Hornification in Commercial Chemical Pulps: Dependence on Drying Temperature

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Hornification is a well-known phenomenon describing what happens during the drying of lignocellulosic materials, often within and between cellulosic pulp fibers. For wood fibers used in papermaking, this phenomenon decreases fiber wall swelling, and internal and external fibrillation. It reduces flexibility of damp fibers, which leads to a diminished ability to form effective fiber networks, resulting in lower paper strength. This work investigates how drying temperature affects the changes in fiber morphology, connects this to the changes in sheet behavior, and proposes a combination of bonding mechanisms for hornification. Results show that hornification depends on drying temperature; higher temperature gives higher degrees of hornification with decreased WRV of about half the numerical value, from 1.5 g/g for never-dried pulp to 0.7 g/g for hardwood pulp samples. Higher temperatures, above 100°C, also change the pulp color, as measured by increased yellowness. Decreased swelling capacity and pulp yellowness are connected. This indicates parallel reactions, which both contribute to hornification. The mechanisms are proposed to be chains of hydrogen bonds, dominating at low temperatures and providing no color change, and dehydration reactions *via* pyrolysis, giving a yellow-to-brown color shift. Compression strength measurements show that major hornification adversely affects sheet strength due to poor network bonding. However, minor hornification can be beneficial for applications where compression strength is an important parameter.

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INTRODUCTION

Hornification of cellulose-containing materials has been known for a long time and is a frequently occurring topic in literature (Jayme 1944; Stone and Scallan 1966; Laivins and Scallan 1993; Weise and Paulapuro 1996; Maloney *et al.* 1997; Oksanen *et al.* 1997; Kajanto and Niskanen 1998; Retulainen *et al.* 1998; Weise 1998; Kato and Cameron 1999; Weise and Paulapuro 1999; Tze and Gardner 2001; Fernandes Diniz *et al.* 2004; Newman 2004; Welf *et al.* 2005; Hubbe *et al.* 2007; Köhnke *et al.* 2010; Claramunt *et al.* 2011; Luo and Zhu 2011; Luo *et al.* 2011; Ferreira *et al.* 2017; Moser *et al.* 2018; Salmén and Stevanic 2018; Mo *et al.* 2022; Wohlert *et al.* 2022; Benselfelt *et al.* 2023; Ferreira *et al.* 2023; Koistinen *et al.* 2023; Solhi *et al.* 2023; Sellman *et al.* 2023; Hashemzehi *et al.* 2024; Hubbe *et al.* 2024). These cited works describe what happens during drying cycles in lignocellulosic materials where cellulose surfaces are close together, often within and

between cellulosic pulp fibers. Hornification occurs when practically irreversible, or at least very stable, chemical bonds form between cellulose surfaces during dewatering and drying, hindering the material from resettling in water to the original structure. This phenomenon brings about changes in lignocellulosic fibers such as increased stiffness/reduced flexibility, diminished rewetting, and decreased chemical reactivity. In the application of wood pulp fibers for papermaking, hornification gives decreased fiber wall swelling, decreased internal and external fibrillation, and decreased flexibility compared with never dried pulp, which leads to a decreased ability to form effective fiber networks with many fiber-fiber bonds, resulting in lower paper strength (Laivins and Scallan 1993; Oksanen *et al*. 1997; Ferreira *et al*. 2023). However, hornification can also be positive in some cases; stiffer fibers provide higher bulk which can be an advantage in certain applications, such as middle layers of packaging boards (Kajanto *et al*. 1998).

There has been a lively discussion regarding the mechanisms that underlie the formation of the actual bonds responsible for hornification (Wohlert *et al.* 2022; Benselfelt *et al.* 2023; Koistinen *et al.* 2023; Sellman *et al.* 2023; Sjöstrand *et al.* 2023; Solhi *et al.* 2023; Hashemzehi *et al.* 2024), although there are no disagreements about the effects of the fibers and the implications in sheet strength. Some claim that multiple hydrogen bonds (H-bonds) are responsible for the hornification, where multiple hydroxyl groups on cellulose surfaces bond to each other, making it difficult for water to break the bonds due to inaccessibility, and the fact that all must be broken simultaneously (Laivins and Scallan 1993; Kajanto and Niskanen 1998; Kato and Cameron 1999; Tze and Gardner 2001; Newman 2004; Luo and Zhu 2011; Luo *et al.* 2011; Mo *et al.* 2022). The fact that H-bonds are reversible in water is one of the arguments against this hypothesis (Fernandes Diniz *et al.* 2004; Wohlert *et al*. 2022). Another idea is that the hornification is due to a combination of hydrophobic interaction, Van der Walls forces, and H-bonds, which may explain why more disordered/amorphous cellulose hornified is heavier than natural crystalline cellulose (von Schreeb *et al.* 2024). It has also been suggested that hornification is related to lactone bridge formation (Fernandes Diniz *et al.* 2004) and capillary forces (Wohlert *et al.* 2022). Lactone bridge formation is when covalent bonds are formed between cellulose chains (Fernandes Diniz *et al.* 2004); the term is somewhat inadequate because lactones are cyclic structures and not crosslinkers between polymers. Capillary forces (Wohlert *et al.* 2022) and co-crystallization (Newman 2004) are not alternative explanations to the above hypothesizes – co-crystallization must involve noncovalent interactions, such as H-bonds and Van der Waals forces, and the capillary forces in water are highly dependent on H-bonds – rather they should be seen as complements on a higher hierarchical level than the strictly molecular. Most likely, several bonding mechanisms can be valid at the same time. A combination of different bonds form between functional groups on the cellulose chain within the fibers, H-bonds, ester bonds, and ether bonds.

Kang *et al.* (2018) developed a method named Critical Point Drying (CPD), in which the morphological structure of *Eucalyptus* cellulose biomass is conserved by replacing water as a solvent with a non-polar liquid, where they use CO_2 fluid. Changing the solvent to one that cannot engage in H-bonding prevented the cellulose surfaces from approaching each other adequately to trigger hornification, resulting in minimal alteration to the morphological structure. The substitution of the liquid solvent could also impact the flexibility of the cellulosic chains, reducing their conformability. Consequently, this would lead to a less compressed morphological structure. However, it is worth noting that an increase in stiffness is not anticipated to lead to greater swelling after drying, as this parameter is closely linked to the flexibility of the fiber walls.

The hornification mechanism was proposed to be driven by chains of H-bonds (Sjöstrand *et al.* 2023), as also reported in other publications (Barrios *et al.* 2024; Hashemzehi *et al.* 2024). However, this concept does not account for the temperature dependence reported in several publications (Luo and Zhu 2011; Salmén and Stevanic 2018; Sellman *et al.* 2023). The ability of H-bonds to form chains in water has also been reported previously by Clark (1985), Fellers and Norman (1998), and Israelachvili (2011). The drying conditions appear to be a crucial factor in hornification, as indicated by the declining water retention value (WRV) observed after successive drying cycles, as demonstrated by both Salmén and Stevanic (2018) and Ferreira *et al.* (2023). Salmén and Stevanic (2018) have noted that this effect persists even when drying is carried out at room temperature. Furthermore, it has been proposed that higher drying temperatures can enhance hornification, as evidenced by the findings of Welf *et al.* (2005), Luo and Zhu (2011) and Salmén and Stevanic (2018). Nevertheless, contradictory results have been reported in studies conducted by Laivins and Scallan (1993) and Newman (2004).

This study investigates how drying temperature affects the changes in fiber morphology, *i.e.*, hornification, and connects this to the changes in sheet behavior, and proposes a combination of bonding mechanisms for hornification.

EXPERIMENTAL

Materials

Never-dried, fully bleached, chemical kraft pulp fibers from birch (*Betula pendula*/*pubescens*) and Norway spruce (*Picea abies*)/Scots pine (*Pinus sylvestris*) mix were supplied by Gruvön Mill, Billerud AB (Grums, Sweden), with an approximate solids content of 4.4% and 7.2%, respectively. These are named Hardwood (birch) and Softwood (Spruce/Pine) in this article.

Table 1. Temperatures Used for the Pulp Samples and the Different Levels of Hornification Induced

Sample / Pulp Type	Temperature Setting (°C)	Achieved Temperature (°C)
Hardwood never dried	No drying	No drying
Hardwood	Room Temperature	20.2 ± 0.9
Hardwood	50	38.0 ± 5.5
Hardwood	75	74.4 ± 0.4
Hardwood	100	100.9 ± 0.2
Hardwood	125	126.7 ± 0.2
Hardwood	150	152.2 ± 0.2
Hardwood	175	175.4 ± 0.2
Softwood never dried	No drying	No drying
Softwood	Room Temperature	20.6 ± 1.4
Softwood	50	44.2 ± 8.3
Softwood	75	75.7 ± 0.5
Softwood	100	101.6 ± 0.2
Softwood	125	124.2 ± 0.2
Softwood	150	148.8 ± 0.3
Softwood	175	177.9 ± 0.2

Temperature settings and achieved temperature differ somewhat due to inaccurate oven heating. The variance of achieved temperature was indicated by maximum and minimum temperature values.

The pulps were extracted from the pulp mill at a point after bleaching but located before refining. The kappa numbers of the pulps were 12 for Hardwood and 14 for Softwood.

Drying Experiments

The never-dried fibers were dried completely, to dryness of > 95%, at different temperatures ranging from 25 to 175°C in a laboratory oven, and compared to their never-dried counterparts (see Table 1 for drying temperatures used in this study).

The drying procedure for all temperatures consisted of manually squeezing out the free water, then distributing the pulps on blotting paper and putting in the correct temperature either in a fume hood or in an oven. The temperature inside the pulp pieces was monitored using a Datalogger Mitec AT40. All samples were left in the ovens until completely dry, at least 24 h.

Characterization Methods

After drying, the WRV was measured for all samples according to a modified version of ISO 23714 (2014). According to the standard, the centrifugal force should be 3000 G, for these experiments. In the present work 740 G was used to be able to capture smaller differences in swelling behavior. In addition, paper sheets with a target basis weight of 100 g/m^2 were made in a Rapid-Köthen sheet former (RL-ASF-A; Rycobel, Belgium), according to SS-ISO 5269-1 (2005), by repulping the dried samples according to ISO 5263-1 (2004) and diluting them to a consistency of 0.2%. All samples were tested in a standard environment after 24 hours conditioning, according to ISO 187 (2022). The yellowness index of all sheet samples was measured with a Minolta CM-3630 according to the standard DIN 6167 (1980). Double measurements of WRV and yellowness were performed, as well as double measurements of the drying, giving four samples of each kind to provide statistical certainty. Rapid-Köthen sheets were also subjected to short-span compression strength measurements with a Zwick Roell Z005 according to ISO 9895 (2009). The density of the sheets was determined by measuring the basis weight (ISO 536:2019) on a Precisa XT 320M scale, and the thickness (ISO 534:2011) on a Lorentzen & Wettre App 141, type 90-0 of the sheets; note that due to limited amount of material, only two measurements of each sheet were made, which is reflected in larger confidence intervals for the density.

RESULTS AND DISCUSSION

The temperature settings from Table 1 did not exactly match the real achieved temperatures, which are shown in Fig. 1. Most notable is the fact when the oven was set to 50 °C, it had trouble maintaining the temperature, with both mean values off by approximately 10°C, with high variation. This was due to the ovens temperature setting with a manual twist-knob, which was not accurate for the lowest settings. For this particular study, it is still interesting to observe the drying for this temperature, although the setting much less stable than the others.

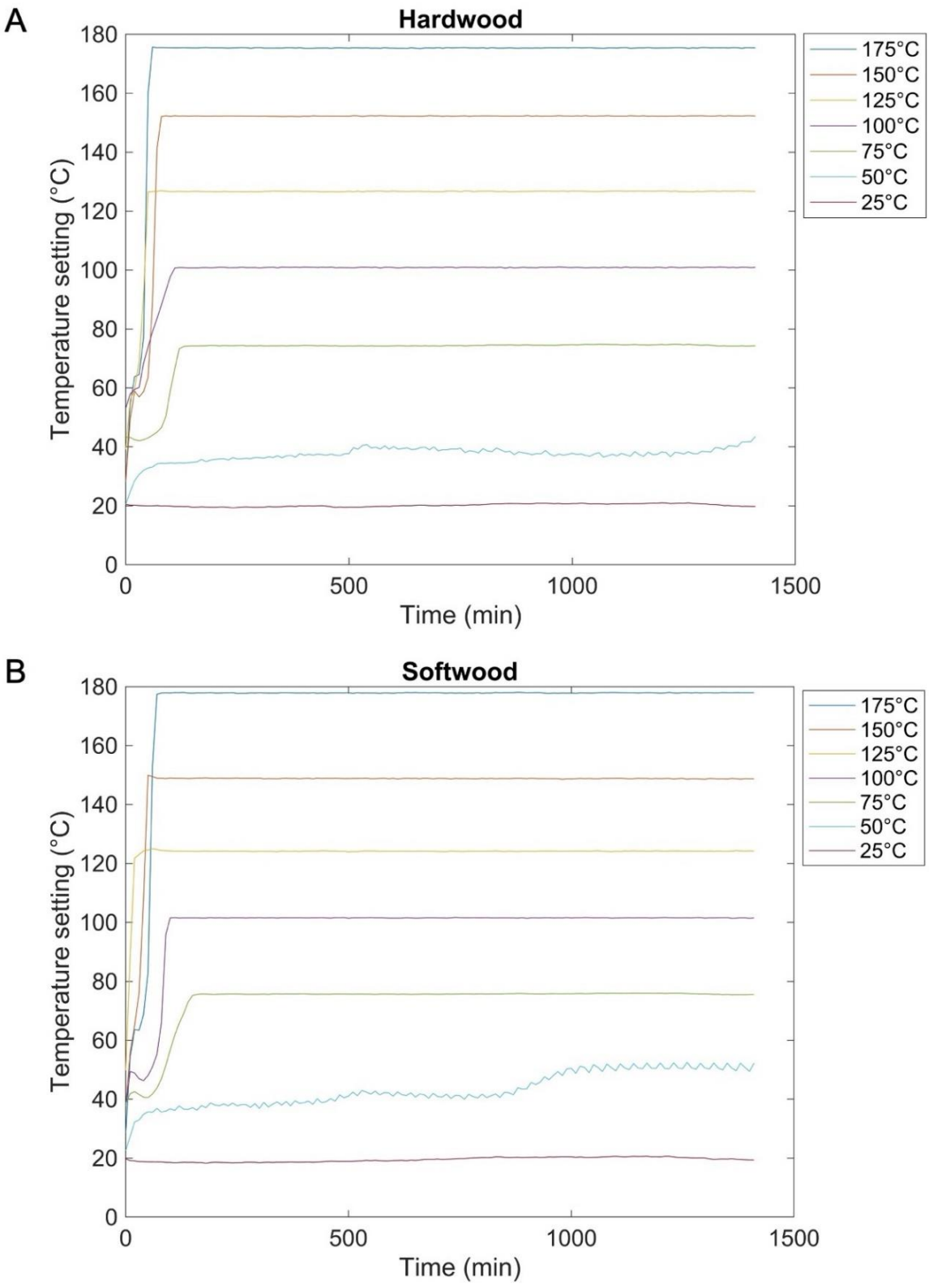

Fig. 1. Logged temperatures, that were compared to temperature settings. Hardwood (A) and Softwood (B). Note that the oven set to 50°C had trouble stabilizing and the mean values are off approximately 10°C as well as showing large variation.

Hardwood and softwood chemical pulps were dried at different temperatures, to the same dryness, 95% solids content. With increasing temperature, the swelling capacity, *i.e.*, WRV, of the pulp fibers, both hardwood and softwood, decreased, as shown in Fig. 2, meaning that the pulps became more hornified at higher temperatures. WRV and hornification were introduced by Jayme (1944), and the phenomenon have been researched widely since then. Hubbe *et al.* (2024) have recently provided a comprehensive description of the connection between cellulosic fiber swelling, hornification, and WRV. Note that the absolute values of WRV are slightly higher than they would be for normal WRV testing, as a lower centrifugal force was used, compared to the standard procedure.

Interestingly, there was also a color development of the pulps during the drying, which became significant with drying temperatures over 100 °C (Fig. 3). Color and hornification have previously been shown for CNF films by Yang *et al.* (2019) and Kato and Cameron (2002). When the WRV is plotted against the yellowness (Fig. 4), the data was in line with a relationship between color and hornification, for the lower WRV values, *i.e.*, drying temperatures over 100 °C.

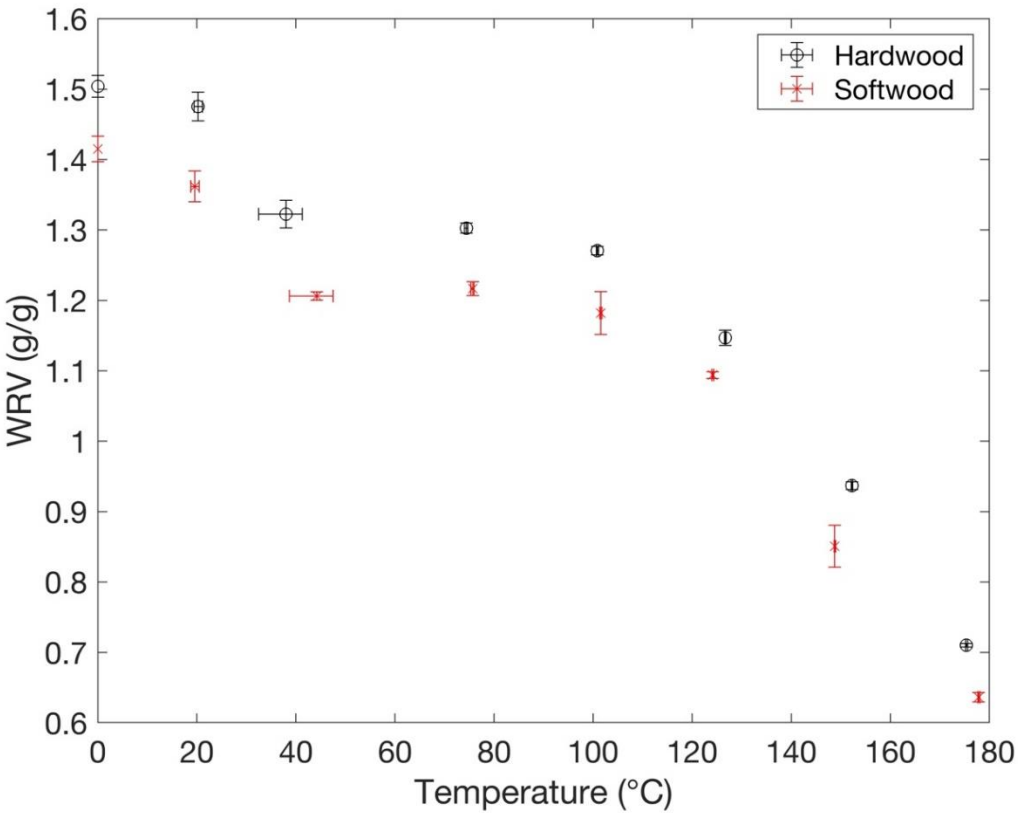

Fig. 2. Fiber swelling capacity as measured by WRV depending on drying temperatures. Reference values for never-dried pulps are placed at a drying temperature of 0°C. Error bars in the X-direction show maximum and minimum temperature values, and error bars in the Y-direction show a 95% confidence interval based on four measurements of WRV.

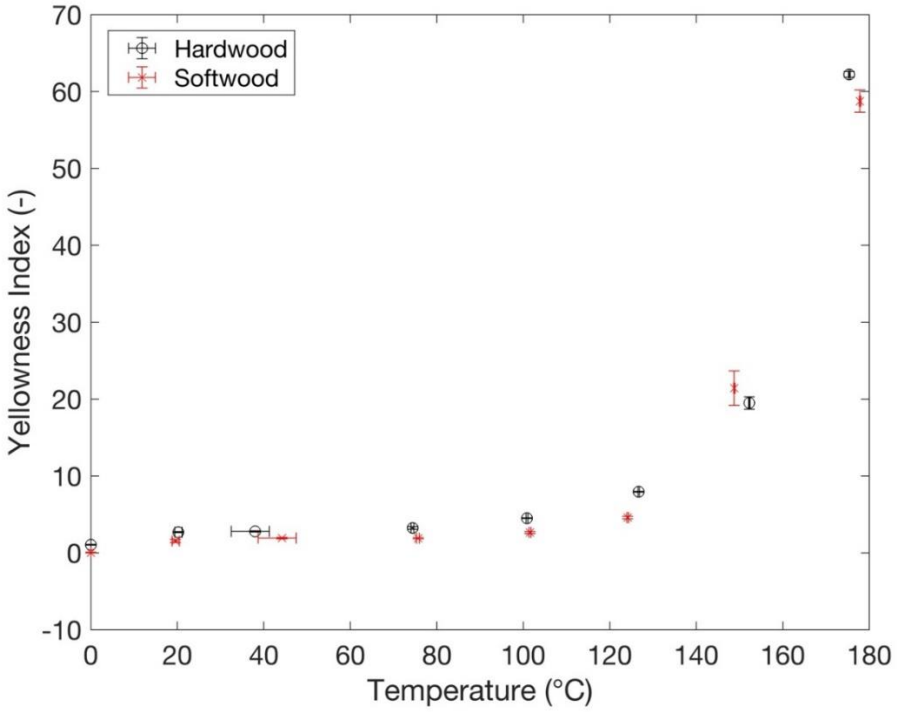

Fig. 3. Pulp yellowness depending on drying temperatures. Reference values for never-dried pulps are placed at a drying temperature of 0°C. Error bars in the X-direction show maximum and minimum temperature values, and error bars in the Y-direction show a 95% confidence interval based on four measurements of yellowness.

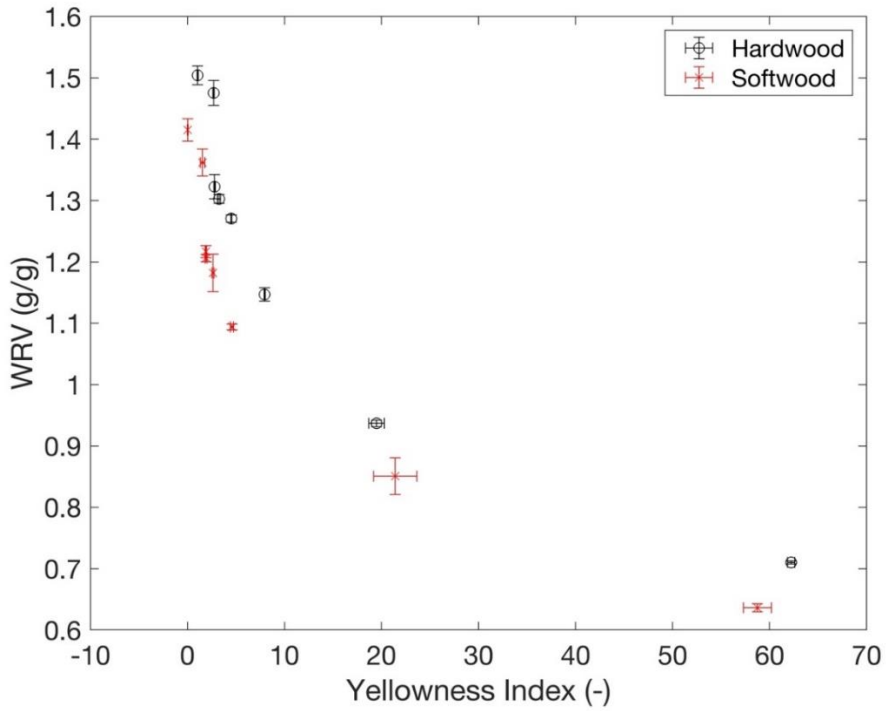

Fig. 4. WRV and yellowness plotted against each other for all drying temperatures from Table 1. Error bars show a 95% confidence interval based on four measurements.

Furthermore, the drying temperatures influenced the mechanical properties of sheets made from the pulps dried at different temperatures; the compression strength of the pulp decreased generally with higher drying temperatures (Fig. 5).

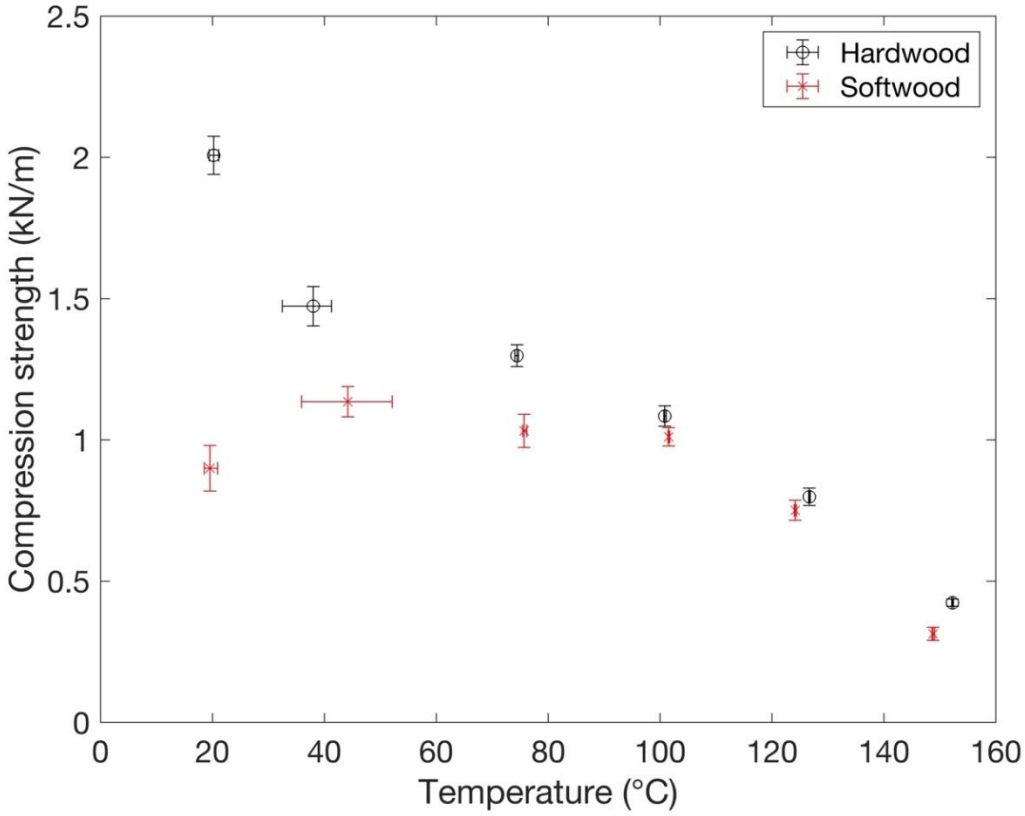

Fig. 5. Compression strength depending on drying temperatures. Error bars in the X-direction show maximum and minimum temperature values, and error bars in the Y-direction show a 95% confidence interval based on 20 measurements of compression strength divided over two sheets. The highest drying temperature (175°C) was excluded because of no failure detection according to the standard.

Figure 6 shows the sheet density for the different temperatures. Note that for both compression strength measurements (Fig. 5) and density (Fig. 6), the results from sheets dried at the highest temperature, 175°C, were excluded. This was because the compression strength method relies on failure detection by a peak in the stress-strain curve, and this was not present for these particular sheets. The compression strength values reported in Fig. 5 were very low compared to industry standard values. This was mainly because unpressed Rapid-Köthen sheets were produced, which had lower density (Fig. 6) than normal papers. Very little of the shift in magnitude can be attributed to the hornification, as the strength values from room temperature also were low.

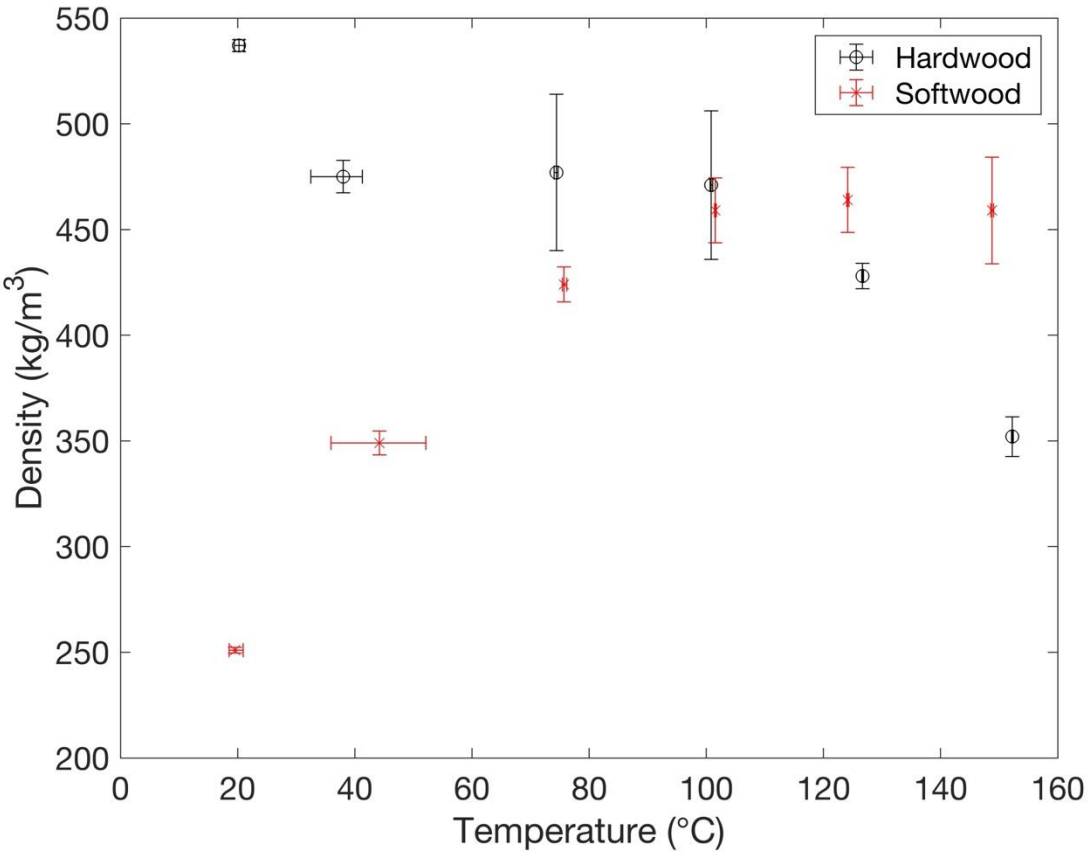

Fig. 6. Density depending on drying temperatures. Error bars in the X-direction show maximum and minimum temperature values, and error bars in the Y-direction show a 95% confidence interval based on two measurements of density. The highest drying temperature (175°C) was excluded because of no failure detection for SCT according to standard.

The results in this work indicate that drying temperature influences the hornification of pulp, so that under 100 °C the hornification increases modestly with drying temperature and increases drastically over 100 °C. There was also a connection shown between color formation during drying and increased hornification. A previously suggested model for hornification is mainly based on that water during drying forms "chains" that eventually direct hydroxyl groups on cellulose surfaces to each other (Sjöstrand *et al*. 2023; Hashemzehi *et al*. 2024). Chains of H-bonds structuring close to the surface of cellulose were also revealed in molecular dynamic simulations by Barrios *et al*. (2024). These chains may be seen as a molecular base for capillary forces. However, capillary forces of water are generally weaker at increased temperatures (Gittens 1969), which is probably due to the fact that such "water chains" are less stable due to the heat moments and increased mobility of the molecules. A possible explanation is related to the idea first introduced by Salmén and Stevanic (2018), who proposed that the fibrils were more mobile. Accordingly, it proposed here that the cellulose chains within fibrils are also more movable at higher temperatures, thus making the fibrils themselves have a larger area available for interactions with each other by hydrophobic interactions and Van der Waals bonds, which also have been suggested to play a role in hornification (Hashemzehi *et al.* 2024; von Schreeb *et al.* 2024). A graphical presentation of this hypothesis is shown in Fig. 7a.

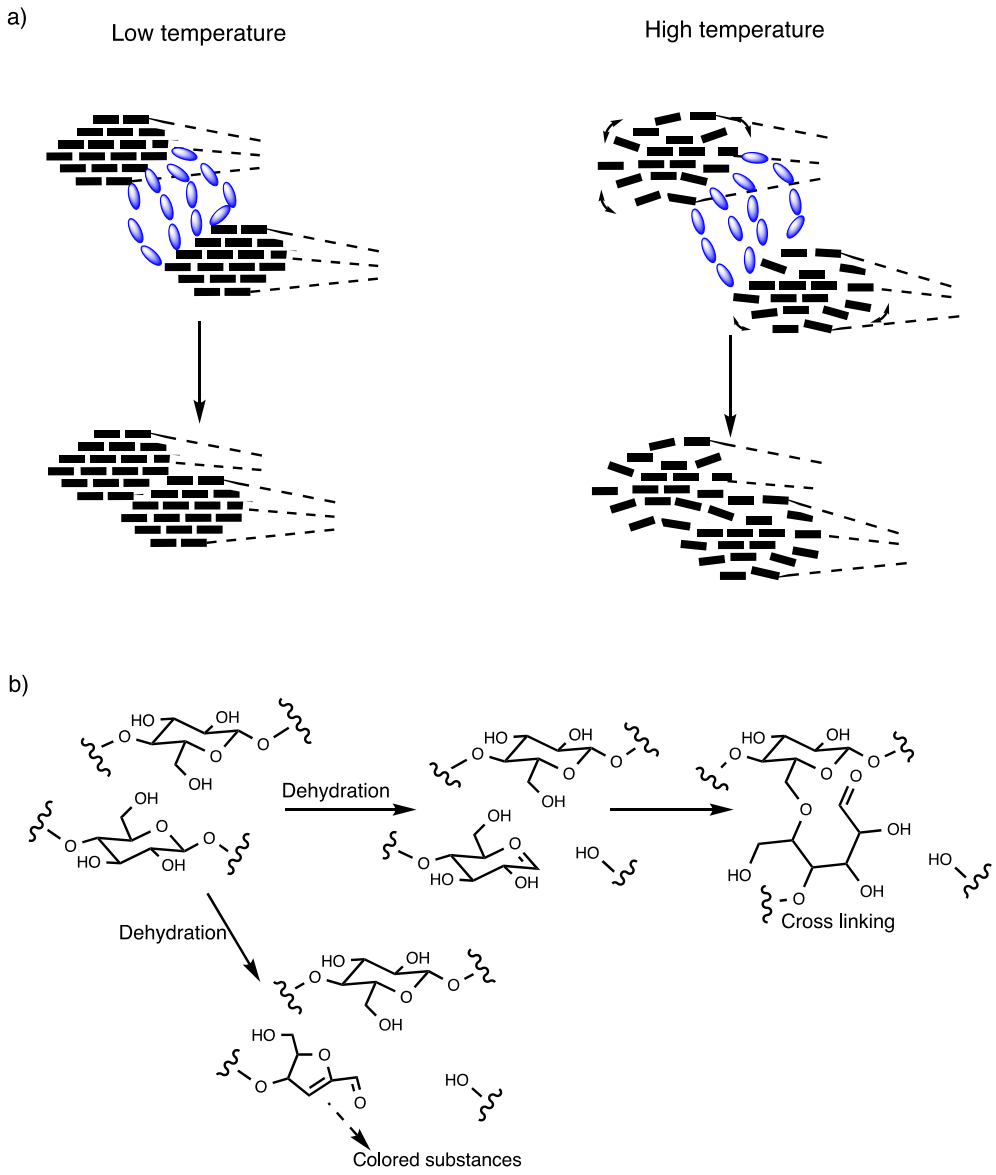

Fig. 7. Schematic presentations of hypothetical explanations for the data in this paper: a) At higher temperatures the cellulose fibrils become more mobile and thus more available to interfibrillar interactions and higher hornification, and b) Hypothetical mechanism for color development and covalent crosslinking of cellulose due to dehydration at high drying temperatures.

The increased hornification observed with increased drying temperatures is also not linear with temperature (Fig. 2); it happens stepwise between never-dried and room temperature is almost the same, 50 to 100 °C a step down, and at higher temperatures than 100 °C decreasing more linearly. It could also be interpreted as first a linear increase although relatively modest up to 100 °C, and above 100 °C the degree of hornification increases quickly. Both interpretations, linear and stepwise, suggest that more than one mechanism is involved. This is because the temperature is important below 100 °C in both cases. The drastically increased hornification at higher temperatures probably needs an additional explanation. Here, the color formation (Fig. 3), which might be connected, may

give a clue; dehydration reactions may cause caramelization reactions on carbohydrates (Yao *et al.* 2021), and reactive species formed during these reactions, might also lead to covalent crosslinking between cellulose molecules, which of course may contribute to the hornification process (see Fig. 7b). It should be underlined that the reaction shown in Fig. 7b is just a hypothetical reaction of an outcome of dehydration redaction in cellulose; the crosslinked structure is not a lactone, but rather a more stable structure as an ether. In support of these suggestions, the yellowness of the pulp samples, where yellow/brownish color indicates dehydration by pyrolysis reactions, plotted against WRV (Fig. 4). It is interesting to observe that the image shows an acceleration of yellowness with decreasing WRV, indicating that after a certain temperature, multiple mechanisms must be present.

Generally, the sheet compression strength was observed to decrease with increased hornification (Fig. 5) with one exception of the sheets from the room-temperature dried softwood pulp. Note again, that the laboratory Rapid-Köthen sheets were not pressed with any significant press loads and thus, the compression strength absolute values will be low compared to conventional sheets. The hornification phenomenon increasing with drying temperature (Fig. 2) mainly affects the fibers by lowering the extent of the external and internal fibrillation and providing stiffer fibers. For these compression strengths – in contrast to earlier presented material – there was a significant difference between the behavior of hardwood and softwood pulps, where the hardwood samples display a semi-linear relationship between compression strength and temperature, whereas the compression strength for the softwood appeared to have a maximum around 40 to 50 °C (Fig. 5). Compression strength, and also hornification, can thus be connected to sheet density. High hornification gives stiff pulp fibers, which would increase fiber density, but on a sheet level, stiffer fibers give lower sheet density.

The compression strength of sheet networks will be influenced by the increased hornification and increased fiber stiffness in two ways: (i) the sheet compression strength will have a slight benefit from stiffer fibers, bearing load under compression, and (ii) the sheet compression strength will decrease due to lower number of fiber-fiber bonds that is an effect of the stiffer fibers. By this reasoning, with two conflicting effects on compression strength, the hypothesis was that the sheet compression strength might increase with moderate hornification and start to decrease when the second mechanism takes over at higher hornification. This is the observed behavior for softwood fibers but not for hardwood (Fig. 5). Softwood sheets exhibited the highest compression strength at the 40 °C drying setting, with an almost linear decline after that temperature. Hardwood sheets did not behave like this. Instead, the compression strength decreased with increased drying temperature. The conclusions drawn from this are that major hornification is negative for all sheet compression strengths due to poor network bonding. However, minor hornification can be beneficial for applications, for certain fiber types, where compression strength is an important parameter. The density measurements (Fig. 6) support this reasoning, where hardwood pulps follow the expected loss of density due to stiffening of the fibers. Softwood pulp, on the other hand showed an increase in density that would explain the initial increase in compression strength. This behavior of softwood pulp is not explained by hornification theory, where stiffening of fibers in a paper network should decrease density. Perhaps the absence of conventional pressing and drying accounts for this; however this issue is not answered by this study. Density measurements were also few and not the core of the study.

CONCLUSIONS

1. Hornification was found to depend on drying temperature, such that higher temperature gave higher degrees of hornification. This is true for both Hardwood and Softwood, unbeaten bleached chemical kraft fibers.
2. Pulp yellowness increase with increasing drying temperature.
3. During fiber hornification, the two indicators: (i) decreased swelling capacity, and (ii) pulp yellowness, are connected. Initially, at low drying temperatures, WRV decreases rapidly with a low increase in yellowness, after around 100 °C WRV decreased more slowly, and yellowness started to increase much more. This indicates parallel reactions, not necessarily connected, which both contribute to hornification.
4. Even before dehydration reactions start at approximately 100 °C drying temperature, the mobility of cellulose chains within fibrils increases with temperatures, causing higher degrees of hornification with higher drying temperatures.
5. Compression strength measurements showed that hornification negatively affected sheet compression strength. This is proposed to be due to poor network bonding. However, minor hornification could be beneficial, as observed in this study for softwood pulps, where increased individual fiber stiffness resulted in increased sheet compression strength.

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