



Elemental composition of raw and torrefied pellets made from pine and pine-eucalyptus blends

Andrés Iglesias Canabal^{a,*}, Jorge Proupín Castiñeiras^a, José Antonio Rodríguez Añón^a,
Cristina Eimil Fraga^b, Roque Rodríguez Soalleiro^b

^a Faculty of Physics, University of Santiago de Compostela, 15782, Santiago de Compostela, Spain

^b Department of Plant Production, University of Santiago de Compostela. Higher Polytechnic Engineering School, 27002, Lugo, Spain

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ABSTRACT

Debarked *Pinus radiata* wood was blended with debarked *Eucalyptus nitens* wood in three different proportions: 100% pine (100P), 90% pine-10% eucalyptus (90P/10E) and 60% pine-40% eucalyptus (60P/40E). The pellets were torrefied in dry and non-oxidative conditions at different temperatures (210, 240, 270 and 300 °C) and residence times (40 and 60 min) to enhance the energy properties and determine the elemental composition (18 elements). For raw pellets, the concentrations of Na, K, Zn, B and Cl increased significantly with the proportion of eucalyptus wood, with Cl levels being 60% higher in the 60P/40E than in the 100P pellets. The concentrations of most elements (C, Mg, Al, P, Ca, Fe, Cu) tended to increase (+35% for C, +200–250% for the others) with torrefaction severity, independently of the mixture. Decreases in H and O concentrations were also independent of the mixture. Torrefaction decreased the Cl content by 63–77%, which compensated for the high levels in mixtures with eucalyptus. Increases in the high heating value (by as much as 37%) with torrefaction occurred in parallel with an increase in carbon content and a decrease in the atomic H:C and O:C ratios, particularly in the 260 to 300 °C transition. Torrefaction compensated for the negative effect of the inclusion of eucalyptus, with the alkali index remaining at a relatively safe maximum value of 0.10 kg GJ⁻¹.

1. Introduction

Pellets made from lignocellulosic biomass are used in Europe to generate thermal energy for domestic heating and for use in agro-industrial processes and even for co-firing, with coal, in power plants. Pellet consumption amounted to 27.7 M tons in 2019 for the EU-28 countries [1], 19.7 M tons in 2020 [2] and 24.5 M tons for the EU-27 countries [3]. Biofuel pellets are cylindrical pieces of compressed wood material, with improved energy density derived from the compaction. The standardized size of the pellets improves their handling and eases transport. In the EU, pellet production was 17.8 M tons in 2019 (EU-28 countries), 18.1 M tons in 2020 and 20 M tons in 2021 (EU-27 countries); in Spain the respective production levels were 0.714 M tons in 2019, 0.616 M tons in 2020 and 0.642 M tons in 2021 [4].

Most pellet factories in Spain produce high quality wood pellets made from debarked pine; however, there is an interest in using mixtures of other species, as pine wood is increasingly in demand for other uses (as fibreboard and sawn wood and in construction). The pine pellets

are generally classified as A1 or I1 quality, according to the UNE-EN ISO-17225-2 standards for respectively domestic and industrial use ($600 \leq BD \leq 750 \text{ kg m}^{-3}$, moisture content $M \leq 10\% \text{ w.b.}$ and net calorific value $Q \geq 16.5 \text{ MJ kg}^{-1}$) [5]. The abovementioned standards also consider A2/I2 classes and B/I3. The chemical composition of solid biofuels has a direct impact on thermal use and thus on the properties covered by the standards [6]. Moreover, one of the most restrictive aspects of the ISO standards is the elemental composition of the biomass: the limits of chlorine (0.02%), sulphur (0.04%) and nitrogen (0.3%) are strongly regulated, because the products that are formed during combustion are released into the atmosphere.

Although the energy quality of the material is improved, biofuel pellets maintain some characteristics of the biomass from which they are made, such as low calorific value relative to fossil fuels and high hygroscopicity, properties that are undesirable in thermal power generation [7,8]. The importance and impacts of the elemental composition of biomass on its thermal utilisation are summarized in Table 1. The information refers to the list of elements covered in this study.

* Corresponding author.

E-mail address: a.iglesias.canabal@usc.es (A. Iglesias Canabal).

Table 1

Significance and impacts of the elemental composition of biofuels for their thermal utilisation. HHV = high heating value. LHV = low heating value. FAP = fly ash particles (volatile elements forming aerosol). Limits in standards refer to domestic use for categories A1, A2 and B.

Element (s)	Effect(s)	Specific limit in UNE-EN ISO-17225-2 (%)	References
N	Air contaminant (NOx)	$N \leq 0.3, \leq 0.5, \leq 1.0$	[6,9]
C	Increases HHV		[6]
H	Increases HHV, but decreases LHV		[6]
S	Air contaminant (SOx). Sulphate contributes to fouling. Corrosive. Formation of FAP	$S \leq 0.04, \leq 0.05, \leq 0.05$	[6,10]
O	Decreases HHV		[6]
Cl	Air contaminant (HCl, PCDD/F). Contributes to fouling. Corrosive. Formation of FAP	$Cl \leq 0.02, \leq 0.02, \leq 0.03$	[6,10,11]
B	Air contaminant (H ₃ BO ₃ , B halogens)		[12]
Ca, Mg	Ash-forming. Increase ash melting point		[13]
K	Ash-forming. Decreases ash melting point. Risk of alkali-related sintering/slagging. Formation of hard sintering if combined with Si. Formation of FAP		[6,10,13]
Na	Ash-forming. Risk of alkali-related sintering/slagging. Corrosive. Formation of FAP		[6,10]
Si	Ash-forming. Formation of hard sintering if combined with K		[6]
Al	Ash-forming. Can prevent sintering and Chlorine deposits		[11]
Cu	Ash-forming. Soil contaminant for ash recycling	$Cu \leq 10$ ppm	[5]
Zn	Ash-forming. Slagging. Soil contaminant for ash recycling. FAP	$Zn \leq 100$ ppm	[6]
P, Fe	Ash-forming		[6]
Mn	Minor nonvolatile, ash-forming		[6]

Several types of biomass pre-treatment have been proposed with the aim of overcoming the drawbacks associated with solid biofuel. Torrefaction at temperatures of between 200 and 300 °C in inert or low oxygen content atmospheres is a thermal pretreatment [14]. This process modifies the structure of the biomass, decreasing the atomic O:C and H:C ratios. It also reduces the biomass hygroscopicity and improves calorific values. The improved biomass properties increase the commercial value of pellets, woodchips or other biofuels and favour their potential use in thermochemical energy conversion processes.

The ISO 17225-8 standard for classifying graded thermally treated and densified biomass fuels for commercial and industrial uses was released in 2016 [15]. Torrefied pellets produced from thermally processed chemically untreated woody biomass can be classified as types TW1 and TW2, with the first being the most restrictive in terms of ash content, bulk density or net calorific value, as well as regards elemental composition.

Debarked wood is known to have favourable levels of the most harmful elements, in comparison with other woody biomass components [6]. Nonetheless, blending pine with eucalyptus wood can potentially increase different levels of elements; torrefaction is a pre-treatment technology that has been suggested to lower the Cl content of pure eucalyptus feedstock [16,17].

This study aimed to determine the effect of different blending and torrefaction severities on the elemental composition (18 elements) of wood pellets. The study was performed using three types of pellets, with eucalyptus always comprising a minor proportion (if any) of the blend (100% pine, 90% pine 10% eucalyptus and 60% pine 40% eucalyptus). The objective of the study was to investigate the elemental composition

of the pellets subjected to a range of torrefaction severities.

2. Material and methods

2.1. Biomass characterization

The samples used in the study were 100% pine (100P), 90% pine and 10% eucalyptus (90P/10E), and 60% pine 40% (60P/40E) pellets. The first sample (100P) was obtained from a pellet factory dedicated to producing biofuels from debarked *Pinus radiata* wood. The factory uses an annular industrial pelletizer with press-channel length of 42 mm. The other two samples (90P/10E and 60P/40E) were produced in this study in the biomass laboratory with the same debarked *Pinus radiata* wood mixed with debarked *Eucalyptus nitens* wood. The wood of eucalyptus came from 12-year-old plantations in the form of 12–15 cm diameter logs and were chipped in the laboratory. According to previous experiences [18], the woodchips were ground to <4 mm and dried to a moisture content of 10–12% (wet basis) before being pelletized. The pellet samples were analyzed in the laboratory to determine the energy properties.

The blends were prepared in the different proportions and were then mixed for 1.5 h in a solids Heidolph mechanical blender to ensure optimal homogenization. The pine and eucalyptus woodchips used as feedstock to produce the pellets were analyzed to determine the heating value and for ultimate and proximate analysis.

2.2. Pelletization

The pellets were produced in a flat die pellet press (Amandus Kahl 14–175). The machine has two rotating steel rollers that force the biomass sample through cylindrical die holes (of diameter 6 mm) to form the pellets (length 20–22 mm). The temperature increases gradually due to friction between the die and the biomass and between the particles until a stable pelletization temperature is reached. Temperature is measured by a thermocouple located in the outer part of the flat die. The pelletization process (5 kg each type of pellet) took 1 h due to the complexity of pelletizing mixtures with eucalyptus and the need to heat the flat die, with a production rate of 10 kg h⁻¹ for each type of pellet. Two cutting knives located 25 mm under the die sliced the pellets as they emerged from the die holes. The pellets were then collected in a recipient. The newly produced pellets were left to cool at room temperature for 48 h in order to improve their durability and moisture content [18].

The processing parameters for pelletization (moisture content, press-channel length and die temperature) were established on the basis of previously reported experience with the same equipment [18–20] and then adapted to the problems associated with the densification of eucalyptus. A press-channel length of 28 mm was suitable for producing pellets with mixture 90P/10E but led to clogging of the die holes when used with mixture 60P/40E. A press-channel length of 24 mm was therefore used for the mixture containing the highest percentage of hardwood. In this study, an average pelletization temperature of 65 °C was applied (range 60–70 °C), and biomass moisture content at the inlet of the pellet press had to be increased to 17–17.5%. The moisture content of the samples required for the pelletization process was adjusted by spraying distilled water onto the mixture. Overall, the pelletization parameters were similar to those to hardwoods such as beech [20].

2.3. Torrefaction process

Pellet samples (25 g) were placed in a muffle furnace (J.P. SELECTA model) at different temperatures (210, 240, 270 and 300 °C) and two holding times (40 and 60 min) in an oxygen-deprived atmosphere. The samples were heated from room temperature to the torrefaction temperature, at a heating rate <15 °C/min. After torrefaction, the samples were cooled on a desiccator with silica gel. Nine treatments of

torrefaction after pelletization (TAP) were applied, with torrefaction severities varying from T210-40 to T300-60. The treatments were factorised with the three mixtures (100P, 90P/10E and 60P/40E). Each treatment was repeated three times, accounting for a total of 81 samples. The samples were weighed before and after torrefaction to enable calculation of the mass yield (MY, %) in all treatments. Control pellet samples were not torrefied.

2.4. Analysis of pellet properties

Proximate and ultimate analyses were used to measure the basic characteristics of control and torrefied pellets according to UNE standards. The samples were dried in an oven at 105 °C for 24 h for determination of the moisture content (MC, %), expressed on a wet basis according to UNE-EN ISO 18134-1 [21].

Ultimate analysis was performed on control and torrefied samples considering the 18 elements listed in Table 1. These include major elements related to energy content (C, H, O), elements covered in the standards, and which are present in non-contaminated forest areas (N, S, Cl, Cu, Zn), ash forming elements (Ca, Mg, K, Na, Si, Al, P, Fe, Mn) and B as a potential contaminant.

N, C, H and S were determined after combustion in a LECO elemental analyzer (Truspec model) to establish the gas contents after the process, following UNE-EN ISO 16948 [22] and UNE-EN ISO 16994 [23]. The oxygen content was calculated by difference, with Eq. (1).

$$O = 100 - C - N - H - S - A \quad (1)$$

where O, C, N, H and S denote elemental composition (% db) and A is ash (% db)

The ash content (%) was determined after combustion at 550 °C following UNE-EN ISO 18122 [24].

The data were represented in a van Krevelen diagram (i.e. by plotting the H:C atomic ratio against the O:C atomic ratio) to enable classification of the different types of biomass.

The pellet samples were digested with HNO₃, HF and H₂O₂ in a microwave oven, and the concentrations of B, Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Cu, Zn were determined by ICP-MS [25].

Chlorine content was determined by ion chromatography (Metrohm 930 Compact IC Flex) according to the UNE-EN ISO 16994 standard. In addition, the Cl release ratio was calculated by the following equation (Eq. 2):

$$R_{Cl}(\%) = \frac{m_{Clc} - m_{Cl_{torr}} * MY}{m_{Clc}} * 100 \quad (2)$$

where m_{Clc} and $m_{Cl_{torr}}$ are the chlorine contents of control and torrefied sample respectively and MY is the mass yield.

The high heating value (on a dry basis) (HHV_{db}) was determined experimentally by combustion of 0.5 g of dry pellet in a bomb calorimeter (IKA C5000) under a 30 bar oxygen atmosphere following UNE-EN ISO 18125 [26].

Finally, the ash alkali index was determined with the ash components (Eq. (3)).

$$ALKALI (kg GJ^{-1}) = \frac{(K_2O + Na_2O)}{HHV_{db}} \quad (3)$$

2.5. Statistical analysis

The data were processed to determine the mean values and ranges of variation. Two-way analysis of variance (ANOVA) was used to determine any significant changes in the elemental composition of the woodchips, according to the following model:

$$E_{i,j,k} = \mu + M_i + S_j + M * S_{ij} + \varepsilon_{i,j,k} \quad (4)$$

where $E_{i,j,k}$ denotes the element, μ the overall mean, M_i the mixture

effect, S_j the effect of torrefaction severity and $\varepsilon_{i,j,k}$ the error term.

Mean classification was performed by using the Tukey's test to examine all possible differences between mixtures and torrefaction severities. Pearson's correlation coefficients were calculated to evaluate the relationships between variables. Test results were considered significant at $p < 0.05$. All analyses were performed using the R statistical package [27].

3. Results

3.1. Feedstock properties

The mean values (and standard deviations) obtained in the proximate analysis and high heating values (on a dry basis) and the concentrations of the major elements and other elements that were very different between the two feedstocks used to make the pellets are shown in Table 2. No significant differences were found in the variables determined in proximate analysis (ash, fixed carbon or volatiles). The pine woodchips yielded an HHV_{db}, which was 0.2 MJ kg⁻¹ higher than that yielded by the eucalyptus woodchips. Significant differences ($p < 0.001$) were observed in the Cl, Na and K concentrations, which were higher (at least 65%) in the eucalyptus woodchips than in the pine woodchips.

3.2. Mass yield and ash content

The torrefaction treatments and different mixtures significantly affected the mass yield and ash content ($p < 0.001$, Figs. 1 and 2). The pattern of change in both variables was similar for all three mixtures tested. The limit of torrefaction severity after which significant changes in MY and ash content occurred was 240 °C. The threshold commonly used in the standard methods for A1 pellets (0.7% ash) was not exceeded in the control pellets, and all torrefied pellets did not surpass the 1.2% limit for TW1 pellets (Fig. 2).

3.3. Ultimate analysis

Regarding the elemental composition, the concentrations of the different elements are shown in Tables 3–5. The ANOVA revealed significant effects ($p < 0.05$) of the mixture for most elements analyzed, with the pattern of variation being particularly clear for Na, K, Zn, B and Cl, the concentrations of which increased with the percentage of eucalyptus wood. Considering all the torrefaction severity levels, the Na and K concentrations were respectively 2.8 and 1.4 times higher for the 60P/40E mixture than for the pure pine pellets (100P). Zn showed the greatest differences in concentrations, which were 2.73 times higher in the mixture containing 40% eucalyptus wood. Differences in Cl and B were less pronounced (35 and 13%, respectively). On the other hand, the

Table 2

Average values (and standard deviations) of ash, volatile matter and fixed carbon content, high heating value and element composition determined in pine and eucalyptus woodchips. Letters denote the mean classification by the Tukey's test.

Property	Pine woodchips	Eucalyptus woodchips
Ash content (%)	0.65 (0.02) a	0.59 (0.03) a
Volatile matter (%)	84.44 (0.18) a	84.23 (0.08) a
Fixed carbon (%)	14.91 (0.16) a	15.18 (0.07) a
HHV _{db} (MJ kg ⁻¹)	19.16 (0.08) a	18.95 (0.04) b
N (%)	0.31 (0.02) a	0.31 (0.03) a
C (%)	47.44 (0.21) a	47.24 (0.19) a
H (%)	6.48 (0.03) a	6.41 (0.02) b
S (%)	0.030 (0.004) a	0.030 (0.004) a
O (%)	45.09 (0.23) a	45.42 (0.24) a
Cl (%)	0.022 (0.003) b	0.036 (<0.001) a
K (mg kg ⁻¹)	805.2 (13.9) b	1331.0 (84.2) a
Na (mg kg ⁻¹)	55.5 (0.54) b	229.3 (18.59) a

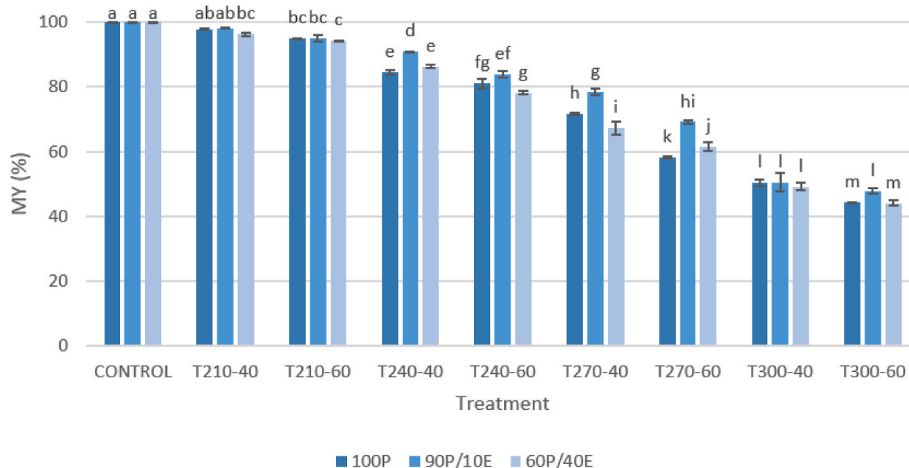


Fig. 1. Mean values (with standard deviations shown as error bars) of mass yield on a dry weight basis (dwb) in the different treatments and mixtures. Letters denote the mean classification by the Tukey's test for torrefaction severity and mixture.

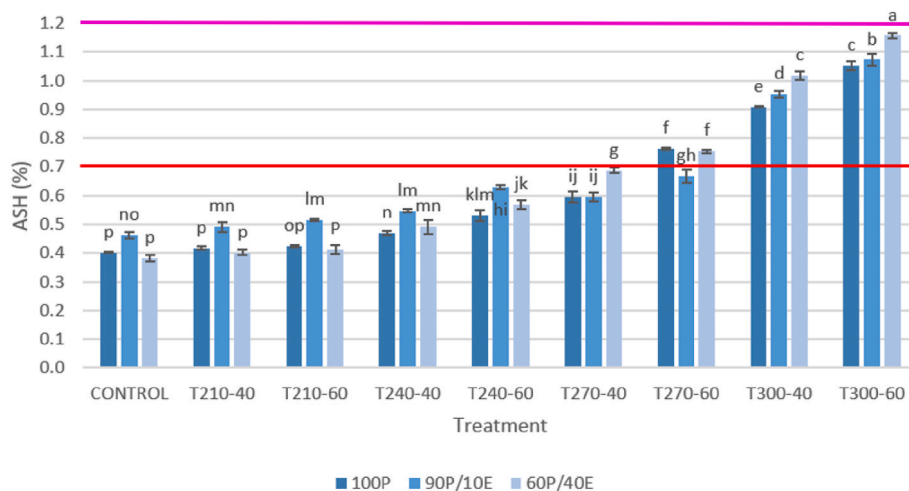


Fig. 2. Mean values (with standard deviations shown as error bars) of ash content value on a dry basis (db) in the different treatments and mixtures. Letters denote the mean classification by the Tukey's test for torrefaction severity and mixture. Thresholds for A1 quality of ISO17225-2 and the TW1 of ISO17225-8 are shown.

Mn concentrations were 50% lower in 100P than in 60P/40E.

The Cl concentrations were 25–50% lower than expected from the woodchip composition, indicating that a reduction derived from the pelletization temperatures had already occurred. Nonetheless, the raw pellets with the highest proportion of eucalyptus used (60P/40E) have levels above the A2 quality threshold of the ISO-17225-2 standards.

The effect of torrefaction severity was also significant for most elements, along with the interaction with the mixture. The patterns of variation in grouping the elements were therefore analyzed. The concentrations of most of the elements (C, Mg, Al, P, Ca, Fe, Cu) increased with torrefaction severity, independently of the mixture (see Fig. 3a). The percentage increase ranged from +35% in the case of C to 218, 226 and 250% for Ca, Mg and P, respectively. For H and O, the concentrations decreased in a pattern also independent of the mixture: both decreased by 35% with torrefaction severity (Fig. 3b). The Cl tended to decrease with torrefaction severity, which compensated for the high levels in mixtures with eucalyptus: the Cl concentrations were 60% higher for raw pellets 60P/40E than for 100P pellets (Fig. 3c). Five elements tended to increase in concentration as torrefaction severity increased, but the differences between mixtures were maintained: B, Na, K, Zn and Mn (Fig. 3d). There were no clear trends in S and N concentrations in relation to torrefaction severity (Tables 3–5).

The strong decrease of Cl concentrations with torrefaction severity

(63–77%) shows that Cl is released by heating. The chlorine release ratio is already evident for the lower torrefaction temperature (Fig. 4). Both the temperature and the residence time clearly affected the release ratio. The higher levels of severity only led to marginal increments in the release ratio. This implied that all torrefied pellets were below the limit for TW1 pellets (0.05%) established in ISO 17225-8. The T240-60 combination was sufficient to maintain the Cl levels at 10% of the first threshold for TW1 pellet quality (30% of the threshold for the A1 class) in all mixtures. This combination of torrefaction severity is also the first that ensures compatibility with the TW1 class in terms of net calorific value ($Q \geq 20 \text{ MJ kg}^{-1}$). Nevertheless, higher proportions of eucalyptus will lead to lower Q values (data not shown).

The H:C and O:C atomic ratios are commonly used as indicators of energy densification during the torrefaction process. The van Krevelen diagram showed that most of the treated samples and the raw pellets are included in the biomass range, except samples subjected to treatments T270–60, T300–40 and T300–60 (Fig. 5). The pellets torrefied at 210 °C and the control pellets occur relatively close together in the diagram because the torrefaction process did not greatly affect the hydrogen, carbon or oxygen contents. These ratios were lower at higher temperatures and carbon contents. The samples subjected to treatments T300–40 and T300–60 are close to the peat and lignite zone, indicating that the high heating value is higher, and the low heating value is thus also

Table 5

Mean values (and standard deviations) of the concentrations of the different elements determined in pellet samples. Letters denote the mean classification by the Tukey's test of each mixture.

Mixture	Treatment	Al (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	P (mg kg ⁻¹)	Fe (mg kg ⁻¹)	Mn (mg kg ⁻¹)
100P	CONTROL	73.3 (6.0) ef	1.60 (0.14) f	10.6 (0.9) g	68.0 (7.4) h	68.2 (6.6) e	60.0 (5.0) f
	T210-40	80.2 (5.5) ef	2.25 (0.16) d	12.7 (1.0) ef	84.1 (7.1) fg	97.3 (6.8) d	69.2 (4.6) ef
	T210-60	69.2 (<0.1) f	1.67 (0.02) ef	11.5 (<0.1) fg	71.9 (1.1) gh	76.4 (0.5) e	64.3 (0.5) ef
	T240-40	83.8 (0.9) e	1.89 (0.01) e	13.5 (0.1) e	88.4 (1.3) ef	99.7 (0.4) d	71.1 (0.4) e
	T240-60	100.3 (8.8) d	2.27 (0.21) d	15.5 (1.4) d	100.6 (8.8) de	131.8 (12.5) bc	82.7 (8.1) d
	T270-40	111.4 (0.8) cd	2.37 (0.04) d	16.5 (0.1) d	113.7 (1.8) d	133.4 (1.6) bc	89.1 (0.8) d
	T270-60	116.4 (0.9) c	2.69 (0.01) c	18.9 (<0.1) c	131.0 (0.4) c	123.7 (0.6) c	104.4 (0.6) c
	T300-40	132.7 (1.8) b	3.17 (0.04) b	21.6 (0.4) b	149.7 (1.1) b	143.0 (2.2) b	119.7 (1.8) b
	T300-60	163.6 (2.2) a	3.72 (0.02) a	25.6 (0.2) a	179.3 (1.1) a	171.2 (1.0) a	138.5 (1.5) a
90P/10E	CONTROL	140.8 (76.1)	1.53 (0.31)	15.8 (3.8) b	157.9 (41.7) def	147.7 (49.7)	60.8 (9.0) d
	T210-40	127.1 (3.0)	1.69 (0.36)	15.2 (0.4) b	146.8 (2.1) ef	145.6 (3.8)	59.9 (0.6) d
	T210-60	99.2 (3.5)	1.33 (0.06)	14.4 (0.2) b	141.4 (2.0) f	113.6 (7.3)	57.9 (0.4) d
	T240-40	109.9 (9.4)	1.55 (0.09)	17.3 (0.6) b	185.1 (12.5) cdef	134.7 (27.0)	69.5 (3.9) cd
	T240-60	104.6 (17.1)	1.35 (0.46)	18.0 (0.1) b	191.4 (4.8) cde	127.1 (8.6)	74.0 (1.4) bcd
	T270-40	101.9 (18.9)	1.28 (0.41)	19.0 (0.3) b	199.6 (11.8) cd	122.4 (11.6)	81.6 (2.0) bcd
	T270-60	120.4 (14.1)	1.62 (0.47)	21.7 (0.2) ab	231.7 (14.1) c	136.7 (32.8)	97.9 (2.5) bc
	T300-40	84.8 (79.1)	1.23 (0.74)	19.1 (11.1) b	316.1 (10.2) b	96.1 (73.7)	102.2 (27.1) b
	T300-60	158.1 (46.7)	1.60 (1.05)	31.2 (1.9) a	367.2 (6.9) a	163.4 (65.3)	139.3 (7.5) a
60P/40E	CONTROL	63.1 (2.7) c	2.47 (0.76) ab	47.1 (5.2) bc	93.9 (2.7) e	70.1 (5.8) bc	43.3 (1.0) f
	T210-40	64.3 (3.2) c	2.99 (1.38) ab	31.3 (0.9) e	92.6 (2.2) e	73.6 (1.4) bc	45.1 (1.0) ef
	T210-60	63.6 (11.9) c	1.62 (0.04) b	22.9 (1.0) f	95.5 (2.5) e	65.8 (2.5) c	44.4 (0.8) ef
	T240-40	59.6 (0.8) c	1.77 (0.41) ab	39.7 (1.0) cd	102.5 (1.4) e	69.1 (1.0) c	48.6 (0.8) e
	T240-60	66.9 (0.8) c	1.69 (0.08) b	32.1 (0.3) de	116.8 (1.3) d	74.9 (0.7) bc	54.4 (0.2) d
	T270-40	69.0 (4.7) c	1.96 (0.26) ab	55.0 (1.2) a	157.8 (5.4) c	76.4 (1.0) bc	57.7 (1.4) d
	T270-60	71.7 (1.9) bc	2.01 (0.07) ab	54.2 (2.6) ab	168.7 (8.1) c	84.7 (2.0) b	63.3 (3.3) c
	T300-40	84.8 (1.6) ab	2.75 (0.38) ab	56.8 (0.7) a	211.3 (4.9) b	108.7 (1.3) a	82.1 (0.8) b
	T300-60	90.7 (3.3) a	3.59 (0.90) a	61.6 (5.0) a	228.8 (7.8) a	123.4 (14.3) a	90.6 (2.8) a

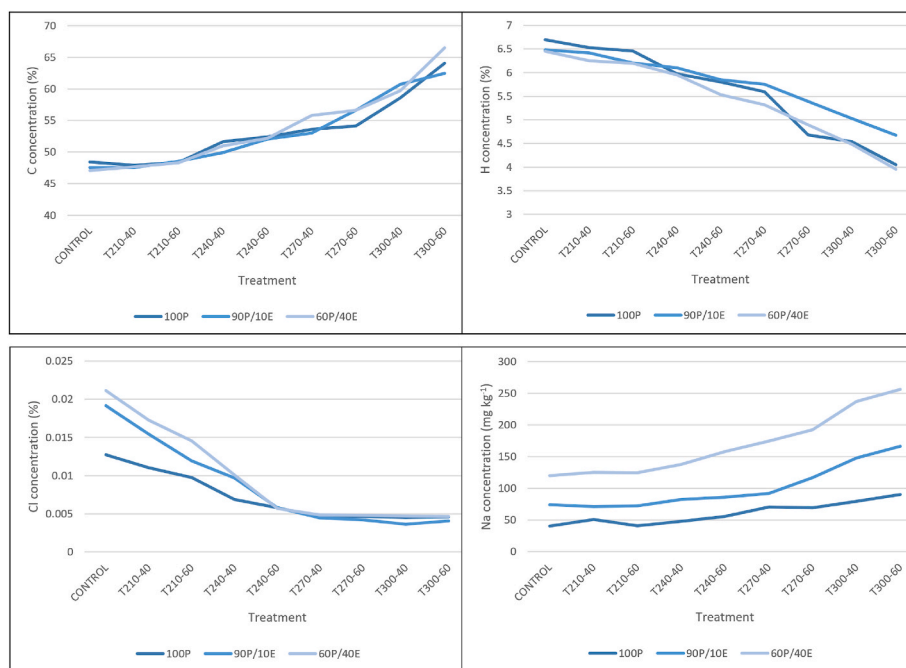


Fig. 3. Carbon, hydrogen, chlorine and sodium concentrations in control and torrefied pellets.

led to an increase in the alkali index; the increase in temperature and residence time was negative due to the high values of the alkali index. Miles et al. (2015) [29] reported that a value higher than 0.17 kg GJ⁻¹ indicates that fouling is likely to occur, and that above 0.34 kg GJ⁻¹ fouling will definitely occur. These levels are still far from being reached with the range analyzed in this study. Nonetheless, this finding must be validated experimentally.

4. Discussion

The study findings showed the effects of different combinations of torrefaction temperature and residence time on the elemental composition of pellets made from three different woodchip mixtures. The relatively high Cl content proved to be the most limiting factor for blending eucalyptus woodchips with pine woodchips, with percentages as low as 10% possibly leading to Cl concentrations close to 0.02%. Relatively high Cl levels have previously been reported even for wood

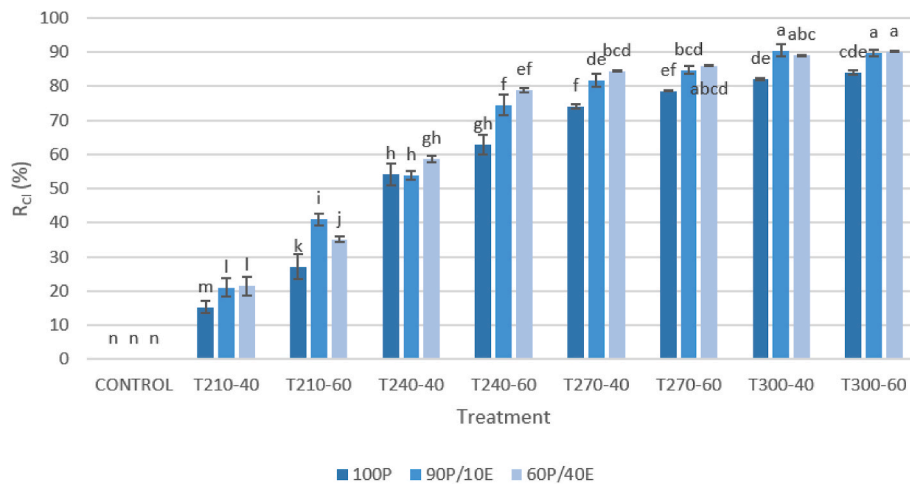


Fig. 4. Mean values (with standard deviations shown as error bars) of chlorine release rate in the different treatments and mixtures. Letters denote the mean classification by the Tukey’s test for torrefaction severity and mixture.

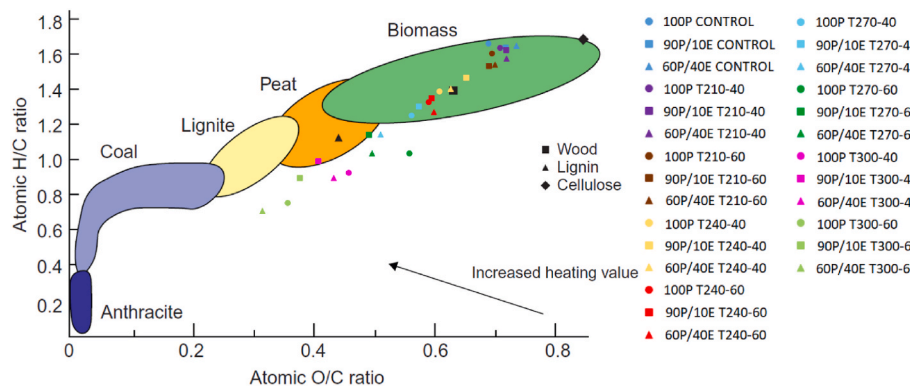


Fig. 5. van Krevelen diagram adapted from Ref. [28] to the present study of control and torrefied pellets.

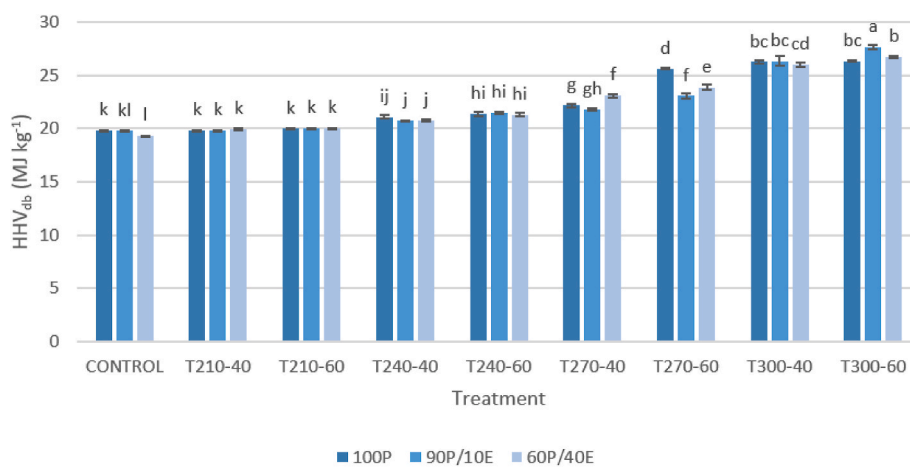


Fig. 6. Mean values (with standard deviations shown as error bars) of high heating value on a dry basis (db) in the different treatments and mixtures. Letters denote the mean classification by the Tukey’s test for torrefaction severity and mixture.

without bark [30] and torrefaction was proposed as a potential pretreatment in order to decrease Cl concentrations to acceptable limits [16,17]. The biomass components to which the figures for non-torrefied samples refer to is a key factor. Most studies report the mean values of various components, whose relative abundance depends on the size of the trees sampled. In this study, the Cl concentrations refer specifically to the wood component, and it was thus assumed that the eucalyptus

logs would have to be debarked prior to chipping in the pellet factory (along with the pine logs). Another important factor to take into consideration is the reduction in Cl concentration brought about by the pelletization process itself, with releases estimated as 25–50% relative to the woodchips used as feedstock.

The observed pattern of Cl release with torrefaction severity in this study involves a wider range than the previously covered. Keipi et al.

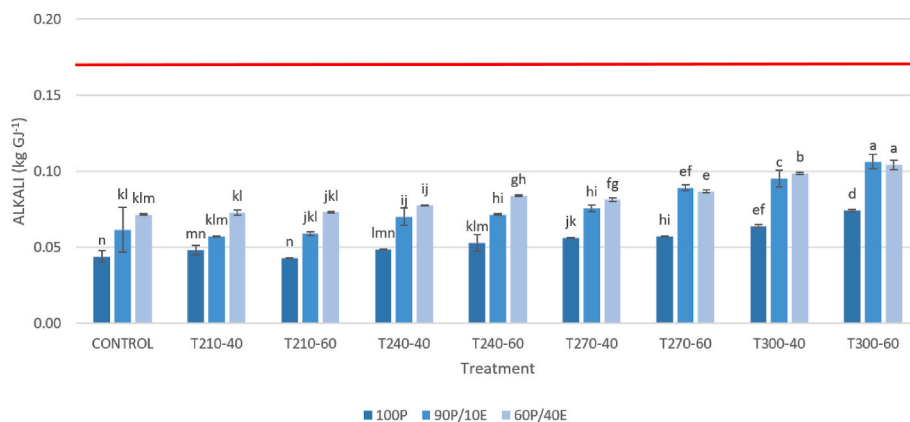


Fig. 7. Mean values (with standard deviations shown as error bars) of the alkali index in the different treatments and mixtures. Letters denote the mean classification by the Tukey's test.

(2014) [30] reported release of 90% Cl in eucalyptus samples with 60 min of torrefaction reaction at 260 °C. Romão et al. (2023) [31] reported three combinations of torrefaction severities (T240–30, T260–30 and T260–60), obtaining releases of 88–96%, with residence time having little effect. Some studies indicated problems in the determination, as Sá et al. (2020) [16] obtained always a null value of Cl for samples torrefied at 240 °C using a chloride titration procedure. The values obtained by De Oliveira Araújo et al. (2017) [32] for eucalyptus, i.e. a mean Cl concentration of 0.29% in untreated wood samples of 8 eucalyptus species, is much higher than the values usually reported. These authors obtained moderate release rates (25–50%) for torrefaction temperatures of 160–230 °C. In this study, the observed release values are much lower than previously reported values for the same range of torrefaction severities, with an evident effect of residence time for temperatures of 210 and 240 °C. Nonetheless, pretreatment reduced the Cl concentrations to levels half of the first thresholds outlined in the ISO 17225-2 standard for the T240-40 combination, despite the high proportion of eucalyptus in the mixture.

The recently approved standard ISO 17225-8 establishes a threshold of Cl content of 0.05% for the TW1 for densified biomass fuels produced from thermally processed chemically untreated woody biomass ([15], table B1). This is 2.5 times higher than the level considered for non-thermally treated pellets (class A.1) and led to a simple classification of all mixtures in the top class of thermally treated pellets in this study.

Although it is not yet clear how chlorine is bound in wood, it has been proposed that K can form discrete KCl particles in the organic matrix [33]. The results obtained in the present study are consistent with those reported by Saleh et al. (2014) [34], who studied different species, including spruce (a conifer), finding that i) a higher Cl fraction is released from the samples with the lower chlorine content and ii) the fraction of chlorine released decreases with the biomass potassium (K) content. In the present study, the pellet samples with the highest Cl or K contents were those containing the highest proportion of eucalyptus. Jensen et al. (2000) [33] demonstrated that 60% of Cl is released at temperatures of 200–400 °C during pyrolysis of straw. Cl is released in the form of KCl and CH₃Cl [34], whereas K can be redeposited as discrete particles of KCl and K₂CO₃ [33]. The formation of KCl deposits can explain the above-mentioned negative relationship, even though chlorine may be released during the reaction between KCl and carboxylic groups [35]. Significant amounts of chlorine are not released at temperatures below 200 °C [33,36].

In parallel to the Cl concentrations and how these vary with torrefaction severity, the present study reports the higher levels of several elements in eucalyptus wood that can release ash-forming material to fine particles: K, Na and Zn [37]. Torrefaction of the pellets also increases these concentrations, following a pattern similar to the mass

yield of this pretreatment. These elements lead to deposition and corrosion in boilers and other heating systems [38]. However, the alkali indices obtained for the mixtures containing 40% of eucalyptus and treated at the highest torrefaction severity level are close to 0.10 kg GJ⁻¹, still below the limit (0.17) proposed by Miles et al. (1995) [29] for probability of fouling. High levels of alkaline elements in eucalyptus wood have previously been reported [39] and are known to be higher in hardwood than in softwood (ISO 17225-1), although some researchers such as Zhang et al. (2022) [40] have reported much higher values for pure pine pellets than those obtained in the present study for the 60P/40E blend (× 2, × 8, × 3 and × 3 for K, Ca, Mg and Na, respectively). Saddawi et al. (2011) [39] proposed a pretreatment involving washing to remove alkali metal ions and chloride to produce high quality torrefied biofuels. The results of this study are consistent with those reported by Singh et al. (2020) [41] regarding the increase in concentrations of ash-forming element during the torrefaction process. High torrefaction temperatures cause an increase in the ash content, as the principal components of ash are alkali and alkaline earth metals, including K, Na and Mg [42].

In the present study, the reductions in H and O contents occurred in parallel with the increase in C content previously observed in biomass torrefaction [43]. The results obtained in this study were compared with those of several other studies involving torrefaction of eucalyptus wood. The gains and losses in C, H and O are summarized in Table 6. Overall, the pattern of C gains and O and H losses are dependent on the torrefaction severity, and the values obtained in the present study for T240-60 (C gain 9–11%, H loss 10–14%, O loss 7–10%) were lower than those reported by Lu et al. (2012) [44] and Cardona et al. (2019) [45] for T250-60. For a torrefaction severity of T270-60, the C gain (12–20%) and O loss (9–19%) observed in this study were lower than the values reported by Romão et al. (2020) [46], whereas the H loss (17–30%) was much higher.

The lower H/C and O/C ratios in the torrefied pellets are related to the dehydration, decarbonylation and demethylation processes that occur during torrefaction [49]. These processes lead to the removal of large amounts of oxygen and a large increase in carbon content of the biomass [40]. The first process to occur during torrefaction is the removal of unbound molecules of water: at higher temperatures (150–160 °C) bound water is removed and formation of CO₂ begins. At 180 °C the decomposition of hemicellulose starts and the biomass changes colour. The next reactions occur during torrefaction (200–300 °C): devolatilization and carbonization of hemicellulose, depolymerization and devolatilization of lignin and cellulose. Torrefaction of lignocellulosic materials results in the decomposition of more hemicelluloses than lignin and cellulose. These decomposition reactions lead to the removal of hydroxyl groups (OH), increasing the specific heating value and the hydrophobicity of the fuel [50,51].

Table 6

Different studies in which properties of torrefied eucalyptus produced under different conditions were determined. Negative values of H loss indicate a gain. Data were transformed to dry basis when necessary.

Severity	Sample	Atmosphere	C gain (%)	H loss (%)	O loss (%)	Reference	
T240-30	Eucalyptus woodchips	Nitrogen	12.26	11.02	9.80	[46]	
T240-60			8.57	9.42	5.55		
T260-30			14.76	8.47	22.02		
T260-60			25.53	15.02	20.94		
T280-30			18.52	9.74	19.68		
T280-60			27.66	15.18	44.11		
T250-60	Eucalyptus leaves, bark and wood	Inert gas with high nitrogen content	21.15	-17.51	21.31	[45]	
T275-60			27.79	-16.71	25.40		
T300-60			42.47	-16.83	39.75		
T265-15	Eucalyptus wood	Nitrogen	12.45	12.89	20.72	[47]	
T250-15	Eucalyptus woodchips	Nitrogen	4.52	5.82	7.43	[48]	
T250-30	Eucalyptus wood	Nitrogen	6.22	5.97	7.94	[44]	
T280-15			9.71	11.49	15.96		
T280-30			14.96	10.60	18.81		
T250-60			13.78	3.92	16.10		
T275-60			17.52	7.84	19.73		
T300-60			34.25	17.65	38.10		
T325-60			47.64	29.41	52.38		
T350-60			47.83	29.41	52.15		
T250-60			Air	19.29	17.65		20.63
T275-60				35.83	41.18		37.19
T300-60				40.35	56.86		40.36
T325-60	44.09	70.59		43.31			
T350-60	47.05	76.47		46.26			

5. Conclusion

Blending pine wood with high proportions of eucalyptus wood increased the chlorine content of pellets; however, torrefaction greatly reduced the Cl concentrations, even at a temperature of 240 °C. Concentrations of alkaline elements were also 1.5 (K) to 3 (Na) times higher in the blend containing the highest proportion of eucalyptus wood. The carbon content increased and hydrogen and oxygen contents of the pellets decreased after torrefaction, with similar patterns to those previously reported in the literature. Most elements analyzed increased with torrefaction, including the alkaline elements and metals, thus resulting in a higher alkali index; however, none of the sample exceeded the 0.17 GJ kg⁻¹ threshold indicating the likelihood of fouling in boilers.

Data availability

Data will be made available on request.

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