THE EFFECTS OF ALKALINE PEROXIDE TREATMENT ON PHYSICAL AND STRUCTURAL PROPERTIES OF LOW CONSISTENCY REFINED PAPER

By

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University of Toronto

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Physical property data was used to test two hypotheses pertaining to the impact of a chemical pre-treatment on the qualities of low consistency refined pulp. The first objective was to determine whether the addition of a chemical treatment would effectively accelerate the refining process when compared to a regular pulp. This involved the measurement of the physical property data and how it changed with increased refining energy. The second objective was to determine how the chemical treatment affected fibre development during refining, and whether its implementation could result in enhancement of inter-fibre bondability. Theoretical models for the physical properties of paper were used to study the fibre-to-fibre bonding properties of the tested paper samples. Additionally, SEM images were obtained to study the differences in morphology of the tested pulp samples.
I would like to thank the supervisors of my work, prof. Mark Kortschot and Prof. Ramin Farnood. They have guided me through the process of carrying this project from start to finish and provided me with the necessary feedback and motivation when I needed it most.

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<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>HC</td>
<td>high consistency</td>
</tr>
<tr>
<td>LC</td>
<td>low consistency</td>
</tr>
<tr>
<td>TMP</td>
<td>thermo-mechanical pulp</td>
</tr>
<tr>
<td>CTMP</td>
<td>chemi-thermo-mechanical pulp</td>
</tr>
<tr>
<td>AP</td>
<td>alkaline peroxide</td>
</tr>
<tr>
<td>T</td>
<td>finite span tensile strengthening</td>
</tr>
<tr>
<td>Z</td>
<td>zero-span tensile strengthening</td>
</tr>
<tr>
<td>g</td>
<td>acceleration due to gravity</td>
</tr>
<tr>
<td>A</td>
<td>fibre cross-sectional area</td>
</tr>
<tr>
<td>P</td>
<td>fibre cross-sectional perimeter</td>
</tr>
<tr>
<td>L</td>
<td>fibre length</td>
</tr>
<tr>
<td>ρ</td>
<td>density of fibrous mass</td>
</tr>
<tr>
<td>τ</td>
<td>fibre-to-fibre bond shear strength</td>
</tr>
<tr>
<td>RBA</td>
<td>relative bonded area</td>
</tr>
<tr>
<td>n_f</td>
<td>number of fibres crossing the rupture zone that take the load at tensile failure</td>
</tr>
<tr>
<td>n_p</td>
<td>number of fibres crossing the rupture zone that pull out intact at tensile failure</td>
</tr>
<tr>
<td>φ</td>
<td>mean fibre strength</td>
</tr>
<tr>
<td>β</td>
<td>force required to pull a fibre from the sheet.</td>
</tr>
<tr>
<td>N</td>
<td>number of fibres crossing the fracture line in the Shallhorn &amp; Karnis models</td>
</tr>
<tr>
<td>W</td>
<td>work required to tear a sheet of N fibres</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
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1 Introduction

1.1 Background

The need for improvements in pulp and paper manufacturing technology is becoming increasingly important. The continuing research and development of new alternative materials is undermining the necessity of using wood pulp. Moreover, the growing presence of electronic media in day-to-day consumer activities is proving to be important competition for such popular applications of paper as newspapers, books, and magazines. In order to remain prosperous within an increasingly more competitive market, the wood pulp industry requires manufacturing options that will provide greater efficiency and reduced operating costs. In Canada, where pulping is an important industry, research into innovative solutions and technological improvements is continuing.

The objective of any pulp-making process is to break up the rigid composition of the wood chips, so that the wood fibres which make up the bulk of a tree are liberated into a free-flowing fibrous mass. This fibrous mass, the pulp, is then subjected to a series of other treatments so that it may eventually become pressed and dried into paper rolls or into bails/sheets of pulp to be shipped for various applications.

Pulping methods may be broadly divided into two categories: chemical pulping, and mechanical pulping. Chemical pulping incorporates the use of chemical agents to convert wood chips into
pulp. During this pulping process, the chips are deposited into a chemical solution (liquor) and cooked at raised temperature. The aggressive nature of the liquor dissolves the rigid matrix which encapsulates the wood fibres and by doing so liberates the fibres. The chemical action of the liquor also attacks the wood fibres, because of this the yields achieved by chemical pulping processes are usually low: typically in the range of 40%-55%. There are a number of chemical liquors that are used in the industry. Kraft pulp involves use of an alkaline solution consisting mostly of sodium hydroxide and sodium sulfide. The sulphide pulping process utilizes an acidic liquor based on a sulphurous acid formulation.

Although chemical pulping yields are low, chemical pulp consists mainly of readily collapsible fibres that form very well bonded paper sheets. As such, the paper obtained from these types of processes is generally quite strong. There are, however, certain drawbacks associated with this: the sheet density of paper made of chemical pulp is high and the distribution of mass is often nonuniform. Due to this, chemical pulp is often blended with other types of pulp [1][2].

In mechanical pulping, mechanical action is what breaks up the wood chips. Traditionally mechanical pulping was performed by a stone groundwood process, where wood chips were pressed against a large cylindrical grinder – and thus were broken up and converted into pulp. Currently, the more prevalent method for mechanical puling relies on passing wood chips between two rotating grinders (usually discs, however conical grinders are in use as well). These machines are referred to as refiners, a diagram of a typical one disc refiner is shown below.
In a traditional disc refiner as shown in the image 1.1.1, the stock is fed in between the centre of the two discs. There it is subjected to the refining action of the grinding discs while gradually moving away from the centre. The refined pulp stock is collected from around the perimeter of the rotating grinders and is passed onto further stages of the pulping process. The surfaces of the discs are patterned with an arrangement of grooves and protrusions referred to as breaker bars; their function is to propagate refining action. The operation of refiners requires vast amounts of kinetic energy, as such the energy consumption required to operate such machines yields considerable costs.

*Image 1.1.1: A typical one disc refiner displaying the stator, rotor, refiner casing, screw feed, and the pulp outlet*
Mechanical pulp usually consists of fibres that are shorter than chemical pulp (the harsh refining action cuts and shortens the fibres during operation), and therefore mechanical pulp tends to be physically weaker than chemical pulp. Mechanical pulp, however, provides good print quality, high bulk (inverse of density), and is a less expensive pulping option when compared to chemical pulp. Mechanical pulping was, and remains to be used to manufacture newsprint (blended with chemical pulp to increase strength), however because of its good print properties, its lesser cost and high bulk it is also utilized as filler for paper blends for various applications [1][2].

Mechanical pulping processes have relatively high yields (usually above 90%); however, they are energy intensive. To address these issues, in some mechanical pulp mills steam (thermo-mechanical pulp - TMP), chemical treatment or a combination of both (chemi-thermo-mechanical pulp - CTMP) is applied to the wood chips prior to refining to soften the chips so that operating costs are lowered and efficiency is improved.

### 1.2 Motivation

Over the course of years, low cost of energy coupled with a source of good quality wood fibre led to a relatively high growth of the mechanical pulping industry in Canada. Today, many research projects – both private and government funded – are under way with aims of improving the cost effectiveness of the numerous existing mills. As was mentioned previously, the energy consumption of mechanical mills is a significant component of mechanical pulp cost. Hence,
even small advancements in the energy efficiency of the mechanical pulping process will yield considerable reductions in operating cost. Because of this, each part of the mechanical pulping process is being scrutinized in order to optimize its operation while maintaining the quality of the final product.

A typical mechanical refining process usually consists of the following stages: wood chipping, chip pretreatment (optional, depends on the mill and if any pretreatments are incorporated), primary refining, secondary refining, tertiary refining, latency chest (curl removal), screening (separation of reject particles), optional reject refining, dewatering, and finally storage or paper manufacture [1].

All of those unit operations are subjects of many studies with aims of overall optimization. However, the most important aspect of a mechanical pulp mill is the pulping operation, which includes the series of refiners as well as any treatments (chemical or thermal) that are implemented as part of the pulping process. Efficiency improvements in this part of the process have the most potential for yielding cost reductions to the whole operation. Estimates of the energy consumption associated with refiner operation indicate that about 80-95% of electrical energy in a typical mechanical pulping mill is dedicated to refiner operation [3][4]. Francis et al., conducted an analysis of electrical energy consumption in typical mechanical pulping mills [5]. He provided the following breakdown of mill components and their respective energy use in units of kWh/ADt (AD means air dried).
Figure 1.2.1 above shows the electrical energy use of various compartments of a mechanical pulping mill as presented by Francis et al. [5]. It is evident that the energy spent on refiner operation is about 90% of the total. Because the energy consumption associated with the operation of refiners is so high, slight improvements in efficiency may yield considerable cost reductions. In fact, if one considers a hypothetical 1% reduction in energy use due to refining in a mill manufacturing say 100,000 tonnes of paper per year, one may expect an annual saving of over $170,000 – a fairly substantial amount considering the relatively insignificant improvement in processing efficiency (calculation based on the data provided by Francis and a price of electricity $0.08 CAD/kWh).
Two avenues for the improvement of refining efficiency that are currently attracting much attention are: low consistency refining and alkali-peroxide pulp pretreatment (described in detail in Background Sections 2.3.1 and 2.3.2). The investigation of these potential improvements to the pulping line of a mechanical pulping process is the focus of this study.

1.3 Objective

The objective of this study is to examine the benefits of alkali-peroxide chemical pretreatment on the performance of low consistency refined mechanical pulp. The assessment will be based on physical property of handsheets made of treated and untreated pulps refined at identical low consistency conditions.

Another aim of this study is to assess the differences between structural properties, specifically the inter-fibre bonding, of the treated and untreated pulp. Theoretical analysis based on fibre network models will be used to better examine bonding characteristics of these pulps from basic physical measurements. This will provide a new insight into the effects of chemical pretreatment on the pulp properties and sheet characteristics.

1.4 Approach

In order to complete the objective, two sets of mechanical pulp samples were obtained from the same wood source. One set was chemically treated while the other was untreated. Both sets were refined at identical conditions in a single stage refiner at low consistency. They were then
subjected to a series of physical tests. The resulting observations were used to assess basic benefits of the novel chemical pretreatment and compare them with literature reports. Additionally, the physical property measurements were incorporated into a theoretical model analysis of paper properties. This was done to evaluate inter-fibre bondability of the tested samples. SEM images were acquired to determine any morphological differences that correlate to the quantitative results.

Based on the above approach, this thesis is organized into 5 chapters. Following this chapter, Chapter 2 contains an overview of the concepts of paper structure and physical properties as well as review of current research on the improvement of the refining line of a mechanical pulping process. Chapter 3 describes the experimental methods that were utilized during this study.

Chapter 4 pertains to the discussion of the results, it is divided into two parts which correspond to the two hypothesis of this thesis. The first part of this chapter is dedicated to the comparison of the basic physical properties of regular and chemically refined pulp. In the second part a comparison of theoretically predicted fibre-to-fibre bonding properties of the two types of pulp is presented. Chapter 5 contains the conclusions and recommendations for future work.
2 Background

2.1 Introduction

This section provides the necessary knowledge needed to better analyze and interpret the results presented in the forthcoming sections. To allow for a better understanding of how process alterations may improve efficiency in a mechanical pulping line, it is necessary to examine the structure of paper and how it translates into physical properties. Following this, the changes imposed onto the fibres by a traditional mechanical pulping process are examined. Then, improvements to the mechanical pulping method such as the adjustments to the mechanical aspects of the pulping process as well as any chemical treatments that are of benefit are discussed. Finally, literature pertaining to the theoretical models for the physical properties of paper is presented.

2.2 Properties of Paper

This section is a review of the concepts of paper structure, micro-structure, physical properties of paper, and how paper structure is related to the observable physical properties.

2.2.1 Basic Structure of Paper

Wood is composed of fibres fitted closely together and arranged almost in parallel with each other. These fibres are held within a matrix composed mostly of a complex polymer compound
named lignin. Hemicellulose – which is a polymer consisting of short chains of various sugar monomers – is also present in smaller amounts. This matrix is what provides the tree with its rigidity as well as its colour. The wood fibres themselves consist of a layered structure made up mostly of another naturally occurring polymer referred to as cellulose (small amounts of hemicellulose are also present in the fibres). Cellulose is produced by the tree from monomers of glucose and composes the bulk of the tree.

Fibres may be considered to be long hollow tubes. Within the wall of these tubes, cellulose chains conglomerate into smaller string formations known as fibrils. These fibrils are fitted closely together and are spirally wound around the hollow centre of the fibre. The fibre wall is generally composed of three layers of such fibril arrangements. Cellulose chains make up the bulk of the wood fibres, and are fibre components that are crucial in the formation of paper sheets.

The chemical structure of the cellulose chains features many oxygen and hydroxyl sites that impart on the fibres a hydrophilic tendency and a susceptibility to form hydrogen bonds upon drying. This hydrophilic behaviour enables the dispersion and hydration of the fibres in water which allows for the formation of pulp slurries. The ability to form hydrogen bonds between the fibre's cellulose chains is the binding force that facilitates the final formation of paper sheets [1] [2].
2.2.2 Micro-Structure of Paper

In the study of paper properties it is important to understand how structural qualities affect physical properties. This point is elucidated by Kortschot: “a complete set of material properties describes the way in which the material interacts with the rest of the universe [...] this is the basic reason that end users cannot be interested in the structure of a material: the interaction between the user and the material is controlled by the properties of the material and not its structure, although the properties are determined entirely by the relative placement of the components”[6].

Knowledge of the detailed structure of studied specimen of paper is beneficial only if it provides insight into its physical properties. Kortschot provides an extensive list of paper structural parameters that contribute to the physical properties of paper, these parameters are in agreement with the factors provided by Page [7] in his review of mechanical beating effects on pulp. Kortschot's list of parameters that are deemed appropriate for the scope of this study is provided below.

**Fibre Morphology**
- fibre length, width and thickness
- fines, fraction and quality – i.e. The specific surface area of the fines
- curls, kinks

**Fibre Properties**
- fibre strength, distribution of strength
- fibre modulus, and stress-strain curve

**Fibre connectedness**
- relative bonded area
- bond strength

**Micro-structural variables which represent useful combinations of the above**
- sheet density (may also be observed as bulk, the inverse of density)
− fibre flexibility, and collapsibility
− specific surface area

This is a long list of structural factors, the combined influence of which composes the physical properties of paper. Some of these parameters may be measured relatively easily (fibre length, density). Conversely, certain parameters are not readily measurable. An example of such a parameter is the bond strength between fibres. Bond strength is an important parameter in the study of effect of chemical pre-treatment on the performance of low-consistency refined mechanical pulp.

The relationship between structural components and physical properties of paper is discussed in the following sections.

2.2.3 Physical Properties of Paper

The pulping industry utilizes a number of physical tests that offer practical measures for the quality of pulp and paper. Better understanding of these physical measurements and their relation with paper micro-structural properties could lead to improvements in the product quality or process efficiency or both. Theoretical paper property models are useful tools that may serve this purpose very well, this will be discussed in further portions of this review. Described below are the physical properties measured and used in this study. They are introduced along with their respective association to paper micro-structural properties.
**Canadian Standard Freeness (CSF):** Canadian standard freeness is a measure of the rate at which pulp may be drained through a sieve of standard size. It was found that specific surface area is a factor that is related to CSF values [8]. In particular, shorter fibre length and higher amount of fines are factors that lower CSF values.

**Tensile Strength:** Tensile strength represents the maximum tensile force that a specimen of paper may sustain before it breaks. Tensile strength is a function of fibre strength, fibre length and fibre-fibre bonding [9]. However, it was established that fibre connectedness is the most important factor affecting tensile strength [10][11]. It was also found that curl in fibres tends to decrease the tensile strength of paper [12].

**Tear:** Tear is a measure of the energy required to tear multiple plies of paper through a specified distance using a force perpendicular to the plane of the paper [13]. This is a practical measurement of paper strength. It is affected by factors such as fibre length, fibre strength and fibre bonding. Tear strength depends on fibre pull-out energy (dictated by bonding and fibre bonded area) and fibre strength [14][15]. However, work required to pull out fibres is significantly larger than work required for breaking them. Hence, for poorly bonded sheets only a small amount of work will be needed to tear a sheet, and conversely for strongly bonded sheets, most of the fibre will break instead of being pulled out and resulting in lower tearing energy. Therefore, a maximum tear is achieved when a proper balance is obtained between inter-fibre bonding and the fibre strength.
**Zero-span Tensile:** Zero-span tensile strength is a measurement which attempts to specifically describe the tensile strength of individual fibres [16]. This is accomplished by removing effects of elongation of the fibre network during a tensile test (to do this the test specimen is clamped between two jaws with minimal separation between them). It was shown that zero-span tensile is a reliable indication of fibre strength although it was postulated that the measurements are usually slightly lower than the real fibre tensile strength [17][18].

**Peel Energy:** Peel energy was established by Skowronsiki to be the energy required to separate a certain area of two sheets of paper that were wet pressed together after forming. He proposed that this is a practical measurement that may be used to accurately and consistently determine fibre to fibre bond breaking energy – which is consequently related to the fibre connectedness properties of the pulp [19].

### 2.3 Mechanical Refining Technology

The pulping line of a mechanical mill is usually composed of a series of three refining stages. The primary and secondary refiners are responsible for the majority of the pulping action and consume the brunt of the overall energy required to run the process [3]. The third stage refiner is traditionally employed to introduce slight adjustments to the pulp properties [20]. Occasionally, a chemical or thermal (steam) pretreatment may be utilized before refining or in between the refining stages.
There are many variables involved in the operation of a mechanical refiner. However, this study is mainly concerned with the amount of energy input into the pulp during refining – this is referred to as specific energy and is expressed in units of energy input per mass of refined pulp. It represents how much energy was transferred into the pulp by refining action. For example, the specific energy for standard TMP in a newsprint production is about 2100 kWh/ADMT, and this value can be reduced to about 1300 kWh/ADMT using modern pulping processes [21]. Another key variable of interest is the pulp consistency that represents the solids content (wood stock) in the feed entering the refiner. As it will be explained later, pulp consistency greatly affects the refiner energy consumption.

As was mentioned previously the work of a mechanical refiner breaks up the lignin matrix of the wood chips and facilitates the releases fibres (this is referred to as defibration). Additionally, the refining action hydrates the fibres and facilitates their dispersion in water and also allows for the formation of hydrogen bonds during paper forming. It is important however to realize that the refining action greatly affects the structure of wood fibres. These structural changes imparted by refining have been extensively reviewed by Page [7] and also in part by Ebeling [4]. The effects that are thought to be most relevant to this study are discussed here.

One important consequence of refining is fibre cutting that reduces fibre length and hence has adverse effect on the physical strength of paper. At the same time, refining increases bulk and improves printability, over-refining may yield to pulps consisting of mainly very short fibres. The physical properties of such pulps make them difficult to use in many application.
Additionally, the risk of linting (separation of loose particles from the paper surface during printing) was found to rise with increased fibre cutting [22].

Production of fines is yet another by-product of refining. Fines are small fibre fragments produced by the erosion of the outer layers of the fibre wall during the refining process. These particles are small enough to readily pass through a wire filter cloth [1]. Fines fill the pores between larger fibres in the sheet of paper and augment the bonding between them – as such they can enhance the strength of paper [23][24].

Refining also results in what is typically referred to as fibre development. Fibre development is a term associated with the increase in overall inter-fibre bonding. This action may be considered as two distinct effects: external fibrillation and external fibrillation [25]. External fibrillation describes what occurs on the fibre wall surface. This pertains to the removal of lignin during refining which exposes the cellulose layers of the fibre. Moreover, the refining action also disrupts the cellulose fibrils of the fibre wall causing them to rise up. The resulting “hairy” surface possesses a high relative bonding area which essentially improves inter-fibre bonding. Internal fibrillation pertains to actions taking place inside fibre walls. During refining the cellulose layers within the fibre wall become delaminated, this causes the whole fibre to be softened, and to become more flexible. This, along with the breaking of the cell wall (external fibrillation), increases the conformability of the fibres. Softer, more flexible fibres can fit more closely together and therefore obtain greater bonded areas.
In addition to the above factors, the degree of fibre curl is modified by the refining action. Curl is an important structural parameter since large amounts of curled fibres have been found to decrease tensile properties of paper [12][6]. It is known that refining consistency affects fibre curl [26].

As mentioned in the Introduction Section, the refining line of a typical mechanical pulping process is currently undergoing extensive research because this stage of pulping requires large quantities of electrical energy to operate. There are two prominent avenues that are of most interest at this time, low consistency refining and chemical pretreatment of pulp. The diagram below illustrates the traditional refining line in a mechanical pulp mill as well as the potential future improvements to this process.

![Diagram of traditional and potential modified refining lines](image)

**Figure 2.3.1:** Illustration of a traditional refining line in a mechanical pulp mill, and the prospective improvements to the refining line
Figure 2.3.1 illustrates the most prominent avenues for the improvement of efficiency in a typical refining line in a mechanical pulping mill. Verification of the practicality of these new processing variants is the focus of this study. The following Background sections review the scientific work pertaining to these two topics.

2.3.1 Refining Consistency

Traditionally, the primary and secondary refiners of a mechanical pulping process are operated at high consistency, which is usually about 30% solids content. This range of consistencies is commonly referred to as high consistency, or HC [2]. Primary and secondary refiners break wood chips into fibres and somewhat defibrillate the fibres. This is typically followed by a third refining stage to introduce minor adjustments to the pulp qualities. The tertiary refining stage is operated at a lower consistency of about 2-5% solids, referred to as low consistency or LC [20].

Currently, a shift toward greater use of the LC refining stage is believed to be the most promising avenue for the reduction of energy consumption in mechanical mills. This is occurring because LC refining has been found to have the potential to reduce energy usage in the pulping process. In fact, the total replacement of the secondary HC stage with an LC refining stage is a prospect that is currently motivating in depth research into LC refining and how it compares with HC refining [27].
The discussion of the differences between HC and LC pulp should begin with a description of how the wood fibres behave in water at various consistency levels. HC pulp is a dense aggregate that may be described as a fibrous mass of moist wood fibres. Under high shear LC pulp is more resemblant of a viscous fluid. It was established that wood fibres at low consistency form small agglomerates, or flocs, when dispersed in water [28][29]. Analysis of the mechanics of refining has shown that during beating these flocs are subjected to highly localized forces both at contact points with the breaker bars of the refiner discs as well inter-fibre tensions and compressions. This highly localized action generates more damaging conditions than what may be expected during HC refining [4].

Morphological studies performed by Murata et al., using SEM imaging have revealed that HC refining yielded gently developed and well fibrillated fibres [30]. In comparison LC refining was shown to be generally more damaging and displayed a stronger tendency to cut fibres than what was observed in HC refining. Additionally LC refining cell wall fragments were removed in localized lumps, as opposed to the gentle fibre development imparted on the fibres during HC refining.

This is congruent with work done by Klinga and Ericksen as well as Kang et al. [31][32][33], who have performed LC and HC refining comparisons. They refined LC and HC pulps to the same specific energy input and found that LC refining tends to produce pulp with both a lower average fibre length and lower CSF values than HC refining. Clark [2] also reported that given the same specific energy input, LC refined pulp had higher tensile strength than HC refined pulp.
However, the measured tear strength of the LC pulp was found to be lower than that of HC pulp. Clark also reported that LC refining generates considerably more fines and debris than pulp refined under HC conditions – this is in accord with the morphological analysis conducted by Murata et al., [30] (described in the paragraph above). A similar result was reported by Ohmori, who assessed LC and HC refined pulps at the same specific energy input [34]. Page has also conducted a comparison of HC and LC refining to determine the effect of consistency on fibre curl [26]. He found that HC refining tends to impose curl into the fibres, whereas LC refining tends to reduce fibre curl.

These experimental observations are consistent with the mechanical action of LC refining process. The high amount of fines in LC refining increases the bonding between fibres and hence tensile strength is strongly increased. On the other hand, due to fibre cutting and reduction of fibre length in LC refining process, less energy is required to pull out these short fibres and hence tear strength of LC pulp is lower than that of HC pulp.

In summary, there was much attention given to the LC refining process to produce mechanical pulp at lower energy inputs. However, LC refining is known to have adverse effects on pulp quality. Implementation of theoretical models that bridge the physical properties of paper to fibre and structural characteristics represents a promising opportunity to better understand and even to optimize the competing effects of the above variables to achieve desired product quality.
2.3.2 Chemical Pretreatments

In mechanical pulping process, the wood chips may be exposed to pretreatment with steam or certain chemical agents – or a combination of both. These preconditioning operations are referred to as TMP (thermo-mechanical pulp) and CTMP respectively (chemi-thermo-mechanical pulp). The objective of these pretreatment processes is to soften the wood chips prior to refining so that less energy is needed during the refining process. Research and development for the optimization of these pretreatment processes presents the possibilities of reduction of energy use in mechanical pulp mills [1].

The focus of most current research is on the chemical pretreatment of wood chips before refining. The two more common pathways for the chemical treatment are alkali-peroxide treatment and sulphonation. The alkali-peroxide (AP) treatment is usually formulated with sodium hydroxide and hydrogen peroxide. During this treatment the lignin of the pulp stock undergoes hydrolysis and oxidation which breaks up the molecular structure of lignin. In sulphonation, sodium sulphite undergoes sulphonation reactions with parts of the lignin network and effectively disconnecting its molecular structure [35][36]. The chemical action of these treatments also alters the surface chemistry of the fibres, which may affect fibre bonding.

It has been reported that these alkali-based pretreatments resulted in noticeable softening and swelling of the fibres, and hence affected the physical properties of pulp. As expected, the softening of fibres increased tensile as well as tear strength; likely due to a greater bonding
ability provided by the presence of soft and conformable fibres [37][38]. Yuan provided similar observations in of his comparison of AP pretreatment and untreated TMP [39]. He showed that the chemical treated pulp required less bleaching chemicals to reach the required brightness and less energy input to reach the target tensile strength – a result of the softening of the fibres, which serves to develop fibres prior to refining.

Extensive work was performed to compare the different chemical treatments with the aim of determining the treatment that is most advantageous. Although the studies were performed on various wood species, the general consensus is that the AP treatment yields changes that are as beneficial or better than the sulphonation treatment. Xu, who studied the effects of chemical treatments on eucalyptus fibres reported very similar physical property changes induced by the treatments, with the AP yielding higher brightness values [40]. Xu also conducted further comparative studies of regular TMP with and without chemical pretreatments using aspen [41] and arrived at similar conclusions as presented by Yuan [39] – described in the paragraph above. Xu's comparison of the chemical treatments showed that both types of chemical treatment affected the pulp in a similar fashion, however the AP process yielded higher brightness and greater tear strength values than the sulphonation treatment. Congruent findings were reported by Francis et al. [42], who analyzed the effects of chemical treatments on silver maple and black locust wood fibres. He reported that both of the pretreatments yielded similar effects on physical properties, however he found that the AP treatment provided higher brightness and light scattering coefficient values.
Despite extensive work related to refining consistency and chemical pretreatment of mechanical pulp, little has been done to examine combined effects of these two factors. In studying AP treated and regular pulps subjected to HC and LC refining, Xu [43] reported that LC refining of AP chemical treatment pulp required less energy to obtain a similar tensile strength than what was obtained by the treated HC refined pulp. However, he also found that the tear strength of the pretreated LC pulp was lower than that of pretreated HC pulp. Some postulations were made by Muenster et al. that the softening action induced by chemical treatment would allow for better absorption of refining intensity [27]. This would in turn yield fibres that are more readily developed and less damaged by the refining action.

### 2.4 Structural Property Models

Theoretical models that are based on paper structure could be utilized to examine differences between treated and untreated pulps. Such an analysis may use typical properties of paper to provide additional insight into the effect of chemical pretreatment on pulp and paper properties. Three key models that were used in this study are discussed in the sections below.

#### 2.4.1 Page Model

Page's objective for the development of his model was to obtain an expression for tensile strength of paper [10]. He has done so by postulating two premises for the interaction of fibres in a paper network. The first premise was concerned with the observation that during tensile
fracture of paper, the fibres laying across the failure line will either carry a load until failure, or pull out of the network and carry no load during failure. This behaviour is described by Page in the following equation:

\[ T = \frac{8n_f Z}{9(n_f + n_p)} \]

Equation 1

Where \( n_f \) is the number of fibres crossing the rupture zone that take the load at failure and then break, \( n_p \) is the number of fibres crossing the rupture zone that pull out intact due to poor bond breakage and carry no load at failure, \( T \) is the sheet breaking length, and \( Z \) is zero-span tensile also expressed in breaking length. Page then combined this equation with an expression that would dictate the relationship between the force necessary for fibre breakage and the force required for fibre pull out. Page assumed that this relation would be best implemented as a simple ratio of the two forces. By combining the two premises he arrived at the following expression.

\[ \frac{1}{T} = \frac{8}{9} \left[ \frac{1}{Z} + \frac{1}{\beta} \right] \]

Equation 2

Where \( \phi \) is the mean fibre strength (expressed in units of force) and \( \beta \) is the force required to pull a fibre from the sheet. By incorporating expressions for the mean fibre strength and the force required for fibre pullout, Page further refined the above equation. For the former he used an equation developed by van den Akker for the mean fibre strength in random sheets [44], while for the latter, he provided a simple representation for the force of fibre pull out that is dependent on the inter-fibre bond strength, the relative bonded area as well as basic geometric parameters of
fibres. The inclusion of these yielded the final expression for Page's theoretical model for the tensile strength of paper:

\[
\frac{1}{T} = \frac{9}{8Z} + \frac{12Apg}{bPL(R.B.A)}
\]

*Equation 3*

Where A is the average fibre cross section area, \( \rho \) is the sheet density, g is the acceleration due to gravity, b is the shear bond strength per bonded area (expressed in units of force per area), P is the perimeter of fibre cross section, L is the average fibre length and R.B.A is the relative bonded area. Using this expression it is possible to deduce information regarding the bonding ability of fibres, which consequently may be used as a representation of the degree of fibre development of the tested samples. The fact that simple physical property measurements are enough to leverage such high level information makes this model quite useful.

For the purposes of this study, the b and R.B.A terms of the above equation have been grouped to form the parameter \( \tau \), which represents the overall fibre-to-fibre bond shear strength. Because the Shallhorn & Karnis models include this parameter, the Page equation was modified like this to normalize the models for the forthcoming analysis. The resulting equation is shown below.

\[
\frac{1}{T} = \frac{9}{8Z} + \frac{12Apg}{PL\tau}
\]

*Equation 4*
2.4.2 Shallhorn & Karnis Tensile-Based

Based on the theory of composite materials, Shallhorn and Karnis proposed a model to predict tensile strength properties of paper [45]. This model was built on the premise that a fracture line of a certain known length (x) will have a known number of fibres (N) that are arranged perpendicularly to the fracture line, while the distance between fibre ends and the fracture line is governed by a normal distribution. Using these assumptions, the tensile strength due to fibre pull of the fibres laying across the fracture line becomes:

\[ T = \int_0^{L/2} \left( \frac{2N}{L} \right) \left( 2\pi \tau x \right) dx = \frac{N\pi \tau L}{2} \]

*Equation 5*

Where \( T \) is tensile strength of the hypothetical sheet expressed in units of force, \( N \) is the number of fibres crossing the fracture line, \( L \) is the fibre length, \( r \) is fibre cross section radius and \( \tau \) is the fibre-to-fibre bond shear strength (units of force per area). Following this, it was possible to account for the effects of sufficiently high bonding between fibres – which, if too high, induces individual fibre breakage. By incorporating fibre strength (\( Z \), measurable by zero-span tensile) the above equation can be simplified as:

\[ T = \int_0^{Z/2r} \left( \frac{2N}{L} \right) \left( 2\pi \tau x \right) dx + \int_{Z/2r}^{L/2} \left( 2N / L \right) Z \pi r^2 dx \]

*Equation 6*

Where \( Z \) is introduced as the zero-span tensile strength expressed in units of force per area. This equation was then simplified to yield the final form of the tensile-based Shallhorn & Karnis model.
This model allows for the estimation of fibre-fibre bonding and fibre development based on measurable physical properties of paper.

The Shallhorn & Karnis model and the Page model are quite similar. However because the S-K model is based on a hypothetical group of fibres defined as \( N \), it presents the flexibility for the inclusion of fibre length distribution data.

### 2.4.3 Shallhorn & Karnis Tear-Based Model

The second model developed by Shallhorn & Karnis was constructed to offer a method for the prediction of tear strength of pulp [45]. This model was based on the same premise pertaining to the fibre arrangement on the fracture line as their tensile-based model. However, since the focus of this model was to predict tear strength – the work required to tear a certain length of paper network was the necessary value that had to be expressed mathematically. First, Shallhorn & Karnis obtained an expression for the total work required to pull apart the fibres of the modelled network:

\[
W = \int_0^{L/2} \left( \frac{2N}{L} \right) \left( \pi r x^2 \right) dx = \frac{N \pi r L^2}{12}
\]

*Equation 8*

Where \( W \) is the work required to tear the sheet (expressed in units of energy or force-distance), \( N \)
is the number of fibres crossing the fracture line, \( L \) is the fibre length, \( r \) is fibre cross section radius and \( \tau \) is the fibre-to-fibre bond shear strength (units of force per area). Following this, it was necessary to account for the breakage of fibres and its effect on the tear strength. The researchers assumed that no work is required to break individual fibres. The resulting expression is shown below:

\[
W = \int_0^{2r/\tau} \left( \frac{2N}{L} \left( \frac{\pi r \tau x^2}{2} \right) \right) dx
\]

*Equation 9*

Where \( Z \) is introduced as the zero-span tensile expressed in units of force per area. This equation, when simplified, became the final form of the tear-based Shallhorn & Karnis model:

\[
W = \frac{N \pi r^4 Z^3}{12L \tau^2}
\]

*Equation 10*

This model, just like the S-K tensile-based model, may be used to observe fibre bonding ability and fibre development. In addition, it may be used in combination with fibre length distribution data to generate more accurate results. Moreover, because this model incorporates an entirely different physical property than the other two models (tear as opposed to tensile) it can offer new insights in the study of paper structure and properties.
2.5 Concluding Remarks

Mechanical refining is a prominent method for pulp manufacturing. However, this process is energy intensive and electrical energy is a significant portion of cost of mechanical pulp production. This provides considerable motivation for the development of technologies that will increase refining efficiency. Two most promising technologies for such saving are the use of low consistency refining and the use of chemical pretreatment methods. Although effects of these two technologies are well studied individually, little is known in terms of the combined effects of these two technologies on pulp and paper properties.

Considering various pulp properties, tear and tensile are among key parameters that represent the pulp quality. The relation between these properties and the structural parameters is well established by various theoretical models. In particular, theoretical models proposed by Shallhorn and Karnis and by Page relate basic physical properties of paper with a structural parameter representing the shear tensile strength of the fibre to fibre bonded area. This variable may be used as a measure of fibre development and can be estimated based on physical properties of paper. These models may therefore be used as a basis for the study of the effect of chemical treatment on low consistency refined pulps.
2.6 Hypothesis

This purpose of this study is to compare untreated and chemically pretreated pulps that underwent low consistency refining. The results obtained from this work will be used to test the validity of two hypotheses outlined below. The first hypothesis is concerned with the testing of findings already presented in current literature, while the second hypothesis pertains to a new approach to the study of chemically treated low consistency refined pulp.

Hypothesis 1: The reports provided by literature that chemical treatment improves physical properties will be validated in this study. This improvement of physical properties without refining will yield an effective acceleration of the refining process.

Hypothesis 2: The chemical treatment enhances the fibre development action induced by low consistency refining, effectively increasing the upper limit of obtainable physical properties.

The validity of these hypotheses will be examined in the following chapters.
3 Methodology

This study required the acquisition of regular and chemically treated pulps that were refined at low consistency. Both types of pulp were sampled at increasing refining energy inputs. The acquisition of pulp was carried out by researchers from the Pulp and Paper centre at University of British Columbia. The refining trials were performed at Andritz research facility located in Springfield, Ohio. Fibre characterization and fractionation were performed by researchers at the University of British Columbia. The pulp samples were then centrifugally dewatered at UBC and shipped at low temperature to the University of Toronto. At the University of Toronto pulp and paper centre, the Canadian standard freeness of the pulp was measured and then the pulps were converted into test handsheets and were subjected to physical testing, as well as SEM imagining. The physical tests involved the measurement of bulk, tensile strength, tearing strength, dry zero-span tensile and peel energy. The results of these tests were used to compare the regular and chemically treated pulp with respect to the rate of the development of physical properties of paper. Additionally, physical property acquired throughout this study was input into three theoretical models. This allowed for the indirect observation of the changes in fibre development in both types of pulp caused by refining. Provided below are the detailed description of the experimental methods implemented in this study.

3.1 Acquisition of Pulp

The pulp samples that were tested in this study were acquired by UBC researchers at a facility
that belonged to Andritz. Whole log Hemlock was used as the source material in this study. The whole log wood was first chipped, then subjected to high consistency refining (at about 20-30% consistency) using a 36" Andritz 36-1CP disc refiner to a target CSF of about 400 mL and a specific energy of about 900 kWh/t. Part of the pulp was subjected to a chemical treatment with a solution of 6%NaOH and 4%H₂O₂. The chemical agents were mixed with the pulp inside the HC refiner at the end of HC refining. Following this step, the regular and the chemically treated pulp were refined at low consistency of 4%, in a 22" Andritz TwinFlow refiner at rpm of 1200 and a net motor load of 100 kW until the target specific energy input was achieved. During this process samples of each pulp were taken at different refining energies. This resulted in a set of regular pulp samples and another set of chemically treated pulp samples, each set composed of pulp samples that were refined up to the to the following specific energies: 0 kWh/t, 150 kWh/t, 300 kWh/t, 450 kWh/t, 600 kWh/t, 900 kWh/t. These pulp samples were centrifugally dewatered and shipped to the University of Toronto for further testing.

3.2 Handsheet Preparation

The handsheet making procedure was based on Tappi Method T 205 [46]. The regular and chemical pulp samples were stored at about 4°C at a consistency of about 20-25%. Since pulp samples were received and stored at about 20-25% consistency, they were diluted to 1% consistency prior to disintegration. The diluted pulp slurry was heated to above 85°C and subjected to disintegration at 15,000 revolutions in a standard disintegrator built in accordance with specifications of Tappi Method 205. After disintegration, the pulp was diluted further with chilled to about 0.3% consistency. Part of this slurry was used for the CSF test (this procedure is
described in detail in the following Section 3.3). and the remaining of the pulp mixture was then used for handsheet making.

Fines content is a very important factor in physical properties of mechanical paper. Because of this, the water used to disperse pulp during handsheet manufacture (referred to as whitewater) was recirculated during the handsheet making process.

In a typical experiment, 400g of the 0.3% consistency pulp stock was inserted into a British standard handsheet making machine (manufactured by Noram, QC) to make handsheets based on the standard procedures. To retain the fines and achieve a stable fines content in the handsheets, initial sheets were discarded until the target weight was reached.

The handsheets were arranged in a stack of no more then 10, with paper blotters and a circular plates separating each handsheet and pressed. For the purposes of this study at least 5 handsheets from each pulp sample were made and pressed at the standard pressure of 50 psi. Additionally for each pulp sample, 5 handsheets were made and pressed at 80 psi and another 5 was made and pressed at 25 psi. Once pressed, the handsheets were air dried under standard conditions at a temperature of 23°C and humidity of 50% as prescribed in Tappi Method T 402 [47]. Dried handsheets were weighed (inside the conditioned room) to determine their grammage (expressed as g/m²). The area of each handsheet was roughly 200 cm².
3.3 Canadian Standard Freeness

Canadian standard freeness (CSF) was measured in accordance with Tappi Method T 227 [8]. The CSF is a measurement of drainability of pulp. It is a standardized measurement where a set amount of pulp is deposited into a tank with a perforated bottom that is suspended above a conical drain. Although the test pulp consistency was aimed to be 0.3% the Tappi standard for the measurement of CSF included correction tables to account for discrepancies in the test pulp consistency. Two 1kg loads were measured per pulp sample to obtain an average.

3.4 Bulk

The bulk of each handsheet involved in this study was measured by the average of 5 thickness measurements from each handsheet, the measurements were taken at equal spacing to obtain a true representation of the thickness of each handsheet. This thickness was then multiplied by the inverse of the grammage measured for each handsheet, the resulting units of bulk were cm³/g. The thickness measurements were performed by an automated micrometer manufactured by Testing Machines Inc. Handsheet grammage was measured inside the conditioning room at 23°C and 50% humidity.

3.5 Tensile Strength

The tensile strength measurements were performed in accordance with Tappi Method T 494 [9]. The tests were conducted under controlled conditions of 23°C and 50% humidity. From each
pulp sample's set of handsheets that were made at three different wet-press pressures, 5 handsheets were used to obtain 2 test specimens from each handsheet – yielding a total of 10 specimens. Each specimen was cut into a strip of 15 mm width, and a sufficient length to present a test length of 10 cm between the clamps of the tensile testing machine.

The image 3.5.1 and image 3.5.2 shown above illustrate a test specimen before and after fracture. The machine that was used was a Sintech computerized system for material testing. The test required placement of the specimen exactly horizontally between the two clamps, and setting the initial clamp separation at 10 cm. Once clamped, the specimen was elongated at a rate of 14mm/min until fracture occurred. The machine software converted the load and elongation data acquired during the test into tensile strength measurements. The units of tensile strength in the
paper industry are usually expressed as tensile strength per unit width: N/m. However, it is more common to use Tensile index, which is the tensile strength (N/m) divided by the handsheet grammage (g/m²) yielding Tensile index units of Nm/g. This is done to account for variations in mass of the different specimens.

3.6 Tear Resistance

Tear strength represents a measure of the work required to tear a paper through a certain distance with a force that is perpendicular to the plane of the torn sheet. The method for the measurement of tear strength that was used for this study was based on the Elmendorf tester type described in Tappi Method T 414 [13] and was performed at 23°C and 50% humidity. During a Elmendorf tear test, a weighted pendulum is used to tear the test specimen through a controlled tear length. The machine uses the measurement of the difference in potential energy of an empty pendulum swing and a swing which resulted in the tearing of a sample to determine the work required to tear a specimen.
The image 3.6.1 and image 3.6.2 shown above display the Elmendorf tester manufactured by Testing Machines Inc., that was used in this study. From each pulp sample, a set of five handsheets that were made at each of three different wet-press pressures were collected, 2 test specimens were cut from each handsheet, yielding a total of 10 specimens for each wet pressure. Each specimen was cut into specimens measuring 63 mm by 54 mm.

Before any samples were tested, the machine was calibrated by swinging the pendulum with and without a standard weight. During testing, single ply specimens were placed into the tear tester with the longer side arranged vertically. Prior to the test, each specimen was clamped, and a tear was initiated in the tested sheet. The length of the initial tear was 20mm so that the length of the
The tear involved in the measurement was 43mm. The recorded tear measurements that were output by the testing machine were in mN. However, tear resistance is often divided by the specimen grammage (g/m²) to account for variations in mass of the different specimens. The property obtained by that division is referred to as the tear index, it has the units: mNg/m².

### 3.7 Zero-Span Tensile

This test was performed in accordance with Tappi Method T 231 [16]. Zero-span tensile is a property which describes the strength of fibres in a paper sheet. This is done by fixing a test specimen between two clamps that are fitted closely together. The distance between the clamps is zero, which allows for the testing of tensile properties of a sheet of paper where only the fibre strength contributes to the strength of the sheet.

*Image 3.7.1: Pulmac TS100 zero-span tester with a specimen after fracture*
Image 3.7.1 displays the Pulmac TS100 zero-span tester that was used in this study. All zero-span testing took place in the conditioned room at 23°C and 50% humidity. In this study 5 handsheets of each pulp sample at each of the three wet-press pressures were used to obtain 2 specimens per handsheet – this yielded a total of 10 specimens per any pulp sample. The specimens were cut into strips of 15 mm width and a length sufficient enough to be fully pressed down by both clamps of the tester – this length was usually greater than 11 cm. The optimal clamping pressure was determined by measuring the zero-span tensile of regular copy paper strips over a range of 80-100 psi clamping pressure, it was determined that the highest zero-span tensile measurement were obtained at a clamping pressure of 90 psi, therefore this pressure was used for all the specimens involved in this study. Zero-span tensile strength is usually reported on a per unit width basis, which yields the following units: N/cm.

3.8 FAQ: Fibre Length/Width

Fibre quality analyzer involves the use of a computerized vision system to discern fibre length and fibre width of a pulp sample. FQA testing was performed by the researchers at UBC in accordance with the Tappi Method T 271 [48]. In this test, a small amount of each pulp sample was dispersed into deionized water. This dilute mixture was then placed into the Optest Equipment HiRes FQA analyzer which processed the sample automatically. The measurements acquired by the FQA were the average fibre width as well as the weight weighted average fibre length. Weight weighted fibre length was used because it offered a more meaningful representation of fibre length properties of pulp sample than simple numerical average [49].
3.9 Bauer-McNett Fractionation

Bauer-McNett fractionation was used to determine the fibre length fractions of the pulps assessed in this study. This analysis was performed by the researchers at UBC. For each pulp sample, a known amount of pulp (based on dry weight) was dispersed in water, and passed through a series of decreasing mesh sizes. The mesh sizes used were: 14 (1.4mm), 28 (0.64mm), 48 (0.32mm), 100 (0.15mm) and 200 (0.08mm). The pulp captured in each mesh stage was then dried, and weighed. The ratio of the weight of the pulp from each stage and the total initial weight was used to determine the fractionation values.

This fractionation data was also used to determine simple fibre length distributions of each pulp sample. To do this, it was first important to determine the maximum fibre length attained by each pulp. Handsheets of the regular and chemically treated pulp at zero energy input were inspected visually, it was determined that the longest fibre length present in both samples was about 6mm. This finding as well as the relative sizes of the meshes used during fractionation allowed for an iterative determination of six average fibre length values that corresponded to the Bauer-McNett fractions of each pulp sample. These distributions were incorporated into the Shallhorn & Karnis model analysis described in section 4.2.2.

3.10 Peel Energy

Peel energy was determined according to a method developed by Skowronski [19]. Peel energy
was determined according to a method developed by Skowronski [19]. In this test the peel energy required to separate two dried, but wet-bonded, handsheets is obtained. This property offered a physical representation of fibre bonding of the tested samples. It required the preparation of special handsheets. During the handsheet manufacture process, 4 additional handsheets from each pulp sample were made and joined together face-to-face while they were still wet. This resulted in two double handsheets that were then wet-pressed as standard handsheets. For each pulp sample 3 sets of double handsheets were made, each set at different wet-press pressure (25 psi, 50 psi and 80 psi pressures were used). After pressing, the double handsheets were dried and stored just like regular handsheets. Once dry, the double handsheets were cut into strips of 1 inch width and a length of at least 2 inches. 3 strips were obtained from each double handsheets, resulting in 6 specimens per sample. The samples were then ready for testing.

This test involved the use of the same machine that was used for tensile strength testing. For this test however, a well oiled pulley was attached to the top clamp of the machine. The objective of this test was to measure the load required to split a double handsheet when it was attached to the rotating pulley. Before the samples could be tested, the test was calibrated by measuring the load required to rotate the pulley. Once calibrated, the sample strips were glued to the pulley, and the bonded handsheets were slightly separated. The split was gently propagated until the free end of the specimen could be clamped in the bottom clamp of the test machine. Once this was possible, the pulley was clamped into the top clamp while the free end of the specimen was clamped into the bottom clamp. At this point, the pulley was raised at a rate of 30mm/min while the steady
The load required to separate the specimen was measured.

Image 3.10.1 illustrates a sample undergoing peel energy testing. The load measured in kg was converted into an energy per area value (J/cm²). This test was performed in a conditioned room at 23°C and 50% humidity.

3.11 Theoretical Model Set-up

The three models that were utilized in this study were introduced in the background section 2.4. These models were developed to model physical properties of paper such as tensile strength (Page model, and tensile-based Shallhorn & Karnis model) as well as tear (tear-based Shallhorn & Karnis model). All three models are equations consisting of various parameters. The variable of importance in this study was the fibre to fibre bond shear strength, $\tau$. The observation of this
parameter and how it changed as a result of refining energy input allowed for the deduction of changes in fibre development in the tested pulp samples. This analysis was possible because the values of all other model parameters were obtained through experimental testing (described in sections above), which consequently allowed for the prediction of $\tau$. The models initially expressed in equations 4, 7 and 10 of section 2.4 were rearranged to isolate $\tau$. The following equations were obtained.

Page Model:

$$\tau = \frac{12 A p g}{P L} \left( \frac{1}{T} - \frac{9}{8Z} \right)$$

*Equation 11*

Tensile-Based Shallhorn & Karnis Model:

$$\tau = \frac{Z r}{2L} \left( 1 - \frac{T}{N \pi Z r^2} \right)$$

*Equation 12*

Tear-Based Shallhorn & Karnis Model:

$$\tau = \sqrt{\frac{N \pi r^4 Z^3}{12 W}}$$

*Equation 13*

The units of $\tau$ are force per unit area. In the Page model analysis the predicted values of $\tau$ were reported in units of N/mm². In the case of the Shallhorn & Karnis models, $\tau$ was presented in arbitrary units of force per area. This was so because those models used hypothetical parameters which prevented the calculation of tear in real units.
4 Results and Discussion

The results obtained in this study were arranged into two main parts which correspond to the two premises of the hypothesis presented previously. The first part presents the physical property comparison of the regular and chemically treated pulp and how these properties were affected by low consistency refining. The aim of the first part was to determine whether the chemical pretreatment yielded an apparent acceleration of the refining process, which would allow for a lesser refining energy input to obtain adequate physical proprieties. The second part of the Results Section is concerned with the effects of the chemical treatment on fibre development of pulp caused by refining, and whether the treatment affected the subsequent refining process other than to merely accelerate it. In the third section of Results, SEM images of the surfaces of the tested handsheets are presented and their morphology is discussed. The final part of the Results contains a simple prediction of the economic gains that might be obtained through the use of the chemical pretreatment, it is based on the results acquired throughout the study.

4.1 Hypothesis 1: Enhancement of Fibre Development

In the first part of the Results Section basic physical proprieties of the chemically treated and regular pulp are discussed. The comparison is mostly made against specific energy input to compare the rate at which physical properties are changed in the two types of pulp. The tensile and tear strength of the two pulps were also plotted against bulk. This was done to normalize certain effects of the chemical treatment and to allow for a more insightful analysis.
4.1.1 CSF/Bulk and Specific Energy

The Canadian standard freeness (CSF) represents the drainability of pulp while the bulk is the inverse of density. Both of these parameters are important in the industry; they are key variables that dictate processing set-points and are easily measurable during manufacture. Most mechanical pulping mills refine their pulp for newsprint manufacture down to a CSF values of about 100. The bulk of commercial paper is usually lower than what is often obtained in laboratory runs. A typical newsprint has a bulk of roughly 1.8 cm³/g [50], such low bulks are obtainable only through considerable calendaring and pressing of the paper.

Figure 4.1.1.1: Canadian standard freeness and bulk of regular and chemically treated pulp plotted against specific energy
The Canadian standard freeness and the bulk values of the regular and chemically treated pulp are plotted against specific energy input in figure 4.1.1.1. It should be noted that both chemically treated and regular pulp displayed a decrease in CSF with increased refining, however it is evident that the chemically treated pulp exhibited a more rapid decrease in freeness than the regular pulp. As was described in the Background Section, CSF is increased by an increase in specific surface area. It may be postulated that the greater increase in specific surface area displayed by the treated pulp was caused by the generation of fines and debris during refining. Such particles drastically increase the specific surface of pulp because of their high surface area and low mass. Both chemical and regular pulp converge on the same CSF value at very high energy input, indicating that the chemical treatment did not change the maximum obtainable specific surface area. It seems that this is limited by the intrinsic fibre properties of the pulp as well as the nature of the low consistency refining itself.

Both types of pulp displayed a decrease in bulk with greater energy input. Nevertheless, the chemically treated pulp reached significantly lower bulk values when compared to the untreated pulp at any specific energy input. This comparison reveals that that the chemical treatment seems cause the fibres to soften noticeably. A softer fibre is more conformable which lends itself to greater compactability, as made evident in the figure above.

In summary, CSF and bulk plots show that the chemical pretreatment accelerates fines generation and softens the fibres, which improves fibre conformability and packing.
4.1.2 Tensile Index vs. Specific Energy

The tensile strength is one of the most important physical properties of paper. It indicates the in-plane strength of a paper sheet. Naturally a higher tensile strength is always an aim for mechanical pulp manufacturers. Tensile strength is typically increased by increased inter-fibre bonding and increased individual fibre strength. Fibre development caused by refining increases inter-fibre bonding and consequently tends to increase tensile strength (refer to the Background Section for more information regarding tensile strength). Often tensile strength is expressed in the form of Tensile Index, which is the tensile strength (N/m) divided by the grammage (expressed as g/m²). Units of the tensile index are Nm/g. This is done to eliminate the trivial dependence of tensile strength (in MPa) on sheet compaction. Typically newsprint exhibits a tensile index of about 40 Nm/g [50].
Figure 4.1.2.1 displayed above displays the tensile index of the regular and chemically treated pulp plotted against specific energy. Both types of pulp exhibited an increase in tensile strength with increased energy input. This is expected since the development of fibres and production of fines associated with refining action increases inter-fibre bondability which in turn improves tensile strength of paper. The rate of increase of tensile strength of both pulp types is similar, however the chemical treated pulp displayed higher tensile values than the regular pulp when compared at any specific energy.

Figure 4.1.2.1: 

Tensile index of regular and chemically treated pulp plotted against specific energy
It is evident that the implementation of the chemical treatment yielded an improvement in tensile strength even prior to any refining. This is congruent with the bulk results discussed in the previous section. The chemical action seemed to soften the fibres, which resulted in them becoming more conformable. This caused the decrease in sheet bulk, as well as an increase in fibre-to-fibre bonding – the cause of the tensile strength increase. These results clearly indicate that the implementation of the chemical treatment prior to low consistency refining may yield pulp that requires less specific energy input than regular pulp to obtain the same tensile properties.

4.1.3 Tear Index vs. Specific Energy

The tear strength of paper represents a paper sheet's resistance to out of plane tearing. This along with the tensile strength are crucial physical properties of paper. A high tear strength is a desirable in paper since it makes it more durable. Tear is measures as the amount of work required to tear a certain length of a paper sheet. It is very much dependant on the degree of inter-fibre bonding present in the sheet as well as the individual fibre strength. During fracture, fibres may be either pulled out – which requires work, or the fibres may break – which requires relatively negligible work. If a network of fibres is weakly bonded the work required to tear it apart will be small, conversely if the bonding is too high a large fraction of the fibre in the network will break and the sheet of paper will become brittle and will tear easily. Therefore the maximum achievable tear of a sheet of paper is usually obtained at some intermediate level of bonding.
Tear strength is often reported in the form of tear index. This is obtained by dividing the tear strength (mN) by the respective grammage (g/m²). The resulting units of tear index are mNm²/g. Typical newsprint achieves tear indexes of about 5.5 mNm²/g [50].

![Graph showing tear index of regular and chemically treated pulp plotted against specific energy](image)

**Figure 4.1.3.1**: Tear index of regular and chemically treated pulp plotted against specific energy

In the figure 4.1.3.1 shown above the tear index values of the regular and chemically treated pulp are plotted against the specific energy. It may be noted that both treated and untreated pulp displayed an initial increase in tear index as energy input increased until a certain maximum tear was reached, followed by a steady decrease of tear strength with increasing energy input. The treated pulp displayed higher tear strength at the start of refining and it reached its maximum tear
strength at a lower specific energy input than the untreated pulp so once again, it appears that the chemical pretreatment accelerated the refining process. However, the treated pulp yielded considerably lower tear strength values at the greatest specific energy input.

This somewhat parabolic behaviour is expected, and was described in the Background Section of this work. Because the bonding of fibres at the start of refining was still relatively low, further refining will developed the fibres and increased inter-fibre bondability, this increased the energy required to pull out fibres and consequently increased the tear strength. The maximum tear strength that was reached by both types of pulp represents the condition at which the bonding between fibres is sufficiently high that it causes an increased number of fibres to break instead of being pulled out. Since relatively less work is required to break fibres, the tear strength begins to decrease beyond this point as the pulp is refined further.

The shapes of both plots are similar. In fact, it seems that one would be able to superimpose both graphs if the specific energy input values of the chemically treated data were increased by a constant of about 150 kWh/t. This would effectively shift the plot of treated pulp to the right, and superimpose it roughly against the plot of the untreated pulp. This signifies that the mere addition of the chemical treatment yields pulp that if untreated would have to be refined up to about 150 kWh/t.
This result is in agreement with what was observed in the tensile strength vs. specific energy analysis. It seems that the chemical action of the pretreatment softened the fibres, which increased fibre conformability and by doing so also increased inter-fibre bondability. This increase in bondability between the chemically treated pulp fibres yielded a relatively higher initial tear strength and provided for the occurrence of the maximum tear strength at a lower specific energy input than that of the untreated pulp.

The maximum tear strength obtained by the chemically treated pulp is noticeably higher than the tear strength of the untreated pulp. To determine the validity of this observation, a statistical analysis was conducted to test whether the two data sets are significantly different. It was determined by a t-test comparison, that on the basis of 10 measurements per each maximum of the two pulp types it may be stated, with 99.9% confidence, that the maximum tear strength obtained by the treated pulp is indeed higher than the maximum tear strength obtained by the regular pulp. This occurrence will be considered further in Section 4.2.3.2 which pertains to the tear resistance based theoretical model analysis.

### 4.1.4 Zero-span Tensile vs. Specific Energy

Zero-span tensile is a parameter that is used to describe the tensile strength of individual fibres. It is a fairly important quality that is very dependant on the species of the source wood.

The Zero-span tensile values measured for all the samples were very similar. The variations between the values obtained by each sample were minute, and were considered to be
insignificant. Therefore, it seems that neither the chemical treatment nor the further low consistency refining affected the strength of individual fibres. This result implies that any changes in mechanical properties of the chemically treated and low consistency refined samples is not the result of changes of individual fibre strength.

4.1.5 Peel Energy vs. Specific Energy

Peel energy is a direct measure of fibre-to-fibre bond strength, and is calculated by measuring the energy required to separate a unit area of two dried sheets of paper that were wet-pressed together. The test and analysis were developed by Skowronska [19]. It may be used as a physical measurement of the bond strength between fibres in the tested samples. Typically refining is expected to increase inter-fibre bondability because of the fibre development of fibres induced by the beating action of the refiners, as such one may expect a rise in peel energy with increased refining.
Depicted above in figure 4.1.5.1 is the plot of peel energy of the two tested types of pulp versus specific energy. It is evident that the energy required to separate, or peel, two wet-pressed handsheets increased as the specific energy of pulp increased. The observed shape and behaviour of these plots is similar to the observations made in the previously described analysis of tensile strength vs. specific energy. The rate at which the peel energy increased with respect to increased specific energy input was nearly the same for both types of pulp. However the chemically treated pulp yielded peel energies that were roughly 20% higher than those of the regular pulp at any given specific energy amount.

**Figure 4.1.5.1**: Peel energy of regular and chemically treated pulp plotted against specific energy with 1 standard deviation error bars
Since peel energy is a fairly direct measurement of inter-fibre bondability, this result clearly shows that the addition of chemical pretreatment introduced a significant increase in fibre-fibre bonding that otherwise would have to be achieved by further refining. Therefore, this analysis made it evident that the chemical treatment would allow for the production of pulp of similar bondability to regular pulp but at a lower specific energy input.

The rate at which peel energy increases with refining for both types of pulp is similar, indicating that the nature of refining does not change and the chemical treatment does not affect the rate of fibre development during refining. This issue is assessed further in the theoretical model discussion section (Section 4.2).

**4.1.6 Tensile Index vs. Bulk**

In the previous sections of this part of results, the chemical treatment was determined to cause softening of fibres and a reduction in bulk prior to any refining taking place. In order to account for this action and to offer a more normalized basis for comparison of physical properties, the tensile index values of both regular and chemically treated pulp were plotted against bulk.
Figure 4.1.6.1: Tensile index of regular and chemically treated pulp plotted against bulk

Figure 4.1.6.1 displays the tensile index values of all of the tested samples plotted against their bulk respective bulk. It may be noted that the chemically treated and the regular pulp values are mostly superimposed on each other and seemingly follow the same decreasing linear trend. This trend of decreasing tensile strength with increasing bulk signifies that there is a strong relationship between these two properties of paper. This relation may be explained by the fact that the refining action developed and softened the fibres, additionally it caused the generation of fines and short fibres. As mentioned in the Background Section of this work, fibre softening results in greater sheet compactability while fines fill the gaps in the fibre network – it is evident that both of these actions were responsible for the reduced bulk of the tested samples. It is also known (see the Background Section) that these actions also increase the degree of bondability.
between paper sheet fibres. Since inter-fibre bonding strength is a crucial parameter affecting tensile strength, it is clear that this is the reason for the observed tensile strength increase with decreasing bulk.

It is also noticeable that the chemically treated pulp reaches the highest tensile strength values at the respectively lowest bulk values. Conversely, the regular pulp displayed the lowest tensile strength at the highest bulk value. Since all the samples have been refined to the same specific energy input, this results indicates that the addition of chemically treatment introduces an immediate decrease in bulk and a consequent increase in tensile strength. This is congruent with the observations described previously, and the implications of this finding are that the use of the chemical treatment may yield pulp of similar properties to regular pulp with a lesser refining energy input requirement.

The fact that both sample plots followed the same trend, and were superimposed on each other suggests that aside from the initial softening of pulp fibres the chemical treatment does not introduce any noticeable changes into the mechanism of fibre development during the refining process. If indeed such fibre development enhancement was present, it would be possible to observe variations in the slopes of the trends exhibited by the two pulp types; no such observation may be made. The theoretical model analysis provided in the following sections of the thesis will provide a more detailed discussion of this issue.
4.1.7 Tear Index vs. Bulk

Just as in the above analysis of tensile strength vs. bulk, tear index was also plotted against bulk. This allowed for a normalized basis for the comparisons of the regular and chemically treated pulp tear qualities. The use of bulk as the independent variable accounted for the initial softening action of induced by the chemical treatment.

Displayed in figure 4.1.7.1 above are tear index values of the regular and chemically treated pulp plotted against bulk. This plot shows that the two pulp types exhibit a somewhat parabolic trend. The tear index values increased with increasing bulk up to a maximum value, after which the tear index values decreased with increasing bulk. As was explained in the Background Section of this thesis, sheets compressed to a lower bulk possess fibres that are more closely connected and

![Figure 4.1.7.1: Tear index of regular and chemically treated pulp plotted against bulk](image-url)

Figure 4.1.7.1: Tear index of regular and chemically treated pulp plotted against bulk

Displayed in figure 4.1.7.1 above are tear index values of the regular and chemically treated pulp plotted against bulk. This plot shows that the two pulp types exhibit a somewhat parabolic trend. The tear index values increased with increasing bulk up to a maximum value, after which the tear index values decreased with increasing bulk. As was explained in the Background Section of this thesis, sheets compressed to a lower bulk possess fibres that are more closely connected and
hence yield greater inter-fibre bondability. Thus, the behaviour observed in the above plots is the expected trend for tear index measured over a range low to high fibre bondability. At low bulk, fibre bonding is high and during fracture fibres tend to be broken instead of being pulled out, resulting in relatively negligible work required to tear a sheet. Conversely high bulk represents low fibre bondability, in which case not much work is required to pull out fibres from the weakly bonded network. The combination of these two effects yields the observed parabolic behaviour.

Although, both pulp types exhibit the same parabolic shape, it is noticeable that the chemically treated pulp yields a higher maximum tear index value than that of the regular pulp. The measurements comprising the maximums of both types of pulp were statistically tested (using a t-test comparison) to determine if they are different. This analysis revealed a significant difference at the 99.9% confidence level. This behaviour may an indication of fibre development enhancement because it seems to increase the maximum potential tear resistance obtainable from the chemically treated pulp. This is not the same as the evidence for the acceleration of refining reported in Section 4.1. Acceleration of refining would not increase the maximum potential physical properties of paper, it would merely reduce the refining energy requirement to obtain the same physical properties. Since fibre strength was shown to be the same for all samples, a logical explanation for a greater maximum tear value obtained by the chemically treated pulp would be that this type of pulp exhibits some superior fibre-to-fibre interaction properties than the regular pulp. However, there other variables that must still be considered – the tear-based theoretical model analysis provided in Section 4.2.3.2 will allow for complete explanation of this behaviour.
4.2 Hypothesis 2: Enhancement of Fibre Development

In this section of results and discussion, three theoretical models for the prediction of physical properties of paper were used to assess the inter-fibre bondability qualities of the regular and chemically treated pulp refined at low consistency. The Page model, as well as the tensile-based and tear-based Shallhorn & Karnis models were rearranged to isolate the variable corresponding to the fibre-to-fibre bond shear strength, symbolized by $\tau$. This allowed for the use of basic physical properties of paper such as tensile strength, tear strength, zero-span tensile to obtain quantitative predictions for the strength of inter-fibre bonding in the tested samples.

In this analysis the predicted values for the fibre-to-fibre bond shear strength ($\tau$) were plotted against the respective bulk values. Bulk was used as the independent variable because it allowed for a fair comparison of the differences in fibre development of the two pulp types. This is so because the bulk measurements accounted for the initial softening action imparted by the chemical treatment. The softening action was determined to decrease bulk and increase fibre-to-fibre bondability (refer to Section 4.1 for a more detailed description). The use of bulk as the basis for comparison normalized these effects, and allowed for a more direct assessment of the effects of refining on the fibre bondability characteristics of these pulps.
4.2.1 Page Model

The Page model was developed to offer a means for the prediction of tensile strength properties of paper sheets and is the most widely used model in the literature. It is founded on the assumption that the tensile strength of paper is related to the force required for fibre pull out and the force required to break individual fibres (zero-span tensile). The force required for fibre pull out is a key component of this equation, its presence allows for the assessment of inter-fibre bondability. This is so because the calculation of this force involves the knowledge of the bonded area as well as the fibre-to-fibre bond shear strength (τ), the latter being of interest since it may be used as an indication of inter-fibre bondability.

It was mentioned in the Background Section that the Page model and the tensile-based Shallhorn & Karnis model are different mainly because the S-K model allows for the inclusion of fibre length distribution data, whereas the Page model relies on fibre length average values. While the introduction of the fibre length distributions precedes the Results Section pertaining to the S-K model analysis, at this point it is important to introduce the average fibre length data to precede the Page model analysis. The section below provides this information.

4.2.1.1 Weight-Weighted Average Fibre Length

The weight-weighted average fibre length data was obtained by FQA analysis. Fibre length is an important parameter because it affects the force required to pull out a fibre, which is crucial for
both tensile strength and tear resistance. The weight-weighted average fibre length data of the samples analyzed in this study is shown below, the values are plotted against bulk because bulk is the basis of the theoretical model assessments.

![Weighted fibre length values of regular and chemically treated pulp plotted against bulk](image)

**Figure 4.2.1.1.1: Weight weighted average fibre length of regular and chemically treated pulp plotted against bulk**

Figure 4.2.1.1.1 displays the weight-weighted fibre length values of the two types of pulp plotted against bulk. It is clear that at high bulk values – which correspond to low specific energy input – both pulps had similar fibre lengths. However, as bulk decreased with further refining, it is evident that the average fibre length of the chemically treated pulp was slightly higher than that of the regular pulp when compared at the same bulk. This is most discernible at a bulk range of 2.5-3cm³/g. This is an indication that the chemical treatment affected the mechanism of fibre
shortening during refining – resulting in the chemically treated pulp retaining a higher average length with increasing specific energy input. The following sections will determine whether the mechanism of fibre development was altered as well.

### 4.2.1.2 Page Model Analysis (vs Bulk)

The Page model equation was rearranged to isolate the parameter, τ, which represents the fibre-to-fibre bond shear strength. The equation was presented in the Methodology Section, it is provided again below.

\[
\tau = \frac{12A_{pg}}{PL} \left( \frac{1}{T} - \frac{9}{8Z} \right)
\]

*Equation 11*

What follows are results of the analysis of the τ values obtained for the regular and chemically treated pulp by the Page model. In this model the units of τ, the fibre-to-fibre bond shear strength, are N/mm².
The figure 4.2.1.2.1 displayed above shows the values of the fibre-to-fibre bond shear strength of the regular and chemically treated pulp plotted against bulk. The values of $\tau$ for both regular and chemically treated pulp were observed to increase exponentially with decreasing bulk. The plots of the two pulp types followed a nearly identical trend, yielding data points that were mostly superimposed on each other. This similarity between the trends is expected since this model is based upon modelling of tensile strength of paper and as it was discussed in Section 4.1.6 the tensile strength was shown to be similar for both types of pulp when compared against bulk. The chemically treated pulp displayed slightly lower $\tau$ values at bulks of about 2.5cm/g. In the previous section the average fibre length values of the tested pulps were show. There it was

Figure 4.2.1.2.1: Fibre-to-fibre bond shear strength of regular and chemically treated pulp plotted against bulk
determined that at bulks of roughly 2.5 the chemically treated pulp yielded longer average fibre lengths than the regular pulp. The other parameters involved in the model (tensile and zero-span strength) were shown to be similar for regular and chemically treated pulp when compared at the same bulk, therefore it seems that the variation in average fibre length between the regular and chemically treated pulp is the cause of the slight difference observed in the Page model analysis.

To explain this difference in fibre-to-fibre bond shear strength one must first consider the impact of fibre length on the tensile strength within this model. The force required to pull out fibres out of a paper sheet is a major factor in the Page model, this force is derived from the geometry of the fibres as well as the bond strength between the fibres. If all variables were held constant while the fibre length was increased, the tensile strength would also increase. In the Page model analysis of this study, the chemically treated samples had a slightly longer fibre fraction than regular pulp at the same tensile strength and bulk – therefore the model predicted a lower fibre-to-fibre bond strength for the chemically treated pulp to account for this discrepancy.

The difference between the fibre-fibre bond strength of the pulps was nevertheless very small. Therefore it seems that the refining action on the pulp was not drastically altered by the introduction of a chemical treatment. From this it follows that the fibre development caused by refining – and consequently the mechanism for increasing inter-fibre bondability, are not fundamentally changed by the chemical treatment. If such an improvement in fibre development was present, then the observable rate at which $\tau$ increased with decreasing bulk would be
noticeably higher than that of the regular pulp. Based on these results it seems that the suppositions made by Muenster et al. [27], stating that the softening action of the chemical treatment would lessen the intensity of refining cannot be supported, rather, the evidence presented suggests that the softening action imparted by the chemical treatment does not reduce the damaging action of refining.

The only discernible effect of the addition of the chemical treatment is the apparent acceleration of the refining process. This seems to be caused by the fibre softening action of the chemical treatment and the consequent changes to fibre conformability, bulk, and fibre bondability. As shown in Section 4.1.1, the highest bulk values achieved by the chemically treated pulp are roughly 3.5 cm³/g – this represents samples at the lowest specific energy input. Both pulp types yield similar fibre-to-fibre bond shear strength at this bulk, however the chemical treated pulps achieved this bulk without any mechanical beating, whereas the regular pulp was refined to reach this bulk. Because of this it seems that it would be possible use the chemical treatment to produce a pulp of similar fibre-to-fibre bonding qualities to a pulp that would otherwise require considerable refining energy input.
4.2.2 Shallhorn & Karnis Model

The two Shallhorn & Karnis models were developed to offer a means for predicting tensile strength and shear strength of paper sheets respectively. The Shallhorn & Karnis models take on a hypothetical approach to the study of the tensile and tear fracture line. In these models the length of the fracture line is arbitrary while a variable, N, is introduced to represent the number of fibres crossing the fracture line.

Although values of N was chosen arbitrarily for the purposes of this study, there were certain adjustments that were implemented to improve the accuracy of the model. Since refining alters fibre dimensions, it was important to account for the fact that the number of fibres crossing an arbitrary fracture length will change for samples refined to different specific energy inputs. A fixed value of N was set for one reference sample, and then this value was scaled for all other samples proportional to their respective fibre widths. This resulted in increased values of N for samples that underwent longer refining.

4.2.3 Incorporation of Fibre Length Distribution

To improve the accuracy of the Shallhorn & Karnis model analysis, an attempt was made to introduce the effects of fibre length distribution into the model equations. This was performed in a manner that partially emulated the work of Kortschot and Feldman [51], who used a scripted random distribution generator for the fibre length data in their analysis. For the purposes of this
study, Bauer-McNett fractionation data was used to measure simplified fibre length distributions. These distributions described the fibre lengths of each sample in terms of six distinct average fibre length values and their relative frequencies of occurrence. To conduct the model assessment, the value of N for each sample evaluation was divided into the fibre length fractions of the distribution, this yielded six separate model equations. The corresponding average fibre lengths relating to each fraction were entered into these model equations, the sum of which resulted in the final value predicted by the model. These fibre length distribution plots are displayed in the following figures.
Figure 4.2.3.1: Progression of fibre length distribution of regular pulp caused by increased specific energy input

Figure 4.2.3.2: Progression of fibre length distribution of chemically treated pulp caused by increased specific energy input
The plots show in figure 4.2.3.1 and figure 4.2.3.2 display the simplified fibre length distributions of the tested pulp samples. Each sample's overall average fibre length was expressed as a weighted average of six average fibre length values. It may be noticed that the distributions are initially very similar for both types of pulp. Both pulps displayed a significantly high fraction of fine fibres even at zero specific energy input, because they were both based on a commercial pulp that had already been refined at high consistency. Refining seemed to progressively reduce the long fibre fraction and increase the short and fine fibre fractions, this behaviour was similar for both types of pulp until a specific energy input value of 600 kWh/t and onwards. At this point as well as at the maximum specific energy input (900 kWh/t) the chemically treated pulp showed a more severe reduction of long fibre fraction and a greater increase in the short fibre fraction than the regular pulp. This result seems to indicate that the chemical treatment effectively accelerated the refining process, which caused a more significant reduction of long fibre fraction than that yielded by regular pulp refined to the same specific energy. Coincidentally, these high specific energy inputs also correspond to the region at which the chemically treated pulp achieves lower bulk values than those yielded by regular pulp.

**4.2.3.1 Tensile-Based Shallhorn & Karnis (vs. Bulk)**

The Shallhorn & Karnis tensile strength model was developed to offer a method for predicting the tensile strength of paper sheets. Similarly to the Page model, this model relates the tensile strength of paper to the force required for fibre pull out and to the force required to break individual fibres. As was the case with the Page mode, the force required for fibre pull out is the component of this model where the fibre-to-fibre bond shear strength is incorporated. While the
similarities with the Page model are significant, this model assessment utilized the fibre length
distribution data while the Page model merely used one single value for the average fibre length.
The tensile-based Shallhorn and Karnis model rearranged for $\tau$ is provided below.

$$
\tau = \frac{Zr^2}{2L} \left(1 - \frac{T}{N\pi r^2}\right)
$$

Equation 12

The results of this analysis are provided below. Because of the hypothetical assumptions made in
this model, analysis of the number of fibres crossing the fracture line, and the units for $\tau$ – the
fibre-to-fibre bond shear strength – are arbitrary in the form of force divided by bonded area.

Figure 4.2.3.1.1: Fibre-to-fibre bond shear strength of regular and chemically treated pulp
plotted against bulk
Figure 4.2.3.1.1 displays the inter-fibre bond shear strength of the regular and chemically treated pulps estimated by the tensile-based Shallhorn & Karnis model plotted against bulk. The trend followed by both types of pulp seems to be similar to what was observed using the Page analysis. The same exponential increase of $\tau$ with decreasing bulk may be observed. Similarly to what was observed in the Page model analysis, it is evident that at bulk values of about 2.5 cm$^3$/g the chemically treated samples yielded a somewhat lower $\tau$ value than that of the regular pulp. The Shallhorn & Karnis model considered the forces required for fibre pull out as well as the forces required for individual fibre fracture – similarly to the page model, this explains the resemblance of the plots obtained by these two models.

The Shallhorn & Karnis model assessment incorporated fibre length distribution data – a parameter that was not accounted for by the Page model. However, the inclusion of these fibre length distributions seemed to have an effect that was similar to what was observed in the Page model – where only single average fibre length values were used. As shown in the above plot, fibre-to-fibre bond strength seemed to be slightly lower for the chemically treated pulp than the regular pulp at bulk of about 2.5 cm$^3$/g. Due to fact that the other parameters which compose the Shallhorn and Karnis model were determined not too change significantly when assessed at the same bulk, it seems that the changes in the fibre length distribution are the cause of this discrepancy. It was established in the Page model analysis that average fibre length affected the predicted fibre-to-fibre bond shear strength of the regular and chemically treated pulp. Now it is important to assess how the fibre length distributions have affected the results of the Shallhorn and Karnis model.
When compared at the same specific energy, chemically treated pulp refined to 600 and 900 kWh/t were determined to have a greater fraction of shorter fibres than the regular pulp samples at the same specific energy. However the chemically treated pulp samples refined to 600 kWh/t were found to have a slightly greater long fibre fraction than the regular pulp sample refined to 900 kWh/t – both of those pulp samples were found to have very similar tensile strength and bulk. In the plot above these two sets of samples represent the region where the values of \( \tau \) of the chemically treated pulp are lower than those of the regular pulp. As it was described in the Page model analysis, a high long fibre fraction in a sample sheet which obtains the same tensile strength as a sample sheet with a lower long fibre fraction necessitates the predication of a lower fibre bond strength. This is what was observed in this analysis.

According to the tensile-based Shallhorn and Karnis model analysis, chemically treated pulp when refined to high specific refining energies retained a greater fraction of long fibres than regular pulp when compared at the same bulk. This was accompanied by an apparent decrease in the strength of inter-fibre bonding of the chemical pulp at low bulk and high refining energy. The effects of this higher retention of long fibre fraction, and decreased inter-fibre bond strength observed in the chemically treated pulp seemed to balance each other out so that when compared at the same bulk, the chemically treated pulp and the regular pulp yield very similar tensile strength. The inclusion of fibre length distribution in the S-K model analysis yielded similar results to what was obtained in the Page model analysis which used single average fibre length values.
In conclusion, there is no evidence that the chemical treatment enhances fibre development during refining, in fact there is some indication that the chemical treatment actually inhibits fibre development at high refining energies. In practical terms, this detrimental effect is countered by the apparent greater retention of long fibres (at a given bulk) observed in the chemical pulp – yielding paper of similar tensile strength to that of regular paper when assessed at the same bulk.

This lack of evidence for the enhancement of fibre development seen in the tensile-based model analysis is in accordance with what was determined in the analysis of the physical properties of paper, especially tensile strength and peel energy – both properties that are influenced heavily by inter-fibre bonding. Both tensile strength and peel energy were observed to increase with refining energy at the same rate for both chemical and regular pulp, a strong indication that the mechanism of fibre development was not altered by the chemical treatment.

4.2.3.2 Tear-Based Shallhorn & Karnis (vs. Bulk)

The tear-based Shallhorn & Karnis model was developed to predict tear strength properties of paper sheets. This model considers the tearing of paper as the balance between the work required to pull out fibres and the lack of work yielded by the breaking of fibres. Whereas the two previous theoretical models were concerned with the force required for fibre pull out, this model pertains to the work required for fibre pull out, as such fibre length becomes exponentially more important than in the tensile-based models (since work required for fibre pull out is the force of fibre pull out multiplied by distance). The tear-based Shallhorn and Karnis model equation
rearranged for $\tau$ is shown below.

$$\tau = \sqrt[3]{\frac{N\pi r^4 Z^3}{12W}}$$

*Equation 13*

Because of the hypothetical assumption of the number of fibres crossing the fracture line, the units of the value of $\tau$ which represent the fibre-to-fibre bond shear strength in this model are arbitrary units of force divided by bonded area. The results of this assessment are provided below.

*Figure 4.2.3.2.1: Fibre-to-fibre bond shear strength of regular and chemically treated plotted against bulk*

The figure 4.2.3.2.1 displayed above shows the fibre-to-fibre bond shear strength of the regular
and chemically treated pulp plotted against bulk. It may be noticed that the plots representing both types of pulp are very similar. The same exponential increase in fibre-to-fibre bond shear strength may be noticed with decreasing bulk for both types of pulp. The close similarity between the plots of the regular and the chemically tread pulp indicates, that according to this model, the chemical treatment did not affect the mechanism of refining and fibre development in any way. This is further evidence that disputes the suppositions that the softening of fibre imparted by the chemical treatment would decrease the intensity of refining and allow for enhanced fibre development during beating. This result is congruent with what was observed in the Page model analysis and the tensile-based Shallhorn & Karnis analysis.

At this point it is possible to provide an explanation for the observations made in Section 4.1.3 and 4.1.7. Those sections pertained to the tear index comparison of the two types of pulp versus specific energy and bulk respectively. In both cases it was determined that the chemically treated pulp acquired a higher maximum tear index than the regular pulp. Now that it was established that there are no significant differences in fibre bonding between the two types of pulp when compared at the same bulk, it is evident that the observed difference in tear index maximum was the results of the greater fraction of longer fibres retained in the chemically treated pulp.

Both the average fibre length values as well as the fibre length distributions have indicated that the chemically treated pulp had generally slightly longer fibres than the regular pulp at high energy inputs and low bulks. Given the same bond strength, it is clear that the longer fibres present in the chemically treated pulp increased the work required for fibre pull out and hence
increased the maximum obtainable tear.

Aside from this slightly increased tendency to retain long fibre the only observable effect of the chemical treatment is the apparent acceleration of the refining process. The chemically treated pulp even at zero specific energy input exhibited a bulk and fibre-to-fibre bond shear strength that was equivalent to regular pulp samples that have been subjected to refining. Additionally it may be noticed that at the maximum specific energy input, the chemically teated pulp obtained both a lower bulk and a higher fibre-to-fibre bond shear strength values than the regular pulp. This is congruent with the findings reported in the other two model assessments.

4.3 SEM Image Analysis

The paper samples of the regular and chemically treated pulps at all the tested specific energies were subjected to a scanning electron microscope analysis. This allowed for a visual inspection of the changes introduced by refining, and direct observation of the differences between the regular and chemically treated pulp. Two sets of images were created, one set at a relatively low magnification (50 times) and another set at relatively high magnification (600 times). These images are presented and discussed below.

4.3.1 Low Magnification Surface Images

In this section the low magnification SEM images of the surface of the assessed pulp handsheets are shown.
Image 4.3.1.1: 50X magnification SEM surface image of regular pulp refined to 0 kWh/t

Image 4.3.1.2: 50X magnification SEM surface image of chemically treated pulp refined to 0 kWh/t

Image 4.3.1.3: 50X magnification SEM surface image of regular pulp refined to 150 kWh/t

Image 4.3.1.4: 50X magnification SEM surface image of chemically treated pulp refined to 150 kWh/t
Image 4.3.1.5: 50X magnification SEM surface image of regular pulp refined to 300 kWh/t

Image 4.3.1.6: 50X magnification SEM surface image of chemically treated pulp refined to 300 kWh/t

Image 4.3.1.7: 50X magnification SEM surface image of regular pulp refined to 450 kWh/t

Image 4.3.1.8: 50X magnification SEM surface image of chemically treated pulp refined to 450 kWh/t
Image 4.3.1.9: 50X magnification SEM surface image of regular pulp refined to 600 kWh/t

Image 4.3.1.10: 50X magnification SEM surface image of chemically treated pulp refined to 600 kWh/t

Image 4.3.1.11: 50X magnification SEM surface image of regular pulp refined to 900 kWh/t

Image 4.3.1.12: 50X magnification SEM surface image of chemically treated pulp refined to 900 kWh/t
The above images show the SEM captures of the surface of the chemically treated and regular pulp at low magnification.

Analysis of the two pulp types at zero energy input shows the significance of the effect of the chemical treatment on the morphology of the paper sheet. It is clear that the surface of the chemically treated pulp is smoother and more uniform in terms of fibre distribution. It is possible to distinguish the difference between the degree of fibre collapse of the two pulp types. The chemically treated pulp yielded fibres that are more conformable and therefore flattened, whereas the regular pulp fibres were more cylindrical. This is in agreement with the observations that were made in previous sections of the thesis, where it was observed that addition of the chemical treatment resulted in immediate softening of the fibres.

Both pulp types showed similar changes with further refining. As the energy input increased the surface of the sheets became smoother and more uniform, the fibres became more collapsed and conformed while the amount of long fibres steadily diminished. The decrease in fibre length, and consequent increase in the amount of short fibres and fines with further refining may also be observed in the fibre length distribution figures shown in Section 4.2.2. Since the chemical treated pulp displayed a greater degree of fibre collapsibility at zero energy input than regular pulp, it is not surprising to see that this quality was also observable in samples that were refined further. In fact it may be concluded that the morphological qualities of any chemically treated sample that was scrutinized in this study are similar to that of the regular pulp but at one less stage of refining. This is further evidence that the chemical treatment may be used to reduce
the required refining energy during a mechanical pulping process.

Although it seems that the chemical treatment has accelerated the refining process, there does not seem to be any morphological evidence that would suggest that the treatment enhances the fibre development during refining. After the initial softening effect of the chemical treatment, both types of pulp seemed to react in a similar fashion to the effects of further refining. There is no indication that the chemical treatment results in a less intense refining action, as it is apparent that the damage imparted during beating is comparable for both types of pulp.

4.3.2 High Magnification Surface Images

In this section the high magnification SEM images of the surface of the assessed pulp handsheets are shown.

*Image 4.3.2.1: 600X magnification SEM surface image of regular pulp refined to 0 kWh/t*

*Image 4.3.2.2: 600X magnification SEM surface image of chemically treated pulp refined to 0 kWh/t*
Image 4.3.2.3: 600X magnification SEM surface image of regular pulp refined to 150 kWh/t

Image 4.3.2.4: 600X magnification SEM surface image of chemically treated pulp refined to 150 kWh/t

Image 4.3.2.5: 600X magnification SEM surface image of regular pulp refined to 300 kWh/t

Image 4.3.2.6: 600X magnification SEM surface image of chemically treated pulp refined to 300 kWh/t
Image 4.3.2.7: 600X magnification SEM surface image of regular pulp refined to 450 kWh/t

Image 4.3.2.8: 600X magnification SEM surface image of chemically treated pulp refined to 450 kWh/t

Image 4.3.2.9: 600X magnification SEM surface image of regular pulp refined to 600 kWh/t

Image 4.3.2.10: 600X magnification SEM surface image of chemically treated pulp refined to 450 kWh/t
Displayed above are high magnification SEM images of the surfaces of handsheets of the pulp samples that were involved in this study. These images will allow for the assessment of the morphological qualities of the fibres at the scale of fibre width.

Although not as discernible as it was in the low magnification comparison, it is possible to note that the chemically treated fibres were slightly more collapsed prior to any refining than the regular fibres. Both types of pulp displayed the presence of some wall fragments and debris even prior to refining, and this is expected since both pulp types were refined at high consistency before being subjected to the low consistency tests of this study. Assessment of the images of both types of pulp at increasing refining energy showed signs of progressive fibre damage and breakage. It seems that continuing energy input introduced more fibre wall delamination. With increasing energy input this is manifested by the more noticeable presence of thin fibre
fragments attached to the fibres, as well as a greater amount of very small fines and debris. The changes imparted by refining occurred gradually for both types of pulp. However, because of the initial softening effect of the chemical treatment, the treated samples displayed a greater degree of fibre collapsibility and more fibre degradation than the regular pulp when compared at the same energy input. Again, it is evident that the addition of the chemical treatment resulted in an observable acceleration of refining.

This effect is most noticeable when one considers the images of the samples subjected to the maximum energy input. It is evident that the chemically treated fibres were much more damaged than the regular pulp. In fact the treated fibres seem to have been almost disintegrated, whereas the regular fibres showed effects of refining that are not nearly as severe – both were refined to the same specific energy input.

The effect of this extensive fibre damage in the chemically treated pulp at high specific energy may be observed in this sample's tensile and tear properties. The tensile strength obtained by this pulp is the highest of all samples, this is so because the high fines content present in this pulp facilitated bridging between fibres and increased the bonding within the sheet. This high bonding is what caused such a high tensile strength.

The tear resistance exhibited by this pulp was conversely the lowest of all samples. This is so because in the case of tear strength, the high degree of bonding induced fibre breakage instead of
fibre pull out – which lowered the tear energy. Additionally the presence of short fibres decreased the work required for fibre-pull out (since work is force multiplied by distance) further decreasing the tear resistance value.

The chemical treatment seemed to accelerate the effects of refining. This is in agreement with the low magnification image assessment, as well as the assessment of the physical data described in previous section. There are no observable indications that the addition of the chemical treatment affected the mechanism of refining. It seems that both type so of pulp have underwent the same damaging beating process, the effects of which are comparable for both types of pulp. The SEM analysis did not seem to produce any evidence of any enhancement in refining fibre development imparted by the chemical treatment.

4.4 Assessment of Economic Gains

The apparent acceleration of refining action imposed by the chemical treatment was observed in all of the assessments discussed in this thesis. The linear fits of tensile index and peel energy plotted against specific energy of the regular and chemically treated pulp were compared. The slopes of those plots were observed to be very similar, however the Y-intercept values of the trend-lines were determined to be different (this is why an acceleration of refining action was noticed). Based on the 95% confidence intervals of the Y-intercept values it was determined that the chemically treated pulp needed between 200 kWh/t to 400 kWh/t less refining energy than
regular pulp to obtain a similar physical property value. This is an imprecise estimation because of the considerable variation in the measured physical property values.

The Introduction Section featured a simple economic assessment of potential gains due to efficiency improvements of the refining line in a mechanical pulping mill. A hypothetical mill was proposed that manufactures 100,000 tonnes of pulp annually. Based on literature estimates, which state that about 90% of electrical energy use in a mill is dedicated to refiner operation, and that a typical mill exhausts about 2160 kWh per tonne of dry pulp, it was determined that a reduction of 1% (or 21.5kWh/t) in the electrical energy used on refining would yield a saving of $170,000 per year.

In the Methodology Section, it was mentioned that both types of pulp were refined up to 900 kWh/t in a high consistency refining stage prior to the LC refining stage. Assuming that both pulps also required at least another 200 kWh/t of LC refining to reach an industry viable CSF value (about 100-150) it may be estimated that both types of pulp would require at least 1100 kWh/t of refining. It was mentioned above that regular pulp needed about 200-400 kWh/t more of refining energy than the chemical pulp to obtain similar physical properties. This evaluation shows that the chemically treated pulp would require between 15-25% less energy than the regular pulp. In a hypothetical mill generating about 100,000 tonnes of pulp annually, this energy saving would translate into a operating cost reduction of about $2.5-4.3 million.
This assessment is very general and considers a relatively small component of the overall operating costs of a mechanical mill. A complete analysis of the economic impact of the chemical treatment would have to account for the cost of chemical reagents, expenses associated with adjustments in the refining process, potential yield losses due to the chemical treatment, as well as other miscellaneous costs. This would require detailed research and could be incorporated in future studies pertaining to chemical treatment in mechanical pulping.
5 Conclusions

The conclusions of the comparison of the physical properties, the theoretically predicted fibre-to-fibre bonding properties, as well as the morphological qualities of the regular and chemically treated pulp are presented in the sections below.

5.1 Hypothesis 1

The analysis of the CSF and the bulk values of the regular and the chemically treated pulp against specific energy suggested that the chemical treatment softened the fibres which lowered bulk before any refining took place. The chemical treatment also increased the rate of fines generation, which resulted in a more rapid decrease of CSF with increasing specific energy than was observed for regular pulp.

The chemical treatment seemed to improve tensile strength by a constant amount when compared to the regular pulp at any specific energy. This indicated that the chemically treated pulp would require less refining energy to obtain a desired tensile strength than the regular pulp.

The tear versus specific energy analysis yielded similar results. The chemically treated pulp yielded paper with tear resistance properties that were comparable to those obtained by regular
pulp that was relatively more refined. The chemically treated pulp yielded higher maximum tear values than the regular pulp, indicating that the chemical treatment improved the development of tear resistance during refining. The tear-based Shallhorn and Karnis model analysis suggested that this was caused by slightly higher long fibre fraction present in the chemically treated pulp at high specific energy.

Zero-span tensile results showed that the individual fibre strength was not significantly affected by the chemical treatment or further refining action.

Peel energy results were very similar to the tensile data, and likewise have show an acceleration of refining action imparted by the chemical treatment.

Tensile index versus bulk displayed a collapsing of the regular and chemically treated pulp data points. This suggested that apart from softening action induced by the chemical treatment which altered the physical properties of the pulp in a manner that would otherwise require refining, the chemical treatment did not introduce any other noticeable effects.

The tear index versus bulk comparison showed similar trends exhibited by regular and chemically treated pulp. The chemically treated pulp displayed higher maximum tear values than the regular pulp. It was determined that this was caused by higher long fibre fraction retained by the chemically treated pulp at high refining energies.
There is strong evidence of accelerated refining, which is an agreement with studies reported in literature. There was no indication of the enhancement of the development of physical properties aside from the slightly higher maximum tear value obtained by the chemical pulp in comparison to the regular pulp.

5.2 Hypothesis 2

The results of the Page assessment did not show any significant difference in fibre-to-fibre bonding qualities of the two types of pulp during refining. The chemically treated pulp yielded slightly lower fibre bonding values at low bulks. This was caused by the slightly higher average fibre length values exhibited by the chemically treated pulp at those bulks.

Similar results were obtained by the tensile-based Shallhorn and Karnis model. This implied that the inclusion of fibre length distributions in the model had a similar effect to the inclusion of a single average fibre length value.

Tear-Based Shallhorn and Karnis model did not show any significant difference between the regular and chemically treated pulp. The inclusion of the fibre distribution did not yield any discrepancies between the fibre-to-fibre bond strength values of the two types of pulp.

The occurrence of the higher maximum tear index obtained by the chemically treated pulp was
explained by the higher long fibre fraction retention in the chemically treated pulp.

In summary, all theoretical models yielded little evidence of enhanced fibre development as a result of chemical treatment. The observable effects of the chemical treatment were the apparent acceleration of refining as well as the slightly greater retention of long fibres with prolonged refining.

5.3 Morphology

Both low and high magnification images showed the immediate fibre softening effects of the chemical treatment. Further refining seemed to have the same effect on both types of pulp, however when compared at the same specific energy input, the chemically treated fibres seemed to be more collapsed and had a greater amount of fines and debris than the regular pulp.

The postulation that the chemical treatment accelerated the refining process was confirmed by the inspection of the SEM images. However the lack of any significant differences in the effects of refining on the regular and the chemically treated pulp indicated that there are no improvements imparted by the chemical treatment on the mechanism of fibre development during refining.
5.4 Future work

A wider range of chemical treatments should be studied to augment the findings that the chemical treatment did not enhance the mechanism of fibre development.

More physical testing of the fibre-to-fibre bonding should be conducted. Single fibre pull-out tests or fracture line mass decay (as developed by Gallage [15]) tests are recommended.

More specialized and complex theoretical models for the physical properties of paper should be implemented, such as the tear energy model developed by Yan [14].

More detailed morphological studies should be made, such as X-ray tomography, to consider the changes in fibre arrangement during refining of chemically treated and regular pulp.

A more detailed economic analysis of the impact of the chemical treatment in the refining process is suggested. So that the electrical energy savings may be compared against the costs of chemical treatment implementation.

An assessment of the effects of pulp pH, polarity, and fibre surface charge effects (zeta potential) in the two types of pulp on the paper properties is suggested.
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