

Hornification in Commercial Chemical Pulps: Dependence on Water Removal and Hornification Mechanisms

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Understanding cellulose hornification provides crucial information regarding drying of pulp, paper, and other cellulosic materials as well as recycling them. By measuring drainage, fiber width, and water retention value of hardwood and softwood pulps before and after sheet forming and after different drying procedures at different achieved levels of solids, the hornification was evaluated. The water retention value was also measured for the pulps when dried from acetone to observe what happens when hydrogen bonds are not available in the liquid phase. The drainage and fiber width decreased with increasing solids content; the fibers became increasingly stiff with increased water removal. Water retention measurements indicated that hornification is a stepwise process with large drops in fiber flexibility as soon as the fibers are being processed and later after a certain amount of water has been removed. In sum, the fibers must achieve a certain solids content to show hornification, and hydrogen bonds in water draw the cellulose surfaces together to create hornification. The mechanism of hornification is believed to be driven by hydrogen bonds and related to the distance between cellulose chains inside the fiber wall. Other types of bonds are probably also present and help with the irreversibility of hornification.

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INTRODUCTION

Hornification is a phenomenon in cellulose-rich materials where irreversible, or at least very stable, chemical bonds form between cellulose surfaces (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; Bensselfelt *et al.* 2023; Ferreira *et al.* 2023; Koistinen *et al.* 2023; Solhi *et al.* 2023). Hornification happens when wet cellulosic materials are dried, and the most notable consequences are stiffness/reduced flexibility, diminished rewetting, and decreased chemical reactivity. In the case of cellulose

pulp for papermaking, hornified pulp fibers exhibit decreased fiber wall swelling, internal and external fibrillation, and flexibility compared with never dried pulp. All these effects of hornification decrease the ability of the pulp fibers to form fiber-fiber bonds, resulting in lower paper strength (Laivins and Scallan 1993; Oksanen *et al.* 1997; Ferreira *et al.* 2023). A similar phenomenon occurs with nanocellulose fibrils (Moser *et al.* 2018). However, hornified pulp fibers are often stiffer, which is an advantage in certain applications, such as middle layers of packaging boards (Kajanto *et al.* 1998). Natural cellulose plant fibers have a complex hierarchic organization, where the cellulose chains are parallelly organized in semi-crystalline fibrils of around 28 chains. These fibrils tend to aggregate into larger units, fibrillar aggregates, that in turn organize in several levels for eventually building of cell walls of plant cells such as tracheids and labriform fibers. This means that that chemical pulp fibers display fibrilized cellulose surfaces with a larger exposed cellulose surface area in comparison to what would be expected from a synthetic fiber of similar dimensions without this hierarchic organization (Kumar *et al.* 2021).

There is an active debate as to the mechanisms of the actual bonds responsible for hornification (Wohlert *et al.* 2022; Benselfelt *et al.* 2023; Koistinen *et al.* 2023; Solhi *et al.* 2023), although there is no ambiguity about the resulting reduced flexibility of the fibers due to reduced swelling ability and therefore reduced sheet strength. Different mechanistic explanations for the hornification are favored by different researchers and studies; a common hypothesis for hornification is that it is based on by hydrogen bonds (H-bonds) with help from free hydroxyl groups that create irreversible or at least rather strong assemblies of H-bonds between cellulose chains inside fibers (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 reasoning behind H-bonds being responsible for hornification is the huge amount of hydroxyl groups present in cellulose surfaces, but all agree that H-bonds are also reversible in water environments. However, if multiple H-bonds have been formed, it will be more difficult for water to break them. The reversibility in water is the main reason for disagreement and doubts (Fernandes Diniz *et al.* 2004; Wohlert *et al.* 2022) that H-bonds can be solely responsible for the irreversible hornification bonds created with drying. There are several studies not content with hydrogen bonding as the sole explanation. Two alternative mechanisms are: (1) co-crystallization where crystalline parts of the cellulose in the fibers end up next to each other, rotate, and cross-link with each other (Newman, 2004) - probably by H-bonds and hydrophobic interactions/ Van der Waals bonds, and (2) lactone bridge formation, which is a covalent bond between cellulose chains that are not be reversible with water (Fernandes Diniz *et al.* 2004). Of course, several mechanisms can be valid and even cooperate, *i.e.*, a combination of different bonds between functional groups on the cellulose chain within the fibers, H-bonds, ester bonds and ether bonds.

According to recent literature reviews (Wohlert *et al.* 2022; Benselfeldt *et al.* 2023; Solhi *et al.* 2023), H-bonds may be involved in hornification, but according to these researchers, H-bonds alone cannot be the explanation. The argument is that H-bonds are not strong enough and do not have the reach to pull the cellulose surfaces close enough to be in range for H-bonds. Wohlert *et al.* (2022) suggest “capillary pressure and capillary forces” instead. The capillary effects are high when the liquid’s surface tension is high and when the contact angle towards the solid is low (Myers 1999; Israelachvili 2011), both these are true for water and cellulose due to H-bonds. When the surfaces of cellulose are close enough, Wohlert *et al.* (2022) accept that H-bonds are formed. However, they suggest that the H-bonds should be weakened by the water present between the cellulose surfaces

(Wohlert *et al.* 2022). The forces in this case are about how water binds to the solid phase cellulose. The H-bond strengths are approximately the same between water-water, cellulose-cellulose and water-cellulose (Medronho *et al.* 2012; Kihlman *et al.* 2013). Several sources report the ability of H-bonds in water to interact with each other and form bridges (Clark 1985; Fellers and Norman 1998; Israelachvili 2011), this might be the mechanism for pulling cellulose surfaces together even when individual H-bonds have very short reach (Wohlert *et al.* 2022; Benselfeldt *et al.* 2023; Solhi *et al.* 2023). Kang *et al.* (2018) describe an interesting method called Critical Point Drying (CPD) where they preserve the morphological structure of eucalyptus cellulose biomass by replacing water as a solvent with a non-polar liquid, in their case CO₂ fluid. By exchanging the solvent to one that cannot form H-bonds, the cellulose surfaces could not come sufficiently close together to enable hornification and the morphological structure remained unchained to a large extent. The liquid exchange could also affect the stiffness of the cellulosic chains, making them less conformable. This would also give a less collapsed morphological structure, but higher stiffness is not expected to give higher swelling after drying since that is a measurement highly connected to fiber wall flexibility.

The presence of different types of hemicelluloses, of which xylans and glucomannans are the most important, was shown to diminish hornification in a study by Oksanen *et al.* (1997). Köhnke *et al.* (2010) showed increased fiber swelling with hemicellulose present. Therefore, since pulps with high content of hemicellulose will be less likely to have hornification effects, these pulps will be more successfully swelled when reintroduced to water (Köhnke *et al.* 2010).

As Oksanen *et al.* (1997) showed results with similar effects when removing both xylan and glucomannan, the chemistry of the respective hemicellulose does not seem to be critical. Even for hemicelluloses that themselves can create hydrogen bonding with cellulose, the hornification is lowered. This is an argument in favor of the hemicelluloses acting as spacers, letting water penetrate the structure, and letting the H-bonds be broken more easily. A suggested mechanism for this is that the hemicelluloses keep cellulose aggregates separated, which would allow water to penetrate the structure and break the bonds. This is in line with the idea of hydrogen bonding being an important part of the hornification mechanism. It is expected that large objects sitting in the way should prevent hornification (Oksanen *et al.* 1997; Köhnke *et al.* 2010). Since additions of glycerol succeed in diminishing hornification by interposing between the cellulose chains, shown by Moser *et al.* (2018), the argument is further strengthened that the mechanism of binding is distance dependent, although not actually demonstrating the binding itself and the mechanism behind it. A mechanistic sketch of this concept is shown in Fig. 1. As proposed by Campbell (1959), capillary forces become extremely strong as a meniscus between two fibers becomes very thin. Such forces would be expected to pull at least the edges of the contacting surfaces into molecules contact, and then the zipper-like mechanism, shown in Fig. 1, is expected to kick in.

One fundamental question about hornification is how it is evaluated. One way is to assess the ability of a pulp to hold water by measuring the water retention value (WRV) (Laivins and Scallan 1993; Oksanen *et al.* 1997; Tze and Gardner 2001; Köhnke *et al.* 2010; Claramunt *et al.* 2011; Luo and Zhu 2011; Luo *et al.* 2011; Mo *et al.* 2022). Higher values of WRV indicate a greater ability to swell for pulps with hemicellulose present in the experiments carried out by Oksanen *et al.* (1997); this is explained with the help of increased charge density of fibers. They also achieved higher density and strength and lower light scattering of the paper sheets, but low degree of hornification, *i.e.*, good

wettability of fibers. Such a situation is also expected to give higher WRV. Increased hornification thus results in stiffer fibers, lower value of WRV, lower density, lower pore volume within cell walls, and lower paper strength (Oksanen *et al.* 1997). Both the water holding capacity of the fibers, which can be measured by centrifugation (WRV), and the strength properties of the paper product can be used to evaluate hornification (Luo and Zhu, 2011). Lessons can be also learned from the lack of hornification in high-yield pulps, the presence of hemicellulose and lignin in the structure prevents cross-linking between cellulose chains to some extent and the effect of hornification is less (Laivins and Scallan 1993; Oksanen *et al.* 1997).

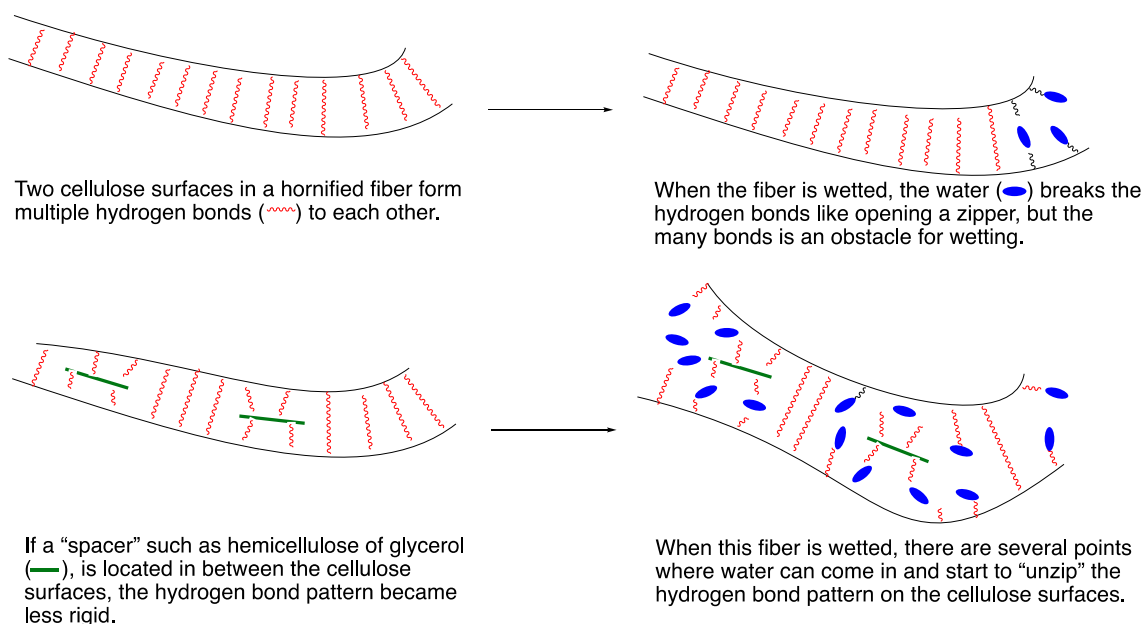


Fig. 1. Multiple H-bonds preventing water from breaking hornification (top), but when a spacer is present, the H-bonds are much more accessible for water penetration and hornification will be lower due to higher number of H-bonds being broken (bottom)

The conditions for drying might have importance for hornification; the WRV value decreases after cycles of drying. This is due to hornification, as shown by Salmén and Stevanic (2018) and Ferreira *et al.* (2023). According to Salmén and Stevanic (2018), this is also true when drying at room temperature. Increased temperature during drying was suggested to increase hornification, as shown by Salmén and Stevanic (2018), and Luo and Zhu (2011). However, opposite results were obtained by Laivins and Scallan (1993) or Newman (2004). Salmén and Stevanic (2018) also interrupted drying around 80% solids, and unexpectedly showed that the hornification was greater than with drying to 95%. Nuclear Magnetic Resonance (NMR) measurements showed that the hornified masses have more compact structure, *i.e.*, increased aggregation. The crystallinity is not affected by the drying method according to NMR, but Wide-Angle X-ray Scattering (WAXS) shows an effect that is consistent with hornification via WRV (Salmén and Stevanic 2018).

This work explores how the actual water removal of commercial hardwood and softwood pulps affect fiber swelling, together with drying from a liquid with lesser tendency to form H-bonds, as a basis for a discussion of the mechanism of hornification. The hypothesis is that the mechanism behind hornification is H-bonds, and that chains of

H-bonds can draw cellulose surfaces closer together during drying. This phenomenon will be demonstrated by drying pulps from both water and acetone acting as solvents.

EXPERIMENTAL

Fibers

Never dried bleached chemical kraft hardwood pulp fibers from birch (*Betula pendula/pubescens*) and softwood pulp fibers from a 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. The pulps were extracted from the pulp mill after full bleaching and before refining. The kappa numbers of the pulps were 12 and 14 for birch and spruce, respectively. To be able to use the same pulp for a long series of experiments without deterioration, they were deep-frozen on delivery at minus 20 °C and thawed at room temperature and diluted to a 0.2% stock solution before each experiment. No chemicals were added. Reference testing was performed before and after the freezing to account for possible effects on the fibers.

Drying from Different Solvents

To test the hypothesis that chains of H-bonds in water pull cellulose surfaces together and thereby increase hornification, pulp was dried in exactly the same way from water and from acetone. If the H-bond chains pull the cellulose together, then the swelling capacity of fibers when drying from water should be lower than when drying from acetone.

Both reference pulps, softwood, and hardwood were dewatered to approximately 10% solids on a Büchner funnel with gentle vacuum, and the filtrate was recirculated one time to make sure all fine material stayed in the pulp. The pulps were then diluted to approximately 0.5% in ethanol for 60 min; this was done to ensure that as much water as possible was removed.

The same procedure was repeated with acetone. After the pulps were completely immersed in acetone for 60 min, they were put back on the Büchner funnel for vacuum exposure one last time, where most of the acetone was removed, and then dried at 105 °C for 24 h until completely dry.

The same procedure was performed for both pulps using water in all steps; these provided reference values for this part of the method. WRV was measured on all four versions of the pulps, after they were diluted to 0.2% in water and disintegrated according to ISO 5263-1 (2004), with 10000 revolutions, to investigate possible differences in swelling capacities.

Water Removal for Inducing Hornification

The pulps were formed to 100 g/m² sheets in a Rapid-Köthen sheet former (RL-ASF-A; Rycobel, Belgium) from 0.2% stock solution, and dried at different temperatures in vacuum according to the setup shown in Table 1. The vacuum level was set to -0.85 to -0.90 bar. At this particular vacuum level, the temperature 65 °C was at the boiling point for water, which was the reason for the large variation in solids for these samples. At least three sheets were made for each sample. The sheets were both for ensuring enough mass for testing and for increasing the amount of material for higher statistical significance in the heterogenous material. The Rapid-Köthen sheets of varying achieved solids content

were all repulped in a pulp disintegrator (ABB AB / Lorentzen and Wettre, Sweden) and diluted back to 0.2% stock solution.

Table 1. Temperature and Drying Times for Sheet Forming to Induce Different Levels of Hornification

Sample / Pulp type	Temperature (°C)	Drying time (min)	Solids (%)
Hardwood never dried	No drying	No drying	4.3 – 4.4
Hardwood	25	10	20.36 – 21.67
Hardwood	50	10	29.97 – 30.61
Hardwood	60	10	35.49 – 40.89
Hardwood	65	10	56.11 – 84.98
Hardwood	75	10	85.96 – 94.27
Hardwood	95	10	94.23
Softwood never dried	No drying	No drying	7.0 – 7.4
Softwood	25	10	23.52 – 23.91
Softwood	50	10	27.73 – 32.0
Softwood	60	10	39.64 – 42.54
Softwood	65	10	56.78 – 85.08
Softwood	75	10	90.31 – 95.55
Softwood	95	10	99.76

Note that the achieved solids are presented as a range between a number of sheets, where some ranges are large and the driest sheets were only measured once.

Evaluating Hornification

Solids content was measured with an IR-scale (DAB moisture analyser, Kern and Sohn, Germany) directly after sheet forming in 120 °C. The never-dried pulp, as well as the disintegrated sheet pulp from the Rapid-Köthen sheets were evaluated according to several standard measurements to be able to evaluate the possible degree of hornification in each sample.

The dewatering ability of the pulps after each process of sheet forming and drying was tested by measuring the drainage resistance according to the Schopper-Riegler method ISO 5267-1 (1999), and the swelling ability of the fibres with water retention value (WRV) ISO 23714 (2014). The fibers were also evaluated with a LandW Fiber Tester (ABB AB / Lorentzen and Wettre, Sweden), mainly to monitor the possible change in fiber width due to differences in collapsibility following hornification in the fiber wall.

RESULTS AND DISCUSSION

Results from changing the solute to acetone from water for never-dried pulp and then measuring swelling ability of the fibers with WRV are shown in Fig. 2. There was a clear difference between the reference and the acetone pulps, for both hardwood and softwood. The pulps where water was exchanged into acetone, a liquid without H-bonds, before drying, showed higher swelling capacity according to WRV measurements. The hornification was significantly lower for these. This difference can be explained by the ability of the H-bonds in water to form chains and pull cellulose surfaces closer together while drying. The different surface tensions of the solvents could also affect the ability of the solvent to pull cellulose surfaces closer, which might be contributing to the hornification mechanism, although in combination with hydrogen bonding.

Another significant difference was that the hornification appeared to be worse for the softwood pulps than for the hardwood pulp (Fig. 2). Although there of course are many chemical and morphological differences between these pulps, it appears plausible that they have to do with the differences in hemicellulose composition; hemicellulose may affect the hornification process, as has been reported earlier (Oksanen *et al.* 1997). The hemicelluloses in softwood and in hardwood are different; in hardwoods xylan dominates completely, and in softwood glucomannans are the most common hemicelluloses. In a recent study of Berglund *et al.* (2020), it was demonstrated that xylylans and glucomannans seem to affect cellulose fibrils in different ways, where xylylans tend to make the fibrils evenly distributed - maybe due to the charges of the uronic acids in the structure, whereas glucomannans tend to flocculate the cellulose fibrils. From this perspective it is not unexpected that glucomannan-rich pulps hornify more than xylan-rich pulps.

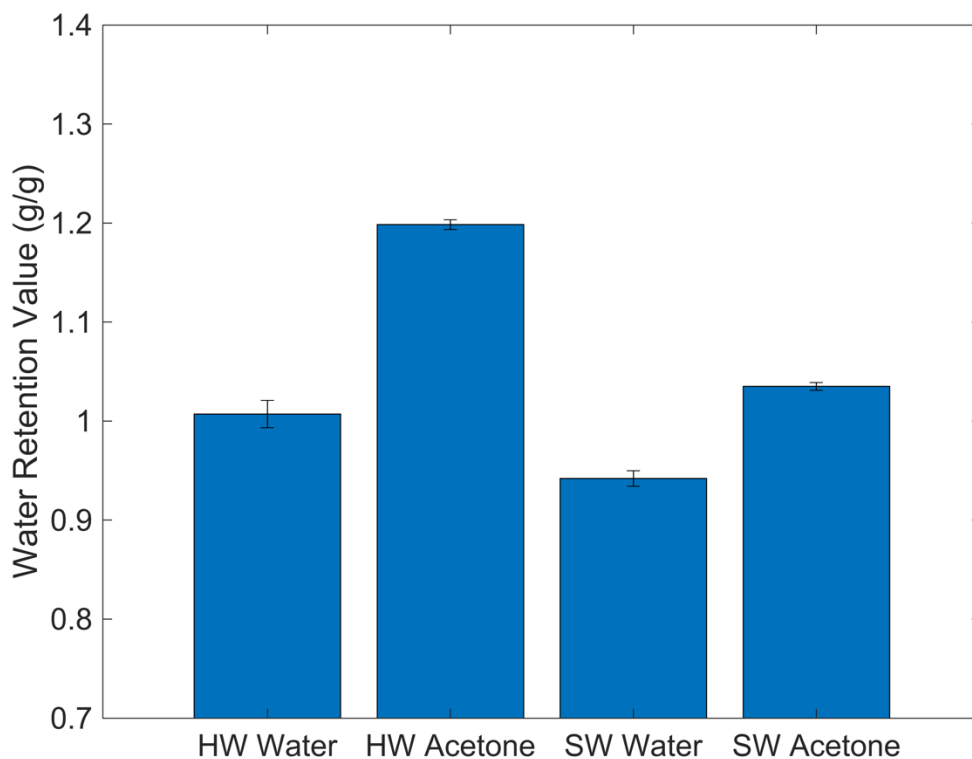


Fig. 2. WRV results for once-dried hardwood and softwood pulps from water and from acetone. Mean values and 95% confidence interval are shown.

In a paper sheet during dewatering, with an environment of cellulose and water, there are, due to H-bonds, forces acting between water molecules, even as dewatering begins to introduce air into the system. These H-bonds between water molecules will form temporary bridges (Clark 1985; Fellers and Norman 1998; Israelachvili 2011), in accordance with Fig. 3, which are proposed to create adhesion forces between surfaces of cellulose. These adhesion forces, driven by H-bonds, will help to draw the cellulose surfaces towards each other when draining and drying.

The results from the evaluations of hornification are shown in Figs. 4 through 6 where the drainage ($^{\circ}$ SR), fiber width (μm), and WRV (g/g) are all plotted against the achieved solids content (%) for the samples introduced in Table 1.

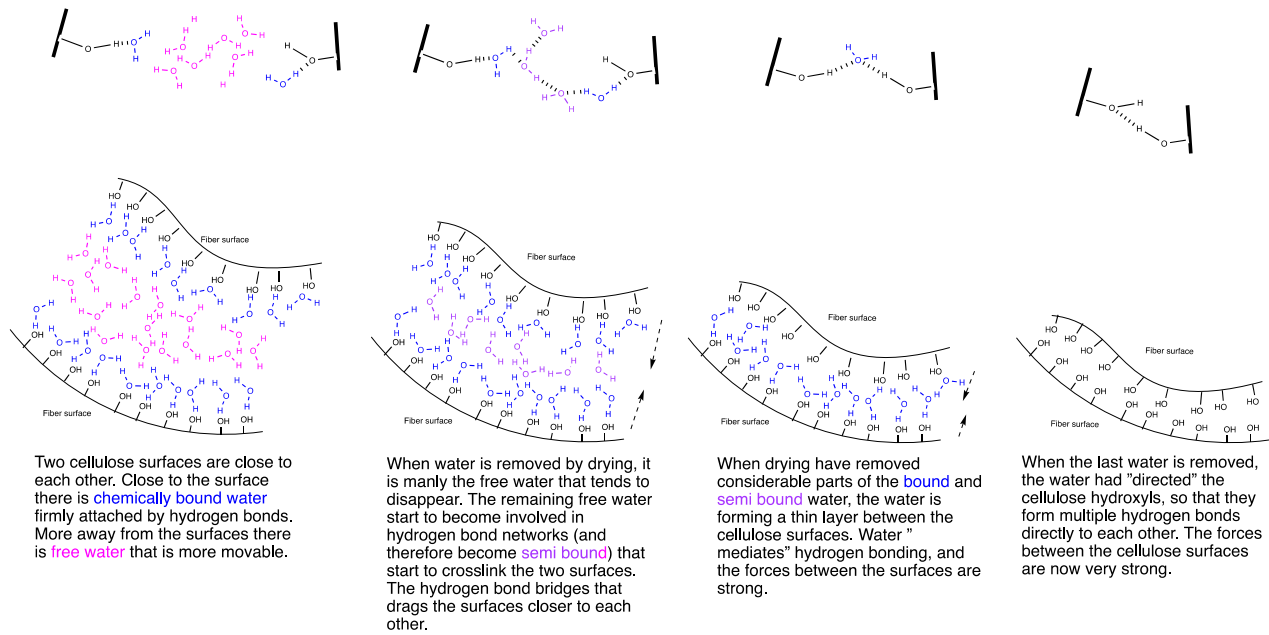


Fig. 3. Interfibrillar cellulose units with decreasing number of monolayers of water molecules between

The drainage for the hornified hardwood pulps showed a significant decrease with achieved solids content (Fig. 4). The drainage for the softwood samples does not show an equally clear trend of decrease.

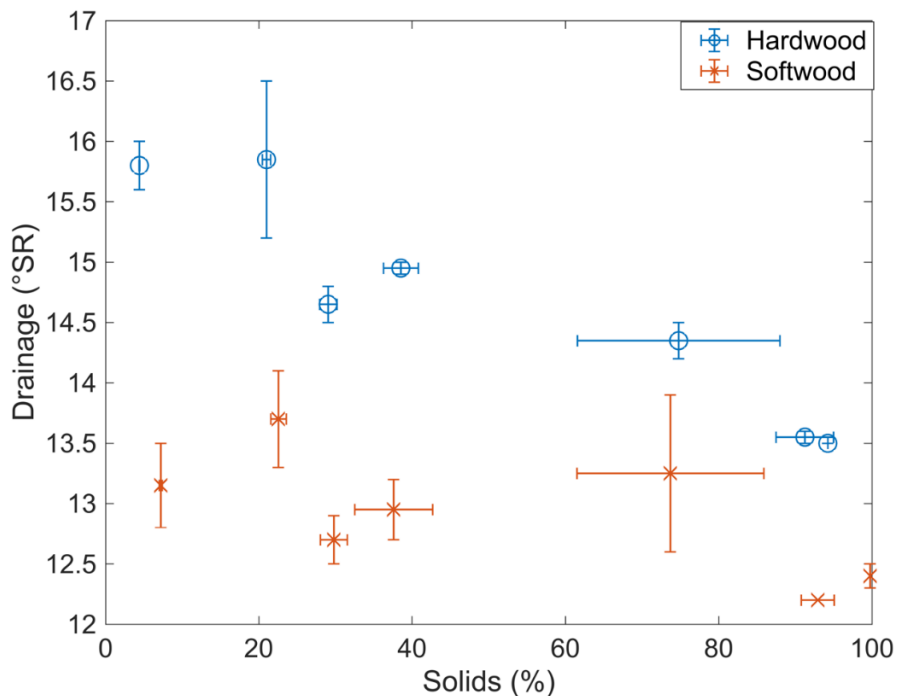


Fig. 4. Drainage measurements (°SR) against achieved solids content (%) for all hardwood and softwood samples. Mean values and 95% confidence interval are shown.

From Fig. 4, it is only evident that the softwood reference was higher in drainage than the two driest samples with solids close to 100%. In theory (Laivins and Scallan 1993, Oksanen *et al.* 1997), the hornified fibers would become more stiff and less flexible, and therefore easier to dewater in the drainage test, which in turn gives lower °SR-values. The downwards trend in drainage for the hardwood pulp looks fairly linear and no clear evidence shows any other behavior for different solids, as was apparent in Fig. 6 for the WRV measurements.

The fiber width behaved quite similarly to the drainage with decreasing width for increasing solids (Fig. 5). Both hardwood and softwood showed similar results for the decrease. The fiber width was obtained by an optical measurement in the Fiber Tester, and a reason for the decrease in width with increasing hornification is the fact that the internal structure of the fiber wall becomes stiffer, which leads to less collapsed fibers after one circulation of drying and rewetting. If a considerable number of the fibers in a sample becomes less collapsed, then the observed fiber-width would therefore decrease, since the fibers will appear more like smaller round cylinders as compared to the collapsed fibers appearing like elliptic cylinders. These initial results could indicate that Fiber Tester could be a quick way of determining changes in hornification for different locations, if the more traditional measurement WRV is unavailable for testing.

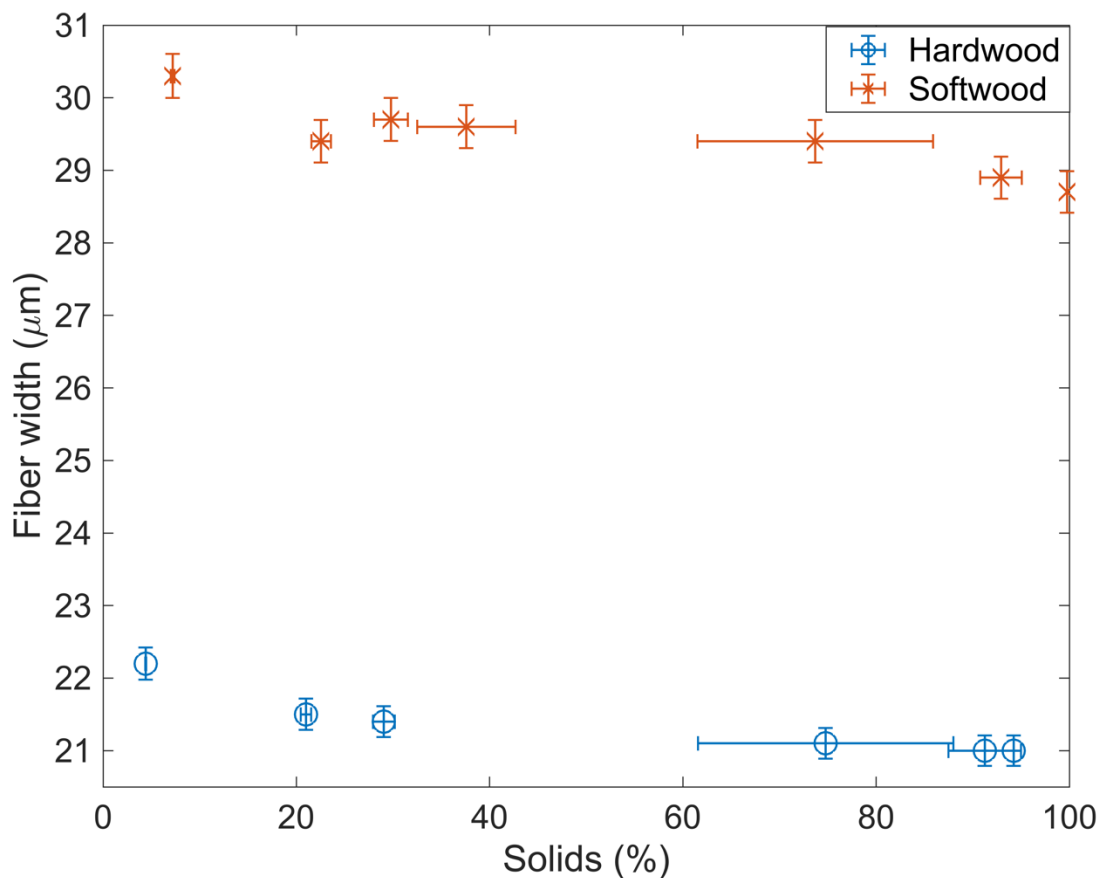


Fig. 5. Fiber width (μm) against achieved solids (%) for all hardwood and softwood samples. Mean values and 95% confidence interval are shown.

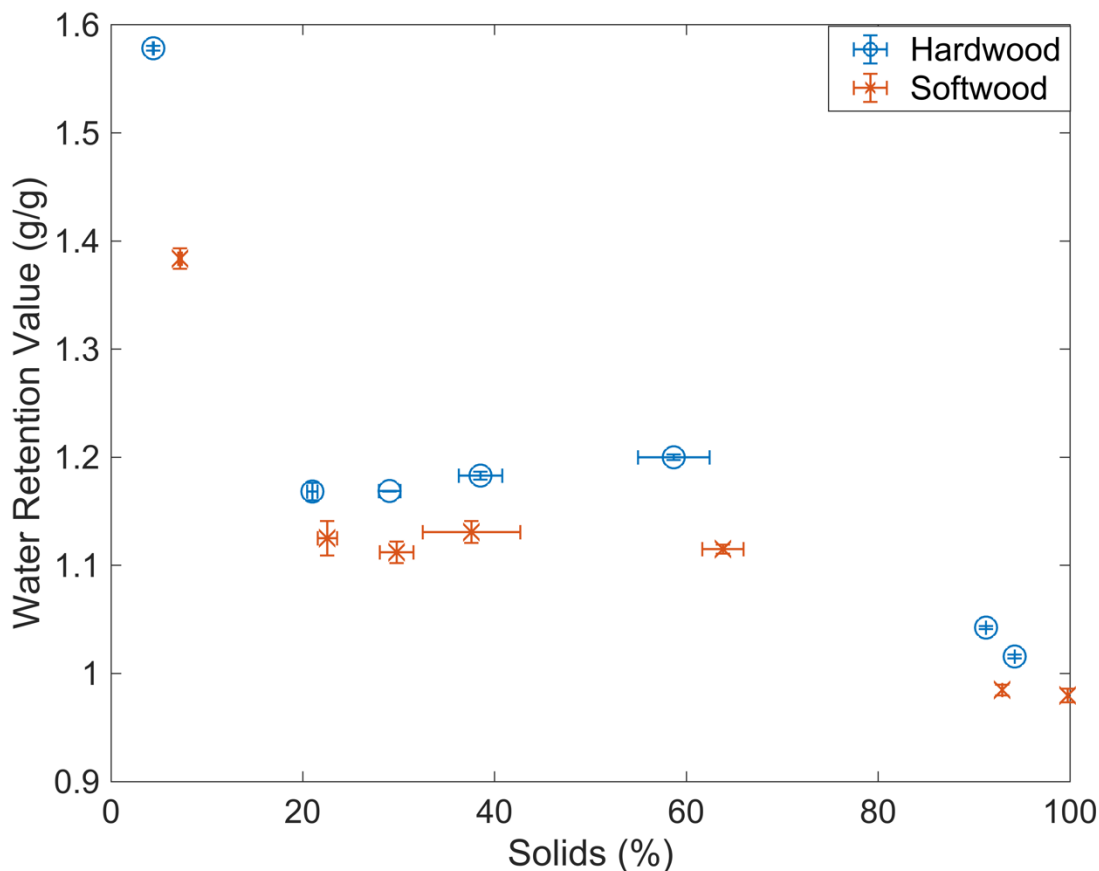


Fig. 6. WRV (g/g) against achieved solids content (%) for all hardwood and softwood samples. Mean values and 95% confidence interval are shown.

Figure 6 shows how the WRV decreases with increased hornification, brought on by increased solids. This has of course been shown and discussed in detail by many researchers before (Laivins and Scallan 1993; Oksanen *et al.* 1997; Tze and Gardner 2001; Claramunt *et al.* 2011; Luo and Zhu 2011; Luo *et al.* 2011; Mo *et al.* 2022). An interesting observation in Fig. 6 is that the WRV seems to decrease in a stepwise manner rather than linear, as has also been reported previously for eucalyptus pulps by Mo *et al.* 2022. This is observed for both hardwood and softwood samples. The never-dried pulp has a high WRV, which is connected to the high ability of fiber wall swelling due to low hornification. Initially when increasing the solids content, the WRV is considerably lower, although not changing. After reaching a certain solids content, the WRV is once again lowered drastically. It is of course of great interest to find, if it exists, the threshold point in solids where the main hornification occurs. The hornification seems constant between 20 and 60% solids. The hypothesis is that the hornification behaves in a stepwise manner, the reasoning behind this is that enough water needs to be removed from between the cellulose surfaces within the fiber wall, as shown in Fig. 3, before the main part of hornification can occur. Once the water layers between the cellulose surfaces are thin enough, chemical bonds can start to pull the surfaces close enough for multiple bonding (Fig. 3). Regardless

of exact bonding mechanism, this would constitute the practically irreversible bonds known as hornification. Once the multiple bonds are present, it becomes really difficult for the water to penetrate and to break enough bonds simultaneously to pull the cellulose surfaces apart and reverse the hornification.

CONCLUSIONS

1. Commercial chemical pulps need to achieve a certain solids content to start showing hornification effects. This is believed to be related to the distance between cellulose chains inside the fiber wall. Enough solvent needs to be removed for the interfibrillar cellulose units to come within range of binding to each other.
2. The mechanism for hornification is proposed to be multiple hydrogen bonding, as indicated by an experiment in which water was replaced by acetone, where higher fiber swelling was achieved upon rewetting in water due to the lack of H-bonds in the liquid phase during drying, and therefore no forces were available to pull the cellulose surfaces close enough together to form bonds and not let water penetrate.
3. Apart from fiber swelling by measuring Water Retention Value, both drainage and fiber width can be used as measurements for the hornification by addressing fiber stiffness which will decrease when the hornification is increased.

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