The effect of drying conditions on the swelling and bonding properties of bleached kraft hardwood pulp

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Summary
The quality of dried chemical pulp depends on the loss of swelling (hornification) which happens during drying. This is a critical issue in the manufacture of fine papers where good fiber bonding is essential. It is apparent that a better understanding of how drying variables affect hornification could lead to improvements in pulp quality.

The purpose of this study was to determine how important drying variables affect fiber hornification and bonding. The following variables were considered: final moisture content, drying temperature, and cellulose/water interaction.

It was found that in the high solids range the final moisture content has only a small effect on hornification for pulp dried at room temperature. Heating the pulp above 70ºC increases the hornification substantially. The magnitude of the heat-induced hornification depends on the amount of water in the cell wall. Hornification results in pulp with lower bonding potential.

An optimum drying strategy has the potential to increase the quality of dried pulp. A high final moisture content, low drying temperature and control of the drying temperature profile are possible ways to reduce hornification.

INTRODUCTION

When a low-yield pulp is dried and rewetted the papermaking properties of the pulp deteriorate. This is related to the loss in fiber swelling (1) which (2)is called hornification. The details of the hornification mechanism have still not been worked out, but many of the essential features are known. When pulp fibers are dried the water's internal tension pulls the microfibrils together allowing them to bond to one another. When the pulp is resaturated some of the bonds which have formed in the cell wall are not broken by the water (1). These are called "irreversible bonds". The exact nature of irreversible and reversible bonding is not known, but it likely involves different types hydrogen bonds.

An essential feature of hornification is the collapse of cell wall pores. Most of the pores which close are the so-called macropores (1, 3, 4). These are a class of larger pores in the cell wall which are formed by the dissolution of lignin and hemicelluloses in chemical pulping.

Most dewatering variables have some influence on hornification. These include the final solids content (3), drying time and temperature (5), wet pressing (6) and drying stresses (2). Pulp variables such as yield (1), type and amount of hemicelluloses (7), the ionization of the acid groups (8) or basically any other factors which affect the structure and chemistry of the cell wall have the potential to affect hornification.

Hornification is an important problem in the manufacture of fine paper in cases where dried pulp is used. For this paper grade good bonding is essential. Fine paper normally uses a mixture of bleached softwood (BSW) and hardwood (BHW) kraft pulps, with the latter making up most of the mix. In Scandinavia the BHW is usually birch.

It is the purpose of this study to determine how important drying variables affect the hornification of birch kraft pulp. The following variables were considered: final pulp moisture content, temperature and the interaction of water and cellulose at elevated temperatures. The effect of hornification on bonding properties was also examined.

EXPERIMENTAL

Pulps

Three different pulp samples were obtained from a Finnish pulp mill. These were an elemental chlorine free (ecf) bleached birch kraft pulp (BHW-ecf), the same pulp bleached with a total chlorine free (tcf) sequence (BHW-tcf) and a tcf bleached softwood kraft pulp (BSW-tcf). The BHW-ecf was used in most of the experiments.

The pulps were adjusted to the H^+ form by first washing with deionized (DI) water, followed by 0.001M HCl and final washing with DI water. The pulp was dried in the manner specified below, re-soaked in DI water for 1 day followed by cold disintegration.

In one experiment BHW-ecf pulp was dried to different moisture contents (water/solids) as follows. About 70 grams of the never-dried pulp was filtered and lightly pressed to about 1.5 g/g moisture content. The pulp was crumbed and placed in dessicators containing saturated salt solutions from 20-98% relative humidity (RH). Some pulp was also placed in a dessicator with a silica gel desiccant. The desiccators above 30% RH were opened each day for a few hours to speed up the drying. Each pulp was mixed several times per day to minimize moisture gradients. Pulps were prepared with final moisture content in the range from 0.61-0.03 g/g. This took 2-3 weeks.

The effect of drying temperature was investigated by placing 70 grams batches of the air-dried BHW-ecf pulp in a convection oven for 16 hours at 50, 70, 90, and 110°C. The pulp was opened to the atmosphere so the small amount of water present after air-drying was free to evaporate. A portion of each pulp was beaten 2500x in a PFI mill.

Pulp and handsheet measurements

The degree of swelling, or fiber saturation point (FSP), was measured with the solute exclusion method. The FSP is the water in the cell wall expressed in mass water/mass solids. The method used to measure FSP (9) was a modification of Stone and Scallan's original technique (10).

Handsheets were made in DI water. Sheet preparation and testing were done according to Scan standard methods.

RESULTS

Final moisture content and drying temperature

The purpose of this experiment was to determine how the final moisture content affects hornification. On a pulp dryer the operating window for final moisture content is probably not greater than 0.05-0.2 g/g. The results in Fig. 1 show that in this range the differences in the FSP are small, and after refining almost non-existent. *When drying at room temperature* it appears that there is little advantage to be gained from increasing final pulp moisture content. However, on a pulp drying machine the final moisture content may have a larger affect on hornification because it will affect other variables such as drying time or temperature.

In Fig. 1 the curves have been extrapolated back to the moisture content where hornification likely begins. The onset of hornification was not measured directly. However, since it has been shown that hornification begins when the pulp moisture content = FSP (1) such an extrapolation seems justified.

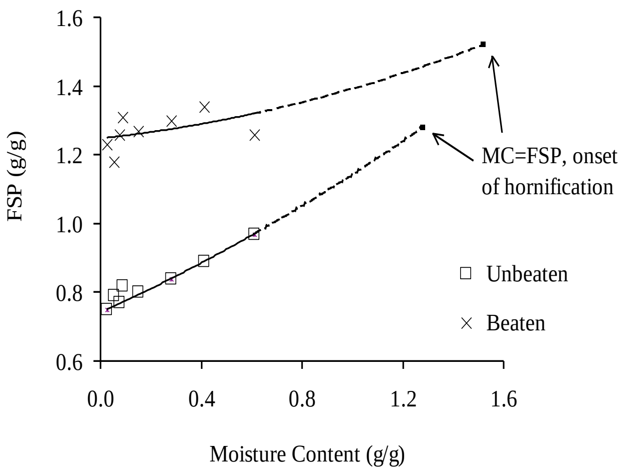

Fig. 1. The FSP for BHW-ecf pulp dried to different moisture contents at room temperature. MC = Moisture content. Beating in this and other figures was done <u>after</u> partial drying. The indicated onset of hornification is an estimate only.

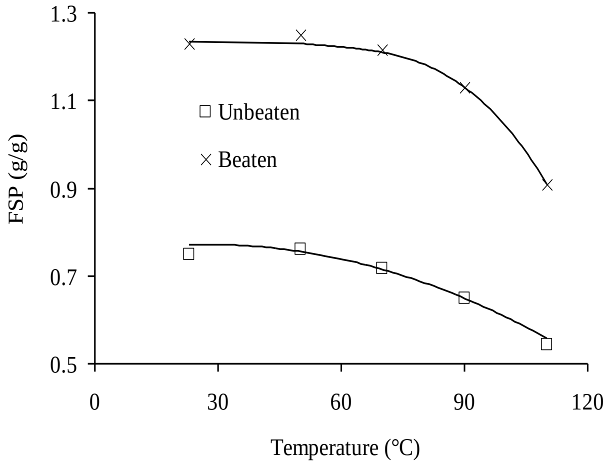

Fig. 2. The effect of temperature on the FSP of air-dried BHW-ecf pulp. The pulp was freely dried in an oven for 16 hours. Pulp was refined after heating.

Fig. 2 shows that there is a significant loss in FSP when the pulp is exposed to temperatures above 70°C. The hornification after exposure to 110ºC was 0.23 g/g (ΔFSP from the air-dried state to 110ºC heated). This is about half the hornification which occurred when pulp was first dried at room temperature (ΔFSP = 0.51 g/g from never-dried to air-dried state). This shows that while the main cause of hornification is the removal of water from the cell wall, temperature has a rather large effect.

One reason for refining the hornified pulp was to get some indication of factors which affect the strength of internal cell wall bonds. The idea here is that refining once-dried pulp breaks bonds inside the cell wall which formed in hornification. Therefore, the increase in FSP after a constant refining can be used to roughly gauge the net strength of the irreversible bonds.

When the pulps dried at room temperature were refined the curve of FSP vs moisture content (Fig. 1) tends to flatten out. In other words the difference between the pulps diminished. This contrasts with the pulps exposed to elevated temperatures. For these pulps the ΔFSP (air-dried pulp – pulp exposed to 110ºC) of the pulp increased slightly from 0.23 to 0.31 g/g after refining. This suggest the formation of relatively strong bonds between microfibrils when the pulp was heated.

Atalla et al. (11) have investigated hornification using Raman scattering and x-ray diffraction. They reported a fairly large increase in the proportion of crystalline cellulose for fibers exposed to high temperatures. This shows that the hornification at high temperatures involves crosslinking or some other mode of cellulose crystallite aggregation. It appears that the cellulose is soft enough above 70ºC to allow for the necessary molecular rearrangements. It is worth noting in Atalla's study that the increase in crystallinity was observed in press drying. This indicates that hornification can occur very quickly.

Water/cellulose/heat interactions

It has been reported (5) that the presence of moisture can accelerate or increase the magnitude of hornification. The purpose of this section is to shed some more light on this phenomenon. This was done by adding different amounts of water to the air-dried pulp, sealing it is a tube, and exposing the sealed tube to 100ºC for 15 minutes. This time and temperature are in line with conditions on typical pulp dryer.

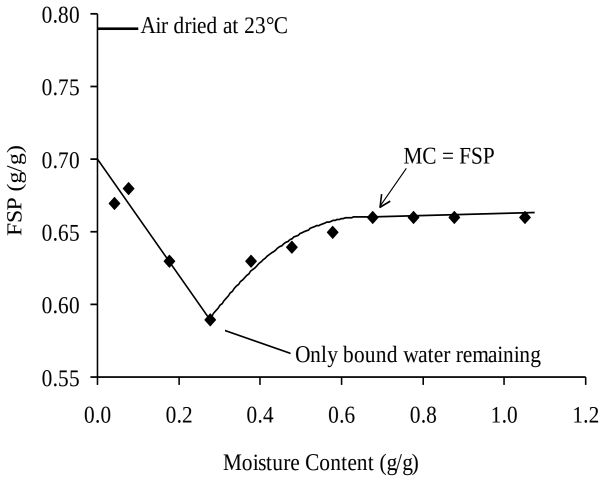

Fig. 3. The effect of pulp moisture content on the hornification of BHW-ecf pulp. A quantity of water was added to the air-dried pulp, this was hermetically sealed and then exposed to 100°C for 15 minutes.

The results from this experiment are shown in Fig. 3. Below 0.25 g/g hornification increases with the amount of added water. A possible explanation for this is that moisture softens the cell wall allowing for increased mobility and bonding of the microfibrils. Another possibility is that the water plays some direct role in the formation of irreversible hydrogen bonds. From a moisture content of 0.25-0.65 g/g the FSP increases. A reason for this increase may be that the microfibril separation increases beyond the point where interfibrillar bonding becomes favorable. Keep in mind that the average distance between microfibrils increases with cell wall's water content. Above the FSP additional water does not influence hornification.

It is interesting in Fig. 3 that the maximum hornification (minimum in the FSP curve) is at the moisture content where capillary water forms in the cell wall. This is sometimes referred to as the "second critical point"(12). In a number of studies (3, 13, 14) it has been found that there are changes to the behavior of the fibers at or near this moisture content. The reason for this apparent correlation is not clear and is certainly worth further investigation.

Swelling and bonding

In this section the effect of hornification on pulp bonding properties was examined. Tensile index, Scott bond strength and light scattering were used to indicate the changes to the fiber bonding. The results from this analysis, are shown in Figs. 4-6. A summary of the results, including the measurement precision, is given in the appendix.

Fig. 4 shows that there is an inverse relationship between FSP and light scattering. This is because less swollen fibers have a lower flexibility and yield a smaller bond area (15). This is reflected in the sheet strength as shown in Fig. 5 and Fig. 6.

In Fig. 4-6 the FSP correlates with scattering or strength within either the unbeaten and beaten series but not between the series. This is because the development of fiber properties in refining goes well beyond fiber swelling. External and internal fibrillation, fines generation and fiber straightening are some of the factors which explain the lack of correlation between the data sets.

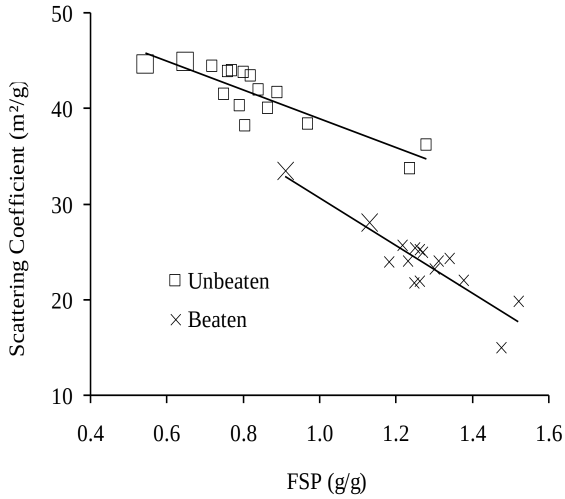

Fig. 4. Light scattering vs FSP for BHW pulp. The larger points are never-dried pulp. See the appendix for point values and confidence levels.

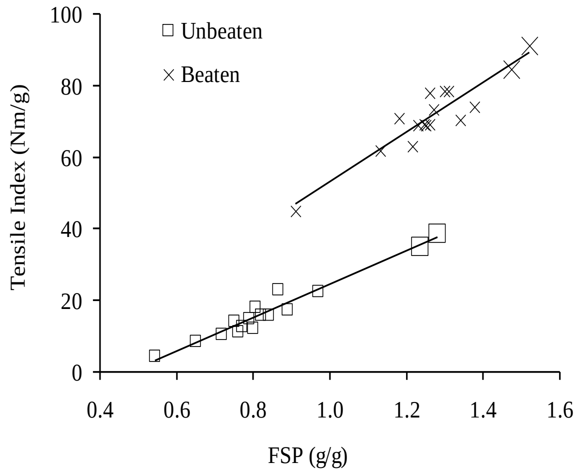

Fig. 5. Tensile index vs FSP for BHW pulp. The larger points are never-dried pulp.

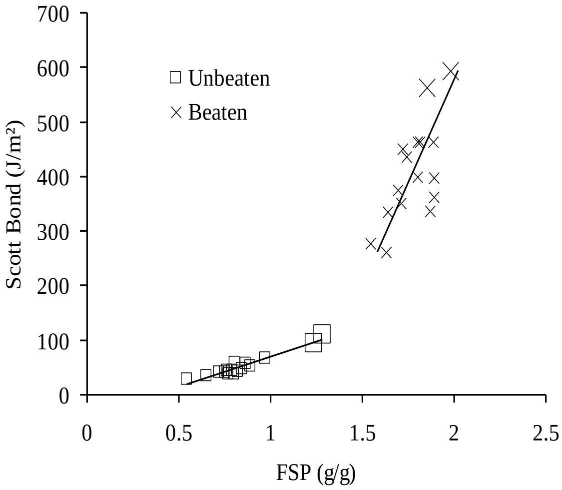

Fig. 6. Scott bond strength vs FSP for BHW pulp. Same series as Fig. 5. The larger points are never-dried pulp.

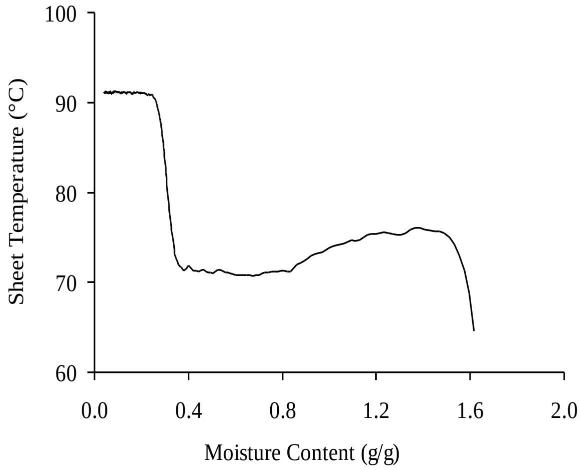

Fig. 7. The web temperature of unbleached softwood kraft pulp as a function of moisture content in contact dryer simulation. Redrawn from (12).

DISCUSSION

There are four likely alternatives to decrease pulp hornification via changes to the drier section. These are: 1) decrease the moisture content into the dryer section, 2) increase the final web moisture content, 3) decrease the average dryer temperature and 4) change the dryer temperature profile.

The moisture content of the web entering the dryer section may be reduced by increasing the amount of wet pressing. This will have an indirect benefit in hornification because it allows for lower drying time or temperature while maintaining production. Excess pressing should be avoided because the closure of pores in the cell wall can increase the fiber hornification (6, 16). A higher final web moisture content also allows a decrease in drying time or temperature. Decreasing the average web temperature is clearly expected to benefit pulp quality, particularly where temperature is already high. Obviously, production concerns will limit this strategy.

Changing the dryer temperature profile is an interesting option. Consider a typical drying temperature profile shown in Fig. 7. Near the end of drying, around 0.3 g/g there is a distinct increase in the drying temperature. This happens when the free water has evaporated from the fibers. Recall from Fig. 3 that this is the same moisture content where the hornification is at a maximum. While the exact temperature profile will depend on the particular dryer section the jump in web temperature near the end of drying is quite usual. It would seem from Fig. 3 that there may be some benefit from adjusting the temperature profile by e.g. increasing the temperature in the early part of the dryer section and decreasing the temperature in the latter stages. The practicality of this approach remains to be seen.

SUMMARY

In the high solids range the final moisture content of pulp dried at room temperature had only a small impact on hornification. Temperatures above 70ºC caused an additional hornification. At 110ºC this was about half the hornification caused by removing the water from the cell wall. The pulp exposed to elevated temperature was not easily reswollen by refining. This may indicate the formation of relatively strong irreversible bonds in the cell wall.

The presence of water in the cell wall increases heat-induced hornification. From a moisture content of 0-0.25 g/g the hornification at high temperature increased with temperature. This is possibly related to the softening effect of water. From 0.25 g/g to the FSP the hornification decreases. This may be due to an increases in the average microfibril separation as water content is increased. The addition of water above the FSP does not affect the heat-induced hornification.

Hornification resulted in lower bonding and sheet strength. This was indicated be a loss in light scattering, Scott bond strength and tensile strength.

The results show that improvements in pulp quality could be realized by optimization of the dryer section.

Acknowledgements

The authors would like to thank Maija Pitkänen for her comments on the manuscript. Funds for this research were generously provided by The Finnish Academy and The Finnish National Technology Agency (Tekes).

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APPENDIX

Table 1. Summary of results

Test point	Pulp[1]	PFI Beating (rev)	Moisture content dried to (g/g)	FSP (g/g)	Apparent Density (kg/m^3)	Tensile Index (Nm/g)	Scott Bond (J/m^2)	Light Scattering (m^2/kg)
Never dried	BHW-ecf	0	N/A	1.28	563	38.6 ± 1.1	111 ± 2.0	36.2 ± 0.2
Dried at room temp	BHW-ecf	0	0.61	0.97	495	22.4 ± 0.5	67 ± 1.6	38.4 ± 0.4
Dried at room temp	BHW-ecf	0	0.41	0.89	482	17.4 ± 0.6	53 ± 1.3	41.7 ± 0.7
Dried at room temp	BHW-ecf	0	0.28	0.84	468	16.0 ± 0.5	48 ± 0.9	41.9 ± 0.5
Dried at room temp	BHW-ecf	0	0.15	0.80	427	12.3 ± 0.3	39 ± 1.2	43.8 ± 0.3
Dried at room temp	BHW-ecf	0	0.09	0.82	459	16.0 ± 0.6	44 ± 1.1	43.4 ± 0.3
Dried at room temp	BHW-ecf	0	0.07	0.77	446	12.7 ± 0.4	39 ± 1.2	44.0 ± 0.5
Dried at room temp	BHW-ecf	0	0.05	0.79	448	14.9 ± 0.6	45 ± 1.4	40.3 ± 0.4
Dried at room temp	BHW-ecf	0	0.03	0.75	429	14.2 ± 0.6	41 ± 0.9	41.5 ± 1.2
Dried at 50°C	BHW-ecf	0	~0.00	0.76	431	11.3 ± 0.4	45 ± 1.1	43.9 ± 0.3
Dried at 70°C	BHW-ecf	0	~0.00	0.72	415	10.5 ± 0.4	41 ± 1.0	44.4 ± 0.3
Dried at 90°C	BHW-ecf	0	~0.00	0.65	404	8.48 ± 0.2	35 ± 1.0	44.9 ± 0.2
Dried at 110°C	BHW-ecf	0	~0.00	0.54	348	4.33 ± 0.2	29 ± 0.6	44.6 ± 0.4
Never-dried	BHW-tcf	0	N/A	1.24	481	34.9 ± 2.2	94 ± 1.4	33.7 ± 0.3
Air-dried	BHW-tcf	0	0.07	0.81	438	18.0 ± 2.5	60 ± 2.2	38.2 ± 0.4
Never-dried	BSW-ecf	0	N/A	1.50	569	39.9 ± 3.1	143 ± 3.0	33.8 ± 0.3
Air-dried	BSW-ecf	0	0.07	1.12	507	22.3 ± 2.4	78 ± 2.1	38.3 ± 0.5
Never-dried	BHW-ecf	2500	N/A	1.52	732	91.1 ± 2.9	594 ± 18	19.9 ± 0.1
Dried at room temp	BHW-ecf	2500	0.61	1.26	697	78.1 ± 1.3	564 ± 24	22.0 ± 0.2
Dried at room temp	BHW-ecf	2500	0.41	1.34	683	70.4 ± 2.4	352 ± 10	24.4 ± 0.3
Dried at room temp	BHW-ecf	2500	0.28	1.30	692	78.4 ± 1.8	464 ± 10	23.3 ± 0.1
Dried at room temp	BHW-ecf	2500	0.15	1.27	666	73.4 ± 2.4	398 ± 11	25.0 ± 0.2
Dried at room temp	BHW-ecf	2500	0.09	1.31	681	78.6 ± 1.4	464 ± 7	24.1 ± 0.1
Dried at room temp	BHW-ecf	2500	0.07	1.26	659	69.2 ± 2.7	363 ± 10	25.3 ± 0.1
Dried at room temp	BHW-ecf	2500	0.05	1.18	677	70.8 ± 2.2	436 ± 10	24.0 ± 0.2
Dried at room temp	BHW-ecf	2500	0.03	1.23	662	69.0 ± 2.2	399 ± 10	24.1 ± 0.3
Dried at 50°C	BHW-ecf	2500	~0.00	1.25	668	68.9 ± 2.1	451 ± 10	25.5 ± 0.3
Dried at 70°C	BHW-ecf	2500	~0.00	1.22	649	63.2 ± 3.4	375 ± 13	25.7 ± 0.2
Dried at 90°C	BHW-ecf	2500	~0.00	1.13	636	61.9 ± 0.9	336 ± 13	28.1 ± 0.2
Dried at 110°C	BHW-ecf	2500	~0.00	0.91	591	45.1 ± 1.0	277 ± 6	33.5 ± 0.1
Never-dried	BHW-tcf	2500	N/A	1.47	665	84.7 ± 1.4	337 ± 9	15.0 ± 0.1
Air-dried	BHW-tcf	2500	0.07	1.25	620	69.3 ± 0.4	261 ± 5	21.8 ± 0.2
Never dried	BSW-ecf	2500	N/A	2.16	784	91.8 ± 1.0	731 ± 13	20.5 ± 0.3
Air-dried	BSW-ecf	2500	0.07	1.75	699	77.8 ± 0.8	476 ± 12	24.2 ± 0.2

[1]BHW-ecf= Elemental chlorine free bleached birch kraft; BHW-tcf total chlorine free bleached birch kraft; BSW-ecf = bleached softwood kraft, ecf pulp.