Article

The Influence of Freezing Temperature Storage on the Mechanical Durability of Commercial Pellets from Biomass

Arkadiusz Dyjakon * and **Tomasz Noszczyk**

Institute of Agricultural Engineering, Wroclaw University of Environmental and Life Sciences,
51-630 Wroclaw, Poland
* Correspondence: arkadiusz.dyjakon@upwr.edu.pl; Tel.: +48-71-320-5945

check for updates

Abstract: The interest in pellets utilization for households heating has been growing significantly in the last several years. However, the pellets need to meet certain quality requirements, including the mechanical durability (D_U) index. In the winter seasons, the pellets are very often stored in unheated in-door systems or are transported by trucks over long distances. As a result, the pellets are exposed to external weather factors, including very low temperatures (even freezing ones), which can have a negative impact on the quality parameters of the fuel. There are several parameters affecting mechanical durability, but little is known about the influence of a very low temperature on the pellet properties. The aim of this research was to analyze the influence of freezing temperature storage on the mechanical durability of commercial pellets made of different biomass. The research was carried out in accordance with the international standard for solid biofuels PN-EN ISO 17831-1:2016-02. The samples were investigated under three different conditions: after normal storage conditions (20 °C), after frozen storage conditions (−28 °C) and after the defrosting of the pellets. The results revealed that the freezing process and subsequent defrosting of the pellets only causes a small drop in their mechanical durability in comparison to the normal storage conditions. The highest mechanical durability was established for digestate pellet and pine sawdust pellet, at 99.0 ± 0.1% and 98.7 ± 0.1% respectively ($p < 0.05$). The greatest change of mechanical durability was observed after the defrosting process of pellets, which in the initial stage and at the normal storage temperature were characterized by low mechanical durability. The pellets made of sunflower husk ($D_U = 87.4\%$) and coal/straw blend ($D_U = 96.2\%$) were distinguished by the highest change in their mechanical durability ($\Delta D_U = 1.7\%$, $p < 0.05$). Based on the obtained results, it was concluded that the storage of pellets at freezing temperature does not significantly affect their mechanical durability. However, if the mechanical durability decreases, this result is related to pellets with low initial mechanical durability.

Keywords: freezing temperature; storage; pellet; biomass; mechanical durability

1. Introduction

Households in European countries are responsible for 25.4% of primary energy usage. Moreover, ca. 64.7% of this value is assigned to household heating [1]. In terms of the environment protection and CO_2 emission reduction, renewable energy sources (RES) play an important role in meeting this trend as part of the strategy proposed by the European Union (EU) [2,3]. Amongst RES, the energy produced from biomass amounts is approximately 50% (ca. 450 Mtoe) [2]. In Europe, biomass has the highest potential of all energy sources and its use for energy purposes is foreseen to continue to increase in the future [3,4]. The new European Commission (EC) Directives [5] relating to the increase of domestic boiler efficiency and reduction of pollutants emission mean that the best form of solid biomass to

be burnt by households is pellets. The biomass pellets are made of various substrates, including forestry and agricultural residues [6,7] and the pellets market has developed significantly in the last few years. The pelletization of biomass significantly increases mass and energy concentration in the organic material, as well as stabilizing its physical and chemical properties [8]. Moreover, the biomass agglomeration enables its economic transportation for longer distances due to higher density of pellets compared to loose biomass [9,10]. However, during the transportation operation (loading, transport, unloading) the pellets might be damaged by friction, impact, compression, and vibration, leading to a reduction in their quality and thus, the financial losses. Therefore, the pellets should be characterized by high mechanical durability.

The mechanical durability of the pellets is understood as their resistance to abrasion and delamination, defined as the percentage loss of the total fuel mass during the mutual attrition of the granulate and its ability to remain intact [11,12]. The pellets made of various raw materials are characterized by a different value of the mechanical durability index [13]. Moreover, there are many other factors influencing the mechanical durability of pellets, like physical and chemical properties of biomass, parameters of the pelletization process, as well as storage conditions.

One of the relevant parameters is the lignin content, which is a natural particle binding component. The lignin content varies across the natural materials. For example, wood contains about 25% of lignin in contrast to grass (less than 20%) [14,15]. The durability tests revealed that wood pellet is characterized by a higher brevity of material particles and higher mechanical durability [16,17].

In other studies [10,18], the influence of moisture content in the pellets on their durability was investigated. The results showed that higher moisture content can decrease the mechanical durability of pellets. Furthermore, after exceeding a certain limit value of the moisture content, the mechanical durability decreases emphatically [19]. Moreover, at higher moisture content in the biomass, the dry matter loss [20], microbial and chemical degradation of the fuel are affected [21], as well as to the self-ignition risk [22]. However, in terms of mechanical durability, the optimal moisture content in the raw material depends on the type of biomass [19]. According to some tests, this value ranges between 6–13% for pine pellet [23–25], 8–15% for wheat straw [26–28] or 9–17% for tulip wood pellet [29]. On the other hand, if the pellets are too dry, the mechanical durability decreases as well. To improve their mechanical durability, natural additives are in use [7].

The particle size of compacted biomass is also important for the mechanical durability. For instance, for wood and miscanthus pellets, the optimal screen size for durability is 3–6 mm [30], for wheat, barley, straw, and oat the optimal screen size is 0.8 mm [31] and for it hay is 4 mm [32]. Additionally, the tests showed that the length/diameter ratios of the produced pellets have influence on its durability as well. Higher length/diameter ratios of pellets increase mechanical durability through growth pressure in the pelleting matrix [25,33].

The biomass compacting parameters, like pressure and conditioning temperature also influence the mechanical durability. Higher pelletization pressure between 115 and 300 MPa increases the durability of pine and beech sawdust pellet [23]. The pellets produced under low pressure at about 1.5 MPa are characterized by lower mechanical durability [29,34]. In turn, the increase of conditioning temperature of pellet results in a more durable pellet [7,12]. In the conditioning temperature range of between 45 °C and 95 °C, the mechanical durability index of the pea pellet increased by 2.5% [19]. At the temperatures above 50–70 °C, an increase of lignin activity was observed that improved the pellets durability [25,35,36].

Finally, the method and storage conditions of the pellets affect the mechanical durability. Long-term storage of pellets (over 20 months in this test) caused the durability to decrease by 30% [18]. The influence of the positive temperatures storage on pellets durability was investigated by Rynkiewicz et al. [16], however, the results did not indicate significant changes. Storage at temperatures of 20 °C, 40 °C and 60 °C caused variation of the mechanical durability index in the range of 0.1%; 0.2% and 0.4%, respectively.

However, there is no data in the literature related to the influence of the freezing temperature storage and defrosting process of biomass pellets on their mechanical durability. These conditions are very common in the winter season, when the pellets are stored in the warehouse without heating

systems (preventing freezing) or transported by trucks over long distances. Therefore, the investigation of the influence of this parameter on the mechanical durability of commercial pellets was the main aim of this study.

2. Materials and Methods

2.1. Materials Used in the Experiments

The aim of the work was to assess the effect of freezing temperature storage on the mechanical durability of pellets, depending on the type of substrate used for agglomerate production.

The subject of the research was pellets made of different biomass materials: wooden biomass (wood pellets) and agricultural residues (agropellets). In detail, eight types of pellets were investigated (Figure 1): chips and sawdust pine wood (a), wheat straw with the addition of rancid straw and hay (b), digestate biomass (c), corn settlements (d), agricultural residues (e), post-hydrolytic wood (lignocellulosic) (f), sunflower husk (g) and 45% of fine coal blend with 55% straw (high calorific pellet) (h).

Figure 1. Commercial pellets investigated in the study: (**a**) chips and sawdust pine wood, (**b**) wheat straw with the addition of rancid straw and hay, (**c**) digestate biomass, (**d**) corn settlements, (**e**) agricultural residues, (**f**) post-hydrolytic wood, (**g**) sunflower husk, (**h**) a blend of fine coal (45%) and straw (55%).

As the commercial pellets were selected in the tests, it was assumed in the manuscript that during pellets production, the optimized value of the moisture content in the given biomass material was kept. According to the commercial pellets production, this is a standard procedure and approach.

2.2. Technical and Chemical Analysis

In order to characterize the commercial pellets, ultimate and proximate analysis were performed. The sampling procedure for technical and chemical analysis consisted of the grinding a randomly collected portion of pellets (500 g) from 15 kg bags of commercial pellets to the fraction below 1 mm. From the obtained pulverized material, the required samples (in accordance with applied ISO Standards) for further analyzes were used, accordingly. The proximate analysis included parameters such as: moisture content (MC), higher heating value (HHV), lower heating value (LHV), ash content (AC), and volatile matter content (VM). Moreover, the relative density, porosity and bulk density were determined as well. All parameters were determined in five repetitions. Relating to the ultimate analysis, the carbon, hydrogen and nitrogen content were investigated.

The moisture content was determined according to PN-EN ISO 18134-2:2017-03E [37] using a laboratory moisture analyzer SARTORIUS MA150 (Sartorius, Goettingen, Germany) (Figure 2a). The higher heating value (HHV) was determined in a calorimetric bomb IKA C200 (IKA, Lucknow, India)

(Figure 2b) in accordance with PN-EN ISO 18125:2017-07 [38]. The lower heating value was determined using the following formula [39]:

$$LHV = HHV - r(MC^a + 8.94 \cdot H^a) \tag{1}$$

where: LHV—lower heating value (kJ·kg^{-1}); HHV—higher heating value (kJ·kg^{-1}), r—heat of water evaporation (r = 24.42 kJ·kg^{-1} for 1% moisture content in fuel) (kJ·kg^{-1}), MC^a—moisture content in the fuel in analytical state (%), H^a—the hydrogen content in the fuel in analytical state (%).

Ash content in pellets was determined according to PN ISO 1171:2010 [40] using the muffle furnace SNOL 8.2/1100 (SNOL, Utena, Lithuania). The following formula was used:

$$AC = \frac{m_A - m_C}{m_M - m_C} \cdot 100\% \tag{2}$$

where AC—ash content in pellet fuel in analytical state (%), m_A—mass of the crucible with ash after heating (g), m_C—mass of the empty crucible (g), m_M—mass of the crucible with material before heating (g).

The volatile matter content (VM) in the pellets was determined according to PN-EN ISO 18123:2016-01 [41] and using following formula:

$$VM = \frac{1 - (m_S - m_C)}{m_M} \cdot 100\% \tag{3}$$

where: VM—volatile matter content in pellet in dry analytical state (%), m_S—mass of the crucible with fuel sample after heating (g), m_C—mass of the empty crucible (g), m_M—mass of the crucible with fuel sample before heating (g).

Ultimate analysis was conducted using elemental analyzer EA 1110 CHNS (CE Instruments Ltd., Wigan, United Kingdom).

Relative density of pellets (ρ_R) was determined using the gas pycnometer HumicPyc (InstruQuest Inc., Boca Raton, FL, USA) (Figure 2d). Meanwhile, the porosity was calculated according to PN-EN 1936:2010 [42] using the following formula:

$$\varepsilon = \left(1 - \frac{\rho_V}{\rho_R}\right) \cdot 100\% \tag{4}$$

where: ε—porosity of pellet fuel in a dry analytical state (%), ρ_V—volume density of pellet fuel in a dry analytical state (kg·m^{-3}), ρ_R—relative density of pellet fuel in a dry-analytical state (kg·m^{-3}).
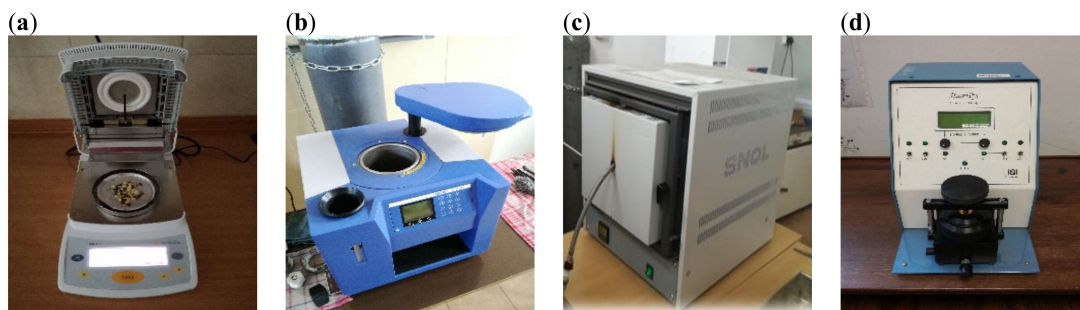

Figure 2. Devices in the technical analysis stand test: (**a**) moisture analyzer SARTORIUS MA150, (**b**) calorimetric bomb IKA C200, (**c**) muffle furnace SNOL 8,2/1100, (**d**) gas pycnometer HUMIPYC.

The bulk density of the material was determined according to the PN-EN 1237:2000 standard [43] using the following formula:

$$\rho_V = \frac{m_i}{V_i} \cdot 100\% \tag{5}$$

where: ρ_v—bulk density (kg·m^{-3}), m_i—mass of pellet (kg), V_i—volume of pellet (m^{-3}).

2.3. Preparation of the Samples

Depending on the storage conditions (variants), three types of pellets samples were prepared for the analysis:

- *Variant 1* (assumed as normal pellets): the reference sample was stored in the warehouse in the temperature of 20 °C at air humidity of 70% (the storage time was one month). The storage conditions (temperature and air humidity) inside the warehouse were controlled using a thermo hygrometer Kimo HD 50 (Kimo, Barcelona, Spain). All the pellets were packed in the 15 kg bags.
- *Variant 2* (assumed as frozen pellets): the pellets were stored in a laboratory freezer. The temperature inside the freezer was −28 °C. The storage time was 5 days. Hermetically packed 10 samples of each material were prepared for further tests. The mass of one sample was 500 g.
- *Variant 3* (assumed as defrosted pellets): after the storage of the pellets in the freezer, five samples of each investigated material were taken out and left for a period of 12 hours in the warehouse (in the temperature of 20 °C at air humidity of 70%) to enable the samples to have a natural defrosting process.

2.4. Mechanical Durability Test

The mechanical durability test of pellets was carried out in the especially constructed apparatus (Figure 3), meeting all the requirements of the PN-EN ISO 17831-1:2016-02 standard [44]. The procedure of the mechanical durability test was as follows: the mass of the pellets (500 ± 10 g for the pellets with a diameter below 12 mm or 500 ± 50 g for the pellets with a diameter over 12 mm) was put into the working chamber. The procedure for the mechanical durability analysis consisted of randomly sampling of pellets (500 ± 10 g) from the 15 kg bags of commercial pellets. The rotational speed of the chamber was 50 rpm, whereas the operation time was 600 s. After the test, the entire content of the chamber was sieved through a sieve with a mesh diameter of 3.15 mm. The sieving process consisted of making 10 circular movements with a sieve containing the investigated pellets. Next, these two separated samples of the pellets were weighed using a laboratory scale Steinberg Systems SBS-LW-7500A (Expondo Poland sp. z o.o. sp. k., Zielona Góra, Poland) with an accuracy of 0.1 g. Finally, the mechanical durability (D_U) index of pellets was determined using the following formula:

$$D_U = \frac{m_2}{m_1} \cdot 100\% \tag{6}$$

where: D_U—mechanical durability index of pellets (%), m_2—the mass of pellets left on the 3.15 mm sieve after the test and sieving (g), m_1—the mass of pellets inserted into the working chamber of the apparatus (g). According to the standard [44], the mechanical durability index for investigated pellets might be higher or lower than 97.5%. As a result, the pellets meet the mechanical durability criterion (if $D_U \geq 97.5\%$) or do not meet the defined criterion ($D_U < 97.5\%$). The mechanical durability of commercial pellets was determined using five repetitions for each type of pellet.
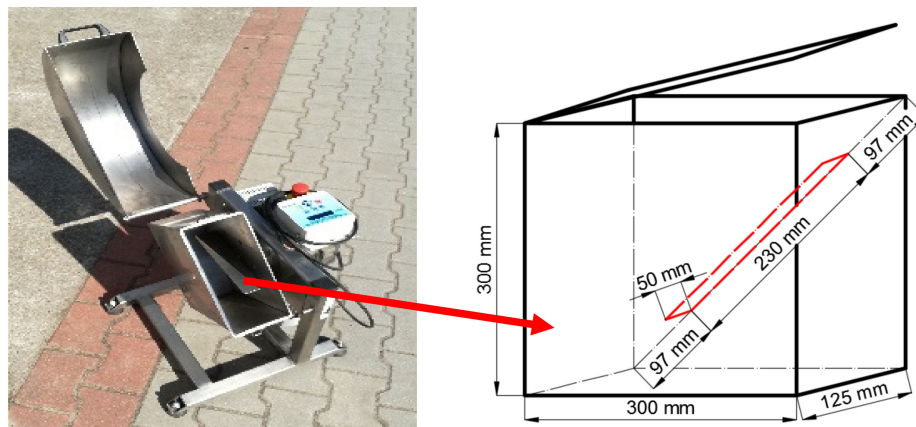
Figure 3. Test stand to mechanical durability with rotating chamber.

The obtained results were statistically developed in the Statistica software (StatSoft–Dell Software, TX, USA). In this study, the analysis of variance (ANOVA) was used. For the statistical development of data, the significance index p-value amounted to 0.05 was adopted.

3. Results and Discussion

The studies were focused on the investigation of the impact of the storage of the pellets at a freezing temperature on the mechanical durability. Therefore, the eight types of biomass pellets in three storage conditions (variants) were evaluated.

3.1. Technical and Chemical Characteristics

The results of the main physical and chemical analysis of the investigated pellets are shown in Table 1. Higher heating values of pellets were between 17.5 MJ·kg^{-1} and 23.3 MJ·kg^{-1}, and were close to the typical values for biomass fuel presented in other literature [45,46]. The highest value was reached for mix of fine coal and straw. It resulted from a significant share of coal (45%) in these pellets which is characterized by much higher HHV [46] in comparison to the biomass substrates. The lower heating values were influenced by hydrogen and moisture content in the given fuel. The LHVs were calculated in the range of 16.0 to 22.0 MJ·kg^{-1}.

In case of ash content, only one type of pellet (pine sawdust pellet) met the pellets quality requirement for class A1 (AC < 0.7% [47]). Its ash content was AC = 0.66%. Other pellets contained greater amounts of ash (up to 9.43% for a blended pellet of coal and straw). Higher value of ash content indicates a higher content of mineral fraction in fuel, which has no energy value in terms of heat production. The value of AC in commercial pellets used in this study was close to the range of AC presented in other studies [48] and was still much lower than for bituminous coals. The moisture content in the investigated pellets varied from 3.0% for pine pellets to ca. 20% for post-hydrolytic wood pellets, which was in the range of optimal values indicated by other researchers [49].

The volatile matter content (VM) in commercial pellets was between 44% and 77%. The lowest VM was determined for the mix of fine coal and straw pellet, due to the addition of fine coal. In relation to the sole biomass pellets, these values are in line with other literature data [46,48,50,51]. Lower content of VM in the pellet including coal resulted in higher carbon content (ca. 54%) and thus much greater HHV. Volatile matter content in bituminous coals is in a range from 20% to 40% [46,51]. It explains the estimated values for a blended pellet. In terms of elemental analysis (Table 1), the values were also typical for biomass residues.

The analysis of the additional properties of tested commercial pellets in this study showed that pellets from biomass were characterized by relative density at the level from 1385 to 1666 kg·m^{-3}, but the most of pellets were characterized by relative density about 1400 kg·m^{-3}. The highest relative density was observed for post-hydrolytic wood pellet and mix of fine coal and straw pellet. In turn,

the porosity of the pellets fuel material was amounted from 50% (post-hydrolytic wood pellet) to 75% (wheat straw pellet). Bulk densities of the investigated pellets were in the range of 432 to 822 kg·m^{-3} and were comparable to the other granulated biomass.

Table 1. Technical and physical analysis of commercial pellets fuel.

Type of Pellet	Proximate Analysis					Ultimate Analysis			Additional Properties		
	MC *	HHV *	LHV *	AC *	VM *	C	H	N	Relative Density	Bulk Density	Porosity
	%	kJ·kg^{-1}	kJ·kg^{-1}	%	%		%		kg·m^{-3}	kg·m^{-3}	%
Pine sawdust pellet	3.01 5.07 **	19523	17887	0.66	77.84	47	6.7	0.11	1385.2	432.4	68.78
Wheat straw pellet	10.33 11.69 **	17574	15992	7.27	72.83	40	6.1	0.69	1429.3	358.3	74.93
Digestate pellet	16.45 16.99 **	19051	17224	7.10	67.28	40	6.5	1.5	1463.4	488.0	66.65
Corn settlements pellet	7.82 8.91 **	18797	17181	1.27	74.91	42	6.4	0.5	1431.3	651.5	54.49
Agricultural residues pellet	10.97 12.41 **	18129	16511	8.27	71.05	39	6.2	1.3	1461.8	467.5	68.02
Post-hydrolytic wood pellet	20.08 20.26 **	21532	19914	8.99	56.17	46	5.7	0.3	1665.5	822.1	50.64
Sunflower husk pellet	13.77 13.80 **	19946	18246	2.99	71.83	44	6.4	0.8	1409.4	533.4	62.15
Fine coal (45%) and straw (55%) pellet	8.89 9.18 **	23269	21880	9.43	44.15	54	5.3	2.1	1653.1	737.9	55.36

* Abbreviations: MC: Moisture Content; HHV: Higher Heating Value; LHV: Lower Heating Value; AC: Ash Content; VM: Volatile Matter Content. ** Moisture content in pellets fuel after freezing and defrosting process.

3.2. Mechanical Durability Index

Having analyzed the obtained values of the pellet mechanical durability index under normal storage conditions (Figure 4), two groups of pellets can be selected: satisfying the defined quality standard, and below the standard.

The group of substrates that reached the values of the mechanical durability index above 97.5% contained digestate pellet, pine sawdust pellet, wheat straw pellet and post-hydrolytic wood pellet (lignocellulosic). These pellets were characterized by the highest mechanical durability in normal storage conditions. The highest value was obtained for digestate pellet (99.0 ± 0.1%). The variations of mechanical durability of commercial pellets in three storage conditions are presented in Table 2.

In the group of investigated materials which did not meet the durability criterion were pellets made of corn settlements, sunflower husk and a coal/straw mix. For agricultural residues pellets the value amounted to 96.5 ± 0.1%. Slightly lower values were achieved for corn settlements pellets (96.0 ± 0.2%) and a fine coal/straw blend (96.2 ± 0.2%). The lowest durability in normal storage conditions was observed in the pellet made of sunflower husk (only 87.5 ± 1.3%).

In case of pellets storage in freezing temperature conditions (Figure 4), the values of mechanical durability coefficient of pellets did not change significantly (pine sawdust and corn settlement pellets) ($p < 0.05$). For the remaining six types of the pellets, the changes of mechanical durability were significant ($p < 0.05$). The tested samples were still divided into two groups, and their mechanical durability

was only slightly lower in most cases in comparison to normal storage conditions. The pellets from digestate biomass and post-hydrolytic wood were characterized by the highest mechanical durability in freezing storage conditions, respectively 98.8 ± 0.1% and 98.6 ± 0.1%. After the freezing process, mechanical durability decreased by 0.2 percentage points for digestate biomass ($p < 0.05$). A decrease in the mechanical durability values was also observed in other agglomerates. In turn, the mechanical durability for the post-hydrolytic wood pellet and sunflower husk pellet increased slightly by 0.3 and 0.8 percentage point, respectively ($p < 0.05$). The highest change in mechanical durability of freezing pellet was observed for pellet from mix of fine coal (45%) and straw (55%). Its decrease reached 1.5 percentage point (94.8 ± 0.1%) ($p < 0.05$). The most stable mechanical durability had pellets from straw with addition of corn settlement. Their mechanical durability was 96.0 ± 0.2% both in normal and freezing storage conditions, and did not change significantly ($p < 0.05$), as well.

Analyzing the obtained values of mechanical durability of the pellets in defrosting storage conditions (Figure 4), the decrease of mechanical durability for almost all of the tested pellets samples was observed. As in case of normal and freezing storage conditions, the tested pellets were divided into two groups (which met and did not meet the mechanical durability standard). During defrosting storage conditions, the highest durability was reached by pellets from pine sawdust. Their mechanical durability was 98.7 ± 0.1%. This change, however, was not significant ($p < 0.05$). Only two types of pellets: pine sawdust and corn settlements were more resistant to freezing and defrosting storage conditions in terms of mechanical durability ($p < 0.05$). Their values were the same as the values in the normal storage conditions (98.7 ± 0.1% and 96.0 ± 0.2%, respectively). The lowest mechanical durability and the highest change in comparison to the reference values (normal storage conditions) was reached by pellet produced from sunflower husk ($p < 0.05$). Its value was 85.7 ± 1.1% and the change was 1.7 percentage point relative to mechanical durability in normal storage conditions ($p < 0.05$).
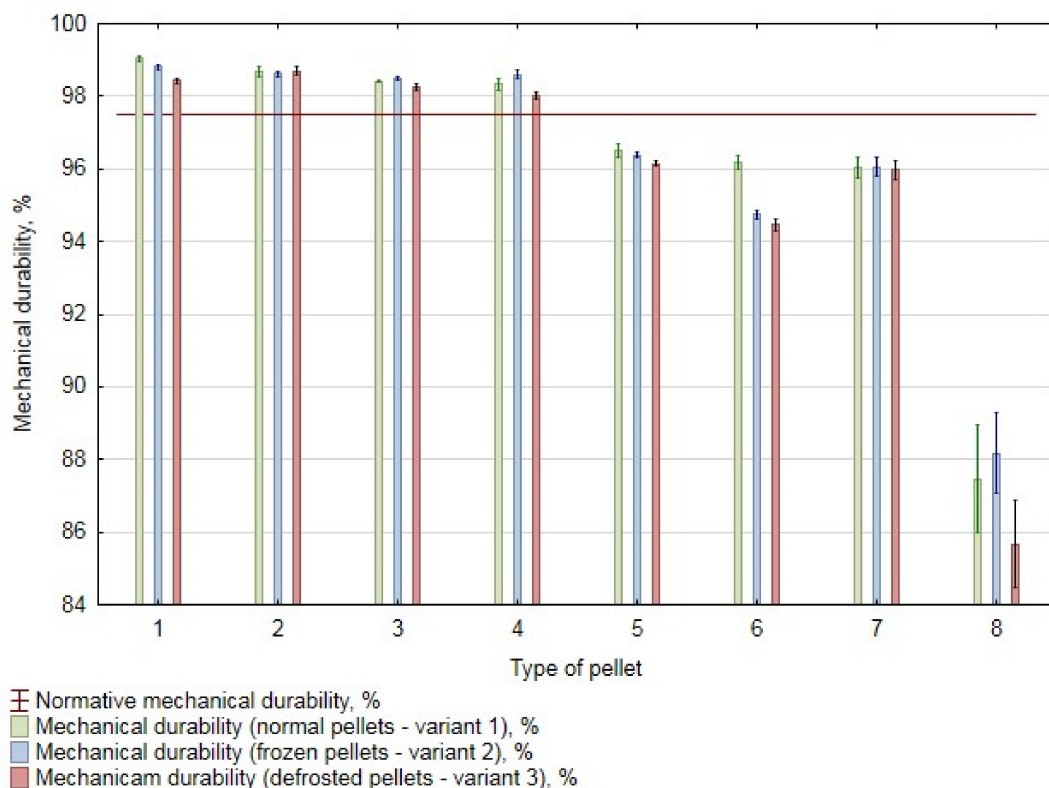

Figure 4. Mechanical durability of commercial pellets from biomass in three storage conditions: (1) Digestate pellet, (2) Pine sawdust pellet, (3) Wheat straw pellet, (4) Post-hydrolytic wood pellet, (5) Agricultural residues pellet, (6) Mix of fine coal (45%) and straw (55%), (7) Corn settlements pellet, (8) Sunflower husk pellet.

Table 2. Mechanical durability of commercial pellets from biomass and its variations in three storage conditions.

Type of pellet	Mechanical Durability and Its Variations *		
	Variant 1 (normal pellets)	*Variant 2* (frozen pellets)	*Variant 3* (defrosted pellets)
	%	Δ%	Δ%
Digestate	99.0	−0.2	−0.6
Pine sawdust	98.7	−0.1	0.0
Wheat straw	98.4	+0.1	−0.2
Post-hydrolytic wood	98.3	+0.3	−0.3
Agricultural residues	96.5	−0.1	−0.3
Fine coal (45%) and straw (55%)	96.2	−1.5	−1.7
Corn settlements	96.0	0.0	0.0
Sunflower husk	87.4	+0.8	−1.7

* The statistical analysis was carried out adopting the significance index $p = 0.05$.

The obtained results of mechanical durability test of commercial pellets indicated that this parameter depends on the type of the raw material used for its production. Values of the mechanical durability of commercial pellet used in this study varied from 86% to 99%. Similar relationship was also noted in other works. The pellets made of agricultural biomass (i.e. straw) were characterized by significantly lower mechanical durability than the pellets made of wooden biomass [52], which is usually assigned to the higher content of lignin in the wood material (a natural compound binding the material particles) [53].

A remarkable decrease in mechanical durability of commercial pellets was observed after freezing and defrosting process. It is known that the phase change of water from liquid to ice in solid materials can results in increase its volume which causes local damages in the material such as delamination, cracks or splashing [54]. However, the scale of the material destruction depends on the water content in the material as well as on the hardness and flexibility of the material. However, in case of the pellets characterized by high mechanical durability ($D_U > 97.5\%$), no correlation has been found between the water content and the mechanical durability of the investigated pellets. The pellets made of pine sawdust, digestate biomass, post-hydrolytic wood and wheat straw had very similar mechanical durability between 98% to 99%, although they were characterized by different moisture content (Table 1): 3.01% (5.07%), 16.45% (16.99%), 20.08% (20.26%) and 10.33% (11.69%), respectively. The lack of this correlation in the investigated pellets probably resulted from the fact that the water content in the agglomerated materials was generally too low to cause their substantial damages. It must be underlined, however, that the increase of water content to the level outside the typical and optimized values for pellets production may change their behavior and their mechanical properties.

After the defrosting process, only a little increase in moisture content in all samples was detected. This change, however, was probably related to the additional water absorption from the air during defrosting process of the pellets. The lower water content in the pellet prior the freezing process was, the more water was absorbed by the material during the defrosting phase (Table 1).

The same relationship was observed for the pellets made of sunflower husk and blend of fine coal and straw, which were characterized by the highest change in their mechanical durability after freezing and defrosting process ($\Delta D_U \approx 1.7\%$). The moisture content in these pellets was 13.77% (13.80%) and 8.89% (9.18%), accordingly. The change of moisture content in the pellets was from 0.03 percentage points for sunflower husk pellets to 2.06 percentage points for pine sawdust pellet.

Based on these results it can be concluded that there is no correlations between mechanical durability after freezing and defrosting process and moisture content in materials (in considered conditions and fuel characteristics). It suggests, that in the range of typical moisture content in the granulates (MC < 20%), the water does not influence the value of mechanical durability index in the investigated conditions. In case of a significant increase of water content in the material

(above recommended values for pellets), the remarkable change in durability of pellets should be expected.

Similarly, in case of the porosity index, no relationship with mechanical durability was noticed. The pellets with the best mechanical durability (D_U ca. 98–99%) characterized by different porosity: 60.78% (pine sawdust pellet), 66.65% (digestate biomass pellet), 50.64% (post-hydrolytic wood pellet) and 74.93% (wheat straw pellet). Also in case of sunflower husk and blend of fine coal and straw pellet (highest change in mechanical durability after the process of freezing and defrosting), the values of porosity were different: 62.15% and 55.36%, respectively.

Only when the pellets quality itself is low, the further drop of the D_U index might be expected. For example, among the investigated pellets, for sunflower husk pellets the D_U index decreased from 87.5 ± 0.8% to 85.7 ± 0.6%. Thus, the initial quality of pellets influences their general mechanical durability and abilities towards a further decrease caused by freezing conditions.

However, in terms of the change of mechanical durability index, this decrease is not decisive and does not cause complete destruction (scattering) of pellets. Other parameters (indicated in the introduction) have more significant influence on this index.

As a result, according to the obtained results it can be concluded that the influence of the defrosting process of the pellets on their mechanical durability is rather irrelevant. It must be noted, however, that in this study the impact of only one cycle of freezing and defrosting process on mechanical durability of commercial pellets was investigated. In practice, the number of such cycles might be different, but low moisture content in pellets should limit this process significantly.

4. Conclusions

The mechanical durability of pellets used for energy purposes is crucial in terms of their storage and transport to the final consumer. There are many parameters or conditions that can lead to the destruction of pellets. Usually, the pellets are stored in unheated in-door systems or warehouses, and transported over long distances by trucks without isolated walls. As a result, in the winter season, the pellets undergo a freezing process which can change their mechanical properties. Therefore, the investigation of the pellets storage in low temperatures, namely in freezing conditions, and its influence on the mechanical durability was important to increase the knowledge in that area.

The performed research and analysis of the results revealed that the storage (or transport) in freezing conditions of pellets affects their mechanical durability in a very limited range. If the initial mechanical durability of the pellet is high in normal conditions, the storage of pellets at freezing temperatures and its subsequent defrosting do not affect their mechanical durability significantly. However, in case of low quality of pellets (low initial mechanical durability index) there might be a further decreasing of their mechanical durability if the material was previously frozen. Therefore, the companies and consumers dealing with the pellets storage should pay attention to their mechanical durability index. In case of a lower mechanical durability index, in order to minimize the risk of further deterioration of properties, it is recommended not to allow freezing of the pellets to occur. Therefore, storage only in temperatures above 0 °C is suggested.

In fact, in comparison to the other parameters, the freezing temperature is not a crucial parameter deciding about the final mechanical durability of commercial pellets available on the market, but the index D_U is very demanding for high quality pellets (D_U > 97.5%) and proper storage might decide to meet this criterion.

This study creates a basis for further research in this subject, namely, to investigate the influence of the number of freezing-defrosting cycles of the pellets on the change in their mechanical durability. Interestingly, there also seems to be an estimation of the maximal value of water content in the pellets that shows that freezing-defrosting conditions cause the destruction of pellets.

Author Contributions: A.D. conceived and designed the research; A.D. and T.N. performed the research; A.D. and T.N. analyzed the data and contributed materials/analysis tools; A.D. and T.N. wrote the paper.

Conflicts of Interest: The author declares no conflict of interest.

Abbreviations

AC	ash content
EC	European Commission
EU	European Union
HHV	higher heating value
LHV	lower heating value
MC	moisture content
RES	renewable energy sources
VM	volatile matter content

References

1. EuroStat. Energy Consumption in Households. Available online: https://ec.europa.eu/eurostat/statistics-explained/index.php/Energy_consumption_in_households (accessed on 29 May 2019).
2. European Commission. *EUROPE 2020: A Strategy for Smart, Sustainable and Inclusive Growth*; European Commission: Brussels, Belgium, 2010.
3. World Bioenergy Association. *WBA Global Bioenergy Statistics 2018*; World Bioenergy Association: Stockholm, Sweden, 2018.
4. Karakashev, D.; Zhang, Y. BioEnergy and BioChemicals Production from Biomass and Residual Resources. *Energies* **2018**, *11*, 2125. [CrossRef]
5. PN-EN. CEN-EN 303-5. In *Heating Boilers. Part 5: Heating Boilers for Solid Fuels, Manually and Automatically Stoked, Nominal Heat Output of Up to 500 kW—Terminology, Requirements, Testing and Marking*; European Committee for Standardization: Brussels, Belgium, 2012.
6. Nilsson, D.; Bernesson, S.; Hansson, P.A. Pellet production from agricultural raw materials—A systems study. *Biomass Bioenergy* **2011**, *35*, 679–689. [CrossRef]
7. Whittaker, C.; Shield, I. Factors affecting wood, energy grass and straw pellet durability—A review. *Renew. Sustain. Energy Rev.* **2017**, *71*, 1–11. [CrossRef]
8. Thek, G.; Obernberger, I. Wood pellet production costs under Austrian and in comparison to Swedish framework conditions. *Biomass Bioenergy* **2004**, *27*, 671–693. [CrossRef]
9. Sahoo, K.; Hawkins, G.L.; Yao, X.A.; Samples, K.; Mani, S. GIS-based biomass assessment and supply logistics system for a sustainable biorafinery: A case study with cotton stalks in the Southeastern US. *Appl. Energy* **2016**, *182*, 260–273. [CrossRef]
10. Adapa, P.; Tabil, L.; Shoenau, G. Grinding performance and physical properties of non-treated and steam exploded barley, canola, oat and wheat straw. *Biomass Bioenergy* **2011**, *35*, 549–561. [CrossRef]
11. Obidziński, S. Influence of selected structure parameters of pellet mill on the quality of the final product. *Pol. J. Food Nutr. Sci.* **2007**, *57*, 121–124.
12. Tumuluru, J.S. Effect of process variables on the density and durability of the pellets made from high moisture corn stover. *Biosyst. Eng.* **2014**, *119*, 44–57. [CrossRef]
13. Kraszkiewicz, A.; Kachel-Jakubowska, M.; Szpryngiel, M.; Niedziółka, I. Analiza wybranych cech jakościowych peletów wytworzonych z surowców roślinnych. *Inżynieria Rolnicza* **2013**, *2*, 167–173.
14. Novaes, E.; Kirst, M.; Chiang, V.; Winter-Sederoff, H.; Sederoff, R. Lignin and biomass: A negative Correlations for wood formation and lignin content in trees. *Plant Physiol.* **2010**, *154*, 555–561. [CrossRef]
15. Lehmann, B.; Schroder, H.W.; Wollenberg, R.; Repke, J.U. Effect of miscanthus addition and different grinding processes on the quality of wood pellets. *Biomass Bioenergy* **2012**, *44*, 150–159. [CrossRef]
16. Rynkiewicz, M.; Dobek, T.K. Wybrane właściwości fizyczne i mechaniczne pelletów w zależności od składu i temperatury ich przechowywania. *Inżynieria Rolnicza* **2013**, *3*, 321–330.
17. Niedziółka, I.; Szpryngiel, M. Ocena cech jakościowych peletów wytworzonych z biomasy roślinnej. *Inżynieria Rolnicza* **2012**, *2*, 267–276.

18. Graham, S.; Eastwick, C.; Snape, C.; Quick, W. Mechanical degradation of biomass wood pellets during long term stockpile storage. *Fuel Process. Technol.* **2017**, *160*, 143–151. [CrossRef]

19. Kulig, R. Wpływ procesu kondycjonowania wybranych surowców strączkowych na właściwości fizyczne granulatu. *Inżynieria Rolnicza* **2009**, *1*, 147–155.

20. Sahoo, K.; Bilek, E.M.; Mani, S. Techno-economic and environmental assessments of storing woodchips and pellets for bioenergy applications. *Renew. Sustain. Energy Rev.* **2018**, *98*, 27–39. [CrossRef]

21. Noll, M.; Jirjis, R. Microbial communities in large-scale wood piles and their effects on wood quality and the environment. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 551–563. [CrossRef]

22. Jirjis, R.; Theander, O. The effect of seasonal storage on the chemical composition of forest residue chips. *Scand. J. For. Res.* **1990**, *5*, 437–438. [CrossRef]

23. Nielsen, N.P.K.; Gardner, D.L.; Poulsen, T.; Felby, C. Importance of temperature, moisture content, and species for the conversion process of wood residues into fuel pellets. *Wood Fiber Sci.* **2009**, *41*, 414–425.

24. Arshadi, M.; Gref, R.; Geladi, P.; Dahlqvist, S.A.; Lestander, T.A. The influence of raw material characteristics on the industrial pelletizing process and pellet quality. *Fuel Process. Technol.* **2008**, *89*, 1442–1447. [CrossRef]

25. Stelte, W.; Holm, J.K.; Sanadi, A.R.; Barsberg, S.; Ahrenfeldt, J.; Henriksen, U.B. A study of bonding and failure mechanisms in fuel pellets from different biomass resources. *Biomass Bioenergy* **2011**, *35*, 910–918. [CrossRef]

26. Sultana, A.; Kumar, A. Development of energy and emission parameters for densiefied form of lignocellulosic biomass. *Energy* **2011**, *36*, 2716–2732. [CrossRef]

27. Stelte, W.; Holm, J.K.; Sanadi, A.R.; Barsberg, S.; Ahrenfeldt, J.; Henriksen, U.B. Fuel pellets from biomass: The importance of the pelletizing pressure and its dependency on the processing conditions. *Fuel* **2011**, *90*, 3285–3290. [CrossRef]

28. Mani, S.; Tabil, L.G.; Sokhansanj, S. Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass Bioenergy* **2004**, *27*, 339–352. [CrossRef]

29. Ahn, B.J.; Chang, H.; Lee, S.M.; Choi, D.H.; Cho, S.T.; Han, G.; Yang, I. Effect of binders on the durability of wood pellets fabricated from Larix kaemferi C. and Liriodendron tulipifera L. sawdust. *Renew. Energy* **2014**, *62*, 18–23. [CrossRef]

30. Carroll, J.P.; Finnan, J. Physical and chemical properties of pellets from energy crops and cereal straws. *Biosyst. Eng.* **2012**, *112*, 151–159. [CrossRef]

31. Adapa, P.; Tabil, L.; Shoenau, G.; Opoku, A. Pelleting characteristic of selected biomass with and without steam explosion pretreatment. *Int. J. Agric. Biol. Eng.* **2010**, *3*, 62–79.

32. Kirsten, C.; Lenz, V.; Schroder, H.W.; Repke, J.U. Hay pellets—The influence of particle size reduction on their physical-mechanical quality and energy demand during production. *Fuel Process. Technol.* **2016**, *148*, 163–174. [CrossRef]

33. Theerarattananoon, K.; Xu, F.; Wilson, J.; Ballard, R.; McKinney, L.; Staggenborg, S.; Vadlani, P.; Pei, Z.J.; Wang, D. Physical properties of pellets made from sorghum stalk, corn stover, wheat straw and big bluestem. *Ind. Crops Prod.* **2011**, *33*, 325–332. [CrossRef]

34. Lee, S.; Ahn, B.J.; Choi, D.H.; Han, G.S.; Jeong, H.S.; Ahn, S.M.; Yang, I. Effect on densification variables on the durability of wood pellets fabricated with Larix kaempferi C. and Liriodendron tulipifera L. sawdust. *Biomass Bioenergy* **2013**, *48*, 1–9. [CrossRef]

35. Stelte, W.; Sanadi, A.R.; Shang, L.; Holm, J.K.; Ahrenfeldt, J.; Henriksen, U.B. Recent developments in biomass palletization—A review. *Bioresources* **2012**, *7*, 4451–4490.

36. Hansen, M.T.; Rosentoft-Jein, A.; Wach, E.; Bastian, M. *Poradnik użytkowania pelet drzewnych*; Bałtycka Agencja Poszanowania Energii S.A.: Gdańsk, Poland, 2009.

37. PN-EN. ISO 18134-2:2017-03E. In *Solid Biofuels. Determination of Moisture Content—Oven Dry Method—Part 2: Total Moisture—Simplified Method*; European Committee for Standardization: Brussels, Belgium, 2017.

38. PN-EN. ISO 18125:2017-07. In *Solid Biofuels-Determination of Calorific Value*; European Committee for Standardization: Brussels, Belgium, 2017.

39. Porowski, R. Analiza metod określania ciepła spalania i wartości opałowej paliw. *Zeszyty Naukowe SGSP* **2016**, *59*, 45–70.

40. PN. ISO 1171:2010. In *Solid Mineral Fuels. Determination of Ash*; European Committee for Standardization: Brussels, Belgium, 2010.

41. PN-EN. ISO 18123:2016-01. In *Solid Fuels. Determination of Volatile Content by Gravimetric Method*; European Committee for Standardization: Brussels, Belgium, 2016.

42. PN-EN 1936:2010. In *Metody badań kamienia naturalnego. Oznaczanie gęstości i gęstości objętościowej oraz całkowitej i otwartej porowatości*; European Committee for Standardization: Brussels, Belgium, 2010.

43. PN-EN 1237:2000. In *Fertilizers—Determination of Bulk Density (Tapped)*; European Committee for Standardization: Brussels, Belgium, 2000.

44. PN-EN. ISO 17831-1:2016-02. In *Solid Biofuels—Determination of Mechanical Durability of Pellets and Briquettes—Part 1: Pellets*; European Committee for Standardization: Brussels, Belgium, 2016.

45. Damirichi, H.; Najafi, G.; Alizadehnia, S.; Mamat, R.; Azwadi, N.; Sidik, C.; Azmi, W.H.; Noor, M.M. Micro Cimbined Heat and Power to provide heat and electrical power using biomass and Gamma-type Striling engine. *Appl. Therm. Eng.* **2016**, *103*, 1460–1469. [CrossRef]

46. Bai, Z.; Liu, Q.; Lei, J.; Hong, H.; Jin, H. New-solar biomass power generation system integrated a two-stage gasifier. *Appl. Energy* **2017**, *194*, 310–319. [CrossRef]

47. Gehring, M.; Wohler, M.; Pelz, S.; Steinbrink, J.; Thorwarth, H. Kaolin as additive in wood pellet combustion with several mixtures of spruce and short-rotation-coppice willow and it influence on emissions and ashes. *Fuel* **2019**, *235*, 610–616. [CrossRef]

48. Lim, C.H.; Lam, H.L. Biomass supply chain optimisation via novel Biomass Element Life Cycle Analysis (BELCA). *Appl. Energy* **2016**, *161*, 733–745. [CrossRef]

49. Tumuluru, J.S. Pelleting of Pine and Switchgrass Blends: Effect of Process Variables and Blend Ratio on the Pellet Quality and Energy Consumption. *Energies* **2019**, *12*, 1198. [CrossRef]

50. Ellis, N.; Masnadi, M.S.; Roberts, D.G.; Kochanek, M.A.; Ilyushechkin, A.Y. Mineral matter interactions during co-pyrolysis of coal and biomass and their impact in intrinsic char co-gasification reactivity. *Chem. Eng. J.* **2015**, *279*, 402–408. [CrossRef]

51. Matali, S.; Rahman, N.A.; Idris, S.S.; Yaacob, N.; Alias, A.B. Lignocellulosic Biomass solid Fuel Properties Anhancement via Torrefaction. *Procedia Eng.* **2016**, *148*, 671–678. [CrossRef]

52. Stasiak, M.; Molenda, M.; Bańda, M.; Wiącek, J.; Parafiuk, P.; Gondek, E. Mechanical and combustion properties of sawdust—Straw pellets blended in different proportions. *Fuel Process. Technol.* **2017**, *156*, 366–375. [CrossRef]

53. Welker, C.M.; Balasubramanian, V.K.; Petti, C.; Rai, K.M.; DeBolt, S.; Mendu, V. Enginnering Plant Biomass Lignin Content and composition for Biofuels and Bioproducts. *Energies* **2015**, *8*, 7654–7676. [CrossRef]

54. Šavija, B. Smart Crack Control in Concrete through Use of Phase Change Materials (PCMs): A Review. *Materials* **2018**, *11*, 654.