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Effects of Kraft Lignin and Corn Residue on the Production of Eucalyptus Pellets

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Abstract

Pellets have become an important renewable energy source. Aiming to contribute for diversifying the Brazilian energy matrix, the goals of this work were to evaluate the quality of the pellets of lignocellulosic residues (Eucalyptus and corn) produced with the addition of different percentages of Kraft lignin. For the production of pellets, mixtures of wood with bark of a *Eucalyptus urophylla* and *Eucalyptus grandis*, and corn residue were used as raw material. The proportions of corn residue in the mixture were 0, 20, 25, and 30% (w/w). Except for the control (0% lignin), 2 and 5% (w/w) Kraft lignin were added to a dry mass of raw material in the 4 different mixtures. Pellets were produced in a laboratory press pelletizer with horizontal circular array. The following properties of the pellets were evaluated: proximate analysis, high heating value (HHV), elementary analysis, energy density, bulk density, diameter and length, hardness, mechanical durability, and fine content. The pellets were classified according to European marketing standards. The addition of Kraft lignin to eucalyptus and corn residue pellets contributed to improving the physical and mechanical pellet properties, as regards the bulk density, mechanical durability, and fine content, allowing the transportation of a greater amount of mass and energy, besides maintaining the integrity of the biofuels during handling and use. The mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. The treatment with higher corn addition, in relation mechanical properties, showed a better performance in accordance with the European standards. The mechanical properties were above to 97.5%, besides that has no impact from the addition of Kraft lignin. The addition of up to 20% of corn residue has the potential to improve physical and mechanical pellet quality, with or without Kraft lignin addition. Thus, similar amounts to that of the treatment with the proportion of 80% eucalyptus and 20% corn residue can be a viable alternative to the production of pellets.

Keywords Additive · Solid fuel · Mechanical strength · Agricultural waste

Introduction

In the search for new energy sources to compete with the fuels currently available in the market, lignocellulosic residues have become one of the most promising options as alternative forms of energy. Lignocellulosic residues can be reused as raw material in a different manner; for instance, it can be used for heat or electricity generation [1–3] or for materials and chemicals, according the principle 7 of green chemistry—use of renewable feedstock [4–6]. In this context, agricultural residues and forest residues are an example of alternative source and contain a considerable reservoir of lignocellulosic wastes.

Agricultural residues such as rice husk, straw, and corn fibers are alternative source of lignocellulosic [7, 8]. The corn fibers are constituted mainly by three structural

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Statement of Novelty The use of lignin and corn residue to improve the physical and chemical properties of eucalyptus pellets for energy generation is a novel approach. Our results show that bulk density and mechanical durability were improved.

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components or fractions—lignin, cellulose, and hemicellulose—and each component has specific properties destined for different uses in biorefineries [9–11]. An integrated corn-based biorefinery can comprise bioproducts as value-added chemicals and fuel ethanol with a lower capital investment. Furthermore, hemicellulose and lignin permit expand the bioproduct possibilities to monomers, polymers, and chemicals of high value-added [12–16].

Forest residues, such as wood residue from harvest and processing, can be directly used as fuels. The definitions of the FAO cover data on the resource of wood processing residues by differentiating in two assortments: (1) wood chips and particles and (2) wood residues [17]. Wood industrial residue includes those materials derived from a manufacturing process, those derived from a logging process, and those that are reused or recycled from a harvest and manufacturing process, those derived from a logging process, and those that are reused or recycled [17–19].

Wood is the most-used raw material for energy production. Brazil has great forest potential, totaling 9.6 million hectares in 2020 [20], of which 7.5 million are dedicated to *Eucalyptus* plantations, although just 14% is destined for charcoal-fired steelworks [21, 22]. Wood residues are commonly used for basic fuel purposes in manufacturing facilities (to produce energy through the burning of this waste) but have also been used as sources of raw material bioenergy processes, the development of wood pellets or smaller wooden articles, and for pulp and paper processes. The use of *Eucalyptus* for energy purposes is mainly due to low ash generation and less corrosion of the combustion equipment, when compared with agricultural biomass [23–25].

However, when it comes to waste, the pretreatment of lignocellulosic materials is required, which is performed by the densification of the material, by using temperature and pressure, resulting in a material with granulometric homogeneity, higher density, and resistance to the generation of fines. This procedure is known as pelletization [22, 23, 26]. The pellet production process comprises the drying and grinding of the raw material, its pelleting, followed by cooling and sieving. During pelleting, the raw material is pressed by rollers through cylindrical compression channels and is converted into an agglomerated material due to the thermal softening of the lignin that promotes the agglutination of the particles [27, 28]. The increase in temperature, according to [27–29], makes lignin "plasticized" and acts as a natural binder of the particles after compaction of particles. The quality of the pellets can be improved by using binding additives in raw material, as Kraft lignin [30–32].

Kraft lignin can be extracted and used as other alternatives with more value-added, one example is the possibility of use as an additive for pellets. The Kraft lignin is obtained from Lignoboost process by black liquor generated by pulp mills, where they produce surplus energy that is obtained by burning the black liquor [33]. Lignin is a macromolecule that makes part of the chemical constitution of wood, and acts on the adhesion of the particles to form the pellets. The properties of Kraft lignin are specific to the extraction process and positively or negatively affect pellet properties [30, 31].

In this context, pellets can be an important alternative to transform biomass into higher value-added product used for energy purposes. Pellets are a new type of compressed fuel that enables the use of more modern firing equipment and facilitates long-distance biomass transportation.

It is very important to diversify the Brazilian energy matrix with the introduction of renewable energy sources and potentiate the use of forest and agricultural residues to reduce costs. Therefore, the objective of this work was evaluated the use of lignin and corn residue to improve the physical and chemical properties of eucalyptus pellets. The quality of produced with the addition of different percentages of Kraft lignin is a novel approach for energy generation.

Materials and Methods

Materials and Properties of *in natura* Particles

Wood biomass, corn residue, and Kraft lignin were used to produce pellets. Mixtures of *Eucalyptus urophylla* [34], *Eucalyptus grandis* [35] chips of a 6-year-old with the percentage of bark were approximately 10%, from sawmills located in state of Minas Gerais in Brazil, and corn residues were obtained from processing industry located in Brazil. Kraft lignin was prepared by the LignoBoost [33] process and was provided by a pilot pulp and paper mill located in São Paulo, Brazil.

Biomass residues were ground using a hammer mill and sieved to ensure particle size uniformity, according to TAPPI T257 cm-85 [36]. Subsequently, samples were dried at 60 ± 2 °C in an air circulation oven to 12 ± 2% humidity. The moisture content (dry basis) of biomass samples was determined using a halogen moisture analyzer. The residues (Eucalyptus and corn) and Kraft lignin were characterized according to the methods described in Table 1.

The bulk density was calculated by the ratio between the mass obtained and the volume of the biomass (100 cm^3). For analysis structural chemical composition, the holocellulose was obtained by the difference between the sum of (extractives, Klason lignin, and ash content) per one hundred percent.

The proximate analysis includes ash, volatile matter, and fixed carbon content. They are determined by means gravimetric tests, both direct and indirect, that allow their calculation. The high heating value (HHV) is defined as heat released when burning a gram of fuel in a calorimeter

Table 1 Characterization of residues, Kraft lignin, and their respective methodologies

Properties (unit)	Procedure
Bulk density (kg m^{-3})	DIN EN 15,103 [37]
Extractives soluble in alcohol/ toluene (%)	TAPPI T264 cn-97 [36]
Acid-insoluble lignin (%)	TAPPI T222 cm-11 [36]
Acid-soluble lignin (%)	TAPPI UM 250 [36]
Proximate analysis (%)	ABNT NBR 8112 [38]
Higher heating value (MJ kg^{-1})	ASTM D-2015–66 [39]
Elementary analysis (%)	DIN EN 15,104 [37]

(closed container). The equipment was used, an adiabatic calorimetric bomb, brand IKA® model 300.

Elementary analysis is defined as the determination of carbon, hydrogen, nitrogen, and sulfur and provides a convenient method for reporting the major organic elemental composition of coal. The equipment used was Vario Micro Cube CHNS, Elementar®. The sulfur content was also determined on the elemental analyzer. The oxygen value was determined by the sum of carbon, nitrogen, hydrogen, sulfur, and ash content decreased by 100, according to DIN EN 15,296 [37].

The estimate of the useful calorific power was carried out according to annex E of the DIN EN 14,918 standard [37]. Energy density was calculated by multiplying the useful calorific value by the bulk density of the material, as suggested by [40].

The results obtained were submitted to the Lilliefors test for normality [41] and the Cochran test for homogeneity of variance [42]. Characterization data of the residues and Kraft lignin were analyzed statistically by analysis of variance to evaluate differences between treatments. When significant differences were found between results, Tukey's *t* test was applied at the 95% significance level.

Pellet Production

Pelletizing experiments were produced from sawdust of the raw materials residues (Eucalyptus and Corn) and the Kraft lignin. Ideally, a woody feedstock should have a moisture content of 8–15% (w/w) [43] before entering the pellet mill. Pellets were produced in a laboratory press pelletizer with horizontal circular array (Amandus Kahl, model 14–175), with capacity for 50 kg h^{-1} production. The compression channels of the array had 6.0 mm internal diameter and 20.0 mm length.

About 1.5 kg of pellets was produced per batch, being three batches per treatment. To feed the pelletizer, a system consisting of an electric motor, a 38-speed controller, and an endless screw was used. The pelletizing temperature ranged from 95 to 100 °C, and the rollers rotation speed was 1500 rpm.

Table 2 Experimental planning

Treatments	Corn residue (%)	Eucalyptus (%)	Kraft lignin (%)
T1	0	100	0
T2			2
T3			5
T4	20	80	0
T5			2
T6			5
T7	25	75	0
T8			2
T9			5
T10	30	70	0
T11			2
T12			5

From this, pellets were produced with 4 different proportions of mixture of the two biomasses, eucalyptus and corn residue, and 3 proportions of the Kraft lignin added, being 12 treatments with 3 replications, totaling 36 pellet batches. Table 2 shows the experimental plan.

Classification of Pellets According to Quality Standards

The mixture of eucalyptus and corn residue pellets was classified as non-woody pellets, whose quality specifications are in accordance with DIN EN 14,961–6 [37] (Table 3). This standard refers to the quality of non-woody pellets for non-industrial use, and was used for classification of pellets in class A or B.

Evaluation of Pellet Properties

Pellets were reduced to smaller fractions, using the Willey mill, according to TAPPI standard T257 cm-85 [36], and later, the particles were selected in a set of sieves of 40 and 60 mesh for proximate analysis (fixed carbon content and volatile content), ash content, elementary analysis (C, H, O), and HHV.

Ash content analysis was determined according to the procedure established in the ASTM—D1762-84 standard [39] and proximate analysis according to ABNT NBR 8112 [38]. The HHV and elementary analysis were obtained according to the DIN EN 14,918 standard [37], using an adiabatic calorimeter pump IKA® model 300.

Moisture content of the pellets, after being stored for seven days, was determined according to the methodology described in the DIN EN 14,774–1 standard [37], in a laboratory oven at 105 ± 2 °C.

Table 3 Specifications for non-woody pellets

Properties (unit)	Origin	
	A	B
	Herbaceous biomass; fruit biomass; biomass mixture	Herbaceous biomass; fruit biomass; biomass mixture
Diameter (mm)	6 ± 1	6 ± 1
Length (mm)	$3.15 \leq \text{length} \leq 40$	$3.15 \leq \text{length} \leq 40$
Moisture content (%)	≤ 12	≤ 15
Ash content (%)	≤ 5	≤ 10
Mechanical durability (%)	≥ 97.5	≥ 96.0
Fines (%)	≤ 2	≤ 3
Net heating value (NHV) (MJ Kg^{-1})	≥ 14.1	≥ 13.2
Bulk density (kg m^{-3})	≥ 600	≥ 600
Nitrogen (%)	≤ 1.5	≤ 2.0
Sulfur (%)	≤ 0.20	≤ 0.20
Chlorine (%)	< 0.20	< 0.30

Source: Adapted from DIN EN 14,961–6 [37]

Mechanical durability and fine content (particles smaller than 3.15 mm) were determined by using the Ligno-Tester, Holmen® according to the DIN EN 15,210–1 standard [37] and the equipment's instructions. Pellet samples were blown by means of an air jet that simulates the natural destruction of pellets during transportation and handling in an inverted quadrangular pyramidal chamber. To determine the fine content, airflow had a pressure of 30 mbar for 30 s, and a sample of 0.300 kg of pellets was used. Subsequently, untreated samples were subjected to another controlled airflow (70 mbar) for 60 s to determine the mechanical durability, using 0.100 kg of pellets.

Bulk density of pellets was determined according to the DIN EN 15,103 standard [37].

Hardness (kg) was determined by the diametral compression test of the pellet in an Amandus Kahl manual durometer, with a scale of 0 to 100 kg. One pellet at a time was inserted in the durometer, and increasing load was applied until sample breakage. Afterwards, the maximum load (kg) the pellet withstands before breaking was read. The hardness of 30 pellets per batch was evaluated.

Diameter (mm) and length (mm) of the pellets were obtained according to the DIN EN 16,127 standard [37], measured in a digital caliper.

Data Analysis

The experiment was carried out in a completely randomized design with 12 treatments and three replications (pellet batches) in StatSoft, Inc. version 10.0 [44]. The results obtained were submitted to the Lilliefors test for normality [41] and the Cochran test for homogeneity of variance [42]. Proximate analysis (fixed carbon content and volatile content), ash content, elementary analysis (C, H, O), and HHV were subjected to analysis of variance (ANOVA), to verify the differences between the treatments. When significant differences were observed, the Scott test was applied at 95% significance.

Results and Discussion

Biomass Properties

Water has a crucial role in the pelletizing process and, along with lignin content, the moisture content of the feed is one of the most important parameters determining pellet durability [26, 45]. The moisture content for the corn residue and eucalyptus particles was on average 8.82% (wb) and 14.0% (wb), respectively. Thus, the corn residue moisture content is in accordance to that suggested by other authors for pellet production, which varies between 8 and 15% (wb) [23, 43].

Table 4 shows the mean values of the physical and chemical properties of the residues and the Kraft lignin. The HHV of wood (18.9 MJ kg^{-1}) and corn (19.2 MJ kg^{-1}), were significantly lower than that Kraft lignin (26.3 MJ kg^{-1}). It is noted that Kraft lignin, because of its agglutinating and energy properties, has a great energetic potential to be used as an additive in pellets [30, 46]. In addition, Kraft lignin has potential application as a binder, emulsifier, dispersant, favor agent, fertilizer, and copolymer adhesive [47–51]. The improvements concern properties such as higher heating values and lower ash contents, as well as lower slagging tendencies, and lower emissions of fine particles during combustion compared to wood (stem) pellets.

Pellet quality is largely a function of the type of feedstock and process parameters. Some feedstock parameters have a greater effect on pellet durability than other. The lignin

Table 4 Mean values of the physical and chemical properties of the particles of lignocellulosic residues and Kraft lignin

Characterization	Residues		Kraft Lignin
	Eucalyptus	Corn	
Bulk density (kg m^{-3})	137 (b)$^{12.78}$	-	492 (a)$^{14.07}$*
HHV (MJ kg^{-1})	18.9 (b)$^{0.32}$	19.2 (b)$^{0.43}$	26.3 (a)$^{0.25}$
Lower heating value (MJ kg^{-1})	17.5 (b)$^{0.56}$	18.0 (b)$^{0.45}$	25.1 (a)$^{0.67}$
Energy density (10^4 MJ m^{-3})	1.5 (b)$^{0.4}$	1.9 (a)$^{0.3}$	-
Elementary analysis (%)	C = 49.2; N = 0.2; H = 5.9; O = 44.3; S = 0.1	C = 50.1; N = 1.3; H = 5.1; O = 41.2; S = 1.4	C = 66.2; N = 0.2; H = 5.6; O = 23.4; S = 2.4
Volatile content (%)	89.13 (a)$^{0.52}$	84.33 (a)$^{0.48}$	1.1 (c)$^{0.3}$
Ash (%)	0.3 (c)$^{0.2}$	0.8 (c)$^{0.1}$	
Fixed carbon content (%)	10.60 (b)$^{0.40}$	14.86 (b)$^{0.56}$	
Extractives soluble in alcohol/toluene (%)	5.2 (a)$^{0.3}$	5.8 (a)$^{0.3}$	-
Acid-soluble lignin (%)	2.6 (d)^{0,4}	8.0 (c)^{0,3}	12.7 (c)$^{0.4}$
Acid-insoluble lignin (%)	33.2 (b)$^{0.2}$	4.0 (d)$^{0.1}$	85.4 (a)$^{0.2}$
Klason lignin (%)	35.8 (b)$^{0.2}$	12.0 (c)$^{0.3}$	98.1 (a)$^{0.3}$
Holocellulose (%)	59.0 (b)	64.8 (a)	0.2 (c)

*Means followed by the same letter in parentheses for wood residues (within the same row), and for Kraft lignin (within the same row), do not differ from each other by the Tukey test at 5% probability. Standard deviations are overwritten

content is possibly the most important parameter, followed by moisture content, as these two factors directly interact to affect the temperature at which lignin softens. There are some conflicting results found in the effect of extractives on pellet durability: some studies suggest they lubricate the passage of material through the mill, whereas a few other studies suggest they have a role in binding [28, 45].

Lignin, extractive, and holocellulose content for the biomass showed different contents in between the feedstocks. The effect of extractive content may be dependent on the particle size distribution and the lignin content. Changes in moisture content may also have positive or negative effects on durability, though it appears that there is some interaction with the extractive content [28, 43].

Pellet Properties

Table 5 shows the elementary analysis, proximate analysis, energy density, HHV, and hardness of pellets.

Biomass is composed of elements C, H, O, N, S, and Cl, where the former three are the major, representing up to 97–99% (w/w) of the biomass organic mass. Elementary analysis gives the weight percent of the elements. In Table 4, the elementary analysis (C, H, and O%) of the three main elements indicates the addition of the Kraft lignin affected the treatments for pellet production. Kraft lignin is an organic compound extracting by pulping black liquor, producing a material with high energy density and low ash content. Already the fixed carbon content increased with the addition of 5% (w/w) of Kraft lignin and the volatile content decreased. It should be noted that fuel materials with high fixed carbon content present slower burning, implying a longer residence time inside the burners compared to other that have lower fixed carbon content [28, 52].

Biomass has not been widely utilized due to its relatively low energy density when compared with fossil fuels. This low energy density results in inhibitive transportation costs and inconvenient storage and handling. In Table 5, it can be observed that with the increase of the corn residue addition, there was a decrease in energy density, which may be related to the lower lignin content of corn residue (12.0% w/w) in relation to eucalyptus (35.8% w/w).

In relation to the hardness (Table 5), a high value was observed without corn residue. According to [24, 28], the compressive strength of the pellets is related to the adhesion forces between particles. Wood of the genus Eucalyptus has greater lignin ratio syringyl/guaiacyl (S/G); it consequently has more points of contact between the particles of the pellets, leading to greater adhesion and therefore greater the hardness [53].

HHV of the pellets (Table 5) was observed higher value with 0% of corn residue. For all treatments, it was similar, with no effect the addition of Kraft lignin, except the treatment with 25% (w/w) of corn residue that presented an addition of HHV with the addition of 5% (w/w) of Kraft lignin. According to [45, 46], higher lignin contents contribute to the increase in the higher calorific value of the fuel, since lignin's HHV of 26.3 MJ kg^{-1} is higher than the

Table 5 Elementary analysis, proximate analysis, energy density, HHV, and hardness of pellets

Corn residue (%)	Kraft lignin (%)	C (%)	H (%)	O (%)	Fixed carbon content (%)	Volatile content (%)	Energy density (10^4 MJ m^{-3})	Hardness (Kg cm^{-2})	HHV (MJ kg^{-1})
0	0	50.4 (a)	6.1 (a)	42.8 (c)	14.9 (b) $^{0.4}$	84.8 (a)$^{0.5}$	5.4 (b)	65.2 (a)	20.0 (a)$^{0.3}$
0	2	50.8 (a)	6.0 (a)	42.6 (c)	13.9 (b) $^{0.5}$	85.3 (a)$^{0.6}$	5.5 (a)	65.8 (a)	20.1 (a)$^{0.4}$
0	5	49.8 (b)	5.9 (a)	43.7 (a)	16.9 (a) $^{0.4}$	82.8 (b)$^{0.5}$	5.5 (a)	58.0 (b)	20.1 (a)$^{0.3}$
20	0	49.6 (c)	6.2 (a)	43.2 (b)	15.1 (b) $^{0.2}$	84.7 (a) $^{0.3}$	4.9 (c)	49.4 (c)	19.3 (c)$^{0.4}$
20	2	50.4 (a)	6.2 (a)	42.2 (d)	14.5 (b) $^{0.4}$	85.2 (a) $^{0.3}$	4.5 (d)	50.2 (c)	19.8 (b)$^{0.4}$
20	5	49.6 (c)	6.1 (a)	43.3 (b)	16.9 (a) $^{0.3}$	82.7 (b) $^{0.2}$	4.4 (e)	56.0 (b)	19.4 (c)$^{0.2}$
25	0	49.5 (c)	6.1 (a)	43.2 (b)	15.3 (b) $^{0.4}$	84.4 (a) $^{0.4}$	4.0 (g)	47.5 (c)	19.4 (c)$^{0.3}$
25	2	50.1(b)	6.2 (a)	42.6 (c)	14.0 (b) $^{0.2}$	85.8 (a) $^{0.2}$	4.4 (e)	51.8 (c)	19.6 (c)$^{0.3}$
25	5	50.5 (a)	6.1 (a)	42.1 (d)	17.3 (a) $^{0.4}$	82.3 (b) $^{0.5}$	4.3 (f)	54.4 (c)	19.8 (b)$^{0.4}$
30	0	49.6 (c)	6.1 (a)	43.1 (b)	13.9 (b) $^{0.5}$	85.7 (a) $^{0.6}$	3.7 (h)	40.4 (d)	19.3 (c)$^{0.2}$
30	2	50.3 (a)	5.4 (b)	43.1 (b)	14.6 (b) $^{0.4}$	85.0 (a) $^{0.4}$	4.0 (g)	48.0 (c)	19.5 (c)$^{0.4}$
30	5	50.0 (b)	6.1 (a)	42.4 (d)	16.1 (a) $^{0.4}$	83.5 (b) $^{0.2}$	3.6 (i)	47.4 (c)	19.5 (c)$^{0.2}$

*Means followed by the same letter in parentheses for wood residues (within the same row), and for Kraft lignin (within the same row), do not differ from each other by the Scott test at 5% probability. Standard deviations are overwritten

other primary components of the wood. Higher HHV means a smaller mass and hence smaller volume of pellets will be needed to provide the desired energy. Therefore, the HHV of Kraft lignin was not high enough to contribute to the increase of HHV of the pellets, for most treatments, since the maximum percentage of lignin added was of 5% (w/w).

Properties of the Pellets in Accordance with DIN EN 14,961–1

The common standard (DIN EN-14961) will form the platform for a certification system with the European Standard Committee, identifying the specifications for different categories of pellets [37]. Generally, the highest grades have the strictest standards and offer the best combustion properties. The specifications for heating pellets are stricter than for industrial pellets, requiring lower contents of ash, fines, nitrogen, sulfur, and chlorine (Table 3). The DIN EN 14,961–1 [37] standard also introduces some sustainability criteria to regulate the environmental impacts of sourcing and trading of non-woody pellets. Figures 1 and 2 show the properties of pellets that meet European quality standards.

Densification of biomass could result in a significant increase in the bulk density of biomass. Bulk density is defined as the mass per unit volume of biomass. Figure 1A shows the results of bulk density of all the evaluated treatments. The observed higher bulk density was with 0% (w/w) of corn residue. Therefore, greater the mass that can be transported or stored in a fixed volume container, thus minimizing transport and storage costs. Reduction of the bulk density is observed as the proportion of the corn residue increases. Conversely, in the addition of Kraft lignin, there is a significant difference, but, as the difference is present at 0% (w/w) of added Kraft lignin. It can be explained that the Kraft lignin composition has higher content and non-structural compounds [30, 31]. Pellets with 30% (w/w) addition of corn residue did not meet the DIN EN 14,961–1 [37], which should be greater than 600 kg m^{-3}.

Biomass, by its nature, is hygroscopic. Stable pellets can be formed with a range of moistures between 8 and 12% (wb) depending on the biomass in question. For the moisture content of the pellets (Fig. 1B) tended to increase due to the higher proportions of corn residues in the mixture and addition of lignin varied according to the different treatments. The higher moisture content increases the extent to which the pellets "relax" after formation. The biomass expansion behavior after compression and extrusion through the pellet matrix, which can decrease durability and reduce the temperature at which lignin plasticizes (Tg), increases the bond between particles [25–27]. An increase in temperature increases diffusion but also increases contraction, which decreases diffusion. As the first phenomenon is more substantial, the resulting effect of the increase in temperature is an accentuated humidity [27]. All treatments met the requirements of DIN EN 14,961–6 [37], which indicates a maximum moisture value of 12% (wb) for Type A pellets.

For fine content, no statistical difference was observed between the evaluated treatments, which evidences that the addition of both corn residues and Kraft lignin did not influence this property of the pellets (Fig. 1C). Regardless of the treatment, percentage of fines was below the maximum allowed by the European standard, which stipulates values lower than 2%. Therefore, they were all treatments all are according to the DIN EN 14,961–1 [37], because they are below the 2% limit.

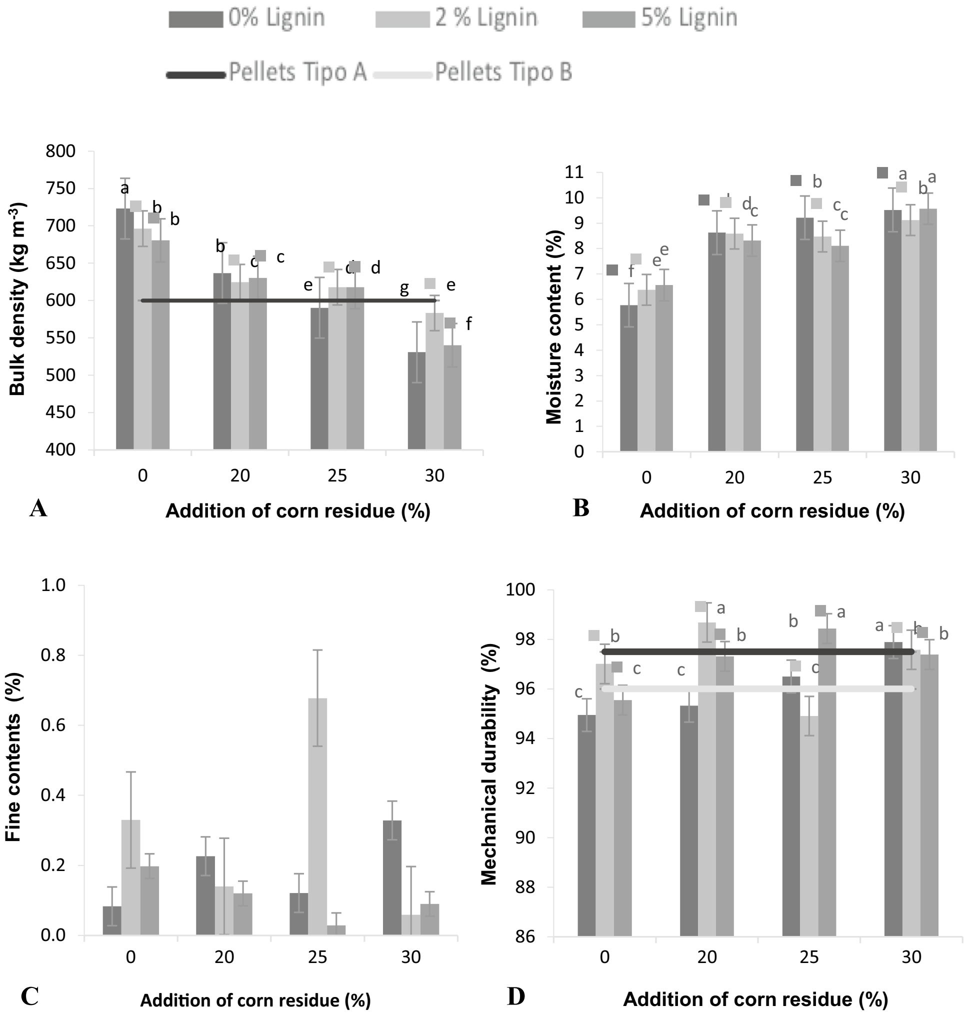

Fig. 1 Properties of pellets for the treatments: **A** bulk density (kg m^{-3}); **B** moisture content (%); **C** fine content (%); **D** mechanical durability (%). Bars followed by the same small letter do not differ among themselves at 5% probability (Scott, $p > 0.05$)

Mechanical durability is the most important physical quality of a pellet [11, 54], which simulates the resistance of the pellets to mechanical impacts during storage and transportation, must be greater than or equal to 97.5%, according to the DIN EN 14,961–2 standard [37]. In Fig. 1D, with 0% (w/w) of corn residue, only the pellets produced with 2% (w/w) lignin were in accordance with the DIN EN 14,961–1 [37]. By adding 20% (w/w) of corn residue, pellets with 2% (w/w) of lignin were in accordance with the DIN EN 14,961–1 [37] how as type A pellets, and with the proportion of 5% (w/w) of lignin were in accordance with the DIN EN 14,961–1 [37] how as type B pellets; however, 0% (w/w) of lignin for this proportion did not meet the standard. In the addition of 25% (w/w) of corn residues, 5% (w/w) of lignin had the best results for the production of pellets. Pellets produced with 0% (w/w) lignin were in accordance with the DIN EN 14,961–1 [37] how as type B pellets, and those produced with 2% (w/w) lignin did not meet the standard. The behavior of the pellets in the proportion of 20% and 25% of corn residues, in relation to mechanical durability, showed that for a 20%, the addition of 2% of lignin was sufficient, while for the 25%, an addition of 5% of Kraft lignin was necessary to obtain a mechanical durability above 98%.

The percentage of 30% (w/w) of corn residue pellets produced with 0% (w/w) and 2% (w/w) of lignin was in accordance with the standard how as type A pellets, and those produced with 5% (w/w) lignin were in accordance the standard how as type B pellets. The treatment with higher corn addition showed a better performance and there is no impact of the lignin addition.

Figure 2 shows the results of the ash contents, nitrogen content, and size of the pellets. Ash content as can be seen in Fig. 2A varied greatly among treatments and was classified as pellets type A, in accordance with DIN EN 14,961–1 [37], because they are below the 5% limit. Higher ash content is undesirable for pellets, since they are inversely proportional to HHV, besides being the combustion residue and depending on the constitution chemistry of the ashes; it is possible to form incrustations in the combustion equipment [40, 54].

In theory, a nitrogen content of agricultural residues is higher than those of woody biomass due to the large amounts of N fertilizer applied during crop growth [28, 55].

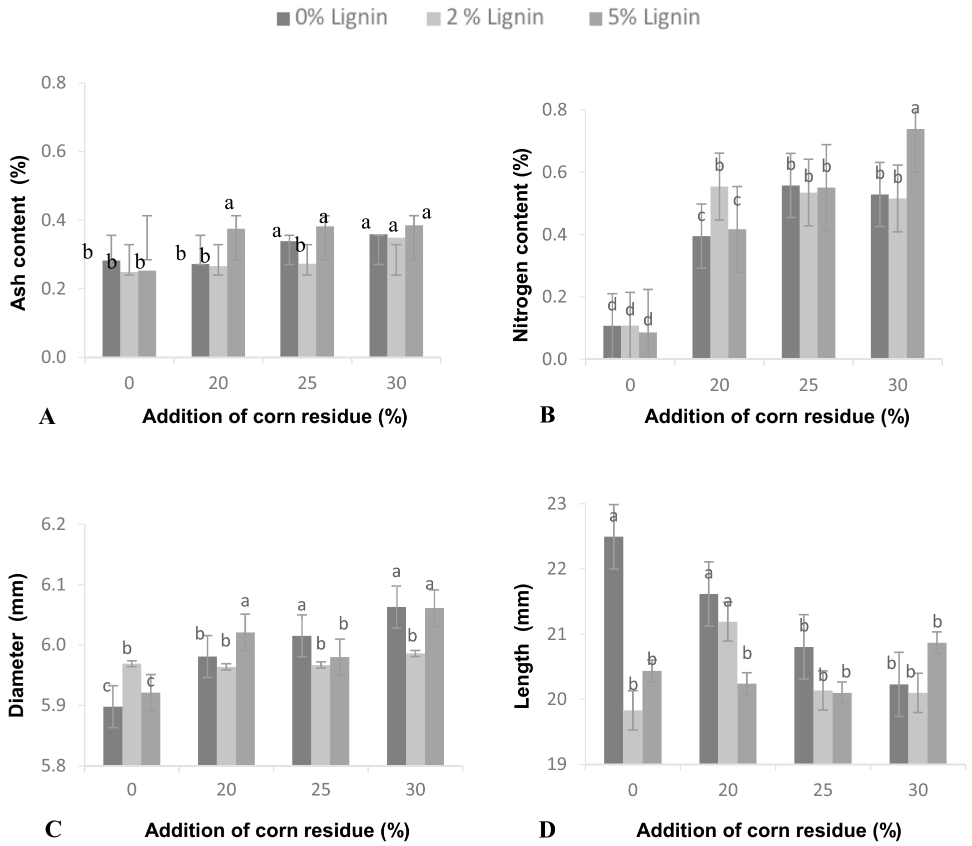

Fig. 2 Properties of pellets for the treatments: **A** ash content (%); **B** nitrogen content (%); **C** diameter (mm); **D** mean length of the pellets (mm). Bars followed by the same small letter do not differ among themselves at 5% probability (Scott, $p > 0.05$)

In Fig. 2B, the higher nitrogen content is the pellets with the addition 30% (w/w) of corn residue and 5% (w/w) of lignin. This is also shown in the EN classes that all treatments of pellets are classified as type A, in accordance with DIN EN 14,961–1 [37], because they are below the 1.5% limit. Higher nitrogen content can lead to elevated NOx emissions which, along with SO_2, has great environmental relevance in terms of acid rain [28].

The strong, uniformed-size of biomass pellets with high bulk density makes them easier handle, transport, and store. The values of diameter (5–7 mm) and length (3.15–40 mm) are in accordance with the requirements of the DIN EN 14,961–2 standard [37], as observed in Fig. 2D, for all the treatments. According to [28, 56], the dimensions and shape of the pellets should be homogeneous for the best functioning of small-scale furnaces and automatic heating equipment.

Conclusions

Besides the technical and operational advantages of pellets, when compared with other fuel sources, the association with residual biomass during the production process makes the product with potential to compete in the pellet market. Regarding the mechanical properties, the treatment with higher corn addition showed a better performance in accordance with the European standards, because they are above the 97.5% limit. Beyond that, it has no impact from the addition of Kraft lignin.

The mixing of eucalyptus with corn residue is an effective way to optimize properties of biomass solid fuel. The addition of up to 20% of corn residue has the potential to improve pellet quality, with or without Kraft lignin addition. Thus, similar amounts to that of the treatment with the proportion of 80% eucalyptus and 20% corn residue can be a viable alternative to the production of pellets.

The addition of Kraft lignin in the pellets of a mixture of lignocellulosic residues (Eucalyptus and corn) contributed to improving the physical and mechanical pellet properties, as regards the bulk density, mechanical durability, and fine content, allowing the transportation of a greater amount of mass and energy, besides maintaining the integrity of the biofuels during handling and use.

Author Contribution Bianca M. Barbosa—experiments for her PhD thesis and manuscript draft. Sílvio Vaz Jr.—manuscript review and submission; Bianca M. Barbosa's thesis co-supervision. Jorge Luis Colodette—Bianca M. Barbosa's thesis supervision. Humberto Fauller de Siqueira—manuscript review and assistance during experiment. Carlos Miguel Simões da Silva—manuscript review and assistance during

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Data Availability The datasets generated during and/or analyzed during the study are available in the Federal University of Viçosa repository for doctorate thesis and for master dissertations.

Declarations

Consent for Publication All authors agree with submission to BioEnergy Research, being represented by the author for correspondence.

Competing Interests The authors declare no competing interests.

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