

Article

Densification of Delignified Wood: Influence of Chemical Composition on Wood Density, Compressive Strength, and Hardness of Eurasian Aspen and Scots Pine

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Abstract: The densification of solid wood is a well-studied technique that aims to increase the strength and hardness of the material by permanently compressing the wood tissue. To optimise the densification process in this study, a pre-treatment with sodium sulphite was used (delignification). With delignification prior to densification, one achieves higher compression ratios and better mechanical properties compared to densification without pre-treatment. The reactivity of syringyl (dominant in hardwoods) and guaiacyl (dominant in softwoods) lignin towards delignification is different. The influences of this difference on the delignification and densification of softwoods and hardwoods need to be investigated. This study aimed to densify wood after delignification and investigate how variations in chemical composition between coniferous and deciduous species affect the densification process. Scots pine and Eurasian aspen specimens with a similar initial density were investigated to study the influence of the different lignin chemistry in softwoods and hardwoods on the densification process. Both timbers were delignified with sodium sulphite and sodium hydroxide and subsequently densified. While the delignification was twice as efficient in aspen than in pine, the compression ratios were almost identical in both species. The Brinell hardness and compressive strength showed a more significant increase in aspen than in Scots pine; however, one exception was the compressive strength in a radial direction, which increased more effectively in Scots pine. Scanning electron microscopy (SEM) revealed the microstructure of densified aspen and Scots pine, showing the crushing and collapse of the cells.

Keywords: delignification; densification; guaiacyl; syringyl; hardness; wood



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1. Introduction

Density is one of the most important characteristics of wood, determining its physical and mechanical properties. Numerous studies show that increasing wood density contributes to higher material stiffness, strength, and hardness [1–4]. The density of the wood depends on the tree species, growth conditions, age of tree, and sampling location in the trunk. Within one species, the density may vary considerably due to variable anatomical features, such as the number of vessels and their diameters, wood fibres, proportion of latewood, or the thickness of cell walls [1,5–7].

As a high density usually improves the physio-mechanical properties, many attempts have been made to manufacture artificially densified wood products [1,8–10]. The densification process reduces the void volume in wood by collapsing the vessels and fibres. The various methods available for this task include compressing wood in hydraulic presses, using heat and steam, impregnating wood with thermosetting resins before densification, or combining either of these methods [8,11]. The above techniques improve key mechanical

parameters such as hardness, stiffness, and modulus of elasticity [12–15]. Moreover, the set-recovery, i.e., dimensional stability, can be improved by resin impregnation prior to densification [16] or thermo–hydro mechanical treatments [17].

Thermomechanical wood densification is one of the well-established methods that uses elevated temperatures in the wood stabilisation process, during which a press with heated plates is used. To minimise internal stresses that would occur if the moisture content of the wood was too high or too low, it is necessary to condition the timber until it reaches a moisture content of approx. 8%–15% [18]. Subsequently, the wood is compressed using heated plates with a temperature between 130 and 180 °C. The compression force is maintained as long as the wood cools below 100 °C. The temperature of the heated plates and pressing time significantly affect the densified wood’s hardness, strength, and dimensional stability [19].

The first patent related to wood densification dates back to 1900 [1,11,17]. Initially, research focused on different densification methods, but over time, more attention was paid to secondary properties, such as the dimensional stability after densification [20]. In the literature, the most important parameters are moisture content before densification, pressing time and temperature, and the degree of densification, i.e., how much the wood was compacted compared to the initial dimensions [13,21]. Between 1930 and 1960, wood densification combined with chemical and heat treatments was investigated because earlier methods lacked dimensional stability and did not fully exploit the compaction capabilities [22]. Densification of wood after a chemical pre-treatment was primarily aimed at reducing set-recovery and increasing the dimensional stability of wood.

Wood densification is carried out on both low and high-density species. As a result, low-density grades can be used where they have not been considered so far due to their otherwise poor strength properties. The properties of wood species with higher density improve further, and their dimensions can be reduced [23–26].

Lignin, the cell wall kit, is a heterogeneous aromatic compound that imparts rigidity to the wood, whereas cellulose is the main load-bearing component in tensile tests [27]. Hence, lignin plays an important role during the densification process, where compressive forces are applied. Hardwood lignin consists of syringyl (S) and guaiacyl (G) units linked by a series of ether and carbon–carbon bonds. In contrast, softwood lignin is essentially composed of G units and is less reactive in the sulphite process, making it more difficult to remove from wood tissue. The share of lignin in typical softwood species ranges from 26% to 32% and in regular hardwood from 20% to 25% [28]. Delignification affects the wood structure, dimensional stability, and bond strength of cellulose [29,30]. Using delignification before densification improves the mechanical properties beyond the level achieved by densification alone. This is due to the breaking and reconstruction of new hydrogen bonds [30–33].

The influence of variable chemical composition, specifically the lignin type, on the combined delignification and densification process remains poorly understood. This work aimed to densify wood after delignification and investigate how variations in chemical composition between coniferous and deciduous species affect the densification process. The effectiveness of the densification process was assessed by analysing selected physical and mechanical parameters (wood density, Brinell hardness, compressive strength).

2. Materials and Methods

2.1. Wood Specimen

The wood of Eurasian aspen (*Populus tremula* L.) and Scots pine (*Pinus sylvestris* L.) were used in the research. The choice of species was based on their lignin’s chemical composition and almost identical initial density. The lignin in pine wood is characterised by a guaiacyl system and a lower reactivity in the sulphite process, which makes it difficult to remove it from the wood tissue, in contrast to aspen wood, which has lignin with greater reactivity, mainly with a syringyl system. The samples were cut according to the anatomical directions to the dimensions of 35 mm in the tangential direction, 25 mm in the radial

direction, and a length of 25 mm. A total of 53 clear wood specimens per species were subjected to the delignification and densification process. Before the delignification process, the samples were oven-dried at 103 ± 2 °C. The density of each specimen before and after the densification process was determined using the stereometric method [34].

2.2. Analysis of the Chemical Wood Composition and Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy (FTIR-ATR)

To analyse the chemical composition of the wood, the specimens were ground using a laboratory mill (Fritsch type Pulverisette 15, Fritsch GmbH, Idar-Oberstein, Germany). The resulting wood powder fraction of 0.5–1.0 mm was utilised for chemical analyses. Cellulose content was determined employing the Kürschner–Hoffer method [35], while pentosan content was assessed following the Technical Association of Pulp and Paper Industry (TAPPI) T 223 cm-01 standard [36]. Acid-insoluble lignin content was tested according to TAPPI T 222 om-06 standard [37], involving the use of 72% sulfuric acid to hydrolyse and solubilise carbohydrates. Each analysis was conducted a minimum of three times per specimen. The chemical composition was evaluated both before and after the delignification process.

FTIR-ATR spectra of both control and densified wood specimens were captured using a Nicolet 8700 FTIR instrument (Thermo Scientific Instrument Co., Waltham, MA, USA) equipped with GladiATR vision (Pike Technologies, Madison, WI, USA). Sample preparation involved milling in a laboratory mill, with subsequent drying of the fraction that passed through a mesh size with a 250 µm nominal sieve overnight at 103 ± 2 °C. The FTIR analysis was conducted on the resulting dry powder. Each spectrum was an average of 32 scans, covering wave numbers from 4000 to 400 cm^{-1} . Background spectra were taken after every two samples to reduce spectral noise and account for peaks associated with CO_2 and water vapour resulting from environmental variations.

2.3. Delignification and Densification of Wood

Delignification was performed using the laboratory method, according to Song et al. [38] and Mania et al. [39]. Pine and aspen specimens were placed in a round-bottomed flask, which was flooded with an aqueous solution of 2.5 M NaOH and 0.4 M Na_2SO_3 . The flask was placed in a heating mantle and connected to a reflux condenser. The liquid solution was boiled by the heating mantle and kept in this state for nine hours. After this time, the specimens were transferred to boiling distilled water and rinsed several times from lignin decomposition products.

After delignification, specimens were placed individually in the central part of specially prepared steel clamps. The steel clamps consisted of two 7 mm thick steel flat bars connected together with four M10 metric screws. All samples were oriented to be densified in the radial direction. Then, the set prepared this way was placed on a testing machine, Zwick ZO50TH (Zwick/Roell, Ulm, Germany). Densification was carried out under the stress of $5 \text{ N} \cdot \text{mm}^{-2}$ and the lowest possible speed of exerting the machine force. The nuts at the steel clamps were tightened during the test to minimise post-deformation recovery. After densification, the samples (still in clamps) were left for one week, during which the tightening of the nuts was monitored continuously. The porosity (C) of wood was calculated before and after densification as in Equation (1):

$$C = \left(1 - \frac{\rho_D}{1540}\right) \cdot 100 (\%), \quad (1)$$

where C is the porosity of wood, 1540 is the cell wall density in $\text{kg} \cdot \text{m}^{-3}$, and ρ_D is the oven-dry density of the specimen in $\text{kg} \cdot \text{m}^{-3}$.

2.4. Compression and Brinell Hardness Test

Compression tests were performed according to the standard of the International Organization for Standardization—ISO 13061-5 [40] in all three anatomical directions using

a numerically controlled test machine, Zwick Z050TH (Zwick/Roell, Ulm, Germany). Ten specimens of each wood species were tested before and after densification. The stress at the proportionality limit, hence, the compressive strength perpendicular to the grain, was measured in the radial (RcR) and tangential (RcT) direction. As the determination of destructive force in compression tests within the radial and tangential directions (for further wood densification) was unfeasible, the force at the limit of proportionality was instead identified. The testing machine's software facilitated this by extrapolating it from the stress–strain curve, specifically at the point where the tangent line diverged from the actual curve (Figure 1). The point described above, corresponding to the proportionality limit, was circled in the figure. Failure stress (RcL) was also determined for the longitudinal direction. After the strength determination, wood moisture content (MC) was determined on selected control and densified samples in accordance with the standard [41]. The moisture content of the samples during the test was similar and averaged 9.5%. However, the MC of the densified samples was slightly higher and was close to 10.5%, despite the similar conditions of sample seasoning.

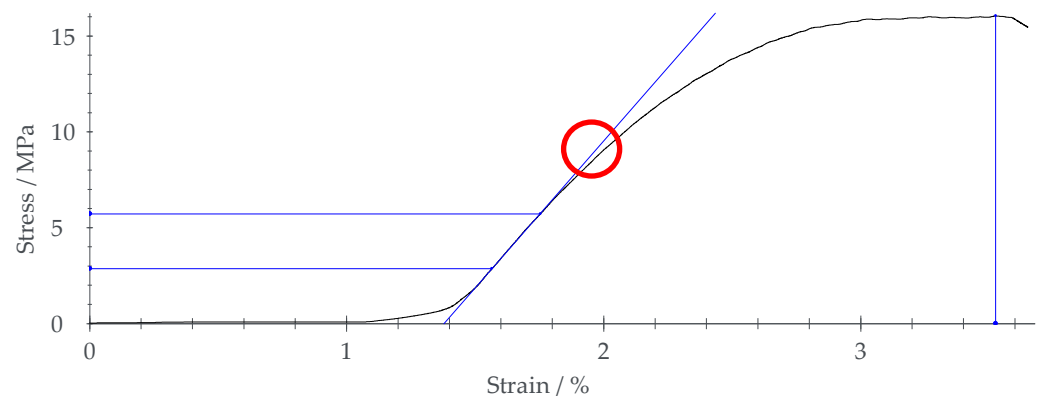


Figure 1. Stress–strain relationship during wood compression test.

Following the guidelines outlined in the European Standard—EN 1534 standard [42], hardness in the radial direction was assessed using the Brinell method. This involved employing a 10 mm diameter steel ball subjected to a 1 kN load. The maximum force of 1 kN was reached within 15 s, maintained for 30 s, and then gradually reduced to zero within the subsequent 15 s. Brinell hardness was calculated as in Equation (2):

$$HB = \frac{2F}{\pi D \left(D - \sqrt{D^2 - d^2} \right)} \quad (2)$$

where HB is the Brinell hardness [$\text{N} \cdot \text{mm}^{-2}$], F is the nominal force [N], D is the diameter of the steel ball (10 mm), and d is the mean diameter of the residual indentation [mm]. Brinell hardness values were determined for both control and densified specimens in the radial direction.

2.5. Scanning Electron Microscopy (SEM)

The densified wood and the controls were prepared for scanning electron microscopy (SEM) observations as follows. The controls were soaked in water for 24 h to soften the tissue. Subsequently, the cross sections of the controls were “smoothed” using a rotary microtome with disposable blades to make several cuts with a thickness of 10 μm . The densified wood was cut in an air-dry state to avoid set-recovery during water soaking. After smoothing, the controls were dried in an oven set to 103 ± 2 °C overnight. Before microtome cutting, the densified wood was prepared in a cone-like shape to minimise the surface that was presented to the blade (approximately 1 mm^2). Then, several cuts with a thickness of 1 μm were made. All samples were placed on carbon tape for SEM observations

(HITACHI, TM4000, Tokyo, Japan), which were performed using an accelerating voltage of 15 kV and a detector for backscattered electrons.

2.6. Statistics

The experimental data underwent analysis utilising STATISTICA 13.3 software by TIBCO Software Inc. (Palo Alto, CA, USA) employing analysis of variance (ANOVA). Subsequently, Tukey's HSD test discerned noteworthy disparities among the mean values of the properties investigated within the control group, as well as densified pine and aspen wood samples. All comparison tests were conducted at a significance level of 0.05.

3. Results and Discussion

3.1. Chemical Composition

Table 1 shows the lignin content for aspen and pine samples before and after delignification and the lignin loss during the process. Among the controls, aspen contained significantly less lignin than pine, which is consistent with the data provided in the literature [43,44].

Table 1. Lignin content of lignin in pine and aspen wood before and after the delignification process.

Specimens	Percentage of Lignin [%]	Reduction of Lignin [%]
Aspen (control)	23.4	39.7
Aspen after chemical treatment	14.1	
Scots pine (control)	29.8	21.1
Scots pine after chemical treatment	23.5	

After delignification, the lignin content was reduced by 39.7% in aspen and by 21.1% in pine (Table 1). This reduction is statistically significant, as shown by single-factor analysis of variance (ANOVA). As mentioned earlier, softwood lignin is more difficult to remove from the wood tissue, therefore the reduction in the lignin content is much lower in Scots pine compared to aspen.

3.2. Attenuated Total Reflectance–Fourier Transform Infrared Spectroscopy

The surface chemical changes caused by delignification and densification were determined by FTIR-ATR (Figure 2). The spectra in reflectance mode are normalised to wavenumber 1033 cm^{-1} , showing some qualitative differences between samples.

Comparing the densified Scots pine to the control, it is evident that the 1730 cm^{-1} peak disappears after densification. Since this peak is exclusive to carbonyl groups in hemicelluloses (esters, carboxylic acids, aldehydes), it can be assumed that hemicelluloses were partly removed or heavily deacetylated during delignification. In Scots pine, wavenumbers 1269 and 1225 cm^{-1} represent the C-O stretching in G-lignin and S-Lignin, respectively [45]. After densification, the former peak becomes more intense compared to the latter, further indicating the partial degradation of S-Lignin. Additionally, in Scots pine, the peaks at 798 and 777 cm^{-1} disappear after densification. These bands correspond to C-H deformations in the aromatic ring of lignin and their disappearance is the result of delignification.

Similar to pine, the aspen wood shows signs of partly hemicellulose degradation at wavenumber 1732 cm^{-1} . Moreover, the 1233 cm^{-1} peak shows a substantial decrease in aspen wood. This peak mainly represents the C-O stretching in S-lignin, constituting around 50% of the total lignin in aspen. The depletion of this band shows that S-lignin is removed more efficiently than G-lignin and supports the data provided in Table 1. Comparing the two species, it can be said that hemicelluloses are removed or at least deacetylated, cellulose is mainly unaffected, and S-lignin is removed more effectively than G-lignin.

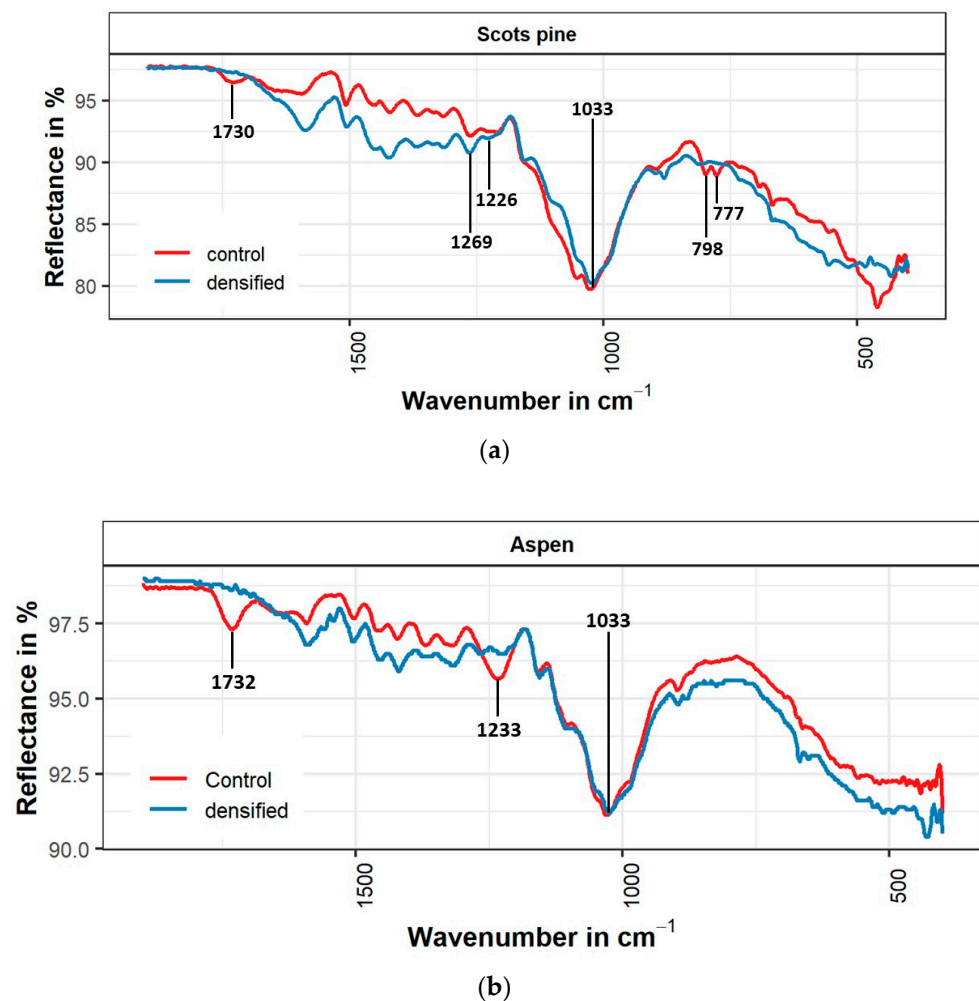


Figure 2. FTIR spectra of Scots pine (a) and aspen (b) wood before and after delignification and densification.

3.3. Densification

Table 2 shows the average density of aspen and Scots pine samples both before and after delignification and densification. Aspen wood, which had an average initial density of $458 \text{ kg}\cdot\text{m}^{-3}$, was densified to $1142 \text{ kg}\cdot\text{m}^{-3}$. Control Scots pine wood had an average density of $462 \text{ kg}\cdot\text{m}^{-3}$ and was densified to $1146 \text{ kg}\cdot\text{m}^{-3}$. The compression ratio (calculated by dividing the density after densification by the density of the wood before) was 2.5 for both woods studied. Hence, both species could be densified to a similar extent. The compression ratio at a similar level for aspen, spruce, and beech wood was obtained by Schwarzkopf (2021) [16]. Tenorio et al. (2022) [46], by densifying several species of tropical wood, obtained a much lower density in the range of $600\text{--}1100 \text{ kg}\cdot\text{m}^{-3}$.

The density of aspen controls and densified samples was more variable than in pine, but the average was similar. ANOVA analysis showed statistically significant differences in density within species. Almost identical compression ratio values result from a comparable density of control wood, regardless of the type of wood species. The use of wood with a very similar density also contributed to an almost identical change in the porosity of the tissue. In aspen, the porosity decreased from 69.4% in the controls to 23.9% after densification. In pine, it decreased from 69.2% to 23.6%. Therefore, the porosity reduction amounted to about 65%, regardless of the species. There were no statistically meaningful distinctions detected among wood species regarding porosity reduction. ANOVA analysis revealed statistically insignificant variations in porosity within the individual species.

Table 2. Wood density (ρ) before and after the densification process.

Material	Number of Specimens	$\rho_{\min}$	ρ_{mean}	$\rho_{\max}$	Standard Deviation ($\pm$ SD)
		[kg·m ^{−3}]			
Aspen (control)	53	429.3	458.4	486.8	18.86
Densified aspen	53	985.3	1141.7	1268.1	64.76
Scots pine (control)	53	450.5	461.9	478.4	9.49
Densified Scots pine	53	1082.9	1145.5	1204.8	27.80

3.4. Brinell Hardness

Brinell hardness tests are presented with basic statistical parameters in Table 3. The indentation was applied in the radial direction. Hardness measurements in other anatomical directions were unfeasible due to the sample geometry of the densified samples. The thickness of the specimens was smaller than the steel ball used for indentation (10 mm).

Table 3. Wood Brinell hardness (HB) before and after the densification process.

Material	Number of Specimens	HBmin	HBmean	HBmax	Standard Deviation ($\pm$ SD)
		[N·mm ^{−2}]			
Aspen (control)	10	9.1	12.4	15.3	1.20
Densified aspen	10	75.5	92.8	143.1	20.30
Scots pine (control)	10	11.2	16.7	24.9	2.12
Densified Scots pine	10	65.4	88.6	121.1	14.79

The average hardness of densified aspen and pine wood is similar. However, there is a large discrepancy between the minimum and maximum values. Within the aspen control, the hardness ranges from 9.1 to 15.3 N·mm^{−2}; after densification, these values increase to 75.5–143.1 N·mm^{−2}. The variable hardness relates to the natural variation in the density of aspen wood. The pine control ranges from 11.2 to 24.9 N·mm^{−2}, increasing to 65.4–121.1 N·mm^{−2} after densification. A single-factor analysis of variance (ANOVA) has shown that the Brinell hardness of densified aspen does not significantly differ from densified Scots pine. However, the relative increase in the average hardness is higher in aspen (748%) than in pine (531%). Other authors also achieved a similar level of hardness improvement. Pelit and Emiroglu [47] obtained an increase in HB for aspen that was more than threefold for densified and styrene-treated wood. A several-fold increase in hardness in surface-densified pine wood was observed by Scharf et al. (2022) [48]. Research on spruce wood also showed a significant increase in the hardness of wood densified and treated with acetylation [49].

3.5. Compressive Strength in Three Anatomical Directions

Table 4 presents the average values of the compressive strength of aspen and Scots pine wood in longitudinal (L), tangential (T), and radial (R) directions.

During the test, short scratches can be observed along the fibres in Scots pine, which increase in size to reveal the damaged zone. When wood is compressed in such a way, changes in cell membranes occur even before the appearance of visible deformations; these membranes are deformed, causing shearing and, finally, crushing of the cell.

The compressive strength along the grain (L) was higher than the compressive strength across the grain (R and T). The control specimens of both species had almost identical strength longitudinal direction. After densification, the strength along the grain increased by 179% in aspen but only by 143% in pine. In the tangential direction, the average strength of aspen increased by 493% and that of pine only by 179%.

Table 4. Wood compressive strength before and after the densification process.

Material	Number of Specimens	L	T	R
		[N·mm ^{−2}]		
Aspen (control)	10	47.8 ± 2.8	1.6 ± 0.2	5.8 ± 0.4
Densified aspen	10	85.3 ± 20.7	7.9 ± 2.2	82.7 ± 19.5
Scots pine (control)	10	47.5 ± 1.6	2.8 ± 0.4	5.3 ± 0.5
Densified Scots pine	10	67.8 ± 13.7	5.0 ± 1.0	130.9 ± 17.7

L—longitudinal, T—tangential, and R—radial directions; ±SD.

For aspen, the strength in the radial direction increased by 14 times compared to the control. For pine, it increased by almost 25 times. However, this is also the direction of densification, so such a significant increase was expected. The compressive strength in the radial direction was even higher in pine than in the longitudinal direction. In aspen wood, the values for both directions are in a similar range.

Compared to the literature, the relative strength increase in this study is low. Song et al. (2018) [38] increased the compressive strength in the tangential direction from 2.6 N·mm^{−2} to 87.6 N·mm^{−2}. In the current study, however, samples buckled very quickly during the compressive strength test. Buckling is, therefore, most likely the cause of a low-strength increase in the longitudinal and tangential directions. Buckling did not occur in the radial compression test, where a massive increase in strength was achieved. As in the case of hardness, a single-factor analysis of variance (ANOVA) was performed for each anatomical direction. The study aims to indicate whether differences between species after densification are statistically significant or not (Table 5). When analysing the ANOVA results, it can be seen that statistically significant differences occur only in the radial compressive strength of wood (the direction of densification).

Table 5. ANOVA of compressive strength in three anatomical directions in densified wood species.

Source of Variation	SSB	df	MSB	SSE	df	MSE	F	p
Longitudinal	998.057	1	998.057	3363.650	11	305.786	3.263	0.09822 ^{ns}
Tangential	25.288	1	25.288	68.981	10	6.898	3.665	0.08455 ^{ns}
Radial	27,824.922	1	27,824.922	16,661.836	46	362.213	76.819	0.00000 ^s

SSB—sum squares between groups; MSB—mean squares between groups; SSE—sum squares within groups; MSE—mean squares within groups; df—degrees of freedom; F—value of test function; p—level of significance; ^s—significant differences, ^{ns}—not significant differences.

3.6. Scanning Electron Microscopy (SEM) Observations

Figure 3 shows micrographs of the material before and after the densification process. The Scots pine wood tissue (Figure 3a) consists of early and late wood tracheids arranged in radial rows and parenchyma cells arranged perpendicular to the grain. The diffuse porous hardwood (Figure 3c) shows vessels, evenly distributed wood fibres, and wood parenchyma cells. Figure 3b,d show both wood species after the densification process. Both show a significant reduction in wood porosity. In pine wood (Figure 3b), outlines of cells (tracheids) can still be observed without clear cell lumens. There are also visible cracks, which run mainly along the wood rays.

The ray parenchyma cells differ in structure and shape from the tracheids and have different thicknesses of the cell walls. The stress is applied in the direction of the parenchyma cell axis by radially compressing the wood. Due to their anatomy and the direction of applied force, parenchyma cells are compressed to a lesser extent than tracheids. A visible crack may also result from the presence of horizontal resin canals in this place. It is an element of wood tissue which, in the case of pine, is mainly composed of thin-walled cells

and can reach a diameter of up to 200 μm . The difference in the degree of densification causes internal stress and makes parenchyma cells a likely place of crack initiation.

More cracks were seen in aspen wood than in Scots pine. However, what appears as cracks might be collapsed vessels. Residual lumens fibres can also be observed. In both cases, however, residual pore spaces are visible. The densification process does not entirely close the lumens of wood cells, bringing them closer together. It should be added that the wood tissue in both cases was cut in an air-dry state with wood moisture not exceeding 6%.

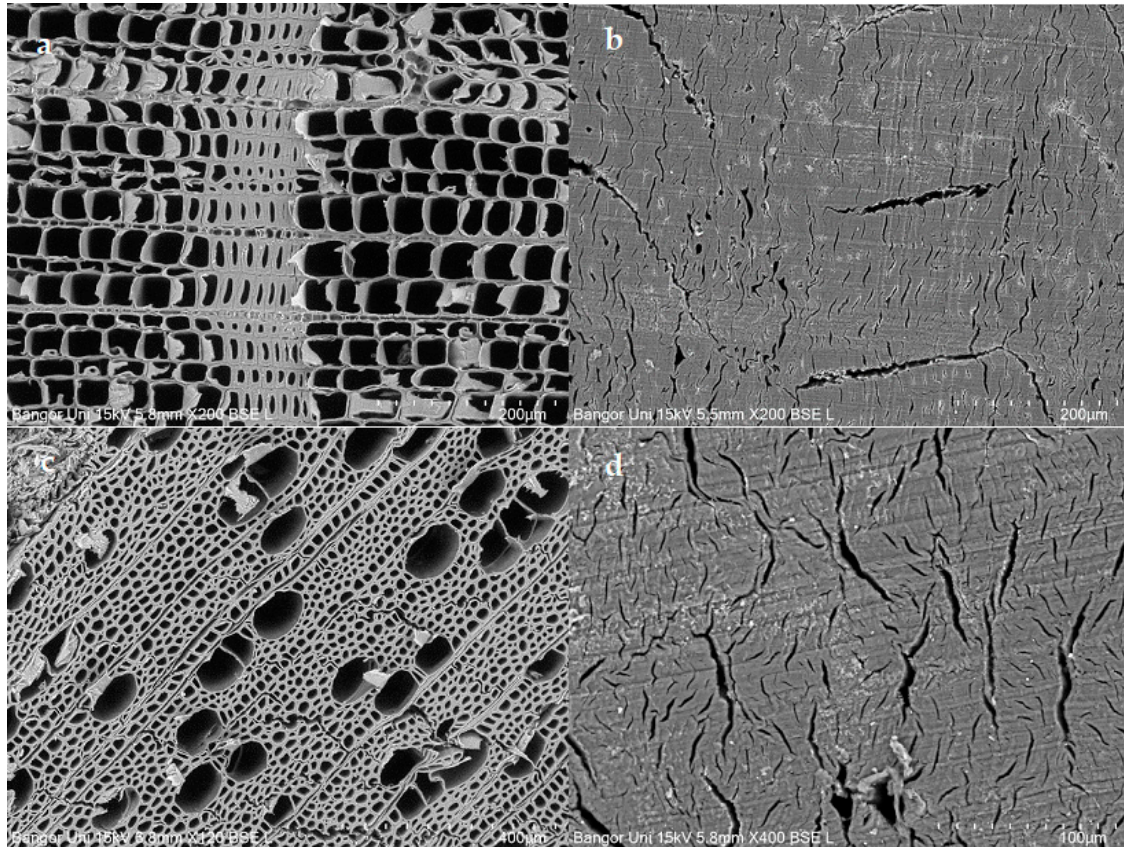


Figure 3. SEM micrographs of pine and aspen wood before and after the densification process. (a) Scots pine control, (b) densified Scots pine, (c) aspen control, (d) densified aspen.

4. Conclusions

This study has shown that Eurasian aspen and Scots pine specimens could be densified to a similar extent, showing an almost identical compaction ratio of 2.5. The delignification process reduced the lignin content in aspen samples from 23.4% to 14.1%, which resulted in a loss of lignin of 39.7%. In Scots pine specimens with naturally higher lignin content, delignification reduced the lignin content from 29.8% to 23.5%, corresponding to a lignin loss of 21.1%. However, the different chemical compositions and degree of delignification of the samples did not contribute to any significant differences in the following densification process.

The densification significantly increased the compressive strength of both aspen and Scots pine in all directions compared to the controls. Densified aspen exhibited a higher increase than Scots pine in compressive strength in the longitudinal and tangential directions. In the radial direction, Scots pine showed a higher increase than aspen. In pine, the stress increase exceeded 24 times, compared to 14 times in aspen. This significant rise in compressive stress (not observed in the hardness test) could stem from the consistent microstructure of pine wood. Densification diminishes the heterogeneity within annual growth rings, equalising the density of earlywood with that of latewood. This effect is

less pronounced in aspen, a diffuse-porous species with lower heterogeneity compared to coniferous species. When the rise in wood strength lags behind the increase in density or shows only slightly more improvement, cell wall destruction occurs. Latewood pine, with its cell structure and notably lesser deformations during densification compared to earlywood, is less susceptible to mechanical cell wall destruction effects.

Author Contributions: P.M. was responsible for the research design, data collection, analysis, and manuscript writing. The conceptualisation and supervision were conducted by P.M. and S.C. The data visualisation was performed by P.M. and C.K. Each author made contributions to the data analysis, review, editing, and assisted with proofreading. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

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