pore structure at low pyrolysis temperature and heating rate, as well as a more occur porous structure with honeycomb or skeletal form with the increase in pyrolysis temperature level and heating rate (Fig. 4d).

SEM images of biochars reveal that different pyrolysis temperature and heating levels produce significant changes in the surface morphology of the crude biomasses. Also, depending on the increase in the pyrolysis temperature level and the heating rate, the formation of more and prominent porous structure in biochar is very important for soil fertility. Biochar with such a structure will be very effective in the retention of water and plant nutrients in the soil in a long time. For example, it has been reported that in wheat culture, biochar addition at 10% in combination with urea improved agronomic efficiency of N by 63% (Abbas et al. 2017), on the other hand P-loaded biochar at 30 g kg^{-1} improved the bioavailability of P (Ahmad et al. 2018). In the SEM images, it is seen that the raw biomasses, which have a non-porous integrated structure, are transformed into a porous and cracked surface profile structure because of pyrolysis processes. Similar results and evaluations have been expressed in various studies. Swapan et al. (2017) has been reported that biochars obtained from tomato wastes at different pyrolysis temperature levels (450, 600 and

900 °C) and at 30 °C/min for 2 h have a porous spongy structure at low temperature. In addition, Ayala-Cortés et al. (2019) reported that the pore widths formed in biochar ranged from 1 µm to 10 µm. On the other hand, in the biochar SEM images obtained because of the pyrolysis of some biomasses, smooth, flat or nearly flat surface formations were observed. Mary et al. (2016) reported that the flattening of fracture surfaces by volatile hydrocarbons during the pyrolysis process is effect in these formations on biochar surfaces.

5 Conclusions

Biochar has many properties that can positively affect soil fertility capacity. From the perspective of sustainable agriculture and soil fertility, biochar may have a bright future in the long term. Biomass source, pyrolysis conditions, application level and economic viability are critical variables in the evaluation of biochar. Based on the findings, the increase in biochar yield, especially with the increase in pyrolysis temperature, heating rate and residence time, reveals that more studies at laboratory scale pyrolysis should be done on this subject. Considering the properties of biochars derived from different agricultural wastes, their effectiveness in improving the fertility capacity of soils may vary from soil to soil. It was envisaged that the use of biochars with increased alkalinity (high pH value) under high pyrolysis temperature, heating rate and residence time, especially in acidic soils, may be more important and effective in terms of improving soil fertility. Due to the high electrical conductivity (EC) levels of the some biochars are likely to pose a risk in terms of plant production. In contrast, considering the many advantages that biochar can have in many aspects such as soil fertility, plant growth and yield, agricultural disease, removal of pollutants and reduction of greenhouse gases, this way of utilizing agricultural wastes could offer significant industrial opportunities. In summary, biochar may not play a positive role in improving the fertility potential of all types of soils. Therefore, the biochar application procedure to be established to improve the fertility potential of soils should be determined considering soil characteristics, differences in environmental conditions and especially the limiting properties of biochar on soil fertility.

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Declarations

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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