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From waste to resource: maximizing olive pomace valorization through advanced thermal treatment

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Abstract

The present study aimed to investigate the thermochemical treatment of olive pomace carbonization to improve its value and use. For this purpose, experimental procedures were carried out at different temperatures, 300, 400, 500, 600, and 700 °C, and heating rates, 10 and 20 °C/min, with a residence time of 1 h. The resulting biochar was characterized through physical–chemical analysis, including elemental analysis, thermogravimetric analysis, and evaluation of chemical kinetics through temperature and heating rate, as well as its morphology and chemical composition by scanning electron microscopy and energy-dispersive X-ray spectroscopy. In addition, different applications for biochar were evaluated using the hierarchical analysis method. The results indicated that the 400 °C treatment showed the highest priority for application as a biofertilizer (26% priority vector), while heating rates of 20 °C/min and treatments at 400 and 500 °C showed the highest priority for application as a biofuel (between 44 and 46% priority vector). For application as a biocatalyst, treatments at 300 and 400 °C showed the highest percentage values of the priority vector (27 and 26%, respectively). These results contribute to expanding the possibilities of using olive pomace as a sustainable resource in various areas.

Keywords Thermochemical treatment · Olive pomace · Biochar · Sustainable resource

1 Introduction

Sustainable processes are often more required in all fields of our society. In the context of olive oil industry and similar ones, waste management poses a significant challenge for sustainability. For each 1000 kg of fresh olives, 800 kg of wastes (mainly olive pomace) is created and needs to have a correct disposal due to the presence of pollutants such as phenolic compounds and fatty acids that are difficult to decompose in the environment [1]. Creating alternative utilization of these wastes is crucial for mitigating environmental impacts and promoting sustainable practices. The global production of olive oil is concentrated in Europe. According to FAOSTAT data, Spain is the leading producer of this resource, followed by Italy and Greece, with their respective average productions being 1.13, 0.51, and 0.34 million tons

Pedro H. Pereira pedromaranhao@unifei.edu.br [2]. Despite not being a significant global producer, Brazil has noticeably increased its local production over the last decade, transitioning from 16.6 tons in 2011 to 500 tons in 2023. The state of Minas Gerais, particularly in its southern region, has a notable production of this resource, resulting from research projects supported by agricultural policies [3].

Previous studies have explored diverse strategies for the treatment and valorization of olive pomace, revealing the potential to transform this waste into a valuable resource. A prevalent method is composting, which consists of the controlled biological decomposition of olive oil waste [4]. This not only reduces waste volume but also yields a nutrient-rich soil amendment applicable in agriculture [5]. Other promising pathways for the utilization of this waste comprise pyrolysis, a thermochemical process. This method transforms lignocellulosic wastes into biochar, biooil, and gases. Biochar is a carbon-rich material with many final applications, including soil improvement and carbon sequestration [6]. The insights provided by recent reviews into the current state of knowledge surrounding crop residue pyrolysis offer a comprehensive understanding of its techno-economics and multifaceted applications, providing a valuable roadmap for sustainable waste management

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practices [7]. Another utilization of olive pomace involves extracting bioactive compounds from this waste, opening avenues for utilization in pharmaceuticals, cosmetics, and food industries [8]. Phenolic compounds, known for their antioxidant and antimicrobial properties, become valuable assets for developing functional products [9]. Furthermore, ongoing research explores the potential of anaerobic digestion of olive oil waste, offering a sustainable route for biogas production as a renewable energy source [10].

Despite these efforts, there is still significant unexplored potential in maximizing the utilization of the olive pomace. The limited utilization rates highlight the need for further research and development of innovative waste valorization strategies. There are many ways to face the challenge of using biomass residues as the application of the analytic hierarchy process (AHP), a decision-making methodology conceived by Thomas L. Saaty [11] that can be applied for choosing a final utilization of biomass residues. AHP is widely used across diverse research fields such as business, engineering, urban planning, and the social sciences [12].

In addition, recent works such as that of Len et al. have advanced the understanding of biochar production thermodynamics by exploring kinetic models and the influence of process parameters. These investigations complement existing knowledge, paving the way for a more comprehensive analysis of the olive pomace pyrolysis process [13].

This work investigates the thermochemical treatment of olive pomace from Minas Gerais Brazil, through pyrolysis, applying AHP methodology to prospect potential applications. Raw samples were submitted to different temperatures and heating rates and the resulting biochar was characterized through physicochemical analyses. Following, different potential utilizations of pyrolyzed residues were evaluated through AHP: use as biofertilizer, use as biofuel, and use as biocatalyst.

The results indicated the highest priorities for application as a biofertilizer, biofuel, and biocatalyst at specific temperature and heating rate conditions. These findings significantly contribute to expanding the possibilities of utilizing olive pomace as a sustainable resource in multiple sectors.

2 Materials and methods

2.1 Biomass acquisition and pretreatment

The raw material used in this study, olive pomace, was obtained from the EPAMIG SUL experimental field (Oliviculture and Temperate Climate Fruit Growing) located in Maria da Fé/MG at an altitude of 1285 m, with the following geographic coordinates: latitude 22° 31′ 46″ south, longitude 45° 37′ 5″ west. The extraction system employed is directly linked to the byproduct obtained; in this case, the two-phase pomace, a byproduct resulting from the extraction of oil by two-phase centrifugation, composed of water resulting from fruit crushing, solid parts of the olive, and fatty residues. The drying of the material was then carried out in a muffle furnace according to the methods described in the CEN/TS [14] standard for sample preparation. The difference between the samples before and after pretreatment is shown in Fig. 1.

The olive pomace samples were ground in a ball mill for 1 h, before the analysis. Subsequently, a particle size classification was performed using standard sieves with different classification numbers. Uniformly sized particles tend to have the same carbonization behavior, resulting in a homogeneous sample. Therefore, after the 1-h particle size separation process, a particle size distribution of approximately 350 µm was achieved.

2.2 Biomass characterization

Proximate analysis was determined with the contents of volatile matter, moisture, ash, and fixed carbon based on ASTM [15] standard. The test was performed in triplicate. For the proximate analysis of olive pomace, a thermogravimetric balance was used, which can provide a continuous record

Fig. 1 Sample preparation: raw olive pomace (left) and pretreated pomace (right)

(a)





Olive pomace



Pre-treated olive pomace

of sample weight loss during the heating period, making it possible to determine moisture, volatile matter, and ash content per sample.

2.2.1 Elemental analysis

The analysis was carried out at the Biofuel Characterization Laboratory at the Federal University of Itajubá (UNIFEI) using a Perkin Elmer 2400 series II elemental analyzer. The ISO [16] "Bioproducts—Biochars—Part 2: Methods of analysis" standard was used for elemental analysis. The raw and biochar samples were characterized to verify the change in the organic composition of the material, mainly the H/C and O/C molar ratios, with the aim of evaluating the use of biochar as a biofuel [17]. For a better visualization of this change, the Van Krevelen diagram was used.

2.2.2 Higher heating value

The higher heating value (HHV) of the samples was determined experimentally, in triplicate, using an IKA C2000 calorimetric bomb available at the Biofuel Characterization Laboratory at the Federal University of Itajubá (UNIFEI). For the determination of the HHV, the BS EN [18] standard was used. Five milligrams of the sample was placed in a stainless-steel crucible set in a pressurized vessel. To achieve complete combustion of the material, the equipment injected a fraction of pure oxygen between 30 and 35 bar (3000 and 3500 kPa) into the pressurized vessel. The raw and biochar samples were characterized to study the increase in the HHV after the carbonization treatment, for possible use of biochar as a biofuel [17].

2.2.3 Statistical analysis

The statistical analysis of the data collected was carried out using the Tukey test, a post-hoc test widely used for multiple comparisons of means. This test was used to assess the differences in C, H, N, S, and O content between different biochars. The significance level adopted was 5% (p < 0.05), which implies that only differences with a p-value of less than 0.05 were considered statistically significant.

The study encompassed five distinct treatments, namely C300, C400, C500, C600, and C700, corresponding to carbonization temperatures of 300, 400, 500, 600, and 700 °C, respectively. The analytical structure was based on a one-way ANOVA model, in which the type of biochar was considered the main factor, with six different levels (C300, C400, C500, C600, C700, and in natura). The dependent variables were the contents of C, H, N, S, and O, in order to provide a comprehensive understanding of the characteristics of each type of biochar.

2.3 Carbonization of biomass (treatment)

The production of biochars in this study was based on the established methodology from previous research by Pires et al. [19]. To ensure a comprehensive exploration of the thermochemical properties of olive pomace, carbonization temperatures ranging from 300 to 700 °C were selected. These temperatures were chosen based on previous studies and their relevance to the thermal transformation of olive pomace, and were maintained for 1 h with a heating rate of 20 °C min⁻¹. The pyrolysis process took place in sealed crucibles to ensure an oxygen-limited environment.

To prepare the crucibles and porcelain lids for the carbonization process, they underwent pre-calcination at 450 °C for 30 min. Following this pre-calcination step, approximately 5 g of pretreated pomace was carefully loaded into the covered crucibles. The crucibles, with their lids securely in place, were then placed inside a Barnstead Thermolyne 1300 muffle furnace, situated in the Biofuel Characterization Laboratory at UNIFEI. After the pyrolysis process, the biochars were cooled to room temperature in a desiccator. The olive pomace underwent controlled thermal treatment under the specified temperature conditions in triplicate.

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a LECO TGA701 thermogravimetric balance at the Biofuel Characterization Laboratory at the Federal University of Itajubá (UNIFEI), Itajubá, MG. To evaluate the influence of process variables on changes in the physical–chemical composition of the products, two heating rates were used. The ISO [20] "Bioproducts—Biochars—Part 3: Physical and chemical analysis" standard was used for biochar thermogravimetric analysis. To explore the influence of different heating rates on the carbonization process, two ramping rates were employed: 10 °C/min and 20 °C/min. The selection of these specific heating rates allowed for an investigation into the effect of the rate of temperature increase on the formation and properties of the resulting biochar.

In addition, the amount of biomass utilized in each experiment was fixed at 1 g. This standardized amount ensured consistency and comparability across the different treatments, enabling a reliable assessment of the impact of temperature and heating rate on the carbonization process.

2.5 Kinetic analysis: activation energy

To calculate the reaction kinetics, the Coast-Redfern method, as described by Rocha [21], was employed. This

method provides a mathematical expression for the firstorder reaction, as shown in Eq. 1:

$$\log\left[\frac{-\log(1-a)}{T^2}\right] = \log\frac{AR}{\beta E_a}\left[\frac{1-2RT}{E_a}\right] - \frac{E_a}{2.303RT}$$
(1)

In this equation:

T represents the temperature in Kelvin (K).

 β signifies the linear heating rate.

A corresponds to the frequency factor.

 $E_{\rm a}$ represents the activation energy in kilojoules (kJ).

R denotes the gas constant.

a denotes the fraction of the sample decomposed at a given time t, as $a = \frac{w_0 - w_t}{w_0 - w_f}$. Here, w_0 represents the initial weight of the sample before the start of the decomposition reaction, w_t represents the weight of the sample at any temperature, and w_f is the weight of the sample after the completion of the reaction.

The Coast-Redfern method allows for the estimation of the activation energy by analyzing the logarithmic relationship between the fraction of sample decomposed (*a*) and temperature (*T*). The activation energy was estimated using the formula ln [ln (1-a)] vs. 1000/*T*, proposed by Paswan et al. [22]. By plotting the natural logarithm of the natural logarithm of (1-a) against the reciprocal of the absolute temperature (1000 divided by *T*), a linear relationship can be observed. The slope of this linear fit corresponds to the activation energy, offering further insight into the thermal decomposition of the olive pomace.

2.6 SEM/EDS

The study and characterization of the surface morphology of olive pomace biochar were performed by scanning electron microscopy (SEM), which has been widely used to evaluate the morphology of biochar particles after different thermal treatments. SEM images are very useful for obtaining precise details about the pore structure of biochar. For elemental mapping of the sample surface and quantitative reading of the chemical elements present, energy-dispersive X-ray spectroscopy (EDS) analysis was used. The analyses were carried out at the Electron Microscopy Center at the Federal University of Itajubá (UNIFEI) using a HITACHI S-4800 field emission gun (FEG) scanning electron microscope at an acceleration voltage of 10 kV and magnifications ranging from 100 to 6000 times.

2.7 Utilizing the analytic hierarchy process for application criteria

To comprehensively analyze the potential of the produced biochars, a decision-making method based on the evaluation of multiple criteria will be implemented. The objective is to determine the optimal temperature for the carbonization process that yields the most suitable biochar properties for each potential application, such as biofertilizer, biofuel, or catalyst.

The analytic hierarchy process (AHP) is a robust and widely recognized methodology introduced by Thomas Saaty [23] that supports decision-makers in establishing priorities and making informed choices [24]. In this study, the AHP methodology was used to systematically evaluate and compare the characteristics of biochar, enabling the identification of the most suitable application among various possibilities, such as biofertilizer, biofuel, or biocatalyst.

The AHP methodology provides a structured and rigorous framework for decision-making, ensuring that multiple criteria and their relative importance are rigorously considered. Through a series of pairwise comparisons, decision-makers assign weights or preferences to the criteria based on their relative significance. This systematic process allows for the quantification of subjective judgments, promoting transparency and consistency in decision-making shown in Fig. 2.

Initially, the problem is structured by defining decision criteria and their relative importance. Subsequently, priorities are calculated based on these criteria [25]. Prioritization of criteria for biochar application involves evaluating the advantageous characteristics for use as fertilizer, biocatalyst, or biofuel, considering their equal importance [25]. The biochar potential is presented according to the property presented in Table 1.



Fig. 2 The AHP process

Table 1Decision criteria forbiochar application	Fertilizer	Biofuel	Biocatalyst	
	Higher carbon content	Higher carbon content	Higher carbon content	
	Lower H/O mole ratio	Higher calorific value	Higher (%) N, P, Mg, K, S	
	Lower O/C mole ratio	Lower activation energy		
	Higher (%) N, P, Mg, K			

In this study, the potential of the AHP methodology was used to comprehensively assess the properties of biochar obtained from various carbonization treatments. To ensure evaluation consistency, a range of crucial criteria specific to each application was considered. For biofertilizer, higher carbon content, lower H/O mole ratio, lower O/C mole ratio, and higher percentages of N, P, Mg, and K were required. For biofuel, higher carbon content, higher calorific value, and lower activation energy were required. For biocatalyst, higher carbon content and higher percentages of N, P, Mg, K, and S were required. These criteria are meticulously selected to capture the desired properties for each application.

To establish the relative importance of these criteria and determine the optimal carbonization temperature, a rating system was adopted, based on absolute values derived from the evaluation of biochars produced at different temperatures. This systematic approach allows the identification of the temperature range that yields biochars with the most desirable properties for each application category. Figure 3 demonstrates the structure of decision criteria to find priorities in each of these applications.

To ensure maximum consistency and reliability in evaluating the criteria, the adhesion to the mathematical property of transitivity is necessary and is a fundamental principle of the AHP methodology. By consistently applying this principle, the logical coherence of the decision-making process adopted in this work is maintained. By summing the values obtained from the priority vectors, it is possible to determine the treatment that emerges as the best overall choice, perfectly aligned with the main objective of each specific application.

By adopting this approach, it is possible to indicate the temperature range that yields biochars with the most favorable properties for each application. This comprehensive analysis plays a pivotal role in maximizing the potential benefits of biochar across diverse fields, including agriculture, energy production, and catalysis. By providing valuable insights into the optimal carbonization temperature for each application, our research aims to unlock the full potential of biochar, paving the way for enhanced sustainability, improved soil fertility, and the development of innovative energy and catalytic solutions.



Fig. 3 Criteria for optimized biochars

3 Results and discussion

3.1 Characterization of the raw biomass

Regarding the raw material used in the tests, biomass derived from olive oil production, known as olive pomace, was used. Table 2 presents the results of all analyzed parameters of the raw biomass.

The values of moisture, ash, higher heating value (HHV), and chemical element content of olive pomace obtained through the analysis performed in this study were different from the values found by Petry [20] in their previous study. Compared to the results of Petry [26], it was observed that the olive pomace analyzed in this study presented lower moisture content (7.70% compared to 12.08%) but higher

Table 2Olive pomace biomasscharacterization

Parameter	Olive pomace
Moisture (%)	7.70
Ash (%)	12.05
HHV (MJ/kg)	22.05
Carbon (%)	55.62
Hydrogen (%)	7.80
Nitrogen (%)	1.88
Oxygen (%)	30.94
Sulfur (%)	3.71

ash content (12.05% compared to 20.02%). The HHV found in the present study was higher (22.05 MJ/kg) than reported by Petry (16.95 MJ/kg), which can be attributed to the difference between carbon and hydrogen contents, which are higher in the material analyzed in this study (55.62% and 7.80%, respectively) compared to the material analyzed by Petry (43.82% and 5.19%, respectively). The nitrogen content was also higher in the biomass analyzed in this study (1.88% compared to 2.68%), while the sulfur content was higher in the material analyzed by Petry (3.71% compared to 0.15%). These differences may be explained by possible variations in the composition of olive pomace depending on the cultivation, harvesting, and storage conditions. Additionally, the analytical methodologies employed in the two studies may have influenced the results obtained.

However, despite the differences found, it is important to note that both studies, the present study and Petry's study, demonstrated that olive pomace can be a promising source of renewable energy due to its high carbon content and higher heating value.

3.2 Characterization of biochar

In the present study, 15 carbonization treatments were carried out using the thermogravimetric analysis technique to evaluate the changes in the physicochemical properties of produced biochars. The proximate analysis with volatile matter, ash, and fixed carbon contents present in the raw biomass used in the assays along with the carbonized biomass produced is presented in Table 3.

Table 3 The proximate analysis

Sample	Moisture (%)	Ash (%)	Fixed carbon (%)
Raw	77.08	4.70	12.46
C300	55.49	13.06	24.68
C400	34.31	14.08	43.20
C500	39.46	17.18	42.80
C600	30.49	17.60	40.09
C700	23.33	26.90	40.04

According to the results presented in Table 3, an increase in carbonization temperature from 300 to 700 °C significantly decreased the percentage of volatiles present in the samples. This can be attributed to the fact that higher temperatures can cause greater thermal decomposition of volatile organic compounds, resulting in a reduction in their content [27].

Moreover, an increase in carbonization temperature also increased the fixed carbon content present in the samples, indicating that carbonization at higher temperatures may favor the formation of graphite or other more stable forms of carbon. This result is consistent with other studies that found this relationship between carbonization temperature and fixed carbon content in biochar [28].

Regarding the ash content, considerable variation was observed among the samples, not necessarily related to the carbonization temperature. Sample C400 showed a relatively high ash content compared to the other samples carbonized at similar temperatures. Ash content is related to the presence of inorganic material in the sample due to soil residue contamination [24].

Thus, by comparing these results with other studies investigating the effects of carbonization temperature on biochar, it is possible to verify that olive pomace biochar production is a complex process, and factors beyond temperature may influence the final product characteristics.

3.2.1 Elemental analysis

The elemental composition (C, N, H, S–O) and atomic ratios (O/C and H/C) of the produced biochars are shown in Table 4. In terms of energy, the most significant elements used in calculating the empirical formula of the fuel molecule are carbon, hydrogen, and oxygen [27].

The elemental analysis shows that there was a significant change in the chemical composition of biomass samples before and after carbonization at different temperatures. In general, the carbonized samples showed higher carbon content and lower content of hydrogen, nitrogen, and sulfur compared to the raw sample [27].

During the carbonization phase of the olive pomace, there was an overall average for the carbon concentration (C) of 63.21, with a standard deviation of 1.52. This average suggests that most of the C values were concentrated around 63.21, indicating a consistent central tendency, with a relatively small dispersion of the data. For the elements hydrogen (H), nitrogen (N), and sulfur (S), the overall averages were 3.80, 2.14, and 2.07, respectively, with corresponding standard deviations of 0.15, 0.11, and 0.17.

An increase in carbon content was observed with increasing carbonization temperature, with sample C500 having the lowest carbon content among the carbonized samples. This can be explained by the fact that

 Table 4
 The elemental analysis

Elemental a	Elemental analysis (C, N, H, S-0) and atomic ratio (O/C and H/C)								
Sample	C (%)	H (%)	N (%)	S (%)	O (%)	O/C	H/C		
Raw	55.67	7.84	1.94	3.68	30.88	0.55	0.14		
C300	63.93	5.29	2.27	2.41	26.10	0.41	0.08		
C400	67.99	3.91	2.45	2.39	23.26	0.34	0.06		
C500	67.42	1.80	2.10	1.30	27.39	0.41	0.03		
C600	62.00	2.29	2.23	1.41	32.07	0.52	0.04		
C700	62.29	1.67	1.82	1.22	33.00	0.53	0.03		

high-temperature carbonization favors the formation of fixed carbon, which is less volatile [28].

The atomic ratios H/C and O/C are useful indicators of the quality of biochar produced, as the excessive presence of hydrogen and oxygen can limit its potential as an adsorbent or soil conditioner [29]. Given the importance of carbon content, H/C, and O/C ratios for biochar valorization, the Van Krevelen diagram was used to better visualize the data obtained in this step.

According to the literature, the H/C and O/C ratios for natural biomass vary between 1.2 and 2.0 and 0.4 and 0.8, respectively [30]. The diagram is shown in Fig. 4.

It can be observed that hydrogen content decreased with carbonization, but its variation was not as great as for carbon. Also, the H/C ratio tended to decrease, suggesting that carbonization caused greater removal of hydrogen atoms relative to the carbon present in the samples.

The atomic ratio O/C also decreased with increasing carbonization temperature, indicating that the carbonized samples had a higher proportion of carbon relative to oxygen. This result is expected since carbonization removes oxygen-rich compounds (such as cellulose and hemicellulose) during the process [29].

Therefore, it can be said that the samples carbonized at higher temperatures had a higher concentration of carbon with respect to the other elements analyzed, which tends to increase the quality of the produced biochar.

3.3 Higher heating value

Table 5 presents the higher heating value (HHV) of biochars produced by traditional carbonization at 300 $^{\circ}$ C, 400 $^{\circ}$ C, 500 $^{\circ}$ C, 600 $^{\circ}$ C, and 700 $^{\circ}$ C.

The results obtained in this analysis indicate that olive pomace biochar has a higher heating value (HHV) in the range of 22 MJ/kg. This value is comparable to findings from other studies, such as the study conducted by Petry [26], where the HHV of carbonized olive pomace was close to the values found in this analysis.

Comparing the biochar of olive pomace with other raw materials used in thermochemical conversion processes, it can be observed that the HHV of olive pomace biochar is



Fig. 4 Van Krevelen diagram of biochars

Table 5The higher heatingvalue of biochars

Higher heating valu (MJ/kg)	ie—HHV
Sample	HHV
C300	22.62
C400	22.71
C500	22.25
C600	22.45
C700	21.44

higher than that of sugarcane bagasse, which was found to be 17.73 MJ/kg by Sahoo and Ram [31]. Additionally, the HHV of olive pomace biochar is greater than that found for coconut shell and rice husk, which were 18.88 MJ/kg and 15.90 MJ/kg, respectively, in a study by García et al. [32].

It was possible to verify that the HHV values are quite similar, with the C400 treatment obtaining the highest HHV value. These results are important for evaluating the energy potential of the biochar produced from olive pomace and its viability for application in combustion or gasification processes. Furthermore, with a high HHV, olive pomace biochar can be considered a promising alternative to replace fossil fuels in applications that require high energy density [17].

3.4 Thermogravimetric analysis (TGA) and kinetic parameters

The study of the results of thermogravimetric analysis (TGA) and kinetic parameters of the biochar showed that it is possible to identify the biomass components that are degraded during the production of biochar, such as cellulose, hemicellulose, lignin, and other organic components. Figure 5 shows the TGA curves of the raw biomass and

biochar produced at different temperatures using two heating rates of 10 and 20 °C/min.

The thermogravimetric analysis (TGA) of olive pomace biochar showed a mass loss in three distinct phases. The first phase (zone 1), between 90 and 180 °C, corresponded to the evaporation of water and other volatile compounds present in the biomass. The second phase (zone 2), between 180 and 600 °C, was the main stage of decomposition of hemicelluloses, celluloses, and lignin present in the material, resulting in a significant mass loss and modification of the physical and chemical properties of the biochar. Finally, the third phase (zone 3), between 600 and 900 °C, represented a final stage of decomposition of lignin and other remaining components.

These results are consistent with other studies that analyzed the TGA of biochars produced from different types of biomasses. For example, a study by Lei et al. [33] analyzed the TGA of biochar produced from *Eucalyptus grandis* and observed a similar behavior, with mass loss in three distinct phases. Another study by Hu et al. [34] analyzed the TGA of biochar produced from marigold waste and observed a mass loss in three distinct phases, with a main decomposition stage between 200 and 500 °C.

TGA provides important information on the thermal behavior of materials under study. To apply a kinetic model to the biomass and biochar decomposition, it is necessary to define a temperature range to be studied [35].

In this study, the Coats-Redfern model was used to analyze the obtained TG curves. This model allows the estimation of the activation energy $(E\alpha)$ of the material's decomposition reaction at different temperature zones.

Figures 6 and 7 show the $\ln[\ln(1-x)]$ vs 1000/T plots for each biomass and biochar decomposition zone, along with the respective slopes of the resulting linear fits of the experimental data. From these plots, it is possible to calculate the $E\alpha$ of the samples under study.



Fig. 5 TGA curves of biochars



Fig. 6 Experimental data of TGA and linear fit with a heating rate of 10 °C/min for biochars

The activation energy (E α) (kJ mol⁻¹) values of all samples are shown in Table 6.

The decomposition behavior of biochars is quite different from that of raw biomass. The results obtained showed that the thermal decomposition reactions of lignin and inorganic matter exhibited high activation energy values ($E\alpha$) of 53.64 and 44.34 kJ/mol, respectively. These values indicate that these reactions are slower and more resistant to the thermal conversion process, which may have important implications for the use of these materials as an energy source.

Among the various characteristics to be evaluated, the activation energy in the devolatilization stage stands out as an important indicator of the material's energy potential [17]. In this sense, the results obtained for zone 2 of the thermal decomposition process showed E α values ranging from 19.81 to 20.90 kJ/mol for raw biomass and from 6.31 to 19.03 kJ/mol for biochars, depending on the temperature and heating rate used.

These results are consistent with previous studies that also reported the influence of heating rate on $E\alpha$ values for biochars. Ferreira et al. [23] observed that activation energy

values decrease as the heating rate increases, suggesting that the choice of heating rate is an important factor to be considered in the production and use of biochars as an energy source.

Previous studies, such as that conducted by Abdullah and Wu [36], have shown that the lower the activation energy in the devolatilization stage, the better the performance of biochar as a fuel source. This is because lower activation energy values indicate that less energy is needed to initiate the thermal decomposition reactions of the material, resulting in a more efficient conversion rate of biomass into useful products, such as combustible gases and liquids.

For this reason, the evaluation of activation energy in the devolatilization stage is a crucial aspect to be considered in the development and utilization of biochars as a renewable energy source.

3.5 SEM/EDS analysis

The scanning electron microscopy (SEM) images are an important tool for analyzing the structure of biochar



Fig. 7 Experimental data of TGA and linear fit with a heating rate of 20 °C/min for biochars

Table 6 Activation energy for biochars		Zone 1		Zone 2		Zone 3	
biochars		10 (°C/min)	20 (°C/min)	10 (°C/min)	20 (°C/min)	10 (°C/min)	20 (°C/min)
		Eα (kJ/mol)					
	Raw	53.64	44.34	19.81	29.9	20.25	10.12
	C300	42.34	32.72	17.9	19.03	24.99	22.05
	C400	30.67	50.8	14.63	13.11	26.25	25.85
	C500	32.36	26.54	9.63	9.39	37.14	39.44
	C600	39.02	34.71	8.18	7.48	24.82	25.61
	C700	46.77	43.49	10.35	6.31	39.7	30.88

produced from olive pomace. Figure 8 shows the pores of the biochars, with an increase of 100 times; subtle differences in the structure of the different biochars, which were identified as C300, C400, C500, C600, and C700 in this study, can be observed. The analysis of the SEM images of the biochars produced from olive pomace allowed for the observation of differences between them. Although the structure of the biochars generally resembled the in natura biomass, the biochar produced at 400 $^{\circ}$ C had few ashes, which affected the quality of the obtained image. This can be attributed to the fact that lower temperatures tend to generate less ash during carbonization, while higher temperatures tend to generate more ash.

Compared with the literature, it is possible to verify that the structure of biochars is influenced by the processing conditions used in their production. A study conducted by Qian

Fig. 8 SEM images and the pore detail



et al. [37] analyzed the structure of biochars produced from different biomasses and observed that the carbonization temperature was a key factor in determining the final structure of the biochars. Another study conducted by Ahmad et al. [38] also found that the carbonization temperature significantly affects the specific surface area and porosity of biochars produced from wood waste.

Therefore, it is important to conduct a detailed analysis of the structure of biochars to identify possible differences between them and understand how processing conditions affect their final structure. The information obtained can be useful for improving the biochar production process and obtaining biochars with specific properties that meet the needs of various applications.

In this sense, as the carbonization temperature increases, there is a loss of mass in the form of volatile compounds, including cellulose, hemicellulose, and lignin. These compounds decompose, forming other compounds with a high carbon content and creating porous spaces on the surface of the biochar. This forms pores of different sizes, including macro-, meso-, and micropores [39].

The chemical composition of the biomass and biochar was also analyzed using X-ray energy-dispersive spectroscopy (EDS). Through EDS analysis, the main chemical elements present in the ash of the carbonized materials were identified as Ca, K, Mg, and P, as demonstrated and analyzed in Table 7.

Table 7 presents the results of the EDS analysis of biochar produced at different temperatures using olive pomace as the feedstock. The analysis allowed the identification and quantification of the chemical elements present in the produced biochars, as well as comparisons between different treatments.

Table 7 EDS analysis

EDS analysis, (%) weight								
	Raw biomass	300 °C	400 °C	500 °C	600 °C	700 °C		
Mg	0.18	0.22	0.44	0.38	0.30	0.52		
Р	0.20	13.36	7.85	4.28	6.43	5.89		
Κ	19.00	12.99	15.58	14.34	12.66	27.04		
Ca	20.03	11.91	7.44	1.46	5.70	8.01		

The increase in temperature also influenced the concentration of other elements. For instance, the concentration of potassium (K) gradually increased up to the production of biochar at C500 but started to decrease in C600 and C700, while for calcium (Ca), there was a significant decrease in concentration in C500 and onwards. Phosphorus (P) presented its maximum concentration value in the biochar produced at 300 °C, being 13.36%. This suggests that the temperature influences these elements, but each element may have a different response as the temperature increases.

Elements Ca, Mg, P, and K are essential not only for plant growth but also for their nutrition and survival. Calcium (Ca), for example, is important for maintaining the integrity of cell walls and regulating the absorption of other nutrients by the plant [41]. Magnesium (Mg) is a key constituent of chlorophyll, which is essential for photosynthesis and therefore for energy production by plants [42]. Phosphorus (P) is a fundamental element for the formation of ATP, a molecule responsible for storing and using energy in living cells [43]. Finally, potassium (K) regulates the water balance of plants and is involved in the processes of opening and closing stomata, which control gas exchange with the environment [42].

The P content of the biochars was significantly higher compared to the raw biomass, with a difference of up to 13% by weight. This can be explained by the fact that carbonization cleaves the organic bonds of P present in the raw biomass, leading to a better recovery of this element at temperatures above 300 °C [40]. Additionally, the EDS analysis revealed that the highest concentration of potassium (K) was obtained in the treatment at 700 °C. Other elements found in relatively small amounts were sulfur (S), manganese (Mn), iron (Fe), zinc (Zn), and aluminum (Al), both in the raw biomass and in the biochars.

These results indicate that the temperature of the carbonization process has a direct influence on the composition and concentration of the chemical elements present in biochar. It is important to note that since olive pomace is a specific feedstock, the results may vary if other types of biomasses are used.

3.6 Evaluation of possible biochar applications

The aim of this study is to optimize the properties of biochar for applications such as biofertilizer, biofuel, and biocatalyst. To achieve this, the most important variables in the carbonization process of olive bagasse were identified and adjusted to maximize the result. Hierarchical analysis of these variables is fundamental for achieving this optimization.

Temperature and heating rate are the main factors in the physicochemical change of the material for different product applications. The results of the hierarchical analysis according to the criteria of biochar application for biofertilizer, biofuel, and biocatalyst are shown in Tables 8, 9, and 10.

After analyzing the priority vectors, the optimal carbonization temperature to obtain a biochar with desirable properties for use as a biofertilizer is 400 °C. This can be explained by the high priority given to the C content (43.9%) and the H/C ratio (4.9%), indicating that a lower carbonization temperature is more suitable for preserving the organic elements of the biochar.

Furthermore, the high priority given to the N (14.6%) and P (21.9%) content suggests that the carbonization temperature should be high enough to remove impurities and

Table 8 Biofertilizer priority vector for AHP process		Biofertili	zer							
		Priority	Priority vector							
		C (%)	H/C	O/C	N (%)	P (%)	Mg (%)	K (%)	Total	
	C300	0.146	0.146	0.146	0.438	0.438	0.067	0.095	1.476	
	C400	0.439	0.049	0.439	0.146	0.219	0.267	0.286	1.845	
	C500	0.293	0.293	0.293	0.088	0.088	0.200	0.190	1.445	
	C600	0.049	0.073	0.073	0.109	0.146	0.133	0.048	0.631	
	C700	0.073	0.439	0.049	0.219	0.109	0.333	0.381	1.603	

Table 9	Biofuel	priority	vector	for	AHP	decision
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	Biofuel							
	Priority ve	Priority vector						
	C (%)	PCS	Ea	Total				
C300-10	0.095	0.100	0.038	0.233				
C400-10	0.190	0.167	0.043	0.400				
C500-10	0.143	0.133	0.068	0.344				
C600-10	0.048	0.067	0.113	0.228				
C700-10	0.024	0.033	0.057	0.114				
C300-20	0.095	0.100	0.038	0.233				
C400-20	0.190	0.167	0.049	0.406				
C500-20	0.143	0.133	0.085	0.361				
C600-20	0.024	0.067	0.170	0.261				
C700-20	0.048	0.033	0.300	0.381				

residues from the biochar, but still maintain its porous structure and organic origin nutrients.

This conclusion is in line with several studies that have evaluated the influence of temperature on biochar formation and its properties as a biofertilizer. A study by Ahmad et al. [38] compared biochars produced at different temperatures from agricultural waste and concluded that the biochar produced at 400 °C had higher nutrient sorption capacity and biological activity in the soil compared to higher or lower temperatures.

Another study conducted by Zhao et al. [44], which investigated the influence of carbonization temperature on biochar formation from wood waste, concluded that the optimal temperature for obtaining biochar with desirable properties as a biofertilizer was 375 °C. The authors observed that higher temperatures led to an increase in carbon concentration but also decreased nutrient retention and biological activity in the soil. Figure 9 shows the percentage of the most relevant treatments to biochar properties for possible use as a biofertilizer.

Therefore, it is possible to conclude that the ideal carbonization temperature to obtain a biochar with desirable properties as a biofertilizer may vary depending on the feedstock used, but the temperature range of 300–400 °C seems to be generally the most suitable. Next, Table 9 shows the priority vectors for biofuel.

Based on an analysis of priority vectors, the temperature range of 400 °C and heating rate of 20 °C/min are generally the most suitable for varying the properties of biochar for possible use as a biofuel, due to the high

	Biocataly	st						
	Priority vector							
	C (%)	N (%)	P (%)	Mg (%)	K (%)	S (%)	Total	
2300	0.146	0.438	0.438	0.067	0.095	0.438	1.622	
2400	0.439	0.146	0.219	0.267	0.286	0.219	1.576	
2500	0.293	0.088	0.088	0.200	0.190	0.109	0.968	
2600	0.049	0.109	0.146	0.133	0.048	0.146	0.631	
2700	0.073	0.219	0.109	0.333	0.381	0.088	1.203	

Fig. 9 Optimizing biochar properties for biofertilizer applications: percentage of key treatments

 Table 10
 Biocatalyst priority

 vector for AHP decision



priority given to carbon content, calorific value, and activation energy.

A study conducted by Chen et al. [45] compared biochars produced at different temperatures and heating rates from agroforestry residues and concluded that the ideal temperature for obtaining biochar with desirable properties as a biofuel was 400 °C with a heating rate of 20 °C/min. The authors observed that this temperature range and heating rate resulted in biochars with high carbon content and calorific value, low ash and sulfur content, and high combustion efficiency. Another interesting study was conducted by Fang et al. [46], which evaluated the influence of heating rate on the formation of biochar from agricultural residues and concluded that a faster heating rate leads to a significant increase in bio-oil and gas production compared to lower heating rates, resulting in biochar with higher potential as a biofuel. Figure 10 shows the percentage of the most relevant treatments for altering the properties of biochar for possible use as a biofuel.

The treatment in the temperature range of 400 °C and heating rate of 20 °C/min proved to be the most viable for altering the properties of olive pomace biochar for possible use as a biocatalyst, although this result may vary depending on the raw material used. The priority vectors for the biocatalyst are shown in Table 10.

When analyzing the priority vectors to determine the most appropriate carbonization temperature to produce a biochar with desirable properties to be used as a biocatalyst from olive pomace, the treatments in the range of 300–400 °C have the highest total score, with a value of 1.622 and 1.576, respectively.

This conclusion is in line with several studies that have investigated the influence of carbonization temperature on biochar formation and its properties as a biocatalyst. For example, a study conducted by Kloss et al. [47] evaluated the influence of carbonization temperature on biochar formation and its heavy metal adsorption capacity. The authors found that a carbonization temperature of 400 °C resulted in a biochar with higher heavy metal adsorption capacity compared to biochars produced at lower temperatures. Additionally, a study conducted by Ahmad et al. [38] evaluated the influence of carbonization temperature on biochar formation from sugarcane bagasse and its capacity to adsorb textile dyes. The authors found that a carbonization temperature of 400 °C resulted in a biochar with higher capacity to adsorb textile dyes compared to biochars produced at lower temperatures.

However, it is important to note that the choice of the ideal carbonization temperature may vary depending on the raw material used and the specific purpose of using the biochar. Therefore, it is essential to perform specific analyses for each case. Figure 11 shows the percentage of the most relevant treatments for altering the properties of biochar for possible use as a biocatalyst.

The treatment at temperature range of 300 °C and 400 °C was found to be more feasible to obtain the properties of olive bagasse biochar for possible use as a biocatalyst with 27.04% and 26.26% preference, respectively. According to studies conducted by Ferreira et al. [25], it was found that the treatment of biochar produced from grape bagasse at 300 °C is the most suitable for altering its properties for possible application as a biocatalyst. On the other hand, biochar obtained at 600 °C showed the best properties for possible use as a biofuel. The schematic of which biochar is best for which direction is demonstrated in Fig. 12.

However, the temperature of 400 $^{\circ}$ C is the most balanced in terms of property alteration for potential applications as a biofuel, biofertilizer, and biocatalyst. Therefore, it is important to note that the choice of the best carbonization temperature may vary depending on the raw material used and the specific objective of using biochar, requiring specific analysis for each case.

Fig. 10 Optimizing biochar properties for biofuel applications: percentage of key treatments









Fig. 12 Ideal process treatment each application

4 Conclusions

By evaluating the chemical kinetics of the carbonization process, encompassing factors such as heating rate, residence time, activation energy, and temperature, a direct correlation between temperature and heating rate and the final properties of the produced biochar has been established.

The analysis of the physical and chemical properties of biochar derived from olive pomace has demonstrated that higher temperature production leads to biochars with lower H/C and O/C ratios, reduced activation energies, and elevated phosphorus content compared to the original biomass.

Exploring diverse applications and potential uses of biochar, considering specific requirements in various industrial processes, soil remediation, and bio-product production, the hierarchical analysis method has been effectively utilized. Through this method, the optimal conditions for producing biochar with high energy value have been identified.

The findings indicate that biochar produced at 400 °C exhibited the highest priority for application as a biofertilizer (26% priority vector), while heating rates of 20 °C/ min and treatments at 400 and 500 °C emerged as the top priorities for biofuel applications (with priority vectors ranging from 44 to 46%). Moreover, for biocatalyst applications, treatments at 300 and 400 °C showcased the highest percentage values of the priority vector (27% and 26%, respectively).

This study has made significant contributions to the development of a biochar production method utilizing olive pomace, aiming to maximize its properties for a wide range of industrial applications. Furthermore, through the implementation of the hierarchical analysis approach, the optimal conditions for producing high-energy bio-products have been successfully identified. As a result, this research is poised to advance the realm of more efficient and sustainable technologies.

In summary, this work establishes a compelling foundation for the valorization of olive pomace through advanced thermal treatment, unlocking its immense potential for waste management, resource optimization, and the transition towards a greener and more sustainable future. Acknowledgements The authors would like to express their sincere gratitude to the NEST research group from the Federal University of Itajubá (UNIFEI) for the support and expertise in the characterization of the biochar. This assistance was very important for results obtaining. The same thanks are given to the technical staff at UNIFEI for the assistance throughout the various stages of this research project. Their knowledge and dedication significantly contributed to the successful completion of this study.

Author contribution All authors contributed to the study conception and design. Pedro H. Pereira primarily contributed to the decisionmaking process and the application of the analytic hierarchy process (AHP) methodology, as well as the calculations related to activation energy. Diego M. Maya was responsible for extensively reviewing the state-of-the-art on thermochemical processes for olive pomace treatment. Ana F. Ferreira played a significant role in developing the methodology, including the carbonization process and the selection of potential applications. Diego C. Oliveira collected and analyzed the experimental data, conducted the characterization of the biochar, and performed data analysis. The first draft of the manuscript was written by Pedro H. Pereira, incorporating the individual contributions of each author. Subsequently, all authors provided valuable feedback and critically reviewed earlier versions of the manuscript. All authors actively participated in discussions and revisions, ensuring the accuracy and completeness of the final manuscript.

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Data availability The datasets generated and/or analyzed during the current study are available from the corresponding author upon request.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

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