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Article

Lignin Use in Enhancing the Properties of Willow Pellets

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Abstract: Shrub willow (*Salix* spp.) is an emerging lignocellulosic biomass utilized in fuel pellets as an energy source. However, improvements are needed to increase the efficacy of pellets in areas such as the energy content, durability, and hazardous carbon monoxide emissions. This study examined the effect of utilizing lignin as an additive on willow pellet properties. Two types of lignin were used in individual treatments: lignin recovered from the hot water extraction of willow (RecL) and commercial softwood kraft lignin (ComL). A statistical analysis of the ash content, energy content, bulk density, durability, pellet length, moisture absorption, and carbon monoxide emissions for the pellets with and without the addition of RecL or ComL lignin was conducted. The observed significant reduction in carbon monoxide emissions from RecL pellets was an important effect of the lignin addition. There were also significant increases in the energy content, bulk density, and durability of lignin-added pellets. While the production of carbon monoxide via pellets continues to be explored, lignin can be utilized as an additive to reduce carbon monoxide emissions and simultaneously improve other pellet properties.

Keywords: lignocellulosic biomass; solid biofuel; carbon monoxide emissions

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1. Introduction

Lignocellulosic biomass (LCB) is an attractive renewable resource consisting of three major constituents: cellulose (a homopolysaccharide of β-D-glucopyranose units connected via β-(1→4) glycosidic bonds), hemicelluloses (heteropolysaccharides that are mostly branched and consist of various pentoses and hexoses), and lignin (an amorphous polymer consisting of phenylpropanoid units) [1,2]. LCB can be utilized to displace a portion of non-renewable fossil fuels and address the increasing energy needs of the growing population. The U.S. Energy Information Administration projected an increase in energy consumption in the United States by up to 15% from 2022 to 2050 [3]. Energy can be derived from LCB in the form of biofuels—such as via the conversion of polysaccharides to bioethanol [2]—or by directly combusting the LCB itself—such as in repurposed coal-fired boilers [4]. Both forest-derived LCB (such as softwood and hardwood trees and forest residues) [5] and agricultural-derived LCB (such as agricultural residues and herbaceous and woody energy crops) [5] are utilized for energy purposes. Exploration into the use of agricultural-derived LCB for energy production has gradually increased as an alternative that does not directly compete for fertile agricultural food crop land [6]. Shrub willow (*Salix* spp.) is a short rotation woody crop that can grow on marginal land [7] and has been examined in recent studies for its use as an energy source [8]. Shrub willow has regional availability in the Northeastern United States due to the Salix Consortium's Willow Biomass project in conjunction with the State University of New York College of Environmental Science and Forestry (SUNY-ESF), through which shrub willow was planted on over 200 hectares in western and central New York in 2003 [9] and on over 500 hectares throughout the

Northeastern region (as of 2018) [10]. As such, shrub willow was selected for this project due to its availability and to further explore the use of willow as an energy source [8].

However, the utilization of LCB for energy has disadvantages. The bulk density of LCB in various forms is lower than that of traditional energy sources such as coal (Table 1) as is its energy content (typically reported as the gross calorific content or higher heating value) (Table 2). LCB is susceptible to absorbing moisture, which can decrease its energy yield (if the latent heat of vaporization is not recovered), [11] as well as make it more prone to physical, chemical, and biological degradation [12,13]. The high ash content of LCB can also cause damage to boilers and prevent efficient combustion [14,15].

Table 1. Comparison of bulk density of various lignocellulosic biomass (LCB) and coal.

Material	Bulk Density (kg/m^3)
Coal	
Lignite	560–574 [A]
Bituminous	670–910 [B]
Anthracite	800–930 [B]
Forest-Derived LCB	
Softwood	
Chips	160–215 [C]
Pellets	578–637 [D]; 681 [E]; 700 [F]
Hardwood	
Chips	180–235 [C]
Pellets	650 [G]
Agricultural-Derived LCB and Energy Crops	
Wheat Straw	
Loose	20–40 [H]
Chopped	20–80 [H]
Baled	110–200 [H]
Pellets	560–710 [H]
Miscanthus	
Chopped	26 [I]
Baled	230 [J]
Pellets	615 [E]; 624 [K]
Willow	
Chips	195–393 [L]
Pellets	655 [E]; 690 [M]

References: [A] [16] [B] [17] [C] [11] [D] [18] [E] [19] [F] [20] [G] [13] [H] [21] [I] [22] [J] [23] [K] [24] [L] [25] [M] [8].

Pelletizing is a process of densification that converts LCB into fuel pellets of increased bulk density more comparable to that of coal (Table 1), and therefore also of increased energy density. During the pelletizing process, LCB ground into a finer particle size (typically using a hammermill of screen size 1 mm to 6.35 mm [19,23,26–32]) is forced through small channels in a metal die, resulting in interactions between the LCB particles. This surface interaction can create an interlocking of the particles for pellet formation [33]. Friction forces resulting from contact between the particles and the die surface also generate heat, which leads to an improved bonding of constituents within the LCB.

Table 2. Comparison of energy content (listed as the higher heating value unless otherwise noted) of various lignocellulosic biomass (LCB) and coal.

Material	Energy Content (MJ/kg)
Coal	
Lignite	13.14–17.31 [A]; 22.04 [B]; 23.21 [C]
Bituminous	17.33 [D]; 21.90–29.19 [A]
Anthracite	19.35–30.00 *[E]
Forest-Derived LCB	
Softwood	17.38 [F]; 19.7–20.2 [G]; 21–21.2 [H]
Hardwood	17.6–19.1 [G]; 19.9–20.1 [I]
Agricultural-Derived LCB and Energy Crops	
Wheat Straw	12.3 [H]; 17.5 [I]
Miscanthus	17–20 [J]
Willow	18.6–18.8 [K]; 19 [L]

* Higher heating value or lower heating value not specified. References: [A] [34] [B] [16] [C] [35] [D] [36] [E] [17] [F] [37] [G] [38] [H] [21] [I] [39] [J] [40] [K] [41] [L] [42].

The exact bonding mechanisms between LCB constituents—mainly cellulose, hemicelluloses, and lignin—and any binders utilized in pelletizing—such as starches—are still being explored. Anukam et al. [43] examined the interactions within Norway Spruce and pea starch during pelletizing. It was found that bonding in Norway Spruce was mostly due to van der Waals forces, while dipole–dipole interactions and hydrogen bonding were mainly present in the pea starch. However, all three mechanisms were present when Norway Spruce and pea starch were mixed prior to pelletizing.

Anukam et al. [44] noted that the polar functional groups—such as hydroxyl, carboxyl, and carbonyl groups—play a significant role in the attractive electrostatic forces between LCB constituents during pelletizing, and that additives can enhance these interactions. Under the compression forces and increased temperature resulting from the pelletizing conditions, the strength of intermolecular forces in the cellulose structure increases, leading to more contact area for improved inter-particle bonding via the -OH groups [44]. Hemicelluloses also influence bonding to the extent that it depends on the degree of branching. Xylans, which are typically more branched than glucomannans, result in greater pressure and energy required to pelletize, contributing to the difference in pelletizing softwoods and hardwoods [45]. Their adhesive properties expressed under dehydration conditions, which are intrinsic to pelletizing, and the reactivity of the hydroxyl groups and other functional groups (such as acetyl groups in acetylated hemicelluloses) present on hemicelluloses are also proposed to affect the bonding [44]. Lignin is considered to play a “glue-like” role because of its ability to interact with polysaccharides. The presence of polar functional groups in lignin promote the formation of intra- and inter-molecular bonds via covalent and hydrogen bonding as well as dipole–dipole interactions that are “activated” under the compression and temperature forces that occur during pelletizing [44]. Additionally, constituents in LCB such as lignin [46] and hemicelluloses [47] reach their glass transition temperature (T_g) during pelletizing in which they begin to soften, and in some cases, become fluid [45]. By softening and resolidifying (upon cooling the pellets), these polymers are believed to promote bridging between the LCB particles, yielding more durable particle–particle interactions [48].

Current studies are aimed to elucidate and improve the interactions between lignin and the other LCB constituents to promote bonding during pellet production. Moreover, as an aromatic polyphenolic polymer, lignin exhibits unique features that may improve other pellet properties. Lignin has radical scavenging capabilities directly related to free phenolic hydroxyl groups and expanded by methoxyl groups that help stabilize the phenoxy radicals [49]. Additionally, compared to cellulose and hemicelluloses in LCB, lignin is more hydrophobic and contains hydroxyl groups that are different in their interaction with moisture [50]. Considering the energy of combustion as critically important for fuel pellets, the lower oxygen content in respect to carbon and hydrogen results in lignin displaying a higher energy content than cellulose and hemicelluloses [51] (21.0–26.6 MJ/kg for lignin [39,52], 17.0 MJ/kg for cellulose [39,52], and 16.6 MJ/kg for hemicelluloses [52]).

Lignin has been utilized in several studies as a binding agent added to the LCB prior to pelletizing (Table 3). However, lignin did not demonstrate a consistent effect on the bulk density of pellets. Additionally, it has been reported that most pellets with lignin as an additive contained more ash than the control pellets, adversely affecting the fuel pellet combustion (Table 3). However, eucalyptus pellets containing 2% and 5% kraft lignin had lower ash than the control [53], while eucalyptus pellets containing 1% and 2% lignosulfonate in a different study [54] reported an inconsistent effect on pellet ash. Regarding moisture absorption, adding lignin to spruce resulted in an increase in moisture absorption at equilibrium compared to when lignin was not added [55]. This is contrary to the expectation that lignin would reduce moisture absorption because of its more hydrophobic nature, as previously noted.

Generally, the energy content of pellets increased with the addition of lignin. However, one study [56] reported that lignosulfonate had a lower energy content than the pine to which it was added; therefore, it reduced the energy content of the resulting pellets. This result demonstrates the presence of impurities, which adversely affect the energy content. Musl et al. [57] reported that lignosulfonates typically contain carbohydrate impurities, such as the high xylan content in eucalyptus and beech lignosulfonate. Kuokkanen et al. [56] reported that the lignosulfonate contained more ash than pine wood and observed an increase in the ash content in pine pellets produced with lignosulfonates as an additive.

Table 3. Effect of lignin addition to lignocellulosic biomass (LCB) on fuel pellet properties.

LCB and Lignin Type	Ash Content	Energy Content	Bulk Density	Durability	Pellet Length	Moisture Absorption
Mixed Softwoods (Pine, Spruce, and Fir) and High Purity Indulin AT Lignin [A]	--	↑	--	--	--	--
Norway Spruce (*Picea abies*) and LignoBoost Kraft Lignin (Dry * and Wet *) [B]	--	↑	X	↑	↑	--
Scotch Pine (*Pinus sylvestris*) and Lignosulfonate [C]	↑	↓	--	↑	--	--
Spruce (*Picea* sp.) and Kraft Lignin [D]	↑	↑	--	↑	↑	↑
Pine (*Pinus* sp.) and Kraft Lignin [E]	--	--	X	↑	--	--
Larch (*Larix kaempferi* C.), Tulip Tree (*Liriodendron tulipifera* L.) and Alkaline Lignin [F]	--	--	--	↑	--	--
Eucalyptus (*Eucalyptus urophylla*, *Eucalyptus grandis*) and Kraft Lignin [G]	↓	↑	↓	↑	↓	--
Eucalyptus (*Eucalyptus nitens*) and Sodium Lignosulfonate [H]	X	↑	--	--	--	--

↑: Value of pellet property increased with lignin addition compared to the control (no lignin addition). ↓: Value of pellet property decreased with lignin addition compared to the control (no lignin addition). --: Not reported/Pellet property not examined. X: Effect of lignin on pellet property inconclusive (implies no direct trend). * Dry refers to <10% moisture content; wet refers to 30%–40% moisture content. References: [A] [58] [B] [18] [C] [56] [D] [55] [E] [59] [F] [60] [G] [53] [H] [54].

Overall, the use of lignin as an additive in pelletizing has been reported to have a generally positive effect on the mechanical properties of pellets (such as the durability and pellet length), as seen in Table 3. Moreover, based on its antioxidizing capacity, lignin has a potential to serve an additional role in improving the quality of fuel pellets in respect to their inherent emission of carbon monoxide (CO).

While pelletizing addresses issues regarding the bulk density of LCB, it exacerbates the generation of CO in storage as a major health and safety concern with utilizing fuel pellets in large quantities. Levitt et al. [61] studied various sources of LCB, such as cotton, paper, and wood (pine), at an ambient temperature and concluded that these materials are constantly releasing small amounts of CO. However, CO production occurs in vastly larger concentrations for fuel pellets because of their densified nature. Tumuluru et al. [62] examined the CO emissions in ground switchgrass, pine wood chips, and pine wood pellets, indicating that the wood pellets produced the greatest amount of CO (1600 ppmv), followed by wood chips (600 ppmv) and ground switchgrass (<200 ppmv). CO emissions were also examined in pellets produced from softwoods, hardwoods, and a blend of softwoods and hardwoods; the softwood pellets were reported to have the highest average concentration of CO emissions (1000–13,440 ppm [13,63,64]), the blended pellets had a range of 300–800 ppm [13,63], while the hardwood pellets were shown to vary between 400 and 1200 ppm [13].

Currently, the proposed mechanism for the production of CO from LCB starts with the autoxidation of lipophilic extractives, i.e., unsaturated fatty acids, with reactive oxygen species to form radicals [63], which then react with hemicelluloses to form CO [63]. However, Siwale et al. [65] examined the addition of lipophilic extractives (linseed oil, tall oil, and pine rosin) to pine sawdust prior to pelletizing and reported that the CO production of these extractives-added pellets did not significantly change compared to the control (fresh pine pellets). The authors noted that this could be due to the saturation of these extractives in the pellets compared to the limited amount of oxygen available in the testing apparatuses [65]. Comparatively, an additional study from Siwale et al. [66] examined the CO production from cellulose pellets containing these lipophilic extractives and reported that pellets containing linseed oil were the only pellets to produce a significant amount of CO [66].

While the role of lipophilic extractives continues to be explored in the literature, the involvement of radicals in the production of carbon monoxide from fuel pellets seems more apparent. Several studies have examined the use of antioxidizing agents or treatments—such as 1-butanol [63], ozone pretreatment of LCB [67], *tert*-butylhydroquinone (TBHQ) [68], propyl gallate (PG) [68], and acetylsalicylic acid (ASA) [69] to reduce CO emissions from fuel pellets. Additionally, Moreira et al. [70] explored the use of tobacco extract from illicit cigarettes as a source of alkaloids, aldehydes, ketones, and terpenoids capable of quenching reactive oxygen species in the production of carbon dioxide (CO_2), a gaseous compound which is commonly co-emitted with CO during the storage of fuel pellets [13,65,70]. Moreira et al. reported that the tobacco extract reduced the off-gassing of CO_2 but negatively affected the combustion of the pellets, resulting in the increased slagging and fouling of pellets, as well as the emission of undesirable combustion gasses. Rahman et al. [67] examined the effect of ozone treatment on the energy content of pellets as well and reported a minimal impact on the energy of pellets after the ozonolysis of the biomass prior to pelletizing. However, most of these studies did not explore any potential effect of these antioxidants on other important pellet properties. Utilizing lignin to act as a radical scavenger could have a multifaceted effect on pellet properties by reducing CO emissions and simultaneously enhancing their mechanical and energy properties.

The purpose of this work was to examine the effect of two types of lignin; commercial softwood kraft lignin (ComL) and lignin recovered from the hot water extraction of shrub willow (RecL) as binding agents on the properties of shrub willow pellets, including CO emissions. Kraft lignin originates from the most dominant chemical pulping technology used currently in the pulp and paper industry. Lignin recovered from the hot water extract of willow is the byproduct of an emerging autohydrolytic pretreatment of hardwoods. In previous studies, industrial kraft lignin has been incorporated in fuel pellets to analyze its effect on pellet quality without addressing CO emissions [18,58], whereas RecL has been investigated for its use in various applications, including novel phenol-formaldehyde-free novolac-type adhesives [71], thermoplastics, and hydrogels [72]; however, its use as a binding agent in fuel pellets has yet to be explored to the best of our knowledge.

2. Materials and Methods

2.1. Procurement of Lignocellulosic Biomass and Lignin

All shrub willow (*Salix* spp.) was procured from mixed cultivars from the SUNY-ESF Tully Field Station in Tully, NY. Willow utilized for the hot water extraction (HWE) experiments was received and processed in Summer of 2016 to obtain the recovered lignin (RecL). Two batches of willow, received in Fall of 2020 and Spring of 2021, were utilized for pelletizing that was conducted with the laboratory scale pelletizer in Fall of 2022. Willow was chipped (2 cm long pieces) without bark removal prior to receiving on-site. Willow was stored indoors in covered supersacks and was allowed to air dry prior to hammermilling and pelletizing (inlet moisture content: 6.83%). The moisture content of the willow was measured with a modified version of TAPPI Standard T-412 [73]. The chemical composition of the willow (acid-insoluble lignin: 22.50%; acid-soluble lignin: 2.42%; polysaccharides content [glucan, xylan, mannan, arabinan]: 50.17%; ash content: 1.47%) was characterized in previous work [72].

Recovered lignin (RecL) from the willow chips was obtained in the following manner. The willow chips were subjected to HWE on a pilot scale using a 1.84 m^3 Struthers-Well batch digester (Santa Fe Springs, CA, USA) with a liquid-to-solid ratio of 4.3–4.5 at an operating temperature of 160 °C for 2 h. Hydrolysate from the HWE was collected, cooled to room temperature, and acidified to a pH of 2.0–2.3 with 20% sulfuric acid to precipitate the lignin. After a settling period of 1–3 d, the supernatant was decanted, and the RecL was air dried [72]. Once dry, the RecL was ground in a coffee grinder to produce a more homogenous powder for the characterization and utilization as a pelletizing additive.

Commercial softwood kraft lignin (ComL) was obtained from the lignin collection at the USDA FS-Forest Products Lab, Madison, WI from Domtar (Plymouth, NC, USA). Kraft lignin was recovered from black liquor via acidification with sulfuric acid as per the Lignoboost method [74,75]. The ComL was in powder form and was utilized as received.

2.2. Characterization of Lignin

The chemical composition of lignin (the acid-soluble lignin and acid-insoluble lignin content and the content of polysaccharides) was determined by conducting conventional two-step acid hydrolysis, followed by the analysis of the hydrolysate for monosaccharides using high-performance anion exchange chromatographic with pulsed amperometric detection [76]. The ash content was measured in accordance with TAPPI Standard T-413 [77] at 900 °C. The sulfur content of lignin was analyzed by Midwest MicroLab (Indianapolis, IN) via the Schoniger Combustion method [78].

The radical quenching ability of lignin was measured following a colorimetric assay using DPPH (2,2-diphenyl-1-picrylhydrazyl) as the free radical generator, following the method previously described [49]. IC_{50}, µg/mL, i.e., the concentration required to reduce or "inhibit" 50% of the DPPH, was calculated. Ferulic acid, a relatively potent natural antioxidizing compound [79], was used as a control in these experiments. The radical quenching capacity of lignin was measured to assess its potential to decrease the carbon monoxide (CO) emission of pellets in relation to the suggested radical-initiated mechanism of the CO formation in pellets [63].

The glass transition temperature (T_g) of lignin was determined with temperature-modulated differential scanning calorimetry (TM-DSC). TM-DSC was utilized as it is a powerful enhancement to the standard differential scanning calorimetry (DSC) technique. The thermogram consisted of three curves: the total heat flow curve, reversible heat flow curve, and non-reversible heat flow curve [80]. The T_g was determined from the reversible heat flow curve. TM-DSC was performed with a Q20 Differential Scanning Calorimeter

(TA Instruments; New Castle, DE) using a modulation amplitude and period of 0.5 °C and 60 s, respectively, and a ramp rate of 6 °C/min.

The energy content of the lignin was determined using a modified version of ISO 18125 [81]. The method for the gross calorific value at a constant volume measurement was utilized. Lignin was compressed with a pellet press for the energy content experiments. A Parr 6200 isoperibol oxygen bomb calorimeter with a 1108 oxygen combustion bomb and a Parr 6510 water handling system (Parr Instrument Company, Moline, IL, USA) was utilized. The moisture content was measured with a modified version of TAPPI Standard T-412 [73] in which the samples were dried in a vacuum oven at 40 ± 5 °C to a constant mass.

The particle size distribution of lignin was determined using atomic force microscopy (AFM). First, the lignin samples were diluted to 100 ppm using acetone as the solvent. Then, to prepare the samples for AFM imaging, a 20 µL drop was dispensed into a freshly cleaved mica substrate and air dried. AFM imaging was done using the TT-AFM (AFM Workshop, Hilton Head Island, SC, USA). Images were obtained using the Z-scan mode at a scan rate of 0.5 Hz, an image resolution of 512 pixels × 512 pixels, and the selected scan sizes ranging from 15 to 5 µm.

Custom-written scripts in Mathematica 13 were used to level the resulting topographical images. First, image leveling was performed utilizing a combination of 2D polynomial, mean value line-leveling, and background estimation functions to approximate the background while minimizing the overfitting. Next, individual particles were identified using pixel connectivity after applying the leveling functions and binary segmentation. Image segmentation was manually performed via intensity thresholding to separate the background (mica) from the foreground (particles).

2.3. Pelletizing of Lignocellulosic Biomass and Lignin-Added Pellets

Willow chips were ground with a laboratory scale hammermill (Farm Feed Systems, Ltd.; Cinderford, UK) equipped with a screen containing 1 mm holes (from Procore-Peerless Inc.; Buffalo, NY, USA) prior to pelletizing. For pellets produced with lignin, lignin was added to ground willow at 5% of the mass of the willow and thoroughly mixed prior to loading into the pelletizer. This 5% addition ratio of lignin was selected based upon prior studies involving lignin as a binder in pelletizing [55,58–60]. Lignin was added as-received (moisture content: RecL, 1.8%; ComL, 22.3%) to the willow. The mass of lignin added was based on the oven dried (O.D.) mass of willow and the lignin samples. The moisture content of the lignin samples was measured with a modified version of TAPPI Standard T-412 [73].

A laboratory scale, Mini Pellet Mill ring die pelletizer (Farm Feed Systems, Ltd.; Cinderford, UK) with a low compression die (pellet diameter: 6 mm, working length: 15 mm, and compression ratio: 1:2.5) was used to make three batches of fuel pellets in succession: the control (containing 100% willow), RecL pellets (95% willow and 5% recovered lignin), and ComL pellets (95% willow and 5% commercial lignin) (Figure 1). Water was added in-line during pelletizing with a peristaltic pump. Pellets were screened with W.S. Tyler RX-812 Screens (Mentor, OH, USA) and pellets of mesh No. 6 (3.36 mm) and greater were collected. Pellets were cooled and placed into a cold room (4 °C) until testing. Approximately 2 kg of pellets were made per batch for examination.

2.4. Characterization of Fuel Pellets

The moisture content of the pellets was determined with a modified version of ISO 18134-2 [82]. The maximum loading specifications for the samples and dishes in this method were followed to test 10–20 g of pellets per replicate. **The ash content** was examined using ISO 18122 at 550 °C [83]. **The energy content** of the pellets was also measured with a modified version of ISO 18125 [81]. The pellets were conditioned to a constant mass in the atmosphere of the laboratory containing the Parr 6200 isoperibol oxygen bomb calorimeter and were directly placed into the oxygen bomb for analysis.

Figure 1. Fuel pellet samples of shrub willow pellets and pellets with additional lignin. From left to right: Control Pellets, RecL-Pellets, and ComL-Pellets. These samples were utilized for the measurement of pellet length.

The bulk density of the pellets was examined with a modified version of ISO 17828 [84]. A 2 L stainless steel cylindrical container (Tablecraft Brand, Amazon.com, accessed on 28 September 2022) with a height-to-diameter ratio of 1.3 (6.5 in and 5 in, respectively) was utilized for the bulk density measurements based on the container guidelines in ISO 17828. **The durability** was measured according to ISO 17831 [85] using an ISO certified TUMBLER 100 R Durability Tester from the Bioenergy Institute (Vienna, Australia). A 3.35 mm screen was utilized to sieve the pellets before and after tumbling, and the durability index was calculated as a ratio between the mass of pellets remaining after the durability test and the initial mass of pellets. **The pellet length** was determined with ISO 17829 [86]. Pellets shorter than 3.15 mm were discarded as per Table 4 in the ISO 17225-1 definition of pellets [87].

Table 4. Chemical composition of lignin recovered from hot water extraction of shrub willow (RecL) and commercial softwood Kraft lignin (ComL). All values are in percent (%) of oven dried (O.D.) lignin.

Content, % OD Lignin	RecL	ComL
Lignin		
Acid-Insoluble	84.58 (±0.08)	92.86 (±0.03)
Acid-Soluble	7.83 (±0.20)	4.21 (±0.19)
Total Lignin	92.41	97.07
Polysaccharides		
Arabinan	0.08 (±0.00)	0.11 (±0.00)
Galactan	0.34 (±0.01)	0.65 (±0.01)
Rhamnan	0.06 (±0.00)	0.00 (±0.00)
Glucan	0.83 (±0.02)	0.24 (±0.00)
Xylan	1.57 (±0.01)	0.45 (±0.01)
Mannan	0.13 (±0.00)	0.07 (±0.00)
Total Polysaccharides	3.01	1.52
Ash	0.41 (±0.12)	1.14 (±0.12)
Sulfur	1.80 (±0.04)	2.61 (±0.11)

The moisture absorption of the pellets was analyzed following TAPPI Standard T-550 [88] with modifications. The pellets were dried according to ISO 18134-2 [82], placed into a desiccator, and stored in a temperature and humidity-controlled room (21.7 °C and 18% ± 2% relative humidity) overnight to adjust to the temperature. The initial mass of the dry pellets was measured. Then, the pellets were exposed to the conditioned atmosphere

(18% ± 2% relative humidity) and the mass of the pellets was recorded at various time intervals until a constant mass was achieved.

The carbon monoxide emissions of the pellets were measured in the dark at constant temperature (22 ± 1 °C) in a Fisher Scientific Isotemp Low Temperature Incubator (Model Number 13-987-626) based upon various studies of carbon monoxide off-gassing at or near room temperature [13,62–64]. Glass jars were filled halfway with the pellets (yielding a headspace of 50%) and each jar contained approximately 150 g of pellets (Figure 2). The selected headspace parameters were chosen based upon the related studies by Soto-Garcia et al. [13] and Rahman et al. [63]. EasyLog EL-USB-CO and EasyLog EL-SIE-1 temperature sensors obtained from LASCAR Electronics (Erie, PA, USA) were utilized for CO emission studies and were placed in the jars prior to sealing. CO was the only gaseous species measured in this study due to the health and safety risks present when exposed to CO in pellet-related working environments [89].

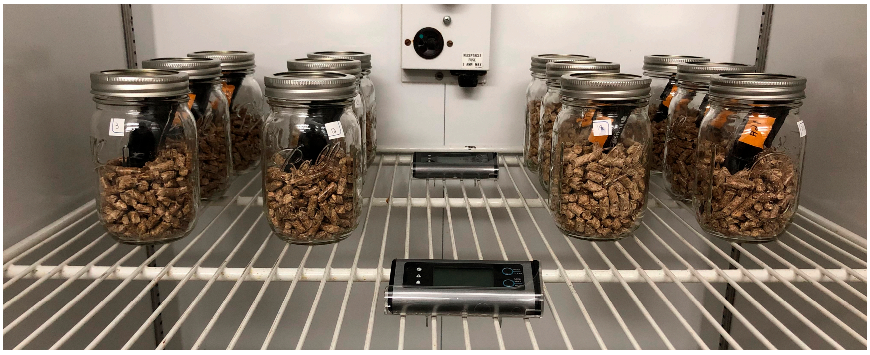


Figure 2. Measurement of carbon monoxide emissions in temperature-controlled conditions. Carbon monoxide sensors were placed in sealed jars. Two temperature sensors were placed on the rack to monitor the temperature of the incubator.

2.5. Statistical Analysis

Statistical analysis was performed using ANOVA (Analysis of Variance) tools on MiniTab (Version 21.2 (64-bit)). ANOVA is a statistical method that uses the variation within each treatment group and variation between treatment groups to analyze the differences between the means of the treatments (μ_i) being compared. A null hypothesis of the means being equivalent ($\mu_1 = \mu_2 = \mu_3$) and an alternative hypothesis of the means being different ($\mu_1 \neq \mu_2 \neq \mu_3$). Fisher LSD ANOVA was used to compare the properties of lignin-added pellets to the control pellets in a 1 × 3 Factorial Design, and the statistics were calculated from the triplicate experiments unless noted otherwise in the method. All statistics were applied with an alpha (α) value of 0.05.

3. Results and Discussion

3.1. Characterization of Lignin

3.1.1. Chemical Composition

The chemical composition of the lignin recovered from the hot water extraction of willow (RecL) and commercial softwood kraft lignin (ComL) can be found in Table 4. Overall, ComL contained a higher total lignin content with a greater fraction of acid-insoluble lignin, whereas RecL contained a greater fraction of acid-soluble lignin. RecL also had a higher carbohydrate content. The variation in the types of detected polysaccharides may be attributed to the difference in hemicelluloses present in ComL (a kraft lignin from softwoods in which galactoglucomannans are the dominant hemicellulose) and RecL (lignin from willow, a hardwood in which glucuronoxylans are the dominant hemicellulose) [90].

The lower ash and sulfur contents of RecL compared to ComL are beneficial in the use of lignin in fuel pellets (combustion) as high ash can damage boilers [14,15] and reduce the energy yield of pellets [55], and high sulfur can corrode boilers [91] and release undesired gasses [92] upon combustion. The higher sulfur content in ComL is expected owing to the use of sodium sulfide in kraft pulping and its incorporation into the lignin structure during delignification [93]. However, the presence of sulfur in RecL may be attributed to the lignin recovery process from the hot water extract, which is promoted via acidification using sulfuric acid.

3.1.2. Radical Quenching Ability

The radical quenching ability of the two lignin samples was 1.8–2.7 times lower than that of the ferulic acid control (27.0 ± 4.3 μg/mL), as revealed by their higher IC_{50} values. However, RecL exhibited a lower IC_{50} (50.0 ± 0.0 μg/mL) than ComL (72.0 ± 6.1 μg/mL), indicating that it is approximately 1.4 times more efficient as an antioxidizing compound. This result reflects the difference in the composition of the two lignins used in this study; RecL originated from willow contains guaiacyl (G) and syringyl (S) units, whereas softwood kraft lignin (ComL) contains solely G units (monomethoxylated) that are, in comparison to S units (dimethoxylated), inferior in their radical quenching ability [49]. The reactive PhOH groups can promote the bonding that occurs between the constituents in LCB during pelletizing and improve the strength and durability of pellets [44].

3.1.3. Glass Transition Temperature

The T_g—as determined from TM-DSC—of RecL is lower than that of ComL (104.16 °C and 148.00 °C, respectively). Thermographs from the DSC analysis can be found in the Supplementary Materials of this publication. The use of the TM-DSC provided a more accurate measurement of T_g than previously reported [72], and the value for ComL falls within the anticipated T_g range for softwood lignin (138–174 °C) [94]. The difference in the T_g values illustrates the difference between the structures of softwood (ComL) and hardwood (RecL) lignins. Hardwood, SG lignin contains more methoxy groups relative to softwood, G lignin [2]. As such, there are fewer bonding sites available for covalent crosslinking to occur within the lignin itself, resulting in a lower T_g [95].

3.1.4. Particle Size Distribution

Figure 3a,b depict the height distribution of the RecL and ComL particles, respectively, as obtained via AFM. The RecL particles are predominantly in the 0–10 nm range, while the ComL particles are in the 10–20 nm range. The ComL particles are also more homogenous than the RecL particles. Figure 3c,d show the AFM images of the RecL and ComL particles, respectively. At the same magnification (5 μm), the RecL particles appear to be larger than the ComL particles with regard to the area, indicating that the RecL particles are pancake shaped.

3.2. Characterization of Fuel Pellets

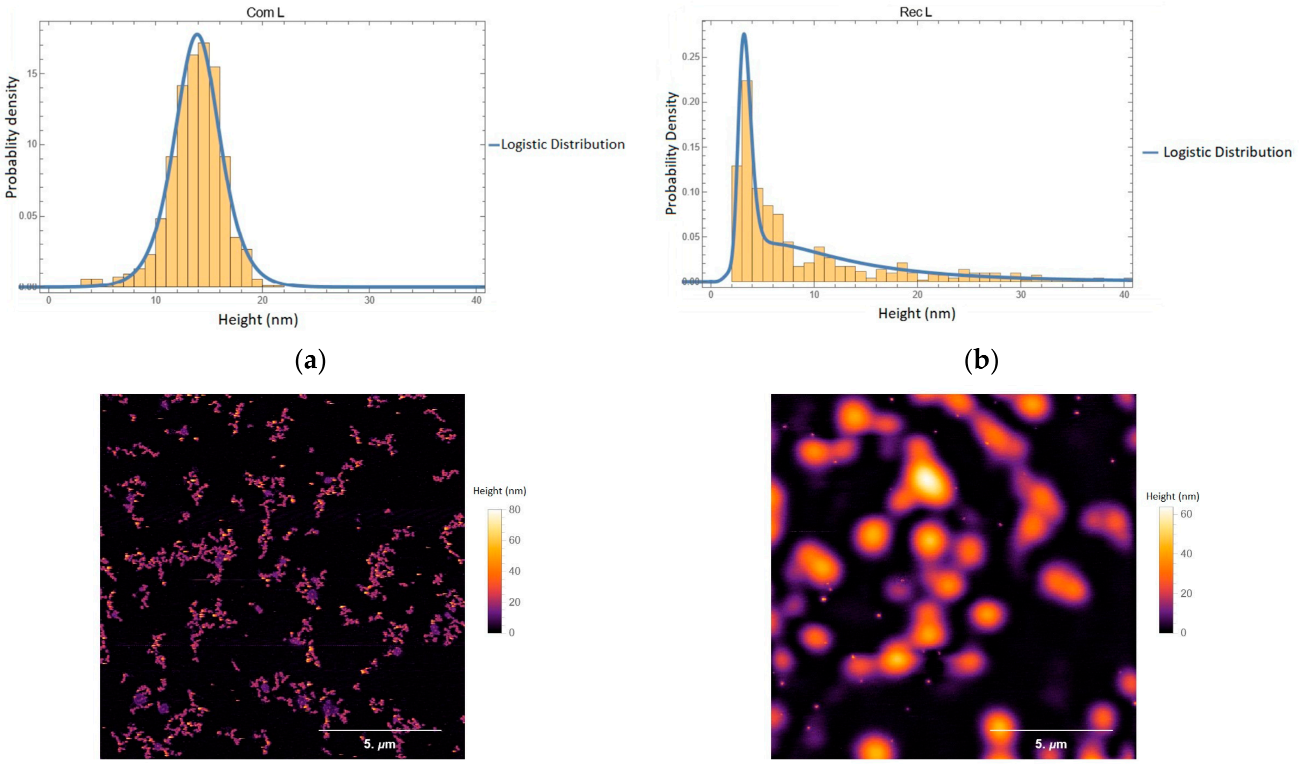
The ash content, energy content, bulk density, durability, pellet length, moisture absorption, and carbon monoxide (CO) emissions of the control pellets and lignin-added pellets are summarized in Table 5. Overall, the energy content, bulk density, and durability significantly increased for both RecL-Pellets and ComL-Pellets compared to the control. The moisture absorption and CO emissions were significantly lower for RecL-Pellets relative to the control.

3.2.1. Ash Content

The effect of lignin on the ash in pellets was not statistically significant between the control and the lignin-added pellets (Table 5). Based on the ash contents in RecL, ComL, and willow pellets, and the composition of lignin-added pellets (lignin:willow, 5%:95%), the RecL-Pellets and ComL-Pellets should have theoretical ash content values of 3.41% and 3.45%, respectively. However, the ash in RecL-Pellets was slightly lower than the calculated value (3.18% vs. 3.41%), in contrast to ComL-Pellets exhibiting a higher ash content (3.72%

vs. 3.45%). The reason for these different values and the unexpected higher ash content in ComL-Pellets is unclear.

Other studies [55,56] utilizing lignin as an additive in pelletizing also reported higher ash relative to the control pellets (Table 3). In the case of Kuokkanen et al. [56], the lignosulfonate used as an additive had more ash (0.6%–0.8%) than the pine to which it was added (0.5%), accounting for the observed increase in ash. Sermyagina et al. [55] reported an increase in pellet ash but did not report the ash in the kraft lignin itself.



(**a**) (**b**)

(**c**) (**d**)

Figure 3. Particle size distribution of RecL and ComL lignin. Height probability density of the (**a**) ComL and (**b**) RecL particles. Atomic force microscopy images of the (**c**) ComL particles and (**d**) RecL particles.

Table 5. Properties of Control, RecL-, and ComL-Pellets.

Pellet Property	Control	RecL-Pellets	ComL-Pellets
Ash Content (% O.D. Biomass)	3.57 (±0.29) ^{A}	3.18 (±0.38) ^{A}	3.72 (±0.36) ^{A}
Gross Calorific Value (MJ/kg)	19.88 (±0.06) ^{A}	20.12 (±0.05) ^{B}	20.19 (±0.03) ^{B}
Bulk Density (kg/m^3, Dry Basis)	612 (±1) ^{A}	642 (±9) ^{B}	633 (±1) ^{B}
Durability Index	90.4 (±0.5) ^{A}	95.4 (±1.0) ^{B}	95.2 (±0.13) ^{B}
Average Pellet Length (mm)	16.43 (±4.91) ^{A}	17.89 (±4.58) ^{A}	17.95 (±4.80) ^{A}
Moisture Absorption (% Moisture Gained)	2.64 (±0.02) ^{A}	2.50 (±0.05) ^{B}	2.62 (±0.01) ^{A}
CO Emissions (ppm)	55 (±13) ^{A}	32 (±4) ^{B}	39 (±4) ^{AB}

Superscript letters for each property indicate whether a significant difference between the reported average values of the treatments is present based upon Fisher LSD ANOVA Analysis. Means that do not share a letter are significantly different.

3.2.2. Energy Content

The energy content of willow pellets produced in this work (19.88 MJ/kg) was greater than the reported values for willow (Table 2) in the literature. Quiñones et al. [31] investigated the higher heating value of three raw materials and their pelletized counterparts and reported that the energy content of the LCB pellets was on average 9.97% higher than the respective raw LCB. Readjusting the energy content of raw willow from Table 2 with this difference in the energy content of pellets from Quiñones et al. [31] results in a range of 20.45–20.89 MJ/kg for willow pellets. However, the reasoning for this difference in the energy content between pellets and raw materials needs further exploration.

Several studies [18,55,58] reported an improvement in the energy content after adding lignin to LCB for fuel pellets, though one study [56] reported a decrease in the energy of pellets owing to the low energy content of the lignosulfonate utilized as an additive. ComL and RecL did not negatively affect the energy content of fuel pellets. Compared to the energy content value of the control pellets (Table 5), those of RecL-Pellets and ComL-Pellets were significantly higher, by 1.21% and 1.56%, respectively. This rise in the energy content was expected because of the difference in the energy content of lignin compared to cellulose and hemicelluloses. It was also expected that ComL-Pellets would have a higher energy content than RecL-Pellets because the energy content of G lignin exceeds that of SG lignin (energy content of G > S) [96]. Accordingly, our results, revealing the expected range for lignin (21.0–26.6 MJ/kg for lignin [39,52], showed that the ComL contained significantly more energy than the RecL (24.20 MJ/kg vs. 22.98 MJ/kg). In addition, these results corroborate the higher lignin contents (97.07% vs. 92.41%) and lower carbohydrate contents (1.52% vs. 3.01%) in ComL than in RecL (Table 4). However, the energy content of ComL-Pellets and RecL-Pellets was not significantly different (Table 5).

3.2.3. Bulk Density

The bulk density of the willow pellets produced in this study (612 kg/m^3) was lower than that reported in the literature (Table 1). One potential source of error was the utilization of a non-standard device to measure the bulk density. A 2 L metal container that followed the height-to-diameter ratio requirements listed in ISO 17828 [84] was selected for this work owing to the limitation of the sample size of the produced fuel pellets and compared to a 5 L ISO certified container. The 2 L container reported a bulk density that was 2.86% lower than that obtained via the 5 L ISO certified container. While this results in an adjusted bulk density of 630 kg/m^3, it is still lower than the reported bulk density of 655–690 kg/m^3 of willow pellets (Table 1).

The bulk densities of RecL-Pellets and ComL-Pellets were significantly higher than that of the control pellets (Table 5), though there was no significant distinction between RecL-Pellets (642 kg/m^3) and ComL-Pellets (633 kg/m^3). However, further studies should examine the extent of this effect by varying the ratio of lignin to LCB. Berghel et al. [18] added kraft lignin to pellets at different ratios and reported a bulk density trend that was inconsistent. Additionally, many pellet standards—such as ISO 17225-2 [97]—state that pellets should not contain more than 2% by weight of additives, while 5% by weight of lignin was utilized in this work; therefore, examining the effect of the lignin content will be beneficial for standardization.

3.2.4. Durability

The durability test examines the ability of pellets to withstand mechanical forces during handling and transportation. Higher durability values represent the ability of the pellet to maintain its shape and form without generating a large amount of dust and fines. The durability of RecL-Pellets and ComL-Pellets was significantly higher by 5.53% and 5.31%, respectively, than that of the control pellets (Table 5) and corroborates with the values previously reported [18,55,56]. The increase in durability observed in RecL-Pellets and ComL-Pellets can be attributed to the improved bonding between the willow particles and lignin, leading to a better formation of the fuel pellet.

RecL had a lower T_g than ComL, which indicates that it required less energy and time to reach the point of softening assisting in particle bonding. The particle size of lignin could have an effect on bonding between the LCB particles, but more work is needed to verify this effect beyond simple speculation. These results underscore the need for additional research on the mechanism of lignin incorporation into pellets and the contribution of different lignin traits (e.g., chemical structure, bonds and functional groups, molecular weight, and polydispersity) on the reinforcement effect. However, it is important to note that the difference in durability between RecL-Pellets and ComL-Pellets was not statistically significant, implying that the pellet durability increases with the addition of 5% lignin to the degree that is largely independent of the lignin origin.

3.2.5. Pellet Length

Overall, the average pellet length of RecL-Pellets (17.89 mm), ComL-Pellets (17.95 mm), and the control pellets (16.43 mm) were not significantly different (Table 5) because the pellet length distribution across the 50-pellet sample of each treatment widely varied (Figure 4). As such, it is not possible to claim that additional lignin improved the average length of fuel pellets.

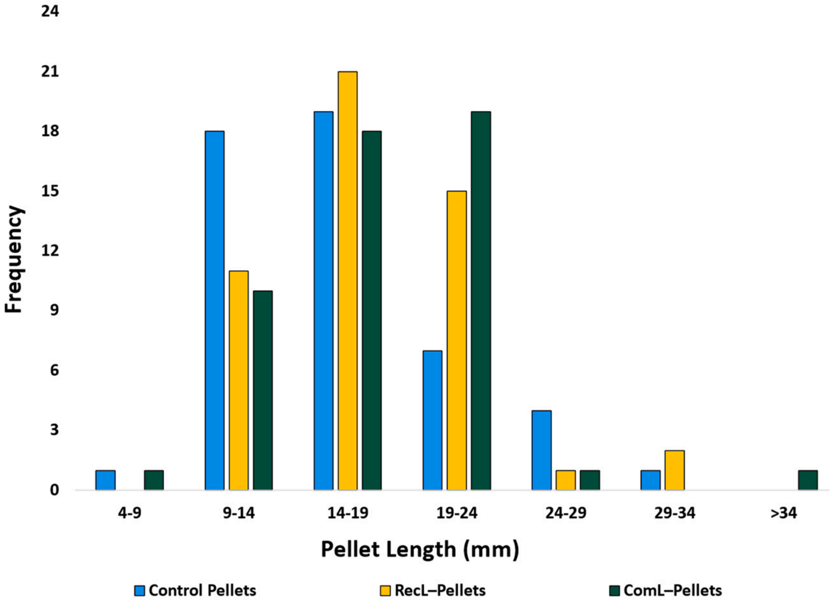


Figure 4. Pellet length distribution of fuel pellet samples (n = 50) for Control Pellets, RecL-Pellets, and ComL-Pellets.

The control pellets had a greater frequency of pellets that were 9–14 mm long compared to RecL-Pellets and ComL-Pellets. The control pellets had a median value of 15.28 mm, RecL-Pellets 17.42 mm, and ComL-Pellets 17.97 mm. This demonstrates that the average length of the control pellets was skewed to the right. The comparison of the median values, however, shows that the influence of lignin as an additive on pellet length was much stronger than what the average values suggest.

The variation in the pellet length distribution between the control pellets and lignin-added pellets can be attributed to similar reasons described in Section 3.2.4. An improvement in bonding between the LCB constituents and particles with the addition of lignin results in a stronger pellet. As the pellets exit the die, they are cut by a knife within the pelletizer set to a desired maximum length as determined by the standards for pellet production (such as 40 mm as a maximum pellet length listed in ISO 17225 [97]). If the LCB particles are not strongly connected, the pellets will break prior to reaching the knife and will result in a greater frequency of smaller pellets. This is seen in the distribution of the control pellets compared to RecL-Pellets and ComL-Pellets. Combined with the results from the durability testing, it can be inferred that the control pellets did not exhibit the same mechanical strength and bonding compared to the lignin-added pellets. However, additional examination of the mechanical strength properties should be conducted considering the statistical insignificance reported for the pellet length values between the control and lignin-added pellets.

3.2.6. Moisture Absorption

Reduced moisture sensitivity is advantageous for LCB-based fuel pellets as LCB is susceptible to moisture that can accelerate physical, biological, and chemical degradation [12,13]. The RecL-Pellets absorbed significantly less moisture than the control pellets (Table 5) with a 5.3% reduction in moisture absorption. This supports the hypothesis of utilizing lignin as an additive to increase the hydrophobicity of fuel pellets; however, this same trend was not observed by Sermyagina et al. [55] (Table 3). Lignin is more hydrophobic than cellulose and hemicelluloses and its hydroxyl groups are different in their interaction with moisture [50]. As such, adding lignin to willow prior to pelletizing increases the total hydrophobicity in the pellet, and it is expected that its moisture sensitivity would decrease. Additionally, when exposed to pelletizing conditions (compressive forces and temperature), lignin can bond with other polar constituents, such as hydroxy groups in LCB [44]; occupying hydroxyl groups in bonding (such as hydrogen bonding), which would interfere with their reactivity to ambient moisture and alter the moisture sensitivity of the fuel pellets.

Additionally, there was a significant difference between the moisture absorption of RecL-Pellets and ComL-Pellets, representing a 4.69% difference in values. This could be due to similar factors as discussed in Section 3.2.4 and those relating to the T_g, particle size, available polar groups, and bonding between the LCB constituents during pelletizing. However, more research should be conducted to elucidate the effect of these properties on fuel pellets.

3.2.7. Carbon Monoxide Emissions

Overall, the RecL-Pellets produced significantly less CO than the control pellets (Table 5) with a 41.8% reduction in emissions. This is a significant finding and confirms the hypothesis of lignin additives lowering the production of CO in fuel pellets. There was a 29.1% reduction in CO emissions for ComL-Pellets compared to the control (Figure 5), however, the average emission values were not significant because of the variability in CO production from the control (Table 5). CO emissions from RecL-Pellets and ComL-Pellets were statistically similar. Comparatively, a 36.1% percent difference in the radical quenching activity of RecL vs. ComL resulted in a 19.7% difference in average CO emissions, indicating that the antioxidant activity of the lignin can be impactful towards reducing CO emissions.

Comparatively, *tert*-butylhydroquinone (TBHQ) was reported to reduce CO emissions by 85% at the laboratory scale at room temperature [68] and acetylsalicylic acid (ASA) lowered CO emissions by up to 70% [69]. One explanation for this difference could be the antioxidant activity of these compounds compared to RecL (50.0 ± 0.0 μg/mL) and ComL (72.0 ± 6.1 μg/mL). Arshadi et al. [68] reported an IC_{50} of 2.0 ± 0.04 μg/mL for TBHQ, though the standard used for comparison was not provided. Sedlmayer et al. [69] did not report the antioxidant activity of ASA, Sharma et al. [98] reported an IC_{50} of 21.34 ± 1.09 μg/mL for ASA in their work via antioxidant testing using the DPPH method with ascorbic acid as a reference compound (4.57 μg/mL). As such, the order of antioxidant activity of these four additives (TBHQ > ASA > RecL > ComL) correlates to the percent reduction in CO emissions. However, it is important to note that the DPPH methods used by each study were slightly different.

Additional purification to a lower polysaccharide content in RecL could further reduce the production of CO as the proposed mechanism of CO generation in LCB involves the reaction of hydroxy radicals to hemicelluloses. Residual carbohydrates in RecL from lignin–

carbohydrate complexes formed with hemicelluloses in LCB have the potential to react with radicals that are not quenched by lignin. Additionally, the further fractionation of the lignin to expose more reactive phenolic hydroxyl groups may also have a positive effect on CO reduction. Nagardeolekar [99] observed an increase in the free phenolic hydroxyl group content of various lignins recovered from hot water extraction (sugar maple, willow, miscanthus, and wheat straw) after both alkali-purification and solvent fractionation. However, this alkali-purification was reported to have a mixed effect on the antioxidant activity of the lignin and further studies were needed to explore these results. Regardless, future work could examine the effect of purifying and further fractionating lignin on the production of CO in fuel pellets.

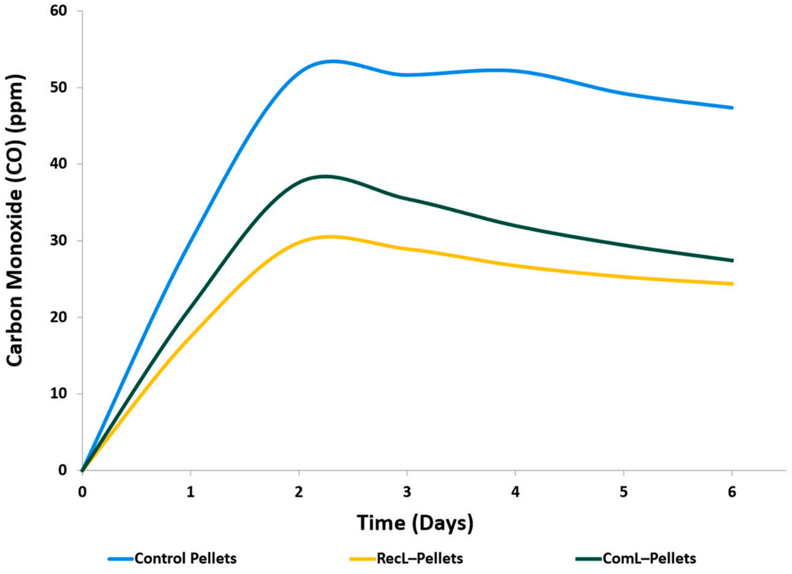


Figure 5. Carbon monoxide emissions of Control Pellets, RecL-Pellets, and ComL-Pellets at 22 ± 1 °C.

4. Conclusions

Commercial softwood kraft lignin (ComL, G lignin) and lignin recovered from the hot water extraction of willow (RecL, SG lignin) were used as additives to the pellets produced from shrub willow. There was a significant increase in the energy content, bulk density, and durability with the addition of lignin compared to the control; however, there was not a difference in performance in these properties between RecL- and ComL-Pellets. RecL-Pellets had significantly lower moisture absorption and carbon monoxide (CO) emissions compared to the control, while ComL-Pellets did not show the same significance of effect. The subtle differences in the pellet properties between ComL-Pellets and RecL-Pellets are attributed to the difference in the characteristics of these two lignins as G- and SG lignins, respectively. Future work should examine the contribution of different lignin traits (such as chemical structure, functional groups, molecular weight, polydispersity, and particle size), lignin purity, and additive-to-pellet ratio on the reinforcement effect lignin provides to lignocellulosic biomass-based fuel pellets.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/f14102041/s1, Figure S1: ComL DSC Thermograph; Figure S2: RecL DSC Thermograph.

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Data Availability Statement: The data presented in this study are available upon request and with approval from the corresponding author. The data are not publicly available due to legal and privacy restrictions with the entities involved in the production of this research.

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