

Experiments and Modeling of the Torrefaction of White Wood Fuel Pellets

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The main purpose of this study was to find the optimal conditions for thermal treatment of white wood pellets. Other goals of this study were to compare torrefied and white pellets and to model the treatment process. Three types of pellets acquired from different manufacturing companies in the pellet market, representing distinct wood species, were torrefied at different temperatures of 160, 180, 200, and 220 °C, for 1, 2, and 3 h. After thermal treatment, the properties of the treated pellets were determined, including their mass loss, calorific value, ash content, and shear strength, and compared with those of the non-torrefied pellets. The calorific value increase was modeled based on the thermal degradation of hemicellulose and cellulose of the pellets and the correlation between the calorific value and mass loss. It was concluded that torrefied pellets have an increase in calorific value up to 22%, because of hemicelluloses degradation.

Keywords: Torrefied pellets; White wood pellets; Calorific value; Mass loss; Shear strength

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INTRODUCTION

Lignocellulosic pellets are engineered products that focus a great amount of energy in a small mass, which helps to reduce transportation costs. Because pellets can be made from wood debris (including municipal sources), a good amount of wood waste is highly valorized, which contributes to a reduction in pollution (Demirbaş 2001). Pellet production in the European Union (EU) has continuously increased every year, from 1 million tons in 2000 (Stelte *et al.* 2011). The EU is the largest producer of pellets in the world, and is responsible for over 50% of the total global production (Kaliyan and Morey 2009). The continuous growth of global pellet consumption, by 1 million tons each year since 2011 up to 20.3 million tons in 2015, is because of the diversification of pellets, and continuous improvement of their properties (Calderón *et al.* 2016). Over 5.2 million tons of pellets are imported to Europe from North America (Calderón *et al.* 2016). This continuous growth is possible because of the global annual increase in the amount of cut trees, approximately 800 million m³/year (representing about 8 m³/ha/year), of which only 62% is exploited annually for sustainability purposes (Kaliyan and Morey 2009; Wolf-Crowther *et al.* 2011; Mitani and Barboutis 2014; Calderón *et al.* 2016). Other researchers (Demirbaş and Sahin-Demirbas 2004; Stelte *et al.* 2011) consider the most important characteristics of pellets to be a moisture content below 10%, bulk density over 500-600 kg/m³ as Swedish standard SS 187120 (1998) stated, ash content from 0.7% to 3%, mechanical durability over 97%, fine sawdust content under 1% during transport and storage, calorific value between 16.5 and 19 MJ/kg, and ash melting point of 800 °C (Zervos 2009; Singer 2011; Gauthier 2014).

Treatment of pellets at high temperatures (thermal treatment) is a process that was developed in recent years. This treatment is used to increase the amount of energy contained in the pellets and enhance their hydrophobic and mycological sustainability (Bergman and Kiel 2005; Karlsson *et al.* 2011). The color of thermally treated lignocellulosic pellets becomes brownish-blackish, which is a disadvantage because the customers are familiar with beautiful natural color of white pellets. However, the color can be used to assess the pellet quality, as it correlates with the mass loss (Tudorović *et al.* 2012). The darker the pellet color, the higher the mass loss. The advantages of torrefied pellets can be determined by degrading the pellets at temperatures above 160 °C for several hours (McKendry 2002). During the degradation process, wood hemicellulose is affected the most, cellulose to a lesser extent, and lignin very little or not at all. Considering that hemicellulose is hydrophilic, it is expected that treated wood would have low hemicellulose content and absorb less humidity/water. Also, considering that hemicellulose and cellulose have lower calorific values than lignin, the calorific value of the treated wood should be greater than that of the untreated wood. Thermal treatment of pellets can be done directly on the pellets or indirectly on the sawdust, after which the dust is compacted into pellets (Lunguleasa *et al.* 2015). In both cases, after thermal treatment, the pellets lose some strength, become brittle, and shatter more easily. However, there is always an optimal balance between the advantages and disadvantages that can be achieved with the optimal treatment conditions. Researchers in the field are interested in determining these conditions (Olarescu *et al.* 2014; Wilén *et al.* 2014). The properties of treated pellets can be improved by eliminating air (use of vacuum autoclaving) or using nitrogen instead (Özbay *et al.* 2015). Thermal treatment in the presence of air is more severe than in the presence of nitrogen or vacuum, and requires lower temperatures or shorter times, with special attention required because of the danger of pellets self-igniting above 220 °C. Torrefaction induces a density loss of 180 to 290 kg/m³ for classic pellets (Esteves and Pereira 2009). Torrefaction time is short, 5 to 15 min, and the pellets have a higher potential of combustion and gasification because of the high energy per mass unit and volume (caloric density of 15 to 18.5 MJ/m³ compared with 8 to 11 MJ/m³ for classic pellets). Also, the thermal efficiency when using new products increases from 92% to 96% (Bergman and Kiel 2005). Bergman and Kiel (2005) examined the effects of heat treatment at 180°C and five different time durations ranging between 2 and 10 h on solid beech wood. More pronounced color changes were observed after the 8- and 10-h treatments, and the best swelling and shrinkage values were obtained with the 8-h treatment (Fabiyyi and Ogunleye 2015). Solid wood swelling decreased when the treatment duration increased up to 8 h only, and then it started to increase, which was a sign that the degradation of the wood was strong, exceeded the degradation of hemicellulose, and started to degrade cellulose. The equilibrium moisture content of the wood decreased by 47% compared with that of the untreated wood (Grîu and Lunguleasa 2014). It was found that the calorific value of the sawdust for four wood species (spruce, larch, beech, and oak) with small particles (less than 2 mm) can be increased by torrefaction in a kiln at temperatures between 200 and 300 °C and treatment times of 3, 5, and 10 min. The high and low calorific values (HCV and LCV, respectively) of pellets made from spruce sawdust and treated at 260 °C for 5 min (HCV = 19,700 kJ/kg and LCV = 19,100 kJ/kg) was higher by 13.1% and 13.2%, respectively, than that of the non-treated sawdust (HCV = 17,000 kJ/kg and LCV = 16,500 kJ/kg). It was revealed that thermal treatment of sawdust from softwood species leads to higher calorific values than for deciduous species (Özbay *et al.* 2015).

The main objective of this research was to determine the optimal conditions for thermal treatment of white pellets from the common market. Moreover, this research aimed to improve the properties of white pellets. A comparative analysis was desired on three types of white and torrefied pellets, in terms of their physical, calorific, and mechanical properties. Modeling of the thermal process of torrefaction was another objective of this work.

EXPERIMENTAL

Materials

Three different categories of pellets, made of spruce (*Picea abies*), oak (*Quercus robur*), and beech (*Fagus sylvatica*), referred to as Type 1, Type 2, and Type 3, respectively, were selected from the common pellet market. These were subjected to analysis of their physical (moisture content, effective density, bulk density, and mass loss), calorific (HCV, LCV, and caloric density), chemical (activated carbon content, volatile content, and ash content), and mechanical properties (shear strength).

Methods

The absolute moisture content (relative to the dry mass of the pellets) was determined by drying the pellets at 105 °C and weighing them when the mass was constant (ASTME1755-01 2003). The following equation was used,

$$M_c = \frac{m_i - m_0}{m_0} \cdot 100[\%] \quad (1)$$

where M_c is the moisture content (%), m_i is the initial mass of the pellets (g), and m_0 is the absolute dry mass (g).

Knowing the effective density of the pellets was necessary to determine the degree of sawdust compaction used during pelletisation and was determined as the ratio between the mass (m , g) and volume of the individual pellets (considered regular cylinder) after their ends were polished to obtain a more accurate length (l , mm). The length was measured with an electronic caliper with an accuracy of 0.01 mm. Each pellet diameter (d , mm), measured with the electronic caliper, was determined as the average of two perpendicular diameters. Fifty pellets were used for determining the average density because the analysis of the density is an uncertain method with a high standard deviation. The final relationship that was used to determine the density took into account the cylindrical shape of the pellets and was as follows:

$$\rho = \frac{4m}{\pi \cdot d^2 \cdot l} \left[\frac{\text{g}}{\text{cm}^3} \right] \quad (2)$$

The same three types of pellets were subjected to torrefaction in an electric oven at 160, 180, 200, and 220 °C for 1, 2, and 3 h. Torrefaction was done in metal crucibles made of chromium-nickel alloy. Inside each crucible, five pellets were placed. Four crucibles were introduced simultaneously into the oven in an atmosphere without oxygen admission. The process of torrefaction was preceded by drying the pellets in an oven at 150 °C for 3 h. The pellets were weighed first at 1.5 h, and then every 20 min until a minor difference between two successive weights was obtained (almost double the precision of the balance measurement). The last value was considered to be the initial mass of the pellets (m_i) before torrefaction. After the treatment period, all of the pellets were extracted from the oven and

cooled in desiccators, and then they were weighed with the same balance, which had an approximate accuracy of 0.001 g. This final mass was noted as m_f (g). Based on the two masses obtained for each type of pellet and thermal treatment, the mass loss (M_l) was determined with the following equation:

$$M_l = \frac{m_i - m_f}{m_i} \cdot 100 \text{ [%]} \quad (3)$$

The bulk density was determined using a vessel with a known volume (usually graded), in which a weighed amount of pellets was placed at a ratio of the effective mass to internal volume of the beaker. Ten values of the bulk density were used to obtain an average. This was the apparent density and was needed to determine the storage space of the pellets.

To determine the influence of torrefaction on the mechanical properties, a procedure was developed to determine the resistance to shear (a measure of strength) of five pellets simultaneously using a shearing device that consisted of two metal parts that generated a shear plane. Ten aftershocks were used to obtain an average resistance. From the general shear equation (force per surface area of fracture), a specific equation for determining the resistance to shear of the pellets was obtained,

$$\tau_s = \frac{4F_s}{5\pi \cdot d^2} \left[\frac{N}{mm^2} \right] \quad (4)$$

where τ_s is shear strength (N/mm²), F_s is shear force (N), and d is diameter of pellet (mm).

The volatile compounds, active carbon, and ash contents are three interrelated chemical properties. To determine these contents, a furnace was used (STC 18.26, Supertherm, Sibiu, Romania) that had air circulation and was capable of attaining a temperature of 650 °C. Additionally, a high-temperature crucible, analytical balance with a sensitivity of 0.001 g, desiccators, and an oven with forced-air circulation that was capable of temperature regulation between 100 and 150 °C were also used. For the determination of the volatile compounds content, approximately 1 g of sawdust that was obtained by grinding and sorting chips with a 1 by 1 mm sieve was dried to a constant mass and calcined at 650 ± 25 °C (ASTMD2866-11 2011). Before calcinations, the crucible was placed on an ashing burner and clay triangle with a stand over a flame until smoke appeared, and the sample was allowed to burn until no more smoke or flames appeared. The approximate content of the volatiles was quantified by the amount of smoke (determined as the mass difference before and after burning) that was removed from the wooden material. The volatile compounds content was expressed as the ratio of mass loss related to the initial mass of the dry sawdust, and used a relationship similar to Eq. 3. The ash content of the pellets was determined by igniting the dried dust in the same electric oven at 650 ± 25 °C for 5 h. The sawdust and ash were stored and treated inside nickel-chromium alloy crucibles that were resistant to high temperatures and whose weight was measured before each treatment. To determine the ash content, the ash mass obtained from the volatile compounds content determination was used, but using the initial value of the dry sawdust mass in the equation. To eliminate the influence of the moisture content, as in the case of the volatile compounds content determination, dust obtained by grinding was heated in an oven to 105 °C for 2 to 3 h and weighed every half hour until a constant mass was obtained. For each type of pellet, ten replicates were made for determination of the volatile compounds and ash contents. The active carbon content, expressed as a percentage, was computed as the difference of the volatile compounds and ash contents from the whole (100%), which is shown with the following equation:

$$Ca_c = 100 - Vo - As [\%] \quad (5)$$

When the volatile compounds content is lower, the wood material is more likely to burn with less smoke, which is more environmentally friendly.

The calorific value was determined experimentally with a bomb calorimeter (XRY-1C, Shanghai Changji Geological Instrument Co., Shanghai, China) equipped with software for calculating and displaying both the HCV and LCV. Samples with a weight of 0.6 to 0.8 g and moisture content of approximately 8% were used. Oxygen was introduced into the bomb at 30 bars. The calorific value for both the white and torrefied pellets was determined using common European standards (DIN 51731 1996; SS 187120 1998; ÖNORM M7135 2000; CTI-R 04/5 2004; EN plus 2013). The formula used by the software is shown by the following equation (Grîu and Lunguleasa 2014),

$$CV = \frac{C \cdot (t_f - t_i)}{m} - q_s \quad [kJ/kg] \quad (6)$$

where CV is the calorific value (kJ/kg), C is the characteristics of the installation determined by calibration, t_f is the final temperature read by the thermocouple in the calorimeter ($^{\circ}C$), t_i is the initial temperature read by the thermocouple in the calorimeter ($^{\circ}C$), q_s is the quantity of heat released by the nickel-chromium wire and cotton thread (kJ/kg), and m is the mass of the pellet sample (g). To alter the calorific value of the pellets from a certain moisture content to a 0% moisture content and *vice versa*, the following equation was used (Finnish Thermowood Association 2003; Krajnc 2015),

$$LCV_{M_c} = \frac{CV \cdot (100 - M_c) - 2.44 \cdot M_c}{100} \quad [MJ/kg] \quad (7)$$

where LCV_{M_c} is the lower calorific value for a certain moisture content M_c (MJ/kg), CV is the calorific value of the dried wooden material (MJ/kg), and M_c is the moisture content (%).

Before determination of each group, calibration with benzoic acid was completed. In this case, a 1-g benzoic acid pill was placed in the crucible and the calorimetric coefficient (C) was determined (Eq. 6), which was used for the next 30 to 50 tests.

The caloric density represents the amount of heat related to the actual volume of fuel, which in this case were the pellets. When the CV of the pellet and its density (ρ , kg/m^3) was taken into consideration, the equation for determining the caloric density became:

$$CD = CV \cdot \rho \left[\frac{MJ}{m^3} \right] \quad (8)$$

The caloric density of pellets is very important because of their high density (approximately 1100 kg/m^3) compared with that of solid wood (between 550 and 780 kg/m^3). It was necessary to determine the caloric density of the torrefied pellets as their density decreased compared with the non-torrefied pellets.

Because the color of the torrefied pellets resembled that of charcoal, and pellets and charcoal are both obtained through the same conversion methods (McKendry 2002), five different sacks of beech coal were sampled to determine their physical properties, calorific value, and ash content for comparison with the torrefied pellets. The same characteristics of the pellets were determined, which were the effective density, bulk density, HCV, LCV, ash content, volatile compounds content, and active carbon content. The calorific value obtained from these measurements was also necessary for modeling torrefaction.

RESULTS AND DISCUSSION

The dimensions and physical properties of the non-torrefied pellets determined during the experiments are presented in Table 1.

Table 1. Dimensions and Physical Properties of the Woody Pellets

Characteristics	Average Values and Limits		
	Type 1 (Spruce)	Type 2 (Oak)	Type 3 (Beech)
Diameter (mm)	6.01 \pm 0.33	6.17 \pm 0.34	6.11 \pm 0.34
Length (mm)	12.06 \pm 0.51	11.71 \pm 0.50	14.97 \pm 0.53
Moisture content (%)	8.2 \pm 0.49	8.1 \pm 0.48	8.3 \pm 0.48
Effective density (g/cm ³)	1.06 \pm 0.07	1.04 \pm 0.08	1.02 \pm 0.06
Bulk density (g/cm ³)	0.321 \pm 0.02	0.311 \pm 0.02	0.305 \pm 0.02

Because the diameters and effective densities of the three types of pellets were close (Table 1), it was concluded that the bulk density was influenced only by their length. The beech pellets with the highest length (14.97 mm) had the lowest bulk density (0.305 g/cm³).

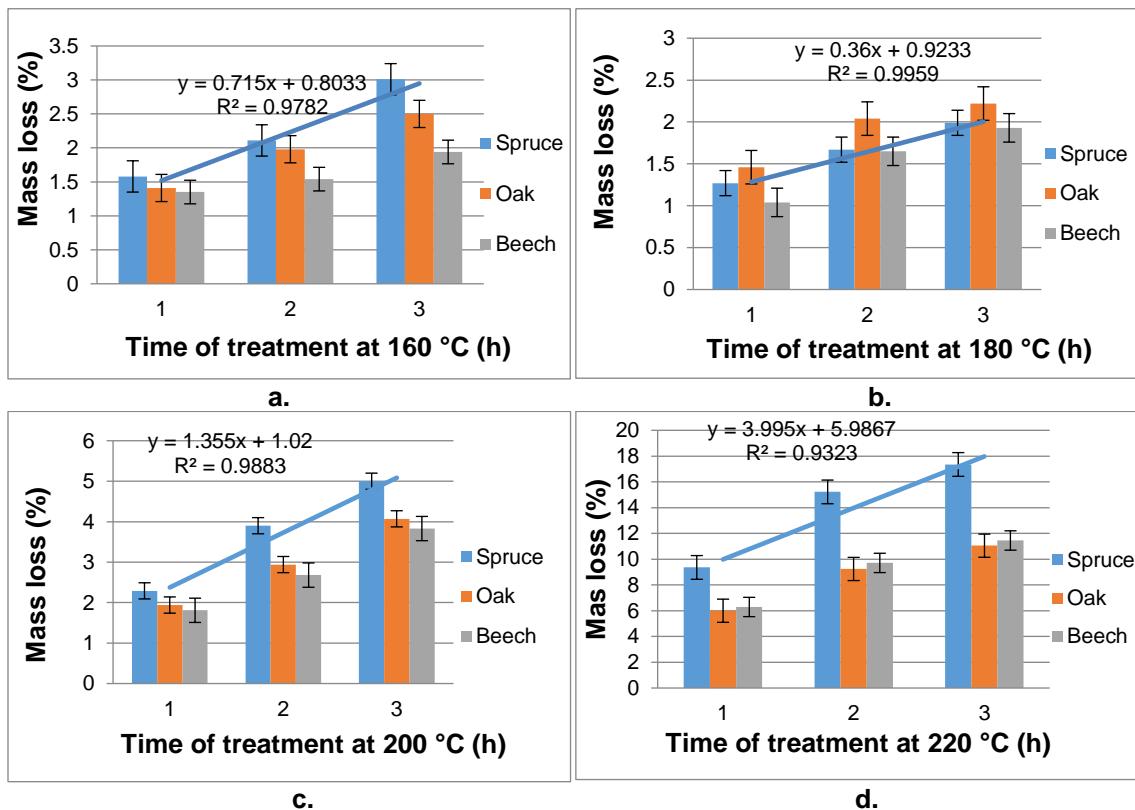


Fig. 1. Influence of the treatment time on the mass loss: (a) at 160 °C, (b) at 180 °C, (c) at 200 °C, and (d) at 220 °C

Within all pellet parameters, the mass loss of the pellets by torrefaction was the most important parameter for analysis (Čermák *et al.* 2015; Fabiyi and Ogunleye 2015). It can be clearly seen in Fig. 1 that for all of the pellet types and treatment temperatures, the mass loss increased as the treatment time increased, usually linearly with a Pearson

coefficient (R^2) of over 0.93. Also, the mass losses of the spruce and oak pellets were generally higher than that of the beech pellets.

The comparative analysis of the four charts in Fig. 1 revealed the influence of the temperature on the mass loss. From this analysis, it appeared that the influence of the temperature on the mass loss was stronger than that of the torrefaction time, especially when the temperature exceeded 200 °C. The mass loss increased from 4% to 11% when the temperature was between 200 to 220 °C. Below 200 °C, the temperature influence was modest, with an almost imperceptible increase of 0.06% from 160 to 180 °C and a 0.9% increase from 180 to 200 °C. Therefore, it is recommended to use temperatures over 200 °C during torrefaction treatment, as other authors stated before (Esteves and Pereira 2009; Chen *et al.* 2015b).

The shear strength of the torrefied pellets decreased when the torrefaction degree increased (the temperature and/or time of torrefaction increased), as can be seen in Fig. 2. For the beech pellets, shear strength values of 2.3 N/mm² at 160 °C and 3 h and 1.8 N/mm² at 220 °C and 3 h were observed, which were low compared with the shear strength value of 3.5 N/mm² for the pellet control samples and was a decrease of 34% and 48%, respectively. Although most researchers consider wood and other lignocellulosic materials to have low resistances after torrefaction, the intensity of the resistance decrease differs greatly and is determined by the treatment environment and temperature (Mitani and Barboutis 2014; Chen *et al.* 2015a).

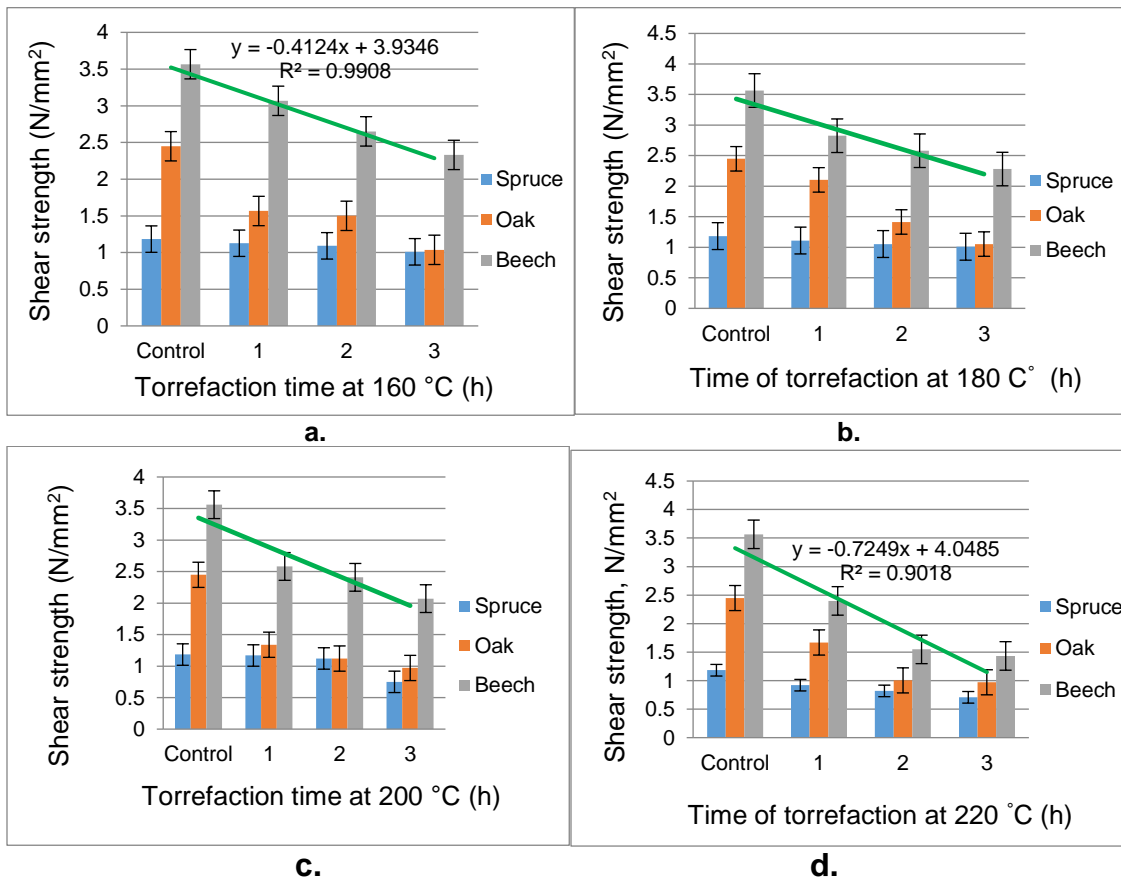


Fig. 2. Shear strength of the torrefied pellets: (a) 160 °C; (b) 180 °C, (c) 200 °C, and (d) 220 °C

The LCV of the pellets, which is the value that is typically used in all of the thermal calculations, increased slightly for the torrefied samples compared with the control samples (3 h at 220 °C), namely from 18.37 to 20.01 MJ/kg for the spruce pellets (8.9% increase), from 16.29 to 19.90 MJ/kg for the oak pellets (22.1% increase), and from 17.54 to 20.11 MJ/kg for the beech pellets (14.6% increase).

The weak influence of the thermal treatment on the calorific value (Fig. 3) was observed in the analysis of the coefficient m from the regression equation ($y=mx+n$). It was observed that the maximum value (0.531 at an angle of inclination of 27.9°) for the calorific value was much lower than the corresponding decrease in the shear strength (0.74 at a tilt angle of 35.7°).

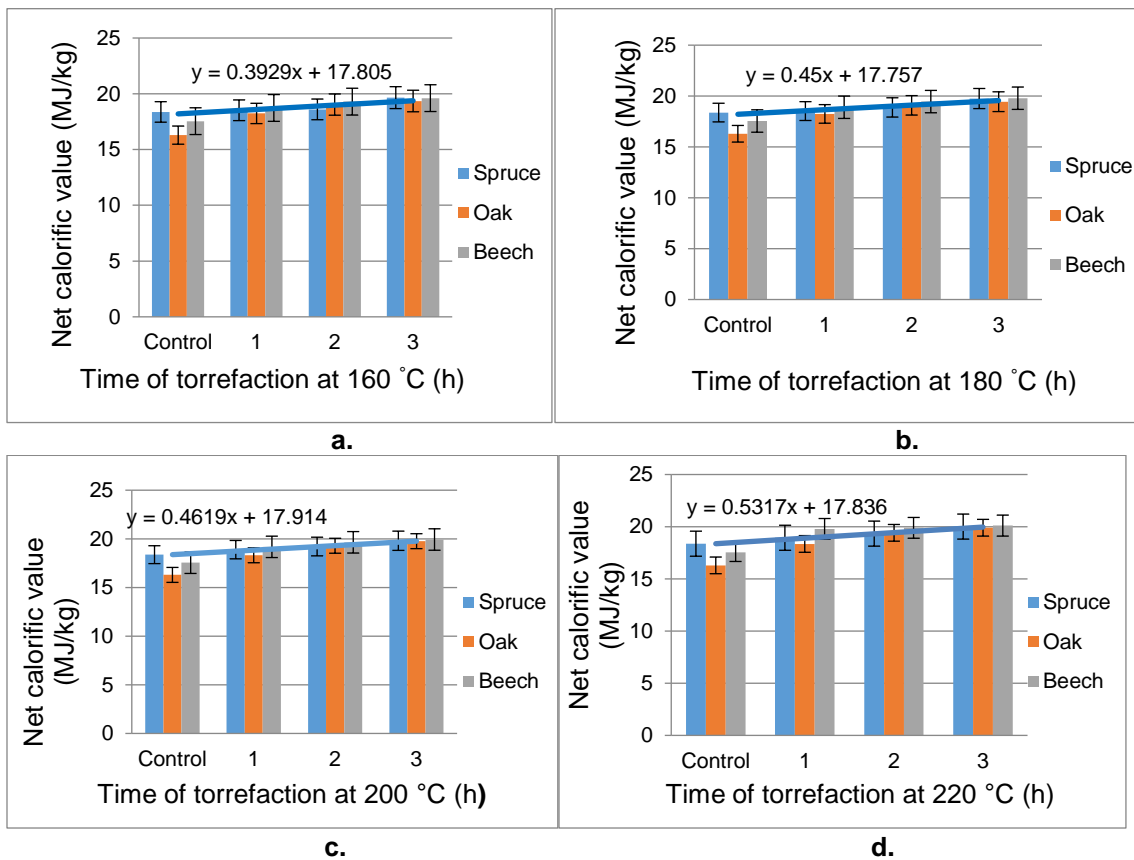


Fig. 3. Influence of the torrefaction degree on the net calorific value: a-at 160 °C, b-at 180 °C, c-at 200 °C, and d-at 220 °C

From the analysis of the volatile compounds, ash, and active carbon contents (Table 2), it was observed that the active carbon content easily increased during torrefaction from 76% to 80% for the spruce pellets, which was an increase of approximately 5.2%. This enrichment in carbon is important (Chen *et al.* 2015b) because of the various uses for activated carbon (fining off/filter for liquid food or enrichment in carbon in iron and steel industry). The black ash content obtained after the volatile compounds content and the light-gray ash content obtained after calcinations were calculated. The black ash content, which was obtained after eliminating smoke from the sawdust, was almost constant, and average contents of 73.7% for spruce pellets, 75.7% for oak pellets, and 75.4% for beech pellets were calculated. The calcined ash content, determined according to the methodology, decreased from 0.91% to 0.47% for the beech pellets compared with that of

the control samples, which was a decrease of 48.3% and was similar to that of the solid wood of the same species.

Table 2. Contents of the Ash, and Activated Carbon

Type	T (°C)	Ash				Activated Carbon			
		C*	1h	2h	3h	C	1h	2h	3h
	160		0.76±0.02	0.79±0.02	0.82±0.04		76.84±3.82	77.41±3.83	78.38±3.91
	180		0.79±0.02	0.81±0.04	0.84±0.04		77.51±3.83	77.79±3.84	79.86±3.98
	200		0.86±0.04	0.92±0.04	0.94±0.04		78.94±3.86	77.98±3.86	80.46±4.05
	220		0.92±0.05	0.96±0.05	1.06±0.05		78.98±3.86	79.14±3.89	80.74±4.02
	160		1.08±0.05	1.03±0.05	1.01±0.05		77.12±3.85	77.27±3.82	77.69±3.95
	180		0.91±0.05	1.01±0.05	1.19±0.06		77.39±3.86	77.69±3.84	78.11±3.94
	200		1.11±0.05	1.12±0.05	1.27±0.06		78.09±3.89	78.28±3.88	78.63±3.96
	220		1.15±0.05	1.22±0.06	1.39±0.05		79.05±3.89	79.18±3.89	79.51±3.98
	160		0.39±0.02	0.43±0.02	0.49±0.02		74.11±3.82	77.17±3.82	77.41±3.95
	180		0.41±0.02	0.43±0.02	0.51±0.03		75.19±3.83	76.27±3.78	76.29±3.87
	200		0.43±0.02	0.44±0.02	0.52±0.03		76.67±3.87	77.16±3.81	77.28±3.88
	220		0.44±0.02	0.45±0.02	0.47±0.02		77.26±3.88	77.45±3.83	78.53±3.89

* C is the control

Table 3. Caloric Density of the Torrefied Pellets

Specification	Torrefaction Degree	Spruce pellets	Oak pellets	Beech pellets
	Control	19.47±1.02	16.94±0.82	17.89±0.81
	160°C/1h	19.31±1.01	18.69±0.81	18.84±0.91
	160°C/2h	19.30±1.01	19.40±0.86	19.37±0.94
	160°C/3h	20.20±1.02	19.62±0.87	19.61±0.95
	180°C/1h	19.38±1.01	18.69±0.81	19.07±0.95
	180°C/2h	19.67±1.01	19.44±0.86	18.95±0.92
	180°C/3h	20.52±1.02	19.77±0.88	19.79±0.96
	200°C/1h	19.56±1.01	18.67±0.82	19.20±0.95
	200°C/2h	19.56±1.01	19.47±0.86	19.44±0.96
	200°C/3h	19.94±1.02	19.71±0.88	19.55±0.96
	220°C/1h	18.19±0.90	17.93±0.81	18.91±0.94
	220°C/2h	17.37±0.85	18.78±0.84	18.31±0.95
	220°C/3h	17.53±0.86	18.41±0.86	18.16±0.94

The caloric density from the experiments, calculated with Eq. 8 (Table 3), was dependent both on the density of the pellets and calorific value, which decreased and increased slightly during torrefaction, respectively. Therefore, the caloric density increased until the torrefaction degree was 180 °C and 3 h, and then it decreased as the torrefaction degree continued to increase, according to the Gaussian curve. The caloric density values of the torrefied pellets (14 to 15 MJ/m³) were higher than that of the white wooden briquettes (14 to 15 MJ/m³) and firewood (13 to 14 MJ/m³).

The beech coal, used as a comparison element, was derived from beech wood (*Fagus sylvatica*) with a density of 690 kg/m³ at 8% moisture content. The coal had a density of 460 kg/m³ with the same moisture content (determined from rectangular pieces

without cracks). The mass loss, which occurred during wood pyrolysis to obtain charcoal, was 33%. This value that was not obtained during the torrefaction process (a maximum of 18% was obtained). Hence, it was concluded that there were some torrefaction reserves, as either the time or temperature increased. The calcined ash content of the beech charcoal was high, 26% to 29%. This was explained by the fact that all of the volatile compounds were removed from the solid wood during carbonization and the term for comparison (denominator) was not the mass of the solid wood, but that of the coal. It was also observed that the period of calcination tripled compared with the treated and untreated pellets. For the calorific value of the charcoal, average values of 31.9 and 31.4 MJ/kg were obtained for the HCV and LCV, respectively. These values represented an increase of 70% compared with the classic pellets and 58% compared with the spruce torrefied pellets. The calorific value of the charcoal was greater than that of bituminous coal (Macias-García *et al.* 2004) and slightly lower than that of plastic waste (Zarringhalam-Moghaddam *et al.* 2011).

Table 4. Correlation between the Mass Loss (*M*) and Low Calorific Value (LCV)

Type	Features	C	200°C/1h	200°C/2h	200°C/3h	C	220°C/1h	220°C/2h	220°C/3h
	<i>M</i> (%)	0	2.29±0.11	3.9±0.19	5.00±0.24	0	9.36±0.46	15.22±0.71	17.35±0.80
	LCV (MJ/kg)	18.37±0.98	18.88±0.98	19.21±0.98	19.80±0.98	18.37±0.98	18.93±0.98	19.33±0.98	20.01±0.98
	<i>M</i> (%)	0	1.94±0.10	2.94±0.15	4.07±0.21	0	6.00±0.31	9.24±0.42	11.05±0.63
	LCV (MJ/kg)	16.29±0.98	18.31±0.98	19.29±0.98	19.75±0.98	16.29±0.98	18.34±0.98	19.41±0.98	19.90±0.98
	<i>M</i> (%)	0	1.81±0.11	2.68±0.11	3.83±0.11	0	6.29±0.11	9.71±0.11	11.45±0.11
	LCV (MJ/kg)	17.54±0.98	19.17±0.98	19.64±0.98	19.93±0.98	17.544±0.98	19.79±0.98	19.88±0.98	20.10±0.98

A correlation between the mass loss and LCV (Table 4) was also completed. It was seen that the highest mass loss and increase in the LCV were recorded for the maximum thermal treatment conditions (220 °C and 3 h), which was why the correlation was done only at these conditions. In the case of the spruce pellets, the increase in the LCV by 1.639 MJ/kg corresponded to a mass loss of 11.05%, which meant that each percent of mass loss increased the LCV by 0.148 MJ/kg. Similarly, for an increase in the LCV by 0.315 MJ/kg for the oak pellets and 0.223 MJ/kg for the beech pellets, a 1% mass loss was observed. This analysis determined that the low growth of the LCV correlated with the mass loss, although it had been assumed that they should be commensurate. After analyzing Table 3, the increase in the LCV after maximum torrefaction was 8.9% for spruce pellets, 22.1% for oak pellets, and 14.6% for beech pellets. These values are important, but it was also seen that torrefaction depended on the wood species the pellets were made of. The oak pellets had the largest increase, while the spruce pellets had the smallest.

Modeling of the Torrefaction Process for the Beech Pellets

The model was based on the fact that wooden materials as pellets are mainly made of three important components, cellulose, hemicellulose, and lignin, and some secondary components, such as some ash mineral and extractible substances (Wilén *et al.* 2014). The mineral and extractible substances are a small portion, and even negligible, usually under 3% to 5%. Therefore secondary components are not taken into consideration in modeling. The wood species chosen for the analysis was beech (*Fagus sylvatica*), which is one of the dominant tree species in Europe (Tudorovic *et al.* 2012; Mitani and Barboutis 2014) and is

composed of 23% lignin, 50% cellulose, and 27% hemicellulose (Krajnc 2015). The choice of beech was also due to the fact that beech pellets and beech charcoal were used in experiments.

It was taken into consideration that with increasing temperature hemicellulose degrades first, cellulose second, and finally lignin (Kers *et al.* 2010). It is also known that at temperatures below 220 °C lignin remains intact, while some authors state that temperatures over 280 °C are needed before there is substantial thermal decomposition of lignin (Esteves and Pereira 2009). The maximum calorific value of the torrefied beech pellets was actually close to the calorific value of the charcoal obtained from the beech wood, as experiments show us.

For the analysis to be performed in good conditions, the experimental value of 17.544 MJ/kg for the beech pellets was changed by Eq. 6 to 18.6 MJ/kg for 0% moisture content. For the beech wood, the calorific values were taken from wood chemistry references (Ververis *et al.* 2004; Esteves and Pereira 2009). The calorific value is 27.1 MJ/kg for lignin, 16.2 MJ/kg for cellulose, and 16.1 MJ/kg for hemicellulose. The calorific value of lignin is close to that of charcoal, and the small difference between the values was because of the activation of chemical compounds during wood pyrolysis (Chen *et al.* 2015b). The calorific value of the torrefied pellets was considered to be a weighted average of the calorific values for holocellulose and lignin. The calorific value for holocellulose represented a weighted average of cellulose and hemicellulose (16.1 MJ/kg). The general relationship of the calorific value is,

$$CV = 27.1 \cdot Li/100 + 16.1(Holce)/100 \text{ [MJ/kg]} \quad (7)$$

where Li is the lignin content(%), and $Holce$ is the holocellulose content(%) ($Li=23\%$; $Holce=77\%$). Because Li and $Holce$ together are 100%, $Holce$ is equivalent to Li subtracted from 100%. Through replacement, the above relationship (Eq. 7) becomes:

$$CV = 27.1 \cdot Li/100 + 16.1(100-Li)/100 \quad (8)$$

When in the regression equation y is replaced with CV and x is replaced with Li , the general equation for the calorific value becomes:

$$y = 0.11x + 16.1, \\ CV = 0.11Li + 16.1 \quad (9)$$

where x equals Li (23% to 100%), and y equals CV both lie in the interval (18.6 to 27.1 MJ/kg).

Equation 9 can also be obtained by determining the calorific value in an Excel graph of the degradation of hemicellulose and cellulose related to the lignin content, from 23% to 100%, as can be seen in Fig. 4. From the first part of Fig. 4a, the model proposed for the thermal degradation of chemical wooden compounds (hemicellulose and cellulose) was identified, with a minimum value of 18.6 MJ/kg at the start of degradation, 21.6 MJ/kg at the moment of total degradation of hemicellulose, and a maximum value of 27.1 MJ/kg when the holocellulose was completely degraded.

When all of the hemicellulose (27%) was degraded (when the value was 50% on the X-axis of the diagram), a calorific value of 21.6 MJ/kg was obtained. As the process of torrefaction continued and all of the cellulose was degraded, the calorific value was 27.1 MJ/kg. This value was closer to the calorific value of the charcoal obtained during the experimental process. The continuation of degradation beyond holocellulose of the wood

obtained from beech pellets included the degradation of lignin and led to a decrease of the torrefied mass. However, the calorific value remained the same.

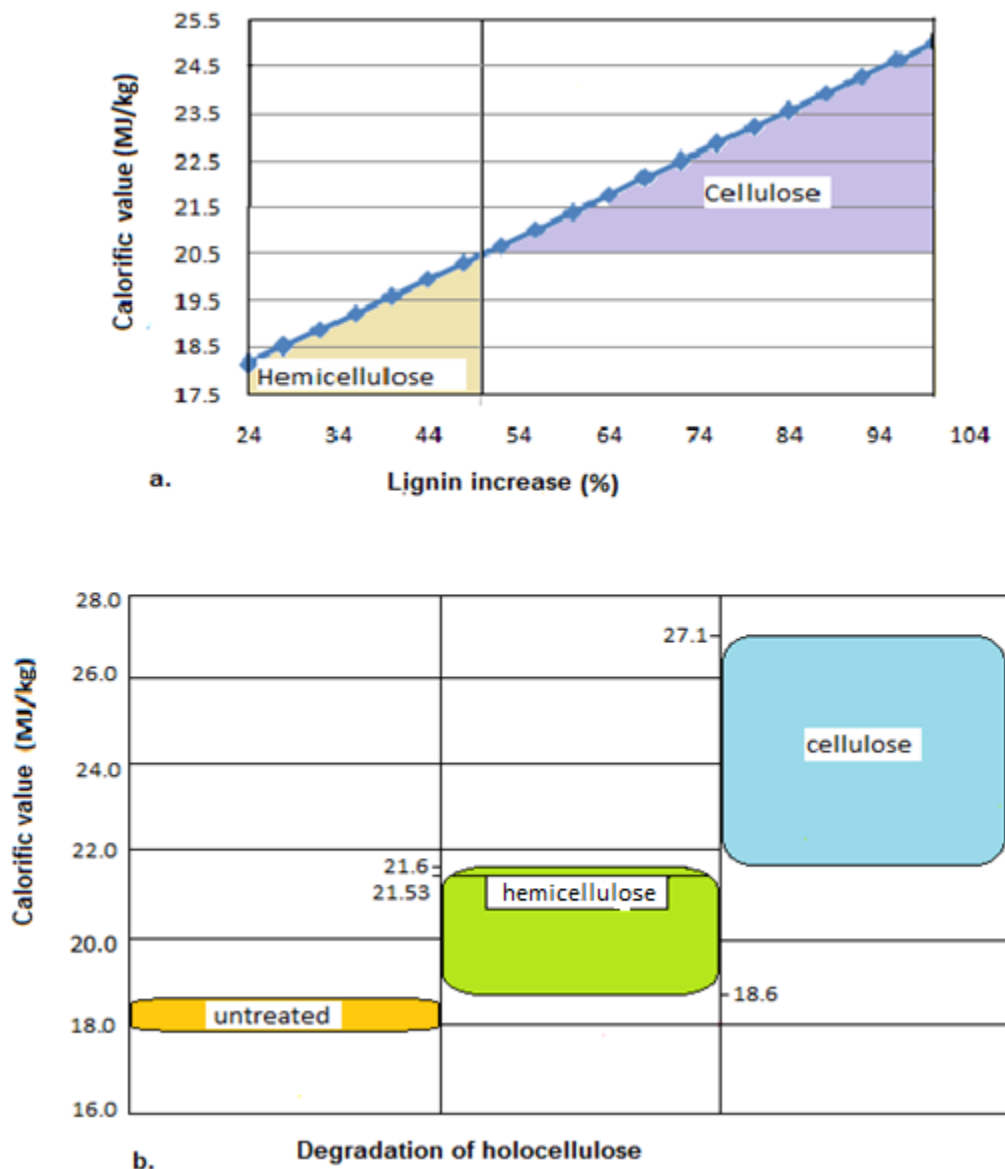


Fig. 4. Influence of the holocellulose degradation on the calorific value: (a) influence of lignin increase, and b) total diagram of the calorific value

In Fig. 4b, the calorific value peak obtained from the modeling is represented. It was observed that although the temperature was very high and the duration of treatment was long, the point of maximum calorific value could not be reached. The calorific value of the classic pellets was also included on the diagram, as well as the minimum value of the torrefaction reference.

The analysis of the calorific value for the experimentally torrefied pellets showed an increase from 17.54 to 20.11 MJ/kg for the beech pellets (14.6% increase) with a moisture content of 8%. For the dried pellets, there was an increase in the calorific value from 18.6 to 21.53 MJ/kg (Fig. 4a). This growth interval can be seen in the total diagram

of torrefaction (Fig. 4b). The maximum calorific value of the torrefied pellets was not the value obtained after mathematical modeling (27.1 MJ/kg), but it was very close to the degradation of total hemicellulose (21.6 MJ/kg). Thus, the degree of torrefaction can be divided into two categories, depending on the total degradation of the hemicellulose or of the holocellulose.

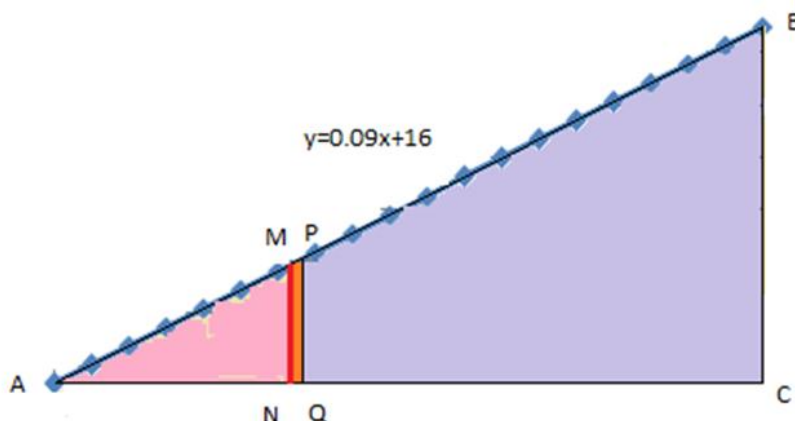


Fig. 5. Determination of the pellet torrefaction degree

To find the relationship for determining the degree of torrefaction, a right-angled triangle ABC (Fig. 5) was drawn, where the holocellulose degradation was on the horizontal axis and the calorific value was on the vertical axis. The right angle was point C (100; 18.6). Point A (23; 18.6) was the starting point of torrefaction and line AB (with equation $y = 0.09x + 16$) represented the line of torrefaction. In this right-angled triangle, the segments AC, BC, MN, PQ, AN, and AQ were known to be 77, 8.5, 2.93, 3, 26.3, and 27, respectively. With this data and using the Pythagorean Theorem, the segments AM, AP, and AB could be computed and were determined to be 26.46, 27.16, and 77.46.

The degree of torrefaction was the percentage ratio between the segment AM and the whole torrefied segment obtained by mathematically modeling AP and AB, which led to the following two relationships:

$$TD_{he} = \frac{AM}{AP} \cdot 100 [\%] \quad (10)$$

$$TD_{holce} = \frac{AM}{AB} \cdot 100 [\%] \quad (11)$$

The appropriate replacements were then made:

$$AM = \sqrt{AN^2 + MN^2} \quad (12)$$

$$AP = \sqrt{AQ^2 + PQ^2} \quad (13)$$

$$AB = \sqrt{AC^2 + BC^2} \quad (14)$$

Returning to the calorific value and percentage of hemicellulose/holocellulose degradation, Eqs. 12, 13, and 14 became:

$$AM = \sqrt{(He_{real} - 23)^2 + (CV_{real} - 18.6)^2} \quad (15)$$

$$AP = \sqrt{(He_{tot} - 23)^2 + (CV_{He} - 18.6)^2} \quad (16)$$

$$AB = \sqrt{(Holce_{tot} - 23)^2 + (CV_{holce} - 18.6)^2} \quad (17)$$

The final relationships of the torrefaction degree of the wooden pellets were as follows:

$$TD_{he} = \frac{\sqrt{(He_{real} - He_i)^2 + (CV_{real} - CV_i)^2}}{\sqrt{(He_{tot} - He_i)^2 + (CV_{He} - CV_i)^2}} \cdot 100 [\%] \quad (18)$$

$$TD_{holce} = \frac{\sqrt{(Holce_{real} - He_i)^2 + (CV_{real} - CV_i)^2}}{\sqrt{(Holce_{tot} - He_i)^2 + (CV_{Holce} - CV_i)^2}} \cdot 100 [\%] \quad (19)$$

where TD_{he} and TD_{holce} are the torrefaction degree of the pellets related to the maximum degradation of hemicellulose and holocellulose (%), respectively, He_{real} and $Holce_{real}$ are the hemicellulose and holocellulose contents (%), respectively, that were degraded during real torrefaction, He_{tot} and $Holce_{tot}$ are the maximum contents of hemicellulose and holocellulose in the pellets(%), respectively, CV_{real} is the final/real calorific value obtained as a result of maximum torrefaction (MJ/kg), CV_{Holce} and CV_{He} are the calorific values of the holocellulose and hemicellulose of the completely degraded pellets(MJ/kg), respectively, according to the modeling, He_i is the initial hemicellulose content when pellet torrefaction began(%), and CV_i is the initial calorific value of the non-torrefied pellets (MJ/kg).

When the fact that the ABC triangle is similar to the AMN and APQ triangles are taken into account, then the following relationships are obtained:

$$\frac{AN}{AQ} = \frac{AM}{AP} = \frac{NM}{PQ}; \frac{AM}{AB} = \frac{AN}{AC} = \frac{NM}{BC} \quad (20)$$

Thus, Eqs.18 and 19 can be simplified and become:

$$TD_{he} = \frac{He_{real} - He_i}{He_{tot} - He_i} \cdot 100 [\%] \quad (21)$$

$$TD_{holce} = \frac{Holce_{real} - He_i}{Holce_{tot} - He_i} \cdot 100 [\%] \quad (22)$$

By introducing the maximum experimental torrefied pellet calorific value of 21.53 MJ/kg to Eqs. 18 and 19 or Eqs. 21 and 22, and keeping in account the modeling values, torrefaction degrees of 97.6% for hemicellulose degradation and 34.15% for total holocellulose degradation from the wooden pellets are obtained. Thus, a new conclusion is reached. It was concluded that the wood pellet torrefaction process in a poorly oxygenated environment conducted at a temperature of up to 220 °C for 3 h resulted only in hemicellulose degradation. This was observed by others researchers as well (Kers *et al.* 2010). The torrefaction of massive wood, plywood, or medium density fiberboard (MDF) has a stronger influence at the same temperatures because of the lower densities and higher porosities of those materials. The larger the pores, the higher the air flow are inside the wooden materials (Ververis *et al.* 2004; Rowell 2005; Lunguleasa and Spîrchez 2015). The literature (Esteves and Pereira 2009) stipulated that the torrefaction process in a nitrogen or vacuum environment, whatever the nature of the wooden material, causes a more pronounced torrefaction degree. It has also been stated that massive wood can be better torrefied (Olarescu *et al.* 2014).

CONCLUSIONS

1. This analysis aimed to clarify some issues concerning the characteristics of torrefied and classic pellets, with special emphasis on the calorific value. An increase of up to 22% in the calorific value for the oak pellets was observed.
2. The torrefaction degree was mathematically determined. Torrefaction degrees of 97.6% for hemicellulose degradation and 34.15% for holocellulose degradation were obtained, when the torrefaction process of the pellets occurred in a weakly-oxygenated environment.
3. By modeling the phenomenon of torrefaction, it was determined that thermal treatment of wooden pellets in a weakly-oxygenated environment at temperatures below 220 °C for 3 h resulted in the degradation of hemicellulose only.
4. This paper highlighted one of the negative influences of the torrefaction process caused by hemicellulose degradation, which was the reduction in the shear strength. The shear strength was decreased by 34% to 48% for the treatment that took place at 220 °C and 3 h. An adequate method for shear strength determination was also specified.

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