

# Evaluation of Biofuel Energy Potential of Barks from Some Conifer Species in Türkiye

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Fuel characteristics were evaluated for bark from four coniferous tree species native to Türkiye (Calabrian pine, Black pine, Scotch pine, and Taurus cedar). Bark samples from varying elevations and age groups were analyzed through calorific value (kcal/kg), ash content (%), volatile organic compounds (VOC, %), sulfur emissions (SO<sub>2</sub>, %), elemental ash composition, Fourier transform infrared (FT-IR) spectroscopy, and principal component analysis (PCA). All calorific values were determined on oven-dried samples. Calabrian pine had the highest higher heating value on a dry basis at 5044 kcal/kg, along with the lowest value for ash (1.55%), while Scotch pine exhibited the lowest energy value (4518 kcal/kg). Black pine, which had the highest ash content (3.84%), appeared less suitable as a fuel source. Sulphur emissions across all species were marginal (0.005% to 0.04%). Ash content increased with altitude in Calabrian pine, while the opposite trend was observed in larch. PCA results showed interspecific variations in mineral composition and combustion traits. In conclusion, Calabrian pine and Taurus cedar bark show strong potential as renewable and cost-effective biomass energy sources due to their favorable calorific and ash properties. However, environmental factors such as altitude remain determining factors in biomass fuel performance.

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## INTRODUCTION

Globally, the demand for energy is increasing each year due to uncontrolled population growth. Although wood has been beneficial since human beings for energy and other applications (Sahin *et al.* 2021), at present, fossil fuels, which include coal, oil, and natural gas, are one of the main energy sources besides those found in some natural resource-rich regions (Sahin *et al.* 2023). However, energy policy has become strategically focused on the promotion of renewable energy sources, considering environmentally friendly materials with an affordable cost (de Bikuña *et al.* 2020; Özkan *et al.* 2025). In this context, there have been numerous studies conducted to investigate new alternative technologies from sustainable sources for energy production. Several scientists have already pointed out that biomass, a sustainable material, is one of the most important renewable energy options compared to other resources (Rose *et al.* 2014; Bryngemark 2020; Dashtpeyma and Ghodsi 2021; Helal *et al.* 2023). It has been reported by numerous

researchers that forest and agricultural residues or wastes could be a potentially important source of renewable energy (Demirbas and Demirbas 2009; Sahin *et al.* 2023; Singh *et al.* 2023). The selection of types of biomass can further help to improve fuel efficiency due to constituent proportions (Fengel and Wegener 2011).

One of the simplest and most cost-effective ways to utilize biomass as an energy source is direct combustion. However, this approach may lead to low-value utilization and significant energy losses, particularly when the biomass has high moisture content. Moisture reduces the effective heating value because a portion of the released energy is consumed for water evaporation during combustion. Therefore, not only calorific value but also the moisture content should be considered when evaluating biomass as a fuel. Researchers have been studying not only to find alternative energy resources, but also to better utilize biomass for effective energy generation. As a result of technological advances, numerous new alternative technologies have also been developed. Demirtas and Demirtas (2009) reported that cellulose has a lower calorific value than lignin due to its higher degree of oxidation. The higher oxygen content in cellulose reduces its energy density compared to lignin, which contains a greater proportion of carbon and aromatic structures. Among wood species, softwoods generally exhibit higher carbon content and greater energy density than hardwoods, primarily due to their higher lignin and resin content in coniferous species. Moreover, extractives usually have a positive impact on the heating value of wood fuels (Telmo and Lousada 2011).

Energy from renewable sources has become a political priority in many developed countries. The European Union had set a goal to reach 20% of energy from renewable sources by 2020 (Zachar *et al.* 2018). It was proposed that short-rotation plantations of fast-growing tree species may provide a promising way to produce heat and electricity from renewable sources (Zachar *et al.* 2018). In general, the chemical portion of the wood is carbon (45% to 50%), oxygen (40% to 45%), hydrogen (5.0% to 6.0%), and the rest of some inorganic substances (Young 2008; Fengel and Wegener 2011; Sahin *et al.* 2023). Therefore, the fuel properties of biomass can be evaluated by elemental and proximate analyses, and determination of the heating value. Some tree species with their residues such as bark, cone, leaf, branch, may be a potential energy source for household or industrial applications due to short rotations in certain conditions. Lamlom and Savidge (2003) evaluated carbon content variation within and between 41 North American tree species. They found that the higher C in conifers agrees with their higher lignin content (~30%, versus ~20% for hardwoods) that impact on fuel values of species. It has suggested by Telmo and Lousada (2011) that the fuel properties of selected 17 wood species are positively correlated with extractive and lignin contents. The impact of genetic variation in 23 *Eucalyptus* hybrid clones at 8.5 years for energy production was studied by Wu *et al.* (2017). They suggested that the clones of higher growth rates had lower values for wood chemical properties and lower energy value (Wu *et al.* 2017).

There have been numerous literature reports on tree barks, such as their physicochemical properties (Routa *et al.* 2021; Vangeel *et al.* 2023) and utilization practices in pulp (Borrega *et al.* 2025), in composites (Palanisamy *et al.* 2023), and related industries (Giannotas *et al.* 2021). However, the geographical growing conditions and their impact on the energy properties of tree barks still needs evaluation. In general, depending on species and age, tree bark constitutes about 10% of the volume of a tree (Konôpka *et al.* 2022). Although bark has been proposed to have similar constituents as wood, some distinct differences exist in chemical constituent proportions, where cellulose and hemicellulose are lower, but the lignin is higher than that of wood (Fengel and Wegener

2011). Due to these chemical characteristics, the higher heating value on dry basis and overall energy-related properties of bark are reported to be comparable to those of the corresponding wood species (Sahin *et al.* 2023). Therefore, bark, as a residual by-product of timber processing, may serve as a cost-effective alternative biomass energy source.

In literature reports, various methods have been suggested to evaluate the energy properties of a given sample (*i.e.*, calorific values, ash content, elemental analysis of ash, and burning gas, *etc.*). One of the objectives of such testing is to find comparable data evaluating suitability for energy production. It has already been reported that the geographical differences of even the same species could impact on the properties of tested biomass. These geographical differences can affect tissue development, chemical composition, and mineral accumulation, leading to variability in calorific performance and combustion characteristics. Therefore, assessments that disregard the geographical context may result in an oversimplified or misleading interpretation of the energy potential of biomass (Sahin *et al.* 2023).

This study investigated the hypothesis that bark fuel properties, including higher heating value on dry basis and ash-related chemical characteristics, are controlled not only by species identity but also by geographically influenced growing conditions. Since moisture content is a critical factor affecting the practical energy yield of biomass fuels, it is important to distinguish between dry-basis calorific measurements and the effective heating value under real combustion conditions. High moisture levels reduce usable energy output because a portion of the released energy is consumed during water evaporation, thereby decreasing overall thermal efficiency. Bark samples from four coniferous species were collected across different elevations and analyzed using standardized methods. The evaluated parameters included higher heating value on dry basis, ash content, volatile organic compounds, sulfur content, and elemental composition of ash, providing an assessment of bark biomass energy potential. Although the present study focuses on dry-basis measurements and does not directly evaluate the influence of inherent bark moisture on effective heating value, the impact of moisture content on practical energy recovery is acknowledged and represents an important consideration for future applications and research.

## EXPERIMENTAL

### Materials

The bark samples from four different tree species (Calabrian pine (*Pinus brutia* Ten.), Black pine (*Pinus nigra* subsp. *pallasiana* Lamb. Holmboe), Scotch Pine (*Pinus sylvestris* L.), and Taurus cedar (*Cedrus libani* A. Rich) were collected at different ages and elevations from Yukarıgökdere and Gölcük forestlands, Isparta, Türkiye. Figure 1 shows the general maps of sampling areas, and Table 1 shows the geographical conditions of sampling areas. The samples were obtained from regions and transported to the Botany lab of Forest Engineering Department at the Isparta University of Applied Sciences. They were carefully cleaned for any dirt or other impurities and homogenized after being crushed to a particle size of less than 0.5 mm. The bark samples were mechanically ground to a fine particulate form suitable for subsequent analysis. The ground material was dried in a forced-air oven at 40 °C until a constant mass was achieved (approximately 72 h) and subsequently placed in sealed glass bottles. The samples were stored in a refrigerator until the experimental procedures were conducted.

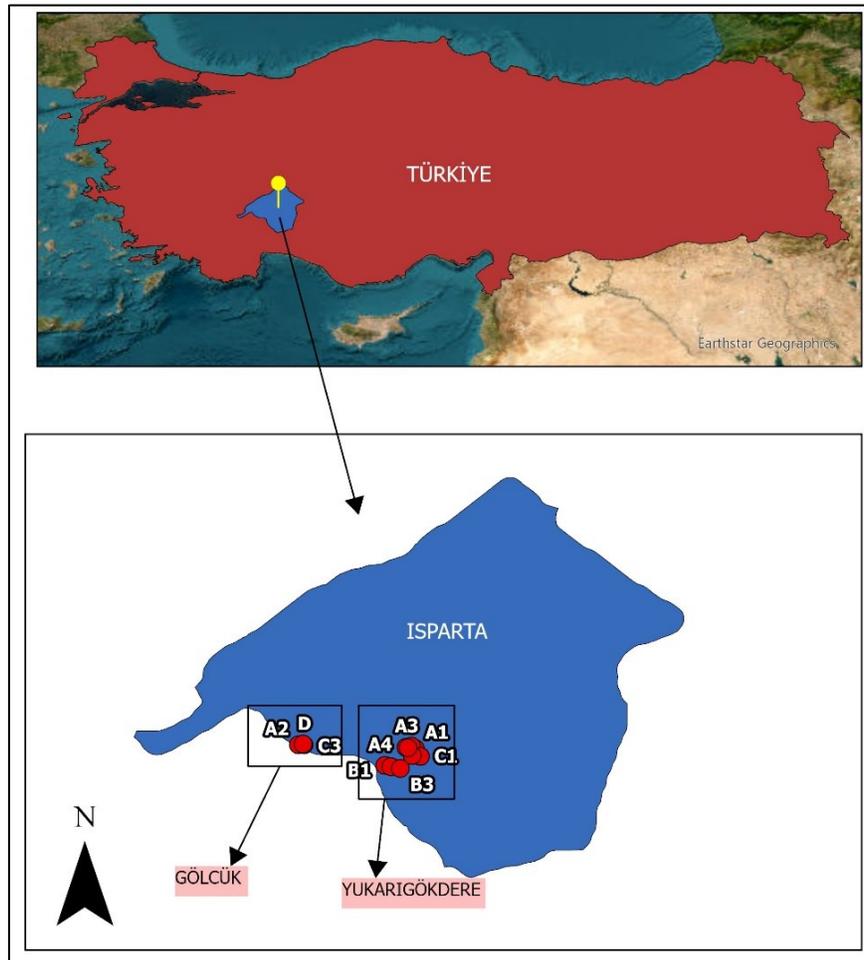


Fig. 1. General map of study area

Table 1. General Geographical and Botanical Properties of Samples

Samples	Sampling Location	Sampling Elevation (m)	Aspect	Age of Tree	Latitude (DMS)
A1	Yukarı Gökdere	1300	East	75	37°43'14.25" N- 30°49'47.81" E
A2	Gölcük	1400	West	70	37°43'53" N- 30°29'10" E
A3	Yukarı Gökdere	1500	Southwest	100+	37°43'39.96" N- 30°49'6.42" E
A4	Yukarı Gökdere	1700	East	100+	37°43'26.16" N- 30°48'8.37" E
B1	Yukarı Gökdere	700	West	90	37°40'17.83" N- 30°44'26.68" E
B2	Yukarı Gökdere	1000	Northwest	75	37°40'5.65" N- 30°45'29.08" E
B3	Yukarı Gökdere	1300	East	75	37°39'48.06" N- 30°47'8.21" E
C1	Yukarı Gökdere	1000	Northeast	90	37°41'55.0" N- 30°50'40.99" E
C2	Yukarı Gökdere	1300	North	110	37°42'2.11" N- 30°49'13.12" E
C3	Gölcük	1400	East	70	37°43'54.44" N- 30°30'8.42" E
C4	Yukarı Gökdere	1600	East	75	37°43'21.13" N- 30°48'30.78" E
D	Gölcük	1400	East	70	37°44'5.25" N- 30°30'1.31" E

(A: Taurus cedar, B: Calabrian pine, C: Black pine; D: Scotch pine)

## Methods

Moisture determination in bark samples was carried out in accordance with the procedures established by the American Society for Testing and Materials, according to ASTM D143-14 (2014). Gross moisture, intrinsic moisture, and total moisture content were determined separately in the measurements.

A bomb calorimeter (LECO AC-500, St. Joseph, MI, USA) was used to determine the higher heating value (HHV) of the bark samples. Prior to calorimetric analysis, the ground samples were oven-dried at  $105 \pm 2$  °C until constant mass was achieved to ensure that the measurements were conducted on a dry basis. Therefore, the reported calorific values correspond to oven-dry conditions. Following the manufacturer's instructions, the instrument was calibrated using certified benzoic acid standards. Approximately 1.0 g of the oven-dried sample was weighed using a precision balance, placed into combustion capsules, and ignited using the bomb calorimeter's self-igniting mechanism.

The ash content (%) and chemical constituents (%) are useful for determining the environmental properties of a given material. Using the sulfur module of the Epsilon EDRX Element instrument (PANalytical, Almelo, the Netherlands) and a LECO AC-500 calorimeter, the total sulfur content (S) was measured. The instrument's detectors picked up the SO<sub>2</sub> gas that resulted from burning samples at high temperatures in an oxygen atmosphere. The instrument software instantly presented the measurement findings as mass percent (%). The elemental analysis of ash was also conducted with the Epsilon EDRX Element instrument.

Tin capsules containing 5.0 to 10 mg of sample were weighed and put into the device. A carrier gas stream (helium) transported the gaseous products (CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>, and SO<sub>2</sub>) to the detector after the samples were fully burned in a high-temperature oxygen atmosphere. The instrument software transformed the measured data into mass percent values. Energy values and the potential for biofuel were evaluated using the elemental composition (%) data.

The FT-IR analyses were conducted using an FT-IR-4700 Diamond ATR Pro spectrometer (JASCO, Tokyo, Japan). Spectral data were collected in the wavenumber region of 400 to 4000 cm<sup>-1</sup>, yielding 3736 data points with a resolution step of approximately 1 cm<sup>-1</sup> ( $\Delta X \approx 0.964$  cm<sup>-1</sup>) for each spectrum. The measurements were recorded in transmittance (%) mode. These experimental parameters represent standard FT-IR operating conditions, enabling the identification and evaluation of characteristic vibrational bands of functional groups in both organic and inorganic compounds.

Principal Component Analysis (PCA) was applied to visualize the relationships between variables in the dataset and identify the primary sources of variance. Prior to the analysis, the data were standardized, and then interpretation was performed by considering components with eigenvalues greater than 1. The PCA results were evaluated using biplot graphs and variance explanation ratios to summarize the multidimensional structure between the variables.

## RESULTS AND DISCUSSION

As mentioned above, there are numerous literature reports on the properties of biomass as a fuel source (Demirbas and Demirbas 2009; Rose *et al.* 2014; de Bikuña *et al.* 2020; Dashtpeyma and Ghodsi 2021; Sahin 2021; Sahin *et al.* 2023). It has consistently been reported that the calorific properties of any given material are a substantial parameter

influencing the final quality of fuel sources. However, some conditions, such as age and growing conditions, could influence not only the botanical properties but also physicochemical properties, including calorific properties.

To find fuel characteristics of four selected different bark samples that were collected from similar elevations in the selected forestlands ( $1350 \pm 50$  m) with similar age group ( $73 \pm 3$  years), three of the commonly used fuel parameters of Calorific value (kcal/kg), VOC (%), and sulfur in burning gas (%) were used to compare samples (Table 2).

The highest higher heating value (HHV) of 5044 kcal/kg was found for the Calabrian pine sample (B3), while the lowest HHV of 4518 kcal/kg was observed for a Scotch pine sample (D). These results indicate an approximate maximum difference ( $\Delta_{\max-\min}$ ) of 522 kcal/kg among the measured samples. Since all calorific values were determined on oven-dried specimens, the observed differences reflect variations in chemical composition rather than differences in moisture content. Such variation is consistent with literature reports on species-specific bark composition and physicochemical heterogeneity (Fengel and Wegener 2011; Vangeel *et al.* 2023). Comparisons with literature values are therefore valid only when based on higher heating value data determined on a comparable dry basis, as effective heating values under practical moisture conditions are not directly equivalent. However, the ash content of samples demonstrated various values, depending on the kind of bark. The black pine (C3) revealed the highest ash content (3.84%), while the Calabrian pine sample (B3) showed the lowest ash content (1.55%), which indicates an approximately 60% lower value than black pine. This could be important considering the Calabrian pine has the highest calorific value with the lowest ash content compared to other samples. Moreover, the volatile organic chemicals were found to be in the range of 56.2% for Scotch pine (D) to 58.0% for Taurus cedar (A2), and there was only a 3.08% difference between the highest and the lowest values, in terms of VOC. It is notable that sulfur contents ( $\text{SO}_2$  % as gas) in burning gas were found to be very low and might be disregarded for all measured samples (0.005% to 0.03%). These experimental findings are consistent with literature and are one of the clear advantages of using bark as a fuel source (de Bikuña *et al.* 2020).

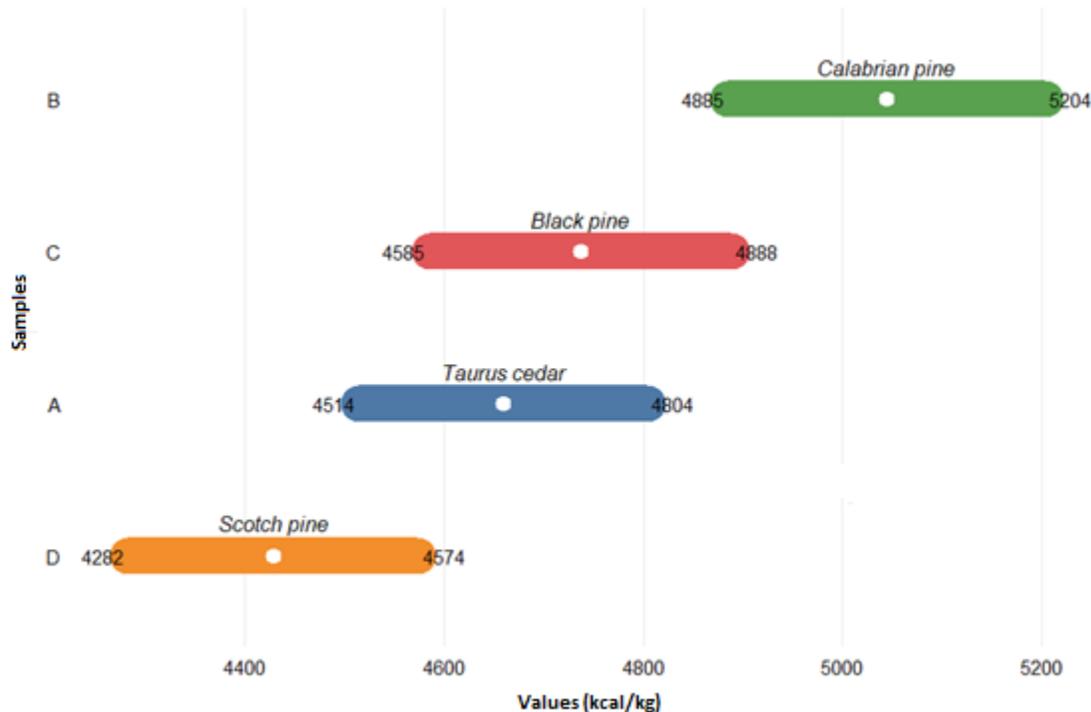
**Table 2.** General Fuel Properties of Some Barks

Samples	HHV (kcal/kg)	Ash (%)	VOC (%)	Sulphur (%)
A2	4659	2.13	58.04	0.02
B3	5044	1.55	57.68	0.005
C3	4737	3.84	56.73	0.03
D	4518	3.01	56.25	0.02

(1350  $\pm$  50 m elevation, 73  $\pm$  3 Years of age of tree)

Figure 2 shows the highest and lowest measured calorific values of samples, for comparison. As shown in Fig. 2, the Calabrian pine (B3) exhibited the highest calorific values (4885 to 5204 kcal/kg), followed by Black pine (C3) (4585 to 4888 kcal/kg), Taurus cedar (A2) (4514 to 4804 kcal/kg), and Scotch pine (D) (4282 to 4574 kcal/kg), in that order. It is also noticeable that a similar range of differences was found for the maximum and minimum calorific values for samples. Values were  $\Delta$ : 290 kcal/kg for Taurus cedar, followed by  $\Delta$ : 292 kcal/kg for Scotch pine,  $\Delta$ : 303 kcal/kg for Black pine, and  $\Delta$ : 319 kcal/kg for Calabrian pine. The relatively similar  $\Delta$  values observed among species indicate comparable levels of intraspecific variability in calorific performance. Nevertheless,

Calabrian pine exhibited the widest calorific range ( $\Delta = 319$  kcal/kg), suggesting greater sensitivity of its bark energy properties to site- or sample-specific factors. Figure 2 further indicates a clear separation among species in terms of calorific performance, with minimal overlap between Calabrian pine and the remaining species. In contrast, partial overlaps in calorific ranges were observed between Black pine and Taurus cedar, suggesting closer energy performance between these two species. Scotch pine consistently exhibits the lowest calorific range, highlighting its comparatively lower suitability as a high-energy biomass fuel.



**Fig. 2.** The calorific properties of samples (1350 ± 50 m elevation, 73 ± 3 years of trees)

To find the effects of different elevations on fuel characteristics of samples with similar age groups of samples (90 ± 20 years), measured general fuel properties are given in Table 3. Within groups, the highest calorific values of 5101 and 4254 kcal/kg were found at the highest elevations with Taurus cedar (A4) (1700 m) and Black pine (C4) (1700 m) samples, while the lowest value of 4203 kcal/kg was also Taurus cedar (A3) at the medium elevation (1500 m). However, Calabrian pine and Black pine samples showed contrasting results regarding ash content, in which Calabrian pine appeared to have a positive correlation between ash content (B1-B3) that increased as elevation increased, while Black pine (C1-C3) showed a negative correlation with ash content (%) that continuously decreased as elevation increased.

Those experimental findings appear to be consistent with literature findings. For instance, Gruber *et al.* (2021) reported a calorific value of birch tree bark as 22.21 MJ/kg (5308 kcal/kg). In a more recent study on a similar topic, Sobol *et al.* (2023) evaluated 14 species of bark from trees naturally occurring in central Europe, in terms of energy suitability. They reported energy values in the range of 4150 kcal/kg (17.4 MJ/kg) for horse chestnuts to 5170 kcal/kg (21.6 MJ/kg) for silver birch bark. Moreover, they proposed that the mean energy values are higher for softwood species than hardwood species. There have

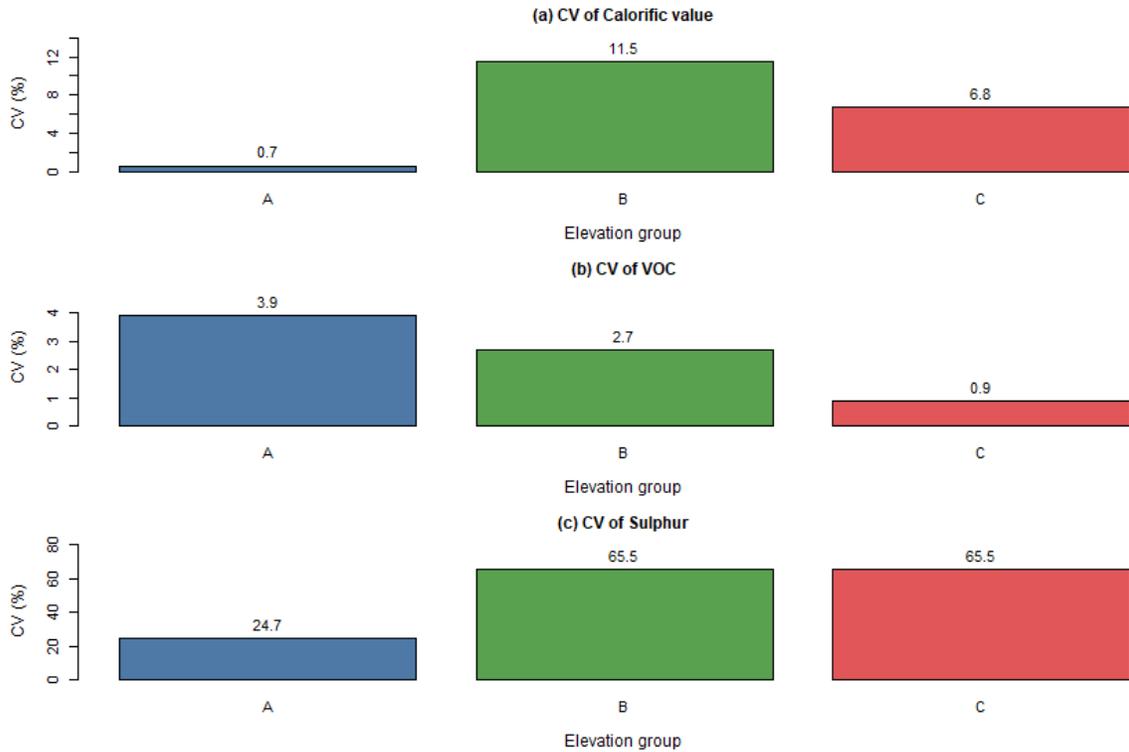
been numerous literature reports that coniferous species tend to be more calorific than deciduous species. Those are related in their chemical composition, primarily in the amount of lignin, cellulose, and hemicellulose, which are the leading energy carriers in biomass (Sobol *et al.* 2023). In addition, Calabrian pine consists of a high ratio of resinous substances not only in wood but also in bark (Fengel and Wegener 2011). In this case, it could be reasonable to suggest that barks from Calabrian pine species (sample B) ability to show higher calorific value due to their special chemical constituents, particularly resinous compounds.

For volatile organic matter, Taurus cedar and Calabrian pine samples appeared to have a positive relation with elevation that increases as elevations increase, and *vice versa*. The highest volatile organic matter of 60.1% for Taurus cedar (A1) and 59.2% for Calabrian pine (B1) were found at the lowest elevations for both species. However, there is no clear trend, and considerable differences were found for Calabrian pine samples ( $\pm 3.0\%$ ). It is also noticeable that the sulfur content of the samples was negligible and at around 0.005% to 0.04%. In many literature suggestions, sulfur release from an energy source has been extensively used to evaluate environmentally friendly fuel material properties. Consistently, they have reported that the lowest sulfur emissions into the air have more environmentally friendly fuel properties (Omer 2017; Demirbas 2004; Jomantas *et al.* 2025).

**Table 3.** Fuel Properties of Barks from Different Elevations (90  $\pm$  20 Years of Age of Trees)

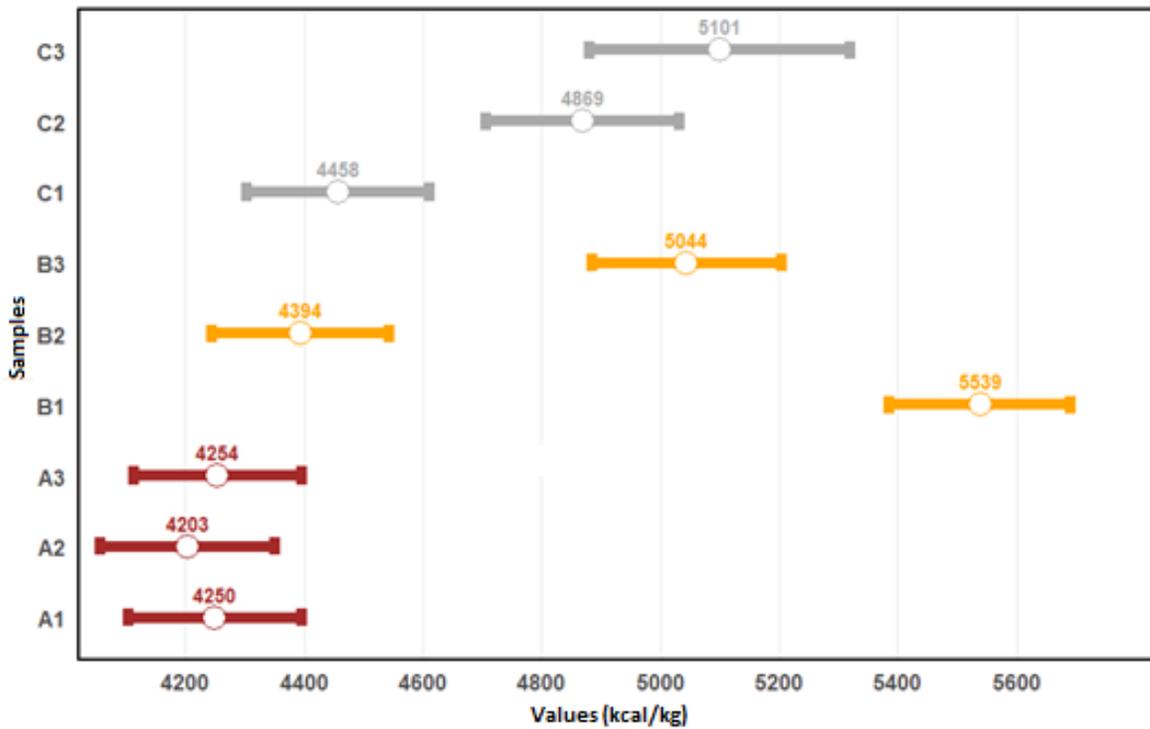
Samples	Values (kcal/kg)	VOC (%)	Sulphur (%)
A1	4250	60.06	0.02
A3	4203	58.98	0.02
A4	4254	55.68	0.03
B1	5539	59.19	0.02
B2	4394	56.10	0.01
B3	5044	57.68	0.005
C1	4458	59.80	0.01
C2	4869	60.63	0.04
C4	5101	60.78	0.02

In the data presented in Table 3, within-group variability was evaluated not only through mean values but also in terms of relative variance. For this purpose, the coefficient of variation (CV) was calculated for calorific value, VOC, and sulfur content according to elevation groups (A-C) and is presented in Fig. 3. The results reveal that VOC values showed a relatively homogeneous distribution, exhibiting low CV values in all groups. In contrast, calorific values showed significant within-group variability with moderate CV values, while sulfur content indicated a heterogeneous distribution, particularly with higher CV values in some groups. These findings demonstrate that the data in Table 3 contain different variable patterns specific to the parameter, rather than a random spread resulting from a few outliers, and support the necessity of considering variance in comparisons between groups.



**Fig. 3.** Coefficient of variation (CV) of calorific value, VOC and sulfur content according to elevation groups

Figure 4 shows the energy properties of samples for comparison.



**Fig. 4.** The calorific properties of samples (90 ± 20 years of age of trees)

When all calorific values were evaluated in terms of calorific differences between the samples, the Calabrian pine sample (B1) from 700 m elevation had a calorific value range of 5386 to 5692 kcal/kg ( $\Delta$ : 306), followed by Black pine sample from 1700 m elevation with calorific value range of 4881 to 5321 kcal/kg ( $\Delta$ : 440) and Calabrian pine sample (B3) from 1300 m elevation with calorific value range of 4885 kcal/kg to 5204 kcal/kg ( $\Delta$ : 319). The experimental data presented in Table 3 and Fig. 4 provide clear evidence that the same biomass (bark) from different elevations could have different physicochemical properties.

The ash values of the samples are shown in Fig. 5. As illustrated, the ash contents of the bark samples from different elevation groups showed notable differences. Group A samples (A1, A3, and A4) had the highest ash values in the range of 3.28% to 4.08%, indicating high mineral accumulation and which negatively affects fuel quality in terms of fuel quality. In contrast, Group B samples (B1, B2, and B3) had lower ash values ranging from 1.12% to 1.55%, indicating cleaner combustion and less potential for solid residue. The lowest ash contents were determined in Group C samples (C1, C2, and C4) at 0.81% to 1.35%, with the C4 sample demonstrating the most favorable fuel characteristics with a value of 0.81%. Overall, there was a systematic decrease in ash content among the groups in the order A > B > C, indicating that the mineral accumulation in the barks varied depending on the tree species and age conditions. These results reveal that the group C samples constituted the most advantageous group for use as biofuel due to their low ash content.

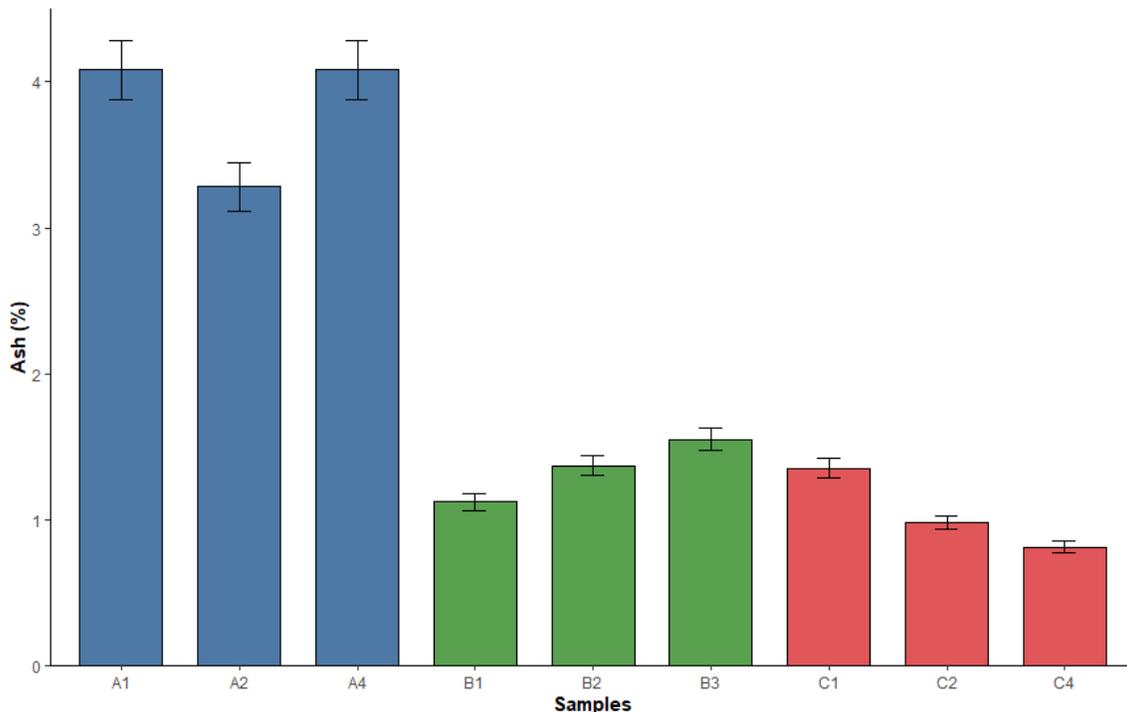
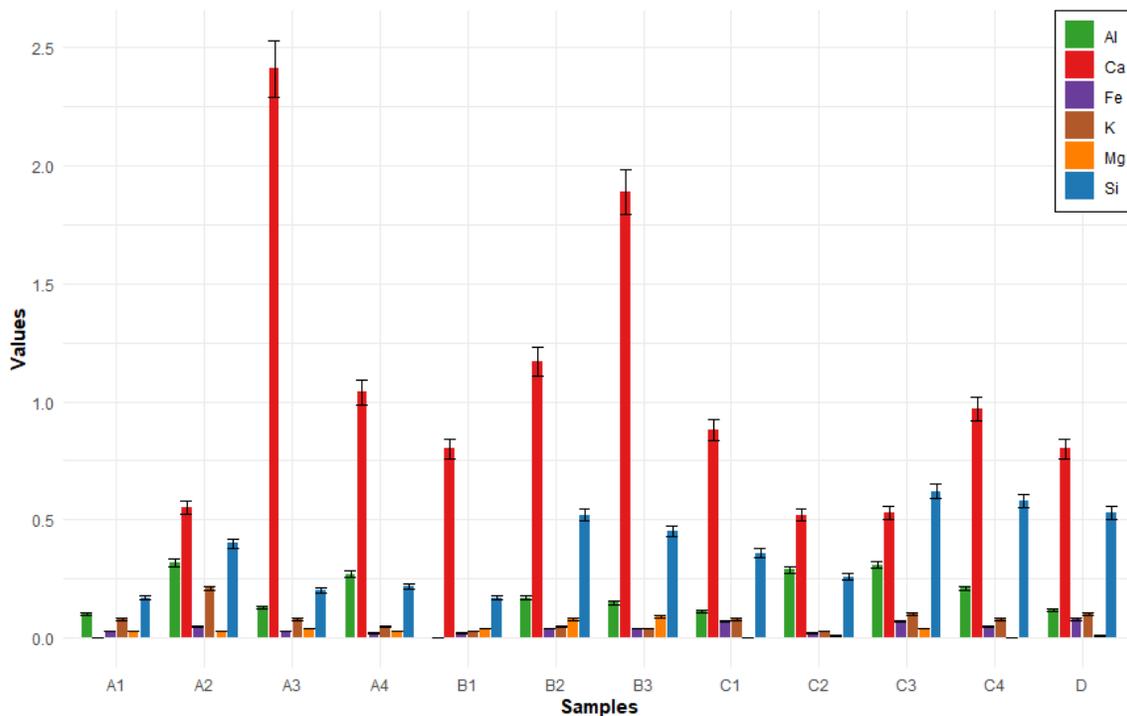


Fig. 5. Ash values of samples

The energy properties of the different biomass types could vary not only for calorific value, but also for ash content (%) and its constituents, even though the constituents were relatively different within a species (Sahin 2021; Sahin *et al.* 2023). This variation is attributed to the influence of geographically growing conditions on constituent

proportions. Figure 6 shows elemental analyses of different bark ashes that were supplied from various geographical locations.

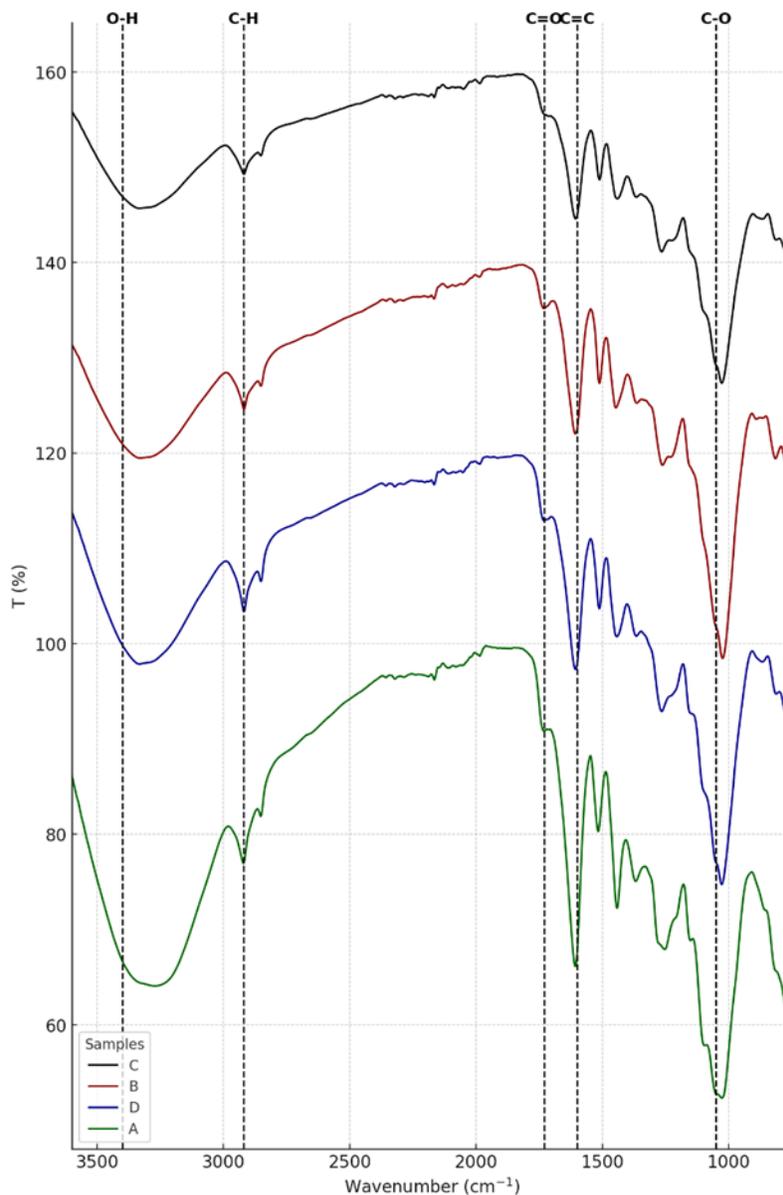
The results indicate that a negligible proportion of iron (0.02% to 0.08%), magnesium (0.01% to 0.04%), and potassium (0.03% to 0.21%) were found in ash. However, the highest Si and Al values of 0.62% and 0.31% were found with a Black pine sample (C3) that was obtained at 1400 m elevation at the age of 70. This sample also showed the highest ash content (3.84%) among all samples, regardless of bark type. The lowest Si and Al values of 0.17% and 0.10% were found with a Taurus cedar sample (A1) that was collected from 1300 m elevation at the age of 75. Notably, the highest and lowest calcium was found with Taurus cedar species that were in the range of 0.01% for sample A1, which was collected from 1300 m elevation at the age of 75 to 2.41% for sample A3 that was obtained from 1500 m elevation at the age of 100-year-old tree. It is worth noting that no clear trend was observed between geographical growing conditions and elemental composition.



**Fig. 6.** Elemental distributions of ash in bark

Figure 7 comparatively shows the FT-IR spectra of selected samples. All the spectra show characteristic bands and stretching properties as similar to each other. It has already been established that biomass, including wood-based samples, show a strong -OH stretching frequency in the  $3300\text{ cm}^{-1}$  band, and C-H stretching in methylene and methyl is prominent in the  $2800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$  band (Ding *et al.* 2016). Other important groups have been identified as: stretching frequencies C=O, -CH<sub>3</sub> asymmetric, -CH<sub>3</sub> symmetric, and C-O and are shown in the  $1680\text{ cm}^{-1}$ ,  $1745\text{ cm}^{-1}$ , and  $2993\text{ cm}^{-1}$  bands, respectively. The -CH<sub>3</sub> asymmetric and -CH<sub>3</sub> symmetric stretching frequencies appear in the  $1361\text{ cm}^{-1}$  and  $1452\text{ cm}^{-1}$  bands, respectively (Chieng *et al.* 2013). When Fig. 7 is examined, although all bark samples exhibited similar chemical constituents and functional groups, differences in band intensity were evident among species. Black pine samples showed weaker

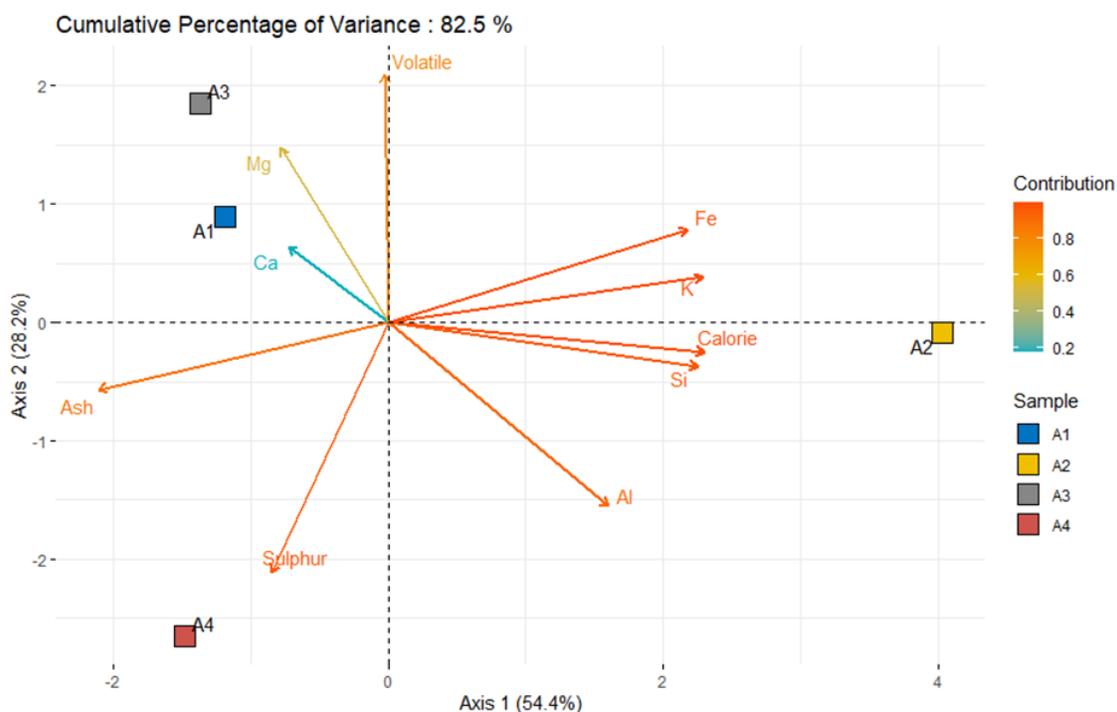
absorbance intensity for the C=O stretching band near  $1745\text{ cm}^{-1}$ . Although the C=O bond typically exhibits strong IR absorption due to its high dipole moment, reduced band intensity may occur in complex biomass matrices where carbonyl groups are involved in esterified structures, hydrogen bonding, or aromatic lignin networks. Moreover, the relatively higher mineral and ash content of black pine bark may partially mask organic functional group signals in FT-IR spectra. In contrast, the Taurus cedar sample exhibited the strongest C=O band intensity, suggesting a higher relative contribution of carbonyl-containing structures.



**Fig. 7.** FT-IR spectra of samples

Figure 8 shows the PCA results for Taurus cedar wood. This PCA graph shows the distribution of data pertaining to Taurus cedar wood (A1-A4) evaluated using PCA. The first component (PC1) explained 54.4% of the total variance, while the second component (PC2) explained 28.2%, with the two axes together representing 82.5% of the total

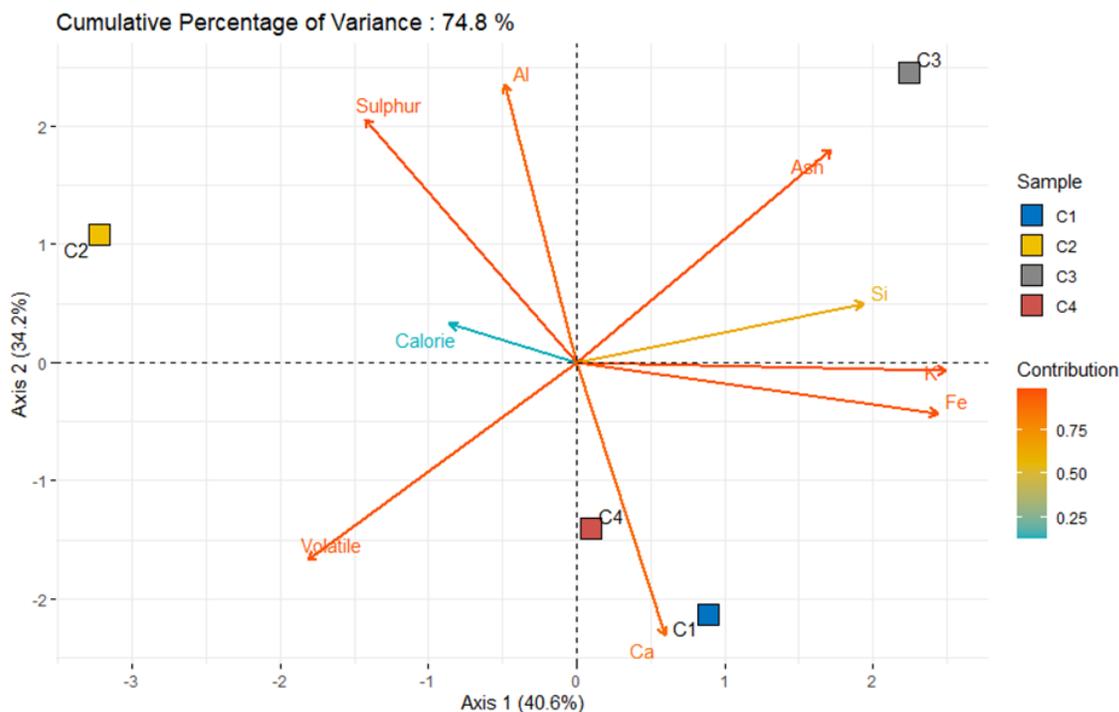
variance. This is a high explanatory power, indicating that the diversity in the data was largely summarized by the first two components. In the graph, sample A2 is distinguished by high positive values in the PC1 direction and is strongly correlated with calorific value, K, Si, and Fe in particular. Sample A1 is positioned closer to the Mg and Ca axes, revealing a different profile in terms of mineral composition. Sample A3 is located on the positive PC2 axis, associated with volatile matter, while sample A4 is positioned in the negative PC1–PC2 region, associated with ash and sulfur content. This distribution indicates that there were significant chemical and energy content differences between Taurus cedar samples and that variables, such as ash, sulfur, and calorific value contribute notably to distinguishing between the samples. Therefore, the PCA results reveal that there were notable variations in mineral content and combustion properties among different Taurus cedar wood samples and that differences that may vary according to elevation or environmental conditions can be observed.



**Fig. 8.** PCA results of Taurus cedar

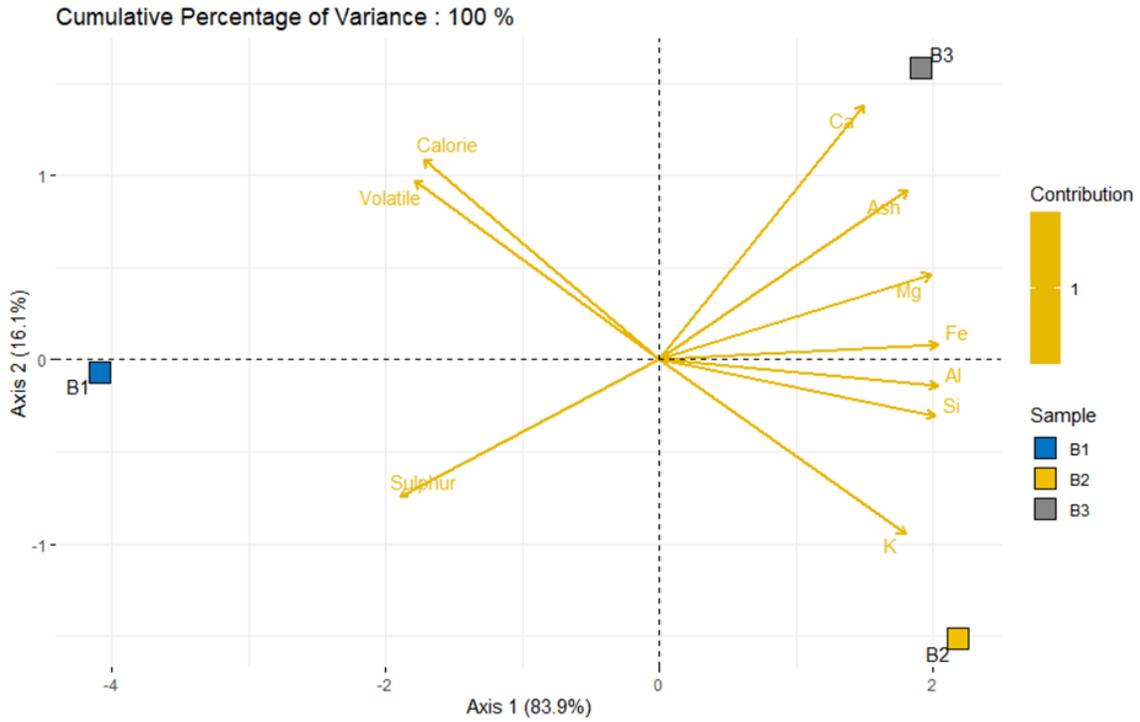
Figure 9 shows the PCA results for black pine. This PCA graph shows the distribution of chemical and energy contents of black pine (C1-C4) samples evaluated by PCA. The first component (PC1) explained 40.6% of the variance, while the second component (PC2) explained 34.2%, together representing 74.8% of the total variance. This ratio indicates that the chemical differences between the black pine samples could be largely explained by the first two components. Upon examination of the graph, it is seen that the C3 sample is located on the positive PC1 and PC2 axes and is strongly associated with Fe, K, Si, and ash content. The C1 sample is located on the negative PC2 axis, correlated with Ca, while the C4 sample is located on the negative PC2 axis, correlated with Ca at a lower level and, to a lesser extent, volatile matter. The C2 sample, on the other hand, is separated into the negative PC1 region and shows a different profile from the other samples. The results further indicate that the Al and S variables contributed to a clear

separation from C3, whereas the calorific value had a weaker effect on the relationships with the variables. These results indicate that black pine samples differed in terms of mineral content (Fe, K, Si, Al, S, Ash) and ash-combustion properties, with the C3 sample standing out in terms of these elements, while C1 and C4 were distinguished more by their Ca and volatile matter characteristics.

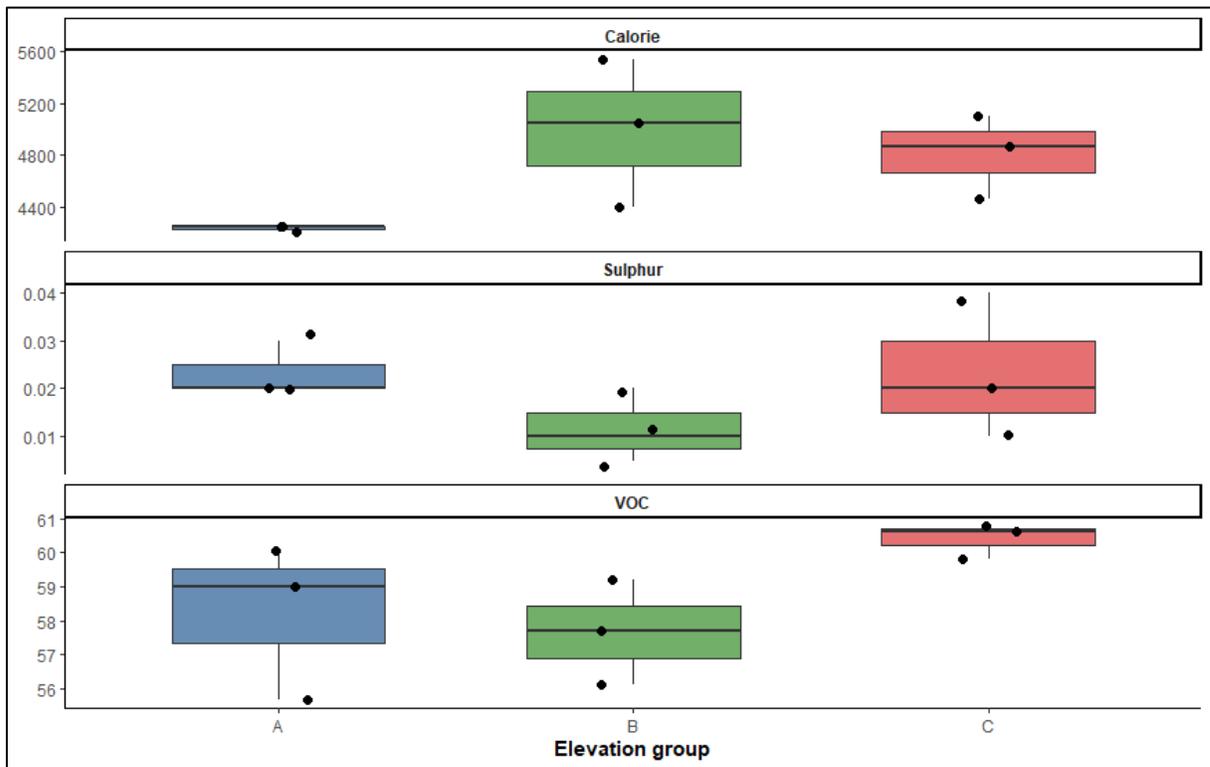


**Fig. 9.** PCA results of black pine

Figure 10 shows the PCA results for Calabrian pine. These results show the distribution of chemical composition and energy-related parameters of Calabrian pine (B1-B3) samples evaluated by principal component analysis. The first two components explain the total variance (100%), with PC1 contributing 83.9% and PC2 contributing 16.1%. This indicates that the differences observed in the Calabrian pine samples could be fully explained by the first two components. When examining the graph, the B2 sample is in the positive PC1 direction and appears to be strongly related to K, Si, Al, Fe, Mg, ash, and Ca content. The B3 sample is in the positive region of both PC1 and PC2, establishing a clear connection with elements such as Ca, Mg, ash, and Fe. In contrast, the B1 sample is separated from the other samples in the negative PC1 direction and stands out with lower mineral content values. Furthermore, volatile matter, calorific value, and sulfur (S) variables are positioned closer to B1 in the negative PC1 direction. This distribution reveals that mineral content parameters (Ca, Mg, K, Si, Fe, Al, and Ash) were particularly decisive in Calabrian pine samples, while a different separation existed in terms of volatile matter and calorific value. As a result, PCA showed that Calabrian pine samples were clearly separated based on their mineral content and combustion properties, with B1 being low in minerals and B2 and B3 being high in minerals.



**Fig. 10.** PCA results of Calabrian pine

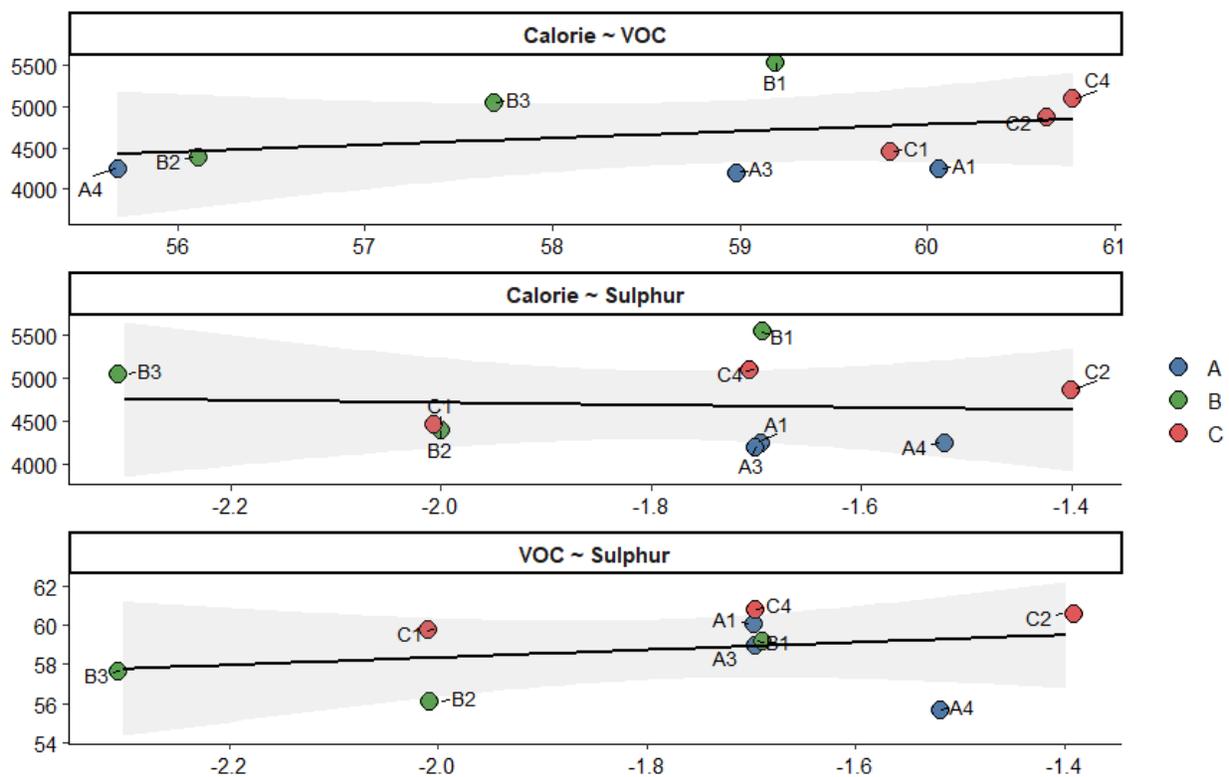


**Fig. 11.** Distribution and variability of calorific value, VOCs, and sulphur content according to elevation groups

Figure 11 shows the differences in distribution and variance among elevation groups for the parameters examined. While VOC values showed limited variability in all groups, significant within-group variance differences were observed in calorific value and sulfur content. It was observed that calorific values exhibited a wider distribution in group B, VOC values showed relatively low variance in all groups, and sulfur content had higher variability in group C.

Figure 12 shows the pairwise relationships between calorific value (kcal/kg), VOC, and sulfur content based on elevation groups (A-C). Scatter plots in each panel reveal inter-sample variability, while linear regression lines and confidence bands visualize possible linear trends between the variables.

The distribution of points in the Calorific value VOC panel showed a wider spread in calorific values despite the relatively narrow VOC range. This indicates that calorific value was also affected by components other than VOC and/or sample characteristics. In the Calorie-Sulphur and VOC-Sulphur panels, sulfur values were scaled using a log<sub>10</sub> transformation to allow for more readable comparisons of differences at low levels. In conclusion, when the findings were evaluated together, the findings suggested that the relationships between variables may show heterogeneity at the group level and that the spread (variation) between samples differed according to the parameters. These findings support the idea that it is appropriate to consider not only mean differences but also distribution/variance characteristics in intergroup comparisons.



**Fig. 12.** Results of the pairwise relationships between calorific value, VOC and sulphur content according to elevation groups

## CONCLUSIONS

1. This study demonstrated that the fuel-related properties of bark residues from selected coniferous species in Türkiye showed notable differences depending on species and growing conditions. The higher heating value on dry basis ranged from 4203 to 5539 kcal/kg. The highest HHV was observed in Calabrian pine (5539 kcal/kg at low elevations), while the lowest HHV was found in Scotch pine (approximately 4518 kcal/kg). Significant interspecies differences were also observed in ash content. Values as low as 0.81% were detected in Black pine samples, whereas values up to 4.08% were measured in Taurus cedar samples. Considering the combination of high HHV on dry basis and relatively low ash content (1.12 to 1.55%), Calabrian pine appears to be the most promising biofuel candidate among the evaluated species. However, these energy values represent oven-dry conditions and should not be directly interpreted as effective heating values under practical moisture conditions.
2. Volatile matter content ranged between 55% and 60%, with elevation-dependent variations particularly evident in Taurus cedar and Calabrian pine samples. Sulphur content in all species ranged between 0.005% and 0.04%, indicating negligible sulfur-related emissions and supporting their environmentally favorable characteristics. Elemental analysis of ash revealed species- and elevation-dependent variations in Si, Al, Ca, and Fe concentrations, with relatively high levels detected in certain Black pine and Taurus cedar samples. FT-IR analysis confirmed functional groups typical of lignocellulosic biomass, and PCA results demonstrated species differentiation based on mineral composition and energy-related parameters.
3. Overall, the findings indicate that bark residues, commonly considered a by-product of the forest industry, possess considerable potential as a renewable energy resource when evaluated on a dry-basis higher heating value. Such work would enable more accurate estimations of real-world energy recovery potential and support the development of sustainable biomass utilization strategies.

## ACKNOWLEDGEMENTS

### Conflict of Interest

The authors declare that there were no funds and no conflict of interest.

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