Effect of Pyrolysis Temperature and Wood Species on the Properties of Biochar Pellets

Safa Arous [1], Ahmed Koubaa [1,*], Hassine Bouafif [2], Besma Bouslimi [1], Flavia Lega Braghiroli [2] and Chedly Bradai [3]

[1] Institut de Recherche sur les Forêts, Université du Québec en Abitibi-Témiscamingue, 445 Boul. University, Rouyn-Noranda, QC J9X 5E4, Canada; safa.arous@uqat.ca (S.A.); besma.bouslimi2@uqat.ca (B.B.)

[2] Centre Technologique des Résidus Industriels (CTRI), Rouyn-Noranda, QC J9X 5E5, Canada; hassine.bouafif@cegepat.qc.ca (H.B.); Flavia.braghiroli@cegepat.qc.ca (F.L.B.)

[3] National Engineering School of Sfax (ENIS), University of Sfax, Sfax 3038, Tunisia; chedly.bradai.enis@gmail.com

* Correspondence: ahmed.koubaa@uqat.ca; Tel.: +1-819-762-0971 (ext. 2579)

Abstract: Thermal treatments such as torrefaction and fast pyrolysis are commonly employed methods to produce biofuels with high-energetic properties. In this study, wood chips were heat-treated at different temperatures of torrefaction (315 °C) and fast pyrolysis (400 and 454 °C) to form energetic pellets. Three softwoods, jack pine (JP), balsam fir (BF), and black spruce (BS), were evaluated. Pellets are produced using 20% moisture content and 15% pyrolytic lignin as a binder. Untreated- and treated-wood residues were characterized by surface chemistry, elemental analysis, and chemical composition, whereas all pellets were characterized in terms of density, high heat value (HHV), and durability. Results showed that both thermal treatments caused significant changes in the physicochemical structure of wood residues. Using temperatures higher than 315 °C leads to the disappearance of hydroxyl groups, a decrease in oxygen and hydrogen contents, and an increase in carbon content. Regardless of the treatment temperature, pellets made from heat-treated JP had the best durability (93%). In contrast, the calorific values of wood-treated pellets reached up to 31 MJ/kg, compared to untreated-wood pellets (19 MJ/kg). Thus, the densification of the thermal-treated wood residues represents a potential approach for producing biofuels with high energetic value.

Keywords: thermal treatment; fast pyrolysis; torrefaction; wood residues; pyrolytic lignin; pellets; durability; calorific value

1. Introduction

Wood chips generated by sawmills represent the principal raw materials for the pulp and paper industry in Québec. However, the decrease in demand for newsprint and other paper grades led to a surplus of wood chips. The chip consumption by the pulp industry decreased from 6293 to 4825 anhydrous metric tons during 2007 and 2017, respectively [1]. Exploring new markets for sawmill residues becomes a necessity for optimum resource use and sawmill profitability. Wood chips are suitable for various products such as particle-board, oriented strand board, wood pellets, wood composites, and wood-based bioenergy. Since biomass is one of the world's largest energy resources, bioenergy produced by wood residues could be a viable alternative to replace fossil fuels such as coal. In addition, it can reduce the world's dependence on natural gas and petroleum products and consequently reduce greenhouse gas emissions and environmental pollution [2].

On the other hand, wood residues have a heterogeneous structure, relatively low calorific values, high moisture contents, are hydrophilic, and are difficult to store [3]. However, several conversion techniques or physical, thermal, chemical, and biological methods improve these properties to satisfy various applications' requirements [4,5]. Thermal treatments are among the biomass conversion processes using heat at temperatures above

200 °C with low or without oxygen [6]. For example, torrefaction is a thermal treatment process between 225 and 320 °C [4,7], whereas pyrolysis is operated within the 300–800 °C range [6]. Solid, liquid, and gas result from such thermal treatments at different proportions. The solid phase, torrefied wood or biochar, has interesting properties, i.e., the material becomes more carbonaceous [3,5] with low moisture content and a higher combustion efficiency [7,8]. For example, the O/C ratio in thermal-treated wood is significantly reduced, enhancing the heating value [7,8]. The mass yield of torrefied wood or biochar is mainly related to the principal parameters of thermal treatments: furnace design, temperature, residence time, heating rate, and the nature of feedstock [9].

In recent years, wood pellets have attracted more interest for energy applications [10]. Europe pellets are ranked among the most important markets globally, accounting for around 50% of worldwide production [10]. Several studies evaluated the efficiency of densification parameters by improving pellets' properties [11–16]. Pelletization is a process that compresses biomass into uniformly sized solid fuel through the application of mechanical force under certain pressure and temperature [16,17]. Combining wood thermal treatments with pelletization could improve fuel properties and provide a better alternative for using extra residual wood residues [15]. Compared to untreated-wood pellets, torrefied or biochar pellets have higher density, lower moisture contents, and higher calorific values [18]. Therefore, these properties can enhance their quality, reduce costs, and better deal with the problems related to biomass transport and storage [17].

Abedi and Dalai [18] pointed out that the quality of treated pellets was improved using binding agents such as lignin and amino acids. Accordingly, binders are needed to assist particles bonded together and improved pellets properties, especially hardness and durability [11,18]. The mixture of small quantities of lignin-rich solid additives during pelletization of torrefied biomass enhanced the densification process and pellet's properties [15]. Kong et al. [19] investigated a method for the conversion of Spruce wood sawdust into biochar pellets by adding different binders (lignin, $Ca(OH)_2$, NaOH, CaO). Results showed that additives reduced disruptive force and improved hardening bonds to ensure safe transportation and storage.

Recent studies investigated the environmental performance of wood pellets through life cycle assessment studies (LCA) [20–22]. Wood pellets from fast growth and short-rotation wood species gave the best environmental performance [20]. Wood torrefaction provides pellets with the best environmental performance compared to nontorrefied wood and other torrefied biomass [21]. The reduction in fossil fuel consumption and greenhouse gas emissions explain the better environmental performance of torrefied wood pellets [21,22] compared to conventional wood pellets. However, the environmental performance of torrefied pellets is strongly dependent on other factors, including the source and type of biomass, the drying requirement, energy requirement for processing, and the outcome of torrefaction gas and pyrolytic oil [21,22].

The main objective of this study was to evaluate the properties of the pellets made from heat-treated wood chips. The specific objectives were to investigate the impact of pyrolysis temperature and wood species on pellets' properties.

2. Materials and Methods

2.1. Sample Preparation

2.1.1. Preparation of Treated Wood Fibers

Wood chips from three softwood species (jack pine (JP), balsam fir (BF), and black spruce (BS)) were collected from the Matériaux Blanchet Inc. sawmill, located in Amos in the Abitibi-Témiscamingue region (QC, Canada). These are the most important species for the forest products industry in eastern Canada and generate important volumes of wood chips. Reported densities for black spruce, jack pine, and balsam fir were 440, 400, and 350 kg/m³, respectively [23]. Wood chips were first ground and sieved at particle size lower than 5 mm. The thermal treatment of dried wood residues was carried out through the CarbonFX unit (Airex-Énergie, Bécancour, Quebec, Canada) at different temperatures

(315, 400, and 454 °C). The selection of these process temperatures insured variability in the chemical composition of the residual biochar. Depending on the moisture content of the wood shavings (between 30% and 60%), several passages in the circuit (conveyor–dust and collector–dryer) were necessary to condition the humidity at 25–35%. They pass from the dryer to the conditioning to the thermal treatment unit based on gravity through an aspiration process. Lighter chips are aspired first, while heavier chips continue to circulate in the dryer until their weight is lowered to be aspired. Thus, only lighter particles pass through to the conditioning chamber and then to a cyclonic bed reactor for heating in an oxygen-poor environment within a few seconds.

2.1.2. Preparation of Pyrolytic Lignin

The pyrolytic lignin (PL) was extracted from pyrolysis oil, produced by Abri-Tech, © Inc. (Namur, QC, Canada). The pyrolysis oil was generated following fast pyrolysis of the linden wood from America (*Tilia Americana* L.) at 450 °C. For the PL extraction process, a 1:3 mass ratio of pyrolysis oil and distilled water was prepared. After eight hours of decanting, the mixture was divided into two phases [24,25]. Subsequently, the aqueous phase containing the water-soluble organic components was removed to recover nonsoluble water components called "pyrolytic lignin." Then, the moisture content of the pyrolytic lignin was determined to take it into account during the pelletization process.

2.2. Characterization of Raw Material

Particle size distribution of wood residues (untreated and treated fibers) was performed with the Ro-Tap RX29, W.S Tyler type sieve shaker (Mentor, Ohio, USA). For the rest of the analyses, wood particles were dried in an oven at 50 °C for 24 h. After the drying procedure, the samples were sieved to the maximum particle size of 40 mesh ($\leq$0.42 mm) according to the TAPPI T264 (1989) standard method [26]. Then, they were placed in plastic bags and stored in a desiccator at room temperature before analyses. The elemental composition of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) were analyzed using a PerkinElmer elemental analysis system, 2400 Series II, CHNS/O (Waltham, Massachusetts, USA). The difference in the total contents estimated the oxygen content in the sample.

According to Sheng and Azevedo [27], a correlation based on the composition of the main elements (C, H, and O in% by weight) was adopted to estimate the high heat value (HHV) of all materials, with an error range of $\pm$5%, according to Equation (1):

$$\text{HHV (MJ/kg)} = -1.675 + 0.3137 \times C + 0.7009 \times H + 0.0318 \times O \tag{1}$$

The hemicellulose, cellulose, lignin, and extractives contents of untreated- and treated-wood residues were determined according to TAPPI T264 [26] and T249 cm-85 [28] standard methods. The five main sugars present in wood: glucose, xylose, mannose, arabinose, and galactose contents, which defined the chemical composition of cellulose and hemicellulose, were determined through high-performance liquid chromatography (Shimadzu HPLC 10 AVP instrument, Canby, Oregon, USA) [29]. Following the T22 OM-88 method [30], Klason lignin content was measured after hydrolysis with sulfuric acid using an autoclave, model 50X-110V-1500W-24L (Manitowoc, Wisconsin, USA). Extractives content was determined using ethanol and hot water, according to the T204 OM-88 method [31]. FTIR analysis of treated and untreated samples was carried through a Shimazhu FTIR device fitted with an ATR total attenuated reflection assembly (Kyoto, Japon) between 4000 and 500 cm^{-1}.

2.3. Pelletization Process

The granulation was carried out using a KAHL granulator (Amandus Kahl, Reinbek, Germany). Preliminary experiments allowed the determination of optimum pelletizing parameters, namely die geometry, moisture content, binder type, and content. Four die geometries (ratio: 1/3, 1/4, 1/5, and 1/6), three moisture contents (15%, 20%, and 25%, wet basis), three binders (starch, lignosulphonate, and pyrolytic lignin), and contents (5%, 10%, and 15%).

Regardless of the binder used, 15% moisture content was insufficient to prepare the pellets due to fines generation at the exit of the granulator. Indeed, the activation of the hydrogen bonding mechanism is incomplete when the particles are not close enough [32]. Thus, the contact between the sites available for hydrogen bonds remained necessary to ensure pellets' good resistance [33]. On the other hand, a humidity of 25% produced very humid granules. Excess water absorbed by the hydrogen bonding sites can attack the particle-particle binding sites leading to a decrease in the durability of the pellet [33]. At 20% humidity, produced pellets had a coherent structure using two geometries of channels at ratios 1:4 and 1:5. Concerning the binder, starch and lignosulphonate could not link torrefied fibers, making pellets easy to crash by hand. Only 15% of pyrolytic lignin produced pellets with good durability. Thus, pyrolytic lignin, a nonvalued product of pyrolysis, is recommended as a low-cost and effective binder to use. Thus, the conditions chosen for producing pellets from thermally treated wood were: moisture of 20%, 15% pyrolytic lignin as a binder, and die geometry at a ratio of 1:5 to ensure good material compaction. Figure 1 shows untreated- and treated-wood pellets from JP, BF, and BS.
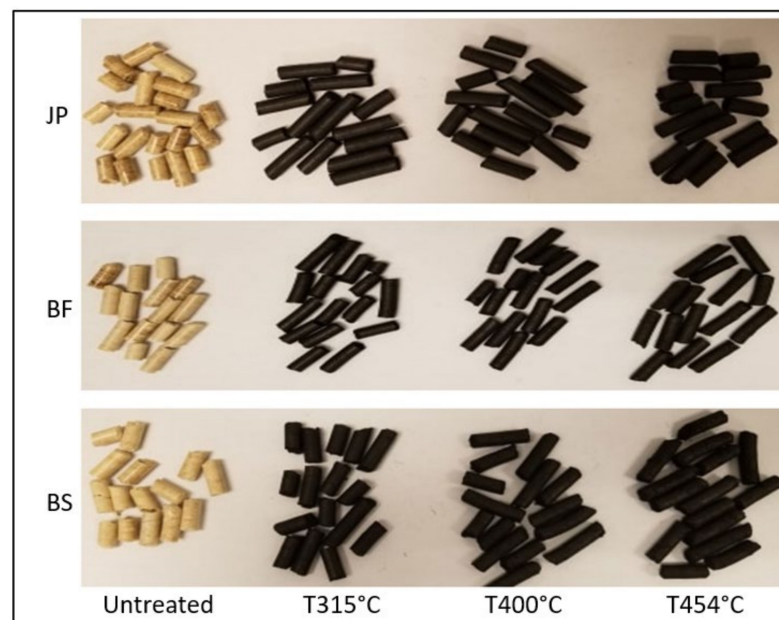

Figure 1. Images of untreated- and treated-wood pellets prepared in the present study.

2.4. Characterization of Wood Pellets

A thermogravimetric analyzer (TGA) (TA instrument, model Q50, Newcastle, Texas, USA) analyzed the pellets' combustion characteristics in the presence of nitrogen (N2). During the test, a drying step was carried out at 100 °C for 5 min followed by 600 °C for 10 min at a heating rate of 20 °C/min. The mass variation was determined as a function of the evolution of temperature and time. A helium pycnometer (AccuPyc 1330, Micromeritics Instrument Corporation, Norcross, GA, USA) determined the pellets' density. An automatic isoperibol calorimeter 6400 (Parr Instrument Company, Moline, IL, USA) determined pellets' higher heating value (HHV, MJ/kg). The moisture and ash contents were measured using a COMPUTRAC MAX 5000 instrument (AMTEK BROOKFIELD, Chandler, AZ, USA).

The durability of pellets was carried out according to the ISO17831 standard, using a pellet durability tester [34]. The durability value describes the intact proportion of pellets after the removal fines by computing the weight difference before and after sieving. In total, 500 g of each pellet type was sieved (3.15 mm screen), placed into a box, and maintained at 50 rpm speed to ensure the rotation of the boxes for 10 min. Each analysis was repeated twice.

2.5. Data Analysis

Statistical analyses were conducted using Statistical Analysis System (SAS) software (SAS Institute Inc: Cary, NC, USA, 2008) [35]. The statistical significance of the fixed effects was determined using the F test at a *p*-value of 0.05. Analysis of variance (ANOVA) was carried out to assess the effects of species (JP, BF, and BS) and the heat treatment temperatures (315, 400, and 454 °C) on the properties of pellets (density, heating value, and durability). Equation (2) describes the general model of the analysis of variance.

$$Y_{ij} = \mu + A_i + B_j + A_i \times B_j + \varepsilon_{ij} \tag{2}$$

where Y_i is the dependent variable (density, high heat value, and durability); μ is the general average effect (intercept); A_i is the wood effect; B_j is the treatment temperature effect; $A_i \times B_j$ is the interaction between the wood type and the treatment temperature; and ε_{ij} is the error term.

3. Results and Discussion

3.1. Properties of Wood Residues and Pyrolytic Lignin

3.1.1. Particle Size Distribution

Figure 2 shows the measured particle size distributions of untreated- and treated-wood residues at 315, 400, and 454 °C of JP, BF, and BS. The particle size of the three softwood species samples was very close to each other. As the thermal treatment temperature increased, the particle size of the three types of wood became smaller. This result was also reported in the open literature [36,37]. At the temperature of 315 °C, the average diameter of JP and BS particles was around 0.65 mm, while the average diameter of BF was about 0.84 mm. On a microscopic scale, particle size reduction is explained by the damage of the material's cell walls [37]. Variation in the cell wall structure of the studied species explains the difference in their particle size. In addition, the particle size distribution depends on the treatment temperature. For example, the mass percentage of BF particles at a particle size lower than 0.5 mm was about 5% for untreated particles and about 20% and 45% for treated particles at 300 and 454 °C, respectively.
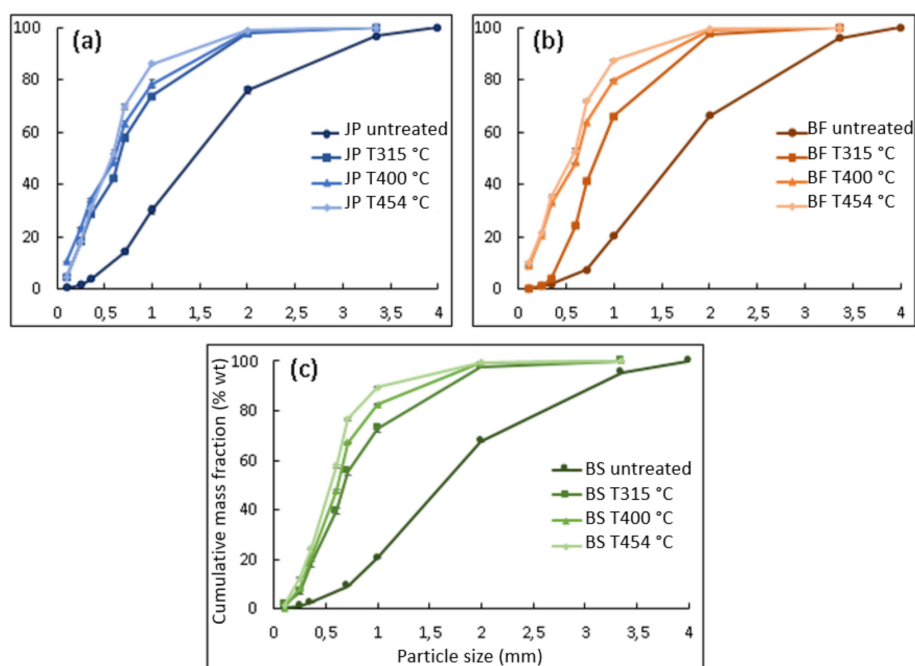

Figure 2. Cumulative particle size distribution for the three types of wood before and after the thermal treatment: (**a**) Jack pine (JP), (**b**) Balsam fir (BF), and (**c**) Black spruce (BS).

3.1.2. Elemental Analysis and Chemical Composition and Chemical Properties

Table 1 shows the elemental analysis and the calorific value of the pyrolytic lignin and the untreated- and treated-wood residues. In agreement with previous findings [37–40], the increasing treatment temperature led to an increase in the carbon content and a decrease in the oxygen and hydrogen contents. The heat treatment decomposes the hemicelluloses and selectively eliminates their –OH groups [41,42]. The reduction in hydrogen content after treatment indicates the increased hydrophobicity of treated wood [39,41]. On the other hand, the elemental analysis revealed similar hydrogen content for untreated-wood residues and pyrolytic lignin (PL) (~6.55 vs. 6.11%). However, the analysis showed that the PL has more carbon content and less oxygen content than the untreated-wood particles. Mullen and Boateng [43] explained the low oxygen content in PL due to the deoxygenation of wood lignin during the pyrolysis process. Indeed, the oxygen released is in the form of water or water-soluble organic compounds remaining in the aqueous phase during the isolation of PL. As listed in Table 1, the HHV increased with the treatment temperature and was higher than the untreated-wood residues derived from the three-wood species. For example, for BF raw and treated residues at 315, 400, and 454 °C, the HHV values were 19.3, 23.8, 22.2, and 27.2 MJ/kg, respectively. Similar observations were reported by Wang et al. [40]. The HHV values of torrefied wood chips increased with the temperature and the reaction time. In addition, the HHV value of PL was higher than that of untreated-wood residues (21.9 vs. 19.4 MJ/kg). Thus, this characteristic makes PL a good choice as a binder for the production of bioenergy.

Table 1. Elemental analysis and estimated calorific value calorific value according to Equation (1) of untreated- and treated-wood residues.

Type	JP				BS				BF				PL
T (°C)	Raw	315	400	454	Raw	315	400	454	Raw	315	400	454	450
	Elemental analysis (%)												
C	46.96	65.21	77	80.7	45.85	75.6	80.55	85.92	46.46	70.01	71.19	83.45	57.18
H	6.55	1.27	2.48	3.34	6.42	3.14	3.03	2.81	6.67	3.34	3.32	2.77	6.11
N	0.05	0.2	0.26	0.21	0.05	0.2	0.11	0.1	0.02	0.17	0.16	0.12	1.51
S	1.09	0.35	0.47	0.58	1.16	0.62	0.52	0.47	1.07	0.59	0.69	0.56	0.59
O	45.35	32.97	19.79	15.17	46.52	20.44	15.79	10.70	45.78	25.89	24.64	13.1	33.61
	Calorific value (MJ/kg)												
HHV *	19.4	21.0	25.2	26.8	19.0	25.2	26.5	27.9	19.3	23.8	22.2	27.2	21.9

* estimated from Equation (1) [27].

The chemical composition analysis (Table 2) showed that the cellulose and hemicellulose contents decreased drastically following the heat treatment. Thus, most of the hemicellulose and part of the cellulose degraded during the heat treatment of wood [44].

Table 2. Chemical composition of untreated- and treated-wood residues.

Type		JP				BS	BF	
Type		JP					BF	
T(°C)	Raw	315	400	454	Raw	400	Raw	400
						BS		
Chemical composition (%)								
Cellulose	45.00	17.13	13.82	2.72	44.66	9.55	40.72	9.9
	(0.30)	(0.52)	(0.06)	(0.01)	(3.44)	(0.03)	(6.39)	(0.12)
Hemicellulose	17.88	1.98	0.42	0.02	23.2	0.28	31.99	0.17
	(0.30)	(0.17)	(0.06)	(0.01)	(3.44)	(0.03)	(6.39)	(0.11)
Lignin	34.06	80.55	83.65	96.76	28.83	89.59	24.29	89.11
	(2.24)	(2.91)	(2.69)	(1.25)	(1.77)	(0.80)	(0.86)	(0.09)
Extractives	3.06	1.03	0.61	0.50	3.31	0.57	3.00	0.79
	(0.13)	(0.06)	(0.01)	(0.04)	(0.21)	(0.06)	(0.10)	(0.04)

In addition, the extractable content decreased with the processing temperature compared to the untreated-wood residues. On the other hand, the lignin content of the heat treated-wood residues increased considerably with the temperature. In the case of JP, the lignin content of the treated-wood residues varied from 80.55% to 96.76% with temperature, compared to 34.06% in untreated residues. The relative increase in lignin content following heat treatment may be due to the volatilization of most carbohydrate components and the formation of acid-insoluble breakdown products during the treatment [40,41]. At 400 °C, BS particles showed the highest lignin content (89.59%). This explains the high value of HHV for BS particles treated at 400 °C, reaching up to 26.52 MJ/kg, compared to other species treated at the same temperature. Similar results were also observed in the literature [44,45].

3.1.3. FTIR Characterization

FTIR spectroscopy investigated the chemical changes induced by the thermal treatment (Figures 3–5). The spectra of the three studied species showed several features in common depending on the temperature. However, the thermal treatment caused significant changes in the spectra of treated wood compared to untreated wood. The wideband in the O–H stretching vibration region at about 3600 and 3200 cm^{-1} is caused by intra- and inter-molecular hydrogen bonds [46–48]. An absorption band appearing in the range of 2889 and 2897 cm^{-1} is due to the stretching of C–H, of the aliphatic $-CH_n$ and aromatic $-CH_3$ groups [46,49–51]. The intensity of these bands almost disappeared after the thermal treatment. Water evaporation and the elimination of most of the hydroxyl groups explain this result [15,52–54]. The peaks between 1585 and 1570 cm^{-1} represent carboxylic groups (C=C) characteristic of the aromatic skeleton of lignin [46] and were strongly present in the absorption spectra of the treated material. The hemicellulose vibration can be found at about 1732 cm^{-1} (the stretching C=O of carboxylic acids) [46,55,56]. The peaks of the aliphatic deformation C–H between 1315 and 1369 cm^{-1} may be derived from hemicellulose or cellulose [57], and the C–O stretching peak at about 1034 cm^{-1} is characteristic of C–O–C in hemicellulose and cellulose [46,48,56]. These peaks were present in the untreated wood but disappeared after the thermal treatment. In good agreement with the chemical analysis data (Table 2), these results indicate hemicellulose and cellulose degradation.
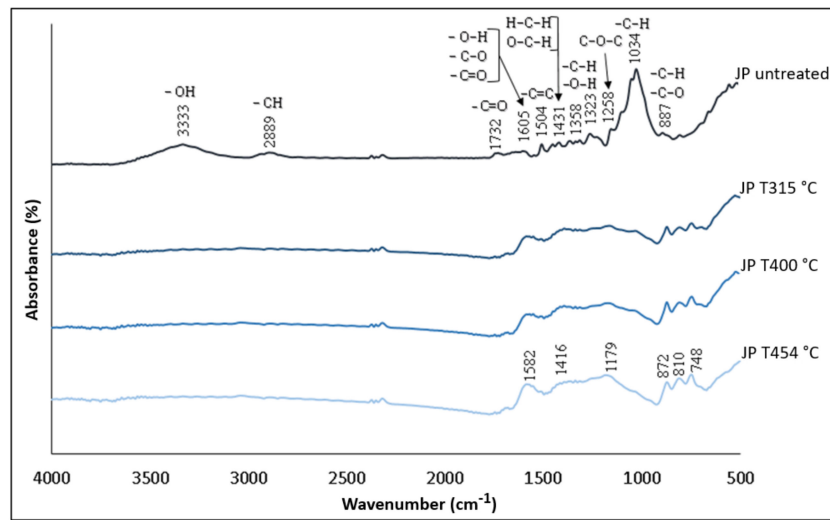
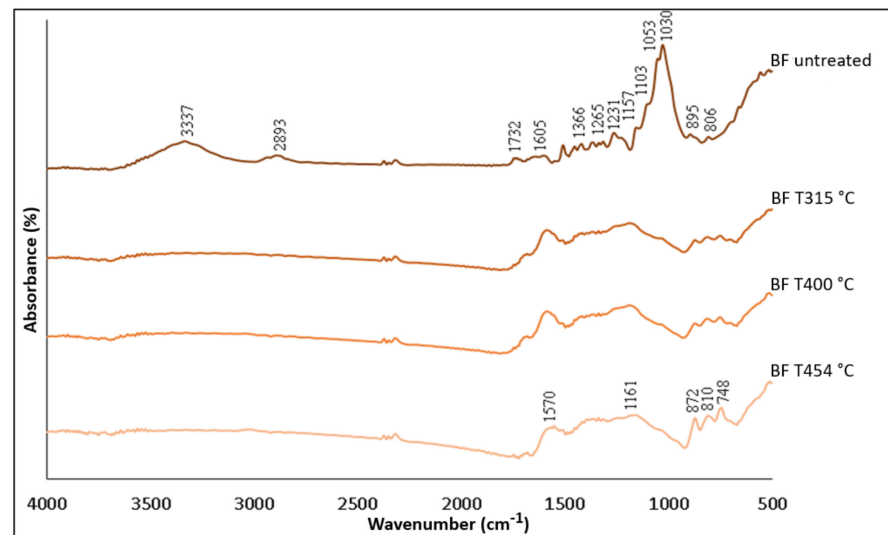**Figure 3.** FTIR spectra of jack pine pellets at different heat temperatures.

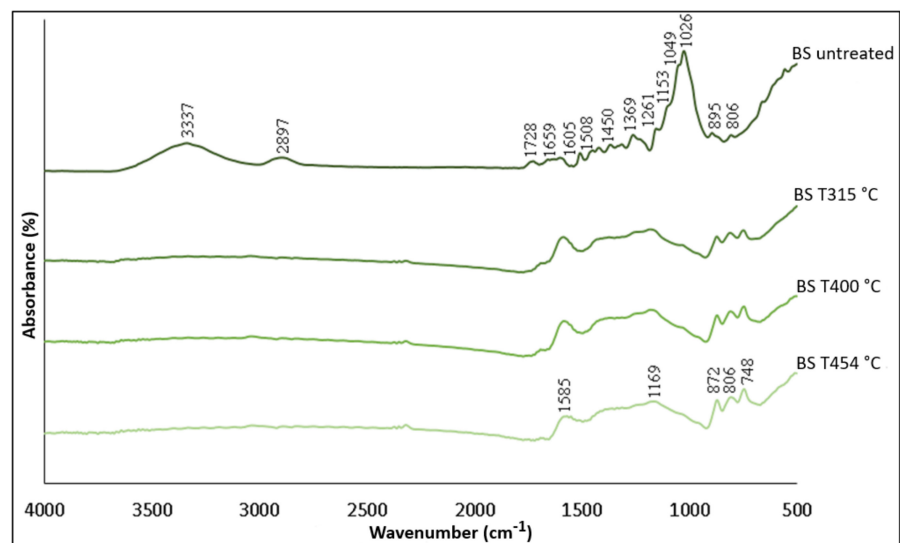**Figure 4.** FTIR spectra of balsam fir pellets at different heat temperatures.

Figure 5. FTIR spectra of black spruce pellets at different heat temperatures.

3.2. Properties of Pellets

3.2.1. Thermal Degradation of Pellets

Figure 6 displays the thermogravimetric analyses of the pellets derived from the three types of wood. TGA curves show three different phases: material dehydration, volatile components release, and combustion [58,59]. At temperatures below 100 °C (i.e., the first phase), the curve of untreated-wood pellets underwent a slight weight loss due to water evaporation. However, the TGA curves of treated-wood pellets showed a delayed onset of weight loss due to the degradation of hemicellulose and cellulose. The thermal degradation of most treated-wood pellets begins at around 380 °C, except for JP treated-wood pellets at 315 °C, where the degradation begins at around 310 °C. This result is surprising and could be explained by the differences in the chemical composition of the studied species. Moreover, the addition of an organic binder (PL) can accelerate the thermal decomposition of pellets. Wang et al. [60] noted that PL has poor thermal stability and decomposes in low temperatures (231–320 °C). The DTG curves show hemicellulose, cellulose, and lignin peaks clearer and higher for JP pellets. This is consistent with the previous results of the wood chemical composition. The thermal degradation of BS-treated pellets illustrates a single prominent peak of DTG (Figure 6d) due to the continuous loss of weight. While the DTG curves illustrated in Figure 6e,f clearly show two degradation peaks: the first peak at around 280 and 300 °C, which corresponds to the release of volatile substances from the PL, and the second peak the remaining degradation weight of the material (at about 420 °C). These results agree with the studies of Hu et al. [61]. They reported that the addition of organic binders in the pellets preparation releases volatile substances during their combustion.
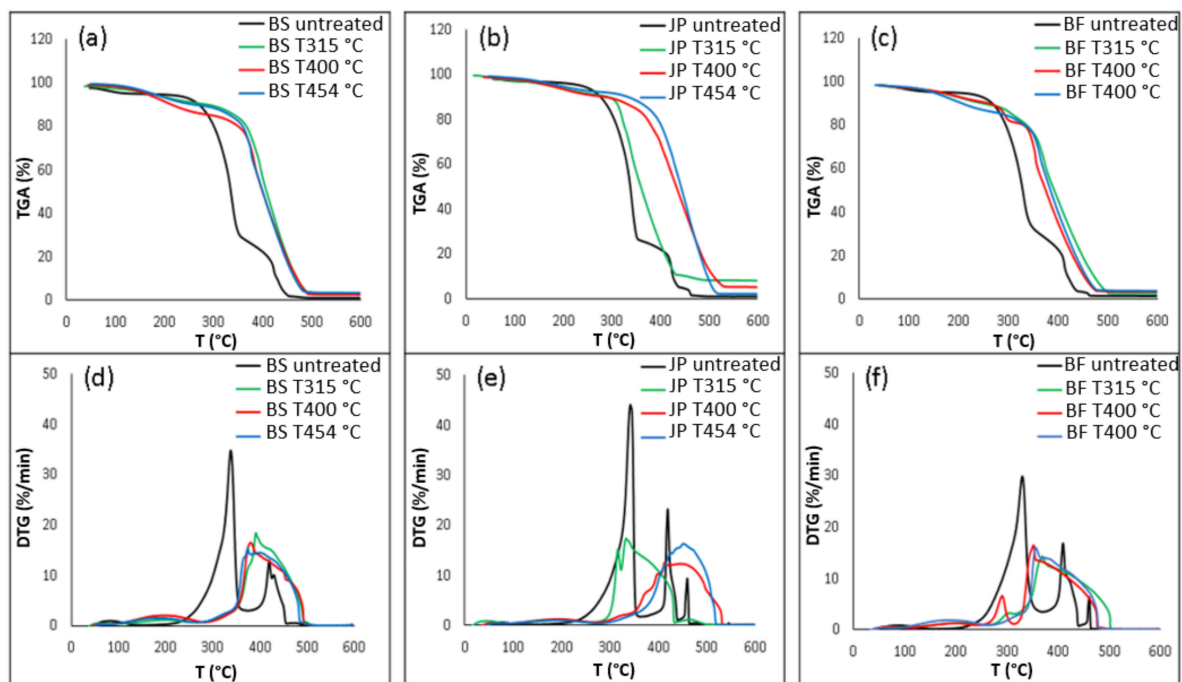

Figure 6. Thermogravimetric analyses curves (TGA and DTG) of pellets derived from the three types of wood: JP (**a**,**d**), BF (**b**,**e**), and BS (**c**,**f**) at different heat temperatures.

3.2.2. Physical and Mechanical Characteristics of Pellets

Table 3 shows the analysis of variance on the effect of wood species and treatment temperature on the properties of the pellets. The type of wood (A), the temperature (B), and the A × B interaction significantly affected the pellets' density, HHV, and durability.

Table 3. Analysis of variance (F-value) of the effects of wood species and treatment temperature on the mechanical and physical properties of wood pellets.

	Density	HHV	Durability
Type of wood (A)	35756.6 **	71.74 **	62.05 **
Temperature (B)	24260.8 **	13952 **	36.75 **
(A) → × (B)	1042.9 **	45.29 **	9.26 **
R^2	0.96	0.99	0.99

** significant at 0.01.

Table 4 presents the results of density, moisture, and ash contents of untreated- and treated-wood pellets. An increase in treatment temperature caused a decrease in pellet density regardless of the species used. The average value of untreated-wood pellet density was about 1392 kg/m^3, while that of treated-wood pellet was around 1353 kg/m^3. For the JP, pellet density decreased from 1438 to 1345 kg/m^3 when the treatment temperature increased from 315 to 400 °C. The decomposition of the wood's hydrophilic groups at high temperatures explains the slight decrease in density. In addition, high temperatures might lead to the irregularity of wood residues [62]. These results are consistent with previous findings [59,63]. According to the statistical analyses, the type of wood and the treatment temperature significantly affected density (Table 3). The JP pellets showed the highest density among the three species studied regardless of the treatment temperature (Table 4). The strong adhesion between the JP treated-wood residues and the pyrolytic lignin explains this result. Hu et al. [61] reported that the highest density was achieved by using the following additives: lignin, starch, NaOH, and Ca(OH)$_2$ during the pelletization. In addition, Hu and al. [62] found that the pellet density increases linearly with the addition of water, and it reaches its limits between 35% and 40%. The moisture content of untreated-wood pellets is between 6.9% and 7.7%, while that of treated-wood pellets decreases slightly with the processing temperature (from 4.0% to 5.5%) (Table 4). The ash content varies depending on the species and the treatment temperature (Table 4). For treated-wood pellets, the ash content decreases with the increasing temperature from 315 to 454 °C. Hu et al. [61] showed that the addition of an organic binder reduces the ash content of wood pellets.

Table 4. Physical properties of pellets.

Pellets	Humidity (%)	Ash (%)	Density (kg/m^3)
Untreated JP	7.7	0.12	1390.57 (0.04)
JP T315 °C	4.80	7.31	1438.37 (0.04)
JP T400 °C	4.30	4.29	1392.50 (0.07)
JP T454 °C	4.50	1.46	1344.63 (0.42)
Untreated BF	7.08	0.52	1395.00 (0.07)
BF T315 °C	5.49	1.72	1343.10 (0.07)
BF T400 °C	5.16	2.56	1334.10 (0.13)
BF T454 °C	5.43	2.32	1337.40 (0.93)
Untreated BS	6.85	0.38	1390.07 (0.04)
BS T315 °C	5.28	2.69	1334.90 (0.07)
BS T400 °C	5.29	2.20	1316.60 (0.33)
BS T454 °C	4.02	1.98	1331.10 (0.47)

Figure 7 illustrates the variation of the calorific values as a function of wood species and pyrolysis temperature. The HHV ranged from 18.48–19.31 to 28.84–31.05 MJ/kg for treated- and untreated-wood pellets, respectively. Pellets prepared at higher temperatures presented the highest calorific values. Indeed, the HHV of treated-BS pellets increased significantly (31.05 MJ/kg) compared to that of untreated BS (18.5 MJ/kg), and it also increased as a function of the temperature (from 29.77 to 31.05 MJ/kg corresponding to 315 and 454 °C, respectively). JP and BF pellets showed the same trend. The highest temperature (454 °C) led to the highest calorific values for JP (30.24 MJ/kg), BF (30.24 MJ/kg), and BS (31.05 MJ/kg) pellets. The increase in carbon content with increasing temperature

compared to hydrogen content explains this trend (Table 1). Azargohar et al. [64] attributed this carbon increase to the reduction in humidity and degradation of hemicellulose during the thermal treatment. The analysis of variance showed that the effects of the type of wood and the temperature are statistically significant (Table 3). However, the temperature has a more pronounced effect on the properties of pellets (Figure 7). These results were consistent with recent studies that reported that increasing the temperature improves the calorific value [42,60,63]. In addition, the HHV of pyrolytic lignin (21.92 M/kg) is relatively higher than that of untreated-wood pellets (18–19 MJ/kg) (Table 1). Thus, using 15% of PL as a binder during the densification of treated-wood residues significantly improves the HHV of pellets. Stevens and Gardner [11] concluded that adding lignin during the densification process significantly increases the fuel value of pellets [11]. Likewise, Cheng et al. [65] found that the calorific value of wheat straw pellets underwent a relative increase of up to 6% with the addition of 35% of coal tar residue.
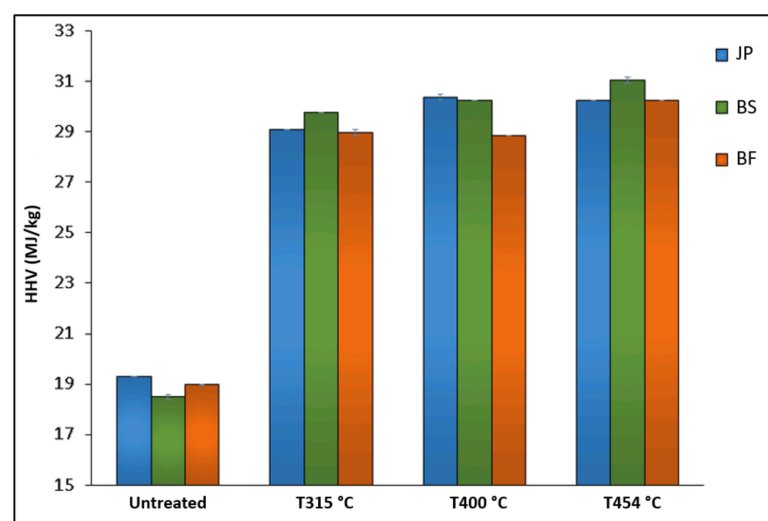

Figure 7. Higher heating value of pellets derived from untreated- and treated-wood pellets derived from the three species: JP, BS, and BF.

Figure 8 presents the results of pellets durability derived from the three untreated- and treated-wood species. The pellet durability is significantly affected by the type of wood and the treatment temperature (Table 3). The mechanical strength of the pellet decreased with the increase in temperature. For example, the durability of untreated BF pellets was around 92%, while that of treated pellets at 315, 400, and 454 °C was 85%, 83%, and 84%, respectively. The degradation of the hemicellulose and the removal of extractives and volatile compounds during the thermal treatment explain this result [48]. These results are in agreement with several other studies [59,63,66]. Indeed, the increase in the temperature considerably reduces the mechanical resistance of pellets, leading to high susceptibility to breakage and the generation of fines during handling, transportation, and storage [59,63]. Although there was a downward trend in the durability of treated-BS and -BF pellets, treated-JP pellets retained excellent durability with a minimum value of 91% at 315 °C. Crosslinking and polycondensation of lignin formed by the thermal degradation can lead to pellets with good mechanical resistance [63]. Thus, the transition of lignin into solid bridges at the pellet's surface and the presence of a minimum amount of water can considerably improve the durability of pellets [62]. As lignin has a high resistance to thermal degradation [63], the increase in temperature favors a higher lignin content, according to the results obtained for the chemical composition of wood residues (Table 2). Therefore, lignin contributes to the self-adhesion of wood residues during the densification process [37] and may explain the excellent durability of JP at T454 °C (93%). In addition, the softening of pyrolytic lignin improves the adhesion of treated-wood residues despite the severe conditions of the thermal treatment. Similar studies show the importance of using

binders to enhance the mechanical strength of pellets. The use of 40% coal tar residues as a binder increases the durability index of sawdust pellets from 69 to 98% [62]. Furthermore, the durability of treated-wood pellets was significantly improved as a function of residence time. The durability of treated pine pellets at 290 °C increased from approximately 89% to 96% after one year of storage [67]. Nevertheless, under the quality criteria of the EN ISO 17225-8 Standard "Fuels based on biomass heat-treated and densified", the durability index of pellets must be greater than 95% [68]. Despite incorporating 15% of pyrolytic lignin in the densification process, all treated pellets produced in this study do not meet this criterion. Therefore, optimizing the pyrolytic lignin content should help lead to better surface wetting during the granulation process. Alternatively, the pellets produced in this study could generate electricity inside or near the manufacturing facility [68].
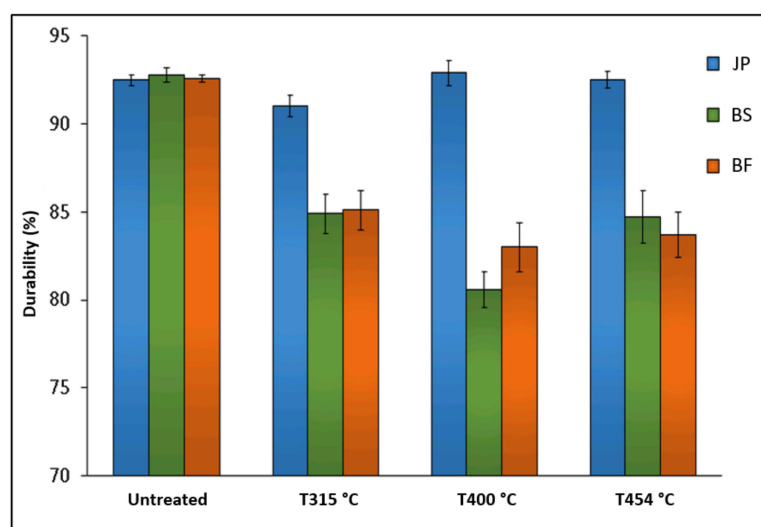

Figure 8. Durability values of untreated- and treated-wood pellets derived from the three species: JP, BS, and BF.

4. Conclusions

The thermal treatment is a promising method for improving the fuel properties of pellets. It significantly affects the chemical properties of wood residues. The increase in the treatment temperature generates friability and reduces the energy required for grinding. Thus, the chemical structure of treated-wood residues is considerably modified. As a result, the thermal treatment causes the degradation of hemicellulose and cellulose. In addition, the use of pyrolytic lignin (15%) ensured a good adhesion during the preparation of treated-wood pellets. Consequently, pyrolytic lignin can constitute an excellent binder and is inexpensive because of its positive impact on the mechanical properties of pellets, such as the durability (e.g., treated-JP pellet at 93%). In addition, the heat treatment significantly improved the calorific value of the pellet. The higher calorific value increased from 18−19 MJ/kg (for untreated-wood pellets) to 27−31 MJ/kg (for treated-wood pellets). Finally, the densification of the treated-wood residues represents a possible way to produce biofuel with a high energy value. This approach also encourages an economical and sustainable supply chain. However, additional research is needed to improve the quality of treated-wood pellets for better handling and storage and to meet current and future legislative requirements.

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