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# THE EFFECT OF SUPERHEATED STEAM DRYING ON THE

PROPERTIES OF PAPER

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemical Engineering McGill University Montréal, Canada

December, 1991

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### DEDICATION

This study is dedicated to the memory of 14 women, slain because they were women, in a bloody massacre on December 6, 1989 at the Polytechrique school of the University of Montréal. They did not live long enough to make their contribution to society as engineers.

I pray that we may never witness another such tragedy, and that the death of these 14 colleagues will not be in vain. May we all become more aware of and attempt to remedy those attitudes and social factors which led to the making of the deranged individual who authored this senseless crime.

#### ABSTRACT

The effect of drying paper by direct contact with superheated steam was determined with respect to the physical, optical and chemical properties of the dried sheet. The results were compared with those for paper dried in a similar fashion by direct contact with hot air.

It was found that the results depended on the type of pulp from which the sheet was made. For thermomechanical pulp sheets, superheated steam drying resulted in improved strength properties; burst index, tensile index and elastic modulus were 20 - 30% higher relative to the air dried sheets. The increase in strength was found to be due to an increase in bonded area, especially of the fine fraction, caused by the higher sheet temperatures occurring in the constant rate period of steam drying. As a result of the increased bonding but not due to any color change, brightness of the steam dried sheet decreased by 5 points. Steam drying of TMP sheets results in strength and optical properties more characteristic of paper made from CTMP.

Superheated steam drying of kraft pulp sheets had a smaller and opposite effect, as strength properties decreased and optical properties increased relative to the properties of sheets dried in air. Unlike mechanical pulp, no increase in bonded area was observed because of the already high bonding potential of kraft fibres; a thermally induced drying stress relaxation is thought to be the cause of the decreased strength properties.

#### RESUME

Nous avons étudié les effets, quant aux propriétés physiques, optiques et chimiques, d'une feuille de papier séchée par contact direct de vapeur surchauffée. Les résultats furent comparés avec ceux du papier séché par contact direct avec de l'air chaud.

Nous avons constaté que les résultats variaient en fonction du type de pâte utilisée. Pour le papier fait de pâte thermomécanique, le séchage par vapeur surchauffée a amélioré la solidité de la feuille; l'indice d'éclatement, l'indice de résistance à la rupture et le module d'élasticité ont augmentés de 20 à 30% comparé aux feuilles séchées à l'air. Cette amélioration est due à une augmentation du nombre de liens dans la feuille séchée par vapeur surchauffée, surtout dans la fraction fine, causée par la température élevée de la période de séchage à taux constant. A cause de cette augmentation du nombre de liens et non à cause d'aucun changement de couleur, l'éclat de la feuille est inférieure de 5 points à celle de la feuille séchée par l'air. Le séchage par vapeur surchauffée de feuilles TMP procure des propriétés physiques et optiques caractéristiques du papier fait de pâte CTMP.

Les feuilles de pâte kraft séchées par vapeur surchauffée démontrent un effect contraire et plus petit; les propriétés de tenacité sont diminuées et les propriétés optiques sont améliorées comparé aux feuilles séchées par l'air. Contrairement aux pâtes mécaniques, aucune augmentation du nombres de liens est produite vu que la feuille faite de pâte kraft est déjà très bien liée; il se peut que la réduction des propriétés de tenacité soit provoquée par un délassement thermique de la tension de séchage.

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The completion of this study coincided with the birth of my first child. I therefore very much appreciate the love, support and patience of my husband Richard, as well as the help and encouragement received from friends and family. Special thanks to my parents who helped take care of my little daughter Bianca while I worked.

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# CHAPTER 1

## INTRODUCTION

#### 1.1 Objectives

The objective was to determine the product quality of paper dried by direct contact with superheated steam. This information is of vital importance in determining the feasibility of the novel process of drying paper in superheated steam.

The physical and optical properties were of primary interest. These properties were measured for steam dried paper and compared to those of paper dried similarly in air. The range of drying fluid temperature was 160°C to 320°C, plus air drying at room temperature. Unlike previous exploratory studies, a much larger set of product quality properties was measured, and more effort was devoted to explaining observed differences between steam and air dried sheet properties in terms of the chemical and physical processes occurring during drying.

#### 1.2 Industry significance

This study makes a direct contribution to the development of a drying process in which paper is dried by direct contact with high temperature superheated steam. This novel technique is being considered as an alternative to conventional drying because of the potential for low capital cost, higher drying rate and energy efficiency, and beneficial effect on paper properties. The superheated steam drying process appears to have the potential of improving the drying operation in paper manufacture, but research is only in the early stages and development work has yet to begin. Research aimed at determining the commercial viability of this process must carefully investigate product quality and property development, as well as drying rate and energy efficiency. The former was investigated in the present study while the latter is being investigated in parallel work. The results of these complimentary studies will indicate whether research should continue and provide preliminary indications of optimum operating conditions.

#### 1.3 Conventional paper drying

From an energy as well as a product quality point of view, the drying of paper products is an important unit operation in the pulp and paper manufacturing process. The moisture content of the paper is typically reduced from 60 - 70% to 4 - 8%. However, drying is more than just the removal of moisture from a wet sheet, for it is during this operation that the mechanical and optical properties of paper are developed as the loose assemblage of fibres becomes a consolidated structure. As many physical and chemical changes occur during drying, the final properties of the product depend greatly on the drying strategy employed.

Conventionally (1), paper has been dried by contact with a series of steam heated rotating cast iron cylinders which alternately heat the top and bottom sides of the web (figure 1.1). The energy costs for such drying may be as high as 75% of the total paper





Figure 1.1: Conventional dryer section

machine operating cost (2). This method suffers from several drawbacks. The low heat transfer rates associated with this conduction-based drying process give rise to long dryer sections containing as many as 60 drying cylinders. This requirement represents a large capital investment. The evaporated moisture eventually leaves the system as humid air discharged to the atmosphere, resulting in an energy intensive process. Finally, operation of the dryer at higher speeds is limited due to web breaks in the many unsupported draws between drying cylinders.

These disadvantages, as well as special drying requirements of some products, have led to the use of various other conventional drying techniques. For example, Yankee dryers used for drying lighter grades such as tissue combine conduction and air impingement drying on a single large diameter steam heated cylinder surrounded by impingement hoods. Dryers using only throughflow of the drying medium also exist. Infrared dryers are used for drying coated sheets which require non-contact drying. Press-drying, involving the application of high pressure at high temperature, has been used for the drying and consolidation of heavy paper boards for years. A process which was tested at the pilot plant scale but which did not achieve commercial adoption is the Papridryer, drying by combined air impingement and throughflow. Impulse drying is an intense form of press-drying and is currently being investigated at the pilot plant scale for paper drying.

#### 1.4 Superheated steam drying

The concept of using superheated steam rather than hot air as a drying medium was discussed as early as 1908 by Hausbrand (3). Superheated steam is currently used industrially to dry such products as granular foodstuffs, pulverized coal, textiles, pulp, bark, veneer and timber. The concept of using impinging jets of superheated steam to dry paper is not new either, as evidenced by patents dating as far back as 1952 (4), although there is no known industrial implementation of the process. Mujumdar et al. (5-7) recently re-examined the idea of drying paper with superheated steam and a renewed interest for the concept has developed.

As a drying medium, superheated steam offers several advantages over air. With superheated steam, the water removed from the wet solids becomes part of the drying medium, as opposed to air drying where the moist air must be continually replaced by heated fresh air. The exhaust steam in superheated steam drying can be re-used directly, with the net steam produced exported for use at that pressure or repressurized by thermocompression or mechanical recompression. In air drying, over 30% of the thermal energy loss is heat in the humid air exhaust stream which is economically unrecoverable (5).

Depending on the temperature of the drying medium, drying rates with superheated steam may be higher than with air at the same temperature and mass flow rate. Although it is generally believed that the rate of water evaporation decreases as the humidity of the drying medium increases, this is not always true. In their comparison of rates of evaporation of water into air, humid air, or superheated steam, Chow and Chung (8) showed that below a certain temperature known as the inversion temperature, water evaporation rate decreases as air humidity increases, as expected. However, above this inversion temperature the evaporation rate increases with air humidity, as shown in figure 1.2. The temperature above which the evaporation rate is faster in steam than in air is approximately 190°C for turbulent flow (8) and 250°C for laminar flow (9, 10). The existence of an inversion temperature results from the opposing effects of higher heat transfer coefficients for steam and depression of the interfacial temperature from 100°C in steam to the wet bulb temperature in air drying.



Figure 1.2: Evaporation rates for various free stream fluids

Chow and Chung (8) also showed that a significant thermal economy may be achieved by using superheated steam. Figure 1.3 from their work shows the energy required to evaporate 1 kg of water into turbulent streams of air and steam, assuming that for air drying the entire drying medium must be replaced by heating fresh air when the amount of water vapor in the medium reaches 10% mass. For most temperatures, the energy used in air drying is at least twice as much as that for steam drying.

Another interesting aspect of steam drying is the absence of oxygen during the drying



Figure 1.3: Effect of drying temperature on energy required for air and steam drying

process, which eliminates the risks of fire and explosion hazards and prevents certain oxidation reactions from occurring. A recent exploratory investigation indicated that superheated steam dried paper had higher zero-span breaking length, burst strength and bulk compared to paper dried under the same conditions with air, without deterioration of paper properties even for overdrying (11). As the mechanisms leading to these changes were unknown, only speculations were offered in that study.

Superheated steam drying could be implemented in a variety of ways. One of the

easiest would be to replace the impinging jets of air with impinging jets of superheated steam in a Yankee dryer, as has recently been proposed by Thompson et al. (12). Some of the difficulties of drying with superheated steam include the confinement of the steam inside the dryer through which the moving web must pass, and possible condensation problems at start-up and during rethreading after web breaks.

Research on superheated steam drying is at the laboratory scale. Besides those at McGill University, no other researchers are known to be currently investigating the concept of superheated steam drying of paper. However, several equipment manufacturers have already expressed interest in the process. A pilot scale dryer able to investigate superheated steam drying and other drying concepts will be available within a year or two at Paprican.

#### 1.5 Summary

Superheated steam drying of paper is a novel drying process in which the moist sheet is dried by direct contact with superheated steam. Research on the process is recent and is at the laboratory stage. The process could potentially improve drying rates, energy efficiency and paper properties.

In this thesis the effect of superheated steam drying on a wide variety of physical, chemical and optical paper properties is quantified for a diverse range of pulps. The conditions experienced by the sheet during superheated steam drying are measured and explanations for the behavior of the paper properties are developed.

#### CHAPTER 2

#### PRIOR KNOWLEDGE

In this chapter, prior knowledge relevant to understanding the phenomena occurring during superheated steam drying of paper is considered. This analysis will serve as a foundation for the discussion and conclusions presented in subsequent chapters.

#### 2.1 Physical and chemical structure of fibres and paper

#### 2.1.1 Structure of fibres

The intricate physical structure and chemical nature of wood fibres is fundamental to the way in which they interact to form paper. This structure and nature varies depending on the wood species. The biggest differences are between softwood and hardwood species, with smaller differences observable within these two major classes. The fibre structure is basically that of a thin-walled, easily collapsible hollow tube (tracheid) having openings (pits) in the walls. The most obvious difference between softwoods and hardwoods are the shorter lengths (1-2 mm vs. 2-7 mm) and smaller diameters (15  $\mu$ m vs 33  $\mu$ m) of the hardwoods, differences which result in significant variation in physical properties of the resulting paper.

All wood fibres are composed of the same wood polymers: cellulose, hemicellulose, and lignin, along with small amounts of various extractives (resins and fatty acids), the individual amount of each component varying with species. Cellulose is the framework of the cell wall, and hemicellulose and lignin are the matrix and encrusting substances, respectively. The typical composition of softwood is approximately 42% cellulose, 27% hemicellulose, 28% lignin, and 3% extractives. Fibres of black spruce, the wood used in the present study, have an average length of 3.5 mm and an average diameter of 25-30 microns (13, 14). The fibre cross-section is almost rectangular.

Figure 2.1 shows a cutaway view of a fibre. The hollow portion down the middle of the tracheid is the lumen. The middle lamella ML, cellulose free, is about 80% lignin and 20% hemicellulose. It acts as an external adhesive, holding the individual fibres together in the structure known as wood. The middle lamella is dissolved in chemical pulping and fractured in mechanical pulping to liberate the fibres. Unlike mechanical pulping, chemical pulping thus results in large reductions of the lignin and hemicellulose fractions of wood, producing fibres which are more flexible and conformable, characteristics which have a significant impact on the properties of the resulting paper.

The cell wall consists of a thin primary wall P and a much thicker secondary wall S. The primary walls, high in lignin and hemicellulose content, also contain 20-25% cellulose. The primary wall and middle lamella together are called the compound middle lamella. The secondary wall is made up of three layers called S1, S2 and S3. These walls consist almost entirely of cellulose with small amounts of lignin and hemicellulose. The secondary wall, the most influential with regard to fibre strength, accounts for approximately 80% of the cell wall thickness and contains over 95% of the total cellulose

content of wood.

Microscopic examination of fibres shows spiral lines on the cell walls. These subfibre structural units, known as macrofibrils, restrain the fibre from swelling. Macrofibrils contain microfibrils, in turn composed of even smaller sub-units known as elementary fibrils. The angle of fibril wrapping to the fibre axis determines the strength of the fibre, with greatest strength occurring at small angles (15). The primary wall has fibrils wrapped at right angles to the fibre axis. The outer and inner layers of the secondary wall have fibrils wrapped almost at right angle to the fibre axis, while those in the middle layer are wrapped at an angle closer to 0°, making it the most important layer in terms of fibre strength.

#### 2.1.1.1 Cellulose

Cellulose, the structural basis of the fibre, is a polymer of the simple sugar glucose. The configurational formula of cellulose is poly- $\beta$ -1,4-D-glucosan and the constitutional formula of cellulose is shown in figure 2.2. For cellulose,  $(C_6H_{10}O_5)_{\alpha}$ , the degree of polymerization, n, ranges from 200 - 30,000 glucose units. The degree of polymerization DP affects strength properties. The tensile strength of fibres with DP < 80 is low, then increases linearly with DP, becoming constant for DP above 1,000 (16). DP can be reduced by dry grinding, ball milling, excessive heating, and exposure to UV light, oxidizing or bleaching agents. An estimate of DP can be obtained from the viscosity of cellulose in solution.



Figure 2.1: Schematic diagram of fibre structure (14)



Figure 2.2: Constitutional formula of cellulose (14)

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Cellulose is unique among the wood polymers in that it is the only fibre component which can exist in the crystalline state; all other components are amorphous. In crystalline regions the cellulose chains, aligned into parallel arrays, are held together by hydrogen bonds to form a crystallite, a perfectly ordered lattice. The cellulose unit cell, the smallest regularly repeating structural unit in the crystal, consists of four glucose anhydride units in two chains. Figure 2.3 shows the structure of the cell wall down to the unit cell level.



Figure 2.3: Structure of cell wall (14)

Crystalline cellulose exists in various polymorphous forms of slightly different unit cell dimensions. Native wood cellulose, cellulose I, can be converted to cellulose II. III or IV. For example, cellulose I can be converted to cellulose II by swelling in concentrated caustic soda. The process is referred to as mercerization. Conversion to cellulose IV can be achieved by heat treatment (17). In some cases such changes are permanent, in others they can be reversed by further treatment.

Cellulose also exists in the para-crystalline form (slightly disordered lattice) and the amorphous form (completely disordered lattice). It is generally assumed that one cellulose chain can pass through crystalline, para-crystalline and non-crystalline regions (17). Disordered cellulose is very accessible compared to crystalline cellulose and readily takes part in chemical reactions. Unlike crystalline cellulose, amorphous cellulose swells readily in the presence of water (17).

Degree of crystallinity is important for strength of the fibre, the strength of disordered cellulose being far inferior to that of crystalline cellulose (18). Orientation of the structural units of cellulose in cell walls is also important. Fibres in which the crystallites are mainly oriented in the fibre axis direction have high tensile strength combined with low stretch (18). Fibres with poorer orientation tend to orient under tension, thus accounting for the greater stretch.

The crystallites of crystalline cellulose are sufficiently aligned to show the phenomenon of double refraction of light or x-rays. Crystallinity is thus often determined by x-ray diffraction, but can also be measured by spectroscopy (raman, infra-

red, NMR) and by chemical techniques. The fact that only amorphous regions of cellulose can absorb moisture or dissolve in various solvents often serves as a basis for the chemical techniques.

#### 2.1.1.2 Hemicellulose and lignin

The highest concentration of hemicellulose occurs in the primary wall, approximately 67% hemicellulose. Hemicelluloses are polysaccharides like cellulose, but differ from cellulose by their lower molecular weights (much shorter chain lengths), by branching of the chains and by their composition of 5 sugar units - glucose, mannose, galactose, xylose and arabinose (17). Hemicellulose readily absorbs water, leading to fibre swelling. Compared to cellullose, hemicellulose is easily degradable. The combined cellulose and hemicellulose fractions are referred to as holocellulose.

Lignin is a complex polymer whose structure consists mainly of phenyl propane units joined in three dimensions. In native form it is considered to be a polymer of unlimited molecular weight. Lignin, found mainly in the middle lamella, serves to bind fibres together in wood.

### 2.1.2 Structure of paper

Paper is formed by dispersing pulp fibres in water, draining the suspension on a screen, followed by pressing, drying and finishing operations. Depending on the severity of processing from wood to pulp to paper, the fibres may not retain their tubular shape

but become flattened ribbons with faces much wider than their thickness, the faces being parallel to the plane of the paper. As these ribbons form a laminated rather than interwoven structure, a paper sheet is a randomly arranged two dimensional array of fibres.

The nature of the forces holding pulp fibres together in a sheet of paper has long been debated. Although mechanical entanglement, friction, hydrogen bonds and van der Waals forces have been proposed, it has now been convincingly demonstrated that polar hydrogen bonds between hydroxyl groups of adjacent fibres and fibrillae are the most important forces holding normally fabricated paper together (19-21). Under certain unusual conditions, to be reviewed later, other types of bonds in paper can be formed.

There is some controversy as to the weak link in paper, variously claimed to be the fibre-to-fibre bonds or the strength of the fibres themselves (16). For a well formed sheet, the strength is a function of both factors, with fibre-to-fibre bonding the most significant factor. In a typical paper only 40% or less of the actual fibre tensile strength is available (21, 22).

Interfibre bonding can be increased by improving the contact between fibres, usually resulting in an increase in sheet density. This can be done by pressing the moist sheet or by beating the fibres prior to sheet formation which makes them more conformable and roughens their surface, liberating fibrils for additional bonding sites. The amount of fibre-to-fibre bonding, expressed as a fraction of the total possible, is termed the Relative Bonded Area (RBA). It can be estimated by various techniques, including by light microscope (19), gas absorption (23, 24), light scattering (25, 26), and x-ray scattering (27). Physical strength tests are also used as indicators of changes in bonding between fibres. These methods provide a relative measure of fibre bonding. Sheet density and RBA are highly correlated with most of the mechanical properties of paper.

The forces holding fibres together in paper are not only due to cellulose-cellulose hydrogen bonds, as evidenced by the poor strength properties of sheets made from cotton and alpha-cellulose (long chain cellulose) pulps which do not contain hemicellulose or lignin. Hemicellulose functions as an adhesive between fibres through the mutual bonding of hydroxyl groups and also introduces points in the fibre structure where fibrillation (the unravelling of fibrils from the cell wall) can occur, leading to additional bonding (21). Strength and stiffness of paper increase with increasing hemicellulose content, up to a certain limit (18, 19).

It is difficult to investigate the effect of lignin on bonding as it is nearly impossible to change the lignin content without affecting the content of the other polymers. However, in general, increasing lignin content does not have beneficial effects on sheet strength due to the increasing stiffness which it causes in the fibres. Lignin, inelastic and non-adhesive compared to hemicellulose, forms bonds with cellulose although much weaker than hemicellulose-cellulose bonds (20). Lignin, while not participating as much as hemicellulose in bond formation, may play an important role by sealing against moisture the bonds formed by other components (28, 29) if added to the sheet, or if the paper is heated to a sufficiently high temperature to initiate lignin flow. The rheology of paper has been described according to phenomenological, structural and molecular theories (30). Phenomenological theories do not take account of the physical or molecular structure of paper but represent the macroscopic behavior of the material by mechanistic models - springs and dashpots. Such descriptions are mainly used in the study of time-dependent mechanical processes.

By contrast, structural theories relate the mechanical properties of paper with the geometry and properties of the constituent fibres. An important parameter in structural theory is the relative bonded area which correlates with many mechanical properties of paper. Structural theories, although unsuccessful in describing the effects of moisture and temperature on sheet mechanical properties, are able to explain differences between machine and cross-machine direction moduli.

Molecular theories treat paper as an isotropic continuous network of hydrogen bonds in three dimensions. They have been successful in describing the effects of temperature and moisture content on Young's modulus, but do not account for contributions to Young's modulus of fibre morphology or distribution.

### 2.2 Fundamental considerations in drying

The sequence of physical and chemical processes occurring during drying and leading to the formation of paper is now reviewed, with emphasis on those factors affecting the final paper properties. The goal of the paper drying operation is to reduce the moisture content of the sheet, usually from approximately 60 - 70%, to a uniform moisture content
profile of 4 - 8%, while keeping the cost at a minimum. The drying process usually involves simultaneous heat and mass transfer by conduction, convection and diffusion. It is typically characterized by a constant rate drying period, where easily removable water is evaporated and during which the sheet temperature remains constant, followed by a falling rate period during which the sheet temperature rises because the water being evaporated is much more difficult to remove due to its intimate association with the fibre network.

## 2.2.1 Water removal and bonding

The first water removed during drying is from between the fibres, often termed free water. After the free water is removed, small menisci of water form between fibres and fibrils, replacing the continuous water. Strong attractive forces are created between the fibres in a direction normal to the surface of the sheet due to the surface tension of water. The consequent sheet thickness reduction increases sheet density correspondingly. Surface tension forces are thereby extremely important in bringing the fibres into intimate contact at 3 to 5 Å so that they may bond.

It is estimated that two round fibres of 30  $\mu$ m diameter lying parallel to each other and having a common water contact will experience an attractive force of 620 kPa (90 psi). For the case of smaller diameter (20  $\mu$ m) fibrils, this estimate increases to 3700 kPa (540 psi) (31, 32). The importance of these attractive forces in drying can be seen by the fact that the presence of even small amounts of surface tension reducing agents lowers the attractive forces to such an extent that the sheets produced are bulky and have little strength. As well, removal of interfibre water by sublimation at  $-6^{\circ}$ C so that no surface tension forces develop also results in a porous, bulky, low strength sheet (21).

As drying continues and intrafibre water is removed, the fibres shrink, building up drying stresses which cause the sheet to contract in the planar dimension if not restrained. Most of the shrinkage occurs between 60 and 85% solids content. The fibres shrink mainly in the transverse direction, but the transverse shrinkage of one fibre bonded to another causes longitudinal shrinkages called microcompressions in the second fibre (33).

The evolution of sheet strength as water is progressively removed during drying is shown in figures 2.4a and 2.4b. According to Robertson (34), line AB (figure 2.4a) represents web consolidation without air intrusion, which begins at point B. Inter-fibre capillary water is removed from B to C. Drying begins at point C, and the line CD represents development of strength due to removal of water from fibrils and contained in the fibre lumens. The onset and development of interfibre bonding occurs in segment DE, beginning anywhere from 50 - 60% solids content. From D onwards the sheet becomes progressively stronger as more bonds are formed.

# 2.2.2 Sheet restraint

The action of restraining the sheet during drying creates tension in the sheet, profoundly affecting paper properties. This drying stress is thought to equalize the load



Figures 2.4a - 2.4b: Evolution of tensile strength during drying

born by each fibrous element, making the sheet more uniform. It also results in increased molecular orientation of the polymers which leads to straighter fibres and reduces microcompressions. Sheets dried under tension generally have higher tensile strength and elastic modulus but lower stretch. However, burst and strength in the thickness direction of the sheet are generally decreased by tension drying. As well, the action of restraining the sheet significantly improves the dimensional stability. In conventional drying, the sheet is well restrained in the machine direction but little restrained in the cross machine direction, a source of anisotropy in sheet properties.

For all types of pulp, the elastic modulus has been shown to be directly proportional and other strength properties directly related to the final drying stress experienced by a restrained sheet (35). The development of drying stress during restrained drying follows 2 a sinusoidal shaped curve as shown in figure 2.5. The highest final drying stresses are attained in sheets dried the most rapidly and at the lowest temperatures (36).

That slower drying or increased drying temperature of a restrained sheet leads to a lower drying stress and lower strength properties is consistent with the viscoelastic and thermoelastic nature of paper. Paper exhibits time-dependent flow behavior, where stress relaxation is achieved by crystallite alignment and orientation of disordered cellulose regions, as well as easement of kinks and microcompressions. Stress can also be relaxed thermally since the fibre polymers are temperature sensitive, as discussed in the next section.



Figure 2.5: Evolution of drying force during restrained drying

# 2.2.3 Effect of temperature

# 2.2.3.1 Thermal softening and glass transition temperatures

Like most amorphous polymers, both hemicellulose and lignin are capable of reversible change at their glass transition temperatures  $(T_g)$  between soft rubber-like materials and hard solids. There is debate as to whether the amorphous regions of cellulose are also capable of this phenomenon. Water acts as a plasticizer, greatly reducing the glass transition temperature. Back and Salmén (37) suggest that for a

softened polymer to flow, a temperature of 25 - 50°C higher than the glass transition temperature is required. The extractives (resins, fatty acids) may also be capable of redistribution due to thermal softening, leading to increased water repellence of the sheet.

The glass transition temperatures of the main wood polymers under dry conditions as measured by various researchers are reviewed by Back and Salmén (37). For moisture-free cellulose, determinations of the glass transition temperature vary between 200 and 250°C, with debate as to whether this softening is due to a glass transition or a thermal degradation of the semi-crystalline material. Although pure crystalline cellulose has been reported to "melt" at temperatures above 400°C, this is actually an irreversible decomposition process unlike a glass transition or a normal phase change. Glass transition temperature determinations for moisture-free hemicellulose vary over a range of 150 to 220°C. For dry "native" lignin (i.e. not sulfonated or oxidized and as close to its natural state as possible), the glass transition temperature ranges from 130 -190°C. Disagreement between the experimentally observed values are ascribed to differences in procedures, definition, crystallinity (for cellulose), or isolation of the polymers.

The lowering of the glass transition temperatures for hemicelluloses, lignin and cellulose of various crystallinity due to the plasticizing effect of water was estimated by Back and Salmén (37). Their results, indicated in Figures 2.6a - 2.6c, compare well to the various experimental measurements. With enough moisture, hemicelluloses and celluloses can reach their  $T_r$  at room temperature, the amounts required being about 25%



Figures 2.6a - 2.6c: Effect of moisture content on softening temperatures of hemicellulose, lignin and cellulose

and 10% respectively for hemicellulose and cellulose of 60% crystallinity. Lignin reaches a softening limit at moisture contents variously reported as 3% (37) or 30% (38). For native lignin this temperature is around 115°C, although temperatures as low as 80-90°C have been reported for modified lignins such as kraft and sulphite lignins (38, 39).

For cellulose, Back and Salmén (37) did not discuss the discrepancy between their results and those of Goring (38) who found that there was no change in softening temperature with absorption of water (or other solvents). This, combined with the fact that Goring (38) reports an average weight loss of 35% for cellulose during the experiments to determine  $T_g$ , is evidence that this softening temperature is not a straightforward glass transition but rather the result of thermal degradation.

#### **2.2.3.2** Thermal treatment for stabilization and wet strength

Overdrying improves the dimensional stability and wet strength of paper (40, 41). More precisely, it is not the overdrying as such which causes the effect, but the heat treatment at low sheet moisture content. The treatment time required to achieve a certain degree of stabilization increases logarithmically with decrease in temperature, being of the order of seconds at 350°C, and weeks at 70°C. Depending on the extent of treatment, the dry strength of paper is generally degraded and the sheet becomes brittle, although short exposure times can actually slightly improve dry strength. However, the most significant improvements are seen in the sheet wet strength properties. Wet tensile and compressive strengths can increase from practically negligible, to one third or even one half the dry strength values. These improvements are accompanied by significant loss in fold, burst and tear strength.

The major source of these wet strength improvements is thought to be cross-linking, i.e. the formation of covalent bonds between adjacent cellulose chains. Unlike hydrogen bonds, these bonds are water resistant and restrict swelling. Cross-linking is brought about by elevated temperatures in moist or dry gases at sheet moisture contents < 15%. Hemiacetal, ether, ester and hemiketal linkages have all been proposed as types of bonds involved in cross-linking.

# 2.2.3.3 Thermal instability and detrimental reactions

Another effect of temperature arises because of the thermal instability of cellulose and carbohydrate structures (16). Thermal degradation of cellulose increases with temperature above 200°C although extended exposure to lower temperatures may also lead to degradation. If the thermal treatment of paper is sufficiently severe, burning or pyrolysis may occur, releasing a number of breakdown products - acetic and formic acids, anhydrosugars, tars, gases and low molecular weight products, water, char,  $CO_2$ and CO.

The rate of degradation of cellulose as measured by weight loss proceeds more quickly in air than in an inert atmosphere such as nitrogen (16). In air the thermal degradation is accompanied by two detrimental reactions, oxidation and hydrolysis, which depolymerize the cellulose and hemicellulose. These reactions are greatly increased by temperature. Oxidation leading to chain scission can be brought about by the presence of molecular oxygen at elevated temperatures, leading to the production of carboxyl and carbonyl groups and peroxide. The degradation products of cellulose oxidation lead to brightness reversion (42). The production of peroxide produces an acid environment which facilitates the hydrolysis to other compounds. More peroxide is produced by aging at high than low humidity, and the fines are the most vulnerable fraction with respect to oxidation as evidenced by their greater generation of peroxide (43).

The difference in degradation rate between air and  $N_2$  gradually disappears around 310°C at which point the degradation pathway changes (44). Reactions which dominate below 310°C involve chain scission, appearance of free radicals, elimination of H<sub>2</sub>O, formation of carbonyl, carboxyl and hydroperoxide groups, evolution of CO<sub>2</sub> and CO and production of a charred residue. The dominant pathway at temperatures above 310°C results in the production of tars containing levoglucosan, other anhydroglucose compounds and glucose decomposition products, but very little char or gases. Interestingly, the combination of heat and moisture produces different results than dry heat alone. Heating in steam or at a relative humidity of 95% is reported to reduce the activation energy for degradation to half the value for dry heat, as well as increasing the reaction rate (16, 45).

## 2.3 Differences between conventional and superheated steam drying

The most apparent differences between conventional and superheated steam drying

will now be discussed with reference to the factors noted above: rate of drying, drying restraint, temperature, and nature of drying medium. The interaction of these factors, many of which are a function of drying time, and effects of sheet moisture content are considered. The complete drying history of the sheet is important in determining the final physical, chemical and optical properties of the dried paper.

### 2.3.1 Drying rate and sheet restraint

Above a temperature known as the inversion temperature, drying proceeds more quickly in superheated steam than in air (8-10). The drying rate of superheated steam drying depends on a variety of factors, especially the dryer design used to implement the process, but will probably exceed those of conduction-based conventional dryers notorious for their low heat transfer rates. Evidently desirable from a process engineering point of view, the higher drying rates in superheated steam may also be desirable from a materials engineering point of view. Assuming other factors (e.g. sheet restraint, temperature, etc.) to remain constant, higher drying rates lead to higher drying stresses which in turn result in higher elastic modulus and strength properties (36).

Sheet restraint is determined by dryer design. The conventional long series of cylinder dryers which alternately heat each side of the wet web provide strong sheet restraint in the machine direction but little restraint in the cross-machine direction. This results in an anisotropic sheet with properties differing in the machine and cross-machine directions. If superheated steam drying were implemented on a Yankee type dryer with

the impinging jets being steam instead of air, the sheet might be entirely dried on a few large cylinders and would be more restrained in the cross-machine direction than in conventional drying. This should result in a more uniform sheet with better strength properties and dimensional stability.

Although drying rate and sheet restraint may be different for superheated steam drying as compared to conventional drying, the above differences are largely due to different dryer design. The next two factors considered, sheet temperature and the nature of the drying medium, are fundamentally different for air and steam drying regardless of the dryer design used.

#### **2.3.2** Sheet temperature

In conventional cylinder drying the web is warmed to a temperature typically around 60°C for the constant rate drying period (17) and 85°C for the falling rate period. In superheated steam drying, regardless of the steam temperature the web very quickly reaches the saturation temperature of the steam which, assuming an atmospheric pressure dryer, is 100°C. Sheet temperature, maintained at this level throughout the constant rate drying period, rises above 100°C in the falling rate period to some temperature intermediate between 100°C and the steam temperature. The constant rate period may be longer for drying in steam than in air. Superheated steam drying thus has the unusual characteristic of the sheet being at a high temperature, 100°C, while at a high moisture content, a temperature impossible to achieve for drying in an air environment.

A high sheet temperature while at high moisture content is important from the point of view of thermal softening of the polymers since at high moisture content the polymer glass transition temperatures are at their lowest values (37). Sheet temperature also affects sheet drying stress (36). Although the higher drying rates of superheated steam drying will increase the drying stress, this will be counteracted by the higher sheet temperature which will tend to lower the drying stress.

### 2.3.3 Nature of drying medium

There are numerous significant differences between air and steam as a drying medium. Some differences, although important for the drying process, have little or no effect on the dried product quality and are not discussed here. The absence of oxygen in a steam dryer, besides reducing explosion and fire hazards, can eliminate oxidation reactions, known to reduce the degree of polymerization and to lower the fibre strength.

As noted earlier, the combination of high temperature and humidity increases thermal degradation relative to just high temperature alone, by lowering the activation energy and increasing the degradation reaction rate (16, 45). The combination of high temperature and oxygen in air drying may benefit from a lower humidity but is subject to the combination of oxidation and hydrolysis. Also, the pure steam environment of superheated steam drying may relax the drying stress achieved during drying. Finally, the equilibrium moisture content of paper in air and steam may be different, possibly making it more difficult to dry to low moisture contents in steam than in air.

### 2.4 Previous drying studies

## 2.4.1 Superheated steam drying of paper

Only two previous exploratory studies have been published on the effect of superheated steam drying on paper properties. In the first, by Cui et al. (46), a static dryer which combined hot surface drying at approximately 100°C and impinging jets of superheated steam at 250°C was used to dry fully restrained handsheets made from a variety of furnishes. For comparison, the handsheets were also dried by hot surface contact alone and by CPPA Standard C.4 drying (sheets clamped between rings and air dried at room temperature). The furnishes used were newsprint repulping pulp, softwood TMP, softwood CTMP, hardwood NSSC pulp (74.5% yield), softwood kraft pulp (62.8% yield) and softwood kraft pulp (46.7% yield). The properties measured on the dried handsheets of basis weight 120 - 200 g/m<sup>2</sup> were bulk, burst index, breaking length, toughness index and tear index. Except for the bulk, these properties all measure different aspects of the physical strength of the handsheets.

For all but the kraft pulps it was found that, relative to the comparison air drying, superheated steam drying increased the burst index, breaking length and toughness index by up to 17% but decreased the tear index only marginally. No significant differences were observed for sheet bulk. For kraft pulp (the only wood-free pulp), superheated steam drying to a final moisture content of 22.5% (no details are given as to completion of the drying) gave physical strength properties the same as for hot surface drying, except for a slightly lowered tear index. However, if the handsheets were superheated

steam dried to 10% moisture or less, the physical strength properties were all lowered by approximately 5%.

Cui et al. (46) proposed that the improved strength properties are due to two factors: improved bond strength and increased bonded area. They suggest that the improvement in bond strength is due to the formation of covalent cross-links which occur because of the higher web temperature. This could have been verified by the measurement of sheet wet strength, which should be improved by cross-linking. The increase in bonded area was attributed to the improved conformability of the stiff high-yield fibres under the elevated temperatures of superheated steam drying. Presumably no such beneficial effect occurs for the low-yield kraft pulp which is already quite flexible. No explanations are offered as to the reason for the reported deterioration of the kraft sheet properties upon full drying in superheated steam.

The second superheated steam drying study, that of David et al. (11), used the drying equipment from the first study with some modifications. TMP and kraft pulp handsheets, dried fully restrained using a combination of hot (100°C) surface drying and impinging jets of superheated steam, were compared to handsheets dried similarly except with jets of air. Drying medium temperatures ranged from 220 - 430°C. Comparison sheets were also dried according to CPPA Standard C.4. The properties measured on the dried handsheets were: bulk, burst index, tear index, zero-span breaking length, and brightness. The effect of impingement jet velocity in the range 40 - 100 m/s was investigated and found to have no effect on properties of the dried sheet.

Some of the results of David et al. (11) do not agree with those of Cui et al. (46). Unlike the first study, David et al. found that paper from kraft pulp as well TMP had a higher burst index by 10 - 15% in steam drying compared to air drying. This was suggested to be due to better bonding between stronger fibres. Tear index remained approximately the same for TMP and kraft sheets, whether dried in steam or air.

Zero-span breaking length is a rough approximation of individual fibre strength. For both pulps, zero-span breaking length was higher in steam drying than in air drying, and increased slightly with increasing steam drying temperature but decreased slightly with increasing air drying temperature. The lower fibre strength obtained in air drying was attributed to progressive oxidative degradation which increased with increased air drying temperature. The absence of this degradation in steam drying was attributed to the nonoxidizing nature of steam, but this does not explain the reported increase in zero-span strength. A possible explanation might be the fact that zero-span breaking length is not entirely independent of the degree of bonding. The small increases in zero-span fibre length observed in steam drying may thus have been due to increased bonding rather than increased fibre strength. The redistribution of resinous material within the fibre was also suggested.

Sheet bulk was higher in steam drying than in air drying for both TMP and kraft, but in different temperature regions. For TMP, the bulk was the same in steam or air except in the higher temperature region, while for kraft the increase occurred in the lower temperature region. This behavior found by David et al. (11) is unlike the previous study, and was explained as possibly due to shorter drying time, higher water vapor evolution from the sheet and earlier onset of fibre bonding.

Sheet brightness is an optical property measuring the ability of the sheet to reflect blue light. The capacity of paper to reflect light is a function of its specific scattering coefficient and specific absorption coefficient. Reductions in brightness may be due to increases in bonded area and/or color changes. Although David et al. (11) claim that there are no brightness differences, careful examination of their data reveals a 5 point brightness loss for the steam dried TMP sheets compared to the air dried ones. David et al. (11) note no apparent difference in brightness for the kraft sheets but the data is very limited.

An interesting finding reported by David et al. (11) was that overdrying the sheets in steam produced different results than overdrying in air. Both TMP and kraft sheet zero-span breaking length remained unaffected in steam overdrying but were severely decreased in air overdrying. Similar results were obtained for brightness.

These two preliminary studies clearly indicate that superheated steam drying affects paper properties, and that more work is needed to quantify these effects as well as determine their cause. Other studies of superheated steam drying of paper (5, 7, 12, 47-52) deal with the design and modelling of the dryer rather than the paper properties. As well, a number of patents describe superheated steam paper dryer designs and processes (53-58).

### 2.4.2 Superheated steam drying of wood products other than paper

Superheated steam drying is used industrially to dry a number of wood products other than paper. Steam drying of market pulp has been used since 1978 at the Rockhammers Bruk CTMP mill in Sweden (59). The process uses steam as the transport process to carry wet pulp through a series of tubular heat exchangers, with high pressure steam is used as the heating medium on the shell side of the heat-exchange column. Energy input into the dryer is 10% lower than for an equivalent flash dryer, and 80% of this energy is recovered in a useful form. The net heat consumption for pulp drying is reduced by 75%. The same drying economy achieved in steam drying of pulp was also obtained for drying hog fuel (bark) in pilot and full scale tests (60).

The dried pulp is said to be of high quality with only minor changes in freeness, brightness and sheet strength properties. The pulp comes into contact with steam at 0.2 - 0.5 MPa and approximately 13°C of superheat. It is claimed that overdrying is impossible because under these conditions the equilibrium moisture content in superheated steam is 7 - 10%. Also, because the pulp comes into contact with a pure steam environment, it cannot be contaminated with soot or sulphur or be oxidized by air.

Numerous types of superheated steam kilns for the drying of wood (lumber) have been available since 1908 (61). Wood veneer is also sometimes steam dried. Advantages claimed are faster drying rates and, by control of the pressure and temperature of the steam, the ability of the process to maintain higher equilibrium moisture contents than in air drying. Overdrying of the wood surface is prevented while the interior is still wet, eliminating steep moisture gradients which result in large internal drying stresses and cause defects in the dried lumber (62).

Although capable, under certain conditions, of maintaining high moisture contents desirable for drying some products, materials can also be steam dried to essentially zero moisture contents provided the degree of superheat is sufficiently high. In a study of steam drying of wood particles for making particle board the required extremely low moisture content of 2% or less was achieved with a superheat of 40°C (63). Also, the strength properties of the board were improved and the net heat consumption reduced.

### 2.4.3 Press and impulse drying studies

Studies of press and impulse drying of paper and board, although quite different from superheated stearn drying of paper, still present certain similarities and can provide useful insights. Most of the studies are performed on static laboratory or dynamic pilot scale equipment, as these two processes are not widely used industrially.

In both press and impulse drying, the moist paper web is supported by a felt and passed through a high pressure nip with one very high temperature surface. Impulse drying uses more intense conditions than press drying, with typical temperatures, pressures and nip residence times of 150 - 500°C, 0.3 - 7 MPa and 15 - 100 milliseconds. Nip residence times are usually longer in press drying. Under these intense conditions the sheet temperature rapidly reaches 100°C or more as the water in the sheet next to the hot surface is vaporized. Especially in impulse drying, the vapor

pressure builds up in the sheet and vapor escapes through the felt side, mechanically displacing water still in liquid form, resulting in drying rates up to 1,000 times faster than conventional drying and using less than half the energy (64).

Press/impulse drying typically results in a well bonded, highly densified sheet with improved strength properties. Small losses in optical properties and tear strength accompany these improvements (64, 65). The disadvantages of the process, especially with impulse drying, are that some combinations of basis weights, freeness and operating conditions produce severe detrimental effects such as sheet delamination and blistering (66 - 68). Apparently this occurs when the mechanical pressure is relieved too quickly, leaving behind a high vapor pressure in the web which blows the sheet apart as it escapes unrestrained. As well, impulse drying cannot be used to completely dry the sheet since the exiting solids content rarely exceeds 80%.

The most striking similarity between press/impulse drying and superheated steam drying is that, unlike conventional drying, the sheet rapidly reaches a temperature of 100°C or higher in a steam environment while still at a high moisture content. As previously discussed, this is of importance with respect to the thermal softening of the polymers. A major difference between press/impulse drying and superheated steam drying is of course the application of intense pressure while the polymers are in a softened state.

In press/impulse drying studies, the improvements in sheet strength properties are generally attributed to the increased densification at high temperature and pressure. This is unlike the strength improvements in superheated steam drying which are not accompanied by decreased bulk (increased density). The benefits for press/impulse drying are far more significant for mechanical and certain hardwood pulps whose stiff unconformable fibres normally bond together poorly. This distinction is apparent from the first study of the properties of superheated steam dried paper, Cui et al. (46). Sheet wet strength for press/impulse drying is also improved, which is thought to be due to cross-linking or flow of certain polymers creating a sizing effect. Wet strength has not yet been measured for steam dried paper.

## 2.5 Summary and conclusions

Superheated steam drying provides conditions sufficiently different from those in conventional drying to change the properties of the dried paper. Differences in sheet temperature and nature of the drying medium may affect many of the chemical and physical processes which can occur in drying: polymer softening and flow, extent and nature of bonding, cross-linking, drying stress, hydrolysis, oxidation, thermal degradation, changes in crystallinity or polymorphy.

For the few sheet properties measured in the exploratory studies, the differences in sheet properties are mostly favorable. More work is now required to obtain a full set of chemical, physical and optical properties of superheated steam dried paper made from a variety of furnishes and dried under a variety of conditions. As well, a fundamental understanding is needed of the chemical and physical processes occurring during steam drying which lead to the different dry sheet properties, so that optimal conditions maximizing beneficial effects and minimizing detrimental ones may be determined.

#### CHAPTER 3

## EXPERIMENTAL EQUIPMENT AND PROCEDURES

### 3.1 Drying apparatus

Primary considerations in design of the drying apparatus were to minimize uncontrolled variables and to provide the needed information in the easiest, most convenient manner. Equipment was required for drying sheets with air or superheated steam at temperatures to 400°C with no leakage of the drying fluid. A provision for pressing the sheet during drying was desired in order to investigate this combination of effects. Monitoring of sheet moisture content and temperature during drying was required. Finally, the experimental facility was to be computer controlled and have a computerized data acquisition system.

Since the objective of the study was to determine the effects of superheated steam drying on paper properties, effects due to other types of drying, in particular conduction drying, were eliminated. The sheet was therefore not supported by any hot surface which would have interfered with or diluted the effects of superheated steam drying and resulted in two sidedness of the sheet; it was therefore suspended in a flow of pure superheated steam.

### 3.1.1 Drying chamber and sliding frame

The drying apparatus which was designed and built is shown as a schematic in figure 3.1, while figure 3.2 shows a photograph. The drying chamber is an insulated rectangular stainless steel box, 33 cm high, 41 cm wide, 20 cm deep, of wall thickness 1.3 cm. The top of the chamber was bolted to a 2.5 cm flange with all other sides welded. Electrical heating tapes were wrapped around the drying chamber underneath the insulation to aid with heat-up and temperature control.

A square sliding frame assembly activated by a computer controlled pneumatic cylinder could be inserted vertically into and withdrawn from a rectangular opening in the top of the drying chamber. This frame carried the paper sample which, when attached to a rigid rod suspended from a load cell mounted at the top of the sliding frame, was centered within the 25 cm square sliding frame. The size of the rectangular slot in the drying chamber top was just sufficient to permit passage of the sliding frame but was smaller than the rectangular plates mounted at the top and bottom of the square frame. The pneumatic cylinder had a 3.8 cm bore, a stroke of 33 cm and a 0.62 MPa air supply. Insertion and retraction were completed in approximately 2 seconds.

The drying chamber was completely sealed when the sliding frame was in the fully inserted or retracted positions. Fully inserted, sealing was provided by contact between the rectangular plate attached to the top of the sliding frame assembly and a 6.4 mm diameter silicon tube wedged into a groove machined around the edge of the rectangular opening on the top of the drying chamber. Fully retracted, sealing was by contact



Figure 3.1: Schematic of drying apparatus



Figure 3.2: Photograph of drying apparatus

between the underside of the drying chamber top and a 6.4 mm diameter silicon tube wedged into a groove around the edge of the top side of the rectangular plate attached to the bottom of the sliding frame assembly.

### 3.1.2 Solids content measurement

Paper solids content throughout drying was required as a key element of the drying history of each sheet. A continuous record was obtained through use of a Schaevitz Gram Range Force Transducer (Model FTD-G-50 DC Unit) to monitor the mass of the paper and holder during drying. Schematics of external and internal views of the Schaevitz load cell are shown in figures 3.3a and 3.3b.

The load cell has a range of  $\pm 50$  grams, a linearity better than 0.2% and a repeatability better than 0.1% full range. A load cell with a small capacity was purposely chosen so that the measurement error would be small relative to the changes in mass to be monitored. As the operating temperature range for this load cell is 25°F to 200°F (-4°C to 93°C) it had to remain outside the drying chamber, away from the hot drying medium.

The load cell contains an LVDT (Linear Variable Differential Transformer) coupled to two elastic elements. Loading of these elastic elements results in a small linear deflection of the LVDT magnetic core, producing a signal directly proportional to axial load. High accuracy, reduced sensitivity to side loading and appreciable overload capacity are important features of this type of load cell.



Figure 3.3a: External view of load cell



Figure 3.3b: Internal view of load cell

Another feature of this load cell is a mechanical zero adjust which can be used to tare out large pre-loads. As well, an electronic zero was built into the load cell signal conditioning box for a finer adjustment yet. This feature was used to tare out the mass of the paper holder and supporting rod, approximately 37 grams. For increased sensitivity, the signal generated by the load cell due to the small mass of the sheet, approximately 3 grams or less upon insertion and around 1 gram upon retraction, was then amplified by a factor of 20 prior to the data acquisition system.

The paper and its holder could evidently not come into physical contact with any part of the drying equipment. A 22 cm long, 1.6 mm diameter stainless steel rod was passed through the axial tube in the center of the load cell, with the ends of this rod threaded at the top and hooked at the bottom. A small retaining nut of diameter larger than the tube diameter was screwed to the threaded end; the rod thus became suspended from the top of the load cell. The paper holder was attached to the hook at the lower end of this rod.

The supporting rod holding the paper holder passed through a 6.4 mm diameter opening in the upper part of the sliding frame. The sheet was thus freely supported by the load cell and could in fact swing somewhat without the rod or sample holder touching anything. A photograph showing the load cell and suspended paper is shown in figure 3.4.

When the sliding frame was inserted, the 6.4 mm diameter opening in the upper part of the frame through which the rod passed created a problem; the hot drying fluid



Figure 3.4: Photograph of load cell with suspended paper

escaped, contacting the temperature sensitive load cell. To protect the load cell it was made air tight with silicone. The top of the load cell was sealed by a metal cap screwed to the threaded upper end of the load cell. A teflon union attached to a metal base with two nipples was placed between the load cell and the top of the sliding frame, serving two purposes. First, cooling fluid at a pressure just slightly greater than that of the drying chamber was passed through the two nipples, thus preventing the hot drying fluid from entering the load cell. (For air drying experiments, the cooling fluid was air, while for steam drying experiments, helium was used). Second, the teflon union minimized thermal conduction from the chamber to the load cell.

For the sliding frame the rapid insertion time of approximately 2 seconds caused the spring-like elastic elements of the load cell to oscillate wildly immediately after insertion and to continue vibrating for about 30 seconds, obscuring the sample mass signal. Since in some cases the drying time itself was less than 30 seconds, a solution to this problem was developed.

A rubber bladder was inserted into the metal cap screwed to the top of the load cell. A 6.4 mm hole was drilled into the top of the cap through which was inserted one end of a 6.4 mm flexible tube. The other end was connected to a hypodermic syringe with the needle removed. To eliminate the vibrations, the air bladder was filled with approximately 5-7 cm<sup>3</sup> of air at half way through the 2 second insertion period. This caused the air bladder to inflate and touch the spring-like elastic element of the load cell, preventing it from bouncing. At 1 second after insertion was completed, the air was slowly withdrawn from the bladder by pulling back on the plunger of the syringe. The entire vibration damping period was thereby reduced from 30 seconds to an acceptable 5 seconds.

#### 3.1.3 Temperature measurement

As shown in figure 3.1, three 1.6 mm diameter stainless steel type K thermocouples with exposed junctions were used, two on the sliding frame and one at the top of the drying chamber. The two sliding frame thermocouples were located immediately upstream and immediately downstream of the paper. A 3.2 mm stainless steel type K thermocouple was placed at the base of the superheater to measure the temperature of the exiting gas.

For occasional monitoring of sheet temperature, the downstream thermocouple in the square frame was removed and replaced by a thermocouple plug. A bare wire thermocouple was embedded in the wet paper, as detailed in section 3.2.2, then connected to this plug.

## 3.1.4 Press-drying apparatus

An arrangement capable of pressing the paper at up to approximately 1 MPa while drying in steam or air, figure 3.5, was designed and built. A 15 cm bore pneumatic cylinder was connected to the 0.62 MPa air supply for this purpose. A hole through which the cylinder shaft could pass was drilled in the center of the front wall of the



Figure 3.5: Schematic side view of press-drying arrangement

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drying chamber. A 6.4 mm thick, 13 cm diameter polished stainless steel pressing plate was fixed to the end of this shaft. Four triangular fillets joining the plate to the shaft were used to distribute evenly the pressing force over the surface of the pressing plate. To prevent leakage of drying fluid from the hole in the front wall, the pneumatic cylinder shaft passed through a flexible sealing sleeve attached at one end to the shaft and at the other end to a bushing welded to the wall.

For pressing experiments, a slightly different sliding frame for the paper was installed to provide the additional function of supporting it during pressing. To achieve this function a 6.4 mm thick, 13 cm diameter backing plate was mounted on a ball bearing in the center of a 1.3 cm thick, 18 cm x 30 cm steel plate held by the two side arms of the sliding frame. The ball bearing provided perfect alignment of the pressing and backing plates. The paper holder was held in place over the backing plate by pins embedded in the steel plate. When press drying experiments were conducted the load cell could no longer be used to monitor sheet solids content.

A pressing arrangement similar to that in the press-drying work of Seth, Michell and Page (69) was used. This method is claimed to provide press-dried sheets of similar internal structure and surface texture as those prepared and dried according to standards established by the Canadian Pulp and Paper Association (CPPA), allowing for meaningful comparison between the properties. Thus the paper was pressed by the polished steel plate and backed by a blotter and a sintered metal-fibre filter sheet (Bekipor ST 60 AL3) fixed to the backing plate. The sintered filter sheet permitted the escape of moisture during press-drying.

#### 3.1.5 Superheated steam and hot air supply

Figure 3.6 shows the piping and ancillary equipment and table 3-1 describes the function of the numbered valves in figure 3.6. The major components include an electrical superheater to heat the steam or air, and a condenser for the drying chamber exhaust. Cold water was sprayed into the condenser which was open to the atmosphere. A safety relief valve in the piping just upstream of the superheater vented into the condenser. The figure 3.7 photograph shows the drying apparatus and piping.

The shop air or steam supply was throttled from 0.62 MPa to 0.21 Mpa prior to the superheater. The drying fluid was piped to the side of the drying chamber where it flowed through an expansion section and a honeycomb flow stabilizer. The drying medium flowed parallel to the paper and exhausted from the opposite side into the condenser. A 3 cm wide slit was made in each of the 5 cm wide side arms of the sliding frame to minimize flow obstruction past the suspended sheet.

## 3.1.6 Control and data acquisition systems

An IBM PC clone and a Data Translation DT2801A board located in an expansion slot of the PC were used for control and data acquisition. The DT2801A is a multifunction analog and digital I/O board with 16SE/8DI channels for analog inputs of



Figure 3.6: Schematic diagram of drying apparatus piping system
12 bit A/D resolution, 2 channels for analog outputs also at a resolution of 12 bits, and 16 digital I/O channels. A Data Translation DT707 screw terminal panel, providing

## Table 3-1

## Valves for drying apparatus

VALVE	DESCRIPTION					
1	Needle valve for another drying apparatus					
2	Ball valve for steam or hot air from superheater					
3	Ball valve for drain					
4	Needle valve for steam or hot air flow					
5	Needle valve for water flow to condenser					
6	Ball valve for steam or hot air exhaust to condenser					
7	Needle valve for cooling air to load cell					
8	Ball valve for air to pneumatic cylinder of press					
9	Solenoid valve for pneumatic cylinder for sample insertion and retrac- tion					
10	Solenoid valve for pneumatic cylinder for press					
11	Ball valve for air flow other than to superheater					
12	Needle valve for air supply					
13	Ball valve for air flow to superheater					
14	Needle valve for water supply					
15	Ball valve for water line					
16	Needle valve for steam supply					
17	Ball valve for steam flow to superheater					
18	Pressure controller					
19	Pressure relief valve					



Figure 3.7: Photograph of drying apparatus and ancillary equipment

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convenient connection points for all signals, was connected by a 50 wire ribbon cable to the DT2801A board.

Signal conditioning boxes were used to amplify thermocouple and load cell signals prior to the DT 707 board. Thermocouple signals were amplified by Analog Devices AD 595 chips. These chips combine an ice point reference with a pre-calibrated amplifier to produce a high level ( $10 \text{ mV/}^{\circ}$ C) output directly from a K type thermocouple signal.

With an excitation source of  $\pm 15V$  DC, the load cell produces a maximum signal of  $\pm 5V$  DC for a  $\pm 50$  gram load. Calibration tests agreed with the factory calibration of 0.101V/g. The load cell signal was amplified by a factor of 20 by the signal conditioning box so that a 5 gram mass (corresponding to a 0.5V signal) resulted in a 10V signal (the saturation voltage) to the data acquisition board. The sensitivity of the data acquisition board for the load cell signal was 0.0012 g/bit. A relay box was used to convert the low voltage output signals from the computer into higher voltages for control of the solenoid valves used to activate the pneumatic cylinders and for control of the superheater.

A QuickBasic program using many of the Data Translation PCLab subroutines was written for data acquisition and control of the experimental facility. A simple on/off control was used for the superheater and found to be adequate for temperature control of the drying fluid. Data from the thermocouples, load cell and system clock could be saved onto diskette at the end of a drying experiment. Several safety features were incorporated into the program. Emergency shut down of the experimental facility was initiated automatically by the computer if specified maximum safe temperatures in the superheater or drying chamber were exceeded. At any time during heat up or an experiment, the sliding frame could be inserted or withdrawn from the chamber by typing certain keystrokes. A switch located near the keyboard could be used to shut off electricity to the superheater instantaneously, or to select manual or automatic (computer) control of the superheater. At all times during heat up or experiments, real time temperature and mass readings were displayed on the computer screen. Temperature set points could be changed at any time from the keyboard.

## 3.2 Experimental procedures

#### 3.2.1 Handsheet preparation

The equipment used for preparation of moist paper samples is described in CPPA Standard Testing Method C.4, "Forming Handsheets for Physical Tests of Pulp". A British Disintegrator was used to prepare the pulp suspension and a British Handsheet Machine to form the suspension into 15.9 cm (6.25 inch) diameter isotropic sheets. A manual press equipped with a pressure gauge was used to press the sheets. All pulps were stored 5°C. Moist sheets were made in batches of 20. The target basis weight was 60 g/m<sup>2</sup>, a standard in paper research.

One minor modification in sheet pressing procedure was introduced. By the standard method, the moist sheet is sandwiched between a blotter and a polished stainless steel plate. A stack of these sandwiches is then pressed, usually resulting in a solids content of about 40% - 50%. The moist sheet does not adhere to the blotter but adheres strongly to the polished stainless steel plate; it cannot be separated from the metal plate without destroying it. To solve this problem, teflon plates were substituted for the polished stainless steel plates in the pressing procedure. The teflon plates of the same diameter as the metal plates were highly polished. After pressing, the moist sheets could easily be separated from the teflon plates. The wet sheets were stored in a zip-lock plastic bag, separated from each other by polyethylene plastic sheets. Samples, stored at 5°C, were equilibrated to room temperature prior to drying.

## 3.2.2 Measurement of sheet temperature

While paper solids content was always monitored during drying, the paper temperature record was obtained only for two drying conditions. Initially the procedure used was to make standard moist sheets except of basis weights  $30 \text{ g/m}^2$  rather than  $60 \text{ g/m}^2$ . A 0.076 mm diameter bare wire thermocouple was placed between two such sheets and the assembly was lightly pressed prior to drying. This procedure gave unsatisfactory results because the two sheets, although pressed well moist, did not bond and in fact were often separated during drying by air or vapor bubbles. The thermocouple thus measured the temperature of the gas between the sheets rather than sheet temperature.

An improved procedure was developed to truly bond the sheets and thermocouple together. A 30 g/m<sup>2</sup> sheet was prepared, couched from the British Sheet Machine wire in the usual manner and left on the blotter. A second 30 g/m<sup>2</sup> sheet was then formed but left on the forming wire. The thermocouple was then gently laid on the surface of this sheet, and the first sheet (still adhering to the blotter) was placed, precisely centered, on top of the thermocouple. This whole assembly was then couched in the usual manner and removed from the British Sheet Machine wire. The resulting dried sheet was so well bonded that it was impossible to delaminate.

## 3.2.3 Drying equipment startup

To prepare the equipment for an experiment the desired drying temperature was entered into the computerized control program, the load cell and data acquisition systems were turned on, air flow for pneumatic cylinders, load cell cooling and drying was started, as was the cooling water flow for the condenser. The square frame was inserted into the drying chamber and the electrical heating tapes and superheater turned on. Air was passed through the superheater and drying chamber until the latter reached the desired temperature, as measured by the three thermocouples in the chamber. Depending on the target temperature, this warm-up period took 0.5 to 2 hours. For steam drying experiments, air was used to preheat the drying chamber well above 100°C to prevent subsequent condensation.

The flowrate of air or steam to the drying chamber was adjusted by means of a needle valve located downstream of the superheater. As the drying study by David (11) showed that air or steam flowrate had no effect on paper properties, the needle valve was kept open two full turns for all experiments. This setting was chosen as a reasonable compromise between rapidity of drying and noisiness of load cell signal; higher flowrates caused excessive sheet flutter, resulting in too noisy a signal from the load cell.

By a dry test meter calibration, 2 full turns open was found to correspond to a flowrate of 0.59 m<sup>3</sup>/min for air at 235°C and 0.76 m<sup>3</sup>/min for steam at the same temperature. These conditions would correspond to a mean superficial velocity in the chamber of 0.18 m/s for air and 0.23 m/s for steam, and Reynolds numbers of 834 for air and 1019 for steam if the chamber depth is taken as the characteristic diameter.

## 3.2.4 Paper drying

Considerations of accuracy in monitoring the weight of the moist paper sample during drying and the low capacity of the load cell made it necessary to minimize the mass of the paper holder. This holder consisted of two concentric aluminum rings of 3.2 mm square cross-section, designed to clamp only the outer 3.2 mm edge of the paper. All sheets were dried fully restrained between these two aluminum rings, as illustrated in figure 3.8. To clamp the sheet between the rings, the moist sheet was placed on a teflon baseplate onto which had previously been placed the inner ring of diameter 6.4 mm smaller than the sheet diameter of 159 mm. The outer ring was then placed on top



Figure 3.8: Paper holder: teflon baseplate and aluminum rings

of the sheet and pressed downwards until it clamped onto the inner ring, firmly catching the outer 3.2 mm edge of the sheet between the two rings in the process. The clamped sheet on the teflon baseplate was then covered with a teflon plate to prevent moisture loss prior to drying. In some experiments this assembly was weighed prior to and after drying in order to determine the solids content of the sheet prior to drying.

The wet sheet in the holder was removed from the teflon baseplate and attached to the hook on the rod suspended from the load cell. The sliding frame assembly was inserted into the drying chamber and the experiment commenced. The criterion used in most cases for terminating the experiment and removing the dried sample from the chamber was that the paper had reached a constant mass as indicated by the load cell, i.e. no more moisture was being removed from the sample. This corresponded to a sheet moisture content of 0 - 2%, as determined from the oven dry mass. In other cases, the sample was purposely removed before or after reaching this constant mass, resulting in underdrying or over drying.

Even though the signal for instantaneous sheet mass obtained from the load cell was visible on the computer screen during the drying experiment, it fluctuated too much to determine by eye when the sheet had reached a constant mass. Therefore several test drying runs were performed where sheets of constant basis weight and moisture content were dried much longer than necessary. The sample mass data from these test experiments were saved on disk. The graphs of sheet mass versus time were generated using a spreadsheet program, from which an appropriate drying time was determined.

An example of the type of curve generated is shown in figure 3.9. The raw data was smoothed using a Fast Fourier Transform technique described by Aubanel and Oldham (70). From the figure 3.9 curve for a TMP sheet in 160°C steam, a drying time of approximately 160 seconds is indicated. The mass versus time curves for other drying conditions can be found in Appendix I.



Figure 3.9: Effect of drying time on sheet mass for TMP sheet in 160°C steam

#### 3.2.5 Paper testing

In order to obtain enough paper for all the property tests, 20 sheets were normally dried for each set of conditions. The dried sheets were immediately removed from the restraining rings and placed into a dessicator to prevent changes in moisture content. Some of the samples were equilibrated for 24 hours prior to testing in the McGill constant temperature and humidity room maintained at 23  $\pm 1^{\circ}$ C and 50  $\pm 2\%$  relative humidity, as specified in CPPA Standard Testing Method A.4. The remainder were sent to the Paprican Pointe-Claire laboratory for tests not available at the McGill laboratory.

The sheets were tested for a variety of physical, chemical and optical properties using instruments and procedures described in the following CPPA or TAPPI Standard Testing Methods (the latter identified by the T preceding the standard number):

- D.4 ..... Thickness and Density of Paperboard
- D.8 ..... The Bursting Strength of Paper
- D.9 ..... Internal Tearing Resistance of Paper, Paperboard and Pulp Handsheets
- D.10 ..... Wet Tensile Breaking Strength of Paper and Paperboard
- D.14 ...... Air Resistance of Paper (Gurley Resistance)
- D.17P..... Folding Endurance of Paper (MIT)
- D.34 ..... Tensile Breaking Properties of Paper and Paperboard
- E.1 .....Brightness of Pulp, Paper and Paperboard
- E.2 .....Opacity of Paper
- F.4 .....Absorption of Water and Ink by Bibulous and Blotting Paper

G.6, G.7 ..... One Per Cent Caustic Soda Solubility of Wood and Pulp

G.25P .....pH of Paper Extracts

T230 om-82 .. Viscosity of Pulp - Capillary Viscometer Method

T412 om-90 .. Moisture in Paper and Paperboard

T453 pm-85 .. Effect of Dry Heat on Properties of Paper

T541 om-89 .. Internal Bond Strength of Paperboard (z-direction tensile)

Other instruments were used to perform the following tests which are not described by CPPA or TAPPI Standard Testing Methods:

> Zero-Span Breaking Length of Pulp (Pulmac Tester) Wet Zero-Span Breaking Length of Pulp (Pulmac Tester) Parker Print Surf Roughness Ultrasonic Measurement of Elastic Modulus Crystallinity by X-ray Diffraction Crystallinity by <sup>13</sup>C MAS NMR Spectroscopy Observation by Scanning Electron Microscopy

In all of these Standard Testing methods, recommendations are made as to the number of measurements, frequently 10, required in order to obtain reliable average values. CPPA Standard Method D.12, "Physical Testing of Pulp Handsheets" shows a convenient method of dividing handsheets in an optimal way.

## 3.3 Experimental plan

The minimum objectives of the study were to:

- Determine a complete set of physical and optical properties of paper from mechanical and kraft pulps, dried in superheated steam and in air at temperatures ranging from 100°C to 400°C.
- 2. Explain the observed physical and optical properties of the dry paper in terms of sheet structure and the physical and chemical processes occurring during drying.

In previous studies, drying conditions were less well controlled and fewer physical and optical properties of superheated steam dried sheets were measured. The explanations suggested for some of the observed differences were speculative and lacked firm experimental evidence.

The optimum objectives included as well to:

- Determine the solids content and sheet temperature as a function of time during drying.
- 4. Investigate the effect on sheet properties of pressing at various stages of drying.
- 5. Determine the effect of steam drying and various degrees of sheet restraint on sheet dimensional stability.

Objectives 1 to 4 were accomplished. Objective 5 became the topic of a separate Master's thesis study.

#### 3.3.1 Pulps

The effect of superheated steam drying was investigated for both mechanical and chemical pulps, made in all cases from black spruce. All pulps were never-dried. Table 3-2 lists the pulps investigated along with their Canadian Standard Freenesses determined according to CPPA Standard Testing Method C.1. Canadian Standard Freeness, CSF, is an indication of the amount of mechanical treatment given to the pulp, which has a significant effect on the final paper properties. In addition, for the chemical pulps the yield (ratio of mass of pulp produced to mass of chips pulped) and Kappa number (indication of degree of delignification as measured by CPPA Standard Testing Method G.18) are also listed.

The TMP was obtained from the Donohue Normick mill in Amos, Quebec. The 5 kg O.D. sample was taken from the disc filter segments prior to any sulfifte or hydrosulfite addition. EDTA (a sequestering agent) had been added. The RMP, obtained from the Paprican mechanical pilot plant in Pointe Claire, was hot disintegrated and screened before use. The kraft pulp was manufactured in the Paprican chemical pilot plant. The semi-bleached and fully bleached kraft pulps were made from this kraft pulp after subjectinon, respectively, to standard CE (Chlorination / Extraction) and CEDED (Chlorination / Extraction / Dioxidation / Extraction / Dioxidation) bleaching sequences

in the Paprican bleaching laboratory. The 5 beaten kraft pulps were made by treatment for various times in a Valley beater.

## <u>Table 3-2</u>

Pulp Type		CSF (ml)	Yield (%)	Kappa No.
Thermo Mechanical Pulp	(TMP)	164	-	-
Refiner Mechanical Pulp	(RMP)	137	-	-
Kraft Pulp	(KRAFT)	698	48	30
Semi Bleached Kraft Pulp	(SBK)	680	-	5
Fully Bleached Kraft Pulp	(FBK)	704	-	0
Beaten Kraft Pulp 1	(BK1)	665	48	30
Beaten Kraft Pulp 2	(BK2)	648	48	30
Beaten Kraft Pulp 3	(BK3)	582	48	30
Beaten Kraft Pulp 4	(BK4)	485	48	30
Beaten Kraft Pulp 5	(BK5)	372	48	30

## List of pulps used

## 3.3.2 Experimental variables

The variables considered in this study include the following:

Pulp Type Drying Medium (Steam or Air) Drying Medium Temperature (20°C - 320°C) Overdrying Mixed Drying Sequence Pressing

Pulp type was of interest because previous studies indicated that superheated steam drying effects varied with pulp type. TMP and kraft pulp were chosen because of their industrial importance and since they had previously been studied, enabling comparison of results.

It is centrally important to determine the effect of superheated steam drying on TMP, the major component of newsprint, since newsprint represents approximately 50% of Canadian production. Kraft pulp is used for wrapping and bag paper as well as board and other important grades. Bleached kraft grades were included because there is an incentive to study the properties of superheated steam dried tissue paper, which is made from this pulp. The incentive lies with the fact that tissue is dried on Yankee dryers, and one of the easiest ways of implementing superheated steam drying would be to substitute superheated steam for the hot air currently used.

Drying medium temperature was varied since paper is a thermally sensitive product and since previous studies have indicated this to be an important variable. In general the temperatures used were 20°C (for air), 160°C, 240°C and 320°C. Overdrying was investigated since previous work indicated that the paper quality deteriorated in air overdrying but not in steam overdrying. For these experiments, the sheet was left in contact with the drying medium three times longer than the time required to achieve a constant mass.

Mixed drying sequence refers to experiments where the sheet was partially dried at one temperature in one drying fluid, with the remainder of the drying completed in another fluid at another temperature. An example of this would be the partial drying of a sheet in air at some temperature followed by steam drying at another temperature. The application of pressure to the sheet while drying was investigated for the first time in steam drying.

Table 3-3 lists the variables investigated for each pulp type. When no effects were observed, not all variables were investigated for all pulp types. Repeats of several experiments were performed. A factorial design was used to investigate the effect of pressing. Table 3-4 summarizes the experimental runs and number of sheets dried in the study.

# Table 3-3

Pulp Type	Air Drying	Steam Drying	T (°C)	Drying Time	Drying Sequence	Pressing
TMP	x	x	x	x	x	
RMP	x	x	x	·		x
Kraft	x	x	x	x		
SBK	x	x				
FBK	x	x				
BK1-5	x	x				

# List of variables investigated

## <u>Table 3-4</u>

# Summary of experiments

Pulp	Drying Conditions	Sheets per condition	Sheets dried
ТМР	<u>Normal Drying</u> : air @ 20, 160, 240, 320°C steam @ 160, 240, 320°C	20 20	80 60
	<u>Overdrying</u> : air @ 160, 240, 320°C steam @ 160, 240, 320°C	20 20	60 60
	<u>Replicates</u> : air @ 160, 160°C steam @ 160, 160°C	20 20	40 40
	Mixed Drying Sequence: air drying @ 40°C to 54, 64, 73, 87% solids content followed by steam drying @ 160°C	10	40
	steam drying @ 160°C to 48, 52, 73, 85% solids content followed by air drying @ 40°C		80
	<u>Fines Removed</u> : air @ 160°C steam @ 160°C	10 10	10 10
	<u>Recycled</u> : air dried, recycled, dried in air steam dried, recycled, dried in steam steam dried, recycled, dried in air (all drying at 160°C)	10 10 10	10 10 10

RMP	<u>Normal Drying:</u> air @ 20, 130, 300°C steam @ 130, 300°C	12 12	36 24
	Pressing and Drying: air @ 20, 130, 300°C steam @ 130, 300°C	12 12	36 24
KRAFT	<u>Normal Drying</u> : air @ 20, 160, 240, 320°C steam @ 160, 240, 320°C	20 20	80 60
	<u>Overdrying</u> : air @ 160, 240, 320°C steam @ 160, 240, 320°C	20 20	60 60
	<u>Replicates</u> : steam @ 320, 320°C	20	40
SBK	<u>Normal Drying</u> : air @ 320°C steam @ 320°C	20 20	20 20
FBK	<u>Normal Drying</u> : air @ 320°C steam @ 320°C	20 20	20 20
BK1-5	Normal Drying: air @ 280°C steam @ 280°C	20 20	100 100
		TOTAL	1280

#### CHAPTER 4

## PROPERTIES OF PAPER FROM MECHANICAL PULP

The effects of superheated steam drying on the physical, optical and chemical properties of two mechanical pulps, thermomechanical (TMP) and refiner mechanical pulp (RMP), are presented and compared to those obtained with air drying under similar conditions. The effects of fines content, initial and final sheet solids content, combined steam and air drying, recycling, overdrying, and pressing in steam drying are included.

## 4.1 Statistical treatment of data

The statistical treatment described here applies to data presented in Chapter 4 as well as 5. In order to obtain sufficient paper for replicate tests (typically 10) in the determination of any one property, usually 20 handsheets made in one batch were dried at each condition investigated. For all sheet properties, the mean value  $\bar{x}$  and the standard deviation s of the sample of n measurements were calculated according to:

$$\overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{(n-1)}}$$

75

The 95% confidence interval for the mean value of a physical property is:

$$\overline{x} \pm (t) (s/\sqrt{n})$$

where t is the t-value, evaluated at (n-1) degrees of freedom from the Student's tprobability distribution function. Statistical results are included in Appendix II.

The values of 95% confidence interval based on a pooled estimate of standard deviation obtained from the standard deviations of replicate experiments is expressed as a percentage of the mean in Table 4-1. Standard deviations vary greatly according to the physical property but remain approximately constant for any particular property regardless of the conditions used to dry the paper. Thus the size of the confidence interval derives mostly from the repeatability of the test itself, and to a lesser extent from variations between samples. The published repeatability of various tests, listed in the Tappi Standard Testing procedures, is defined as the limit within which agreement may be expected 95% of the time between two test results obtained under well controlled conditions and from the same homogeneous sample of material. These values are reproduced in Table 4-1.

# <u>Table 4-1</u>

# Experimental variability of physical tests

Physical Test	95% confidence	Repeatability
	interval (%)	from Tappi (%)
Bulk	± 2	1
Burst Index	± 4	5
Tear Index	± 3	4
Fold	± 11	6
Tensile Index	± 3	5
Stretch	± 5	9
Tensile Energy Absorption Index	± 8	10-16
Elastic Modulus	± 2	
Wet Tensile Strength	± 10	9
Zero-span Breaking Length	± 3	5
Wet Zero-span Breaking Length	± 3	
Air Resistance	± 16	12
Scott Internal Bond Strength	± 4	6
Brightness	± 0.3	0.3
Opacity	± 0.3	0.6
PPS Roughness	± 1	
CED Viscosity	± 6	4
Solubility in 1% NaOH	± 10	

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The variations arising from differences in individual batches of handsheets and the precision to which experimental conditions could be controlled can be observed from replicate drying experiments performed on separate days. Three replicate experiments were performed for steam drying at 160°C and air drying at 160°C, with complete replication of the tests on the paper thereby obtained. The replicates show that it is not possible to exactly control all experimental variables, but in general the differences in the replicates are smaller than the differences observed between steam and air drying. Experiments were not performed in any particular order with respect to drying conditions investigated.

For most graphs the 95% confidence intervals are not plotted as error bars because overlapping error bars would detract from the clarity of the graphs. The lines through the data points are for visual enhancement; they were drawn by hand rather than from regression analysis because of the limited number of data points and the variety of functional relations possible. In all graphs, the abbreviation "stm" is used for steam.

#### 4.2 Sheet temperature, solids content and drying rate

The conditions experienced by the sheet during drying are critical in determining the dry paper properties. One of the most obvious differences between steam and air drying is the sheet temperature during drying. Thus experiments were performed to obtain the temperature and solids content history of the sheet drying in both steam and air at 160°C. The typical results for steam and air drying, figures 4.1a and 4.1b, show the large

difference in sheet temperature for the two drying fluids. As industrial drying is normally terminated at about 93 - 95% solids content, these laboratory data show extended overdrying to 100% solids content for illustrative purposes. In steam drying (figure 4.1a), the sheet temperature immediately rises to 100°C as required by thermodynamics and achieved by condensation of steam on the sheet which, in the laboratory technique, was at room temperature when inserted into the dryer. After much of the drying is completed, the sheet temperature rises to approach the superheated steam temperature of  $165^{\circ}$ C.

In air drying (figure 4.1b), the sheet warms more slowly by convective heat transfer to reach a temperature of about 52°C, in the vicinity of the wet bulb temperature. As in steam drying, the sheet temperature subsequently increases to approach the drying medium temperature of 175°C. The air dried sheet thus experiences a temperature about 50°C lower than the steam dried sheet during most of the drying cycle.

The solids content versus time curves for steam and air drying are of similar shape. For both steam and air drying, when the sheet is at 95% solids content (a typical target solids content for industrial drying) it has just reached the drying fluid temperature. Also, for the laboratory conditions used, the solids content at which the constant rate period ends and the sheet temperature begins to rise is about the same for steam and air drying, with an average of 75% for steam and 77% for air. (The averages were determined from 7 repeat experiments for each drying fluid).





Figure 4.1: Paper Temperature and Solids Content for (a) Steam Drying at 165°C and (b) Air Drying at 175°C

Figures 4.1a and 4.1b are characteristic of the sheet temperature difference between steam and air drying. In superheated steam drying, regardless of the degree of superheat, the sheet temperature rises immediately to the saturation temperature of steam, as is required by thermodynamics. In air drying, the sheet approaches more slowly the much lower wet bulb temperature, as required by the interplay of rates of convective mass and heat transfer which is dependent on the drying fluid conditions. For adiabatic conditions, and an absence of other heat transfer contributions, the wet bulb temperatures for dry air at 160, 240 and 320°C are about 41, 49, and 55°C respectively, all significantly lower than 100°C.

Although the object of the present study was not to investigate drying rates, the load cell arrangement in the experimental setup provides the data required to do so. Drying rate for the constant rate drying period can be calculated from the slope of the steadily decreasing linear portion of the sample mass versus drying time curves obtained from the load cell, an example of which was shown in figure 3.9. Drying rates thus calculated for the constant rate period of each drying condition investigated in the study are presented in Table 4-2.

## <u>Table 4-2</u>

Pulp	Drying Fluid	Temp. (°C)	Ave. Drying Rate (kg/h m <sup>2</sup> )	No. of Experiments	Range
ТМР	Air Steam	20 160 240 320 160 240 320	0.9 8.3 13.0 15.8 6.9 12.4 22.1	1 7 5 1 12 4 3	6.7 - 10.1 10.7 - 16.4 4.9 - 8.7 11.6 - 13.6 21.3 - 23.1
Kraft	Air Steam	20 160 240 280 320 160 240 280 320	0.7 5.1 7.9 11.2 13.2 4.8 9.0 17.6 21.7	3 2 3 1 2 4 1 3 2	0.62 - 0.76 4.5 - 5.7 6.9 - 9.3 12.8 - 13.6 2.6 - 5.7 16.6 - 18.6 19.9 - 22.5

Constant rate period drying rates for various conditions

For both TMP and kraft sheets, the drying rates in steam are higher than those in air only at temperatures of 280°C and greater, which is in agreement with the laminar flow inversion temperature of 250°C discussed in (9, 10). Dividing average drying rate by temperature driving force gives a value proportional to heat transfer coefficient. The ratio of steam to air heat transfer coefficients determined in this manner is 1.7.

#### 4.3 Paper from thermomechanical pulp

In the manufacture of thermomechanical pulp (TMP), wood chips are steamed prior to and during the refining process. This steaming heats the chips to the glass transition temperatures of the wood polymers holding the fibres together, enabling removal of complete fibres rather than tearing and fragmenting them. TMP thus has a greater percentage of long fibres than the two other most common mechanical pulping methods, refiner mechanical pulp (RMP) and stone groundwood (SGW), which are lower temperature processes.

The higher proportion of long fibres in TMP paper results in greater sheet strength properties than that obtained from the other types of mechanical pulp. Even so, TMP sheets are not able to match the strength of paper made from chemical pulps because of the comparatively high lignin content of TMP fibres. This high lignin content renders the fibres quite stiff compared to chemical pulp fibres and inhibits the degree to which the fibres can conform and bond. Much of the bonding between mechanical pulp fibres occurs via the intermediary of the fines fraction, which act as bridges between the stiff whole fibres (71).

## 4.3.1 Effect on physical properties

 $Q_{5}$ 

A significant amount of interdependence exists between the properties measured. The documentation of this is mostly qualitative because of the inherently arbitrary nature of many of the tests, the existence of different standard methods, the complicated nature of the forces acting in the tests and the large number of variables affecting their outcome (72). Direct correlations between different properties could only be established under such restricted conditions and arbitrary methods that they are not generally made. Despite the theoretical limitations, a complete set of comparative physical property data measured under similar conditions provides much valuable information, for example, about the nature, arrangement and bonding of the fibres.

#### 4.3.1.1 Sheet bulk and surface roughness

Sheet specific volume, commonly referred to as sheet bulk (cm<sup>3</sup>/g), the inverse of sheet density, was determined by dividing average sheet caliper (cm) by average sheet basis weight (g/cm<sup>2</sup>). Figure 4.2 shows that sheet bulk is similar for air and steam drying except at 160°C where steam dried sheets are slightly bulkier by a few percent. The differences in bulk between the steam and air dried sheets are too small to account for the differences in sheet properties which will be presented. In fact, the comparison of steam and air dried sheet properties can be made assuming constant sheet density. This is important because of the correlation which usually exists between sheet density, amount of interfibre bonding and physical strength properties. For any one pulp, large differences in strength without variation in sheet density are unusual. They have been reported in certain press/impulse drying studies, where for example, hot pressed sheets having the same density as cold pressed sheets were found to have improved strength properties (17). Such improvement in strength is usually attributed to plasticization of the fibre components at high web temperatures resulting in increased bonded area.

Surface roughness as measured by the Parker Print Surf (S10) test is higher for sheets dried in steam than in air, figure 4.3. The major reason for this is discussed in section 4.3.4.1, although it may also be partially due to the condensation of steam on the sheet which occurs in laboratory steam drying. From a heat balance for a typical sheet with initial temperature of 20°C, solids content of 40%, and oven dry mass of 1.2g, the calculated amounts of water condensing on the sheet at 160, 240 and 320°C steam temperature are 0.31, 0.29 and 0.27g, respectively, resulting in a decrease of solids content from 40% to 36.3, 36.5 and 36.7% respectively. There is thus little difference in the amount of condensation between steam drying at 160 and 320°C.

# 4.3.1.2 Burst index and stress-strain curve properties (tensile index, stretch, tensile energy absorption index and elastic modulus)

Burst index, measured by the pressure (corrected for basis weight) required to rupture a sheet, is controlled by interfibre bonding, individual fibre strength and stretch (17). Figure 4.4 shows that steam dried sheets have consistently higher burst index, by up to 30%. This is a substantial increase, especially when achieved with no reduction in sheet bulk. These results agree with trends identified in earlier work (11, 46), although the increases previously reported were 10% rather than the 20 - 30% observed here.

The information obtained from a stress-strain curve, a fundamental engineering description of the mechanical behavior of a material under stress, has been recorded for

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Figures 4.2 - 4.4: Effect of Drying Fluid and Temperature on Bulk, PPS Roughness and Burst Index

inumerable materials. Stress-strain curves for paper usually consist of an initial linear section, representing elastic deformation, followed by the nonlinear behavior of an inelastic material which retains a permanent deformation upon removal of the stress.

The stress at which the paper fails determines the tensile strength, stretch is obtained from the maximum strain, and tensile energy absorption index from the area under the stress-strain curve. Elastic modulus is the slope of the initial linear section. Examination of stress-strain curves of paper can be highly informative. For example, stress-strain curves in which elastic modulus is high, with little curvature and a low elongation before rupture indicate a brittle material. A tough material is characterized by a more viscoelastic behavior and has a stress-strain curve with a pronounced curvature and a high elongation to break.

Tensile strength, combined with basis weight gives the tensile index. As with burst strength, the factors of predominant importance in determining tensile strength are the amount of interfibre bonding and the individual fibre strength (17). In fact, the curves showing the development of these two properties as a function of beating time in a typical pulp beating cycle are roughly parallel. It is thus not surprising to see, in figure 4.5, improvements in tensile index for steam dried sheets similar to those observed for burst index. The approximately 20 - 30% improvement in tensile index is considerable, again especially when achieved without reduction in sheet bulk. Tensile strength was measured in only one of the previous studies (46) where increases of 15% were noted for the steam dried TMP sheets, again a smaller improvement than that now documented.

Stretch is greatly influenced by the degree of sheet restraint imposed during drying; it decreases with increasing sheet restraint, which leads to a tighter more rigid structure having fibres which are less curled and crimped. Overdrying or exposure of paper to high temperatures at low moisture content results in cross-linking which also decreases stretch and embrittles the paper (40). Normal paper does not usually stretch more than 5% before rupture. Figure 4.6 establishes that there is no significant difference between the stretch for sheets dried under total restraint in steam and in air.

Tensile energy absorption index is often more important in characterizing sheet durability than is tensile index (17). A sheet with a high tensile strength may have a lower work to rupture (toughness index) than one with a lower tensile strength. Figure 4.7 shows that, compared to air dried sheets, the mean value of the tensile energy absorption index for the steam dried sheets, measured here for the first time, is 20 - 40% higher for the steam dried sheets. The increase in energy absorption index is mainly due to the increased tensile strength of the steam dried sheets since there was little difference in stretch.

Elastic modulus, normally obtained from the slope of the linear portion of the stressstrain curve, can also be determined by measuring the velocity of ultrasound in the sheet (73). The latter technique was used here since elastic modulus and stress-strain curves were not available from the tensile tester used. The results (figure 4.8), shown as specific elastic stiffness (elastic modulus divided by sheet density), indicate a significant increase of 20% for the steam dried sheets compared to those dried in air.



Figures 4.5 - 4.7: Effect of Drying Fluid and Temperature on Tensile Index, Stretch and Tensile Energy Absorption Index

The elastic modulus of paper,  $E_p$ , is of particular interest, having been thoroughly studied. Unlike many of the other physical properties, mathematical relations exist to relate it to basic papermaking factors. In a theory developed by Cox (74), it was determined that for an isotropic sheet of long, straight well bonded fibres,  $E_p$  is approximately equal to 1/3 the elastic modulus of the fibre, i.e.  $E_p \approx 1/3 E_r$ . Page et al. (75) give the elastic modulus of pulp fibres of softwoods in the most common range of fibril angles as 4.5 - 5.5 GPa (29 - 35 km<sup>2</sup>/s<sup>2</sup>), independent of pulping process and yield in the normal ranges. The values of  $E_p$  obtained in the present study were less than 1/3 the elastic modulus of the fibres, ranging from 5 - 7 km<sup>2</sup>/s<sup>2</sup>, although these values are typical (or for the steam dried sheets slightly high) for mechanical pulp paper (75).

In a plot of elastic modulus as a function of light scattering coefficient (generally accepted as an indication of the degree of bonding) the asymptotic value of  $E_p$  at high degrees of bonding has been referred to as the "levelling off modulus". Page et al. (75) established that for any pulp, increased bonding results in increased elastic modulus up to this "levelling off value", due to improved efficiency of stress distribution within the sheet. This limiting value decreases with increasing degree of curl and crimp in the fibres. If it were found that the levelling off  $E_p$  was higher for the steam than the air dried sheets, this could imply that the steam dried sheets have fewer crimps and kinks in the fibres, a condition which could be due to the higher temperatures attained by the steam dried sheets. In the figure 4.9 plot of average value of  $E_p$  for steam and air at each drying condition, elastic modulus increases with decreased light scattering (increased


Figure 4.8: Effect of Drying Fluid and Temperature on Elastic Modulus



Figure 4.9: Effect of Scattering Coefficient and Drying Fluid on Elastic Modulus

bonding), for both steam and air drying, as would be expected. These results suggest that  $E_p$  for steam dried sheets would reach a higher levelling off value than for air dried sheets.

It should be noted that the changes in light scattering coefficient reported here are due to different drying media and temperatures rather than different levels of pressing, as is often the case in other studies. In order to obtain data over a wider range of light scattering coefficients, a series of steam and air dried sheets pressed at different pressures in order to change bonded area was prepared. Unfortunately, the high presssures resulted in sheets with solids content of 60 - 65% rather than the usual 40%. Because of the important effect of initial sheet solids content on the results obtained with steam drying, which was only discovered afterwards (see 4.3.5.1), the results had to be discarded.

### 4.3.1.3 Tear index and folding endurance

After burst index and properties obtained from the stress-strain curve, the next two most commonly measured physical properties are tear index and folding endurance. Despite the values quoted in Table 4-1, in practice the precision of these two tests, especially folding endurance, is not as high as for burst and tensile (14).

Tearing strength (the force required to tear the paper after a tear has been initiated), depends on many factors and is especially sensitive to the physical properties of the fibre. Any degradation of fibre strength results in a loss of tear strength greater than that of tensile strength for example (17). Unlike burst and tensile strength, both of which increase with interfibre bonding, the effect of interfibre bonding on tear index is not as straightforward.

Very low degrees of interfibre bonding result in low tear strength, but as interfibre bonding increases, tear strength passes through a maximum. Beyond this maximum, tear index decreases because more fibres are ruptured than are pulled out of the bonded network and this surprisingly requires less energy. In papermaking, normally a compromise is made since maximizing the tensile and burst strength typically results in low tear strength. The effect is less pronounced for mechanical than chemical pulp, because the former rarely achieves the critical bonding levels beyond which tear strength begins to decrease. Often, plots of tear index versus tensile index are made to compare the behavior of various pulps. These were not very informative in this study because of the limited amount of data points and the small range over which the tensile strength varied for the steam and air dried sheets.

Figure 4.10 shows that in superheated steam drying, in contrast to the conventional behavior noted above, the improved burst and tensile strength is not accompanied by a reduction in tear index except at the highest temperature of 320°C. The decrease in tear for drying in 320°C steam could be due to increased interfibre bonding or to fibre degradation; evidence of the former rather than the latter is presented further on. Again, these results agree quite well with those from the previous two studies of superheated steam dried paper (11, 46) where virtually no difference was observed in the tear index

of steam dried TMP sheets relative to those dried in air.

Folding endurance (the number of double folds endured by the sample before it ruptures at the fold line) is particularly sensitive to embrittlement of the paper caused by aging, heat treatment or degradation of fibres (40). Because of the large standard deviations for the figure 4.11 data, no conclusion can be made concerning any significant difference in the folding endurance of steam and air dried paper. Folding endurance was not measured in the two previous studies of superheated steam dried paper.

### 4.3.1.4 Zero-span breaking length

As the physical properties discussed so far (burst, tensile, tear and fold strength) all depend on a combination of fibre strength and interfibre bonding, it is not evident which factor causes the significant improvements observed for steam dried sheets. One measurement which attempts to isolate fibre strength is the zero-span tensile test. The difference from a normal tensile strength test is that there is no separation between the jaws holding the sample under tension. This test gives an indication of average ultimate strength of individual fibres, which substantially exceeds the normal tensile strength (17). Although not completely independent of interfibre bonding, the test is predominantly influenced by fibre strength. Figure 4.12 shows that there is no difference in the fibre strength of steam and air dried sheets, as measured by zero-span breaking length. In the work of David et al. (11), zero-span breaking length was measured at only one temperature below 350°C and, as in the present study, no difference was found between



Figures 4.10 - 4.12: Effect of Drying Fluid and Temperature on Tear Index, Fold and Zero-Span Breaking Length

steam dried and air dried sheets.

It has been suggested that one way of eliminating the effect of interfibre bonding and obtaining a truer indication of fibre strength is to measure the zero-span breaking length on a wet sample, since wetting destroys the strength of the polar hydrogen bonds holding the fibres together (76). However, recent work by Gurnagul and Page (77) indicated that the difference between dry and wet zero-span strength relates more to pulp type than bonding degree. Nevertheless, wet zero-span tests were performed on samples soaked overnight in 23°C deionized water. From figure 4.13, no differences between steam and air dried wet zero-span breaking length can be concluded.

Since, according to the (dry) zero-span breaking length results, fibre strength is not the reason for the improved strength properties, these presumably derive from the nature and amount of interfibre bonding. One way of estimating degree of bonding is from the ratio of normal tensile strength expressed as breaking length (which depends on interfibre bonding and fibre strength) to zero-span breaking length (which depends almost entirely on fibre strength) (17). From this ratio, shown in figure 4.14, the degree of bonding is clearly higher for the steam dried than the air dried sheets, although neither sheet approaches the strength of the individual fibres.

### 4.3.1.5 Scott internal bond strength

A test specifically designed to measure the extent of interfibre bonding is the zdirection tensile test, also referred to as the Scott internal bond strength test. Double faced tape is applied to two platens between which the paper is clamped and the force required for rupture in the z-direction perpendicular to the plane of the sheet is measured. The mechanism of fracture is not one in which fibre strength can easily come into play since the fibres lie mostly in the x-y plane of the sheet.

It is clear from figure 4.15 that the internal bond strength is 10 - 20% greater for the steam dried than the air dried sheets, an important finding which explains the significant improvements in burst and tensile strength observed for steam dried paper. It does not however indicate whether the improvement in bond strength is due to an increased amount of bonding or to bonds having a greater strength.

### 4.3.1.6 Wet strength

Covalent bonds, which can be formed in paper under certain conditions (40), have about ten times the strength of the polar hydrogen bonds normally holding fibres together. Another characteristic is that covalent bonds, unlike hydrogen bonds, are not destroyed by water, so their presence can be detected by increases in the sheet wet strength. Therefore wet strength was determined for paper soaked in 23°C deionized water for 3 hours (no differences in the results were observed if samples dried at 160°C were soaked for longer periods). Excess water was removed by placing the samples between blotters. The samples were then tested as in a standard dry tensile strength test.

Figure 4.16 shows that there is no difference between the wet tensile strength of steam and air dried paper up to 240°C, while at 320°C steam drying results in a 50%



Figures 4.13 - 4.15: Effect of Drying Fluid and Temperature on Wet Zero-Span Breaking Length, Breaking Length/Zero-Span Breaking Length and Scott Internal Bond Strength

higher wet paper strength. Wet tensile strength increases with temperature of the drying fluid for both steam and air dried paper. This increase is probably due to the formation of covalent bonds near the very end of drying, when the sheet temperature approaches the drying medium temperature. It is well documented that exposure to high temperature at low moisture content results in cross-linking (40). The amount of covalent bond formation depends on the exposure time and temperature and appears to be about the same for both the steam and air dried sheets, except at 320°C.

It can thus be concluded that the increases observed in Scott internal bond strength for steam dried paper relative to air dried are probably not due to increased bond strength resulting from covalent bonding, since the wet strength tests did not indicate that steam dried sheets were more covalently bonded than air dried sheets, except at 320°C. The differences in internal bond strength are thus more likely to be due to increased bonded area, i.e. to a larger number of hydrogen bonds.

# 4.3.1.7 Water absorptivity: dynamic and equilibrium

The time required for a sheet to absorb a drop of water is an indication of the degree of sizing or water repellence. In this dynamic water absorptivity test, the time for complete absorption of 0.1 ml of water is recorded, as indicated visually by no further reflection of light from the water drop. The rate of penetration of liquid into the paper, described by the Washburn equation (17), depends on pore size distribution, surface tension and viscosity of the liquid, contact angle between the liquid and the paper, and depth of liquid penetration. The contact angle depends on whether the surface is hydrophobic or hydrophilic; cellulose is normally hydrophilic but the redistribution of fatty acids, resin or lignin on the sheet surface may make it hydrophobic.

Figure 4.17 shows that below 240°C there is little effect of drying medium temperature on water absorptivity. When dried at 320°C, both steam and air dried sheets become more repellent. The repellancy increase with increasing drying temperature is presumably because of redistribution of hydrophobic compounds onto the sheet surface caused by the high paper temperatures reached near the end of drying.

The equilibrium moisture content of the paper after drying was also investigated. The moisture content after equilibration for 24 hours at the same conditions under which physical properties were measured, 23°C and 50% relative humidity was determined, since sheet moisture content influences physical strength properties through its weakening of interfibre bonding. The mass after the 24 hour conditioning was recorded for 5 sheets dried in 160°C steam and 5 sheets dried in 160°C air. The dry mass was determined by drying overnight in a 105°C oven.

Steam dried sheets had lower moisture content than those air dried (5.49%  $\pm$  0.24 versus 6.31%  $\pm$  0.15%). Decreased sheet moisture content results in decreased folding endurance, stretch, and tear index and increased tensile and burst strength (14), but the changes in physical properties from the lower moisture content of steam dried sheets cannot explain the large differences in physical strength properties observed between steam and air dried sheets (14, 78). For example, the maximum increase in burst or

tensile index arising from decreased sheet moisture content is about 3% relative to a sheet with normal moisture content equilibrated at 23°C and 50% R.H. (14).

Differences in equilibrium moisture content can be indicative of changes in crystalline to amorphous cellulose ratio since the latter absorbs water far more readily than the tightly bonded orderly structure of the former; in fact water sorption isotherms are often used as a means of determining cellulose crystallinity (79). Investigation of differences in steam and air dried cellulose crystallinity is presented in section 4.3.1.9.

### 4.3.1.8 Air resistance

The air resistance of paper is evaluated by measuring the time for a given volume of air to flow through the sheet under specified conditions. The test has a very low precision. Air resistance, an indirect indicator of permeability, porosity and sheet density, is influenced by sheet internal structure which depends largely on the nature and bonding of the fibres, their orientation, and the compaction of the sheet. Figure 4.18 shows that within the precision of the test, the air resistance for steam and air dried sheets seems to be comparable.

## 4.3.1.9 Crystallinity

There are inconsistent results from the number of studies investigating the effect of steam treatment on the ultrastructure of wood fibres. Increased degree of crystallinity and average size of crystallites was observed by Tanashi et al. (80) when wood was



Figures 4.16 - 4.18: Effect of Drying Fluid and Temperature on Wet Tensile Strength, Water Drop Absorption Time and Air Resistance

treated with saturated steam for 4 minutes, while Marchessault et al. (81) found no change in crystallinity for a similar 30 second steam treatment of aspen. Atalla (82) found that cellulose crystallinity increased during press drying of paper even though the dwell times were very short.

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Crystallinity, which can affect the fibre strength and resulting paper properties, was determined by x-ray diffraction as well as C<sup>13</sup> MAS NMR spectroscopy for steam and air dried sheets. The crystallinity as measured by x-ray diffraction was 71% for sheets dried with 20°C or 320°C air as well as 320°C steam. Similarily, no difference in crystallinity for sheets dried in air at 20°C or 350°C, or in steam at 350°C, could be observed by NMR spectroscopy. This is consistent with the zero-span breaking length results (figure 4.12) which showed that steam and air dried sheets had the same fibre strength.

## 4.3.2 Effect on optical and chemical properties

The optical properties of paper are in many cases just as sought after as its physical strength properties. Sheet whiteness and the extent to which one can see through the sheet are important qualities for printed material. The change in optical properties with time as paper ages is also important, especially for mechanical pulp. The two most commonly measured optical properties are brightness and opacity, which depend on the ability of paper to reflect, refract, transmit and absorb incident light.

### 4.3.2.1 Brightness

The brightness of paper is primarily dependent on its ability to intensively scatter light, since most of the material making up the sheet is essentially "water white" or transparent (especially for fully bleached pulp). Brightness is defined as the ratio of diffuse reflectance of blue light, having a specified spectral distribution peaking at 457 nm, for a stack of sheets to that of a perfectly reflecting, perfectly diffusing standard surface. The blue portion of the spectrum is chosen because it is the most sensitive to changes in brightness brought about by bleaching. Brightness is not the equivalent of whiteness but provides an excellent measure of the whiteness potential which can be achieved with proper tinting (17). Decreases in sheet brightness are usually associated with increased bonding which decreases the number of fibre-air interfaces available for scattering light. Increased light absorption by colored material, either added to the sheet or formed during thermal degradation, also results in decreased brightness.

Figure 4.19 shows that the brightness for sheets dried in steam is always about 5 points lower than for those dried in air, which is consistent with the increased strength of steam dried sheets from having more interfibre bonding. As well, brightness for sheets dried in either air or steam decreases with increasing drying fluid temperature, especially at 320°C, the cause of which is discussed in section 4.3.2.3. Brightness was measured in only one previous study (11), where a drop of up to 5 points in brightness for drying in steam, relative to that in air, can be observed upon careful examination of the data.

# 4.3.2.2 Opacity

Printing opacity, the ability of paper to obscure matter printed on an underlying sheet, is defined as the ratio of the reflectance of a single sheet of paper over a black backing to the reflectance of the sheet backed by an opaque pad of similar paper. Unlike brightness, which is measured in the blue portion of the spectrum, opacity is measured in the green portion at a peak wavelength of 557 nm. Opacity can be increased by the addition of fillers or fines which increase the amount of light scattering or by the addition of dark or colored material which absorbs the light. Figure 4.20 shows that the opacity of the steam and air dried sheets is comparable. The opacity of both sheets rises sharply for drying fluid temperatures of 320°C, due to thermal degradation products formed in the falling rate period of drying when the sheet temperature approaches the drying fluid temperature; evidence of this is provided by the darkened color of the sheets.

# 4.3.2.3 Scattering and absorption coefficients

Brightness and opacity are parameters indicating the final optical quality of the paper. However, brightness and opacity do not distinguish between changes in optical properties due to differences in color (light absorption) and in amount of light scattering (17). This information can be obtained from the Kubelka-Munk theory and the reflectance values obtained for opacity, from which specific scattering and absorption coefficients can be calculated (83). Theoretically, the scattering coefficient gives a measure of the ability of the material to reflect light independent of its ability to absorb light, while the absorption coefficient indicates the ability of the sheet to absorb light independent of its ability to scatter light. A brightness loss due to increased light absorption can thus be distinguished from one due to decreased light scattering.

The results for steam and air dried sheets shown in figure 4.21 establish that, except at 320°C, the specific absorption coefficient is independent of drying medium and drying medium temperature. Thus up to drying temperature of at least 240°C, the color of steam and air dried paper is the same. Up to 240°C therefore, the brightness decrease of 5 points for steam dried sheets relative to air dried sheets is not due to absorption effects but to changes in the nature of the light scattering surface of the sheet brought about by increased bonding. At 320°C the absorption coefficient rises sharply for both steam and air dried sheets because of the previously mentioned darkening of the sheet.

This darkening is due to thermal degradation occurring in the falling rate drying period when the temperature of the sheet approaches that of the drying fluid. It is not particular to steam drying, occurring in air drying as well. The amount of thermal degradation increases with temperature and exposure time; it can therefore be eliminated by stopping the drying at a lower solids content, thus reducing the maximum sheet temperature, or by increasing the drying rate so that the sheet spends a smaller amount of time at high temperatures. Thermal degradation is not expected to be a problem in industrial drying which would proceed at much higher drying rates and to lower solids content than the laboratory study.

The specific scattering coefficient (figure 4.22) follows exactly the trends seen in the



Figures 4.19 - 4.21: Effect of Drying Fluid and Temperature on Brightness, Opacity and Specific Absorption Coefficient



Figure 4.22: Effect of Drying Fluid Temperature on Specific Scattering Coefficient

brightness measurements; steam dried sheets are less efficient at scattering light than those dried in air, because of the increased amount of bonding. The ability of both steam or air dried sheets to scatter light decreases with increasing drying medium temperature because of the increasing formation of covalent bonds in the falling rate drying period (as seen from the wet tensile strength results).

An estimate of the relative bonded area (RBA) of the steam and air dried sheets can be obtained from specific scattering coefficients and tensile index values according to the method of Ingmanson and Thode (26). The RBA is determined by:

$$RBA = \frac{S_o - S}{S_o}$$

where S is the scattering coefficient for the sheet and S<sub>o</sub> is the scattering coefficient for a totally unbonded sheet of the same fibres. An estimate of S<sub>o</sub> = 76 m<sup>2</sup>/kg is obtained by extrapolating a tensile index - scattering coefficient plot to zero tensile index, at which point the sheet is considered to be totally unbonded. The results at 320°C are not included because of the darkening of the sheets caused by thermal degradation reactions, a mechanism totally different from fibre bonding. Although the data is very limited, the calculated RBA values shown in Table 4-2 indicate that the steam dried sheets are more bonded than those dried in air. Thus the RBA values are in accordance with the improvement in bonding indicated by Scott internal bond strength and that predicted by the ratio of tensile strength to zero-span breaking length.

### <u>Table 4-3</u>

Drying Fluid T (°C)	RBA for air drying	RBA for steam drying
20	0.16	-
160	0.19	0.32
240	0.23	0.36

# Estimated relative bonded areas for steam and air dried paper

It should be noted that this method of determining RBA, originally developed for chemical pulp, provides only a relative measure of fibre bonding. Criticisms of the technique include the fact that light is not appreciably scattered by unbonded surfaces which are separated from each other by distances less than one half the wavelength of the light used. For example, with 650 nm light, free surfaces 0.3  $\mu$ m apart will appear bonded, yet this is 1000 times greater than the distance at which hydrogen bonds form (84).

## 4.3.2.4 Brightness reversion

The thermal and light induced yellowing of paper from mechanical pulps is referred to as brightness reversion. Much effort has been directed towards solving this problem, which would greatly enhance the value of mechanical pulp. Years of research have established that carbonyl groups are one of the main causes of brightness reversion (42). Since carbonyl groups are one of the degradation products of oxidized cellulose, it was thought that the amount of carbonyl groups might be lower in steam dried sheets because of the absence of molecular oxygen.

Accelerated aging was achieved by heating samples in a  $105^{\circ}$ C oven for 1 hour, a procedure found to replicate normal aging. Brightness of both steam and air dried sheets was found to decrease by roughly the same amount (0.20 - 0.35) and no trends were observed. As well, folding endurance, which is very sensitive to aging, was measured for the aged sheets. Again no difference between steam and air dried sheets was observed.

# 4.3.2.5 Chemical properties

Because of the very high lignin content of mechanical pulp, it is not possible to perform most of the chemical tests used for kraft pulp (see chapter 5) without first delignifying the pulp, since lignin interferes with the tests. However, delignification of mechanical pulp is difficult, and can significantly alter the nature of the fibres. Nevertheless, overnight acid chlorite treatments were used to delignify dried TMP sheets and several chemical tests (cold pH and solubility in 1% NaOH) were performed on steam dried and air dried paper. No difference was detected between the two types of dried sheets. The significance of these and other chemical tests will be discussed further in chapter 5.

## 4.3.3 Discussion

The data presented thus far reveals a great deal about superheated steam drying and its effect on properties of TMP paper. Firstly, through to the end of the constant rate  $\rightarrow$ drying period the sheet temperature is significantly higher in steam than in air drying. Secondly, compared to air drying, superheated steam drying results in a sheet of similar bulk but with significant improvement of those properties which are affected by interfibre bonding (e.g. burst index, tensile index, Scott internal bond strength). Fibre strength (zero-span breaking length) is independent of the drying fluid. Thirdly, the improved interfibre bonding occurring in steam drying derives not from stronger bonding but from more bonding. Wet strength tests showed no evidence of differences in covalent bonding between steam and air dried sheets. Finally, steam dried TMP sheets have lower brightnesses and scattering coefficients, each by about 5 points, effects commonly associated with increased amount of bonding. The data thus provides evidence that the major effect of superheated steam drying is a higher degree of hydrogen bonding in the sheet compared to air drying under similar conditions. What is less clear is the mechanism by which this increased hydrogen bonding is occurring. Presumably, one of the most obvious differences between steam and air drying, the sheet temperature, plays an important role in the softening of the amorphous polymers contained in the wood fibres. Assuming the wet sheet to have a typical value of 60% moisture content as it leaves the press section, warming to 60 - 70°C in a conventional dryer is sufficient for the hemicellulose but not the lignin be in a soft rubber-like state. At the sheet temperatures reached in conventional drying, the hemicellulose would become glassy near

the end of the drying. For a superheated steam dryer with the sheet temperature at 100°C at high moisture content, in addition to the hemicellulose being in an even softer rubber-like state, the lignin is also at or very near its glass transition temperature. At a sheet temperature of 100°C, the hemicellulose would stay soft until the end of the drying period and may be capable of some flow and redistribution. The softened lignin would become hard some time prior to the end of drying. The possible flow of hemicellulose and softening of lignin have important implications. The former can provide additional sites for bonding. The latter may result in improved conformability of the fibres leading to increased bonded area and sheet strength properties, as reported in press and impulse drying studies. It is instructive at this point to explore the work of others.

A study by Byrd (29) of mild press drying is of particular interest for several reasons. First, the sheet temperature in the press drying experiments rapidly reached 100°C and remained constant until the water was mostly evaporated before rising again; this is identical to what happens with sheet temperature in steam drying. Second, the drying times used were of the same order as those used in the present study. Third, the focus of the press drying study was on the role of hemicellulose and lignin in the development of sheet strength properties. Sheets of different lignin and hemicellulose content, prepared in various ways, were dried. The key difference between press drying and steam drying is the application of pressure during press drying.

Byrd (29) concluded that wet hemicellulose flowed readily at temperatures of about

 $60^{\circ}$ C and was responsible for the development of bonding strength during press drying; wet lignin flowed only after the sheet was exposed for some time to temperatures of about 100°C, and contributed little to the bonding and strength development. This is in agreement with the published literature on thermal softening temperatures of wet hemicellulose and lignin, reported as 20 - 50°C and 70 - 115°C respectively (37). It is thus probable that there is flow of hemicellulose and to a lesser extent lignin in the steam dried sheets, since they reach the same temperatures as the press dried sheets. Such flow probably does not occur to a very significant extent in air drying beause of the lower temperatures reached in the constant rate drying period.

In another interesting study, Nordman and Levlin (85) investigated the influence of drying on the optical properties of paper from mechanical pulp. They dried mechanical pulp sheets, each supported on a blotter, by restraining them blotter side up with a cloth against a hot plate of high heat capacity and temperature adjustable from room temperature to 140°C.

They found that as plate temperature was increased, the light scattering coefficient of the sheets decreased although the absorption coefficients remained constant. The decreased light scattering coefficients, attributed to a change in size of the light scattering surface, were accompanied by increased tensile strength, although the sheet bulk remained essentially constant. They concluded that these effects resulted from increased bonding at the higher drying temperatures. Their results parallel exactly the differences observed in the present study between steam dried sheets (higher sheet temperature) and air dried sheets (lower sheet temperature).

These authors concluded that because bulk remained constant, the increased bonding was due to an enlargement of bonded surface area in very close proximity to fibre crossings, and to a rebonding of fibrils and fines to the fibres; the network of stiff mechanical pulp fibres was stable enough that this type of increased bonding did not change the paper structure. The increased bond formation at the higher drying temperatures was attributed to plasticization of lignin and hemicellulose. The fines fraction was found to be especially sensitive to the phenomenon of increased bonding with increased drying temperature. Light scattering coefficients decreased the higher the solids content at which hot drying ended, but the decrease was much smaller when the fines fraction (P200) was removed from the pulp.

Thus in steam drying the probable mechanism leading to the increased amount of bonding at constant bulk is a thermally induced softening and/or flow of the wet lignin and hemicellulose because of the characteristic of this process of providing high sheet temperatures while the sheet moisture content is still high. The constant bulk indicates that the increased bonding is not due to thermal deformation of the stiff whole fibres, which would result in increased fibre conformability and consolidation of the sheet structure. Rather, the high temperature - high moisture content conditions lead to a softening of the finer material, held between or on the surfaces of the stiff whole fibres, which can deform without affecting the gross structure of the sheet. It would be expected that the effect of superheated steam drying would be diminished with increasing sheet consolidation achieved for example by stronger pressing prior to drying.

Additional experimental work was performed to investigate these concepts more closely and to examine other superheated steam drying phenomena.

### 4.3.4 Effect of fines content on superheated steam drying

The fines content of mechanical pulp is more rich in lignin, hemicellulose and resin than the rest of the pulp. It consists of thin ribbons of unwound lamellas, flake-like material from the middle lamella, and ray cells (86). In order to test the hypothesis that it is the softening of this fraction of the pulp which in superheated steam drying is largely responsible for the increase in bonded area without decrease in sheet bulk, the fines fraction was removed from the TMP and new handsheets were made and dried in steam and in air at 160°C. For the TMP used in this study, the P200 fraction of the pulp representing 27.1% of the pulp by weight and the P100/R200 representing 5.4% were both removed. The steam and air dried sheet properties were then measured and compared.

The results confirmed the hypothesis, in that the strength improvements and increased bonding for steam dried sheets relative to air drying were diminished or eliminated when the sheets were made of pulp without the fine material. The results, which include only a few key sheet properties, are summarized in Table 4-4.

### Table 4-4

Property	160°C Steam Dried	160°C Air Dried
Bulk, cm <sup>3</sup> /g	$6.65 \pm 0.13$	6.73 ± 0.35
Burst Index, Pa m <sup>2</sup> /g	354 ± 14	344 ± 22
Tensile Index, N m/g	9.94 ± 1.71	6.07 ± 0.95
Stretch, %	$0.81 \pm 0.16$	$0.68 \pm 0.10$
Tensile Energy Absorption Index, mJ/g	47 ± 10	25 ± 5
Scott Internal Bond Strength, J/m <sup>2</sup>	35 ± 4	34 ± 7
Brightness, %	43.17 ± 0.17	45.07 ± 0.25
Opacity, %	91.18 ± 0.37	$91.52 \pm 0.67$
Specific Scattering Coefficient, m <sup>2</sup> /kg	34.29	36.21
Specific Absorption Coefficient, m <sup>2</sup> /kg	4.87	4.62

# Properties of steam and air dried sheets with fine fraction removed

Without the fines, steam dried TMP has the same bulk, burst index, and internal bond strength as the air dried sheets. Increases in tensile index and small losses in optical properties are still perceivable, indicating that some improvement in bonded area is still occurring in steam drying. This is probably due a better bonding of the remaining fine material attached to the fibres, rather than to a thermal softening of the stiff fibres which would result in decreased bulk. These results show that the fines play a key role in developing the superior strength properties of superheated steam dried paper.

As can be seen from the decreased strength and optical properties of fines free sheets

relative to sheets made from whole pulp, regardless of drying method, fines are essential for the development of adequate quality of paper made from mechanical pulp. Much of the bonding between mechanical pulp fibres occurs via the intermediary of the fines which act as bridges between the stiff whole fibres (71).

### 4.3.4.1 Scanning electron microscope analysis

TMP sheets dried at 160°C in steam and in air were examined by scanning electron microscope. Photographs at 64X magnification of the top side of steam and air dried sheets are shown in figures 4.23a and 4.23b. The most striking difference is that the air dried sheet appears to have much more surface fibrillation than the steam dried sheet, in which the fines seem to have disappeared. This can be explained by the thermal plasticization of the fine material which then flows into the structure of the steam dried paper, below the level of the stiffer whole fibres. It can be seen from the photographs that the long fibres are raised above the surface of the steam dried sheet, which appears rougher than the air dried sheet. This is in agreement with the higher roughness of steam dried sheets as measured by the Parker Print Surf roughness test.

Figures 4.23c and 4.23d are scanning electron micrographs of cross-sectional views of the steam and air dried paper magnified 200X. The steam dried sheet appears to have much less fines and fibrils and a far more open structure with larger pore size than the air dried sheet, although both sheets were made from the same pulp. In the steam dried sheet the fines and fibrils have evidently softened and collapsed back onto the fibres.



Figure 4.23a: Scanning Electron Micrograph of Steam Dried TMP sheet surface (mag. X 64)



Figure 4.23b: Scanning Electron Micrograph of Air Dried TMP sheet surface (mag. X 64)



Figure 4.23c: SEM cross-sectional view of steam dried TMP sheet (mag. X 200)



Figure 4.23d: SEM cross-sectional view of air dried TMP sheet (mag. X 200)





Further evidence of this is the diminished rugosity of the fibre contours which are covered with a film of softened fines material. No fibre collapse is observable. The increased roughness of the steam dried sheet surface is also evident. The micrographs thus serve as further proof for the hypothesis that it is mainly the fines fraction which is plasticized by the higher temperatures reached in superheated steam drying.

## 4.3.5 Effect of sheet solids content on superheated steam drying

A series of experiments was performed in order to determine during which period of superheated steam drying most of the strength improvements occur, and to investigate the effects on paper properties of combinations of superheated steam and air drying.

## 4.3.5.1 Effect of initial sheet solids content

In this series of experiments, the sheet solids content at which steam drying began was varied. The restrained sheets were partially air dried to various solids contents (54, 64, 73 and 87%) using low velocity air at 40°C from a hair dryer, then dried in the superheated steam dryer with  $160^{\circ}$ C steam. The entire set of results for a variety of properties is shown in figures 4.24 to 4.37. In these figures, data points at 39% solids content are the average of the three replicate experiments presented earlier for sheets completely dried in steam at  $160^{\circ}$ C, while data points at 100% solids content are the results obtained for completely air dried paper at  $20^{\circ}$ C.

As sheet bulk, tear index, stretch, and zero-span breaking length both dry and wet

were already demonstrated to be the same for complete drying in steam and in air, the additional measurements, figures 4.24 to 4.28 confirm that, as expected, these properties are independent of the solids content at which steam drying is started. However burst index, tensile index, tensile energy absorption index, folding endurance and Scott internal bond strength (figures 4.29 to 4.33) are all markedly affected by the initial sheet solids content. These properties are best when steam drying begins at low solids content. Figure 4.29, for example, clearly shows that the high values of burst index obtained with steam drying are lost if steam drying is initiated at sheet solids content of 60% or higher; after this point the burst index is similar to what would be obtained if the sheet had been completely air dried. This implies that the increased amount of bonding characteristic of steam drying is obtained only if the sheet is initially sufficiently wet. The relationships for the tensile and tensile energy absorption index are even more pronounced, indicating that any deferral of the start of superheated steam drying above a solids content of 40% results in some loss of the potential improvement in tensile properties with superheated steam drying.

Correspondingly, the optical properties brightness and specific scattering coefficient, figures 4.34 and 4.35, are at their lowest values when steam drying is begun at 60% solids content or less. Again, these figures show that increased amounts of bonding, resulting in increased strength and decreased optical properties, occurs only if the sheet is sufficiently wet when steam drying begins. Up to 70% initial solids content, opacity (figure 4.36) improves with increasing solids content at which steam drying is started because of the increase in light scattering coefficient, figure 4.35. For initial solids



Figures 4.24 - 4.26: Effect of Initial Sheet Solids Content on Bulk, Tear Index and Stretch



Figures 4.27 - 4.29: Effect of Initial Sheet Solids Content on Zero-Span Breaking Length, Wet Zero-Span Breaking Length and Burst Index



Figures 4.30 - 4.32: Effect of Initial Sheet Solids Content on Tensile Index, Tensile Energy Absorption Index and Fold


Figures 4.33 - 4.35: Effect of Initial Sheet Solids Content on Scott Internal Bond Strength, Brightness and Specific Scattering Coefficient



Figures 4.36 - 4.37: Effect of Initial Sheet Solids Content on Opacity and Specific Absorption Coefficient

contents in the range 70 - 90%, opacity remains constant, as does light scattering coefficient. The decrease in opacity from 90% initial solids content to pure air drying (100% solids content) is because of the slightly lower absorption coefficient (figure 4.37) of the completely air dried sheets, the only sheets which did not come into contact with high temperature drying steam.

This series of experiments thus shows that in order to obtain the maximal benefits of improved strength properties associated with steam drying through the mechanism of increased amount of bonding, the sheet solids content at the start of steam drying must be less than 60%, preferably about 40%. Above 60% solids content, most of the benefits are lost and the properties become similar to those of a sheet dried completely in air.

There are two possible mechanisms which, when steam drying starts at too high a solids content, could hinder the formation of the increased bonded area otherwise observed. The first is due to the reason for the increased amount of bonding occurring in steam drying - plasticization of the lignin and hemicellulose polymers, especially in the fines fraction. The glass transition temperatures of these polymers, low only when they are wet, rises to around 200°C when dry (37). When the sheet initial solids content is 60% or more, the amount of water available to interact with these polymers appears insufficient to reduce their glass transition temperatures to less than the 100°C sheet temperature obtained from the start of steam drying to the end of the constant rate drying period. The other mechanism which might come into play is that hydrogen bonds are

reported to begin to form at approximately 50 - 60% solids content in air drying; perhaps it is necessary for the plasticization of hemicellulose and lignin to occur before the onset of bonding in order to achieve the benefits of steam drying.

In the previously discussed paper by Nordman and Levlin (85), a set of experiments similar to that discussed here was also performed; the effect of varying the initial solids content of a mechanical pulp sheet dried at elevated temperatures by contact drying on a hot surface was investigated. The solids content for contact drying was varied by partial pre-drying of the restrained sheet in room temperature air. The results paralleled closely those of the present study in that the lower the solids content at which hot contact drying began, the greater the drop in light scattering coefficient. Drying at high temperatures no longer decreased the light scattering coefficient when the initial sheet solids content was 70 - 75% or higher, which agrees very well with figure 4.33 from the present study.

### 4.3.5.2 Effect of final sheet solids content

A complimentary set of experiments was performed to determine to what sheet solids content steam drying had to proceed in order to obtain the benefits associated with the increased amount of bonding. Sheets, with initial solids content of approximately 40%, were dried in superheated steam at 160°C to various solids contents (48, 52, 73, 85 and 100%), then removed from the dryer. For the incompletely dried sheets the remainder of the drying was done in air at  $40^{\circ}$ C with a hair dryer, with the sheet remaining fully restrained. The data at 100% solids content is the set of three replicates for completely steam dried sheets at 160°C, while that at 40% solids content is for sheets completely dried in air at 20°C. The complete set of results for the variety of properties tested is shown in figures 4.38 to 4.52.

Sheet bulk, tear index, stretch, and dry and wet zero-span breaking length (figures 4.43 to 4.48) remains essentially unaffected by solids content at which steam drying ended. For the sheet strength properties - burst index, tensile index, elastic modulus, tensile energy absorption index, folding endurance and internal bond strength - figures 4.39 to 4.44 show that improvements occur the longer steam drying is continued. Some of the properties, i.e. burst index, tensile energy absorption index, folding endurance and scott internal bond strength show no further improvement for steam drying continued past 70% solids content. Other properties, e.g. tensile index and elastic modulus, improve approximately linearly with continuation of steam drying to complete dryness as they are known to do in air drying, presumably because of the formation of covalent bonds in the high temperature falling rate period.

For the optical properties, figures 4.49 and 4.50 show that brightness and scattering coefficient are reduced as the extent of steam drying is increased. This is again indicative of increased bonded area and corresponds to the improved strength properties. As for some of the strength properties, all deterioration of the optical properties in steam drying occurs prior to the sheet reaching 70% solids content. Figure 4.51 shows that opacity decreases for steam drying from 50 to 70% solids content after which it remains



Figures 4.38 - 4.40: Effect of Final Sheet Solids Content on Bulk, Tear Index and Stretch



Figures 4.41 - 4.43: Effect of Final Sheet Solids Content on Zero-Span Breaking Length, Wet Zero-Span Breaking Length and Burst Index



Figures 4.44 - 4.46: Effect of Final Sheet Solids Content on Tensile Index, Elastic Modulus and Tensile Energy Absorption Index



Figure 4.47 - 4.49: Effect of Final Sheet Solids Content on Fold, Scott Internal Bond Strength and Brightness



Figures 4.50 - 4.52: Effect of Final Sheet Solids Content on Specific Scattering Coefficient, Opacity and Specific Absorption Coefficient

constant, parallelling the trend observed for specific scattering coefficient. The drop in opacity at 40% solids content is due to the slightly decreased absorption coefficient (figure 4.52) of the completely air dried sheets which had no contact with high temperature steam. Except for these sheets, absorption coefficient is independent of extent of steam drying. It is interesting to note from figures 4.1a and 4.1b that for both steam and air drying, 70% solids content is achieved before the sheet temperature starts to increase in the falling rate period of drying.

This set of results shows that steam drying must be continued to a certain sheet solids content in order to reap the benefits of steam drying. This solids content is around 70% for most of the properties. For the drying conditions used in the present study, the sheet is still at the temperature of the constant rate drying period at this solids content and does not begin to increase until about 75%. It is thus not sufficient to bring the sheet at low solids content to  $100^{\circ}$ C in steam, followed by drying to high solids content at the lower adiabatic saturation temperature in air drying, as this probably only results in a successive softening and hardening of the hemicellulose and lignin fractions with insufficient time for flow and bond formation. It is known that for conditions of drying in air, hydrogen bonding begins to occur around 50 - 60% solids content; the polymers must be kept soft at least to somewhat beyond this point.

In a series of experiments with similarities to the present study, Nordman and Levlin (85) dried mechanical pulp sheets to various solids contents by contact drying on a hot plate, with the remainder of the drying accomplished in room temperature air. For TMP paper they found, as in the present study, that the light scattering coefficient decreased as hot drying at 130°C was extended, but levelled off once solids contents of approximately 70% or more were reached.

### 4.3.6 Effect of recycling

The objective of these experiments was not primarily to investigate the effect of recycling, although this in itself is quite interesting, but rather to determine whether any effects of superheated steam drying are permanent and persist even after recycling followed by air drying, or intensify after recycling and drying again with steam. Thus sheets which had been steam or air dried at 160°C were reslushed in the British disintegrator for approximately 10 minutes according to standard procedure, reformed on the British Sheet Machine, and redried in steam or air at 160°C. No effort was made to retain the fines fraction which presumably was lower in the reformed sheets. Five drying strategies were investigated, identified as follows:

AIR = air dried unrecycled sheets

AIR/AIR = air dried sheets recycled and redried in air

STM = steam dried unrecycled sheets

STM/STM = steam dried sheets recycled and redried in steam

STM/AIR = steam dried sheets recycled and redried in air

The comparative "AIR" and "STEAM" data are the average results from the set of three replicates dried in 160°C air and steam.

Figure 4.53 shows that for AIR/AIR or STM/STM, recycling reduces the bulk, although the bulk of the STM/STM sheets remains slightly higher than that of the AIR/AIR sheets. This increase in bulk disappears if the steam dried sheet is redried with air (STM/AIR).

Recent work at Paprican (87) has shown that recycling of mechanical pulp sheets, including TMP sheets, results in decreased sheet bulk and increased strength properties, with no significant loss in fibre strength. It is thought that recycling causes the fibres to become flatter and more flexible, resulting in a higher bonded area.

The strength properties burst index, tensile index, tensile energy absorption index, tear index, Scott internal bond strength, folding endurance and stretch are shown in figures 4.54 to 4.60. For the AIR/AIR sheets, most of the strength properties remain about the same or show a slight increase after recycling and redrying in air, except for decreased tear index and stretch. This behavior is similar to that noted in (87). The STM/STM sheets, however, show the opposite behavior, with all of the strength properties decreasing after recycling and redrying in steam, assuming values intermediate between those of STM and AIR (or AIR/AIR) sheets. The reason for the decrease in strength properties after recycling for the STM/STM sheets rather than the increase seen for the AIR/AIR sheets is probably due to the loss of fines in the way these particular experiments were carried out. The presence of fines, which plays such an important role in steam drying as shown earlier, is more significant than any flattening or increase in flexibility of the fibres which may occur due to recycling. Steam dried sheets which are



Figures 4.53 - 4.55: Effect of Recycling and Drying Fluid on Bulk, Burst Index and Tensile Index



Figures 4.56 - 4.58: Effect of Recycling and Drying Fluid on Tensile Energy Absorption Index, Tear Index and Fold

recycled and air dried (STM/AIR) show strength properties distinctly lower than the STM/STM case, of the same order or slightly lower than the properties of AIR/AIR sheets.

The optical properties, figures 4.61 to 4.64, show that for both the AIR/AIR and STM/STM sheets, recycling causes a loss of brightness, opacity and specific scattering coefficient, presumably in this specific case due primarily to the loss of fines which are quite efficient at scattering light. The loss of optical properties which normally accompanies the improved strength properties of steam dried sheets is apparent for the STM/STM sheets, which have lower values than the AIR/AIR sheets. The optical properties are restored to those of the AIR/AIR sheets if steam dried sheets are recycled and redried with air (STM/AIR). There is little difference in the specific absorption coefficients, although the value for the AIR dried sheets is slightly lower. Dry and wet zero span breaking lengths (figures 4.65 to 4.66) remain relatively constant, indicating no change in fibre strength with recycling.

Thus, from this series of experiments it can be seen that the effects of steam drying persist even after recycling, including improved strength properties accompanied by somewhat decreased optical properties. The strength improvements would have been even better if the loss of fines during these recycling tests were avoided.

## 4.3.7 Overdrying in superheated steam and in air

Sensitivity to overdrying, especially for radically different drying conditions such as



Figures 4.59 - 4.61: Effect of Recycling and Drying Fluid on Scott Internal Bond Strength, Stretch and Brightness



Figures 4.62 - 4.64: Effect of Recycling and Drying Fluid on Opacity, Specific Scattering Coefficient and Specific Absorption Coefficient





Figures 4.65 - 4.66: Effect of Recycling and Drying Fluid on Zero-Span Breaking Length and Wet Zero-Span Breaking Length

those investigated in the present study, is of intrinsic interest and potential industrial relevance. Severe overdrying in steam and in air was investigated by drying sheets 3 times longer than the time required for normal drying, as determined by the load cell with the procedures described in Chapter 3. Thus for 160, 240 and 320°C, normal drying times in air were approximately 55, 50 and 30 seconds, and approximately 140, 65 and 40 seconds for steam, with three times these values used for overdrying. Most properties measured for the normally dried sheets were also measured for the overdried sheets, and the results are shown in figures 4.67 to 4.83.

#### 4.3.7.1 Effect on physical properties

Figure 4.67 reveals that the sheet bulk of the steam and air overdried samples is virtually the same and does not differ from the non-overdried bulk. The sheet properties can thus still be compared assuming constant sheet density.

For burst index, figure 4.68 shows no significant differences between overdrying and normal drying until the sheets are overdried at 320°C, at which point burst is significantly reduced by about the same amount for both the steam and air overdried sheets. Interestingly, the steam dried sheets maintain their approximately 30% improvement in burst for all drying temperatures, regardless of whether dried normally or overdried. The tensile index, figure 4.69, behaves in a similar fashion as the burst index. Tensile energy absorption index and stretch are also decreased by overdrying at



Figures 4.67 - 4.69: Effect of Drying Fluid and Temperature on Bulk, Burst Index and Tensile Index

240°C and higher (figures 4.70 and 4.71).

Tear index, figure 4.72, which is very sensitive to fibre degradation, does not vary much except at 320°C where both the steam and air overdried tear indices have decreased about 1/3 their original values. This is because of weakened fibres, as will be seen from the zero-span breaking length results further on. Folding endurance, figure 4.73, a significant indicator of embrittlement in the sheet, shows that the steam and air overdried sheets have been deteriorated by overdrying only at the highest temperature of 320°C.

Figure 4.74 shows that overexposure at 160 or  $240^{\circ}$ C leads to no loss in fibre strength, while overexposure to a  $320^{\circ}$ C drying medium, whether air or steam, decreases the fibre strength. The results from this test are in disagreement with those from the previous study (11), which were obtained for the temperature range of  $360 - 430^{\circ}$ C. Even for this higher temperature range, they observed degradation in zero-span breaking length only for overdrying in air, not in steam.

For internal bond strength, figure 4.75 shows the same pattern, i.e. that overdrying in steam or air at 160 or 240°C is unimportant but at 320°C results in a sharp decrease. Again however, as in normal drying, the steam overdried sheet maintains a considerably higher internal bond strength than the one overdried in air.

Extended exposure to a high temperature drying fluid should improve wet strength due to cross-linking, and this is indeed confirmed. Figure 4.76 reveals however that at 160°C overdrying produces only a small change in wet tensile strength. A longer



Figures 4.70 - 4.72: Effect of Drying Fluid and Temperature on Tensile Energy Absorption Index, Stretch and Tear Index



Figures 4.73 - 4.75: Effect of Drying Fluid and Temperature on Fold, Zero-Span Breaking Length and Scott Internal Bond Strength

exposure time at 160°C would probably be necessary to obtain this effect. At 240°C, where the wet strength improvement was already substantial in normal drying, this further increase in wet strength is even greater. Where the improvements in wet strength due to cross-linking for drying of normal duration at 320°C were much higher yet than at 240°C, overdrying at 320°C in either drying medium reduces wet strength slightly. This reduction could be due to the counterbalancing effect of thermal degradation of fibre strength at this temperature, as seen in figure 4.74.

The sizing effect obtained by subjecting paper to high temperatures is evident in figure 4.77. The effect is negligible at 160°C, becomes strong at 240°C, and is so intense at 320°C that even after 1 hour the overdried sheets had not absorbed the water droplet. The sizing effect is stronger in steam than in air drying. As measured by air resistance, figure 4.78, the steam overdried sheets have a lower permeability than those overdried in air, although both have decreased permeability compared to their normally dried counterparts, perhaps because of the increased amount of sizing or the plasticization of the fine material which forms a film. This effect also reduces the sheet surface roughness, as seen from figure 4.79.

# 4.3.7.2 Effect on optical properties

The decrease in optical properties accompanying overdrying is evident for both steam and air dried sheets (figures 4.80 to 4.83). At 160°C, extended overdrying produces no loss in brightness or scattering coefficient but at higher temperatures, the loss of these



Figures 4.76 - 4.78: Effect of Drying Fluid and Temperature on Wet Tensile Strength, Water Drop Absorption Time and Air Resistance



Figures 4.79 - 4.81: Effect of Drying Fluid and Temperature on PPS Roughness, Brightness and Opacity

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Figures 4.82 - 4.83: Effect of Drying Fluid and Temperature on Specific Scattering Coefficient and Specific Absorption Coefficient

optical properties (figure 4.80 and 4.82) becomes pronounced. The loss in brightness and scattering coefficient is greater for air overdried sheets, which when normally dried have higher brightness and scattering coefficient values than provided by steam drying. The brightness results do not agree with the overdrying results from the previous study (11), which found that overdrying reduced the brightness only for overdrying in air. Opacity and absorption coefficient (figures 4.81 and 4.83) show comparable increases with overdrying because of the brown colored products of thermal degradation.

#### 4.3.7.3 Discussion

The results of the present study establish that extended overdrying, i.e. drying three times longer than normal, at a sufficiently high temperature causes deterioration of sheet strength and optical properties, whether the drying medium is air or superheated steam. With the drying medium at 160°C, neither the physical nor the optical properties of the TMP paper are affected by such excessive overdrying. With the drying medium at 240°C, the physical strength is unaffected but overdrying significantly degrades the optical properties. At 320°C, the extended overdrying severely degrades both the strength and the optical properties of TMP paper.

The lack of agreement between the overdrying results of this study and those of the only other study investigating overdrying (11) appear to be due to differences in the experimental setup. In the present study, the fully restrained handsheet was suspended vertically in an atmosphere of superheated steam or hot air which flowed parallel to the plane of the sheet. Thus both sides of the sheet were exposed to the drying fluid. In the previous study, fully restrained handsheets were dried by jets of steam or air which impinged at 90° on the sheet supported by a metal baseplate at 100°C. As the nozzle plate open area ratio was about 16% (11), not 1.8% as given incorrectly earlier (88), the supporting baseplate played a greater role in the heat transfer than was originally believed. Evidently the sheet temperature did not attain the drying medium temperature when the sheet was dry, but remained at some temperature intermediate between the baseplate temperature and the drying fluid temperature.

One piece of evidence obtained in the present study confirms that the sheet temperatures did not attain the drying fluid temperature in the previous study. It was found here that overdrying by a factor of 3 in air at 380°C resulted in ignition and combustion of the sheet. As the previous study included overdrying by a factor of 3 or 4 in air at 430°C without burning the sheet, it is evident that in those experiments the sheet temperature was significantly below the drying fluid temperature.

# 4.4 Paper from refiner mechanical pulp

Refiner mechanical pulp (RMP) is made in a process similar to that used for making

TMP except that the chips are not steamed prior to refining. The pulps are quite similar although RMP has lower proportions of long fibres and produces sheets of slightly lower physical strength.

## 4.4.1 Superheated Steam Drying compared to Air Drying

RMP sheets were dried in steam and in air at temperatures of 20°C (for air), 130°C and 300°C using the sheet support and special sliding frame for press drying described in Chapter 3. A limited number of sheet properties were measured (figures 4.84 to 4.90).

The effect of steam drying on RMP is almost identical to that observed for TMP. It is therefore concluded that the same mechanisms are operating, namely softening of the lignin and hemicellulose fraction at the high sheet temperatures, resulting in increased bonded area. Figure 4.85 shows that bulk remains essentially constant, while burst index, tensile index and tensile energy absorption index (figures 4.86 to 4.88) increase in steam drying by about 20%. Tear index, folding endurance and stretch are the same for steam dried sheets as those dried in air (figures 4.89 to 4.91). The properties of these RMP sheets and the improvements achieved by steam drying are similar to those obtained for TMP, except for tear index which is slightly lower.

# 4.4.2 Effect of pressing in superheated steam drying

Experiments were made to determine whether pressing could take advantage of the



Figures 4.84 - 4.86: Effect of Drying Fluid, Temperature and Pressing on Bulk Standard Deviation, Bulk and Burst Index



Figures 4.87 - 4.89: Effect of Drying Fluid, Temperature and Pressing on Tensile Index, Tensile Energy Absorption Index and Tear Index



Figures 4.90-4.91: Effect of Drying Fluid, Temperature and Pressing on Fold and Stretch

high sheet temperatures and softened state of the wood polymers to produce a very well bonded sheet of increased strength. The combination of press drying in a superheated steam or hot air environment was investigated using the pneumatic press and attachments described in Chapter 3. With the press, the load cell measuring the sample mass could not be used, nor was sheet temperature monitored during drying with pressing (although this could have been done). Drying times selected for the pressed sheets were the same as for the unpressed paper. For all sheets, pressing was started 10 seconds after sheet insertion into the dryer and was continued for 10 seconds, at a pressing pressure of 0.45 MPa. (Pressures used in other studies range from 0.1 to 7 MPa, although studies where the pressure is above 2 or 3 MPa are usually referred to as impulse drying rather than press-drying). In all graphs, the abbreviation "pr" is used for pressing.

Figure 4.84 shows that the bulk standard deviation is no higher for the pressed than the unpressed RMP sheets, indicating that fairly uniform pressing was achieved over the sheet surface, and figure 4.85 shows that pressing reduces sheet bulk as would be expected. The physical strength properties (figures 4.86 to 4.90) are generally higher for the pressed sheets than the unpressed sheets in both air and steam, except tear index which was reduced. Stretch (figure 4.91) is unchanged by pressing except for pressing at 130°C in air where, for unknown reasons, it apparently increased. Pressing at room temperature has less of an effect than hot pressing. For all properties, the effect of pressing is more significant at 130°C than at 300°C, in both steam and air. The pressed sheets have the same properties regardless of whether they were pressed in air or steam, although improvement in properties due to pressing is greater in air than in steam. For

example, in air at 130°C, burst and tensile indices are increased 60-70% by pressing, but at 300°C the improvement is only approximately 30%. In steam, the improvements due to pressing are a much lower 40% at 130°C and 15% at 300°C. The differences in mechanisms are highlighted by the observations that the strength increases brought about by pressing are accompanied by a bulk reduction of about 40%; the smaller 20% improvement in strength properties arising from steam drying relative to drying in air is accomplished with no reduction in bulk. The reduction in bulk implies improved sheet consolidation and bonding due to the pressing together of the softened sheet components.

It is believed that the greater effect of pressing at 130°C than at 300°C is because the sheet was wetter prior to pressing at the lower temperature, as pressing always began 10 seconds after sheet insertion into the drying chamber. This observation shows the necessity of applying press drying while the sheet is still sufficiently moist. Byrd (89) recommends pressing at a maximum of 60% solids content to ensure adequate interfibre bonding. From the load cell signal, in the present work the sheet solids content after 10 seconds at 130°C is 40%; at 300°C it is about 50%.

The reason pressed sheets have the same strength properties regardless of drying fluid in which they were pressed is that the stainless steel pressing plate was located inside the drying chamber in contact with the hot drying fluid. Because the pressing plate was at the drying fluid temperature, the sheet quickly reached 100°C and presumably increased to 148°C, the saturation temperature of water at 0.45 MPa, regardless of drying fluid. The improvement due to pressing is greater in air than in
steam because of the already improved strength properties of the unpressed steam dried sheets.

### 4.5 Industrial significance of superheated steam drying effects

The industrial significance of the effects produced by superheated steam drying of paper made from mechanical pulp can be evaluated by comparing the properties of this paper with those of paper from other types of pulp and different processes. Such an examination establishes some quantitative bases for evaluating the importance of superheated steam drying effects.

Figure 4.92 (90) shows the typical ranges of tensile index - density relations for a variety of pulps. Also shown are the range of these values in the present study for TMP paper dried in superheated steam and in air, as recorded in figures 4.2 and 4.5. The 20 - 30% increase in tensile strength obtained with steam drying without change in sheet density would permit a steam dried RMP sheet to have a tensile strength approaching that of a conventionally dried TMP sheet, or a steam dried TMP sheet to have the tensile strength of an air dried CTMP sheet. The results should be quite similar for burst index as well. These approximate equivalences are quite significant as the complexity and cost of producing pulp increases from GWD to RMP to TMP to CTMP to SBK.

Figure 4.93 (90) shows the analogous ranges of light scattering coefficient - tensile index relations for these same pulps. The ranges of these properties are also shown for TMP paper dried in superheated steam and in air, as recorded for the present study in



Figure 4.92: Relation between Tensile Index and Density for Various Pulps



Figure 4.93: Relation between Light Scattering Coefficient and Tensile Index for Various Pulps

figures 4.5 and 4.22. For a specific mechanical pulp (GWD, RMP and TMP), increased fines content and external fibrillation leads to higher tensile strength as well as improved light scattering coefficient. The results reported in section 4.3.4 of the present study establish that with superheated steam dried TMP paper as well, the fines content of the paper affects tensile strength and light scattering coefficient in the same way as noted above. Moreover, it can be seen from figure 4.93 that GWD, the pulp with the highest fines content, has higher light scattering coefficients than all the other pulps.

From the perspective of the properties of paper from a broad range of pulp, figure 4.93 shows that as one changes to pulps giving stronger paper, there is an inevitable trade-off in loss of optical properties. The primary mechanism of improved strength for the higher grade pulps is improved bonding between the fibres. The improved strength for TMP paper dried in superheated steam instead of air derives from the same mechanism - improved bonding between the fibres. Thus with the mechanism of better bonding, the coupling of strength increase to brightness decrease, which applies for the range of pulps shown on figure 4.92, applies likewise for the change of drying process from drying in air to drying in steam.

The improvements in tensile strength obtained with steam drying are accompanied by a loss of scattering coefficient of about 10  $m^2/kg$ . By reference to figures 4.92 and 4.93, it is seen that this loss is of the same order as the loss in scattering coefficient which occurs when going, for example, from an RMP sheet to a TMP sheet at the same sheet density. As a rough approximation, then, for a given sheet density superheated steam drying can make an RMP sheet about like a conventionally dried TMP sheet, and a TMP sheet about like a conventionally dried CTMP sheet, in terms of both strength and optical properties. The popularity of CTMP indicates that despite its greater production cost, the market values the increased strength properties more than the decreased optical characteristics of this pulp. The benefits of superheated steam drying are obvious if it can be shown that the process produces a product similar to CTMP but with the less expensive TMP pulp, for example, while at the same time improving the drying efficiency.

The improvement of strength properties without reduction of bulk brought about by steam drying is also important from the point of view of sheet stiffness. The stiffness of a beam of rectangular cross-section is proportional to the third power of thickness, and this relation is approximately true for paper (17). Density is commonly associated with sheet stiffness, although several contradictory factors are involved. At equal basis weight, a dense sheet has a decreased thickness which tends to decrease stiffness; however high density sheets are usually associated with high levels of interfibre bonding which increases sheet stiffness. Although the stiffness of steam dried sheets was not measured, it would be expected that the increase in bonding without decrease in bulk would result in an increase of stiffness, which is highly desirable for many products, such as packaging and writing paper, tabulating and index cards, paper cups, etc. Often the basis weight of a product is determined by the stiffness required; increasing stiffness

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by steam drying could permit lower basis weight and saving of material.

Most paper grades are not made entirely from one type of pulp, but from pulp blends, and may contain a wide variety of fillers and additives. The blend depends on the particular paper product. For newsprint, mechanical pulp is the primary component, strengthened by the addition of small amounts of chemical pulp to increase the sheet wet and dry strengths. The profitability of the newsprint manufacture is highly influenced by the percentage of costly chemical pulp required as a strengthening agent.

Conventional newsprint is a pulp blend of GWD strenghtened by 15 - 20% semibleached kraft pulp (91). To decrease the percentage of chemical pulp, the strength of the mechanical pulp must be increased. Replacement of part of the GWD by TMP or other higher strength mechanical pulp can reduce the addition of chemical pulp content by 10%. Replacement of all of the GWD by TMP or other higher strength mechanical pulp further reduces the chemical pulp requirement, and in some cases a 100% TMP furnish can be used.

The Mohlin and Wennberg study (92) of the interaction between mechanical and chemical pulps indicates the strength improvements achieved by adding bleached softwood kraft to GWD. Addition of 20% lightly refined chemical pulp to the GWD results in a 10% improvement in the tensile index, while 20% of highly refined chemical pulp gives a 20% improvement, presumably with some loss in opacity due to the lower fines content of the chemical pulp, although this information is not provided. Improvements in strength of this order could be obtained by steam drying and would

eliminate the need for the costly reinforcement chemical pulp.

However, improvements in dry strength are not the only reason chemical pulp is added to GWD; the improvements obtained in wet strength are large and are very important for runnability in conventionally designed dryers. This benefit would not be obtained by steam drying. However for the case of TMP and other higher strength mechanical pulps, the wet strength is much greater than for GWD, and the improvement of wet strength by the addition of chemical pulp becomes less critical. Superheated steam drying could then be used to eliminate the reinforcement chemical pulp, provided the optical and other properties of the dried sheet remained satisfactory. More research would be needed to determine for which paper grades and blends the use of superheated steam drying would be useful, but it can be seen that there are interesting possibilities. An incentive for such research is the substantial range in price of various grades of pulp, currently in the range of \$230/ton for GWD and TMP, \$300/ton for CTMP and \$700/ton for SBK. These approximate commercial values again indicate the extent to which the market places more value on the increased strength than on the decreased optical properties.

It is difficult to compare the strength improvements obtained by superheated steam drying with those obtained by press or impulse drying, since the sheet density is greatly increased by the latter processes. However, the results from press and impulse drying studies are useful in establishing whether the improvements in strength properties obtained in the present, low intensity, laboratory dryer could be realized in an industrial dryer section with high drying rates and short sheet residence times in the dryer. Press and impulse drying studies show that elevating the sheet temperature to high values, 100°C or more, for even very small nip residence times of the order of milliseconds, results in a sheet with greater strength than a sheet cold pressed to the same density and dried. This evidence implies that, with a sufficiently moist sheet at 100°C, thermal softening of the polymers and the resulting increased bonding occurs quickly relative to the time required for superheated steam drying under industrial conditions.

One aspect requiring investigation in future work is the behavior of superheated steam dried sheets in calendering, since they generally have a rougher surface than air dried sheets. Temperature gradient calendering could perhaps be used to flatten only the surface fibres without much reduction in bulk.

# 4.6 Summary and Conclusions

The effect of superheated steam drying on the properties of paper made from mechanical pulp has been determined. Superheated steam drying provides a unique way of raising the sheet temperature which, unlike press or impulse drying, does not necessitate strong z-direction restraint resulting in substantially decreased bulk. For drying where the sheet is in contact with the drying fluid on both sides, superheated steam drying results in a significantly higher sheet temperature than air drying. For an atmospheric pressure superheated steam dryer, the sheet temperature is at 100°C until the end of the constant rate period of drying, while in air drying it is much lower,

controlled by the wet bulb temperature which is in the range 40 to 55°C for dry air in the temperature range 160 to 320°C.

The higher sheet temperature reached extremely quickly in steam drying while the sheet moisture content is high has the effect of softening the temperature and moisture sensitive hemicellulose and lignin polymers and allowing them to flow to some degree. The fine fraction of the pulp, particularly rich in hemicellulose and lignin, is especially important. This plasticization of hemicellulose and lignin results in a greater bonded area between the fine material and at those areas where the stiff mechanical fibres are already in close proximity with fine material. As seen from the constant bulk, the increase in bonded area does not result in any contraction of the sheet structure since it is not the stiff whole fibres which are deforming but primarily the fine material between the fibres.

For mechanical pulp, the increase in bonded area obtained in superheated steam drying regardless of steam temperature results in improved strength properties; burst index, tensile index, elastic modulus, etc. are improved by 20 - 30%, with little change in folding endurance or tear index. Fibre strength remains unchanged. As a result of the increased bonding, but not due to any color change, the optical properties are slightly decreased; brightness drops by 5 points and the specific scattering coefficient loss is up to  $10 \text{ m}^2/\text{kg}$ . The sheet surface is a little rougher, perhaps as a result of the condensation of water which occurred in the early stages of steam drying as carried out in the laboratory and/or the plasticization of the fine fraction which sinks slightly into the surface of the sheet below the level of the stiff whole fibres.

To obtain these effects, it was found that the initial sheet solids content must be approximately 60% or lower when steam drying is initiated, and the drying must be continued to approximately 70% solids content or higher. The effects of superheated steam drying are retained when steam dried sheets are recycled and steam dried again; however, if steam dried sheets are recycled and dried in air the improvements are lost. Overdrying in steam appears to be just as harmful as overdrying in air, with deterioration increasing strongly with temperature; it results in a decrease in the fibre strength properties, sheet strength properties, and optical properties.

These findings can have important industrial implications. For example, TMP dried in superheated steam may approximate the properties of the more costly CTMP. Depending on the fines content and the application, mechanical pulp dried with superheated steam may no longer require reinforcement chemical pulp to achieve the required strength properties. The loss in optical properties is not insignificant, but is no different from losses occurring when changing from RMP to TMP at any given sheet density, for example. Moreover, optical properties may be less of a concern than in the past since recycled products have become more common. If it is confirmed that the steam drying process has a higher drying rate, higher energy efficiency, and lower capital cost, in addition to the paper properties benefits and reduced fire and explosion hazard, it will be considered a most attractive alternative to conventional drying techniques.

#### Chapter 5

#### PROPERTIES OF PAPER FROM CHEMICAL PULP

The effects of superheated steam drying on the physical, optical and chemical properties of handsheets made from untreated, bleached or beaten kraft pulp are presented and compared to those obtained with air drying under similar conditions. The effect of overdrying is also discussed.

# 5.1 Paper from Kraft Pulp

Paper from kraft black spruce pulp has higher physical strength properties than that made from any other pulp. Kraft pulp is thus aptly named, as "kraft" means strong in Swedish and German. In kraft pulping, the world's dominant pulping process, a liquor composed of sodium hydroxide and sodium sulfide dissolves the lignin holding the individual fibres together in wood. For a typical yield of 48%, the lignin and hemicellulose contents of kraft pulp are about 5% and 12%, compared to 28% and 27% for TMP. The large decrease in lignin content results in long flexible fibres capable of high degrees of bonding compared to mechanical pulp fibres.

# 5.1.1 Effect on Physical Properties

Figure 5.1 shows that the bulk of steam dried sheets is higher than that of sheets dried in air by about 3%, except at 320°C where it is about 14% higher. The air dried

sheet bulk is independent of drying temperature. The difference in sheet bulk is perhaps the result of a small amount of unintentional overdrying, as section 5.1.4 shows that overdrying in both air and steam results in increased bulk.

David et al. (11), in their superheated steam drying study, also found that the bulk of steam dried sheets was higher than for air dried sheets. Unlike the present study, the air dried sheet bulk in their study was not independent of temperature, increasing from approximately 2.2 cm<sup>3</sup>/g at 20°C to 3 cm<sup>3</sup>/g for drying fluid temperatures of 225°C and higher, indicating that some overdrying probably occurred. The only other superheated steam drying study, Cui et al. (46), found that kraft sheet bulk was about 1% higher for steam drying compared to hot surface drying in air.

Contrary to the results obtained for mechanical pulp in Chapter 4, burst index, tensile index, folding endurance, and tear index (figures 5.2 to 5.5) of the steam dried sheets are up to 10% lower than for those dried in air. Figures 5.6 to 5.9, show that the differences in strength properties are in large part associated with changes in sheet bulk. The high experimental variability of the measured tensile index with air drying, apparent in figure 5.3, limits the conclusions possible from figure 5.7 as well. Stretch and tensile energy absorption index, figures 5.10 and 5.11, are similar for steam and air dried paper except at 320°C where they are somewhat decreased for steam drying.

The results for burst index disagree with those from David et al. (11), where it was found that burst index for the steam dried kraft paper was about 13% higher than for the air dried sheets, even though steam drying gave higher bulk. The probable cause of this



Figures 5.1 - 5.3: Effect of Drying Fluid and Temperature on Bulk, Burst Index and Tensile Index

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Figures 5.4 - 5.6: Effect of Drying Fluid and Temperature on Fold and Tear Index, Effect of Bulk on Burst Index



Figure 5.7 - 5.9: Effect of Bulk on Tensile Index, Fold and Tear Index

anomaly is that their sheets dried in air were overdried; proof of which is that for air drying the burst index of their paper dried at 20°C is much higher than for drying at higher temperatures. As in the present study, they found little difference between the tear index of steam and air dried sheets. The strength property results of Cui et al. (46) for kraft paper are similar to those found here in that burst index, tensile breaking length and tear index were somehwat lower for their steam dried sheets.

Fibre strength as measured by dry and wet zero-span breaking length (figure 5.12 and 5.13) is unchanged by steam drying or by the temperature of the drying fluid. This observation disagrees with David et al. (11), who found that with increasing drying fluid temperature, zero-span breaking length increased with steam but decreased with air.

The amount of bonding as measured by z-direction tensile strength is lower for the steam dried sheets (figure 5.14), as would be expected from their slightly higher bulk and lower sheet strength properties. The formation of covalent bonds is not an important factor since wet tensile strength (figure 5.15) is the same for air and steam drying, except at 320°C where it is lower for the steam dried sheet. The degree of sizing, as indicated by the time required to absorb a drop of water, figure 5.16, is about the same for steam and air dried sheets.

Unlike paper from mechanical pulp, the roughness of steam and air dried kraft paper is practically the same, (figure 5.17). As the main mechanism proposed for increased roughness of TMP paper was thermal softening of the lignin and hemicellulose rich fines



Figures 5.10 - 5.12: Effect of Drying Fluid and Temperature on Stretch, Tensile Energy Absorption Index and Zero-Span Breaking Length



Figures 5.13 - 5.15: Effect of Drying Fluid and Temperature on Wet Zero-Span Breaking Length, Scott Internal Bond Strength and Wet Tensile Strength

fraction and its sinking into the sheet surface, this mechanism evidently does not occur in steam drying of kraft paper.

### 5.1.2 Effect on Optical Properties

Steam dried sheets have higher brightness than those dried in air, while opacity remains essentially the same (figures 5.18 and 5.19). The specific scattering coefficients (figure 5.20) for the steam dried sheets are also higher than for drying in air, by about  $4 \text{ m}^2/\text{kg}$  or 12% over the 160 - 320°C range of drying temperature. Absorption coefficients (figure 5.21) show no difference with drying fluid or its temperature, indicating that the gain in brightness for steam dried sheets is not due to a change in color but rather to a change in the scattering surfaces of the sheet commonly associated with decreased strength properties and increased bulk. In previous work, David et al. (11) measured no difference in brightness between the steam dried and air dried sheets, despite the differences they observed in sheet bulk and strength properties.

## 5.1.3 Effect on Chemical Properties

Unlike high lignin content mechanical pulps, kraft pulp is amenable to a variety of wet chemical tests. The viscosity of a 0.5% cellulose solution in 0.5M cupriethylenediamine (CED) solvent indicates the average degree of polymerization (DP) of the cellulose, considered to be more degraded the lower the DP. Fibre strength is dependent on DP, and CED viscosity often shows degradation of the cellulose structure



Figures 5.16-5.18: Effect of Drying Fluid and Temperature on Water Drop Absorption Time, PPS Roughness and Brightness



Figures 5.19 - 5.21: Effect of Drying Fluid and Temperature on Opacity, Specific Scattering Coefficient and Specific Absorption Coefficient

before any loss in fibre strength can be detected by such tests as the zero-span breaking length (93). Figure 5.22 shows that viscosity decreases as drying fluid temperature increases. Exposure to high temperature at the end of the drying period in either air or steam thus degrades the cellulose, with the extent of degradation not dependent on the drying fluid.

The 1% sodium hydroxide solubility test extracts low molecular weight components consisting mainly of hemicellulose and degraded cellulose, and indicates the degree of degradation by heat, light, oxidation or other processes (93). Dried sheets are extracted with hot 1% sodium hydroxide solution for 1 hour and the loss in mass calculated as a percentage. Within the scatter of the data shown in figure 5.23, it is difficult to conclude any difference between steam and air dried sheets.

# 5.1.4 Overdrying in Superheated Steam and in Air

The procedure used for overdrying kraft sheets in steam and in air is the same as that described in Chapter 4 for TMP paper; the sheets were dried three times longer than the time used for normal drying. For drying fluid temperatures of 160, 240 and 320°C, normal drying times in air were approximately 60, 45 and 30 seconds, and 140, 80 and 20 seconds in steam.

Overdrying in steam or in air results in an increase of sheet bulk (figure 5.24) and a decrease in all the sheet strength properties (figures 5.25 - 5.31). Only the effect of overdrying on tensile index (figure 5.28), is not clear because of the scatter in the data.



Figures 5.22 - 5.23: Effect of Drying Fluid and Temperature Viscosity and 1% NaOH Solubility



Figures 5.24 - 5.26: Effect of Drying Fluid and Temperature on Bulk, Burst Index and Tear Index



Figures 5.27 - 5.29: Effect of Drying Fluid and Temperature on Fold, Tensile Index and Stretch

With either drying fluid the loss in strength properties becomes progressively worse as the drying fluid temperature is increased from 160 to 320°C.

Overdrying in either steam or air has no effect on dry or wet fibre strength at drying fluid temperatures of 160 and 240°C, while at the temperature of 320°C the zero-span strengths are greatly reduced, figures 5.32 and 5.33. At 320°C, overdrying in steam seems to degrade the strength more than in air. Unlike the present study, David et al. (11) found that overdrying in air reduced zero-span breaking length while overdrying in steam had no effect.

The increase in wet tensile strength that occurred with increasing drying fluid temperature in normal dryin<sub>b</sub>,  $c_{,c}$  ure 5.15, is found again with overdrying (figure 5.34) as would be expected because of the formation of covalent bonds (94). Sheet roughness (figure 5.35) is not affected by overdrying at all temperatures, just as was found for normal drying.

The optical properties (figures 5.36 - 5.39) show no effect of overdrying in either steam or air at 160 or 240°C, but at 320°C, both air and steam overdrying significantly reduce sheet brightness and increase opacity. The decrease in brightness for overdrying at 320°C is due primarily to a large increase in the specific absorption coefficient of the paper which has darkened at this temperature, although there is some loss in scattering coefficient as well. This finding is in disagreement with the results from study (11) where overdrying in air but not in steam resulted in decreased brightness.



Figures 5.30 - 5.32: Effect of Drying Fluid and Temperature on Tensile Energy Absorption Index, Scott Internal Bond Strength and Zero-Span Breaking Length



Figures 5.33 - 5.35: Effect of Drying Fluid and Temperature on Wet Zero-Span Breaking Length, Wet Tensile Strength and PPS Roughness



Figures 5.36 - 5.37: Effect of Drying Fluid and Temperature on Brightness and Opacity



Figures 5.38 - 5.39: Effect of Drying Fluid and Temperature on Specific Scattering Coefficient and Specific Absorption Coefficient

# 5.1.5 Discussion

The results show that for kraft paper, the effect of steam drying is entirely different from that for paper from mechanical pulp. For TMP paper, superheated steam drying improved fibre bonding, which results in increased strength but reduced optical properties. For steam drying of kraft paper the findings are just the opposite - reduced strength and improved optical properties. The slightly higher bulk for steam dried sheets has the expected effect of causing small decreases in the strength properties and small improvements in the optical properties. For paper that is overdried, there is little difference in properties whether dried in steam or in air, both of which result in increased bulk, increased brightness and scattering coefficient, accompanied by deterioration of the strength properties, especially at the higher temperatures. Overdrying in steam or air at 320°C is sufficiently severe to seriously degrade the fibre strength, which would probably be observed at lower temperatures as well for even longer overdrying.

Without further experimentation it is not possible to conclude with certainty the mechanisms leading to the observed effects, but plausible explanations can be advanced. If the results obtained for drying in steam at 320°C are excluded (since it is suspected that a certain amount of overdrying occurred at this condition), the paper properties show essentially the same trends with drying fluid temperature regardless of drying fluid, with a relatively constant difference between the steam and air dried properties. Therefore, the differences between steam and air dried kraft sheets must be related in some way to

the higher sheet temperature reached in the constant rate period of steam drying, 100°C instead of 40 - 55°C for drying in air. For kraft paper however, unlike paper from mechanical pulp, this difference results in beneficial effects for optical properties but detrimental effects on strength. The probable explanation is that chemical pulp fibres, very flexible and conformable, produce sheets of high relative bonded area; no further increase in bonding potential is accomplished by softening of the limited amount of lignin and hemicellulose at the higher temperatures reached in the constant rate period of steam drying relative to that for drying in air.

Another effect of high sheet temperature during the constant rate period of drying is a decrease in drying stress of a fully restrained sheet. Htun (36) found that for constant drying time, a bleached kraft fully restrained sheet dried in air at 30°C had a final drying stress about 45% higher than a similar sheet dried in 80°C air because of thermal stress relaxation effects. He observed that final drying stress was also influenced by drying time, but to a lesser extent than by temperature; for constant drying temperature, a ten fold increase in drying time resulted in a final drying stress decrease of about 20%, for constant drying temperature. In the present study, differences in steam and air drying times for any drying fluid temperature were twofold or less; thus differences in sheet temperature but not drying time differences could have resulted in significant differences in final drying stress of steam and air dried sheets.

It has been well documented that decreased drying stress, achieved for example by decreasing the degree of restraint under which a sheet is dried, leads to decreased

strength properties and decreased density (95). These effects are thought to be due to reduced stress distribution, increased microcreping at fibre crossings and increased modulus of elasticity of the fibres. For example, a softwood unbleached kraft sheet having a CSF of 700 (similar to the pulp used in the present study), had a bulk of 2.29 cm<sup>3</sup>/g when dried unrestrained and 2.02 cm<sup>3</sup>/g when dried restrained. The unrestrained sheet had 25% lower tensile strength, 67% lower elastic modulus and a stretch almost three times greater (95). For a waste newsprint furnish which would be expected to behave similarly to the TMP furnish used in the present study, the effects were much smaller; the bulk difference between unrestrained and restrained drying was negligible, 2.49 and 2.48 cm<sup>3</sup>/g, and the tensile strength, elastic modulus and stretch properties for the unrestrained and restrained sheets were much more similar than for the kraft pulp unrestrained and restrained sheets (95).

Thus, although thermally induced stress relaxation must occur to some extent in steam drying of paper from mechanical pulp, the strength decrease which is observed with kraft paper is not seen with paper from mechanical pulp because any such effect is overshadowed by the beneficial effects of increased bonded area arising from the thermal softening of lignin and hemicellulose. For kraft paper, the detrimental effects on sheet strength of decreased drying stress arising from the higher temperatures reached in the constant rate period of steam drying are apparent in the absence of the strong beneficial effects on sheet strength that apply for TMP paper.

# 5.2 Beaten Kraft Pulp

Beating, a laboratory process frequently used for chemical pulp, simulates refining using controlled and reproducible conditions. The purpose of beating is to determine the papermaking potential of the pulp. In this mechanical process, pulp slurry passes between rotating bars and a stationary bedplate, resulting in increased wet fibre flexibility, swelling, amount of fines, sheet density, relative bonded area (RBA), and strength properties (14). Handsheets formed from kraft pulp beaten to five different levels in a Valley beater and dried with 280°C superheated steam were compared to sheets dried in air under similar conditions. The objective of this was to determine whether the effect of superheated steam drying is influenced by degree of bonding potentially attainable by the sheet.

Figures 5.40 to 5.47 show, for both steam and air drying, the trends expected to occur with increased amount of beating, i.e. sheet bulk reduction accompanied by increased burst index, folding endurance, tensile index, stretch, tensile absorption energy index, internal bond, and decreased tear index. As with sheets made from unbeaten pulp, the steam dried sheets made from beaten pulp have higher bulk (up to 6%) and decreased strength properties (up to 13%) relative to comparable sheets which are dried in air.

The decreased amount of bonding of the steam dried sheets also affects their optical properties; brightness and scattering coefficients are higher than for air dried sheets (figures 5.48 and 5.49), while the lower absorption coefficient leads to a slightly decreased opacity (figures 5.50 and 5.51). There is no significant difference between



Figures 5.40 - 5.42: Effect of Beating Time and Drying Fluid on Bulk, Burst Index and Fold



Figures 5.43 - 5.45: Effect of Beating Time and Drying Fluid on Tensile Index, Stretch and Tensile Energy Absorption Index


Figures 5.46 - 5.48: Effect of Beating Time and Drying Fluid on Scott Internal Bond Strength, Tear Index and Brightness



Figures 5.49 - 5.51: Effect of Beating Time and Drying Fluid on Specific Scattering Coefficient, Specific Absorption Coefficient and Opacity

fibre strength as measured by dry or wet zero-span breaking length (figures 5.52 and 5.53). The roughness of steam and air dried sheets are very similar (figure 5.54).

Thus, the effect of steam drying on sheets made from beaten pulp is the same as for sheets from unbeaten pulp; the postulated reduction of drying stress caused by steam drying again results in increased bulk, decreased strength properties and slight improvements in optical properties.

### 5.3 Bleached Kraft Pulp

The main effect of bleaching is to remove lignin which contains the chromophoric groups responsible for the dark color of pulp. The 5% lignin content of kraft pulp is typically reduced to 1% when semi-bleached and 0% when fully bleached, with little change in hemicellulose content. Kraft unbleached, semi-bleached and fully bleached handsheets dried at 320°C in steam were compared to sheets dried in air under similar conditions. Figure 5.55 shows that, as with the unbeaten and beaten kraft sheets, the steam dried semi-bleached and bleached kraft sheets have higher bulk than their air dried counterparts, resulting in the expected decrease in burst index, folding endurance, tensile index, tensile energy absorption index and internal bond strength (figures 5.56 to 5.60). Tear index normally increases with decreased bonding for kraft paper; this is the case for the air dried sheets, but for unknown reasons the steam dried sheets do not follow this trend and have lower tear than the air dried sheets even though they are less well



Figures 5.52 - 5.54: Effect of Beating Time and Drying Fluid on Zero-Span Breaking Length, Wet Zero-Span Breaking Length and PPS Roughness



Figures 5.55 - 5.57: Effect of Bleaching and Drying Fluid on Bulk, Burst Index and Fold

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Figures 5.58 - 5.60: Effect of Bleaching and Drying Fluid on Tensile Index, Tensile Energy Absorption Index and Scott Internal Bond Strength

bonded (figure 5.61). Stretch for the air dried sheets is lower than for the steam dried sheets as was observed for the beaten sheets in the preceding section.

The optical properties are shown in figures 5.63 to 5.66. The scattering coefficient is higher for the steam dried sheets (figure 5.65), indicating the larger number of unbonded surfaces available to reflect light, although this does not show up as consistently higher brightness (figure 5.63) because of erratic differences in the absorption coefficients (figure 5.66) between the steam and air dried sheets. As would be expected, the air and steam dried fully bleached sheets have higher brightness and lower opacity (figure 5.64) than the unbleached or semi-bleached sheets.

There is little difference in the dry or wet zero-span breaking length of the steam and air dried sheets, except for the paper made from fully bleached pulp which has lower fibre strength when steam dried (figures 5.67 and 5.68). This measurement is probably not significant since it does not show up in the viscosity test (figure 5.69) which is more sensitive than zero-span breaking length for detecting fibre strength degradation. A decrease in fibre strength with increasing amount of delignification can be observed in both the zero-span breaking length and viscosity tests. This decrease is the reason for the diminished strength properties of steam or air dried paper made from fully bleached kraft pulp. The roughness of the sheets is not affected by the drying fluid (figure 5.70).



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Figures 5.61 - 5.63: Effect of Bleaching and Drying Fluid on Tear Index, Stretch and Brightness



Figures 5.64 - 5.66: Effect of Bleaching and Drying Fluid on Opacity, Specific Scattering Coefficient and Specific Absorption Coefficient



Figures 5.67 - 5.68: Effect of Bleaching and Drying Fluid on Zero-Span Breaking Length and Wet Zero-Span Breaking Length





Figures 5.69 - 5.70: Effect of Bleaching and Drying Fluid on Viscosity and PPS Roughness

#### 5.4 Summary and Conclusions

The effect of superheated steam drying on the properties of kraft pulp are smaller and in the opposite direction than those observed with mechanical pulp. Thus, while steam drying of TMP paper results in an increase in bonded area from thermal softening of lignin and hemicellulose in the constant rate drying period leading to improved strength properties and slightly decreased optical properties when compared with sheets dried with air, steam drying of kraft paper has the effect of increasing sheet bulk, decreasing strength properties and slightly improving optical properties relative to air drying. The basic mechanism leading to these results that is proposed here is the decreased drying stress arising from the higher sheet temperature obtained during the constant rate period when the drying fluid is steam. There does not appear to be any significant improvement in bonded area due to the thermal softening of the lignin and hemicellulose polymers; presumably the conformable kraft pulp fibres already have a sufficiently high bonding potential and unlike mechanical pulp fibres do not benefit from this phenomenon. The same effects are observed when sheets made from beaten or bleached kraft pulp are steam dried.

The special effects of steam drying on kraft pulp in certain cases may be advantageous. For example, an increase in bulk accompanied by improved optical properties may be desirable for certain grades of tissue made from chemical pulp where surface and absorption properties are more important than sheet strength.

# CHAPTER 6

# CONCLUSIONS

#### 6.1 Contributions to knowledge

- 1. Continuous measurement for the first time of TMP paper internal temperature and solids content via novel techniques while drying unsupported in an atmosphere of superheated steam at 165°C showed that sheet temperature immediately rises to and remains at 100°C for the constant rate drying period. The falling rate period begins at about 75% solids content at which point sheet temperature rises to the steam temperature. Comparative measurements for TMP paper drying in air under similar conditions showed that the constant rate sheet temperature was much lower (50°C) but that the falling rate period began at the same solids content. Drying rates for constant rate drying in steam and air up to temperatures of 320°C were calculated from continuous measurements of TMP and kraft sheet solids content.
- 2. A wide variety of physical and optical properties never before measured revealed that steam drying of TMP as well as RMP paper results in increased hydrogen bonding compared to paper dried under similar conditions in air. This improved bonding results in higher strength properties by up to 30% accompanied by small losses in optical properties without reduction in sheet bulk.
- 3. It was found, via novel experiments altering the fines content of TMP as well as

by scanning electron microscopy, that the hemicellulose and lignin rich fines fraction of the pulp was largely responsible for the increased bonding occurring in steam drying. It is proposed that the high sheet temperature reached at high moisture content in the constant rate period of steam drying allows the hemicellulose and lignin in the fines to reach their glass transition temperatures, permitting them to soften and perhaps flow to some extent. It is thought that the increase in bonded area is due to a rebonding of fines and fibrils to the stiffer whole fibres, which themselves do not deform as evidenced by the constant bulk of the sheet.

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- 4. The effect of initial and final sheet solids content in superheated steam drying was determined experimentally for the first time. It was found that to achieve the benefits of superheated steam drying, the initial solids content of the paper must be less than 60%, and superheated steam drying must be continued past a solids content of 70%.
- 5. The effect of recycling was investigated for the first time. Steam dried sheets which were recycled and steam dried again continued to show improved strength properties relative to air dried sheets which were recycled and dried in air, but these improvements were lost if the steam dried sheet was recycled and air dried.
- 6. Overdrying of TMP paper in steam or air resulted in deterioration of strength and optical properties, contrary to what has been found in previous work.

- 7. Mild press-drying of RMP paper in a superheated steam environment, performed for the first time, produced results no different from those obtained for pressdrying in air.
- 8. The industrial significance of superheated steam drying is that with this process, mechanical pulp furnishes may require much less or no addition of reinforcement chemical pulp, and may be able to produce paper of strength approximating that obtained with higher grade furnishes.  $J_{u} \cup J_{u} \cup J_{u}$
- 9. From a wide variety of never before measured physical, chemical and optical properties, it was found that for paper made from kraft pulp, as well as beaten and bleached kraft pulp, the effect of superheated steam drying was opposite to that obtained with mechanical pulp, resulting in a decrease in strength properties and a small improvement in optical properties relative to sheets dried in air under similar conditions. It is proposed that this is due to a thermally induced stress relaxation arising from the higher sheet temperature in the constant rate period of steam drying.
- 10. Unlike previous work, it was found that intense overdrying of kraft paper in both steam and air resulted in significant degradation of fibre strength.

## 6.2 Recommendations for future studies

1. Further experimental work investigating the effect of superheated steam drying

on paper made from other furnishes should be performed. These might include pulps from species other than kraft black spruce, furnishes with various chemical additives which may react differently at the higher temperatures obtained in the constant rate period, RMP and TMP produced at different energy levels than in the present study, GWD (groundwood), CTMP (chemi thermo mechanical pulp), chemical pulp furnishes other than kraft, and blends of mechanical and chemical pulp.

- 2. The effect of superheated steam drying on paper made from various furnishes but pressed to different levels prior to drying should be investigated.
- Sheet temperature and solids content histories should be recorded for a wide variety of steam drying conditions.
- 4. Drying stress developed during steam drying should be carefully measured under various degrees of sheet restraint and compared to that produced by air drying under similar conditions.
- Superheated steam dried paper should be subjected to calendering and printing trials to determine how it may differ from conventionally dried paper in these processes.

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# APPENDIX I - Raw Data

Paper mass versus time plots



Mass (g)

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Mass (g)



Mass (g)



(g) 889M



MASS (g)



Mass (g)



Maas (g)



Mass (g)



Mass (g)

A10



Mass (g)



Mass (g)

.



(g) 889M





A14


Mass (g)



Mass (g)



Mass (g)

APPENDIX II - Statistical Data

(Experiments listed in same order as in Table 3-4)

## DRYING FLUID: Air

# TEMPERATURE: 20°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.82	0.11	20
Burst Index	1120	195	5
Tear Index	_ 6.3	1.2	5
Fold	3	1	10
Tensile Index	24.6	1.5	10
Stretch	1.7	0.1	10
T.E.A. Index	233	24	10
Wet Tensile Strength	0.038	0.005	9
Zero-Span Breaking Length	10.2	0.9	10
Wet Zero-Span Br. Length	8.5	0.6	10
Scott Internal Bond Str.	80	5	5
Air Resistance	10.2	1.2	5
PPS Roughness	7.62	0.12	10
Brightness	53.03	0.13	5
Opacity	97.04	0.37	5
Water Drop Abs. Time	170	11	2

## DRYING FLUID: Air

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.58	0.15	16
Burst Index	1421	200	6
Tear Index	7.0	0.4	4
Fold	6	2	6
Tensile Index	27.0	2.3	8
Stretch	1.8	0.2	8
T.E.A. Index	257	61	8
Elastic Modulus	5.44	0.13	4
Wet Tensile Strength	0.06	0.01	5
Zero-Span Breaking Length	10.3	0.7	10
Wet Zero-Span Br. Length	6.9	0.6	10
Scott Internal Bond Str.	82	5	5
Air Resistance	9.4	1.7	5
PPS Roughness	7.93	0.23	10
Brightness	51.53	0.16	5
Opacity	96.64	0.19	5
Water Drop Abs. Time	309	16	2

#### DRYING FLUID: Air

# TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.70	0.13	16
Burst Index	1465	110	5
Tear Index	6.8	0.3	4
Fold	5	1	8
Tensile Index	30.2	1.5	8
Stretch	1.7	0.1	8
T.E.A. Index	290	38	8
Elastic Modulus	5.52	0.41	4
Wet Tensile Strength	0.38	0.06	7
Zero-Span Breaking Length	10.0	0.7	10
Wet Zero-Span Br. Length	8.3	0.4	10
Scott Internal Bond Str.	77	1	5
Air Resistance	9.5	1.0	5
PPS Roughness	7.85	0.13	10
Brightness	48.01	0.79	5
Opacity	97.09	0.14	5
Water Drop Abs. Time	387	93	2

## DRYING FLUID: Air

## TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.67	0.09	20
Burst Index	1537	60	5
Tear Index	6.0	0.3	5
Fold	4	1	10
Tensile Index	30.3	4.0	10
Stretch	1.5	0.3	10
T.E.A. Index	244	68	10
Elastic Modulus	5.89	0.22	4
Wet Tensile Strength	0.70	0.09	10
Zero-Span Breaking Length	9.6	0.8	10
Wet Zero-Span Br. Length	8.0	0.4	10
Scott Internal Bond Str.	81	5	5
Air Resistance	10.5	0.7	5
PPS Roughness	8.28	0.31	10
Brightness	25.93	5.24	5
Opacity	99.62	0.38	5
Water Drop Abs. Time	2245	1053	2

## DRYING FLUID: Steam

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.83	0.13	20
Burst Index	1843	134	5
Tear Index	6.6	0.3	5
Fold	6	2	10
Tensile Index	34.5	2.8	10
Stretch	1.7	0.2	10
T.E.A. Index	333	78	10
Elastic Modulus	6.27	0.55	4
Wet Tensile Strength	0.11	0.03	10
Zero-Span Breaking Length	10.6	0.8	10
Wet Zero-Span Br. Length	8.3	0.4	10
Scott Internal Bond Str.	90	10	5
Air Resistance	12.0	2.0	5
PPS Roughness	8.50	0.08	10
Brightness	46.75	0.37	5
Opacity	96.29	0.29	5
Water Drop Abs. Time	645	134	2

DRYING FLUID: Steam

# TEMPERATURE: 240°C

#### TYPE OF DRYING: Normal

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.78	0.13	18
Burst Index	1804	193	10
Tear Index	6.6	0.7	5
Fold	5	2	8
Tensile Index	37.1	2.8	9
Stretch	2.0	0.3	9
T.E.A. Index	418	100	9
Elastic Modulus	6.90	0.45	4
Wet Tensile Strength	0.32	0.05	9
Zero-Span Breaking Length	10.1	0.5	10
Wet Zero-Span Br. Length	8.3	0.7	10
Scott Internal Bond Str.	90	6	5
Air Resistance	9.0	2.2	5
PPS Roughness	8.80	0.11	10
Brightness	43.25	0.22	5
Opacity	96.12	0.34	5
Water Drop Abs. Time	430	94	2

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#### DRYING FLUID: Steam

# TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.67	0.16	20
Burst Index	1791	194	5
Tear Index	4.7	0.5	5
Fold	3	2	10
Tensile Index	38.0	4.0	9
Stretch	1.5	0.2	9
T.E.A. Index	296	77	9
Elastic Modulus	6.33	0.18	4
Wet Tensile Strength	1.04	0.08	9
Zero-Span Breaking Length	9.6	0.6	10
Wet Zero-Span Br. Length	6.5	0.5	10
Scott Internal Bond Str.	96	13	5
Air Resistance	9.9	2.7	5
PPS Roughness	8.43	0.11	10
Brightness	20.08	1.59	5
Opacity	99.81	0.14	5
Water Drop Abs. Time	464	60	2

#### DRYING FLUID: Air

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.66	0.17	20
Burst Index	1483	210	5
Tear Index	6.9	0.6	5
Fold	6	1	9
Tensile Index	29.7	2.6	10
Stretch	1.6	0.2	10
T.E.A. Index	268	56	10
Wet Tensile Strength	0.11	0.02	9
Zero-Span Breaking Length	10.2	0.7	10
Wet Zero-Span Br. Length	7.1	0.4	9
Scott Internal Bond Str.	82	5	5
Air Resistance	10.6	1.3	5
PPS Roughness	7.92	0.12	10
Brightness	50.64	0.42	5
Opacity	96.83	0.15	5
Water Drop Abs. Time	371	10	2

## DRYING FLUID: Air

# TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.69	0.13	20
Burst Index	1553	82	5
Tear Index	6.7	0.9	5
Fold	4	1	10
Tensile Index	29.6	3.9	10
Stretch	1.6	0.2	10
T.E.A. Index	254	65	10
Wet Tensile Strength	0.51	0.11	8
Zero-Span Breaking Length	10.2	1.3	10
Wet Zero-Span Br. Length	7.6	0.6	10
Scott Internal Bond Str.	84	5	5
Air Resistance	11.6	1.9	5
PPS Roughness	8.04	0.22	10
Brightness	37.39	1.01	5
Opacity	98.71	0.16	5
Water Drop Abs. Time	1020	120	2

#### DRYING FLUID: Air

#### TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.75	0.21	20
Burst Index	843	114	5
Tear Index	2.2	0.3	5
Fold	1	0	10
Tensile Index	23.3	1.7	10
Stretch	1.0	0.1	10
T.E.A. Index	109	17	10
Wet Tensile Strength	0.66	0.07	9
Zero-Span Breaking Length	6.7	1.5	10
Wet Zero-Span Br. Length	5.0	1.4	10
Scott Internal Bond Str.	67	8	5
Air Resistance	13.0	2.2	5
PPS Roughness	7.53	0.16	10
Brightness	11.26	0.39	5
Opacity	99.54	0.41	5

## DRYING FLUID: Steam

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measuremen
Bulk	3.66	0.09	20
Burst Index	1908	172	5
Tear Index	6.8	0.3	5
Fold	6	1	10
Tensile Index	36.7	1.6	10
Stretch	1.8	0.2	• 10
T.E.A. Index	367	58	10
Wet Tensile Strength	0.17	0.02	10
Zero-Span Breaking Length	10.5	0.7	10
Wet Zero-Span Br. Length	8.0	0.4	10
Scoti Internal Bond Str.	91	6	5
Air Resistance	12.9	2.4	5
PPS Roughness	8.60	0.20	10
Brightness	46.37	0.58	5
Opacity	96.01	0.15	5
Water Drop Abs. Time	586	12	2

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## DRYING FLUID: Steam

## TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.72	0.19	20
Burst Index	1976	210	5
Tear Index	7.4	0.8	5
Fold	6	2	9
Tensile Index	32.3	5.1	10
Stretch	1.5	0.3	10
T.E.A. Index	253	80	10
Wet Tensile Strength	0.62	0.16	10
Zero-Span Breaking Length	11.1	1.2	10
Wet Zero-Span Br. Length	8.9	1.1	10
Scott Internal Bond Str.	89	3	5
Air Resistance	17.4	2.2	5
PPS Roughness	8.49	0.20	10
Brightness	37.68	0.53	5
Opacity	97.77	0.34	5
Water Drop Abs. Time	2645	64	2

DRYING FLUID: Steam

## TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.71	0.11	20
Burst Index	1267	204	5
Tear Index	2.7	0.3	5
Fold	1	0	10
Tensile Index	31.1	2.3	10
Stretch	1.3	0.2	10
T.E.A. Index	192	39	10
Wet Tensile Strength	0.65	0.20	6
Zero-Span Breaking Length	7.5	1.2	10
Wet Zero-Span Br. Length	4.8	0.3	10
Scott Internal Bond Str.	75	3	5
Air Resistance	15.4	0.6	5
PPS Roughness	7.98	0.17	10
Brightness	14.04	1.19	5
Opacity	99.42	0.41	5

# DRYING FLUID: Air

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.70	0.16	20
Burst Index	1320	94	10
Tear Index	6.0	0.3	10
Fold	5	1	8
Tensile Index	25.6	1.9	10
Stretch	1.9	0.2	10
T.E.A. Index	268	50	10
Elastic Modulus	5.25	0.50	4
Zero-Span Breaking Length	10.1	0.6	10
Wet Zero-Span Br. Length	7.8	0.7	10
Scott Internal Bond Str.	72	6	5
Brightness	49.78	0.07	5
Opacity	98.04	0.15	5

#### DRYING FLUID: Air

# TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.74	0.18	18
Burst Index	1234	153	10
Tear Index	6.2	0.6	9
Fold	4	1	9
Tensile Index	23.8	2.3	8
Stretch	1.7	0.2	8
T.E.A. Index	_219	49	8
Zero-Span Breaking Length	10.0	0.9	10
Wet Zero-Span Br. Length	8.2	3.2	10
Scott Internal Bond Str.	79	4	5
Air Resistance	11.3	4.2	5
Brightness	49.32	0.34	5
Opacity	98.18	0.55	5

# DRYING FLUID: Steam

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.77	0.10	20
Burst Index	1648	144	10
Tear Index	6.2	0.6	10
Fold	7	3	10
Tensile Index	30.9	2.9	10
Stretch	1.8	0.2	10
T.E.A. Index	299	58	10
Elastic Modulus	6.07	0.21	4
Zero-Span Breaking Length	10.3	0.8	10
Wet Zero-Span Br. Length	7.7	0.6	10
Scott Internal Bond Str.	91	4	5
Brightness	45.29	0.37	5
Opacity	97.04	0.39	5

DRYING FLUID: Steam

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.79	0.09	20
Burst Index	1562	134	10
Tear Index	7.1	0.6	10
Fold	6	2	10
Tensile Index	33.2	1.7	8
Stretch	1.7	0.2	8
T.E.A. Index	331	54	8
Zero-Span Breaking Length	10.4	0.4	10
Wet Zero-Span Br. Length	8.0	0.6	2
Scott Internal Bond Str.	84	4	5
Air Resistance	16.1	1.8	5
Brightness	44.24	0.09	5
Opacity	98.09	0.92	5

#### DRYING FLUID: Air, Steam

## TEMPERATURE: 40°C, 160°C

# <u>TYPE OF DRYING</u>: Sheets dried to 54% solids content in 40°C air, remainder of drying done in 160°C steam

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.64	0.13	10
Burst Index	1662	191	10
Tear Index	6.5	0.2	3
Fold	5	2	5
Tensile Index	28.9	2.4	5
Stretch	1.6	0.3	5
T.E.A. Index	260	55	5
Zero-Span Breaking Length	10.1	0.7	10
Wet Zero-Span Br. Length	7.9	0.6	10
Scott Internal Bond Str.	85	4	5
Brightness	44.35	0.09	5
Opacity	98.06	0.27	5

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#### DRYING FLUID: Air, Steam

## TEMPERATURE: 40°C, 160°C

# <u>TYPE OF DRYING</u>: Sheets dried to 64% solids content in 40°C air, remainder of drying done in 160°C steam

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.65	0.13	10
Burst Index	1353	123	10
Tear Index	6.2	0.1	3
Fold	6	1	5
Tensile Index	26.0	2.2	5
Stretch	1.5	0.1	5
T.E.A. Index	217	45	5
Zero-Span Breaking Length	10.3	0.8	10
Wet Zero-Span Br. Length	7.7	0.6	10
Scott Internal Bond Str.	86	6	5
Brightness	45.37	0.33	5
Opacity	97.89	0.30	5



#### DRYING FLUID: Air, Steam

#### TEMPERATURE: 40°C, 160°C

# <u>TYPE OF DRYING</u>: Sheets dried to 73% solids content in 40°C air, remainder of drying done in 160°C steam

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.71	0.12	12
Burst Index	1285	153	10
Tear Index	6.0	0.4	6
Fold	4	2	4
Tensile Index	24.5	2.4	4
Stretch	1.7	0.2	4
T.E.A. Index	219	60	4
Zero-Span Breaking Length	9.2	0.6	10
Wet Zero-Span Br. Length	6.5	0.7	10
Scott Internal Bond Str.	76	6	5
Brightness	47.79	0.34	5
Opacity	98.59	0.42	5

#### DRYING FLUID: Air, Steam

#### TEMPERATURE: 40°C, 160°C

# <u>TYPE OF DRYING</u>: Sheets dried to 87% solids content in 40°C air, remainder of drying done in 160°C steam

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.64	0.08	10
Burst Index	1261	99	10
Tear Index	6.5	0.4	3
Fold	4	1	5
Tensile Index	23.7	1.2	5
Stretch	1.7	0.1	5
T.E.A. Index	218	31	5
Zero-Span Breaking Length	10.3	0.9	10
Wet Zero-Span Br. Length	7.4	0.7	10
Scott Internal Bond Str.	75	4	5
Brightness	49.0	0.09	5
Opacity	98.41	0.20	5

#### DRYING FLUID: Steam, Air

#### TEMPERATURE: 160°C, 40°C

# <u>TYPE OF DRYING</u>: Sheets dried to 48% solids content in 160°C steam, remainder of drying done in 40°C air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.79	0.14	20
Burst Index	1274	114	10
Tear Index	6.2	0.5	10
Fold	5	2	10
Tensile Index	24.5	2.2	10
Stretch	2.0	0.2	10
T.E.A. Index	285	45	10
Zero-Span Breaking Length	10.4	0.7	10
Wet Zero-Span Br. Length	8.0	0.7	10
Scott Internal Bond Str.	79	4	5
Air Resistance	9.8	0.8	5
Brightness	50.11	0.39	5
Opacity	97.91	0.16	5

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#### DRYING FLUID: Steam, Air

## TEMPERATURE: 160°C, 40°C

# <u>TYPE OF DRYING</u>: Sheets dried to 52% solids content in 160°C steam, remainder of drying done in 40°C air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.71	0.09	20
Burst Index	1453	165	10
Tear Index	7.0	1	10
Fold	6	2	10
Tensile Index	25.1	2.8	10
Stretch	1.9	0.2	10
T.E.A. Index	267	72	10
Elastic Modulus	4.64	-	4
Zero-Span Breaking Length	10.4	0.9	9
Wet Zero-Span Br. Length	8.4	0.8	8
Scott Internal Bond Str.	100	8.68	5
Brightness	49.58	0.17	5
Opacity	98.08	0.07	5

#### DRYING FLUID: Steam, Air

## TEMPERATURE: 160°C, 40°C

# <u>TYPE OF DRYING</u>: Sheets dried to 73% solids content in 160°C steam, remainder of drying done in 40°C air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.59	0.14	18
Burst Index	1664	144	10
Tear Index	6.5	0.4	9
Fold	10	4	9
Tensile Index	28.6	2.6	9
Stretch	2.0	0.2	9
T.E.A. Index	327	75	9
Zero-Span Breaking Length	9.7	0.9	10
Wet Zero-Span Br. Length	7.4	0.8	10
Scott Internal Bond Str.	101	6	5
Air Resistance	15.6	3.0	5
Brightness	46.06	0.71	5
Opacity	96.88	0.54	5

#### DRYING FLUID: Steam, Air

## TEMPERATURE: 160°C, 40°C

# <u>TYPE OF DRYING</u>: Sheetd dried to 87% solids content in 160°C steam, remainder of drying done in 40°C air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.75	0.18	20
Burst Index	1614	181	10
Tear Index	7.0	0.4	10
Fold	7	2	10
Tensile Index	29.7	3.4	9
Stretch	1.9	0.3	9
T.E.A. Index	284	113	9
Elastic Modulus	5.73	-	4
Zero-Span Breaking Length	10.5	0.7	9
Wet Zero-Span Br. Length	8.2	0.5	8
Scott Internal Bond Str.	78	1	5
Brightness	46.89	0.91	5
Opacity	97.30	0.61	5

#### PULP: TMP with fines (P100 fraction) removed

DRYING FLUID: Air

#### TEMPERATURE: 160°C

#### TYPE OF DRYING: Normal

.

Property	Mean	Standard Deviation	No. of Measurements
Bulk	6.73	0.41	8
Burst Index	344	18	7
Tensile Index	6.1	0.7	4
Stretch	0.7	0.1	4
T.E.A. Index	25	4	4
Scott Internal Bond Str.	34	10	10
Brightness	45.07	0.20	5
Opacity	91.52	0.54	5

#### PULP: TMP with fines (P100 fraction) removed

DRYING FLUID: Steam

#### TEMPERATURE: 160°C

## TYPE OF DRYING: Normal

Property	Mean	Standard Deviation	No. of Measurements
Bulk	6.65	0.18	10
Burst Index	354	12	8
Tensile Index	9.9	1.2	4
Stretch	0.8	0.1	4
T.E.A. Index	47	7	4
Scott Internal Bond Str.	35	6	10
Brightness	43.17	0.14	5
Opacity	91.18	0.30	5

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## DRYING FLUID: Air

## TEMPERATURE: 160°C

TYPE OF DRYING: Sheets dried in air, recycled, redried in air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.40	0.26	14
Burst Index	1347	214	10
Tear Index	6.1	0.8	7
Fold	5	2	7
Tensile Index	27.3	4.6	7
Stretch	1.7	0.1	7
T.E.A. Index	268	95	7
Zero-Span Breaking Length	10.7	0.6	10
Wet Zero-Span Br. Length	7.9	0.6	10
Scott Internal Bond Str.	78	1	5
Air Resistance	9.6	0.8	5
Brightness	47.26	0.13	5
Opacity	96.89	0.12	5

A46

#### DRYING FLUID: Steam

## TEMPERATURE: 160°C

TYPE OF DRYING: Sheets dried in steam, recycled, redried in steam

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.72	0.12	10
Burst Index	1415	211	10
Tear Index	6.2	0.8	5
Fold	5	2	5
Tensile Index	29.1	3.4	5
Stretch	1.6	0.2	5
T.E.A. Index	242	72	5
Zero-Span Breaking Length	10.5	0.6	6
Wet Zero-Span Br. Length	7.9	0.3	4
Scott Internal Bond Str.	80	3	5
Air Resistance	7.4	0.4	3
Brightness	43.44	0.10	5
Opacity	96.09	0.17	5

A47

#### DRYING FLUID: Steam, Air

## TEMPERATURE: 160°C

TYPE OF DRYING: Sheets dried in steam, recycled, redried in air

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.43	0.11	6
Burst Index	1173	155	6
Tear Index	6.0	0.2	3
Fold	3	1	3
Tensile Index	25.8	1.4	3
Stretch	1.6	0.1	3
T.E.A. Index	238	40	3
Zero-Span Breaking Length	10.0	0.5	4
Wet Zero-Span Br. Length	8.5	0.6	4
Scott Internal Bond Str.	80	2	5
Air Resistance	8.2	0.9	3
Brightness	46.70	0.31	5
Opacity	97.11	0.09	5

## DRYING FLUID: Air

## TEMPERATURE: 20°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.55	0.18	24
Burst Index	1240	230	12
Tear Index	5.4	0.1	3
Fold	3	1	12
Tensile Index	21.4	3.3	8
Stretch	2.5	0.5	8
T.E.A. Index	332	123	8

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DRYING FLUID: Air

# TEMPERATURE: 130°C

#### TYPE OF DRYING: Normal

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.33	0.13	20
Burst Index	1424	117	10
Tear Index	5.0	0.3	5
Fold	3	1	10 +
Tensile Index	25.3	1.7	9
Stretch	1.7	0.1	9
T.E.A. Index	260	36	9

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#### DRYING FLUID: Air

## TEMPERATURE: 300°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.45	0.16	24
Burst Index	1437	144	12
Tear Index	5.0	0.2	5
Fold	4	1	10
Tensile Index	25.4	2,4	9
Stretch	1.7	0.3	9
T.E.A. Index	261	76	9

DRYING FLUID: Steam

## TEMPERATURE: 130°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.51	0.16	20
Burst Index	1705	163	10
Tear Index	4.8	0.2	5
Fold	4	1	7
Tensile Index	29.9	4.5	8
Stretch	1.7	0.3	8
T.E.A. Index	278	83	8

DRYING FLUID: Steam

## TEMPERATURE: 300°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.50	0.11	22
Burst Index	1751	101	11
Tear Index	5.2	0.4	4
Fold	4	1	10
Tensile Index	31.1	1.8	9
Stretch	1.8	0.3	9
T.E.A. Index	325	71	9

## DRYING FLUID: Air

# TEMPERATURE: 20°C

#### TYPE OF DRYING: Press-drying

Property	Mean	Standard Deviation	No. of Measurements
Bulk	3.06	0.13	20
Burst Index	1520	140	10
Tear Index	5.1	0.3	7
Fold	4	1	11
Tensile Index	24.5	1.0	8
Stretch	2.3	0.4	8
T.E.A. Index	351	76	8

#### DRYING FLUID: Air

## TEMPERATURE: 130°C

## TYPE OF DRYING: Press-drying

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.97	0.19	26
Burst Index	2429	152	13
Tear Index	4.4	0.6	4
Fold	13	5	9
Tensile Index	39.6	2.6	6
Stretch	2.3	0.2	6
T.E.A. Index	535	78	6

## DRYING FLUID: Air

## TEMPERATURE: 300°C

## TYPE OF DRYING: Press-drying

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.26	0.14	22
Burst Index	1835	221	10
Tear Index	4.3	0.5	5
Fold	3	1	5
Tensile Index	33.7	3.6	5
Stretch	1.7	0.2	5
T.E.A. Index	301	27	5

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DRYING FLUID: Steam

## TEMPERATURE: 130°C

## TYPE OF DRYING: Press-drying

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.82	0.08	20
Burst Index	2394	315	10
Tear Index	4.0	0.3	5
Fold	18	11	10
Tensile Index	31.1	6.3	5
Stretch	1.6	0.2	5
T.E.A. Index	263	104	5

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DRYING FLUID: Steam

## TEMPERATURE: 300°C

## TYPE OF DRYING: Press-drying

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.22	0.15	24
Burst Index	1980	162	10
Tear Index	4.2	0.4	5
Fold	7	5	10
Tensile Index	36.2	6.0	8
Stretch	1.6	0.3	8
T.E.A. Index	322	112	8

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DRYING FLUID: Air

## TEMPERATURE: 20°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.27	0.13	20
Burst Index	4024	396	10
Tear Index	20.1	4.9	10
Fold	547	289	10
Tensile Index	49.1	3.5	10
Stretch	2.7	0.5	10
T.E.A. Index	814	161	10
Wet Tensile Strength	0.067	0.0087	10
Zero-Span Breaking Length	18.0	0.9	10
Wet Zero-Span Br. Length	17.2	0.8	10
Scott Internal Bond Str.	101	3	5
PPS Roughness	8.49	0.07	10
Brightness	26.36	0.27	5
Opacity	97.94	0.26	5
CED Viscosity	33.9	1.6	4
1% NaOH Solubility	3.8	0.45	2
Water Drop Abs. Time	101	5	2

#### DRYING FLUID: Air

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.38	0.19	20
Burst Index	3578	375	10
Tear Index	20.6	4.5	9
Fold	499	154	10
Tensile Index	42.6	5.5	10
Stretch	2.3	0.6	10
T.E.A. Index	588	226	10
Wet Tensile Strength	0.071	0.014	7
Zero-Span Breaking Length	17.1	1.3	10
Wet Zero-Span Br. Length	15.7	1.1	10
Scott Internal Bond Str.	91	9	5
PPS Roughness	8.29	0.09	8
Brightness	26.67	0.15	5
Opacity	98.31	0.20	5
CED Viscosity	33.2	1.5	4
1% NaOH Solubility	3.5	0.2	2
Water Drop Abs. Time	104	21	2



DRYING FLUID: Air

## TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.31	0.15	24
Burst Index	4006	384	10
Tear Index	16.8	2.0	10
Fold	619	172	10
Tensile Index	54.4	5.1	8
Stretch	2.3	0.2	8
T.E.A. Index	742	153	8
Wet Tensile Strength	0.29	0.03	10
Zero-Span Breaking Length	17.1	0.7	10
Wet Zero-Span Br. Length	16.5	0.7	10
Scott Internal Bond Str.	97	7	4
PPS Roughness	8.07	0.13	5
Brightness	25.39	0.71	5
Opacity	97.90	0.51	5
CED Viscosity	23.0	0.9	4
1% NaOH Solubility	3.42	0.11	2
Water Drop Abs. Time	74	4	2

DRYING FLUID: Air

#### TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.32	0.18	20
Burst Index	4079	280	10
Tear Index	14.6	2.6	10
Fold	402	133	10
Tensile Index	54.8	5.7	10
Stretch	2.5	0.4	10
T.E.A. Index	818	192	10
Wet Tensile Strength	0.81	0.10	10
Zero-Span Breaking Length	17.4	0.9	10
Wet Zero-Span Br. Length	15.1	1.7	10
Scott Internal Bond Str.	99	5	5
PPS Roughness	8.44	0.06	10
Brightness	22.53	0.56	5
Opacity	98.31	0.27	5
CED Viscosity	20.2	0.6	4
1% NaOH Solubility	4.03	0.11	2
Water Drop Abs. Time	154	-	2



DRYING FLUID: Steam

#### TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.42	0.14	20
Burst Index	3344	259	10
Tear Index	18.3	3.7	9
Fold	368	176	10
Tensile Index	46.6	3.5	9
Stretch	2.7	0.4	9
T.E.A. Index	768	140	9
Wet Tensile Strength	0.085	0.018	8
Zero-Span Breaking Length	17.0	1.0	8
Wet Zero-Span Br. Length	17.5	1.0	8
Scott Internal Bond Str.	81	3	5
PPS Roughness	8.44	0.18	10
Brightness	26.73	0.50	5
Opacity	98.42	0.23	5
CED Viscosity	41.3	1.7	4
1% NaOH Solubility	2.62	0.60	2
Water Drop Abs. Time	184	4	2

DRYING FLUID: Steam

## TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.41	0.13	20
Burst Index	3677	269	10
Tear Index	15.9	2.2	10
Fold	313	119	10
Tensile Index	47.5	4.3	10
Stretch	2.8	0.5	10
T.E.A. Index	857	207	10
Wet Tensile Strength	0.33	0.03	10
Zero-Span Breaking Length	16.7	0.7	10
Wet Zero-Span Br. Length	16.5	0.9	10
Scott Internal Bond Str.	89	13	5
PPS Roughness	8.42	0.11	10
Brightness	26.50	0.16	5
Opacity	98.30	0.05	5
CED Viscosity	23.4	0.7	4
1% NaOH Solubility	4.75	1.40	2
Water Drop Abs. Time	90	-	2



DRYING FLUID: Steam

## TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.73	0.17	20
Burst Index	2714	345	10
Tear Index	12.2	1.3	10
Fold	223	120	10
Tensile Index	51.5	4.7	10
Stretch	1.8	0.4	10
T.E.A. Index	489	156	10
Wet Tensile Strength	0.62	0.11	8
Zero-Span Breaking Length	16.5	1.8	10
Wet Zero-Span Br. Length	14.5	2.0	10
Scott Internal Bond Str.	69	3	5
PPS Roughness	8.60	0.02	10
Brightness	24.69	0.53	5
Opacity	98.93	0.79	5
CED Viscosity	12.8	0.1	2
1% NaOH Solubility	3.71	0.07	2
Water Drop Abs. Time	125	13	2

#### DRYING FLUID: Air

#### TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.40	0.16	23
Burst Index	3835	254	10
Tear Index	18.2	2.0	12
Fold	306	194	10
Tensile Index	48.8	4.9	10
Stretch	2.5	0.6	10
T.E.A. Index	746	216	10
Wet Tensile Strength	0.070	0.008	8
Zero-Span Breaking Length	17.6	1.0	10
Wet Zero-Span Br. Length	16.3	0.8	10
Scott Internal Bond Str.	80	9	5
PPS Roughness	8.60	0.08	10
Brightness	27.23	0.17	5
Opacity	97.93	1.07	5
CED Viscosity	25.1	0.7	2
Water Drop Abs. Time	141	53	5

## DRYING FLUID: Air

## TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.51	0.14	20
Burst Index	3415	464	10
Tear Index	16.1	1.9	10
Fold	341	52	9
Tensile Index	54.9	4.4	10
Stretch	2.0	0.4	10
T.E.A. Index	611	186	10
Wet Tensile Strength	0.39	0.07	10
Zero-Span Breaking Length	18.1	1.3	10
Wet Zero-Span Br. Length	16.8	0.8	10
Scott Internal Bond Str.	75	1	10
PPS Roughness	8.43	0.11	5
Brightness	26.78	0.20	5
Opacity	97.80	0.12	5
CED Viscosity	38.5	1.7	2
1% NaOH Solubility	2.04	0.15	2
Water Drop Abs. Time	166	_	2

DRYING FLUID: Air

# TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.6	0.12	20
Burst Index	2714	395	9
Tear Index	7.5	1.3	9
Fold	76	88	9
Tensile Index	51.8	5.3	10
Stretch	1.6	0.3	10
T.E.A. Index	419	118	10
Wet Tensile Strength	0.27	0.05	10
Zero-Span Breaking Length	12.1	0.6	10
Wet Zero-Span Br. Length	7.9	0.3	10
Scott Internal Bond Str.	80	3	5
PPS Roughness	8.55	0.08	10
Brightness	14.82	1.86	5
Opacity	99.38	0.36	5
CED Viscosity	5.2	0	2
1% NaOH Solubility	5.64	0.15	2
Water Drop Abs. Time	100	21	2



DRYING FLUID: Steam

## TEMPERATURE: 160°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.59	0.13	18
Burst Index	3182	265	10
Tear Index	17.3	1.8	9
Fold	277	139	13
Tensile Index	46.4	4.4	9
Stretch	1.8	0.2	9
T.E.A. Index	490	96	9
Wet Tensile Strength	0.11	0.02	8
Zero-Span Breaking Length	17.9	0.7	10
Wet Zero-Span Br. Length	18.3	0.9	10
Scott Internal Bond Str.	72	4	5
PPS Roughness	8.53	0.09	10
Brightness	27.21	0.22	5
Opacity	97.97	0.05	5
CED Viscosity	39.2	2.0	2
1% NaOH Solubility	2.56	0.25	2
Water Drop Abs. Time	155	4	2

DRYING FLUID: Steam

#### TEMPERATURE: 240°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.59	0.15	20
Burst Index	3029	272	10
Tear Index	11.6	1.0	9
Fold	174	78	10
Tensile Index	54.6	4.2	10
Stretch	2.0	0.2	10
T.E.A. Index	805	605	10
Wet Tensile Strength	0.60	0.13	9
Zero-Span Breaking Length	17.0	1.0	10
Wet Zero-Span Br. Length	15.9	1.1	10
Scott Internal Bond Str.	79	9	5
PPS Roughness	8.50	0.05	10
Brightness	25.78	0.56	5
Opacity	98.15	0.11	5
CED Viscosity	13.9	0.1	2
1% NaOH Solubility	3.38	0.30	2
Water Drop Abs. Time	124	11	2



DRYING FLUID: Steam

## TEMPERATURE: 320°C

#### TYPE OF DRYING: Overdried

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.6	0.14	20
Burst Index	1817	509	10
Tear Index	3.8	0.9	6
Fold	2	3	10
Tensile Index	41.5	5.4	8
Stretch	1.2	0.2	8
T.E.A. Index	226	71	8
Wet Tensile Strength	0.76	0.11	9
Zero-Span Breaking Length	8.1	0.6	10
Wet Zero-Span Br. Length	4.5	0.5	10
Scott Internal Bond Str.	68	7	5
PPS Roughness	8.67	0.05	10
Brightness	13.07	0.44	5
Opacity	99.75	0.34	5
CED Viscosity	4.8	0.1	2
1% NaOH Solubility	5.32	0.22	2
Water Drop Abs. Time	119	1.4	2

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DRYING FLUID: Steam

## TEMPERATURE: 320°C

## TYPE OF DRYING: Normal, Replicate

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.55	0.10	18
Burst Index	3380	415	10
Tear Index	13.6	1.0	10
Fold	220	70	10
Tensile Index	52.8	3.6	10
Stretch	2.2	0.2	10
T.E.A. Index	711	89	10
Wet Tensile Strength	0.29	0.12	9
Zero-Span Breaking Length	16.7	0.6	10
Wet Zero-Span Br. Length	18.0	1.2	10
Scott Internal Bond Str.	75	3	5
PPS Roughness	8.49	0.07	5
Brightness	26.23	0.93	5
Opacity	98.16	0.45	5
CED Viscosity	20.6	1.6	2
1% NaOH Solubility	1.51	0.11	2
Water Drop Abs. Time	201	13	2



## PULP: Kraft

DRYING FLUID: Steam

## TEMPERATURE: 320°C

## TYPE OF DRYING: Normal, Replicate

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.62	0.15	20
Burst Index	3151	431	10
Tear Index	14.2	1.3	10
Fold	248	106	10
Tensile Index	48.4	3.8	10
Stretch	1.9	0.3	10
T.E.A. Index	562	129	10
Wet Tensile Strength	0.46	0.09	9
Scott Internal Bond Str.	84	4	5
PPS Roughness	8.50	0.06	10
Brightness	27.07	0.57	5
Opacity	98.08	0.47	5
CED Viscosity	23.0	1.0	2
1% NaOH Solubility	2.65	0.15	2
Water Drop Abs. Time	130	3	2

### PULP: Semi-Bleached Kraft

DRYING FLUID: Air

## TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.18	0.14	20
Burst Index	4055	190	10
Tear Index	15.9	1.6	10
Fold	424	152	10
Tensile Index	56.0	3.9	10
Stretch	2.4	0.3	10
T.E.A. Index	832	194	10
Wet Tensile Strength	0.30	0.08	8
Zero-Span Breaking Length	16.9	1.3	10
Wet Zero-Span Br. Length	16.0	1.5	10
Scott Internal Bond Str.	107	6	5
PPS Roughness	8.12	0.06	10
Brightness	31.29	1.43	5
Opacity .	96.20	0.32	5
CED Viscosity	13.2	0.1	2
1% NaOH Solubility	3.74	0.15	2
Water Drop Abs. Time	410	22	2



## PULP: Fully Bleached Kraft

DRYING FLUID: Air

# TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.40	0.15	20
Burst Index	2469	270	10
Tear Index	20.8	8.0	3
Fold	64	33	10
Tensile Index	44.0	3.1	10
Stretch	2.0	0.3	10
T.E.A. Index	558	118	10
Wet Tensile Strength	0.19	0.06	9
Zero-Span Breaking Length	15.3	0.7	10
Wet Zero-Span Br. Length	13.4	1.3	10
Scott Internal Bond Str.	73	5	5
PPS Roughness	8.31	0.11	10
Brightness	52.52	3.41	5
Opacity	84.03	0.66	5
CED Viscosity	9.18	0.18	2
1% NaOH Solubility	5.27	0.33	2
Water Drop Abs. Time	260	28	2

### PULP: Semi-Bleached Kraft

DRYING FLUID: Steam

#### TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.41	0.12	14
Burst Index	2325	350	10
Tear Index	10.8	2.8	4
Fold	110	78	7
Tensile Index	43.3	4.0	7
Stretch	1.4	0.2	7
T.E.A. Index	350	81	7
Wet Tensile Strength	0.28	0.05	4
Zero-Span Breaking Length	16.7	2.6	10
Wet Zero-Span Br. Length	17.0	1.5	10
Scott Internal Bond Str.	76	3	5
PPS Roughness	8.55	0.07	10
Brightness	29.55	1.79	5
Opacity	99.47	1.89	5
CED Viscosity	10.7	0.1	2
1% NaOH Solubility	3.97	-	1
Water Drop Abs. Time	176	15	2



## PULP: Fully Bleached Kraft

DRYING FLUID: Steam

## TEMPERATURE: 320°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.52	0.12	20
Burst Index	2074	232	9
Tear Index	11.0	3.0	6
Fold	16	9	10
Tensile Index	37.6	3.5	10
Stretch	1.5	0.2	10
T.E.A. Index	326	77	10
Wet Tensile Strength	0.20	0.04	9
Zero-Span Breaking Length	13.4	0.7	10
Wet Zero-Span Br. Length	10.5	0.6	10
Scott Internal Bond Str.	64	3	5
PPS Roughness	8.53	0.07	10
Brightness	47.53	2.37	5
Opacity	89.33	3.17	5
CED Viscosity	8.65	0.21	2
1% NaOH Solubility	4.57	0.11	2
Water Drop Abs. Time	170	21	2

## PULP: Kraft, Beaten 5 min.

DRYING FLUID: Air

#### TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.30	0.10	20
Burst Index	4905	405	10
Tear Index	13.4	1.0	10
Fold	706	32	10
Tensile Index	71.7	2.1	10
Stretch	2.4	0.2	10
T.E.A. Index	1017	127	10
Wet Tensile Strength	0.71	0.10	10
Zero-Span Breaking Length	18.5	0.7	10
Wet Zero-Span Br. Length	17.1	0.7	10
Scott Internal Bond Str.	112	7	5
PPS Roughness	8.26	0.08	10
Brightness	24.40	0.31	5
Opacity	98.16	0.24	5
CED Viscosity	25.4	0.7	2
1% NaOH Solubility	2.59	0.15	2
Water Drop Abs. Time	268	11	2



#### PULP: Kraft, Beaten 20 min.

DRYING FLUID: Air

## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.92	80.0	20
Burst Index	6248	502	10
Tear Index	11.1	0.5	10
Fold	588	150	10
Tensile Index	83.7	4.6	10
Stretch	2.6	0.2	10
T.E.A. Index	1309	141	10
Wet Tensile Strength	0.85	0.14	9
Zero-Span Breaking Length	18.8	0.5	10
Wet Zero-Span Br. Length	17.8	0.5	10
Scott Internal Bond Str.	158	19	5
PPS Roughness	8.04	0.08	10
Brightness	23.30	0.16	5
Opacity	97.54	0.31	5
CED Viscosity	23.0	0.7	2
1% NaOH Solubility	1.24	0.20	2
Water Drop Abs. Time	777	30	2

## PULP: Kraft, Beaten 40 min.

DRYING FLUID: Air

#### TEMPERATURE: 280°C

#### TYPE OF DRYING: Normal

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.75	0.08	20
Burst Index	7867	727	10
Tear Index	10.4	2.0	10
Fold	680	99	10
Tensile Index	95.1	9.0	10
Stretch	3.1	0.3	10
T.E.A. Index	1728	263	10
Wet Tensile Strength	1.1	0.2	9
Zero-Span Breaking Length	20.0	1.5	10
Wet Zero-Span Br. Length	18.0	1.4	10
Scott Internal Bond Str.	216	10	5
PPS Roughness	2.78	0.11	10
Brightness	21.31	0.49	5
Opacity	96.99	0.72	5
CED Viscosity	25.6	0.5	2
1% NaOH Solubility	1.19	0.04	2
Water Drop Abs. Time	896	51	2



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PULP: Kraft, Beaten 60 min.

DRYING FLUID: Air

## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.59	0.08	20
Burst Index	8260	549	10
Tear Index	8.4	0.8	10
Fold	748	220	10
Tensile Index	105.5	8.7	9
Stretch	3.2	0.4	9
T.E.A. Index	2057	381	9
Wet Tensile Strength	0.64	0.09	10
Zero-Span Breaking Length	19.4	1.2	10
Wet Zero-Span Br. Length	18.2	1.1	10
Scott Internal Bond Str.	266	14	5
PPS Roughness	7.58	0.10	10
Brightness	20.54	0.18	5
Opacity	94.31	0.85	5
CED Viscosity	42.9	1.4	2
1% NaOH Solubility	1.8	0.4	2
Wat.r Drop Abs. Time	904	71	2

### PULP: Kraft, Beaten 80 min.

DRYING FLUID: Air

## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.52	0.04	20
Burst Index	8505	820	10
Tear Index	8.0	0.7	10
Fold	1118	339	9
Tensile Index	104.8	5.6	10
Stretch	3.2	0.3	10
T.E.A. Index	2073	316	10
Wet Tensile Strength	0.71	0.11	10
Zero-Span Breaking Length	19.2	1.6	10
Wet Zero-Span Br. Length	17.9	1.5	10
Scott Internal Bond Str.	342	19	5
PPS Roughness	7.80	0.07	10
Brightness	20.15	0.58	5
Opacity	95.68	0.78	5
CED Viscosity	28.4	0.7	2
1% NaOH Solubility	1.29	0.30	2

PULP: Kraft, Beaten 5 min.

DRYING FLUID: Steam

## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.42	0.15	20
Burst Index	4262	194	5
Tear Index	14.0	1.2	10
Fold	626	165	10
Tensile Index	63.0	7.0	10
Stretch	2.1	0.3	10
T.E.A. Index	749	187	10
Wet Tensile Strength	0.37	0.12	10
Zero-Span Breaking Length	18.8	1.3	10
Wet Zero-Span Br. Length	17.9	1.2	10
Scott Internal Bond Str.	83	4	5
PPS Roughness	8.52	0.08	10
Brightness	26.16	0.68	5
Opacity	97.73	0.18	5
CED Viscosity	27.5	1.2	2
1% NaOH Solubility	2.51	0.14	2
Water Drop Abs. Time	128	12	2

PULP: Kraft, Beaten 20 min.

DRYING FLUID: Steam

## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	2.06	0.15	20
Burst Index	5658	450	10
Tear Index	11.9	0.9	10
Fold	570	120	10
Tensile Index	70.9	9.0	10
Stretch	2.1	0.3	10
T.E.A. Index	826	276	10
Wet Tensile Strength	0.75	0.12	10
Zero-Span Breaking Length	19.3	1.5	10
Wet Zero-Span Br. Length	17.4	1.3	10
Scott Internal Bond Str.	132	14	5
PPS Roughness	8.23	0.12	10
Brightness	24.25	0.57	5
Opacity	97.21	0.27	5
CED Viscosity	21.65	0.64	2
1% NaOH Solubility	2.01	0.08	2
Water Drop Abs. Time	284	114	2



PULP: Kraft, Beaten 40 min.

DRYING FLUID: Steam

# TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.85	0.09	20
Burst Index	7338	855	10
Tear Index	10.0	1.3	10
Fold	654	80	10
Tensile Index	93.4	6.2	10
Stretch	2.5	0.3	10
T.E.A. Index	1336	289	10
Wet Tensile Strength	0.95	0.12	10
Zero-Span Breaking Length	19.1	2.1	10
Wet Zero-Span Br. Length	17.0	1.9	10
Scott Internal Bond Str.	200	16	5
PPS Roughness	7.99	0.10	10
Brightness	22.69	0.42	5
Opacity	16.47	0.47	5
CED Viscosity	22.7	0.7	2
1% NaOH Solubility	2.16	0.1	2
Water Drop Abs. Time	727	137	2

PULP: Kraft, Beaten 60 min.

DRYING FLUID: Steam

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## TEMPERATURE: 280°C

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.62	0.04	20
Burst Index	7436	605	10
Tear Index	7.70	0.55	10
Fold	601	174	10
Tensile Index	94.4	7.3	10
Stretch	2.7	0.3	10
T.E.A. Index	1456	321	10
Wet Tensile Strength	1.1	0.1	9
Zero-Span Breaking Length	19.0	1.4	10
Wet Zero-Span Br. Length	17.8	1.0	10
Scott Internal Bond Str.	276	33	5
PPS Roughness	7.57	0.08	10
Brightness	20.37	0.31	5
Opacity	95.09	0.19	5
CED Viscosity	17.2	0.3	2
1% NaOH Solubility	3.3	0.3	2
Water Drop Abs. Time	5970	400	2
PULP: Kraft, Beaten 80 min.

DRYING FLUID: Steam

## TEMPERATURE: 280°C

## TYPE OF DRYING: Normal

Property	Mean	Standard Deviation	No. of Measurements
Bulk	1.52	0.07	20
Burst Index	7564	947	10
Tear Index	8.0	0.8	10
Fold	819	218	10
Tensile Index	99.1	6.5	10
Stretch	2.8	0.1	10
T.E.A. Index	1877	198	10
Wet Tensile Strength	1.06	0.12	9
Zero-Span Breaking Length	19.1	1.5	10
Wet Zero-Span Br. Length	19.3	1.2	10
Scott Internal Bond Str.	294	33	5
PPS Roughness	7.82	0.09	10
Brightness	21.03	0.20	5
Opacity	95.61	0.43	5
Water Drop Abs. Time	11210	1690	2