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Eucalyptus Kraft Lignin as an Additive Strongly Enhances the Mechanical Resistance of Tree-Leaf Pellets

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Abstract: Pelleted biomass has a low, uniform moisture content and can be handled and stored cheaply and safely. Pellets can be made of industrial waste, food waste, agricultural residues, energy crops, and virgin lumber. Despite their many desirable attributes, they cannot compete with fossil fuel sources because the process of densifying the biomass and the price of the raw materials make pellet production costly. Leaves collected from street sweeping are generally discarded in landfills, but they can potentially be valorized as a biofuel if they are pelleted. However, the lignin content in leaves is not high enough to ensure the physical stability of the pellets, so they break easily during storage and transportation. In this study, the use of eucalyptus kraft lignin as an additive in tree-leaf pellet production was studied. Results showed that when 2% lignin is added the abrasion resistance can be increased to an acceptable value. Pellets with added lignin fulfilled all requirements of European standards for certification except for ash content. However, as the raw material has no cost, this method can add value or contribute to financing continued sweeping and is an example of a circular economy scenario.

Keywords: eucalyptus kraft lignin; tree leaf; pellet; additive; biofuel; circular economy

1. Introduction

Lignocellulosic biomass generally has a low bulk density (30–100 kg/m^3). Pelleting process growths the specific biomass density to more than 1000 kg/m^3 [1–3]. Pelleted biomass has a low, uniform moisture content and can be handled and stored cheaply and safely using well-known handling systems developed for grains [4,5]. Pellets can be produced from any one of five general categories of biomass: industrial residues and co-products, food waste, agricultural residues, energy crops, and virgin lumber [6,7]. Wood pellets are the most common type of pellet fuel and are generally made from compacted sawdust and related industrial wastes from the milling of lumber, manufacturing of wood products and furniture industry. However, as a result of limited supplies of sawdust in many countries, particularly those in central and northern Europe, agricultural products are increasingly being used as raw material for pellet production [6]. Wood pellets are becoming more popular worldwide; in the last

five years, the production and exportation of pellets has increased by 73% and 93%, respectively [8]. Regardless of their many attributes, biomass pellets have a higher cost that fossil fuel sources because it is still too expensive to densify biomass. Raw materials are also a major contributor to cost [7].

The manufacturing process consists of drying the biomass and reducing the particle size to be suitable for pelleting by means of a hammer mill. The crushed biomass is compacted in the press mill to form pellets. Individual pellet density ranges from 1000–1200 kg/m^3, and the bulk density varies between 550–700 kg/m^3 depending on the pellets size. The higher heating value of wood pellets varies between 17,000 and 22,000 kJ/kg [9,10]. Pellet density and abrasion resistance are influenced by the physical and chemical properties of the raw material and the temperature and applied pressure during the pelleting process [2].

The quality of pellets is determined by a few main parameters including moisture content (MC), net heating value, abrasion resistance, particle density, ash content, and ash melting point [11]. Pellets must fulfill the requirements for these parameters for commercialization. Several institutions have created standards for pellet quality [12,13].

Mechanical resistance of pellets has been measured in terms of compressive resistance, abrasive resistance and impact resistance [14]. Compressive resistance (crushing resistance or hardness) is the maximum load a pellet can tolerate before breaking. It is related to the adhesion forces between particles in the pellet and is normally used for testing pills in pharmaceutical industry. The test provides a quick measure of the quality of pellets and can be used to improve pellet quality. However, the compressive resistance does not quantify the amount of dust that is formed during the transport, handling and storage of the pellets, and that is the main reason why this test is not normally used to adjust pelleting processing condition [14,15]. The safe and effective transportation and processing of biomass pellets is critical for bioenergy application. Low pellet mechanical resistance leads to high dust emissions, system blockages and an increased risk of fire and explosions during pellet handling, storage and transport [16].

The durability or abrasion resistance is one of the most important parameters in pellet production and is defined as the ability of densified biomass units to remain intact during handling [16,17]. High durability implies high quality pellets with a low number of fines. The most widely used laboratory methods to measure the durability of pellets, are: the tumbling box method, the Holmen durability tester, and the Ligno tester. In the tumbling box method, a sample of pellets is sieved to remove fines and then 0.5 kg of sieved pellets is placed in a tumbling can device. After tumbling for 10 min at 50 rpm, the sample is removed, sieved and weighted. Pellet durability index (PDI) is calculated as the ratio of weight after tumbling over the weight before tumbling and is expressed as a percentage [14,18,19]. The Holmen durability tester simulates pneumatic management of pellets. In this device, a sample of pellets pneumatically circulates through a square conduit of pipe, and the pellets are impacted repeatedly on hard surfaces. After procedure, pellet sample is sieved, and durability index is calculated in a similar way. The Holmen tester is severer than the tumbling can method and, therefore, yields lower PDI [19,20]. The Ligno tester device uses air to rapidly circulate 0.1 Kg of pellets around a perforated chamber during 30 s. The chamber is an inverted square pyramid with perforated sides. Forced air is the destructive force. Fines are removed continuously during the test and there is no need to screen the pellet. PDI is calculated in a similar way [19]. The tumbling box method is the most popular method for abrasion resistance determination.

Impact resistance test (drop resistance or shattering resistance) simulate the forces produced during emptying of densified products from trucks onto ground or bins. It can be used to determine the safe height of pellet production [21]. Pellets are dropped from a standardized height of 1.85-m onto a stainless-steel plate in the floor, four times. The weight of the remaining pellets, as the percentage of the initial weight is the impact resistance index (IRI) [14].

Pellet quality may be improved by using different binding agents or additives during production. Additives can form a bridge, a film, a matrix or can cause a chemical reaction to make strong inter-particle bonding. They can act in several ways, such as improving fuel quality, decreasing

emissions, or increasing burning efficiency. All the current regulations for the classification of pellets limit the use of additives at 2% for wood pellets. The most used additives are lignosulphonate, starch, dolomite, corn or potato flour, and some vegetable oils. These binding agents also affect the production economics of the final product [11,17,22].

When lignin-rich biomass is compressed under high pressures and temperatures, the lignin becomes soft, because its thermosetting properties. The softened lignin acts as a glue [11,23]. If the feedstock (e.g., leaves) does not contain enough lignin, a binding agent needs to be added. Otherwise, the finished pellets have poor mechanical stability and typically break down into powder very easily. Binding agents improve production efficiency but also can increase lubricity during the grinding procedure, thus decreasing wear and tear on the machinery. Many substances can be used as additives, including molasses, starch, gluten, dry distiller, rapeseed cake, etc. Nowadays, ongoing research has sought to extract new additives from waste materials, to develop circular economy processes. Materials that are more sticky or oily are more likely to be used as binding agents. The lignin content of leaves is normally smaller than in wood. Although lignin content in leaves varies with species, it is usually less than 10–12%, and in some cases as low as 3–6%, whereas in wood, the lignin content ranges from 18–30% [24].

In some European countries, the final disposal of leaves collected in street sweeping is problematic, since burning is not allowed, leaves are generally disposed in landfills. In Germany the number of deciduous trees in the streets is particularly high, and only in Berlin there are more than 430,000 trees in the streets [25]. In this work, we study the possibility of using tree leaves as raw material for manufacturing pellets. However, due to the low lignin content of the leaves, it is necessary to add a binding agent to improve the stability of the pellets. As an additive, the use of lignosulfonates was studied by several authors with good results [5,11,12,26] however, as the availability of lignosulfonates has decreased and its price increased, the use of eucalyptus kraft lignin is proposed, given the predominance of the kraft process for the production of cellulose pulp and the use of fast-growing species such as eucalyptus, particularly in South America. In this approach, two sub products from the forest are valorized.

2. Materials and Methods

Wood leaves were collected from streets and gardens in the Bergisches Land (North Rhine-Westphalia, Germany), washed, dried to a moisture content of 30% (wb), and stored in plastic containers. Eucalyptus kraft lignin was obtained by acid precipitation with CO_2 from Eucaliptus kraft black liquor, kindly provided by the UPM-Fray Bentos pulp mill (Fray Bentos, Uruguay) [27]. Then, a washing stage with mineral acid (pH 2) was performed to remove inorganic impurities. As very high purity is not a requisite, the acid washing was performed in only one stage. Lignin was characterized in terms of moisture content (ISO 18134), ash content (ISO 18122), Klason and soluble lignin (Tappi standard T-222). Lignin glass transition temperature (Tg) was measured using a Perkin Elmer DSC 6000 device (Perkin Elmer, Waltham, MA, USA). To manufacture the pellets, a pellet press EverTec WKL120C of 3 kW was used. During pellet manufacturing, the temperature in the rolling press was monitored with an infrared thermometer.

Pellets were characterized in terms of yield, moisture content (ISO 18134), ash content (ISO 18122), durability (ISO 17831-1), calorific value (ISO 18125), ash chemical composition (ISO 16968), and ash melting point (ASTM D 1857—04). The cross section of the pellets was inspected via Scanning Electron Microscopy (SEM) after gold sputtering. To determine the calorific value, a calorimeter IKA C200 (IKA, Staufen, Germany) was used; to determine the metal content, a Perkin Elmer AAnalyst 200 Atomic Absorption Spectrometer was used; to determine the ash melting point, a LECO AF700 device (LECO, St. Joseph, MI, USA) was used.

To study the influence of the moisture content of the raw material, the leaves were crushed and conditioned with different water content values on a wet basis: 10, 14, 18, 22, and 25% (samples labeled

as P-10, P-14, P-18, P-22, and P-25, respectively). To study the influence of kraft lignin as an additive, 1.0, 1.5, 2.0, and 3.0% (db) were added (samples named as L-1, L-1.5, L-2, and L-3).

3. Results and Discussion

Lignin characteristics are shown in Table 1. Lignin ash content was high because the washing stage at the pilot plant was performed with a minimal amount of water. The purpose of this process is to produce technical-grade lignin without further refinement in order to keep production costs as low as possible. Pure lignin content was considered for the pellet formulations. Figure 1a shows the yield of the pelleting process, which was calculated as the dry mass of the pellets obtained divided by the dry mass of the raw material used. Results shows that 22–25% is the best moisture content for pellet formation and when the moisture content is less than 18% pellet formation was poor, resulting in a low process yield. This fact is not in agreement with literature since it is widely reported that the moisture content of raw material for pellet production should be around 15% [5,6,12,14,22,28]. The explanation may be given by the friction of the rolling press, which raises the temperature to between 90–110 °C and causes water to evaporate prior to extrusion. The moisture content of the pellets after the production process is indicated in Table 2 and is independent of the moisture content of the raw material. The average moisture of the pellets in wet basis was (8.7 ± 0.2)%. This value is lower than 10%, as required for certification [13,21,22,29].

Table 1. Physical properties of lignin used in this work.

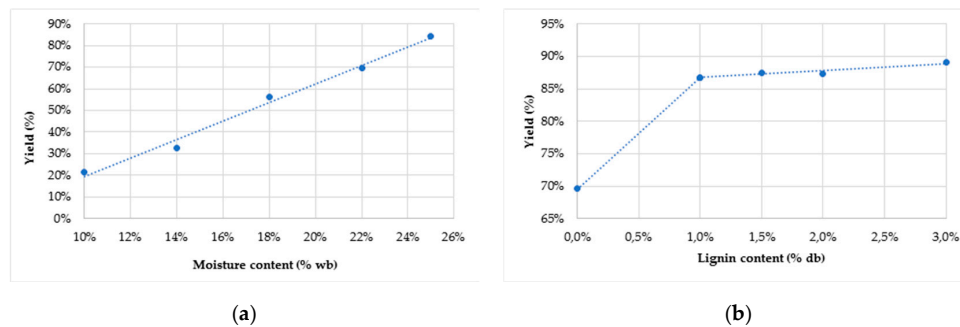| Property	Value
Ash content (%)	12.0 ± 0.9
Klason lignin (%)	73.0 ± 0.5
Soluble lignin (%)	11.3 ± 0.8
Total lignin (%)	84 ± 1
Tg (°C)	132 ± 1
Net heating value (MJ/kg)	29.1 ± 0.1

| (a) | (b) |

Figure 1. (**a**) Yield of pellet production versus moisture content of raw material, (**b**) yield production versus lignin content.

Table 2. Moisture content of pellets versus moisture content of raw material.

Sample	Raw Material Moisture Content (% wb)	Pellet Moisture Content (% wb)
P-10	10.0 ± 0.2	9.2 ± 0.1
P-14	14.0 ± 0.3	8.5 ± 0.3
P-18	18.0 ± 0.1	8.0 ± 0.1
P-22	22.0 ± 0.2	9.1 ± 0.1
P-25	25.0 ± 0.1	8.9 ± 0.1

For the addition of eucalyptus kraft lignin as a binding agent, raw material with a moisture content of 22% was selected. The yield increased drastically with the lignin content, as shown in

Figure 1b. This can be explained because of the bonging effect of lignin on the pellet structure. Also, lignin-added pellets showed a brighter finish.

A pellet with low durability disintegrates easily during handling, which can cause difficulties during its storage and transport, as well as health and environmental problems due to the dust generated. The durability index of the pellets varies with the moisture content of the raw material as well as with the amount of lignin added, as shown in Figure 2. The New European Pellets Standards EN 14961-1 states that the minimum durability value for a commercial pellet is 95%, which was not reached in leaf-pellet production without the inclusion of an additive. When lignin was added at 2.0% and 3.0%, the durability was acceptable for pellet commercialization and fulfilled the requirements for certification [22], but the values were lower than for wood pellets, which usually have a durability above 97.5% [13,22,29].
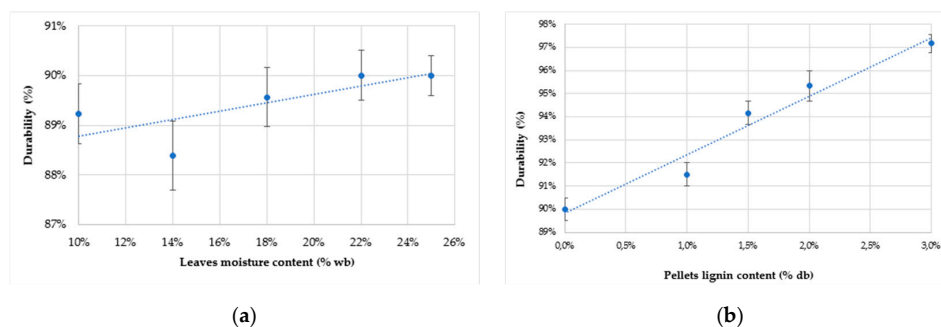

(**a**)　　　　　　　　　　　　　　　　　　　　　(**b**)

Figure 2. Durability of pellets. (**a**) Influence of the moisture content of leaves, (**b**) influence of the lignin content of pellets.

Figure 3 shows the SEM cross sections obtained with pellets P-22, L-1, L-2, and L-3 in which the only difference was lignin content. All pellets exhibited a homogeneous structure, and no large leaf particles could be observed. This finding confirms the quality of the applied leaf pelletization process. Unfortunately, SEM images of tree-leaf pellet cross sections could not be found for comparison in the literature.
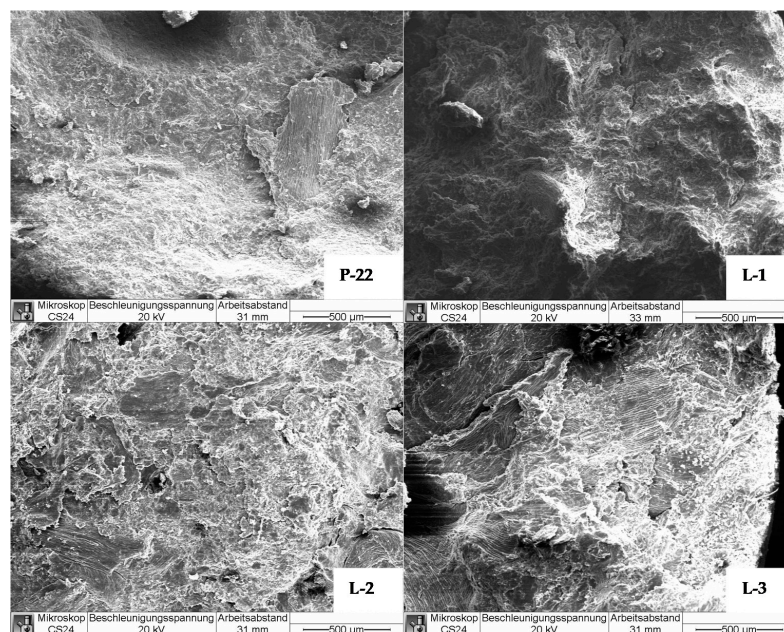

Figure 3. SEM images of pellets without lignin (P-22) and with different lignin contents (L-1, L-2, L-3).

The net heating value of the pellets in dry basis varies with the moisture content of the raw material, as can be seen in Figure 4a, which was quite surprising. One possible explanation is the volatilization of compound with low net heating value during the process, which is higher at low moisture contents. When lignin is used as an additive, the higher heating value increases by approximately 0.11 MJ/kg per each 1% of lignin added, as shown in Figure 4b, because of the higher net heating value of lignin. The minimum net heating value for pellet certification is 16.56 MJ/kg, which is lower than the values achieved with the leaf pellets [22,29].
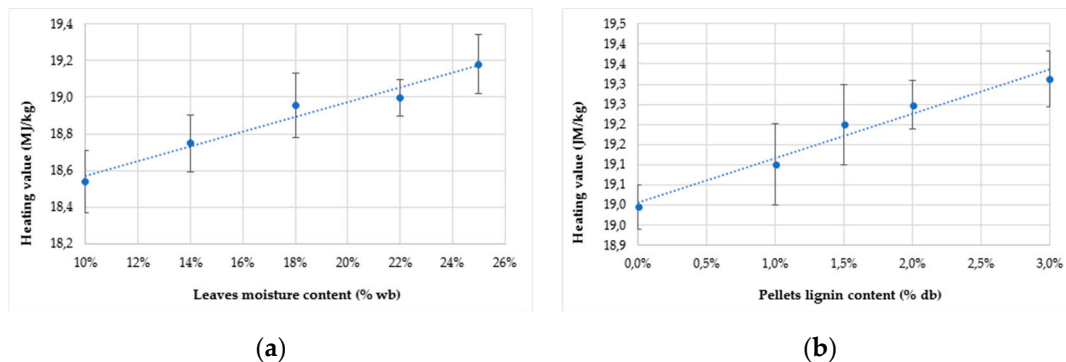

(a)　　　　　　　　　　　　　　　　　　　　　　　(b)

Figure 4. Net heating value (dry basis), (**a**) influence of the moisture content of leaves, (**b**) influence of the lignin content of pellets.

In Table 3, the ash content of the raw materials and the pellets produced is listed. The ash content of leaves is much higher than in wood because of its botanic nature and its function in the plant. The amount of ashes could be problematic for both domestic and industrial uses of these pellets, as it is five times higher than the requirements for wood pellets. One option to diminish the ash content is to formulate pellets with both leaves and sawdust since sawdust has a very low ash content. In this scenario, the need for an additive has to be evaluated. In addition, end users may prefer pellets made from tree leaves if the cost is considerably lower than that of wood pellets, and this is possible since the cost of the raw material is negligible and the equipment for production is the same as for wood pellets.

Table 3. Ash content of leaves and pellets.

Sample	Ash Content (% db)
Leaves	10.2 ± 0.1
P-10	11.0 ± 0.4
P-14	10.9 ± 0.9
P-18	10.9 ± 0.5
P-22	11.6 ± 0.2
P-25	12.3 ± 0.2
L-1.0	10.7 ± 0.4
L-1.5	11.1 ± 0.6
L-2	11.8 ± 0.1
L-3	12.7 ± 0.2

Regarding the fusibility of ash, results can be seen in Table 4. Only the initial deformation temperature (IT) is considered by quality standards. In all cases, the initial deformation temperature was above 1200 °C, except for sample P-14, in compliance with specifications for the highest quality pellets [17,22]. All pellets with lignin fulfilled this requirement. Regarding softening temperature (ST), hemispherical temperature (HT) and fluid temperature (FT) in most cases are higher than the maximum temperature that can be determined with the equipment used (1500 °C).

Table 4. Fusibility of pellet ash.

Sample	IT [1] (°C)	ST [2] (°C)	HT [3] (°C)	FT [4] (°C)
P-10	1232	>1500	>1500	>1500
P-14	1119	1310	1371	1398
P-18	1232	>1500	>1500	>1500
P-22	1281	>1500	>1500	>1500
P-25	1227	1416	1437	1440
L-1	1304	>1500	>1500	>1500
L-1.5	1336	>1500	>1500	>1500
L-2	1314	>1500	>1500	>1500
L-3	1240	>1500	>1500	>1500

[1]: IT: initial deformation temperature. Is the temperature at which the first rounding of the sample occurs. [2]: ST: softening temperature. Is the temperature at which the sample has fused down to a spherical lump in which the height is equal to the width at the base. [3]: HT: hemispherical temperature. Is the temperature at which the cone has fused down to a hemispherical lump at which point the height is one half the width of the base. [4]: FT: fluid temperature. Is the temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of 1.6 mm.

The chemical composition of the pellets is shown in Table 5 for major (Na, K, Ca, Mg) and minor (As, Cd, Cr, Cu, Ni, Pb, Zn) elements. Although metal composition is not regulated, there is an indication of the maximum content of the minor elements in the pellets showed in the first row of Table 5 [17,22]. The results show that in all conditions, the metal content is below this indication, which ensures good environmental performance.

Table 5. Metal composition of pellets.

Sample	Ca (mg/g)	Mg (mg/g)	Na (mg/g)	K (mg/g)	As (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Max. Content					≤1	≤0.5	≤10	≤10	≤10	≤10	≤100
P-10	19.0	3.0	0.5	7.9	<0.2	<0.5	<5.0	8.1	2.0	6.0	23.9
P-14	20.3	3.3	0.1	8.4	<0.2	<0.5	<5.0	3.5	1.8	5.9	17.2
P-18	17.8	2.8	0.1	7.4	<0.2	<0.5	<5.0	4.3	1.5	6.0	15.2
P-22	15.8	2.6	0.1	6.5	<0.2	<0.5	<5.0	2.9	1.3	5.5	11.3
P-25	20.0	3.2	0.3	8.3	<0.2	<0.5	<5.0	2.8	1.5	7.6	16.8
L-1	15.2	2.5	0.2	6.3	<0.2	<0.5	<5.0	1.3	0.8	4.1	21.3
L-1.5	16.7	2.7	0.8	6.9	<0.2	<0.5	<5.0	2.2	1.1	5.1	12.5
L-2	21.8	3.6	1.5	9.1	<0.2	<0.5	<5.0	4.6	1.4	5.3	17.2
L-3	19.8	3.3	1.9	8.2	<0.2	<0.5	<5.0	4.1	1.4	7.0	17.2

4. Conclusions

The main objective of this work was to determine if tree leaves obtained in the sweeping of the streets, can be used as raw material for the production of pellets, going from being a residue to becoming a useful product. The results showed that this is possible but that it is necessary to add an additive that improves the yield of the process and the mechanical resistance of the product.

Lignin is the second most abundant polymer on the planet, and although the technology for production is developed, its uses are still preliminary. This research shows an alternative for the use of eucalyptus lignin kraft, as an additive to produce tree-leaf pellets.

This process can be useful for municipalities because they already have all the logistics of collection and stockpiling established, especially in those cities where the number of deciduous trees is high.

For both domestic and industrial use, the greatest disadvantage in the use of these pellets is given by the amount of ash obtained, a consequence of the starting raw material. For industrial use, a use for the ashes must be found, which could range from filler in cement production to silica production.

Therefore, the process is an example where two forms of biowaste -tree leaves and lignin- are utilized in a circular economy development.

References

1. Lehtikangas, P. Quality properties of pelletised sawdust, logging residues and bark. *Biomass Bioenergy* **2001**, *20*, 351–360. [CrossRef]

2. Mani, S.; Tabil, L.G.; Sokhansanj, S. Evaluation of compaction equations applied to four biomass species. *Can. Biosyst. Eng./Le Genie Des Biosystemes Au Canada* **2004**, *46*, 55–61.

3. Mitchell, P.; Kiel, J.; Livingston, B.; Dupont-Roc, G. Torrefied biomass-A foresighting study into the business case for pellets from torrefied Biomass as a new solid fuel. *All Energy* **2007**, *24*, 1–27.

4. Fasina, O.O.; Sokhansanj, S. Storage and handling characteristics of alfalfa pellets. *Powder Handl. Process.* **1996**, *8*, 361–366.

5. Tumuluru, J.S.; Wright, C.T.; Hess, J.R.; Kenney, K.L. A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application. *Biofuels Bioprod. Biorefin.* **2011**, *5*, 683–707. [CrossRef]

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. Mani, S.; Sokhansanj, S.; Bi, S.; Turhollow, A. Economics of producing fuel pellets from biomass. *Appl. Eng. Agric.* **2006**, *22*, 421–426. [CrossRef]

8. Food and Agriculture Organization of the United Nations, FAOSTAT. Available online: http://www.fao.org/faostat/es/?#data/FO (accessed on 11 November 2019).

9. Telmo, C.; Lousada, J. Heating values of wood pellets from different species. *Biomass Bioenergy* **2011**, *35*, 2634–2639. [CrossRef]

10. Quirino, W.F.; Do Vale, A.T.; De Andrade, A.P.A.; Abreu, V.L.S.; Azevedo, A.C.D.S. Poder calorífico da madeira e de materiais ligno-celulósicos. *Revista Da Madeira* **2005**, *89*, 100–106.

11. Tarasov, D.; Shahi, C.; Leitch, M. Effect of additives on wood pellet physical and thermal characteristics: A review. *ISRN For.* **2013**, *2013*, 876939. [CrossRef]

12. García-Maraver, A.; Popov, V.; Zamorano, M. A review of European standards for pellet quality. *Renew. Energy* **2011**, *36*, 3537–3540. [CrossRef]

13. International Organization for Standardization. *Solid Biofuels–Fuel Specifications and Clases–Part 2: Graded Wood Pellets*; ISO 17225-2:2014; International Organization for Standardization: Geneva, Switzerland, 2014. Available online: https://www.iso.org/obp/ui/#iso:std:iso:17225:-2:dis:ed-2:v1:en (accessed on 25 February 2020).

14. Kaliyan, N.; Vance Morey, R. Factors affecting strength and durability of densified biomass products. *Biomass Bioenergy* **2009**, *33*, 337–359. [CrossRef]

15. Williams, O.; Taylor, S.; Lester, E.; Kingman, S.; Giddings, D.; Eastwick, C. Applicability of mechanical test for biomass pellet characterization for bioenergy applications. *Materials* **2018**, *11*, 1329. [CrossRef] [PubMed]

16. Hedlund, F.H.; Astad, J.; Nichols, J. Inherent hazards, poor reporting and limited learning in the solid biomass energy sector: A case study of a wheel loader igniting wood dust, leading to fatal explosion at wood pellet manufacturer. *Biomass Bioenergy* **2014**, *66*, 450–459. [CrossRef]

17. Obernberger, I.; Thek, G. *The Pellet Handbook: The Production and Thermal Utilization of Pellets*; Taylor & Francis: London, UK, 2010.

18. International Organization for Standardization. *Solid Biofuels–Determination of Mechanical Durability of Pellets and Briquettes–Part 1: Pellets*; ISO 17831-1:2015; International Organization for Standardization: Geneva, Switzerland, 2015. Available online: https://www.iso.org/standard/60695.html (accessed on 25 February 2020).

19. Kaliyan, N.; Vance Morey, R. Factors affecting strength and durability of densified products. In Proceedings of the American Society of Agricultural and Biological Engineers meeting, Portland, OR, USA, 9–12 July 2006. [CrossRef]

20. Thomas, M.; van del Poel, A.F.B. Physical quality of pelleted animal feed. 1-Criteria for pellet quality. *Anim. Feed. Sci. Technol.* **1996**, *61*, 89–112. [CrossRef]

21. Pietsch, W. *Agglomeration Processes–Phenomena, Technologies, Equipment*; Wiley-VCH: Weinheim, Germany, 2002.

22. European Pellet Council. *Handbook for the Certification of Wood Pellets for Heating Purposes*, 3rd ed.; ENplus: Brussels, Belgium, 2015.

23. Van Dam, J.E.G.; van den Oever, M.J.A.; Teunissen, W.; Keijsers, E.R.P.; Peralta, A.G. Process for production of high density/high performance binderless boards from whole coconut husk: Part 1: Lignin as intrinsic thermosetting binder resin. *Ind. Crop. Prod.* **2004**, *19*, 207–216. [CrossRef]

24. Petisco, C.; García-Criado, B.; Mediavilla, S.; Vázquez De Aldana, B.R.; Zabalgogeazcoa, I.; García-Ciudad, A. Near-infrared reflectance spectroscopy as a fast and non-destructive tool to predict foliar organic constituents of several woody species. *Anal. Bioanal. Chem.* **2006**, *386*, 1823–1833. [CrossRef] [PubMed]

25. The Official Website of Berlin, City Trees: Overview of the Stock Data. Available online: https://www.berlin.de/senuvk/umwelt/stadtgruen/stadtbaeume/en/daten_fakten/uebersichten/index.shtml (accessed on 20 December 2019).

26. Tumurulu, J.S.; Wright, C.T.; Kenny, K.L.; Hess, J.R. *A Review on Biomass Densification Technologies for Energy Application*; Idaho National Laboratory. U.S. Department of Energy: Idaho Falls, ID, USA, 2010.

27. Dieste, A.; Clavijo, L.; Torres, A.I.; Barbe, S.; Oyarbide, I.; Bruno, L.; Cassella, F. Lignin from *Eucalyptus* spp. kraft black liquor as biofuel. *Energy Fuels* **2016**, *30*, 10494–10498. [CrossRef]

28. Sokhansanj, S.; Fenton, J. *Cost Benefit of Biomass Supply and Pre-Processing*; BIOCAP Canada Foundation: Kingston, ON, Canada, 2006.

29. Alakangas, E. *New European Pellets Standards–EN 14961-1*; Eubionet3; VTT: Jyväskyla, Finland, 2011.