

Fuel Pellets from Wheat Straw: The Effect of Lignin Glass Transition and Surface Waxes on Pelletizing Properties

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Abstract The utilization of wheat straw as a renewable energy resource is limited due to its low bulk density. Pelletizing wheat straw into fuel pellets of high density increases its handling properties but is more challenging compared to pelletizing woody biomass. Straw has a lower lignin content and a high concentration of hydrophobic waxes on its outer surface that may limit the pellet strength. The present work studies the impact of the lignin glass transition on the pelletizing properties of wheat straw. Furthermore, the effect of surface waxes on the pelletizing process and pellet strength are investigated by comparing wheat straw before and after organic solvent extraction. The lignin glass transition temperature for wheat straw and extracted wheat straw is determined by dynamic mechanical thermal analysis. At a moisture content of 8%, transitions are identified at 53°C and

63°C, respectively. Pellets are pressed from wheat straw and straw where the waxes have been extracted from. Two pelletizing temperatures were chosen—one below and one above the glass transition temperature of lignin. The pellets compression strength, density, and fracture surface were compared to each other. Pellets pressed at 30°C have a lower density and compression strength and a tendency to expand in length after the pelletizing process compared to pellets pressed at 100°C. At low temperatures, surface extractives have a lubricating effect and reduce the friction in the press channel of a pellet mill while no such effect is observed at elevated temperatures. Fuel pellets made from extracted wheat straw have a slightly higher compression strength which might be explained by a better interparticle adhesion in the absence of hydrophobic surface waxes.

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Introduction

Wheat is one of the most common grown crop species worldwide and its annual production has been estimated to be about 685 million tons for the year 2009 [1]. Wheat straw is therefore a large potential resource for heat and power production and a possible alternative to woody biomass in countries with little forest resources. The bulk density of loose straw is only about 40 kg/m³ [2]. Therefore, it is usually compacted into bales of about 120 kg/m³ directly after the harvest [3]. Wheat straw's low bulk density makes handling expensive since volume limitations of carriers are reached before the load limit, and large spaces are required for its storage. One way to overcome this limitation is to compact wheat straw into fuel pellets or briquettes, which

have a much higher density and allow long distance transportation for a fraction of the cost [4]. Fuel pellets made from agricultural residues are of increasing interest to researchers [5–10] and are also successfully being used by energy providers in large scale combined heat and power plants [11]. Recently, the pellets have also been successfully tested in different household-size pellet boilers demonstrating their suitability for small-scale applications [12]. Nevertheless, there are still significant drawbacks to overcome such as ash deposit formation and corrosion.

Wheat straw pellets are produced in pellet mills in which the chopped straw particles are forced through cylindrical press channels. The high pressure in combination with an elevated temperature of about 80–100°C, results in a softening and flow of the wheat straws amorphous polymers. Polymer interpenetration between the straw particles during pelletization increases the bond strength due to macromolecular entanglement [13, 14]. Much work has already been done to determine the optimal processing conditions for pellet production from agricultural residues [5–10]. Nevertheless, the mechanical properties of wheat straw pellets are lower as compared to conventional fuel pellets made from wood [14]. This is likely due to the different chemical composition and structure of wheat straw. In general, the lignin content in grasses is lower and its structure is different compared to wood, i.e., many monolignols in grasses are substituted with acetyl or ferulic acid residues [15]. Another important difference is that wheat straw contains a cuticula, which is present on the outer surface of all grasses and is basically a hydrophobic layer composed of cutin and hydrophobic waxes. Cutin is a polymeric network of polyhydroxylated C₁₆ and C₁₈ fatty acids cross-linked by ester bonds [16]. It is amorphous and insoluble in water and closely associated with semicrystalline wax particles. The plant cuticula acts as a barrier allowing the plant to regulate its water balance and protecting it against physical, chemical, and biological aggression (i.e., fungi and insects) [16]. This layer is likely to have a negative effect on the bonding between the biomass particles within a pellet since weak boundary layers between adjacent fibers and particles can be formed during biomass densification processes resulting in poor mechanical stability of the densified products [14, 17, 18].

The softening, flow, and subsequent hardening of lignin is likely the major bonding factor and, as such, is worth studying in greater detail. The temperature at which a polymer softens and passes from a glassy into a plastic state is called the glass transition temperature (T_g) and is an important characteristic of a polymer.

Many studies have investigated the T_g of wood lignins [19–23] and have shown that they depend on species, moisture content, and sample preparation. In general, the T_g decreases with an increasing moisture content (water acts as plasticizer) and degree of substitution. For example, the presence of many acetyl groups in hardwood lignins lowers its T_g [22, 23].

The present work investigates the lignin T_g of both untreated and organic solvent-extracted wheat straw, where the hydrophobic waxes from the surface have been removed. The removal of surface waxes was monitored by means of attenuated total reflectance—Fourier transform-infrared spectroscopy (ATR-FTIR) that allows surface analysis of a very low depth. The T_g was determined by means of dynamic mechanical thermal analysis (DMTA). Pellets were produced well below and above the T_g from untreated and organic solvent-extracted wheat straw. The impact of the lignin T_g and the surface extractives on the pellet stability are investigated by means of compression testing, density and expansion measurements. Scanning electron microscopy (SEM) was used for fracture surface analysis and determination of the bonding type.

Materials and Methods

Wheat (*Triticum aestivum* L.) was harvested in late summer of 2007 on the island of Sjælland, Denmark and straw collected after being air dried in the field. The wheat straw was milled to particles less than 5 mm in size using a hammer mill (Model 55, Jensen and Sommer Aps, Denmark). The material was packed in paper bags permeable to air and moisture and stored in a dry and dark storage room.

Material Pretreatment

After about 2 years of storage, samples were taken from the bags and particles less than 1 mm and greater than 2.8 mm in size were removed using analytical sieves and a sieve shaker (Retsch, Germany). Extractives were removed from the wheat straw by soxlet extraction in n-hexane for 8 h.

Prior to the experiments, the materials were conditioned in a climate chamber at 65% RH and 27°C for at least 1 week. The equilibrium moisture content was 8.0% for straw and 8.1% for extracted straw.

Determination of Extractives Content

About 8 g of wheat straw particles were dried at 105°C overnight and extracted as described above. The extracted sample was dried again and the extract content was calculated based on the weight difference.

Attenuated Total Reflectance Infrared Spectroscopy

To verify the extractives removal, ATR-FTIR was used to study the surface of the biomass particles. Spectra were recorded at 30°C using a Fourier transform infrared spectrometer (Nicolet 6700 FT-IR, Thermo Electron Corporation, USA), equipped with a temperature-adjustable ATR accessory (Smart Golden Gate diamond ATR accessory, Thermo Electron Corporation, USA). Samples were dried at 105°C for 4 h and stored in

airtight containers until used for testing. A minimum of five measurements per sample was performed. To ensure good contact, all samples were pressed against the diamond surface using a metal rod with consistent pressure. All spectra were obtained with 200 scans for the background (air) and 100 scans for the sample with a resolution of 4 cm^{-1} from 500 to $4,000\text{ cm}^{-1}$. Spectra were normalized using the $760\text{--}790\text{ cm}^{-1}$ segment of the spectra where no distinct IR peaks were found.

Dynamic Mechanical Thermal Analysis

The glass transition temperatures of wheat straw's amorphous polymers were determined by means of DMTA (Q800, TA-Instruments, USA) using a single cantilever grip. Specimens were prepared by pressing the conditioned wheat straw into round fiber mats using a laboratory hot press at 154°C applying a pressure of about 50 MPa for 5 min. The resulting fiber mats were cut into rectangular specimens ($17.5 \times 12\text{ mm}$) and conditioned at 65% relative humidity and 27°C for 1 week. The resulting moisture content of the specimen was determined to be 8.2% ($\pm 0.15\%$) for the wheat straw and 8.3% ($\pm 0.15\%$) for the extracted wheat straw. Measurements were conducted between -60 and 200°C with an amplitude of 15 μm and 1 Hz. The storage modulus (E'), loss modulus (E''), and loss factor $\tan\delta$ were determined and used for finding the transition temperatures of wheat straws amorphous polymers. Measurements were repeated twice to verify the results. It has to be noted that the samples may not be identical in particle size and orientation which limits the comparability of E' and E'' .

Pelletizing

Pellets were produced using a single pellet press, designed and built at the workshop of the Technical University of Denmark, as described earlier [14, 24]. The press consisted

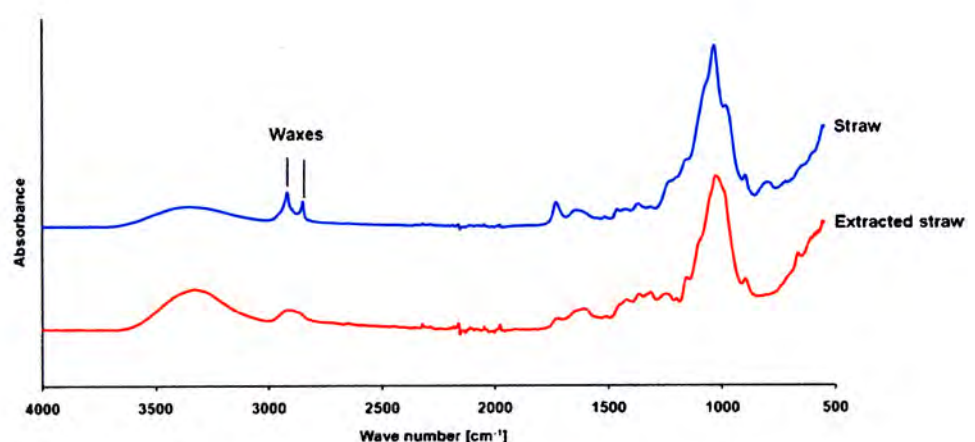
of a cylindrical die 7.8 mm in diameter, made of hardened steel, lagged with heating elements and thermal insulation. The end of the die was plugged using a removable backstop. Pressure was applied to the biomass using a piston made out of hardened steel connected to a pneumatic laboratory press (P25, Compac, Denmark) and a load cell (C2S, NTT-Nordic Transducer, Denmark) connected to a data collection system. To simulate the pelletizing process in a commercial rotating die pellet mill, the pellets have to be built up in sequential layers [25]. The die temperature was adjusted to 30°C or 100°C and 0.25 g of particles were loaded in the die and compressed until a maximum pressure of 200 MPa was reached. The pressure was held for about 30 s and then released. The process was repeated four times until the pellet had a mass of 1 g. Then the backstop was removed and the pellet was pushed out of the die. The maximum force required to press the pellet out of the die was detected by the load cell and the back pressure (P_r) was calculated based on the pellet surface area. P_r has earlier been shown to be an important parameter in pelletizing processes [24]. The produced pellets were stored at 65% relative humidity and 27°C in a climate chamber for 1 week.

Pellet Characterization

The strength of the manufactured pellets was analyzed by compression testing and determined as the force at break as described elsewhere [14, 26]. The conditioned pellets were placed on their side (i.e., the pellet's cylindrical axis oriented horizontally) in a compression tester (Model 5566, Instron, USA) equipped with a 10 kN load cell and data collection system. Pellets were compressed between two metal plates at a rate of 1 mm/min until the pellet broke. The average force at break and its standard deviation were calculated based on at least five tests per sample.

Weight and pellet expansion were determined directly after pressing and after 1 week conditioning time using a

Fig. 1 ATR-FTIR spectra of the particle surface of wheat straw and extracted wheat straw. The spectra were displaced vertically for clarity



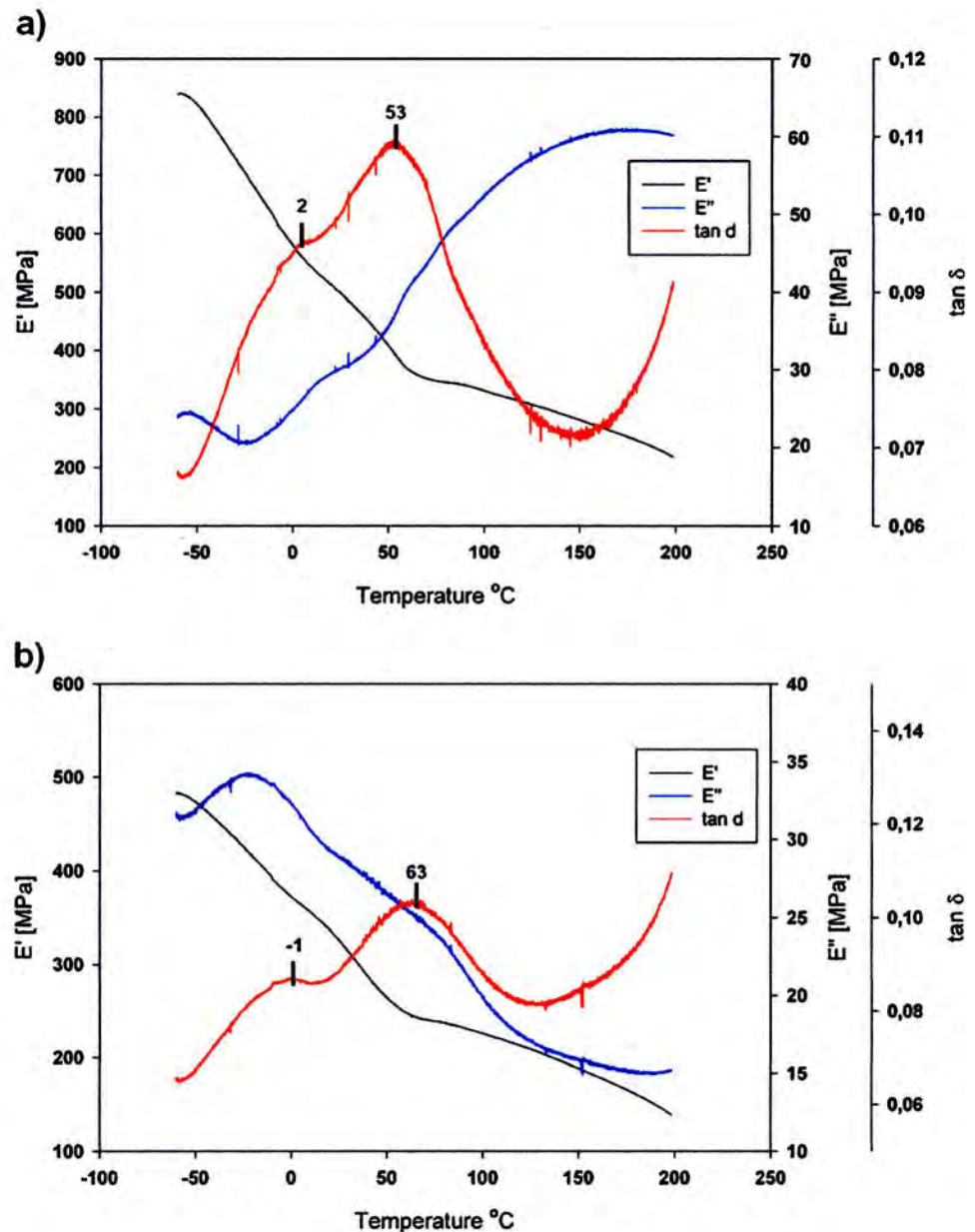
caliper. The measured values were used to calculate the unit density. Density and expansion data is based on at least five measurements per sample.

Fracture Surface Analysis

SEM was used to study the bonding mechanism of the biomass pellets by fracture surface analysis of broken pellets. The compression test resulted in total disintegration of the pellets, and therefore fracture surfaces were prepared by manually breaking a pellet in two parts. Care was taken to replicate the way each pellet was broken and ensure that the same region was fractured. A tiny notch was cut in the center of

the pellet using a razor blade, and the pellets were then snapped into two. Care was taken to examine the fracture surface away from the notch. The two halves of the fractured pellet were attached to metal stubs using a conductive carbon paste (Leit-C, Neubauer Chemikalien, Germany) that was carefully applied below and around the sample to prevent electric charging of the specimen. The upper surface was coated with a thin layer of palladium and gold using a sputter coater (SC7680, Polaron, UK). Electron micrographs were recorded using a scanning electron microscope (FEI Quanta 200, FEI Company, The Netherlands) operated at 2–10 kV. Multiple samples were observed for each type of pellet and representative images were selected for each sample type.

Fig. 2 DMTA spectra of **a** wheat straw and **b** extracted wheat straw



Results and Discussion

Removal of Surface Waxes

The extraction of wheat straw in n-hexane resulted in a weight loss of 1.8%. The surface of the straw and extracted straw particles were analyzed using ATR-FTIR spectroscopy.

The wheat straw spectra (Fig. 1) shows distinct peaks at 2,850 and 2,920 cm^{-1} originating from C-H bonds within a methyl group of the plant cuticula waxes [24, 27]. They are absent in case of extracted straw sample which leads to the conclusion that the extractives removal was successful.

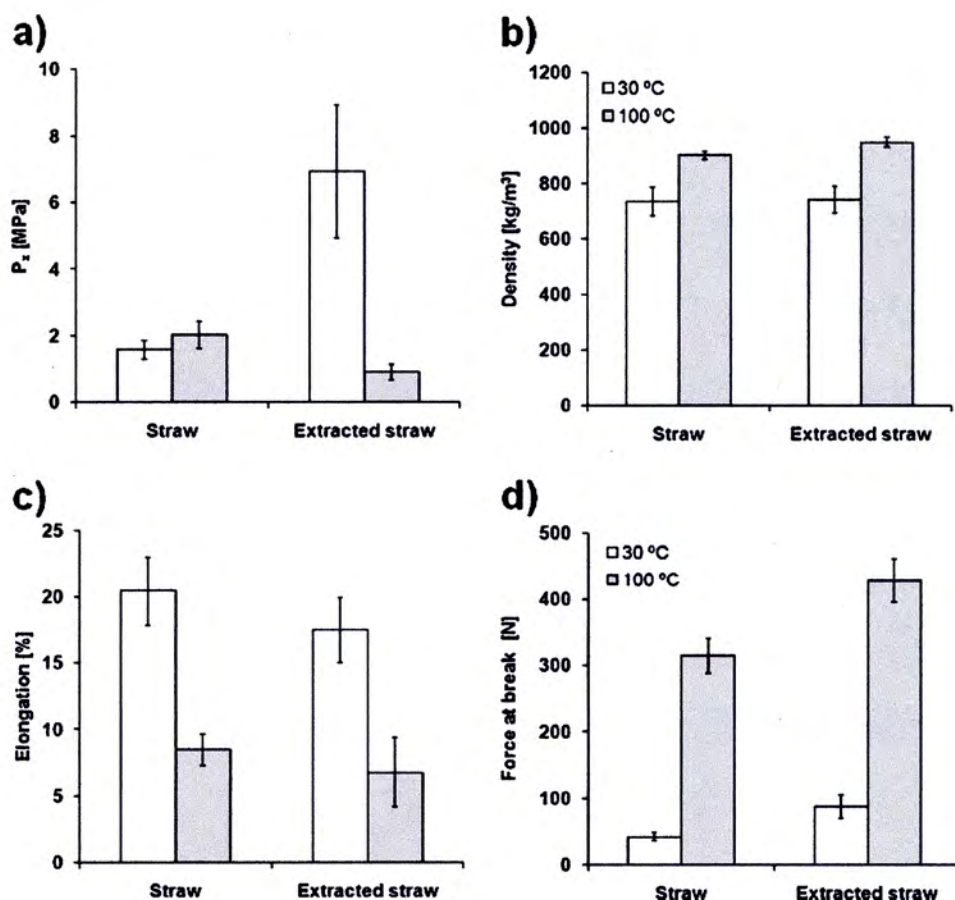
Transitions of the Amorphous Polymers in Wheat Straw

Figure 2 shows the DMTA spectra of wheat straw (Fig. 2a) and extracted wheat straw (Fig. 2b). The transitions can be seen clearest when looking at the $\tan\delta$ graph. Two distinct peaks can be seen at about 53–63°C and around 0°C. The peak assignment was based on earlier data obtained for wood which, like straw, is a lignocellulosic composite material and can therefore be expected to have similar viscoelastic

properties. A study by Salme and Olsson [20] has shown that the T_g of lignin in moist wood occurs at about 60–95°C. For dry wood, it can be well above 160°C [19].

Lignin transitions were found at 53°C for wheat straw and 63°C for solvent extracted wheat straw. One can speculate about the reason for this difference. For example, the wheat straw waxes themselves may undergo a thermal transition at about 40–50°C that might overlap with the lignin transition [28]. Furthermore, there could be unknown effects due to the solvent extraction that might have caused chemical and/or structural changes of the biomass. Further studies are needed to explain these observations. The wheat straw samples used in this study were relatively dry (about 8% moisture content) and, based on the data for wood at similar moisture contents [21], a higher T_g could be expected. Wheat straw lignin is composed differently and has a higher degree of substitution than wood lignin. This is likely to be responsible for a lower T_g than wood lignin under the same conditions. The peak at about -1°C to 2°C can likely be assigned to hemicelluloses. The T_g of hemicelluloses in wood is at about room temperature, assumed to be well below the lignin T_g [21]. Nevertheless, further studies are required to prove this.

Fig. 3 **a** Pressure (P_x) required to push the pellet out of the die. **b** Pellet density after 1 week storage. **c** Springback effect: Pellet elongation after 1 week. **d** Pellet compression strength



Effect of Temperature and Waxes on Pellet Formation

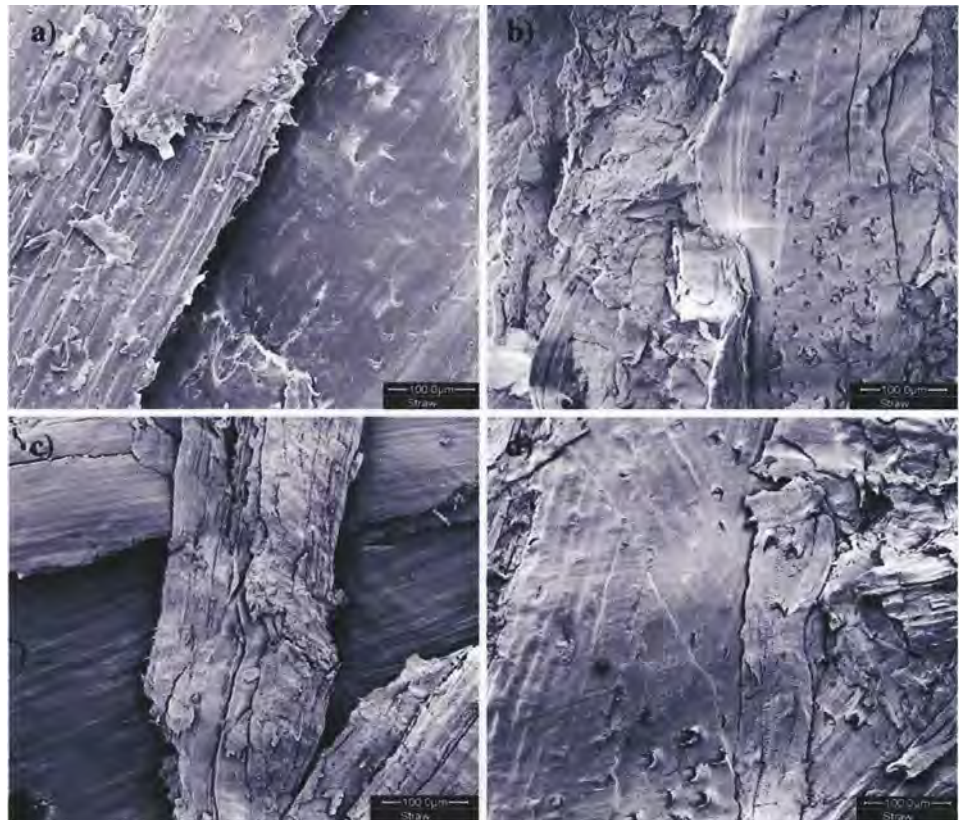
We investigated the pelletizing properties of wheat straw and extracted wheat straw at 30°C and 100°C, well below and above the lignin T_g . The parameters investigated were:

1. Pressure in the press channel during pellet production (P_p), which is a measure of the process energy consumption (Fig. 3a).
2. The pellet density, which is an important indicator for the efficiency of the pelletizing process (Fig. 3b).
3. The elongation 1 week after pelletization, which is an indicator for the inter-particle bonding strength (Fig. 3c).
4. The compression strength, which reveals the mechanical stability and pellet quality (Fig. 3d).

Figure 3a shows that at 30°C, the P_x to press out a pellet made from extracted wheat straw, is significantly higher as when pressing out a pellet made from natural wheat straw at the same temperature. Therefore, it is likely that the waxes on the straw surface have a lubricating effect that reduce the friction between the press channel walls of the pellet press and the biomass. An earlier study made by Nielsen et al. [29] showed that extractives on the pellet surface have a strong influence on the energy consumption of the pelletizing

process. Nevertheless, this effect was not observed for pellets pressed at 100°C. This could be explained by the thermal softening of the biomass after its temperature is raised above the lignin T_g , thereby reducing the friction [24]. It has been shown to be a function of the friction coefficient and the Poisson ratio, which are expected to change with temperature [30, 31]. However, the temperature dependency of P_x increases with pellet length [24] and results might be different for longer pellets. Therefore, further studies are required to fully understand this phenomenon. The pellets unit density is shown in Fig. 3b and is an indirect measure for the pellet quality. The pellets compressed at 30°C have a tendency to expand after pelletization (Fig. 3c), a phenomenon that is also known as "spring back effect" [10]. It is a measure for the bonding quality between the biomass particles within a pellet. If there is poor adhesion, the particles do not bind well together, the pellet expands like a spring. Pellets compressed at 100°C expand much less, which indicates that their particles adhere much stronger to each other. Figure 3d compares the compression strength of pellets made from wheat straw and extracted wheat straw at 30 and 100°C. The compression strength of wheat straw pellets depends on the processing temperature and is greater at 100°C, both for the treated and untreated wheat straw pellet. This is to be expected since a softening and subsequent polymeric flow of lignin is necessary for polymer interpenetration and the formation of

Fig. 4 SEM micrographs of the fracture surface of wheat straw pellets. a Straw pellet pressed at 30°C and b at 100°C. c Extracted wheat straw pressed at 30°C and d at 100°C. The selected images are regarded to be representative for the specific samples



strong bonds between the particles [13, 14]. At 30°C, the T_g was obviously not reached (Fig. 2) and thus less strong interparticle bonds were formed, resulting in less stable pellets.

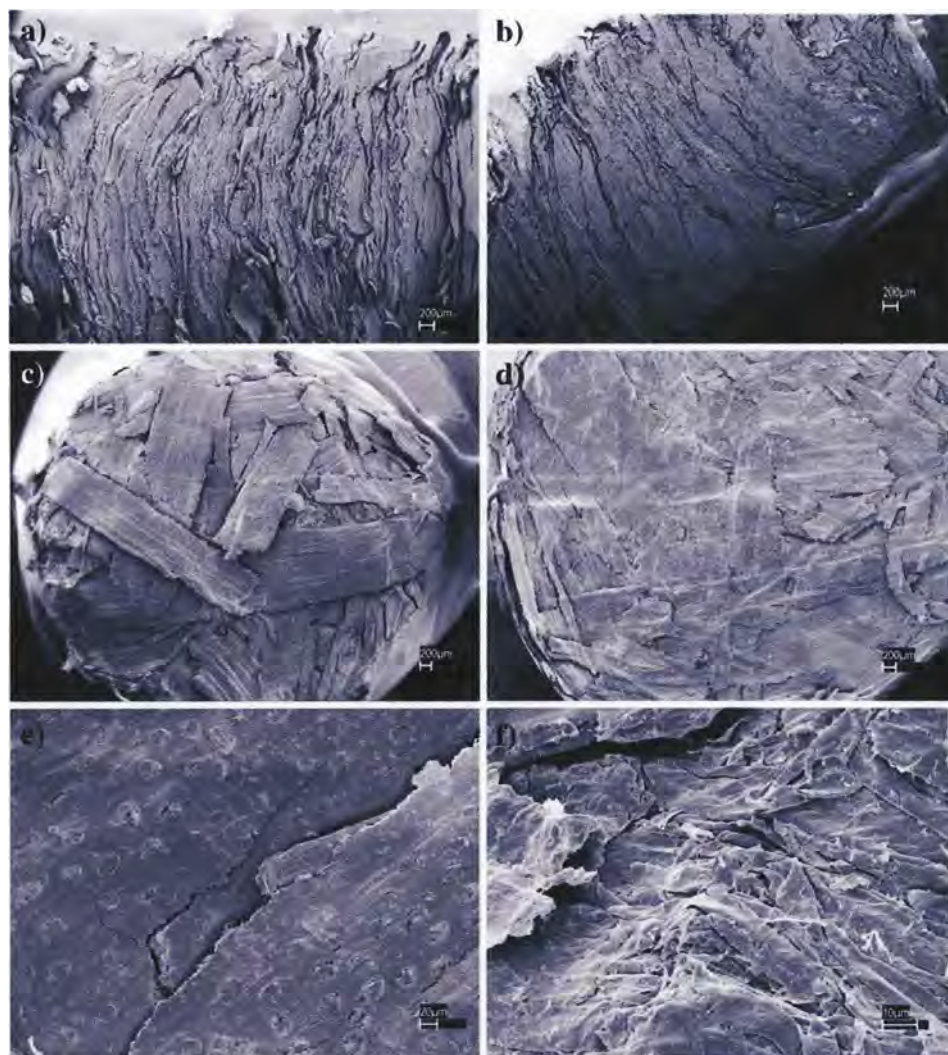
Compared to the compression strengths with those obtained for pellets made from spruce and beech using the same method [14], it was shown that the compression strength values of wood pellets are greater than for all straw pellets included in this study. This could be explained by the lower lignin content in wheat straw compared to wood. Lower lignin content is likely to result in fewer bonds formed between the particles. Furthermore, there are other chemical and structural differences between wood and wheat straw that may contribute to a weaker bonding between the particles. The wheat straw cuticula contains high amounts of cutin, which is a polyester derived from fatty acids and that forms a layer on the wheat straws outer surface [27]. It is likely that parts of this layer are still intact after solvent extraction and reduce the area of interaction where strong bonding can

occur. These polyester surfaces may cover the subjacent cellulose, hemicelluloses, and lignin polymer chains, preventing participation in bond formation either through solid bridge formation or hydrogen bonding. This likely limits the interparticle bonding to weak van der Waals interactions and fiber interlocking.

Effect of Temperature and Waxes on Bonding (Fracture Surface)

To further study the bonding within the pellets, SEM micrographs were recorded of the fracture surfaces of pellets made from straw and extracted straw at 30°C and 100°C (Fig. 4). The images were taken at the interphase between two or more particles and indicate that the gaps between the straw particles are smaller when pelletizing at higher temperature. This has shown to be valid both for untreated (Fig. 4a and b) and extracted (Fig. 4c and d) wheat straw. The smaller

Fig. 5 SEM micrographs of pellets made from wheat straw (a, c, e) and extracted wheat straw (b, d, f). Perpendicular cut through a straw pellet and b a pellet pressed out of extracted straw. Fracture surface at low magnification of c a straw pellet and d a pellet pressed out of extracted straw. High magnification of the fracture surface of a pellet made from e wheat straw and f extracted wheat straw. All pellets were pressed at 100°C according to the described procedure. The selected images are regarded to be representative for the specific samples



interparticle gaps are indicating good adhesion between the biomass particles, which is also reflected by the greater compression strength of the straw pellets pressed at 100°C compared to pellets pressed at 30°C (Fig. 3d). The good adhesion between the particles reduces also the expansion of the pellet after it has been manufactured, the so-called spring back effect. This is reflected by a greater unit density of pellets pressed at 100°C (Fig. 3c).

It is possible that polymeric softening of the lignin at temperatures above its T_g results in polymer interpenetration between the straw particles and as such result in a better adhesion. Under high pressure and temperature, the cell structure of the biomass will be crushed and lignin will be released from the cell wall and middle lamella. At 100°C, it is likely that lignin flows and comes into close proximity with lignin from adjacent particles. Upon cooling, the lignin transfers from its rubbery state back into a glassy state and a network of solidified lignin is formed between the biomass particles, making the straw particles adhere to one another. Nevertheless, the presented SEM micrographs are not able to finally prove this and further studies are needed to confirm this.

Stelte et al. [13] have suggested in an earlier study that waxes found on the surface of wheat straw (cuticula) might reduce the adhesion between two straw particles due to the formation of a weak boundary layer. It can therefore be expected that the mechanical properties of pellets made from extracted wheat straw should be significantly higher. The experimental data recorded in this study shows an improvement of pellet compression strength (Fig. 3d) and density (Fig. 3c), although it is only improving on a small scale. The fracture surfaces of pellets made from untreated (Fig. 4a and b) and extracted wheat straw (Fig. 4c and d) are showing some differences. The interparticle gaps in pellets made from extracted wheat straw are smaller as in pellets made from untreated wheat straw.

Figure 5 investigates the difference between these pellets in greater detail. Comparing the pellets made from wheat straw and extracted wheat straw, there are differences that become first visible when cutting pellets along their perpendicular axis as shown in Fig. 5a for wheat straw and in Fig. 5b for extracted wheat straw. The pellet made from extracted wheat straw appears to be more compact with fewer and smaller gaps between the particles which is a sign for better adhesion and also reflected by the slightly higher pellet strength (Fig. 3d). It has to be noted that it was not possible to cut the pellets pressed at 30°C without destroying them since their mechanical properties were too low. Those differences were also reflected when looking at the pellets fracture surface at low magnification (Fig. 5c and d) where the whole pellet surfaces can be compared. The surface of the pellets made from extracted wheat straw appears more compact with fewer and smaller interparticle gaps.

Looking at higher magnifications (Fig. 5e and f), it seems that the fracture surface of pellets made from extracted wheat straw is rougher, indicating a less brittle failure. But since we looked only on two specimens per sample and since there seems to be only little difference in the mechanical strength of the pellets made from straw and extracted straw when pressed at 100°C, further studies will be needed to confirm whether there is a significant difference.

Conclusion

The glass transition of wheat straw lignin is at about 53–63°C at an 8% (wt) equilibrium moisture content and is likely to have a strong impact on the pelletizing properties of wheat straw. The thermal softening of lignin and the subsequent flow and polymer interpenetration with adjacent biomass particles in a pellet result in the formation of bonds and strong interparticle adhesion. As a consequence, pellets formed above the glass transition temperature of lignin have significantly higher compression strength, a greater unit density, and expand less in length after pelletization. The fracture surfaces have indicated a better interparticle adhesion for straw pellets pressed at a temperature above the lignin glass transition temperature. The surface waxes of straw have been shown to be extractable using hexane. They can act as lubricant and reduce friction between the biomass and the pellet press channels and furthermore lower the mechanical properties of the pellet likely due to the formation of a weak boundary layer. Comparing pellets made from natural and extracted wheat straw indicated that the removal of wax improved the interparticle adhesion resulting in slightly higher compression strength. The effect of extractives is ruled out by the influence of the compression temperature.

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