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Predicting the energy properties of torrefied debarked pine pellets from torrefaction temperature and residence time

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

In this study, high quality radiata pine pellets were torrefied at a range of temperatures (T = 210, 240, 270 and 300 °C) and residence times (t = 20, 40 and 60 min). The effects of these treatments on mass yield (MY), ash content (A), volatile matter (VM) and fixed carbon (FC), high heating value on a dry basis (HHV_{db}) and low heating value on a wet basis (LHV_{wb}) were investigated, and models were constructed to predict these energy properties from T and t. Untreated pellets were analysed as control samples. Threshold conditions of 240 °C 40 min yielded significant increases in HHV_{db} and carbon content and a significant decrease in oxygen content. This combination significantly increased A and FC and significantly decreased VM. Logistics models using T, t, t × T and T^2 were able to predict A accurately, with no bias, whereas FC values tended to be underestimated. The variation in HHV_{db} and LHV_{wb} was explained by linear models with t and t × T as variables. Use of the models enabled definition of torrefaction severity that ensures an A below 0.7% and a LHV_{wb} value 30% higher than obtained with raw pine pellets. Torrefaction conditions of T = 260–270 °C and t = 50–60 min are proposed.

1. Introduction

Torrefaction is a thermochemical treatment in which raw biomass is slowly heated at temperatures of between 200 and 300 °C in an inert or limited oxygen atmosphere [1]. This process modifies the structure of the biomass, increasing the C content and reducing the O content. Torrefied biomass is also hydrophobic rather than hygroscopic. The changes in properties increase the commercial value of the pellets and the potential number of industrial applications, including use with coal in biomass cofiring in large coal-fired power plant boilers, as fuel in decentralized or residential heating systems, as a convenient fuel for gasification, as a potential feedstock for chemical industries and as substitute for coke in blast furnaces to reduce the carbon footprint of the operations [1].

Torrefaction was first used in 1930 in France to improve the properties of wood, and torrefied biomass was used as fuel. The first industrial application of torrefaction was developed in France in 1980 with the Pechiney process [2]. To date, various studies have investigated different types of biomass torrefaction using different wood species (Scots pine [3] and beech or pine sapwood [4]), grass species (Miscanthus [4] or reed canary grass [5]), agricultural bioproducts (almond shells, kiwifruit and vine pruning remains [6]) and algae [7].

Current torrefaction methods can be classified in three groups: dry torrefaction, wet torrefaction and steam torrefaction [8–10]. Dry torrefaction is performed by placing the material in a non-oxidative atmosphere (N_2 or CO_2) or in an oxidative atmosphere (air or other gases with different O_2 content) and heating at 200–300 °C. Wet torrefaction involves the use of compressed water or dilute acid as medium, with heating at 180–260 °C. Steam torrefaction requires high pressure steam at temperatures of between 200 and 260 °C. The different stage of biomass torrefaction are summarised in Fig. 1.

Two pathways can be used to produce densified and torrefied biomass [14]. The combined torrefaction and pelletization (TOP) process involves drying the wood chips, torrefaction, grinding and densification [15,16]. The torrefaction after pelletization (TAP) process involves drying wood chips, milling, densification and finally torrefaction. The TAP process, which is the one used in this study, yields a product of adequate durability, higher energy/carbon value, reduced moisture content and greater stability in water. This pathway has also been shown to be more efficient in terms of overall energy and material

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[*] Corresponding author.
E-mail address: a.iglesias.canabal@usc.es (A. Iglesias Canabal).

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balance [14] and can be more easily included in existing industrial pellet production processes. The TAP pathway may therefore be key to enhancing the commercialization of torrefied pellet production [15]. Negative effects of TAP on pellet properties have been reported to depend on torrefaction temperature, residence time and the raw material used [17]. Studies concerning the TAP process have reported both positive and negative effects of torrefaction, and it is difficult to reach any conclusions about the balance between the different effects. Moreover, tools for predicting the effects of torrefaction severity on energy properties have seldom been reported, thus reducing the possibility of defining optimal combinations of temperature and residence time based on quantitative analysis.

The study was performed using high quality pellets obtained from debarked radiata pine wood and of the maximum quality level for domestic use (A1 of ISO 17225-2 standard). The objectives were i) to investigate the effects of torrefaction conditions (temperature and residence time) on the mass yield, proximate composition and heating values, ii) to provide models able to predict these properties and iii) to use the models to explore the optimal combination of temperature and residence time.

2. Material and methods

2.1. Biomass samples

The samples used in the study were obtained from a biofuel factory located in Galicia (north-west Spain) and dedicated to producing high-quality pellets from debarked *Pinus radiata* wood. Pellet factories in Spain, whether utilizing sawmills by-products or small diameter pine logs, do not use the bark fraction as raw material. Wood chips are ground to <4 mm and dried to a moisture content of 10–12% (wet basis) before being densified in an annular die pelletizer with compression matrix of 42 mm. The pellets, of diameter 6 mm and length 20–22 mm, are classified as premium quality (class A1) according to UNE-EN ISO-17225-2 standards for domestic or industrial use [18]. Pellet particle density, bulk density and mechanical durability were 1154 kg/m^3, 628 kg/m^3 and 98.46% respectively. The pellet samples were transported to the laboratory to carry out the torrefaction process and determination of the energy properties of the raw (untreated) pellets and the torrefied pellets.

2.2. Torrefaction process

The pellets were torrefied in a limited oxygen atmosphere in a muffle furnace (J.P. SELECTA model). Samples (25 g) were placed on ceramic trays in the furnace at different temperatures (T = 210, 240, 270 and 300 °C) for different residence times (t = 20, 40 and 60 min). The samples were heated from room temperature to the selected torrefaction temperature, at a heating rate <15 °C/min. After torrefaction, the samples were cooled in a desiccator containing silica gel. A total of 12 treatments were carried out, with three replications per treatment, (i.e. n = 36 for the variables evaluated). The samples were weighed before and after torrefaction to enable calculation of the mass yield (%) in all treatments. Untreated (raw) pellets were also included in the study as control samples.

Mass yield (MY, %) was evaluated for each sample. The changes in colour and structure after torrefaction are shown, along with the codes used to refer to each treatment, in Fig. 2. As previously observed [3], the pellets became darker as the temperature and residence time increased, and the surface of the biofuel lost its brightness. The colour change is an indicator of the severity of the process and is directly related to changes in acid-insoluble substances [19].

2.3. Analysis of pellet properties

The pellet samples were milled to pass through a 0.5 mm sieve before the proximate analysis, which was carried out following UNE standards. The samples were dried in a convection oven at 105 °C for 24 h for determination of the moisture content (MC, % on a wet basis, wb), according to UNE-EN ISO 18134-1 [20]. The ash content (A, % on a dry basis, db) was determined after combustion at 550 °C following UNE-EN ISO 18122 [21]. The volatile matter (VM, %, db) was determined by application of the UNE-EN ISO 18123 standards [22] and calcination of the samples in an oven at 900 °C. The fixed carbon (FC, %, db) was obtained by difference of ash and volatile matter contents.

Ultimate elemental composition was also determined for all torrefied samples and later used to calculate the low heating value. Total N, C, H and S were analysed by combustion in a LECO elemental analyzer (Truspec model) to determine the percentage of gases after the oxidative process, following UNE-EN ISO 16948 [23] and UNE-EN ISO 16994 [24]. The oxygen content was calculated by difference, with Eq. (1). All elements were determined on a dry basis.

$$O = 100 - C - N - H - S - A \tag{1}$$

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

The higher calorific value (as-received or wet basis, wb) (HHV$_{wb}$) was determined experimentally by combustion of 0.5 g of pellet in a bomb calorimeter (IKA C5000) under an oxygen atmosphere (30 bar) following UNE-EN ISO 18125 [25]. The higher calorific value on dry basis (HHV$_{db}$) was calculated using Eq. (2), and the lower heating values (LHV$_{db}$ and LHV$_{wb}$) were calculated from the HHV$_{db}$ using Eq. (3) and Eq. (4) [25], respectively. The moisture content of raw pellet samples

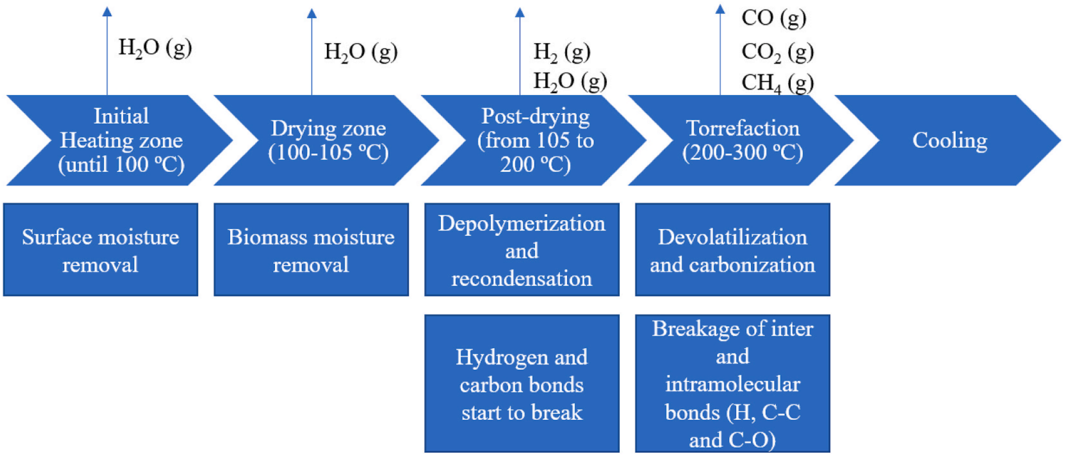

Fig. 1. Stages of the torrefaction process including the main processes and gas molecules formed. Adapted from Refs. [11–13].

Fig. 2. Photographs of untreated (raw) pellets and torrefied pellets.

(control) was 6.24%, which is the value used in Eq. (4) to determine LHV_{wb}.

$$HHV_{db} = HHV_{wb}\,\frac{100}{100 - MC} \tag{2}$$

$$LHV_{db} = HHV_{db} - 212.2\,H - 0.8\,(O + N) \tag{3}$$

$$LHV_{wb} = [LHV_{db}\,(1 - 0.01\,MC)] - 24.43\,MC \tag{4}$$

where db denotes dry basis, wb indicates wet or as-received basis, HHV, high heating value and LHV, low heating value.

2.4. Statistical analysis

The data were processed to determine the mean values and ranges of variation. One-way analysis of variance (ANOVA) was used to determine significant effects of the treatment. Multiple comparison of means was performed by using the Tukey's test to examine all possible differences between untreated and torrefied pellets. Differences were considered significant at $p < 0.05$.

Energy variables were estimated by considering temperature (T, °C) and residence time (t, min) along various combinations and quadratic transformations as predictive variables. A logistic model (Eq. (5)) was used to predict the variables evaluated as percentages (MY, A, FC and VM), which should be bounded between 0 and 100 [26]. A quadratic model, in the form of a second order polynomial model with two independent variables, was used to predict HHV_{db} and LHV_{wb} (Eq. (6)) [27]. Only the explanatory variables found to be significant ($p < 0.05$) were retained in the models. The proposed predictive models were used to construct three-dimensional response surface plots.

$$\widehat{y} = \frac{100}{1 + e^{\left(a_0 + a_1 T + a_2 t + a_3 T t + a_4 T^2\right)}} \tag{5}$$

$$\widehat{y} = b_0 + b_1 T + b_2 t + b_3 T t + b_4 T^2 \tag{6}$$

where $\hat{y}$ is the predicted variable and a_i or b_i are the parameters to be estimated, a_0 and b_0 are the intercepts, a_1, a_2, b_1 or b_2 the coefficients of the linear terms, a_3 and b_3 are the coefficients of the interactions, and a_4 and b_4 are the coefficients of the quadratic term for temperature.

To evaluate the goodness-of-fit of the models, the mean residue (MRES) was used as a measure of accuracy (Eq. (7)) and the root of mean square error (RMSE) (Eq. (8)) and the adjusted-R^2 (Eq. (10)) were used to define the model precision. Predicted and observed values were plotted to visually assess the accuracy and precision of the models. All analyses were performed using the R statistical package [28].

$$MRES = \frac{\sum_{i=1}^{n} (y_i - \widehat{y}_i)}{n} \tag{7}$$

$$RMSE = \sqrt{\sum_{i=1}^{n} \frac{(y_i - \widehat{y}_i)^2}{n}} \tag{8}$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i - \widehat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \overline{y}_i)^2} \tag{9}$$

$$Adj - R^2 = 1 - \frac{(1 - R^2)(n - 1)}{n - k - 1} \tag{10}$$

where $\widehat{y}_i$ denotes the predicted data, y_i is the experimental data, $\overline{y}_i$ is the mean value of y_i, n the sample size (36) and k the number of independent variables finally included in each model.

3. Results

3.1. Effect of torrefaction severity on pellet properties

The mean values (and standard deviations) of mass yield (on a dry basis) for the raw and torrefied pellets are shown in Table 1. Significant differences between the treatments ($p < 0.001$) were observed. The mass yield was significantly higher in the treatments carried out at lower temperatures.

The torrefaction treatments significantly affected the ash, volatile matter and fixed carbon contents ($p < 0.001$, Table 1). Torrefaction at 210 °C (irrespective of residence times) and at 240 °C for 20 min did not produce any significant change in these variables. The ash content ranged from 0.40 for raw pellets and 1.05% in treatment T300-60. The threshold commonly used in the standard methods (0.7% ash) was exceeded in three combinations of temperature and residence time, in treatments T270–60, T300–40 and T300-60. The fixed carbon content increased greatly with temperature; in the treatments carried out at the same temperature it also increased with residence time, but only when a minimum temperature of 240 °C was reached. The most extreme torrefaction treatment (T300-60) yielded a fixed carbon content 3.8 times higher than in the raw pellets. The opposite trend was observed for the volatile matter content (Table 1).

Table 1
Average values (and standard deviations) of mass yield (MY), ash (A), volatile matter (VM) and fixed carbon (FC) content in pine wood pellets torrefied at different severities. Letters denote the mean classification by the Tukey's test.

Treatment	MASS YIELD (%)	ASH CONTENT (%)	VOLATILE MATTER (%)	FIXED CARBON (%)
Control	100 a	0.40 (<0.01) g	84.10 (0.02) a	15.49 (0.02) i
T210-20	98.9 (0.09) ab	0.40 (<0.01) g	84.24 (0.30) a	15.36 (0.30) i
T210-40	97.8 (0.13) b	0.42 (0.01) g	84.07 (0.42) a	15.51 (0.42) i
T210-60	95.1 (0.02) c	0.42 (<0.01) g	83.58 (0.52) a	16.00 (0.52) i
T240-20	95.5 (0.32) c	0.41 (0.01) g	83.64 (0.15) a	15.95 (0.16) i
T240-40	84.5 (0.74) e	0.47 (0.01) f	76.12 (0.07) c	23.41 (0.07) g
T240-60	81.1 (1.51) f	0.53 (0.02) e	73.50 (0.10) d	25.97 (0.08) f
T270-20	88.8 (0.17) d	0.48 (0.01) f	80.46 (0.23) b	19.06 (0.24) h
T270-40	71.6 (0.39) h	0.60 (0.02) d	68.71 (0.44) f	30.70 (0.44) d
T270-60	58.3 (0.34) i	0.76 (0.01) c	55.03 (0.01) g	44.20 (0.01) c
T300-20	73.7 (0.28) g	0.56 (<0.01) e	71.19 (0.05) e	28.25 (0.06) e
T300-40	50.4 (0.86) j	0.91 (<0.01) b	48.03 (0.26) h	51.06 (0.27) b
T300-60	44.2 (0.08) k	1.05 (0.01) a	40.41 (0.07) i	58.54 (0.08) a

The moisture content of the torrefied pellets was zero, except in treatment T210-20 (0.22% wb).

Regarding the composition of elements needed to calculate the heating values, the concentrations obtained are shown in Table 2. The variables analysed did not follow the same trend in all treatments, with different effects depending on the temperature and residence time. The ANOVA indicated that the treatment had a significant effect ($p < 0.001$) on N, C, H and O concentrations. The torrefaction process increased the biomass carbon content and decreased the hydrogen and oxygen contents (Table 2). The variations in N or S concentrations did not follow any clear pattern.

The results revealed a highly significant effect of the torrefaction treatments on the energy properties ($p < 0.001$). As expected, both HHV_{db} and LHV_{wb} increased as a result of the torrefaction process (Table 2). This increase was parallel to the increase in carbon content and was particularly marked at higher temperatures. The HHV_{db} and LHV_{wb} were much higher in the T300–60 and T300-40 samples, followed by T270-60 samples, than in the raw biomass and 210 °C torrefied pellets. For example, the LHV increased by 49% and 48% in the T300–60 and T300-40 samples relative to the raw pellet sample. Small non-significant differences were observed for HHV of the raw pellets and all samples torrefied at 210 °C and the samples in the T240-20 treatment (Table 2).

3.2. Predicting the energy properties of torrefied pellets

The results of the regression analysis and the relationship between observed and predicted values are shown in Table 3 and Fig. 3, respectively. Parameter a_0 in the logistic regression (Eq. (5)) was not significant for any of the predicted variables. Among the variables evaluated as percentages, MY was the most difficult to model and the predicted values tended to be underestimated. In this case, parameter a_4, affecting the squared torrefaction temperature, was not significant. Logistic regression enabled particularly accurate and unbiased prediction of A, but also tended to underestimate the FC values (Fig. 3).

Table 2

Average values (and standard deviations) of the elemental concentrations (N, C, H, O and S), higher heating value on a dry basis (HHV_{db}) and the lower heating value on an as-received (or wet) basis (LHV_{wb}) determined in pine wood pellet samples with different torrefaction treatments. Letters denote the mean classification by the Tukey's test.

Treatment	N (%)	C (%)	H (%)	O (%)	S (%)	HHV_{db} (MJ kg^{-1})	LHV_{wb} (MJ kg^{-1})
Control	0.20 (0.01) ab	48.42 (0.44) fg	6.69 (0.03) a	44.28 (0.48) abc	0.029 (0.004)	19.82 (0.02) g	17.06 (0.02) i
T210-20	0.16 (0.01) cde	47.07 (0.10) g	6.69 (0.05) a	45.67 (0.08) a	0.029 (0.005)	19.82 (0.06) g	18.32 (0.06) h
T210-40	0.15 (0.01) de	47.90 (0.19) fg	6.53 (0.03) b	45.00 (0.18) ab	0.022 (0.004)	19.83 (0.01) g	18.41 (0.01) gh
T210-60	0.14 (0.02) de	48.37 (0.09) fg	6.46 (0.02) b	44.60 (0.09) ab	0.030 (0.005)	19.98 (0.04) g	18.57 (0.04) gh
T240-20	0.17 (0.01) cd	48.19 (0.02) fg	6.50 (0.01) b	44.73 (0.02) ab	0.018 (0.003)	20.07 (0.07) g	18.65 (0.07) g
T240-40	0.16 (0.01) cde	51.65 (0.08) de	5.98 (0.02) d	41.74 (0.10) cde	0.021 (0.004)	21.06 (0.15) f	19.76 (0.15) f
T240-60	0.15 (0.01) de	52.42 (0.11) cde	5.80 (0.02) e	41.10 (0.11) de	0.019 (0.003)	21.37 (0.19) ef	20.11 (0.19) e
T270-20	0.14 (0.01) e	50.14 (1.87) ef	6.25 (0.03) c	42.99 (0.13) bcd	0.021 (0.004)	21.39 (0.16) e	20.03 (0.16) ef
T270-40	0.15 (<0.01) de	53.62 (0.68) cd	5.59 (0.01) f	40.04 (0.68) e	0.024 (0.006)	22.15 (0.12) d	20.93 (0.12) d
T270-60	0.17 (0.01) cd	54.17 (1.82) c	4.68 (0.04) g	40.21 (1.84) e	0.019 (0.004)	25.59 (0.04) b	24.56 (0.04) b
T300-20	0.17 (0.02) bcd	54.09 (0.27) cd	5.81 (0.01) e	39.36 (0.24) e	0.020 (0.004)	22.52 (0.10) c	21.26 (0.10) c
T300-40	0.18 (<0.01) bc	58.60 (2.25) b	4.54 (0.09) h	35.77 (2.33) f	0.032 (0.007)	26.25 (0.14) a	25.26 (0.14) a
T300-60	0.21 (0.01) a	64.08 (0.19) a	4.05 (0.01) i	30.70 (0.18) g	0.030 (0.007)	26.32 (0.06) a	25.44 (0.06) a

Table 3

Results of the regression analysis showing the parameter estimates and measures of accuracy and precision of models predicting mass yield (MY), ash (A), fixed carbon (FC), volatile matter (VM), high heating value on a dry basis (HHV_{db}) and the low heating value on an as-received (or wet) basis (LHV_{wb}). The parameters refer to equations (5) and (6). RMSE is the root mean square error, MRES is the mean residue and Adj-R^2 is the adjusted coefficient of determination.

Variable	Equation	Parameter estimates					RMSE	MRES	Adj-R^2
		a_0	a_1	a_2	a_3	a_4			
MY (%)	5	ns	−0.00806	−0.1912	$8.108\ 10^{-4}$	ns	6.446	1.1643	0.862
A (%)	5	ns	0.04509	0.03029	$-1.511\ 10^{-4}$	$-9.044\ 10^{-5}$	0.042	−0.0001	0.953
FC (%)	5	ns	0.01918	0.05925	$-3.097\ 10^{-4}$	$-4.696\ 10^{-5}$	2.358	−0.0277	0.969
VM (%)	5	ns	−0.01885	−0.06055	$3.153\ 10^{-4}$	$4.609\ 10^{-5}$	2.362	0.0518	0.970
		b_0	b_1	b_2	b_3	b_4			
HHV_{db} (MJ kg^{-1})	6	19.83	ns	−0.3047	0.001427	ns	0.706	−0.0012	0.907
LHV_{wb} (MJ kg^{-1})	6	18.34	ns	−0.3258	0.001533	ns	0.732	−0.0032	0.914

Estimation of VM using the model proposed in Table 4 did not ensure the additivity of the proximate composition, i.e. the sum of predictions of A, FC and VM would be different from 100. Alternatively, VM could be estimated as a difference to ensure additivity ($\widehat{VM} = 100 - \widehat{A} - \widehat{FC}$). This approach would increase the RMSE to 2.385 (1% increase) and also generating a MRES of 0.028, thus denoting a slight overestimation of the values.

As regards the calorific values, only three parameter estimates were significant: those affecting the residence time and the product of residence time and temperature, along with the intercept. The precision was lower in this case, but the adjusted coefficient of determination was >0.9 for both the HHV_{db} and the LHV_{wb}. The RMSE values obtained for both variables (Table 3) represent 3.2% and 3.5% in relative terms.

The influence of temperature and residence time on the variable responses were evaluated by plotting three-dimensional response surface graphics (Fig. 4).

The proposed models enable the definition of torrefaction severity, as a combination of t and T, that provides desired values of the energy properties. A graphical application of the fitted models for A and LHV_{wb} can provide isolines for both variables by plotting the torrefaction temperature (T, °C) on the X-axis and the residence time (t, min) on the Y-axis. If constant values for A and LHV_{wb} are considered, solving for t provides isolines that could be obtained analytically (equations (11) and (12)).

$$t = \frac{\ln\left(\frac{100-A}{A}\right) - 0.04509T + 9.044\ 10^{-5}T^2}{0.03029 - 1.51110^{-4}T} \tag{11}$$

$$t = \frac{LHV_{wb} - 18.34}{-0.3258 + 0.001533T} \tag{12}$$

Fig. 5 shows the isolines obtained for three constant values of the ash content: the ISO-17225-2 threshold for A1 quality class of wood pellet (A = 0.7%) and 0.6 and 0.5%. As regards the isolines for LHV_{wb}, a target of 22 MJ kg^{-1} was considered (corresponding to an increase of 30% relative to the raw pellets), and two more isolines below that value were considered (21 and 20 MJ kg^{-1}). Thus, the use of the models yields isolines that can be used to define the optimal combinations of t and T for other torrefied biomass, at least for the range of torrefaction severities covered by the data.

Considering the models should be used in the area covered by the data used for regression, it can be proposed a range of temperatures of between 260 and 270 °C and residence times of 50–60 min as the combinations that would be most likely to produce torrefied pellets with the target properties.

4. Discussion

In the present study, pellets made from debarked radiata pine wood were used as a baseline for comparison. Although the debarking operation has an associated cost, it allows use of the bark as a biofuel for a boiler to provide all the thermal energy needed to dry the wood chips. Several studies have shown that, because pine bark has high lignin and extractive contents, blending pine wood and bark could enhance the mechanical properties of the pellets, which maintaining low values of ash, provided that the proportion of bark is limited [29,30].

The results of this study show the effects of different combinations of torrefaction temperature and residence time on the energy properties of high-quality pellets. Most of the studied effects were positive, such as the reduction in the moisture content, the increase in fixed carbon, decreases in the O and H contents, increase in FC content, decrease in VM and the increase in calorific values. Other effects can be considered negative and are intrinsic to the process, particularly the increase in ash content.

The results obtained in this study were compared with those of several studies in which the TAP process was applied. The optimal combinations of temperature and residence time concluded in the

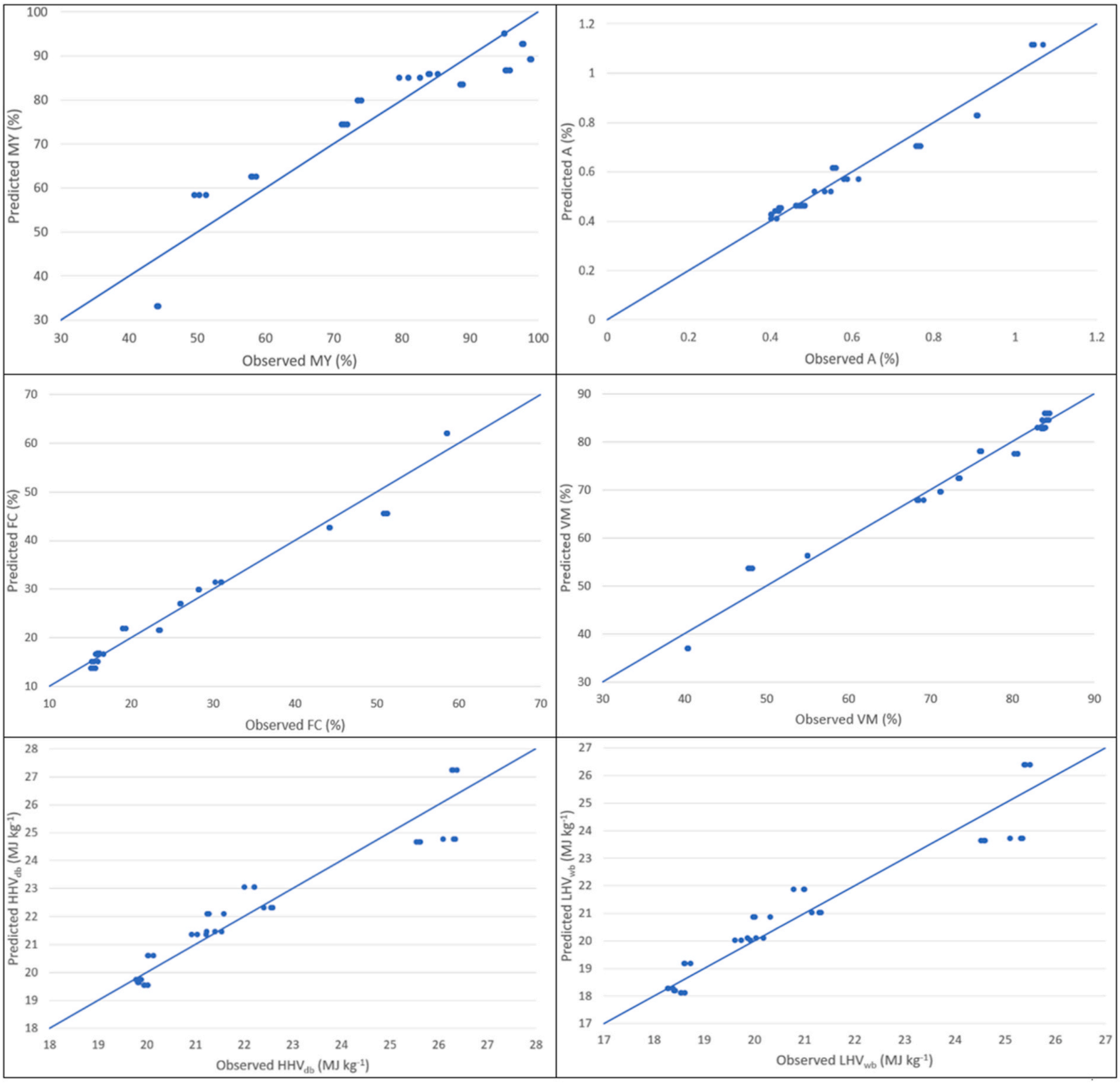

Fig. 3. Observed versus predicted values for the six variables under study, compared to the target line Predicted = Observed. Mass yield (MY), ash (A), fixed carbon (FC), volatile matter (VM), high heating value on a dry basis (HHV$_{db}$) and the low heating value on an as-received (or wet) basis (LHV$_{wb}$).

different studies are summarised in Table 4. Importantly in regard to direct comparison, some of the studies did not specify the raw material from which the pellets were made and others did not identify the species within the *Pinus* genus (Table 4). Additionally, the base reference for the percentages or heating values are not always evident. Only a few of the studies reported the whole range of properties determined in the present study.

The torrefaction conditions most commonly proposed as optimal in the previous studies are 250–275 °C for 30–45 min, combinations which are less severe than the optimal conditions recommended in the present study. Percent increases in HHV$_{db}$ are higher than the values obtained in the present study, although the comparison is restricted to conifer wood pellets. The increases in HHV for pine pellets (*Pinus sylvestris* and other unspecified species, Table 4) are higher than observed in the present study for *Pinus radiata* pellets [17]. However, similar results were obtained for Norway spruce stem wood [38]. Although several studies have reported HHV and LHV, studies specifying whether the calculations of these variables are expressed on a dry basis or as-received (wet) basis are scarce.

The moisture content of torrefied pellets is not generally reported in the relevant literature. In the present study, all the torrefaction treatments, except the least severe one, yielded pellets with zero moisture content. Biomass with low moisture is very stable during storage and is less likely to deteriorate. Moreover, transportation of torrefied biomass is cheaper than transportation the hygroscopic raw biomass due to the hydrophobic nature of the torrefied product [39]. Nonetheless, for practical application, the storage and transportation conditions would induce some rehydration. As combustion energy decreases greatly with increasing moisture content, the effect of torrefaction on the heating values is better indicated by the LHV$_{wb}$.

Loss of mass is directly related to the degradation of hemicellulose at temperatures above 200 °C [8,16], a process that mainly affects the outward appearance of the pellets and which is related to the colour changes. Regarding the mass yield, similar results were observed for torrefied pellets of other species for temperatures and times comparable to those in the present study (Table 4). Although not reported in the data used for the study, severe torrefaction treatments would result in a reduction in durability that should be considered. Preliminary data indicated a reduction in the durability of raw pallets (98.5%) to levels of around 96%, at least for treatment T240-40.

Table 4
Studies in which properties of torrefied pellets produced under different conditions were determined. The optimal torrefaction conditions proposed in each study are shown. HHV_{db} refers to high heating value on a dry basis; A denotes ash (%), DU denotes durability (%) and MY is mass yield (%). Data were transformed with HHV equations and to dry basis when necessary.

Authors	Species	Optimal torrefaction conditions	Increase HHV_{db} (%)	A (%)	DU (%)	MY (%)
Zhang et al., 2020 [17]	Soybean straw	250 °C, 45 min	8.38	4.20	92.78	75.00
	Pine wood sawdust	300 °C, 45 min	14.52	3.80	87.53	60.50
Ghiasi et al., 2014 [14]	Douglas fir	260 °C, 15min	17.65	–	97.00	–
Yu. Y et al., 2021 [31]	Caragana	275 °C, 20 min	9.44	4.17	–	71.07
Shang et al., 2012 [3]	Scots pine	250 °C, 60 min	16.22	–	95.00	87.25
Setkit et al., 2020 [32]	Leucaena	260 °C, 30 min	21.20	5.60	–	77.90
Chicaiza & Palacios, 2020 [33]	Red mangrove	230 °C, 60 min	26.40	14.08	–	75.94
Manouchehrinejad & Mani, 2018 [15]	Yellow pine	250 °C, 30 min	12.67	0.83	86.90	85.20
	Mixture	250 °C, 30 min	14.41	1.70	83.70	77.79
Peng et al., 2014 [34]	White pellet	270 °C, 30 min	20.54	–	–	83.06
	Brown pellet	270 °C, 30 min	15.34	–	–	82.47
	Pine	270 °C, 30 min	13.83	–	–	79.11
Yu. S et al., 2019 [35]	Unknown	250 °C, 30 min	22.38	3.05	–	76.11
Manatura et al., 2016 [36]	Rice husk	250 °C, 60 min	7.33	16.98	–	62.00
Gilvari et al., 2020 [37]	Miscanthus	270 °C, 45 min	–	–	95.00	80.00
	Poplar	285 °C, 45 min	–	–	89.00	75.00
Wang et al., 2020 [38]	Stem wood (N. spruce)	275 °C, 30 min	8.04	0.36	97.08	77.40
	Bark (N. spruce)	275 °C, 30 min	11.82	4.18	96.08	71.30
	Forest residue (N. spruce)	275 °C, 30 min	12.08	3.14	96.00	70.80
This study	Radiata pine	240 °C, 40 min	6.30	0.47	96.04	84.47

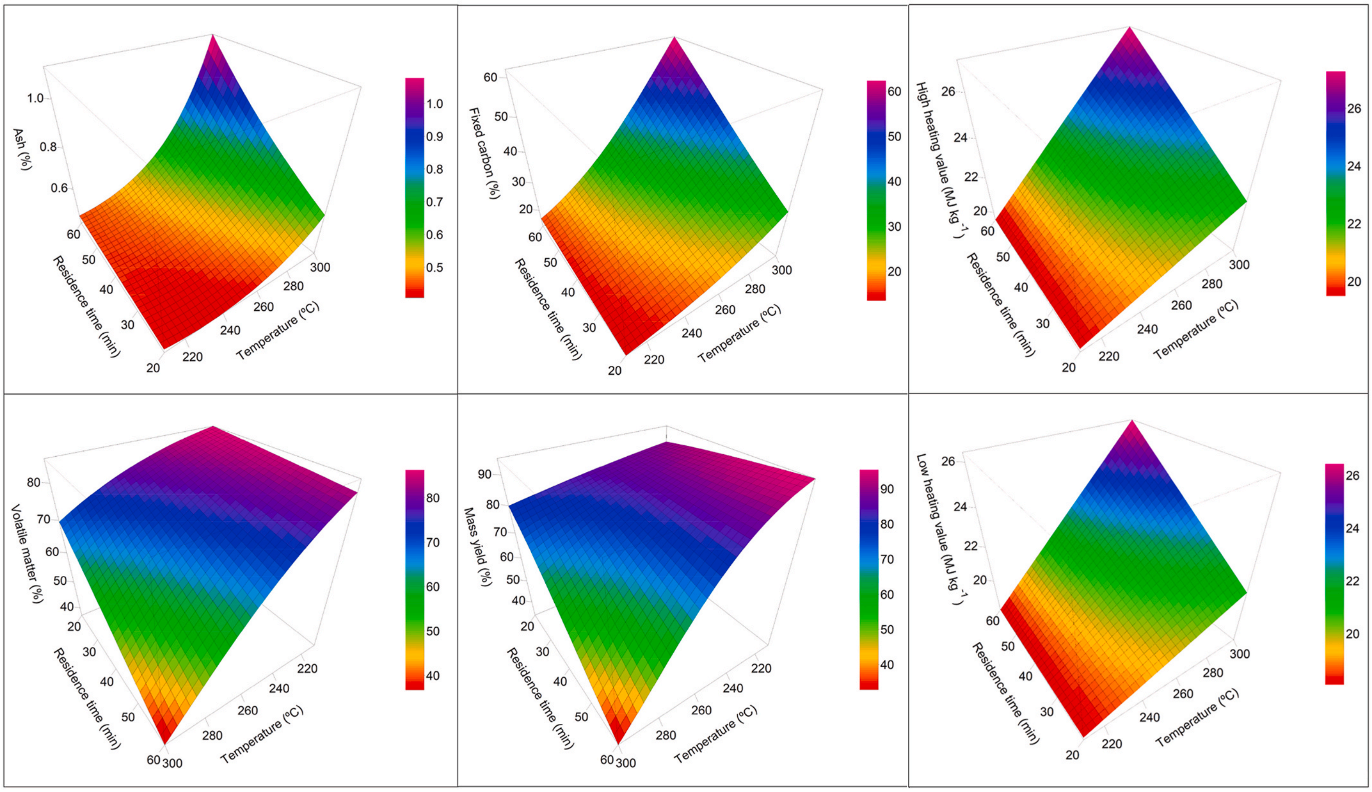

Fig. 4. 3D response surface plots for the six variables under study. Mass yield (MY), ash (A), fixed carbon (FC), volatile matter (VM), high heating value on a dry basis (HHV_{db}) and the low heating value on an as-received (or wet) basis (LHV_{wb}).

The ash content of fuel provides an indication of the lower heating value of the biomass and is one of the most important parameters in the wood pellet industry, with very restrictive levels in the quality standards for solid biofuel. As well as decreasing the lower heating value, a high ash content also increases the mineral content, which can cause fouling and slagging problems in thermal conversion systems working at high temperatures, such as boilers [40]. The ash contents reported in the relevant literature are much higher than those observed in the present study, with some exceptions for pellets made from stem wood of Norway spruce [38] subjected to similar temperatures and residence times (Table 4).

The effects of torrefaction on the proximate analysis of biomass pellets have seldom been reported, although increased fixed carbon and decreased volatile matter are expected. In the present study, fixed carbon began to increase dramatically at a temperature of 240 °C, yielding biofuel that will burn more slowly [6]. On the contrary, the volatile matter content mainly decreased due to the decomposition of the hemicellulose during the heating process. The decrease has a positive

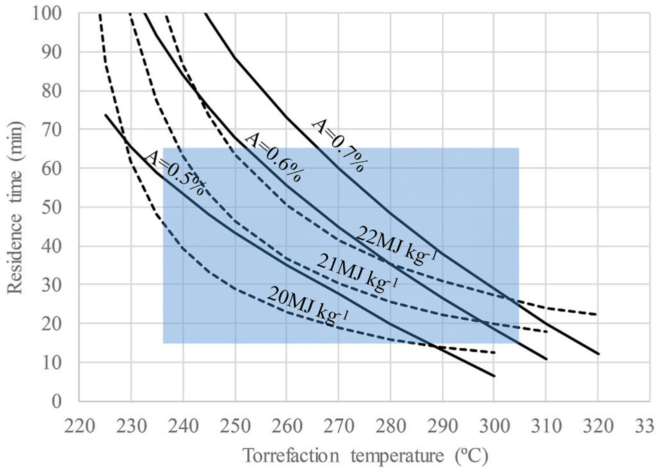

Fig. 5. Isolines for ash content (solid lines, A, %) and as-received low heating value (dotted lines, LHV_{wb}, MJ kg^{-1}) derived from the regression models obtained in the present study. The shaded area refers to the combinations of torrefaction temperature (°C) and residence time (min) covered by the data, where the model could be proposed for predictions.

effect in reducing particulate matter and carbon dioxide emissions, because a high volatile content in biomass is linked to the increased emission of particulate matter (PM) during combustion, poor gasification performance, low thermal output, high ash clinker and tar production, and increased carbon dioxide (CO_2) emission [41].

Several studies have used surface response methodologies to study the effects of torrefaction severity on different energy properties, mainly the mass and the energy yield [42,43]. All of the models used were second degree polynomials and the most frequent explanatory variables were the temperature and residence time. Pelletization temperature and moisture content were used successfully to predict the energy properties of residual blend pellets [44]. Proximate analysis variables that are very relevant for pellet quality, as the ash composition, has not predictive models proposed. Moreover, the present study shows the capacity of the logistic model to produce robust predictions for variables measured as percentages, and also to deal with the problem of the additivity of the predictions. In addition, the plot of diagrams including isolines for different variables of interest is a tool that has not previously been used to define the energy properties of torrefied biomass.

Current standards for pellets only consider the classification of wood pellets for commercial, residential and industrial applications. Although these standards do not include specifications for torrefied pellets, most of the treatments produced pellets that could be classified as A1 or I1 quality in the UNE-EN ISO-17225-2 standards for domestic or industrial use. The ash contents of the torrefied samples are within the threshold proposed in the standards ($\leq$0.7% for A1 and $\leq$1.0% for I1), except in the samples subjected to treatment T300-60. The N concentrations increased relative to those in the raw pellets and were below the threshold values considered in the standard ($\leq$0.3% for A1 and I1). The concentration of S was higher in samples from three of the treatment than in the raw pellets; however, all values were lower than those indicated in the standard ($\leq$0.04% for A1 and $\leq$0.05% for I1). Both of these elements are very important because of their relationship with contamination hazards. The LHV_{wb} increased clearly in all torrefaction treatments, being higher than 16.5 MJ kg^{-1} in all samples.

5. Conclusion

The threshold conditions for yielding significant effects of torrefaction severity in increasing higher heating values on a dry basis (HHV_{db}), increasing carbon (C) content or decreasing oxygen (O) content were 240 °C, 40 min. This combination was also the first providing significant effects on increasing ash content, decreasing volatile matter and increasing fixed carbon. A torrefaction T of 210 °C significantly increased the low heating value (LHV_{wb}) and decreased the hydrogen (H) content. Logistic and linear regression equations are provided for predicting the effects on mass yield, proximate composition and heating values of torrefaction treatments with severities within the region represented by the data. The process defined at temperatures of 260–270 °C and for residence times of 50–60 min increased the low heating value (as-received basis) of the pellets by 30% relative to raw pellets, reaching an as-received lower heating value of 22 MJ kg^{-1} and fixed carbon of 35.6%, with a mass yield of 70%. The negative effects of these combinations were minimal, the ash content remained lower than 0.7%, the current threshold for the A1 quality of wood pellets for domestic use.

CRediT authorship contribution statement

Andrés Iglesias Canabal: performed the experiments and contributed to the analysis of results and to the writing of the manuscript. **Jorge Proupín Castiñeiras:** performed calorimetry experiments and contributed to the analysis of results. **José Antonio Rodríguez Añón:** performed calorimetry experiments and contributed to the analysis of results. **Cristina Eimil Fraga:** contributed to the analysis of results and to the writing of the manuscript. **Roque Rodríguez Soalleiro:** contributed to the analysis of results and to the writing of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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