



Opportunity for sustainable biomass valorization to produce biochar for improving soil characteristics

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Abstract

Biochar, a byproduct obtained from valorization of waste biomass, is utilized in environmental management to restore or improve soil functions where it alters chemical, physical, and biological processes. Therefore, in this study, vastly available oak sawdust was evaluated as a potential feedstock for biochar production with the aim to identify the influence of carbonization conditions on biochar characteristics. Slow pyrolysis with temperatures ranging from 400 to 600 °C and residence times from 15 to 120 min was performed. The feedstock material and resulting biochar were characterized for physical, chemical, and hydraulic properties that are significant for their ability and characteristics as a soil amendment. The pH, BET surface area, carbon content, nutrient content, alkaline functional groups, and water holding capacity increased with increasing pyrolysis temperature and residence time while biochar yield, O/C ratio, and acidic functional groups decreased. Although the effect of holding time on biochar physicochemical properties is less significant than that of temperature, it is an essential parameter to obtain desired biochar properties. It can be concluded that pyrolysis has the potential to add value to regionally available oak sawdust on a sustainable basis and help to restore or improve essential soil functions.

Keywords Oak sawdust · Biomass wastes · Pyrolysis · Biochar · Soil amendment

1 Introduction

Production of value-added outputs from biomass residues is a sector of great interest as it can provide benefits from an

This paper is dedicated to our dear colleague Basak B. Uzun, who tragically deceased during the drafting of this manuscript.

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environmental point of view. The transformation of biomass into a carbon product is becoming increasingly popular to provide a sustainable material for soil remediation [1]. Especially woody biomass, such as agricultural and forestry by-products, can be utilized as a renewable and sustainable source of biochar. Oak sawdust as a biowaste from forestry or timber industry is traditionally used as a solid fuel, but it is also an essential feedstock to produce biochar for environmental engineering [2].

Biochar is a carbon-rich, solid product of the thermochemical conversion of biomass that can be applied as a soil amendment to enhance or restore soil functions and fertility [2, 3]. The pyrolysis process represents thermal conversion of biomass in an environment of limited oxygen while representing a sustainable transformation of biomass to biochar and biofuels [4, 5]. Because of its prominent physicochemical properties, biochar has a wide range of potential applications in various areas, such as soil conditioning, soil remediation, waste management, climate change mitigation, carbon sequestration, catalysis or activated carbon with specific materials, and energy production [6–9]. Biochar has the potential to restore soil functions as a catalyst for microbial activity and nutrient cycling [10]. By variation of pyrolysis conditions and feedstock selection, environmental properties of biochar, such as carbon content, aromaticity, pore structure, nutrient

content, pH, water holding capacity, and functional groups can be altered to address specific issues at a given site in any environmental setting [11].

In general, there are two main types of pyrolysis processes: slow and fast pyrolysis, depending on the residence time, temperature, and heating rate. Pyrolysis process results in both primary and secondary reactions such as dehydration, depolymerization, cleavage of glycosides, decarboxylation, decarbonylation, and debranching [12]. The primary cracking reactions lead to the release of volatile components including water vapor, CO₂, CO, and CH₄ from the biomass structure. The secondary reactions support the formation of heavy molecules such as tar and char with increasing pyrolysis temperature. The physicochemical properties of biochar, such as surface characteristics, organic and inorganic composition, stability, and nutrient and water adsorption abilities, are mainly determined from feedstock properties and pyrolysis parameters. In particular, the driving factors are biomass characteristics and composition, such as lignin content and mineral content [13–16], pyrolysis temperature [13, 17–22], residence time [15, 23], and heating rate [10].

Among these parameters, the pyrolysis temperature is the most significant one in terms of resulting biochar properties, determining its suitability for soil amendment by altering reaction mechanisms and ecological recalcitrance [24, 25]. In general, biochar produced at high pyrolysis temperatures (> 600 °C) is characterized by high pH, large surface area (porosity), and higher aromaticity. On the contrary, lower process temperatures and slow heating rates result in higher char yield and greater amounts of volatiles and oxygen, and thus, it provides high electrical conductivity and cation-exchange capacity [7, 26–28]. These properties provide higher adsorption capacity and larger potential for stable carbon in the soil [29, 30]. Higher condensed aromatic C contents result in a higher cation-exchange capacity for biochar as beneficial cations can interact within condensed aromatic carbon pores [31]. In addition, increasing the pyrolysis temperature leads to the reduction of easily degradable components [26, 32] and loss of acidic functional groups. However, fractions of degradable carbon can be desirable in certain application scenarios for stimulating microbial activity and enhancing nutrient cycles. In addition, biochar produced at low temperatures contains more unstable organic substances such as aliphatic and cellulose-type structures that promote microbial activity in soil [6, 33, 34].

Residence time is an important carbonization condition influencing biochar physicochemical properties. Char yield and volatile matter content decrease with time and remain stable after around 1 h. Conversely, the ash content increases with residence time. Moreover, at low (300 °C) or high (700 °C) pyrolysis temperatures, the residence time is more effective on ash, volatile matter, and fixed carbon than in the moderate temperature range of 450–600 °C [35]. An increase in

residence time significantly increases the stability of biochar produced at low temperature (350 °C) [36]. Long residence times produce more carbonized biochar, with a larger fraction of recalcitrant carbon and more resistance against microbial decomposition [37]. However, a clear judgment between the effects of residence time and temperature on biochar properties is difficult [38].

In this study, sawdust from oak (*Quercus* sp.) was used, since it is a widely available feedstock in many Mediterranean and sub-Mediterranean regions and especially in Turkey. *Quercus* sp. forests cover the largest area in Turkey (~ 6 million hectares, 26.34% of all forest area) [39]. Oak sawdust is a residue of the forestry, timber, and furniture industry. During the typical manufacturing of wood, approximately 12 wt% of sawdust is produced. Due to its firing capacity and similar characteristics with wood, it is used as fuel for combustion furnaces or gasification reactors. However, its calorific value is lower than that of high-rank coal, and therefore, it is normally combusted for only domestic heating purposes after further processes, increasing feedstock costs (pelletizing, briquetting). Upgrading this sustainable feedstock material by pyrolysis to produce a soil amendment with distinct features adds value and can generate additional income in rural areas while addressing specific soil issues and sequestering carbon. Biochar from woody feedstock material, such as oak wood, is considered suitable for soil amendment [32, 40, 41]. The current study is designed to examine and compare biochar key properties that determine its suitability for soil amendment by varying pyrolysis temperature and residence time. The structure and chemical properties of biochar are investigated by using standard analytical and instrumental techniques. The most important properties for soil restoration capability of oak wood-based biochar are discussed in this study.

2 Materials and methods

2.1 Biomass feedstock origin and characterization

Oak (*Quercus* sp.) sawdust was obtained from Bolu, north-western Turkey. This region has large forest resources, and a recent report suggested that only about 50% of the annual increment is harvested at current [42]. Consequently, we assume that the provision of oak feedstock from this region likely increases and can be maintained at sustainable levels in future management scenarios. Untreated sawdust was dried at 105 °C in a laboratory oven for 24 h and sieved to remove large chunks. The analyses were carried out using established procedures presented in Table 1.

The characterization tests were duplicated to ensure the reliability of results, and mean values are presented in Table 2.

Table 1 Characterization methods for feedstock analysis

	Parameter	Method
Proximate analysis	Moisture	EN ISO 712:2009
	Ash	ASTM E1755-95
	Volatile matter (VM)	ASTM D3175-11
	Fixed carbon (FC)	From difference
Component analysis	Cellulose	[43]
	Lignin (acid soluble)	[43]
	Extractives (alcohol-benzene soluble)	ASTM E 1690-08
Ultimate analysis	C, H, N content	Elemental analyzer
	O content	From difference
	Nutrient content	Spectrometer

2.2 Biochar production

Slow pyrolysis was performed in the current study, in order to maximize solid product (biochar) output. A stainless steel fixed bed reactor with 70-mm DI and 350-cm³ volume was used, which has been used in several other studies [54, 55]. A schematic description is provided (Fig. 1). Temperature was

controlled with a thermocouple that was placed inside the reactor during experiments. A proportional–integral–derivative (PID) controller ensured constant pyrolysis temperature during residence time. The reactor was subsequently allowed to cool down.

The pyrolysis experiments were conducted at 400, 500, and 600 °C under constant residence time (30 min) to investigate

Table 2 Proximate, ultimate, component analyses of oak wood and several wood-based biomasses from reference studies

Woody feedstock	Proximate analysis, wt%			Ultimate analysis, wt%					Fiber analysis, wt%			Reference
	VM ^a	Ash ^a	FC ^{a,c}	C ^b	H ^b	O ^{b,c}	N ^b	S	Cellulose ^a	Lignin ^a	Hemicellulose ^a	
Oak wood	78.52	0.99	12.43	46.6	6.4	46.6	0.4	nd	39.25	24.38	26.7	This study
Olive wood	79.6	3.2	17.2	49	5.4	44.9	0.7	0.03	nd	nd	nd	[44]
Pine wood	72.4	6	21.6	52.8	6.1	40.5	0.5	0.09	nd	nd	nd	[45]
Pine pruning	82.2	2.7	15.1	51.9	6.3	41.3	0.5	0.01	nd	nd	nd	[46]
Wood	84.1	0.2	15.7	49.6	6.1	44.1	0.1	0.06	nd	nd	23.15	[47]
Mix sawdust	84.6	1.1	14.3	49.8	6	43.7	0.5	0.02	43.7	28.8	nd	[48]
Mix sawdust	70.4	1.2	18.5	48.4	5	46.3	0.4	nd	nd	nd	22.3	[49]
Olive wood	84 ± 1	3 ± 1	12.9 ± 0.4	50	6.4	41	1.4	nd	nd	nd	nd	[15]
Pine wood	84 ± 1	2.4 ± 0.3	13.0 ± 0.9	47	5.9	47	nd	nd	50.3	23.4	nd	
Poplar wood	81 ± 2	5 ± 1	14 ± 2	45	5.6	48	0.6	nd	49.8	30.3	nd	
Wood mix (pine:spruce 5:95%)	77.2	5.7	17.2	53.7	6.7	33.9	0	nd	48.4	23.5	nd	[50]
Pine wood	73.2	2	21.6	49.5	5.9	44.7	0	nd	41.9	23.1	nd	[36]
Spruce wood	83.5	0.5	16.1	48.3	6.3	44.6	0.4	nd	50.8	27.5	21.2	[41]
Beech wood	85.9	0.4-0.7	13.4	46.9	6.2	45.9	0.3	nd	45.8	21.9	31.8	
Birch wood	78.7	0.3	20.9	48.4	5.6	45.8	0.2	nd	25.7	15.7	40	
Pine wood	88.1	1.1	10.3	nd	nd	nd	nd	nd	45.6	26.8	24	
Soft wood	78.5	0.3-0.4	11.2	46.1	6.6	46.6	0.2	0.1	nd	nd	nd	[51]
Pine wood chips	75.7	2	22.3	50.7	4.8	42.4	0	nd	52	12.6	21	[52]
Blackbutt (wood)	79.5	1.6	18.9	48.9	6.6	44.2	0	0.3	nd	nd	nd	
White oak	nd	2	nd	50.3	6.4	43	0.3	nd	50.4	22.8	14.3	[53]

^a Dry basis

^b Dry-ash-free basis

^c Calculated from difference

nd not detected

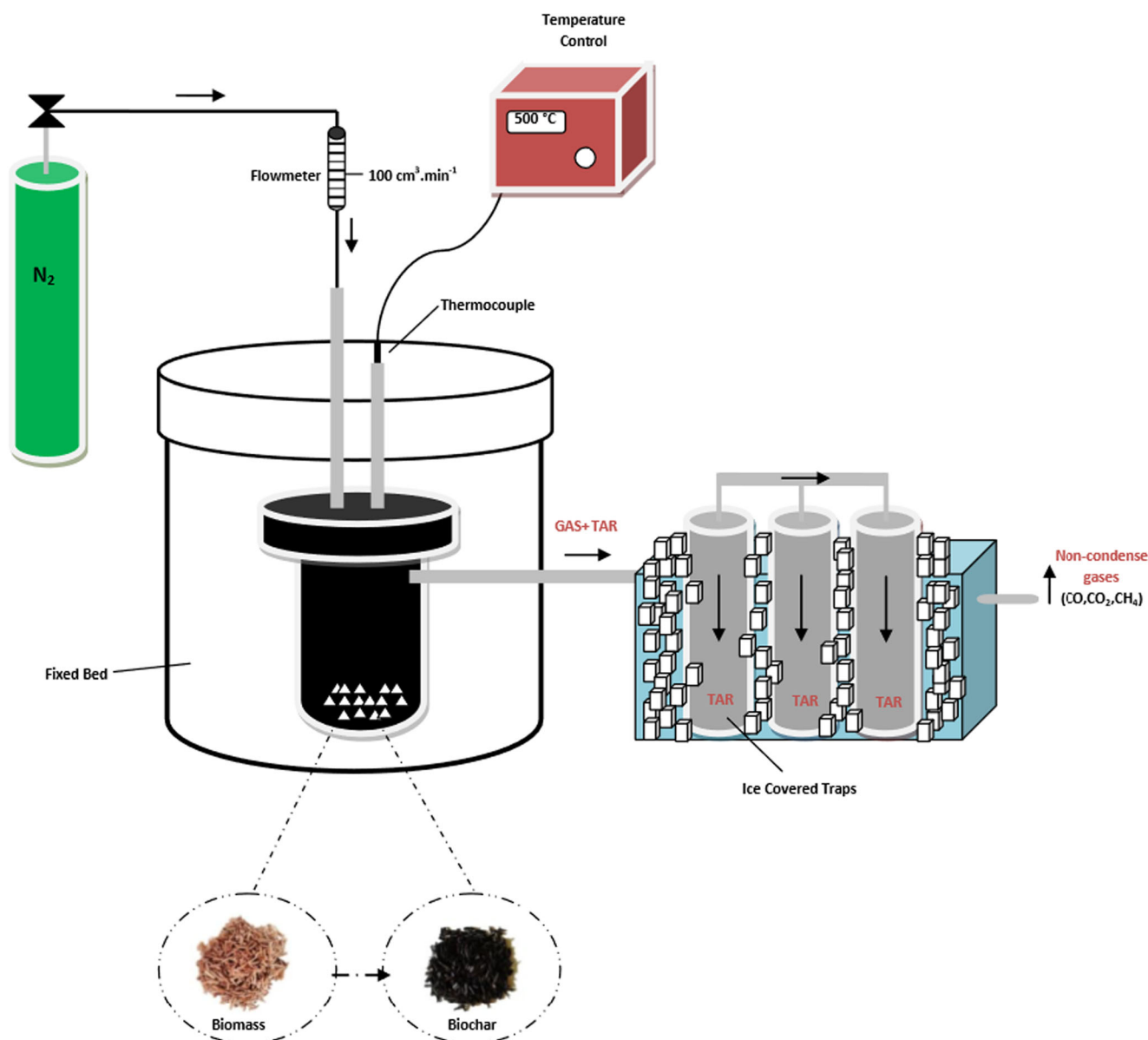


Fig. 1 Pyrolysis unit

the influence of temperature on biochar properties. Nitrogen gas flow rate was set to $100 \text{ cm}^3 \text{ min}^{-1}$ which was controlled by flowmeter during pyrolysis to ensure an oxygen-limited environment. The second group of experiments, aiming at the detection of residence time effects, was carried out at $500 \text{ }^\circ\text{C}$ at residence times of 15, 30, 60, and 120 min. We selected this temperature since it represents an optimal range for bio-oil production, and it was shown that it is an optimal temperature for favorable biochar characteristics for soil amendment [19, 27]. About 20.0 g of oak sawdust ($D_p = 1.63 \text{ mm}$) was used for each pyrolysis batch, and the solid product was collected and stored at room temperature in a desiccator for further analysis. Each pyrolysis experiment was performed at least three times, and the average yields were calculated to confirm the reproducibility of the results.

2.3 Characterization

2.3.1 Chemical composition analyses

The proximate analysis of oak sawdust biochar was performed according to the ASTM D1762-84 standard method. We used a CHN elemental analyzer for ultimate analysis. The total nutrient content of biochar was assessed by means of ICP-OES. The biochar samples were digested with 6 mL concentrated HNO_3 , 2 mL H_2O_2 (30%), and 0.4 mL concentrated HF in a 45-mL Teflon cylinder vessel in the microwave oven according to standards DIN 22022-2, DIN 22022-7, and DIN EN ISO 17294-2/DIN EN 1483 [56]. The filtered digest was analyzed for the total concentrations of K, Ca, Mg, Na, Al, and Fe.

2.3.2 Pore structural characteristics

The true density (ρ_s) is determined with a He pycnometer (Quantachrome Instruments, USA, UltraFoam™1200e). Bulk density was determined according to standard ASTM E 873-82. The BET surface area (S_{BET}) of biochar samples was determined by N_2 adsorption at 77 K using a Quantachrome Instruments (USA), Autosorb 1C analyzer. Prior to the experiment, the samples were degassed at 130 °C. Total pore volume (V_t) was obtained at $P/P_0 = 0.95$. The particle density (ρ_p) and porosity (ε_p) were calculated from the equations below [57, 58].

$$\rho_p = 1/(V_t + 1/\rho_s) \quad (1)$$

$$\varepsilon_p = \left(\rho_p / \rho_s \right) \quad (2)$$

The porous structure was monitored by scanning electron microscopy (SEM) using a Zeiss-SUPRA 50 VP (Carl Zeiss Microscopy GmbH, Germany) at 15 kV.

2.3.3 Electrochemical surface characteristics

The pH of biochar was measured in 0.1 M KCl (1:20, v:v) with a pH meter (Sartorius PP-20, Germany) after the slurry was mixed at room temperature for 20 min. The surface functional groups were determined using a titrimetric method. The surface acidity or basicity (mmol.g^{-1}) was calculated from the amount of acid or base retention on biochar [59, 60]. To determine exchangeable cations, biochar was mixed with deionized water for 24 h. Subsequently, the solutions were filtered through 0.45- μm filter paper and Ca^{+2} , Mg^{+2} , K^{+1} , Na^{+1} , Fe^{+2} , and Al^{+3} contents were measured with ICP-OES. The cation-exchange capacity was calculated based on the amount of cations in cmol.kg^{-1} [61].

2.3.4 Hydraulic properties

The moisture content of biochar samples was determined according to ASTM D 2016-74. To determine the water holding capacity of biochar samples, biochar was soaked with deionized water in a glass column for 24 h [62]. The mixture was vacuumed at 0.7 bar for 10 min. After removing excess water, the moist biochar samples were weighed. To obtain water-free samples, the glass column was settled in the oven at 40 ± 2 °C until reaching a constant mass [56]. The amount of water retained by biochar was defined as the difference between the biochar weight after soaking and the biochar weight after oven drying. The water holding capacity (WHC) was calculated according to Eq. 3:

$$\text{WHC (\%)} = \left[\frac{\text{water retained (g)}}{\text{biochar mass (g)}} \right] \times 100 \quad (3)$$

3 Results and discussion

3.1 Feedstock properties

The properties (fiber components, proximate, ultimate analyses) of oak sawdust feedstock are presented in Table 2. Oak sawdust contains a large amount of volatile matter (78.52 wt%) and has a low ash content (less than 1%) indicating the suitability of this feedstock material for biochar production [41]. The volatile matter and C content of oak wood were the lowest, while ash and fixed carbon content were higher than general. The ash content of pine, olive, and poplar wood is in the range of 2 to 6 wt%, whereas other samples have relatively low ash contents. Several studies which used oak wood as feedstock indicated that the ash content is below 1 wt% [41]. The ultimate analysis revealed high contents of carbon (46.57 wt%) and oxygen (46.55 wt%) similar with other specific woody feedstocks which have 45–50% C and 40–45% O. In general, cellulose content of wood-based biomass is in the range of 25.7 to 52 wt% while lignin content is between 12.6 and 30.0 wt% (Table 2). Oak sawdust also shows a similar trend with 39% cellulose content. The main elements relevant for soil nutrient provision in biomass are Ca, K, and Mg, where a high Ca supply is typical for oak [63]. The nutrients in oak sawdust were determined as $0.74 \mu\text{g g}^{-1}$ Na, $5.29 \mu\text{g g}^{-1}$ K, $108.8 \mu\text{g g}^{-1}$ Ca, and $1.81 \mu\text{g g}^{-1}$ Mg.

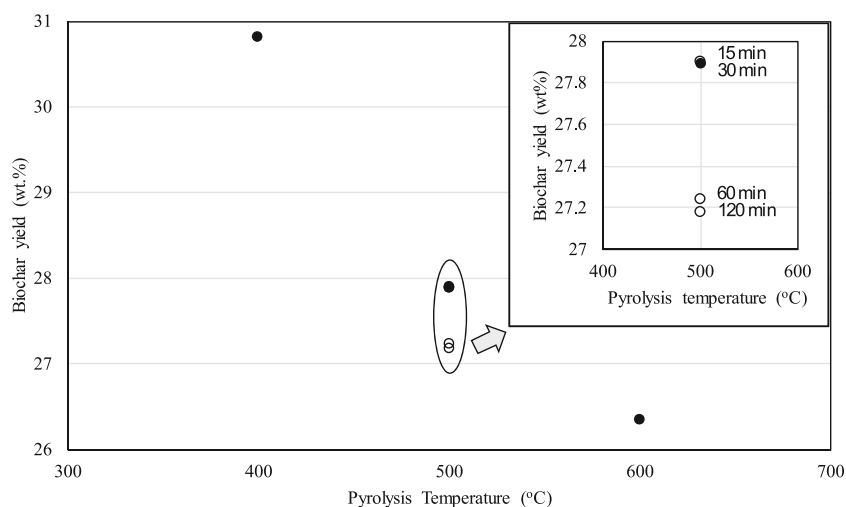
3.2 Biochar yield

Biochar yield was calculated on dry-ash-free basis (Fig. 2). It depends on the two limiting parameters temperature and residence time and decreased with increasing pyrolysis temperature from 30.82 to 26.35%. In addition, biochar yield decreased slightly with increasing residence time from 27.90 to 27.18%. Temperature was found to be more significant than residence time in this regard. Volatile components that include O, H, and N are being progressively removed at higher temperatures with the consequence of increasing mass loss [5]. The rate of mass loss decreased with further increasing temperature as confirmed in other studies [64, 65]. The biochar yield decreased by 2.93% at the temperature range from 400 to 500 °C, while at the range from 500 to 600 °C, it decreased only by 1.54% (Fig. 2).

3.3 Chemical composition of biochar

Results of proximate, ultimate analyses and nutrient elements of oak sawdust biochar samples are shown in Table 3. Pyrolysis temperature and residence time greatly affect the chemical composition of biochar. The increase in pyrolysis temperature and residence time leads to an increase in the ash, fixed carbon and carbon contents, BET surface area, and pH, while volatile matter and H and O contents decrease.

Fig. 2 Biochar yields at different pyrolysis conditions (filled circular marker indicates variation of temperature; empty circular marker indicates variation of residence time at 500 °C)



This is consistent with the reaction mechanism of thermochemical decomposition of biomass.

The content of volatile matter decreased from 15.74 to 5.14 wt% when the temperature increased from 500 to 600 °C. A prolonged residence time of 120 min at 500 °C decreased volatile matter from 15.50 to 5.45 wt%. An increase in temperature reduces the volatile matter content of biochar mainly due to dehydration and devolatilization reactions during pyrolysis [38]. The ash content of the obtained biochar samples increased slightly with the increase of both parameters. The most obvious difference between biomass and the resulting biochar, however, was the loss of volatile

components and aggregation of fixed carbon. In addition, a sharp increase of the C concentration between 400 and 500 °C was observed. The C content increased from 81.64 to 92.35 wt% with a corresponding depletion of O and H. The C concentration of biochar was also increasing with residence time due to ongoing carbonization reactions. Both H/C and O/C ratios represent a proxy for the stability of biochar and correlate negatively with the percentage of aromatic C [66]. The surface chemistry behavior of biochar depends on the oxygen content due to the position of oxygen in the composition of substituted functional groups. These oxygen-containing functional groups play an important role as a driver

Table 3 Proximate, ultimate analyses and nutrient elements of oak sawdust biochar samples

Property	Temperature (30 min residence time)			Residence time (500 °C)			
	400 °C	500 °C	600 °C	15 min	30 min	60 min	120 min
Proximate analysis (%)							
Moisture	5.23	5.17	5.01	5.14	5.17	4.36	4.35
Ash	4.05	4.32	4.75	4.33	4.32	4.55	4.72
Volatile matter	16.79	15.74	5.14	15.50	15.74	5.76	5.45
Fixed carbon ^a	73.93	74.77	85.01	75.03	74.77	85.33	85.5
Ultimate analysis (%)							
C	81.64	89.9	92.35	89.0	89.9	91.08	92.19
H	3.44	2.73	1.81	2.42	2.73	2.71	2.93
O ^b	14.24	6.68	5.05	7.94	6.68	5.27	3.94
N	0.67	0.69	0.79	0.64	0.69	0.97	0.94
Several nutrients (g kg ⁻¹)							
Ca	4.64	5.03	5.76	4.05	5.03	5.17	5.75
K	4.49	5.03	5.35	4.22	5.03	5.02	5.11
Mg	0.13	0.14	0.14	0.10	0.14	0.19	0.21
Na	0.27	0.35	0.28	0.25	0.35	0.27	0.48
Total nutrients	9.53	10.55	11.53	8.62	10.55	10.65	11.55

^{a,b} By difference

for degradation potential [67]. Consequently, biochar produced at 600 °C had the lowest O:C and H:C ratio. In addition, the lower H:C ratio suggests that biochar produced at higher pyrolysis temperatures becomes more aromatic which corresponds to its recalcitrance in soils [68]. The aromatic carbon represents the recalcitrant fraction of biochar, while it also includes aliphatic carbon, carboxyl, and carbohydrate, which are relatively unstable and easily mineralized. These fractions are more common at low pyrolysis temperature [69]. The van Krevelen diagram of the biochar confirms that residence time is less effective for the alterations in elemental composition (Fig. 3). This indicates higher temperatures and longer residence times have a stronger occurrence of C–C bonds compared with C–H and C–O bonds.

In addition to the organic fractions, inorganics in biochar, such as metal compounds or minerals, also affect the agronomic properties. For instance, the presence of carbonates may affect the carbon sequestration capacity via dissolving abiotically under acidic conditions [70]. Likewise, alkaline compounds can influence the mechanism between biochar and soil [13]. The oak sawdust biochar included various nutrient elements that are beneficial for soil fertility. In general, the concentration of each nutrient element increased with increasing temperature and residence time. Residence time was more effective than temperature in increasing Na, Mg, and Ca as these elements show a tendency of thermal decomposition. In terms of nutrient concentration, oak sawdust biochar produced at 500 °C and 120 min residence time exhibited the best conditions.

3.4 Structural properties of biochar

The bulk density of biochar produced at 600 °C was higher than that of 400 °C, indicating a larger volume in relation to mass loss at elevated temperatures (Table 4). The true density

(ρ_s) of biochar increased with temperature, since low-density disordered carbon is converted to higher-density turbostratic carbon [57]. However, the residence time had no significant effect on density. The particle density decreased with increasing pyrolysis temperature and the residence time (Table 4). At high temperature and long reaction time, more porous and less dense biochar was produced. During pyrolysis, the devolatilization of biomass leads to the final pore structure of biochar. S_{BET} increased significantly with increasing temperature and residence time. Biochar obtained at the highest temperature had 244.8-m² g⁻¹ BET surface area and 0.112-cm³ g⁻¹ total pore volume. Furthermore, biochar generated at the highest residence time had the largest BET surface area (368 m² g⁻¹) and hence the highest porosity.

Higher porosity and consequently larger surface area are obtained at higher pyrolysis temperatures. The ongoing degradation of the aliphatic alkyl and ester groups causes the aromatic lignin matrix to be exposed at elevated temperatures. In a similar study, biochar BET surface area, microporous surface area, and total pore volume mainly increased with increasing temperature (300–750 °C) [35]. Biochar produced at very high temperatures ($T > 700$ °C) has better adsorption ability due to its higher surface area and pore volume. While this might be beneficial for certain applications, lower temperatures are more effective for soil amendment, because biochar produced at temperatures of around 400–500 °C exhibits more functional groups and therefore increased CEC [7, 8].

The SEM images of the feedstock material and resulting biochar produced at 600 °C and 30 min residence time confirm little changes from a microscopic point of view (Fig. 4). In terms of BET surface area, the differences are obvious. However, surface morphology of the biochar is similar to the feedstock material. The majority of the macropores on biochar surface resemble the typical capillary structure of

Fig. 3 Van Krevelen diagram for oak sawdust biochar samples

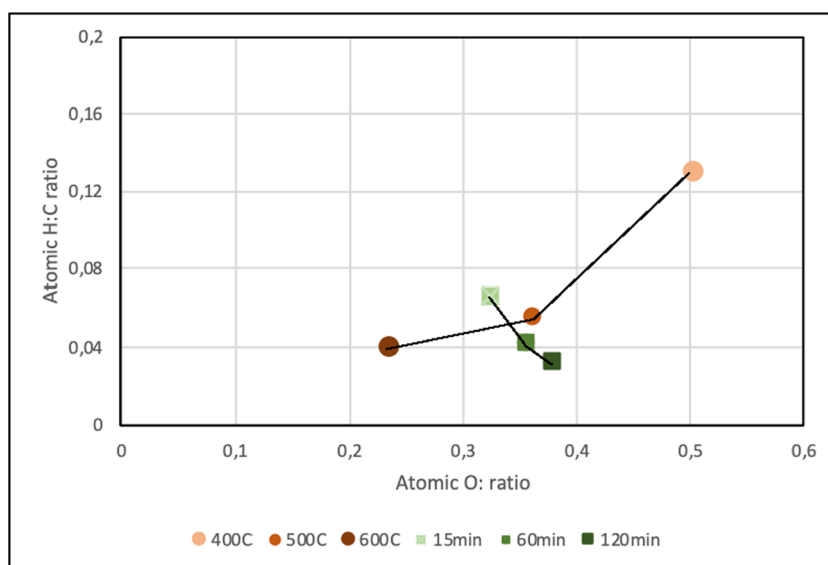


Table 4 Structural properties of biochar produced at different conditions

Property	Pyrolysis temperature (30 min)			Residence time (500 °C)			
	400 °C	500 °C	600 °C	15 min	30 min	60 min	120 min
Bulk density (g cm^{-3})	0.1926	0.1907	0.1954	0.1757	0.1907	0.2036	0.1935
True density ρ_s (g cm^{-3})	1.4301	1.5443	1.6069	1.6356	1.5443	1.6307	1.5647
Particle density ρ_p (g cm^{-3})	1.414	1.339	1.362	1.610	1.339	1.362	1.235
Porosity ε_p	0.011	0.133	0.152	0.016	0.133	0.165	0.211
S_{BET} ($\text{m}^2 \text{g}^{-1}$)	41.9	228.8	244.8	97.7	228.8	277.7	364.8
V_t ($\text{cm}^3 \text{g}^{-1}$)	7.9×10^{-3}	99.1×10^{-3}	112×10^{-3}	9.7×10^{-3}	99.1×10^{-3}	121×10^{-3}	171×10^{-3}

lignocellulosic raw material. The increase in the surface area is mainly due to the formation of micropores on cell walls.

3.5 Electrochemical properties of biochar

The pH increased with temperature and residence time, indicating that biochar produced at higher temperature and residence time included structures that are more alkaline. The pH of the biochar samples ranged from 7.41 to 8.97 (Table 5). This can be related to the increasing ash content at higher temperatures (Cao and Harris, 2010). The main components of ash are salts of alkaline elements (Na, K, Mg, Ca) [70]. Generally, an increase of pH supports the degradation of phenolic-OH groups on the biochar surface, increasing the net negative surface charge, thereby increasing the electrostatic attractiveness [7]. At low temperatures (200–300 °C), cellulose and hemicelluloses decompose and form organic acids that decrease the pH during pyrolysis. The surface functional groups such as carboxylic, lactonic, and phenolics are enhanced during pyrolysis (Table 5), which is also confirmed by other studies [71, 72]. These functional groups support the sorption capacity of biochar [62]. Especially oxygen-containing groups lead to increased water adsorption capacity due to the role of hydrogen bonds in the adsorption mechanism. Hydrogen bonds can occur between oxygen-containing

groups on the biochar surface and the adsorbed molecules [73]. The oak sawdust biochar had more alkaline than acidic functional groups; they represent 2.107 and 0.175 mmol/g at 600 °C, respectively (Table 5). In addition, the acidic functional groups decreased, while the basic functional groups increased with elevating temperature. Among the acidic groups, the carboxylic groups accounted for 25.64–64.71%, lactone groups 23.36–53.3%, and phenol groups 6.3–50.0%.

3.6 Hydraulic properties

The water which is available to plants is adsorbed in soil macro- and mesopores. The main factors that affect the water holding capacity (WHC) of biochar are surface functional groups, total pore volume, porous structure, and surface area [68]. Therefore, the pyrolysis temperature and the holding time are essential parameters that influence the WHC of biochar. The WHC of the obtained biochar samples were 1.16, 1.35, and 1.49 mL g^{-1} for biochar samples produced at 400, 500, and 600 °C, respectively. For prolonged residence times at 500 °C, WHC increased slightly up to 1.39 from 1.12 mL g^{-1} while residence time was changing to 120 from 15 min as a result of the pore formation through volatilization during the long residence time. According to the results, it can be seen that the pyrolysis temperature is more effective than residence

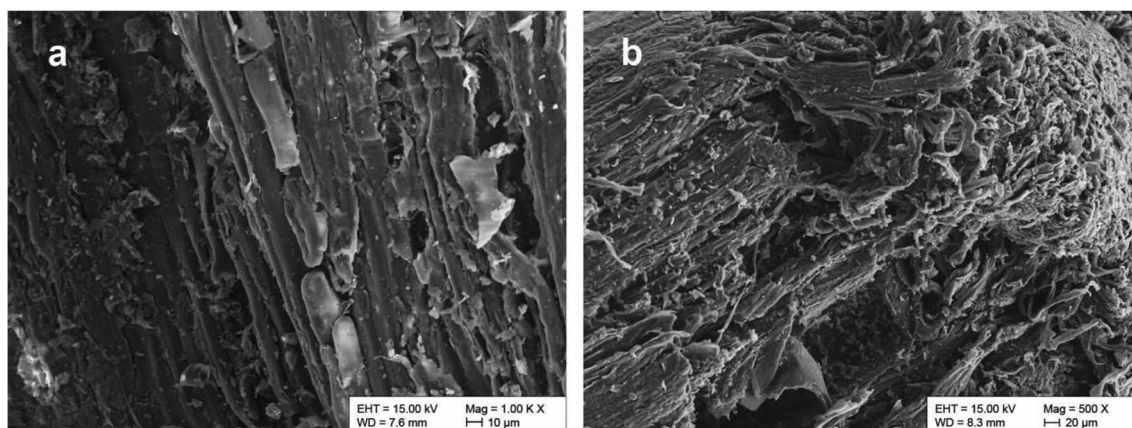


Fig. 4 SEM images of oak sawdust (a) and biochar (b) obtained at 600 °C and 30 min residence time

Table 5 pH and surface functional groups (mmol g⁻¹) of biochar samples

	pH	Acidic	Lactones	Carboxylics	Phenolics	Basic	Total
Temperature (30 min)							
400 °C	7.41	0.784	0.392	0.198	0.194	1.792	2.576
500 °C	7.73	0.300	0.019	0.124	0.156	2.047	2.347
600 °C	8.97	0.175	0.021	0.111	0.042	2.107	2.282
Residence time (500 °C)							
15 min	7.54	0.387	0.023	0.171	0.193	2.020	2.407
30 min	7.73	0.300	0.019	0.124	0.156	2.047	2.347
60 min	8.47	0.250	0.081	0.114	0.128	2.103	2.353
120 min	8.73	0.200	0.066	0.099	0.094	2.139	2.339

time on WHC. The highest capacity was observed at 600 °C, where the S_{BET} was relatively low. This result confirmed that surface area was not the only criterion for high WHCs, whereas other factors such as porous structure and oxygen-containing surface functional groups also affect the WHC significantly [73]. Our results indicate that the surface functional group ratios contributed to the differences in WHC since samples with the highest share of carboxylic and therefore hydrophilic groups did not represent high WHC. This confirms the findings of a recent study by [74].

4 Conclusions

In this study, we confirm that oak wood sawdust, as a lignocellulosic raw material, resembles an excellent feedstock for biochar production based on proximate, component, and nutrient analysis. Oak wood biochar can be considered as a valuable soil amendment, and its properties can be engineered by setting particular pyrolysis conditions. Final temperature and residence time are critical pyrolysis conditions in determining biomass conversion and biochar characteristics. The environmental properties of biochar that are widely affected by pyrolysis temperature and residence time are (1) contents of ash and fixed carbon; (2) elemental composition CHNO, especially carbon content; aromaticity; (3) surface area; total pore volume; (4) pH; surface acidity; cation exchange capacity; functional groups and their ratios; (5) water holding capacity; and (6) nutrient content. The physical, chemical, and hydraulic properties of the biochar was observed with instrumental techniques and its properties were investigated by using state-of-the-art analytical and instrumental techniques. Pyrolysis temperature was found to be the essential parameter defining the agronomic characteristics of biochar produced by slow pyrolysis of woody biomass. The pH and alkaline functional groups increased with the increasing pyrolysis temperature; thus, it provides low surface acidity. Carbon content, micronutrient content, and recalcitrance increased with increasing pyrolysis temperature from 400 to 600 °C. Also, BET surface area and water holding capacity were found larger at higher temperatures;

thus, it offers enhanced porosity. In contrast, biochar yield, acidity, and surface functional groups decreased at higher temperatures. Low residence time results in higher char yield, with greater amounts of volatiles and oxygen content; thus, it provides higher surface functional groups. Conversely, longer residence time generates more aromatic, alkaline, and micro-porous biochar. We found that the optimal conditions for slow pyrolysis lie between 500–600 °C and 60–120 min when taking into account the key properties of biochar for soil amendment.

Oak wood (*Quercus* sp.), which is widely grown in Turkey and has several industrial applications, has been shown to be a suitable feedstock material for biochar production. As a biowaste of forestry and timber industry, the sawdust is usually used directly as solid fuel. Alternative utilization of biowastes as sustainable feedstock in agricultural and forestry applications [11] is an important research subject with a life cycle and carbon sequestration perspective. Oak sawdust biochar can be used to address some of the challenges that Mediterranean soils are facing. As a result, together with the stable regional availability of this feedstock, biochar production can be a viable option for adding value to sawdust, while contributing to carbon sequestration.

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Data availability All data are available upon request

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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