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## IMPROVING THE PAPERMAKING PROPERTIES OF KRAFT PULP BY CONTROLLING HORNIFICATION AND INTERNAL FIBRILLATION

Doctoral Thesis

Xinshu Wang 汪 忻 曙 Helsinki University of Technology, Laboratory of Paper and Printing Technology Reports, Series A26 Espoo 2006

## IMPROVING THE PAPERMAKING PROPERTIES OF KRAFT PULP BY CONTROLLING HORNIFICATION AND INTERNAL FIBRILLATION

## Xinshu Wang

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## ABSTRACT

The objective of this thesis was to improve press dewatering and paper properties of kraft pulps by controlling hornification and internal fibrillation. Hornification was induced by drying and by pressing pulps, and internal fibrillation was developed in refining.

Hornification and internal fibrillation are related to the change in fibre pore structure. In this thesis, a thermoporosimetry technique with cyclohexane as an absorbate was tested and found suitable for detecting the change in pore size and pore volume during drying and refining. The results show that for never-dried fibres, refining mainly expands the large pores in the cell wall, whereas it has only a slight effect on the small pores. Drying closes most of the large pores and a substantial amount of the small pores. For dried fibres, refining not only expands the large pores but also reopens the small pores to a certain extent. Even though the pore volume of previously dried pulps can be recovered by refining (i.e., the pulp can be reswollen), some small pores, which are closed in drying, are not reopened by normal levels of refining. In other words, refining does not completely reverse hornification.

Drying of pulps greatly reduces pulp swelling, enhancing dewatering but impairing tensile strength. Dried pulps offer a far better combination of dewatering and tensile strength than never-dried pulps. One possible reason is that some small hard-to-dewater pores in the fibre wall are irreversibly closed by drying, which enables better dewatering. However, pulp drying is energy-consuming. Pressing pulps may provide an economical way to improve dewatering, while maintaining paper strength properties. Pressing hornifies pulps, which promotes dewatering but impairs tensile strength to a certain extent. On the other hand, pressing causes fibres to flatten, with the flattened fibres providing more surface contact for bonding, thus increasing density and tensile strength. Never-dried pulps which were pressed before refining were found to give both improve dewatering and better tensile strength.

The refining results support the earlier view that internal fibrillation is largely produced by a cyclic compressive action. It is suggested that fibres need to be turned over in refining and compressed from different directions in order to disrupt their internal structure and cause internal fibrillation. Compression also facilitates fibre straightening, but does not promote external fibrillation and fines generation. At the same swelling level, more straightened pulps give higher tensile strength, and pulps with less fines and external fibrillation enable better dewatering. Hence, to achieve an optimum combination of dewatering and tensile strength, chemical pulp refining should aim at increasing internal fibrillation, straightening fibres, and keeping the amount of fines and external fibrils at a low level.

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## **AUTHOR'S CONTRIBUTION**

- I Designing and conducting the experiments and writing the draft version of the manuscript
- II Conducting the pore size distribution and fibre saturation point measurements and writing the draft version of the corresponding part in the manuscript
- III, IV, V Designing the experiments, conducting part of the experiments, and writing the draft version of the manuscript

## LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
DSC	Differential scanning calorimeter
ECF	Elemental chlorine-free
FSP	Fibre saturation point
MC	Moisture content in g water/g solid
MTS	Material test system
ND/OD/AD	Never-dried/oven-dried/air-dried
PSD	Pore size distribution
P200	Passing 200 mesh wire
R50, R100, R200	Retained by 50, 100, or 200 mesh wire
SW/HW	Softwood/hardwood
TCF	Totally chlorine-free
TMP	Thermomechanical pulp
WRV	Water retention value

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## **1 INTRODUCTION**

Pulp property improvements are essentially concerned with their impact on the performance of the paper machine and the end product. For chemical pulps, hornification (loss of pulp swelling) and internal fibrillation are an inverse pair which have a profound effect on the papermaking process and paper properties, especially dewatering in the press section and tensile strength. When the pulp swelling level is changed, either by hornification or internal fibrillation, dewatering and tensile strength will change in opposite directions. It is still unclear how the combination of dewatering and tensile strength can be improved by controlling hornification and internal fibrillation.

Hornification and internal fibrillation involve closing or opening of the pores in the fibre wall. A good way to gain a better understanding of this phenomenon is to examine the fibre pore structure in drying and refining. Many studies have been devoted to this subject (1-6, I, II), and good progress has been made. In this thesis, a cyclohexane thermoporosimetry technique, based on conventional water thermoporosimetry (7), was applied to measure the pore size distribution (PSD) particularly of chemical pulps.

Hornification occurs when water is removed from the fibre wall (4), so drying and pressing of pulps can be used to induce hornification. Pulp drying is common practice in some integrated mills: virgin pulp is dried on a pulp drying machine, reslushed and formed into paper. This results in substantially improved dewatering and therefore higher paper machine speed. The main disadvantage of this practice is that it is expensive, both in terms of energy consumption and additional production stages. In addition, the properties of dried pulps are inferior to those of never-dried ones.

Hornification induced by pressing has been referred to as wet hornification (8). Pulp pressing might provide an economical way to improve dewatering, because it is cheaper to remove water from the fibre wall by mechanical means than by evaporation in drying. Pressing can also cause lumens to collapse and fibres to flatten, thus providing more surface contact for bonding. However, it is not certain how treating never-dried pulps by pressing before refining affects paper tensile strength.

Internal fibrillation is usually developed in refining, together with other major refining effects including external fibrillation, fines generation and fibre straightening. It would be of great practical importance to the paper industry to find ways of refining pulps which give the desired paper properties, combined with improved dewatering properties. This is clearly a difficult problem, as we are still lacking knowledge about how to control pulp properties independently in refining, and in which situations it would be an advantage to do so. In the present thesis work, various laboratory refiners were used to treat pulps, with

the aim to determine how fibre properties develop in refining and how pulps should be refined to obtain an optimum combination of dewatering and tensile strength.

The objective of this thesis was to find out how to improve the papermaking properties of kraft pulp in terms of dewatering and paper properties, particularly tensile strength, by controlling hornification and internal fibrillation.

## 2 MATERIALS AND METHODS

### 2.1 Pulps

The pulps used were mostly bleached kraft pulps from Finnish pulp mills, made from pine (*Pinus silvestris*), spruce (*Picea abies*), and birch (*Betula pendula/pubescens*). They are listed in the following, and more information is given in the articles included in the appendix.

- In the experiments described in Chapter 3 'Fibre pore structure in hornification and internal fibrillation', never-dried ECF bleached kraft softwood and hardwood pulps were used. The never-dried softwood pulp (sw-nd) was a mixture of about 60% pine and 40% spruce; the never-dried hardwood pulp (hw-nd) was made from birch. A portion of these pulps was dried at 105 °C in an oven overnight (sw-od and hw-od). In addition, another ECF bleached pine kraft pulp was used in the PSD measurement. This pulp was prepared by flow-through cooking, producing a lower amount of hemicelluloses. The results obtained with this pulp are shown in Figure 5. Two TMP pulps made from 70% pine and 30% spruce were used for measuring the fibre BET surface area, and the data are shown in Figure 4.
- In the experiments described in Chapter 4 'Hornification induced by pressing and drying', never-dried and dried (92% solids content from a pulp drying machine) TCF bleached kraft softwood pulps were used. The pulps were a mixture of about 75% spruce and 25% pine. The never-dried pulp was pressed to a solids content of approximately 60%. In the other pressing trial, never-dried ECF bleached kraft softwood pulp made from 58% spruce, 41% pine and 1% birch was pressed to different solids contents of approximately 61%, 66% and 68%, and it was also air-dried to a solids content of 93% (ad). The results are given in Section 4.5 'Hornification by pressing to varying degrees'.
- In the experiments described in Chapter 5 'Internal fibrillation in refining', never-dried TCF bleached kraft softwood pulp was used, consisting of a mixture of about 75% spruce and 25% pine. The PSD data were obtained with another similar pulp made from about 50% spruce and 50% pine, and this pulp was used also in the work described in Chapter 6.
- In the experiments described in Chapter 6 'Refining for optimum dewatering/tensile strength combination', never-dried TCF bleached kraft softwood pulp was used. This pulp consisted of about 50% spruce and 50% pine.

#### 2.2 Thermoporosimetry

The thermoporosimetry technique is based on the melting temperature depression of an absorbate in the capillaries of porous materials caused by increased pressure. The well-known Gibbs-Thomson equation describes the relationship between the melting temperature depression and pore size as:

$$D = f(\Delta T) = \frac{-4V_m \sigma_{ls}}{\Delta H_m \ln \frac{T}{T_0}}$$
(1)

Where *D* is the pore size,  $V_m$  is the molar volume of ice,  $\sigma_{ls}$  is the surface energy at the ice-water interface,  $\Delta H_m$  is the latent heat of melting, *T* is the melting temperature, and  $T_0$  is the melting point of water at normal pressure.

In the present work, cyclohexane was used as an absorbate, and it was introduced into the fibre cell wall through a solvent exchange procedure in which water was replaced by acetone, and then acetone by cyclohexane. The solvent exchange was carried out by sealing the pulp and fresh solvent in a jar and mixing them thoroughly. The replacement for each solvent was performed 12 times in 2 days. The experiments show that additional replacements have no effect on the PSD, thus indicating that the exchange was complete. After solvent exchange, approximately 3-5 mg of each sample was sealed in a tube and centrifuged to a cyclohexane content of about 2.5-4 g cyclohexane/g solids, and then the sample was sealed in a 40  $\mu$ L aluminium pan for measurement.

The thermoporosimetry measurements were performed with a Mettler 821<sup>e</sup> differential scanning calorimeter (DSC). An isothermal step method was used to measure the PSD. In this method, the sample is first frozen, and then the frozen cyclohexane is melted in steps. The temperature steps used are -6.0, -4.0, -2.0, -1.0, 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 5.5, 5.8, 6.0, 6.2, 6.3 °C, which are below the melting point of cyclohexane of 6.5 °C. At each step, the temperature is kept constant until melting is completed. The heat absorbed at each temperature is obtained by integrating the endothermic peaks. The melting heat is used to calculate the amount of melted cyclohexane. The pore size, D, is related to the melting  $\Delta T$ . It is calculated using the derived equation temperature depression,  $D = 117(nm \cdot {}^{\circ}C)/\Delta T$  (7). It is assumed that the pores are cylindrical, and that the pore size is the diameter. At the end of the temperature program, the sample is refrozen and then melted completely. This generates the melting peak of the total freezing cyclohexane. The nonfreezing cyclohexane is calculated by subtracting the total freezing cyclohexane from the cyclohexane content in the sample.

#### 2.3 Pressing treatment

The pressing treatment was carried out with a device called Material Test System/810 (MTS), which can exert a force of up to 100 kN between two plates. Two pressing trials were conducted. In the first trial, pulp pads (13-13.5 cm in diameter, 1.6 kg o.d.) made from the never-dried pulp were pressed at a pressure of 7.4 MPa. The pulp pads were pressed 5 times for 2 min each time. After this treatment, the solids content of the pressed pulp was about 60%. The never-dried, dried and pressed never-dried pulps were then refined using a Voith LR40 laboratory refiner. In the second trial, pulp pads (10-12 cm in diameter, 30 g o.d.) made from another never-dried pulp were pressed at a pressure of 2.6, 6.3, or 8.8 MPa. At each pressure, the pads were pressed 5 times for 2 min each time. After pressing, the solids content of the pulps was about 61%, 66%, or 68% for the respective pressure. Because these pulp pads contained a much smaller amount of pulp and had a lower pad basis weight, they reached higher solids contents even at lower pressures. The pulps were then disintegrated and refined using a PFI mill.

## 2.4 Refining

The refining experiments were conducted with different laboratory refiners, including a Lampén mill, a PFI mill, a Voith LR40 laboratory refiner with standard disc plates, and a Masuko Super Masscolloider (9). The refining conditions and pulp consistencies are generally described in the following chapters when the corresponding results are presented, and the details of refining are given in the articles in the appendix.

## 2.5 Testing

The procedures for testing pulp and paper properties are listed in the following.

- <u>Pore size distribution</u>: The pore size distribution was measured by the cyclohexane thermoporosimetry technique.
- <u>Fibre saturation point (FSP)</u>: The FSP was measured by the solute exclusion technique (10).
- <u>Fibre BET surface area</u>: The measurement was carried out with a Micromeritics FlowSorb II 2300. The nitrogen desorption data were used in conjunction with the BET equation for the calculation of the fibre surface area (11). In sample preparation,

the fibres were solvent-exchanged with the water-acetone-cyclohexane sequence and then dried in a nitrogen stream at room temperature overnight.

- <u>External fibrillation</u>: Twenty transmitted light images of never-dried fibres (R100) in water medium were taken using a Leica DMLAM light microscope with a phase contrast objective 10× and polarizer. Each image contained 4-6 fibres. The surface area of fibrils and fibres was obtained by calculating the area of pixels occupied by fibrils and fibres, using a program made with the Matlab software (12). The degree of external fibrillation is shown as the surface area ratio of external fibrils to fibres in per cent. Besides the microscopy method, the SR value was measured, because the SR value is closely related to the external surface area of fibres when fines are absent.
- Fibre curl: The curl index was determined with a Kajaani FiberLab apparatus.
- <u>Fines content:</u> The fines content was determined with a dynamic drainage jar. Both the fines (P200) and fibre fraction were collected for calculating the fines content.
- <u>Press dewatering characteristics</u>: Wet handsheets were formed according to the ISO standard but without pressing and drying. The wet pressing experiments were performed with the MTS, and the moisture content after pressing was determined according to the ISO standard.
- <u>Paper properties:</u> Handsheets were made, conditioned and tested according to the relevant ISO standards.

# 3 FIBRE PORE STRUCTURE IN HORNIFICATION AND INTERNAL FIBRILLATION

#### **3.1 Introduction**

A generally accepted model of the cell wall structure is that the microfibrils of the cellulose, together with the lignin-hemicellulose matrix surrounding them, form an interrupted lamella structure (10, 13–16). The intralamellar space within the lignin-hemicellulose matrix and between microfibrils forms a fraction of small pores called micropores (6, 10, 13). In chemical pulping, the lignin and a certain amount of hemicelluloses are dissolved, leaving a space between lamellae which forms relatively large pores referred to as macropores (6, 10, 13).

The fibre pore structure, i.e., pore size and volume, changes in hornification and internal fibrillation. When water is removed from the fibre wall, hydrogen bonds form within the cell wall which are not completely broken upon rewetting, which leads to a loss of fibre swelling and pore volume. This phenomenon is known as *hornification* (4, 17–21). Earlier studies suggest (2, 4, 22) that drying primarily closes the macropores and has only a small effect on the micropores. Recent results suggest (6, 23) that hornification can cause partial collapse of the micropores.

In refining, the mechanical action causes some of the internal bonds between microfibrils within the cell wall to rupture, thus allowing osmotic and entropic forces to produce increased fibre swelling. This refining effect has been termed *internal fibrillation*. Earlier results show (2, 3, 22) that refining opens or expands the macropores and has little influence on the micropores.

Because of the significance of the fibre pore structure, a variety of techniques have been developed and modified continuously to study the fibre pores. These techniques include microscopy (24–26), centrifuging (27), solute exclusion (10, 28), nuclear magnetic resonance spectroscopy (3), inverse size-exclusion chromatography (5, 29), and thermoporosimetry (7, 30). However, due to the complex structure of the fibre cell wall, there remain issues that are not fully understood. For example, while it is well known that the loss of swelling due to drying can be recovered by refining, it is still unclear how the internal cell wall structure of refined hornified pulps differs from that of never-dried pulps. The aim of the experiments described in this chapter was to gain a deeper understanding of hornification and internal fibrillation by examining the fibre pore structure in drying and refining.

In the experiments, a modified thermoporosimetry technique with cyclohexane as an absorbate was used. The thermoporosimetry technique was recently developed by Maloney and Paulapuro to measure the PSD of wood and pulp fibres (7). The conventional method with water as an absorbate has been successfully used to detect the opening of pores in chemical and mechanical pulping (22, 31). However, with chemical pulps refining opens large pores in the cell wall which are outside the range of water-based measurements. Additionally, the crystallization of water in the fibre wall tends to distort the pore network of chemical pulps (7). For these reasons, a thermoporosimetry technique based on a cyclohexane absorbate was applied. The cyclohexane was introduced into the fibre cell wall through a solvent exchange procedure.

Cyclohexane thermoporosimetry has three significant advantages over the conventional method. First, due to the different thermodynamic properties of cyclohexane and water, cyclohexane thermoporosimetry covers pore size up to about 600 nm, while the conventional method measures pore size up to about 200 nm. The larger pore size coverage of cyclohexane thermoporosimetry makes this technique highly suitable for chemical pulps. Second, upon freezing during the measurements, the cyclohexane forms soft crystals, which do not distort the pore structure in the cell wall, whereas the crystallization of water damages the fibre cell wall in an unknown manner. Third, because of the presence of ions and the partial dissolution of cell wall polysaccharides, the osmotic pressure in water-saturated pulps also leads to the melting temperature depression of water. This does not occur when cyclohexane is used. The major shortcoming of cyclohexane thermoporosimetry is that the fibre cell wall contracts in non-polar cyclohexane. However, the results (7, I, II) show that a large fraction of the fibre pores are preserved for samples solvent-exchanged to cyclohexane.

Cyclohexane thermoporosimetry can be used to measure PSD, pore volume, and nonfreezing cyclohexane, i.e., the amount of cyclohexane which does not freeze in the cell wall. It has been suggested (7) that nonfreezing cyclohexane is an interfacial layer on the cell wall components, and that it is closely related to the fibre internal surface area.

#### 3.2 Pore size distribution with thermoporosimetry

Figures 1 and 2 illustrate the cumulative pore volume as a function of pore size of softwood and hardwood fibres, respectively. They clearly show the changes in PSD and pore volume resulting from drying and refining. This indicates that the cyclohexane thermoporosimetry technique is suitable for studying fibre pore structure in hornification and internal fibrillation.



Figure 1. PSD of never-dried (left) and oven-dried (right) softwood fibre fraction (R50). The numerical suffix indicates the number of PFI refining revolutions (I).



Figure 2. PSD of never-dried (left) and oven-dried (right) hardwood fibre fraction (R50).

The PSD curves do not reach a plateau, so it is uncertain which fraction of the actual pore volume is covered by this technique. In order to clarify this, the pore volume, taken from the most right-hand point on the PSD curve, is plotted against the FSP. Figure 3 shows that there is a good correlation. However, the pore volume obtained from cyclohexane thermoporosimetry is slightly lower than the FSP. The likely reason is that fibres contract in non-polar cyclohexane.

The nonfreezing cyclohexane, denoted by the first left-hand point in a PSD curve, varies with the drying and refining treatment. In order to verify its connection to the fibre surface area, the nonfreezing cyclohexane is plotted against the fibre BET surface area, shown in Figure 4. The fibre BET surface area was measured with fibres solvent-exchanged to cyclohexane and dried in a nitrogen stream, and the nonfreezing cyclohexane was determined with these dried samples rewetted by adding fresh cyclohexane. They correlate

well; in particular, the correlation line almost passes through the origin of the coordinate system. Around the origin, there are three samples of softwood pulps dried from water. When fibres are dried from water, all the pores in the cell wall collapse, and there only exists the external fibre surface area. The surface area for these samples, taken from the literature, was about  $1 \text{ m}^2/\text{g}$  (26); and no nonfreezing cyclohexane was detected. Figures 1 to 4 demonstrate that thermoporosimetry with cyclohexane as an absorbate provides adequate results when used to characterize changes in fibre pore structure in hornification and internal fibrillation.



*Figure 3. Correlation between pore volume from cyclohexane thermoporosimetry and FSP (I).* 



Figure 4. Correlation between nonfreezing cyclohexane and fibre BET surface area (I).

#### 3.3 Pore structure in drying and refining

According to Figures 1 and 2, never-dried fibres have a considerable amount of pore volume in the small pore region. For never-dried fibres, refining has only a slight effect on these small pores and mainly expands the large pores, particularly in the early stage of refining. This is in agreement with previous results (2, 3, 22). The PSD data also show that drying causes most large pores and a substantial amount of the small pores to collapse, and that refining reopens both the small and large pores to a certain extent. It can be seen that the opening of the small pores by refining is more pronounced for hardwood fibres. Hardwood fibres in general contain more hemicelluloses than softwood fibres. The results here suggest that part of the small pores are in the region occupied by the hemicelluloses.

The effect of hornification on fibre pore structure can also be seen in Figure 5, in which never-dried fibres were first refined and then dried. The refined and then dried fibres show almost the same PSD as the unrefined dried fibres, indicating that drying closes most large pores expanded in refining. Drying also closes a large amount of the small pores. In comparison, more hornification appears to occur in the small pore region than in the large pore region.



*Figure 5. PSD of never-dried and oven-dried fibre fraction (R200). The pulp was refined with a Voith laboratory refiner.* 

#### 3.4 Surface area

Pulp fibres have a large internal surface serving as hydration and adsorption sites (32). The surface area is closely associated with the fibre pores, especially the fraction of the small pores. Moisture sorption and nitrogen sorption have often been used to determine the fibre surface area. In the moisture sorption method, the water vapour isotherm is used together with the BET equation for calculating the total surface area, based on the monolayer moisture adsorption on the entire surface. It has been summarized (3) that the moisture content of monolayer adsorption is in the range of 0.028-0.08 g water/g fibre for pulp fibres of various origins, and that the surface area is about 130-350  $m^2/g$ . Nitrogen sorption has proven a promising technique with a solid theoretical basis of a complete monolayer adsorption of nitrogen gas on a given absorbent (11, 26, 33-35). Its advantages include only physical adsorption of nitrogen, the ability of molecular nitrogen to access small-sized pores, and highly accurate results. However, this technique requires samples in dry state. Drying pulps from polar liquid such as water causes collapse of pores and a loss of internal surface. Several techniques, such as solvent exchange (26, 36, 37), freeze drying (38, 39), and critical point drying (40, 41), have been used to remove water in a manner that prevents collapse of the fibre pores to a certain degree. In the present work, a solvent exchange procedure was applied in which water was first replaced with acetone, an intermediate water-miscible organic solvent, and then acetone with cyclohexane, a nonpolar solvent. The fibres were subsequently dried in a nitrogen stream overnight. This sample preparation preserves a large fraction of the fibre pores and surface area.

In Figure 6, the fibre BET surface area determined using nitrogen sorption is plotted as a function of refining. With increased refining, the fibre surface area increases only a little for never-dried fibres, whereas it increases substantially for dried fibres. This is consistent with the results from thermoporosimetry, showing that for never-dried fibres refining primarily opens the large pores and has only a small effect on the small pores, and that for dried fibres refining reopens the pores, including the large and the small ones, thus expanding the surface area. The surface area of dried fibres is smaller than that of never-dried ones, indicating that drying irreversibly closes some small pores which are not reopened by refining.



*Figure 6. BET surface area of never-dried and oven-dried softwood and hardwood fibres (R50). The samples were solvent-exchanged and dried in a nitrogen stream. The figure was drawn with data from (I).* 

#### 3.5 Difference between never-dried and dried fibres

It has long been known that never-dried fibres are more swollen, or have more pore volume, than dried ones. This difference has been cited as the key difference between never-dried and dried fibres, explaining many of their differences in papermaking and paper properties (42). Besides fibre swelling or pore volume, it is reasonable to assume that pore size also plays a role. Many researchers have reported (23, 43–45) that in press dewatering the size of fibre pores affects water removal, and that it is more difficult to remove water from small pores than from large ones. In Figure 7, the cumulative pore volume and pore size are compared for never-dried and oven-dried fibres refined to the same level. It is seen that the difference in pore volume or swelling between the never-dried and dried fibres arises chiefly from the small pores. This phenomenon can be observed consistently at other refining levels.



Figure 7. PSD of never-dried and dried softwood and hardwood fibres refined to PFI 3,000 revolutions.

#### 3.6 Structural change in dried and then refined fibres

It has been shown through the use of solute exclusion that refining can recover pore volume in hornified pulps (4, 10). However, it does not seem likely that all the effects of hornification could be completely reversed. In Figure 8, the PSD of never-dried unrefined fibres is compared with that of dried fibres in which the pore volume has been recovered by refining. The FSP is 1.24 ml/g for the never-dried unrefined fibres and 1.25 ml/g for the dried and then refined fibres. The results show that at the same swelling level, the dried and then refined pulp contains fewer small pores and more larger pores. This indicates that structural changes are induced in the cell wall by hornification which are not reversed by refining. The fibre BET surface area is  $143 \text{ m}^2/\text{g}$  for the never-dried unrefined fibres and  $130 \text{ m}^2/\text{g}$  for the dried and then refined ones, which supports the finding that the dried and then refined fibres have fewer small pores and more large pores. The likely explanation is that strong irreversible hydrogen bonding is formed between microfibrils during drying which is not broken when the fibres are refined. Thus, refining mainly disrupts and loosens macrofibrils (aggregated microfibrils), creating large-sized pores.

Figure 9 presents a schematic of how this might occur. Drying causes the closure of pores between microfibrils by forming hydrogen bonds and possibly Van der Waals bonds (4, 46). When dried fibres are refined, inter-fibril bonds in some regions of the cell wall might be strong enough to resist compression and shear forces. Lundberg and de Ruvo proposed (47) that when fibres are dried, a reorientation of microfibrils and a better alignment of carbohydrate chains might lead to more intense hydrogen bonding; hence, dried fibres have a lower tendency to delaminate than never-dried ones.



*Figure 8. PSD of never-dried unrefined fibres (sw-nd FSP=1.24 ml/g), and dried and then refined fibres (sw-od5000 FSP=1.25 ml/g) (I).* 



Figure 9. A schematic illustrating possible change in fibre pore structure resulting from refining previously dried pulps. Even though the pore volume of previously dried pulps can be recovered by refining, the permanent changes in the pore structure may have occurred: some pores, which are closed during drying, are not reopened by normal levels of refining (I).

### 4 HORNIFICATION INDUCED BY PRESSING AND DRYING

#### 4.1 Introduction

Hornification has a large negative effect on tensile strength and a large positive effect on dewatering. It reduces fibre flexibility and conformability, ultimately resulting in decreased tensile strength. On the other hand, decreased pulp swelling reduces the resistance of compression in wet pressing, which improves dewatering (45). Many studies have shown (44, 48, 49) that the moisture content after wet pressing generally correlates with pulp swelling.

Dewatering particularly concerns highly swollen never-dried pulps. Common practice in some integrated mills is to dry virgin pulp on a pulp drying machine, reslush the pulp, and then form paper. This is done in both fine paper mills and mills using chemical pulp as reinforcement fibre. Although this practice is expensive, both in terms of energy consumption and additional production stages, it can result in a net saving because the paper machine speed is substantially increased. Although it has been demonstrated that the properties of dried pulps are inferior to those of never-dried pulps (42, 50, 51), the industry practice suggests that this is of less concern than the realized improvements in dewatering.

However, much better ways to improve the dewatering of virgin pulps can most likely be found without having to dry them completely to reduce the swelling level. Other routes to minimize pulp swelling include changes to the pulping and bleaching process, chemical treatments, pre-pressing, and changes to the refining process. One attractive way is to dewater the cell wall at some stage, thus inducing hornification and improving dewatering. This does not necessarily demand bulk dewatering, since it is the water in the cell wall which is relevant here, and the extra-fibre water plays little part in dewatering.

Pressing of pulps might provide an economical way to induce hornification. Carlsson and Lindström have shown (52) that increased pressure or increased pressing time at constant pressure causes the pulp solids content after wet pressing to increase and the swelling measured by the water retention value (WRV) to decrease. Other studies suggest (23, 53) that hornification by wet pressing involves closing of pores in the fibre cell wall and that this influences press dewatering. On the other hand, pressing as a means to induce hornification will cause lumens to collapse and fibres to flatten. Page et al. showed (54) that the percentage of collapsed fibres in a sheet increases with increased pressure in wet pressing. The collapsed or flattened fibres provide more surface contact for interfibre bonding, and this leads to denser and stronger paper. Although pressing can hornify pulps

to a certain extent, it is unclear how paper properties can be changed by pressing pulps before refining.

In this chapter, hornification by pressing and drying was examined to find a means to improve dewatering and to control paper properties. Never-dried pulps were treated by pressing at different pressures to different solids contents, followed by refining to varying levels.

#### 4.2 Hornification and dewatering

In Figure 10, the FSP is plotted against refining energy. The pressed pulp was treated by pressing to a solids content of about 60%, and the refining was conducted with a Voith laboratory refiner. The FSP is 1.22 ml/g for the unrefined never-dried pulp and 1.11 ml/g for the unrefined pressed pulp, indicating that the pressing treatment hornifies the pulp. Consequently, at different refining levels, the pressed pulps show lower swelling than the unpressed never-dried pulps. Drying causes more hornification than pressing. The unrefined previously dried pulp has a FSP of 0.99 ml/g, and the refined dried pulps also have the lowest swelling.



Figure 10. FSP versus refining energy for never-dried, previously dried (from a pulp drying machine), and pressed never-dried pulps (III).

In Figure 11, the moisture content of the handsheet after wet pressing is plotted against the refining energy. The dried pulps have the lowest moisture content and thus the best dewatering. The moisture content of the pressed pulps is lower than that of the never-dried pulps, indicating that the pressing treatment improves dewatering. The pressing did not

completely dewater the cell wall, so the amount of hornification was less and the dewatering thus worse than for the previously dried pulp.



Figure 11. Moisture content after wet pressing versus refining energy (III).

#### 4.3 Paper properties

Figure 12 shows dry sheet properties, including tensile index, tear resistance, apparent density and light scattering coefficient, as a function of refining. At a given input of refining energy, the refined dried pulps have the lowest tensile strength and density but the highest tear resistance and light scattering coefficient, which is primarily due to severe hornification caused by drying. Compared with the untreated never-dried pulps, the pressed pulps were found to give higher tensile strength, higher tear resistance, higher density, and a lower light scattering coefficient. In particular, the increase in tensile strength caused by the pressing treatment is substantial: it is about twice the difference between the untreated never-dried and dried pulps.

Hornification reduces the flexibility of pulp and the tensile strength of paper, but the pressing treatment appears to improve tensile strength. So the pressing treatment under the currently applied conditions must cause some other effect which not only offsets, but also outweighs, the effects of hornification. It is seen that the pressing treatment increases density and decreases the light scattering coefficient. These two properties generally indicate interfibre bonding. It seems that the increase in tensile strength brought about by pressing is due to the enhanced densification and consequently improved bonding. The pressing treatment may cause the lumens to collapse and fibres to flatten. The flattened fibres provide a larger area for bonding. As a result, density and tensile strength increase, and the light scattering coefficient decreases.



Figure 12. Paper properties, including tensile index, tear resistance, apparent density and light scattering coefficient, versus refining energy (III).

In Figure 13, the tensile index is plotted against apparent density. There is an excellent correlation, which confirms that the increase in tensile strength caused by pressing is mainly due to enhanced sheet densification and interfibre bonding.



Figure 13. Correlation between apparent density and tensile index (III).

#### 4.4 Combination of dewatering and tensile strength

In Figure 14, the combination of dewatering and tensile strength is compared for neverdried, previously dried, and pressed never-dried pulps. At the same tensile strength, the dried pulps give the lowest moisture content after wet pressing and thus the best dewatering. One reason might be that the dried pulps have fewer small pores and more water in large pores, which promotes water removal and enables improved dewatering. However, although the best combination of dewatering and tensile strength can be obtained with the dried pulps, this occurs at the expense of energy consumption. Pulp drying consumes a huge amount of energy, typically 2.8-4.0 GJ/ton water (55), and dried pulps need to be refined more intensively to reach the desired tensile strength. Pulps treated by pressing offer a markedly better combination of dewatering and tensile strength than never-dried pulps. The main advantage of pressed pulps is that the improved dewatering and higher tensile strength can be achieved with a lower input of refining energy.



Figure 14. Comparison of the combination of dewatering and tensile strength for neverdried, previously dried, and pressed never-dried pulps (III).

#### 4.5 Hornification by pressing to varying degrees

In the experiments described in this section, never-dried pulp was pressed to different higher solids contents, and the never-dried, pressed never-dried, and air-dried pulps were then refined to 5,000 revolutions in a PFI mill. Figure 15 shows the FSP for the pulps before and after refining. The pressing treatment lowers the FSP of the unrefined never-dried pulp from 1.23 ml/g to 1.14, 1.12, or 1.05 ml/g for the pulps pressed to the respective increased solids content. Drying causes more hornification of the pulps, reducing the FSP to 0.86 ml/g. After refining, the same trend of swelling prevails.



Figure 15. FSP for never-dried, pressed, and air-dried pulps before and after refining (III).

Figure 16 shows the dewatering and tensile index of the refined pulps. The pressed pulps are more effectively dewatered than the untreated never-dried pulp, and dewatering improves with increased solids content up to about 66-68%. At a solids content of about 66%, the pulps are dewatered to roughly the same degree as the air-dried pulp. Meanwhile, the pressed pulps give almost the same tensile strength as the untreated never-dried pulp. It appears that when the pulps are pressed to a solids content of around 66-68%, their dewatering can be substantially improved without sacrificing tensile strength.



Figure 16. Moisture content after wet pressing (left) and tensile index (right) for refined never-dried, pressed, and air-dried pulps (III).

#### 4.6 Discussion

In the pressing treatment, a large amount of water (about 0.55-0.76 g/g) was removed from the fibre cell wall. Earlier studies have shown (43–45) that during pressing the water between fibres and in the lumens is removed first, followed by the water in the fibre cell wall. So the pressing treatment probably causes lumens to collapse and further hornifies fibres. On the other hand, Görres et al. have shown (56) that chemical pulp fibres start to collapse rapidly at low pressures, and at high pressures of about 2-5 MPa they tend to approach complete collapse. Previous studies also suggest (57, 58) that fibres are plastically deformed in pressing. In addition, the pulp pads after pressing were very dense and rigid, and there was no discernible expansion in thickness. All these facts support the view that pressing causes lumens to collapse and fibres to flatten. The flattened fibres provide more surface for interfibre bonding, resulting in higher density and tensile strength, as seen in the case where the pulps were pressed to about 60% solids content. At about 66-68% solids content, the pressed pulps have roughly the same tensile strength as the untreated pulps and much improved dewatering. This is probably because the degree of hornification increases with an increase in solids content. The results suggest that it might be worthwhile exploring alternative drying schemes in integrated pulp mills. One possibility that might offer some advantage over current pulp drying machines is to use impulse drying to reach solids contents in the range of 65-75%. This could be followed by immediate reslushing for internal use or formation of moist sheets for market pulp. This would eliminate the need to remove the energy-consuming bound water and would allow construction of shorter and cheaper pulp drying machines. However, the author acknowledges that logistical considerations and the operation of sheeters favour production of ordinary pulp sheets with a solids content of 92-95%.

#### **5 INTERNAL FIBRILLATION IN REFINING**

#### **5.1 Introduction**

Internal fibrillation can be generally described as the breakage of the crosslinks between microfibrils. In an earlier study, Hartman has demonstrated (59) that a cyclic compressive action delaminates fibres internally. This view is supported by many others (60–62). Recently, Kerekes suggested (60) that to produce internal fibrillation, fibres need to be turned over when undertaking compression.

Besides internal fibrillation, other important fibre properties developed in refining include external fibrillation and fibre straightening. External fibrillation refers to fine cellulosic hairs being raised on the fibre surface chiefly by an abrasive action (59, 60). Kerekes has proposed (60) that in bar refiners, the amount of external fibrils produced during refining depends on the forces exerted on the fibres and the sliding distance over which these forces act when the bars cross. There is still no convenient method for accurately quantifying external fibrillation. In the present experiments, the surface area of external fibrils was calculated from the area of pixels occupied by fibrils in images taken with a light microscope (12). Fibre straightening can be promoted by tension and by increased fibre swelling (63, 64). Seth found (63) that fibre straightening increases with increased swelling caused by a progressive carboxymethylation treatment.

The purpose of the experiments described in this chapter was to improve the understanding of how the above-mentioned fibre properties are developed in refining and how they can be controlled independently. Four devices, a Lampén mill, a PFI mill, a Voith laboratory refiner and a Masuko Super Masscolloider (9), were used to simulate refining actions. In the Lampén mill, a motor drives the refiner housing which causes a 10-kg ball inside the housing to rotate, imposing a largely compressive action (65, 66). The PFI mill has been reported to be a largely compressive refiner, generating a high ratio of compressive force to shear force (66, 67). The Voith laboratory refiner is a typical bar refiner that simulates current industrial practice, generating relatively more shear force and surface abrasion. The Masuko Super Masscolloider is a grinding device with a lower rotating plate and an upper stationary one (9). The plates have an abrasive surface, which can produce a large amount of external fibrils.

#### 5.2 Internal fibrillation generated by different refiners

Figure 17 illustrates the PSD measured with cyclohexane-based thermoporosimetry from never-dried fibres refined in the Voith laboratory refiner and the Lampén mill. The increased pore volume originates mainly from the large pores expanded or opened primarily in the early stage of refining. Both the Voith refiner and the Lampén mill have a similar impact on the PSD. Besides thermoporosimetry, another good method for measuring internal fibrillation is to measure the fibre pore volume, the FSP. The FSP measurement was considered adequate here, because the PSD curves show that the pore volume expands in a rather similar fashion in different refiners.



Figure 17. PSD of fibre fraction (R200) refined in a Voith laboratory refiner (left) and a Lampén mill (right) (V).

In Figure 18, the surface area ratio of external fibrils to fibres is plotted against the FSP to illustrate the development of external fibrillation and internal fibrillation in different refiners. It is seen that the different refiners fibrillate fibres internally and externally to different levels. The Lampén mill generates high internal fibrillation but low external fibrillation, whereas the Masuko Super Masscolloider generates low internal fibrillation but high external fibrillation. The PFI mill and the Voith refiner are in between, with the PFI mill closer to the Lampén mill. Taking into account the design and operation of these devices, the results support the earlier view (59–62) that compression causes internal fibrillation.



Figure 18. External fibrillation versus internal fibrillation for fibre fraction (R100) (IV).

In Figure 19, the SR value is plotted against the surface area ratio of external fibrils to fibres. External fibrils have a large specific surface area, which causes them to impede water drainage. The SR value correlates well with the degree of external fibrillation, suggesting that the SR value of a fines-free furnish gives a simple and reasonable measure of external fibrillation. Earlier studies have shown (68, 69) that the freeness correlates with the pulp's specific surface area determined with a liquid permeability method.



Figure 19. Correlation between SR value and external fibrillation (surface area ratio of external fibrils to fibres) (R100) (IV).

The effectiveness in straightening fibres in relation to internal fibrillation is significant in improving pulp properties. The highly straightened fibres require less internal fibrillation to reach a desired tensile strength, which leads to higher bulk and light scattering coefficient and also improves the dewatering and drying rate. In Figure 20, the fibre curl index is plotted against the FSP. The order of the refiners in terms of their effectiveness in straightening fibres is the following: the Lampén mill, the PFI mill, the Voith laboratory refiner, and the Masuko Super Masscolloider. Earlier studies have shown (63, 64) that fibres can be straightened by tension and by increased fibre swelling. However, in the present work, the Lampén mill, which imposes a highly compressive refining action (65, 66), was found to be very effective in straightening fibres. It appears that compression can also promote the straightening of fibres.



Figure 20. Fibre curl index versus FSP (R100). The lower curl index denotes increased fibre straightening (IV).

#### **5.3 Development of internal fibrillation**

As seen in Figure 18, the Lampén mill generates high internal fibrillation. Figure 21 shows the FSP for the whole pulps from the Lampén mill treated at different consistencies, but for an equal number of revolutions. At the standard refining consistency of 3%, internal fibrillation is highly developed. At consistencies above about 10%, the Lampén mill does not internally fibrillate fibres. This is probably because the fibres are fairly immobilized above 10% consistency and do not turn over from the action of the ball rolling over the pulp pad. This means that the fibres are compressed repeatedly, but only in one direction. Kerekes has established (60) that fibre network turnover is a prerequisite for efficient refining. PFI mills can produce high internal fibrillation at 10% pulp consistency; the likely reason is that the bars and grooves of PFI mills are efficient in mixing and turning over fibres. The turning over of fibres enables them to be compressed from different directions, which allows efficient internal fibrillation.

Figure 22 illustrates how compression might cause internal fibrillation in the cell wall. Disruptive forces at the creasing Point B tear bonds between microfibrils. In order to effectively swell the fibres and loosen the cell wall, the fibre needs to be compressed from different directions so that multiple creasing points occur. One of the advantages of a rotating disc refiner is that it effectively mixes the fibres and at the same time compresses and shears them.

In addition, when fibres are in a high-consistency network, the network strength resists compression, making it difficult to deform fibres plastically. This, on the other hand, suggests that the water present during refining plays a pivotal role, probably by lubricating and dispersing fibres.



Figure 21. FSP for whole pulps treated at different consistencies to 7,500 revolutions in a Lampén mill (IV).



Figure 22. A proposed mechanism of how internal fibrillation may be created by a compressive action. Compression in region A flattens and compresses the fibre and causes the disruption to the cell wall lamellar structure at the crease in region B, resulting in the breakage of the crosslinks between microfibrils (IV).

# 6 REFINING FOR OPTIMUM DEWATERING/TENSILE STRENGTH COMBINATION

#### 6.1 Introduction

Chemical pulps are refined to meet the requirements of many end-product properties, particularly strength and surface properties. However, refining causes the pulps to swell, which slows the dewatering rate. This chapter examines how the combination of tensile strength and dewatering properties can be optimized in refining.

Internal and external fibrillation, fines generation and fibre straightening have been generally considered amongst the most important refining effects when aiming at improved tensile strength (70, 71). Internal fibrillation reduces the effective moment of inertia of the fibre wall, thus increasing wet fibre flexibility and collapsibility. This results in improved interfibre bonding (72) and the straightening of the slack fibre segments in the fibre network during drying (73–75), thus increasing tensile strength. Internal fibrillation has a negative effect on dewatering (44, 45, 48, 49).

If sufficient forces are applied to the fibres in the right direction, fibrils are partially torn loose from the fibres. The fibres' external surface area increases, which further promotes bonding and retards dewatering. External fibrillation does not appear to have a major impact on tensile strength (59, 71).

Secondary fines are generated when the fibrils and fibre fragments are completely liberated from the fibres. These fines are highly swollen (76, 77) and have a very positive effect on bonding and a very negative effect on dewatering (78).

Fibre straightening by refining has gained more attention recently (64, 70, 79–81). It improves tensile strength as a result of the improved load-transferring efficiency (70).

Although refining increases the tensile strength of paper and slows the dewatering rate, there seems to be potential to refine pulps in a way that optimizes the combination of dewatering and tensile strength. The purpose of the experiments described in this chapter was to determine how pulps refined to produce different amounts of internal and external fibrillation, fines content and curl behave in terms of dewatering and tensile strength development. Two laboratory refiners – a Voith refiner and a Lampén mill – were used, as it is known (IV, V) that the Lampén mill creates more internal fibrillation and fibre straightening but less fines and external fibrills than the Voith laboratory refiner.

#### 6.2 Results and discussion

In Figure 23, the moisture content after wet pressing is plotted against the FSP for the fines-free and the whole pulps. As expected, the moisture content increases with increased FSP. At equal FSP, both fines and external fibrillation decrease the water removal significantly. This indicates that while water transport from the cell wall is a limiting and important factor in press dewatering, factors that influence the transport of water within the interfibre capillaries must also be considered. Figure 23 shows that in principle it is possible to produce a pulp with a high degree of internal fibrillation, which still has good water removal properties.



Figure 23. Moisture content after wet pressing versus FSP for fines-free pulps and whole pulps (V).

In Figure 24, the tensile index is plotted against the FSP. The tensile index increases with increased FSP, indicating the significance of internal fibrillation and pulp swelling for tensile strength. At the same FSP, the pulps from the Lampén mill give higher tensile strength than those from the Voith refiner. The Lampén mill straightens fibres more effectively, which is one reason why it gives higher tensile strength.



Figure 24. Tensile index versus FSP (V).

In Figure 25, the moisture content after wet pressing is plotted against the tensile index. The results demonstrate that there is great potential to produce pulps with improved dewatering characteristics and adequate tensile strength. In present single-disc, double-disc and conical refiners, it is largely impossible to vary internal fibrillation, external fibrillation, fines content, fibre curl and other fibre properties independently. In these commercial refiners, the refining action is a rather similar shearing action. The current main process variables, i.e. specific energy, intensity, consistency, plate and refiner design, do not give enough flexibility to develop the full potential of fibres for various paper grades. The results presented here show that if radically different refining actions are brought into play, there is potential for improved fibre development. In particular, there is a need to find industrially feasible ways to impose cyclic compression on fibres in the absence of abrasion and shear, as both the Lampén mill and the device employed by Hartman (59) would be very difficult to scale up.

In addition, at equal tensile strength, the sheets from the Lampén mill have lower density and thus higher bulk, and a higher light scattering coefficient. This is probably due to effective fibre straightening, which allows a targeted tensile strength to be obtained with lower pulp swelling, with the lower swelling resulting in higher bulk and a higher light scattering coefficient. Both fines and external fibrils contribute significantly to Scott bond strength, and the Voith refiner gives superior Scott bond strength (82, IV, V).



*Figure 25. Comparison of the combination of dewatering and tensile strength. Redrawn from* (*V*).

## 7 CONCLUSIONS

The objective of this thesis was to find new ways to improve dewatering and paper properties, by controlling hornification in pressing and drying and by promoting internal fibrillation in refining.

Hornification and internal fibrillation cause a significant change in the cell wall pore structure. In the present work, thermoporosimetry with cyclohexane as an absorbate was tested and found to be a good method for studying the pore structure of chemical pulps, because it is able to detect the change in PSD during drying and refining. The pore volume determined with cyclohexane thermoporosimetry correlates with the FSP. However, it is lower than the FSP, probably because fibres contract in cyclohexane. The nonfreezing cyclohexane correlates with the fibre BET surface area, providing information on the fibre internal surface area.

The PSD from thermoporosimetry and the surface area from nitrogen sorption show that for never-dried fibres, refining mainly expands the large pores and has only a slight effect on the small pores. This is consistent with earlier results. Drying closes the large pores and a substantial amount of the small pores. For dried fibres, refining not only opens the large pores but also the small pores to a certain extent. At a given refining level, the difference in swelling between never-dried and dried pulps is largely due to the closing of small pores in drying.

Even though the pore volume of previously dried pulps can be recovered by refining, some small pores, which are closed by drying, are not reopened by normal levels of refining. The likely explanation is that strong irreversible hydrogen bonding is formed between microfibrils during drying which is not broken when the fibre is refined. Therefore, refining mainly disrupts and loosens macrofibrils, creating large-sized pores.

Drying hornifies pulps to an extent that significantly decreases tensile strength, but also greatly improves dewatering. Dried pulps offer a much better combination of dewatering and tensile strength than never-dried pulps. One reason might be that drying closes a large amount of the small pores in the fibre wall which are not completely reopened by normal levels of refining, thus resulting in improved dewatering.

Pressing of pulps before refining may provide an economical way to improve the properties of never-dried pulps. The tensile strength and dewatering characteristics of the pressed pulps appear to be affected by two mechanisms: fibre flattening and hornification. Pressing of the pulps may cause fibres to flatten, with the flattened fibres providing more surface contact for bonding, thus improving the tensile strength. Pressing also reduces

swelling and hornifies the pulps, which improves dewatering but impairs tensile strength to a certain extent, depending on the degree of hornification induced by pressing.

When pressed to a solids content of about 60%, the pulps display improved dewatering, higher tensile strength and better tear resistance, but also higher density and a lower light scattering coefficient. The effects of fibre flattening on sheet densification appear to outweigh the effects of hornification; therefore the pressed pulps develop higher density and tensile strength. When pressed to a higher solids content of about 66-68%, the pulps show substantially improved dewatering, with the tensile strength remaining at the same level as that of the untreated never-dried pulps. This is probably due to the increased effect of hornification on dewatering and tensile strength.

The data from different refiners show that the Lampén mill generates high internal fibrillation and low external fibrillation, the Masuko Super Masscolloider generates low internal fibrillation and high external fibrillation. The PFI mill and the Voith laboratory refiner are in between, with the PFI mill closer to the Lampén mill. These results support the earlier view that a compressive action causes fibres to fibrillate internally and an abrasive action externally. The Lampén mill causes internal fibrillation at low pulp consistencies, but not at high consistencies. It is suggested that this is because the fibres need to be turned over in refining and compressed from different directions in order to disrupt their internal structure and break crosslinks between microfibrils.

At an equal degree of internal fibrillation, the fibres from the Lampén mill are highly straightened, followed by the fibres from the PFI mill, the Voith laboratory refiner, and the Masuko Super Masscolloider. This suggests that, in addition to tension and increased fibre swelling as proposed earlier, compression also helps to straighten fibres.

The fact that compression causes more internal fibrillation and facilitates fibre straightening, but does not promote external fibrils and fines, has significant implications for the efforts to improve pulp properties. At an equal level of swelling, more straightened pulps give higher tensile strength, and pulps with a lower amount of fines and external fibrils enable better dewatering. Therefore, in order to achieve an optimum combination of dewatering and tensile strength, chemical pulp refining should aim at increasing internal fibrillation, straightening fibres, and minimising the amount of fines and external fibrils.

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