IMPROVED PENETRATION OF CHEMICALS DURING CHEMI-MECHANICAL PULPING WITH ANTHRAQUINONE

by

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FOREWORD

This thesis deals with the improvement of chemical penetration during chemi-mechanical pulping (CMP) using the catalyst anthraquinone (AQ) in conjunction with variations in pulping process parameters. These parameters are: wood chip thickness, pre-treatment agents, compression ratio, hydraulic crushing of wood chips, pre-steaming and evacuation, concentration of liquor chemicals, anthraquinone charge, and liquor soaking time.

The work presented here is a part of a post graduate research program sponsored by the Network and Centres of Excellence, in cooperation with the Department of Chemical Engineering at McGill University.

This thesis is presented in 5 chapters. The introduction to the necessity of this research and the objectives of the thesis are presented in Chapter 1. Chapter 2 discusses the effect of wood structure and its properties on a pulping process, and of anthraquinone as a pulping redox catalyst. A literature review pertaining to the research involved in this thesis is also presented. Chapter 3 explains the experimental procedures and equipment used for the completion of this project. Chapter 4 presents the results and effects of the process parameters investigated and gives a thoughtful discussion of the benefits and drawbacks of these parameters. A conclusion and knowledge contribution based on the results of these experiments is given in Chapter 5.

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ABSTRACT

The objectives of this work were to investigate and improve impregnation of regular (2-8mm thickness range) black spruce wood chips in CMP-AQ pulping. Impregnation and pulping experiments were performed while varying several pulping parameters. Experiments were analyzed in terms of yield, lignin content, percent screen rejects, and strength properties. The goal was to determine optimum pulping conditions that would improve chemical impregnation. Impregnation is a function of percent screen rejects: well impregnated chips have fewer rejects.

Cooking temperature and cooking time were held constant in all experiments at 170°C and 30 minutes, respectively. The liquor pH was adjusted to 7.9 and a liquor-to-wood ratio of 6:1 was used. Presteaming pressure was held constant at 138 kPa and soaking temperature was maintained isothermal at 90°C.

Process variables which can influence the chemical penetration were investigated. These are: wood chip thickness, pre-treatment agents, compression ratio, partial crushing of wood chips, and also pre-steaming and evacuation prior to chemical treatment as a possible method of entrapped air removal. Additional process parameters investigated were the concentration of pulping chemicals and dosage of AQ catalyst.

The advantages provided by the use of thinner wood chips, caustic pretreatment and high compression prex-impregnation were confirmed for improving chemical impregnation. The addition of SAQ catalyst to the CMP pulping process produced pulps of unusually high screened yield for a given lignin content. Improvements were also observed in strength properties compared to the control cook where no SAQ was used.

RÉSUMÉ

Les objectifs de ce travail étaient d'étudier et d'améliorer l'imprégnation de copeaux d'épinette noire de taille normale (2 à 8 mm d'épaisseur) durant la mise en pulpe de type CMP-AQ. L'imprégnation et la mise en pulpe ont été effectuées en faisant varier plusieurs paramètres de mise en pulpe. Les résultats analysés ont été le rendement, la teneur en lignine, le pourcentage de rejets de tamis et les propriétés de résistance. Le but était de déterminer les conditions de mise en pulpe optimales pour améliorer l'imprégnation chimique. L'imprégnation varie en fonction du pourcentage de rejet de tamis : les copeaux bien imprégnés présentent moins de rejet.

La température et le temps de cuisson ont été maintenus à 170°C et 30 minutes pour toutes les expériences. Le pH de la liqueur a été fixé à 7.9 et le rapport liqueur/bois à 6 pour 1. La pression de vapeur a été maintenue constante à 138 kPa et la température de trempage constante à 90°C.

Les variables influençant la pénétration chimique ont été étudiées : épaisseur des copeaux de bois, agents de pré-traitement, rapport de compression, écrasement partiel des copeaux, ainsi que la vaporisation et l'évacuation avant traitement chimique comme méthode possible pour ôter l'air captif. La concentration des produits chimiques de mise en pulpe et le dosage du catalyseur AQ ont été également étudiés.

Les avantages fournis par l'utilisation de copeaux plus fins, le pré-traitement caustique et le prex-imprégnation à haute compression ont été confirmés améliorer l'imprégnation chimique. L'addition du catalyseur SAQ au procédé CMP de mise en pulpe a produit un rendement inhabituellement haut pour un taux de lignine donné. Des améliorations des propriétés de résistance ont également été observées par rapport à la cuisson de contrôle où aucun SAQ n'était utilisé.

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CHAPTER I
INTRODUCTION

1.1 INTRODUCTION TO PULPING PROCESSES

There are four categories of pulping processes, listed here in order of increasing mechanical energy required to separate fibres, and decreasing chemical action: Chemical, semi-chemical, chemi-mechanical, and mechanical pulping. Chemical pulping methods use chemicals to separate fibres. Mechanical pulping methods involve shredding and defibering wood chips between the rotating discs of a device called a refiner, and rely completely on physical action. The more chemicals are involved in the process, the lower the yield and lignin content (chemical action degrades and solubilizes components of the wood, especially lignin and hemicellulose) (1).

In this thesis research, the chemi-mechanical pulping (CMP) process was studied. It involves steaming the wood chips for a short period of time prior to pressurized impregnation. The chemically impregnated wood chips are then cooked in a digester for a short period of time prior to refining. During chemi-mechanical pulping, using Na_2SO_3 as a pulping chemical, the lignin and cellulose are preserved, and only a small fraction of hemicellulose is lost. Improvement in bonding strength and fibre conformability are observed when compared to purely mechanical pulping methods which is due to the softening of lignin in wood and sulphonation.

1.2 THE IMPORTANCE OF GOOD CHEMICAL IMPREGNATION

One major problem often encountered in the pulping of wood is the difficult penetration of the cooking liquor into the wood chips. Although much work has been put forth to investigate methods to facilitate penetration, it still warrants much attention today. Uniform and complete penetration of cooking liquor into the wood chips must occur at the start of the cook before the increasing temperature in the digester exceeds the critical value of 140°C where the undesirable lignin condensation reaction can occur. Otherwise the unpenetrated portions of the wood chips are rejected from the process (2). The complete penetration of the cooking liquor helps reduce the cooking time and improves the quality, uniformity and bleachability of pulp (2).

1.3 ANTHRAQUINONE AS A PULPING CATALYST

From many technological advances in the pulp and paper industry in recent years, the discovery of anthraquinone (AQ, See Figure 1) as a pulping catalyst was one which has had a major impact on the industry. The use of AQ has opened new possibilities for the development of better pulping processes. AQ is an alkaline pulping catalyst which, when added in small amounts, accelerates the pulping process dramatically and gives a lower lignin content for the same pulp yield, thus protecting carbohydrates from degradation (3-14).

The effect of AQ on chemi-mechanical pulping (CMP) has been studied by Fleming, 1984; Tay and co-workers, 1984; Kubes and co-workers, 1993. Their studies have shown that in a pulping yield range of 70 to 90 percent, AQ improved the pulping selectivity (a higher yield pulp was obtained for a given lignin content) and pulp strength properties while saving time and energy during both cooking and refining (4,5,12,13,14).

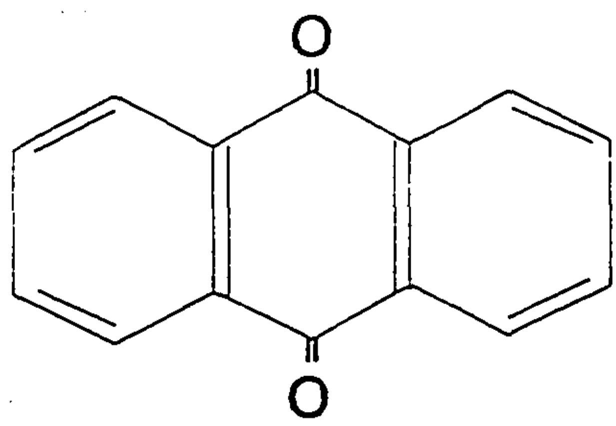


FIGURE 1 ANTHRAQUINONE, "AQ"

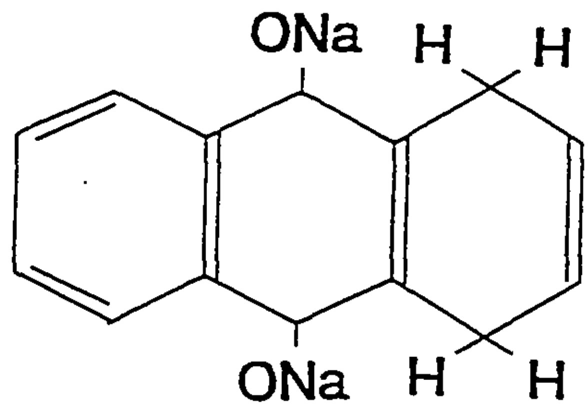


FIGURE 2 SODIUM SALT OF 1,4-DIHYDRO-9,10DIHYDROXYANTHRACENE, OR "SAQ"

The main disadvantage of AQ-pulping is its inability to quickly penetrate to the centre of the wood chips which results in nonuniformity of pulping. In mill operation, the AQ penetration problem results in production of high screen rejects and shives.

Disodium salt of 1,4-dihydro-9,10-dihydroxyanthracene is a soluble form of anthraquinone (SAQ, See Figure 2) which might have an advantage over insoluble anthraquinone (AQ) in high yield pulping processes. All experiments described in this thesis used anthraquinone catalyst in its soluble form, to avoid any potential solubility problem.

1.4 SCOPE AND OBJECTIVES OF THE THESIS

The penetration problem of AQ is more pronounced for shorter cooking times, as in the case of CMP-AQ pulping, because the AQ must reach the reactive sites faster. The penetration and optimization of AQ in CMP-AQ pulping has become an objective of a major project intended to investigate AQ penetration into wood chips and to study the parameters affecting CMP-AQ pulping in order to obtain a higher yield and better quality of pulp. The scope and objectives of this thesis can be summarized as follows:

1. To investigate those pulping variables which can influence the chemical penetration, such as: wood chip thickness, pre-treatment agents, compression ratio, partial crushing of wood chips, and also pre-steaming and evacuation prior to chemical treatment as a possible method of entrapped air removal. Additional process parameters will be concentration of pulping chemicals, soaking time, and dosage of AQ catalyst.

2. To analyze these experiments in terms of yield, lignin content, percent screen rejects, and strength properties.

3. To evaluate the results and determine optimum CMP-AQ pulping conditions for complete penetration of AQ into wood chips.

CHAPTER II
LITERATURE REVIEW

2.1 CHARACTERISTICS OF WOOD

Black spruce wood is used in this study. Softwoods are more suitable than hardwoods for conventional pulping processes. With fibre lengths varying from 2-5mm, they are the preferred wood type for the industry since hardwoods have a denser structure and shorter and less uniform fibres (1-2mm) (1).

Wood structure plays an important role with respect to the ease and speed of chemical penetration. The vertical structure of softwoods is composed almost entirely of long, hollow fibres, called tracheids (see Figure 3). These tracheids have tapered ends which close off the cavities. Transportation between tracheids occurs through bordered pits of which there are between 50 and 300 pits per tracheid. Penetration of liquor into the wood chips occurs almost entirely through the tracheids and connecting pit pores (2,15).

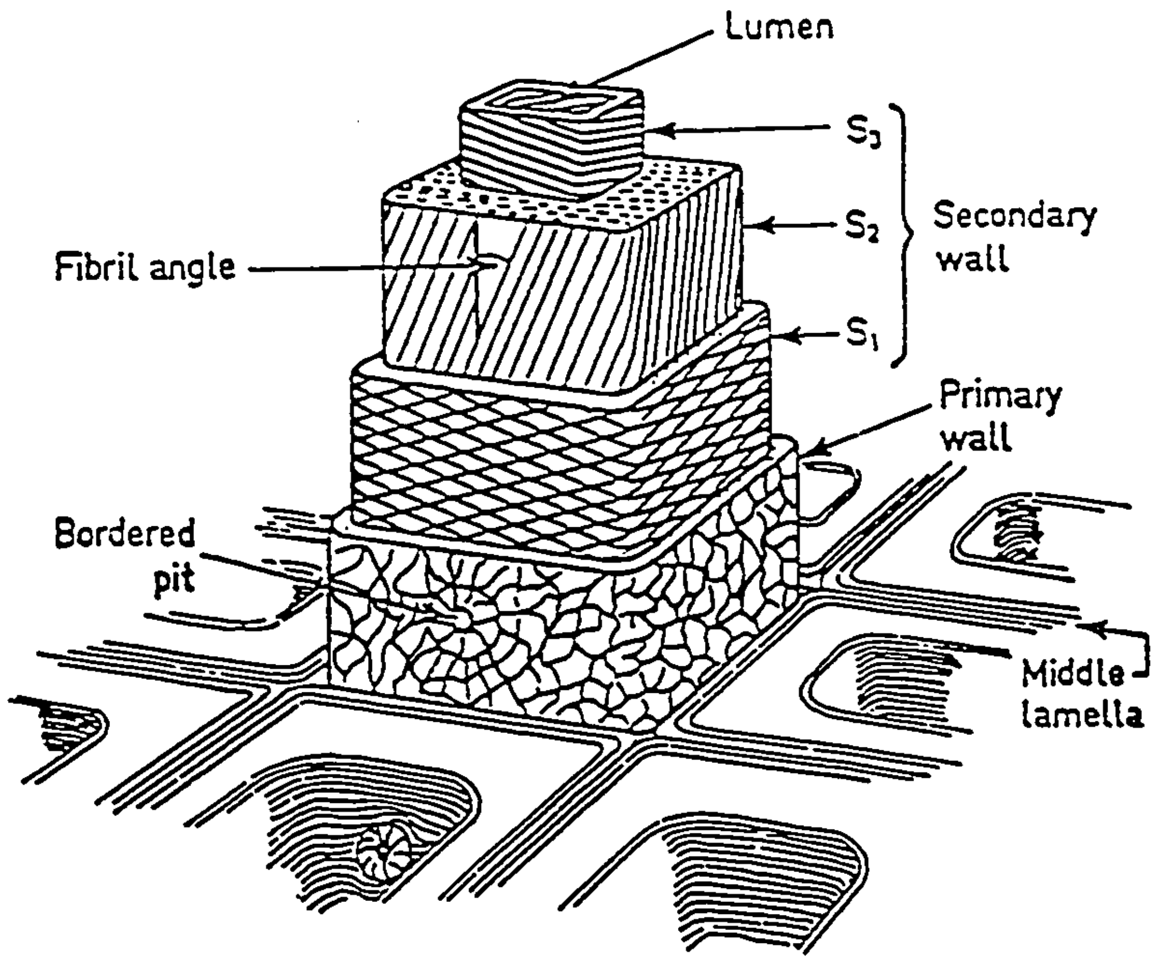


FIGURE 3 DIAGRAMMATIC SKETCH OF A SOFTWOOD (SMOOK, 1992)

Wood, although very difficult to define chemically, has been classified into three major components: extractives, carbohydrates, and lignin. Extractives account for the various compounds that can be removed with organic solvents (2% to 10% of the wood weight) (1).

Carbohydrates are found in the fibre cell wall and are by far the most important component of wood in the pulping process. Making up 60% to 80% of the total wood weight, carbohydrates are made up of cellulose and hemicellulose. Cellulose determines the character of the fibre (1).

Wood contains about 25% to 35% by weight lignin, which is concentrated mainly between the fibre cells and outer layers. It acts as a glue which cements the fibres together. Lignin is an amorphous, highly-polymerized substance of phenyl propane units linked together in three dimensions (1).

2.2 ANTHRAQUINONE AS A PULPING CATALYST

Quinones and their derivatives have been studied by many scientists in attempts to improve pulping processes. In 1972, Bach and Fiehn (16) found that wood cellulose was partly protected from alkali degradation when treated with 2-anthraquinone-monosulfonic acid (AMS). It was also noticed that delignification rate accelerated.

Although these results were very encouraging, the large dosage of AMS required made it impractical in industry. This research prompted other scientists to get involved in finding practical applications for quinonoid additives as pulping catalysts. Holton (6) then discovered in 1977 that anthraquinone accelerated delignification in alkaline pulping of both hardwoods and softwoods, even with relatively small doses (0.1% on oven-dried wood).

Nomura and Nakamura (17) were the first to use anthraquinone as a sulphite pulping catalyst. Their results showed a reduction in total lignin content and improvements in strength properties when compared to control cooks with no anthraquinone addition, at a given pulp yield. Cameron (18) then reported in 1981 that the anthraquinone catalyst produced effective results in the neutral sulphite semi-chemical (NSSC) process. Virkola et al. (19) demonstrated that neutral-sulphite-anthraquinone pulping could produce liner board with quality comparable to the conventional, lower yield kraft process. Fleming et al. (5) confirmed the virtues of sulphite-AQ pulping using black spruce in 1984. Today AQ is used as an additive in a number of kraft, soda and sulphite mills (20).

The various benefits of quinone additions to alkaline, sulphite, and NSSC processes have included shortened cook cycles, reduced chemical consumption, higher yield for a given lignin content, better bleachability, improved pulp strength properties and reductions in refiner energy requirements (3-14). However, most of these results arise from lower yield (up to 75%) pulping processes where the cooking liquor pH exceeded 10.

In 1978, Fleming et al. (4) proposed a reduction-oxidation cycle for anthraquinone in alkaline pulping where AQ is reduced by carbohydrates and re-oxidized in the oxidative cleavage of lignin (Refer to Figure 4). Several scientists (Lowendahl and Samuelson, 1978 (21); Algar et al., 1979 (22)) confirmed these results and since then, many papers were published on the degradation of lignin by the reduced forms of AQ. Keskin (23) then studied the kinetics of sulphite pulping with and without the AQ catalyst in the laboratory of the McGill Pulp and Paper Research Centre. Her results, which were obtained by pulping black spruce wafers with and without the addition of soluble anthraquinone, indicated evidence that anthraquinone functions as a redox catalyst also in sulphite pulping.

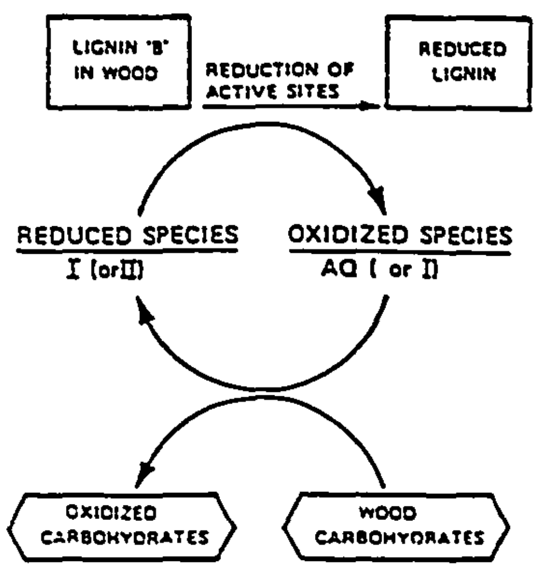


FIGURE 4

AQ REDOX MECHANISM FOR ALKALINE PULPING OF WOOD

(Fleming et al., 1978)

2.3 THE ROLE OF CHIP THICKNESS ON IMPREGNATION

Screen rejects are the result of inadequate diffusion of cooking chemicals to the centre of oversized wood chips and may be taken as a measure of impregnation. Hatton (24) showed that screen rejects, in conventional pulping processes, are controlled by wood chip dimensions. In addition, Cameron et al. (18) and Morin (25) showed that anthraquinone diffuses much more slowly into chips than sodium sulphite, and Falk et al. (3) showed that anthraquinone diffuses much more slowly into chips than sodium hydroxide.

In attempts to determine which wood chip dimension controls screen rejects, Wearing (26) used hand-cut Balsam Fir chips and found that in alkaline sulphite-anthraquinone pulping, screen rejects are controlled by wood chip thickness. Wearing also discovered that only chips thinner than 3mm produce rejects lower than 1% in AS-AQ pulping, but that in practice, slightly thicker chips may give similar results since mill chips have surface lamellations, cracks and fissures which may act to lessen the diffusion path.

2.4 THE ROLE OF PRETREATMENT AGENTS ON IMPROVING IMPREGNATION

During impregnation, the following sequence of events occurs: 1) the pulping reagent diffuses to the reaction site in the wood chip, 2) the reagent reacts with the lignin, and 3) the reaction products diffuse out of the chip (27). A homogeneous and uniform pulp is obtained when the reaction within the wood is rate controlling. However, when the diffusion of the pulping reagent is rate controlling, the outer fibres undergo extended delignification before the inner portions of the wood chip has had the chance to react. This leads to nonuniformly pulped wood, and hence a poorer quality pulp (27).

Minor and Springer (27) found that when wood chips were pretreated with alkali, the rate of diffusion into and out of the internal wood structure was increased significantly, producing a much more uniform pulping. Their experiments used matchstick-sized pieces of wood which were pre-treated with alkaline solutions and pulped with acidified peroxymonosulphate solutions. The pulped fibres were separated from the incompletely pulped core by placing the wood stick in water, pressing it, and stirring it with a glass rod and the extent of fiberization was measured. As a control, water-soaked sticks were used. It should be noted here that most of their experiments were carried out using hardwoods (aspen, red oak).

Their work proved that when hardwood sticks were pre-treated with alkali, the rate and uniformity of the peroxymonosulphate pulping was significantly improved when compared to the water-soaked control (Refer to Tables 1 and 2). When the same experiments were carried out using softwood (slash pine and white pine), the pre-treatment effect was not as clear since the earlywood of softwoods is more easily penetrated than the denser latewood. An uncooked core was not readily definable after pulping, even with the control sticks. The chemical penetration appeared to be more uniform, however, through white pine than through slash pine and delignification was faster in the white pine sticks which were pretreated with alkali when compared to the control (see Table 2).

TABLE 1 EFFECT OF PRETREATMENT ON PEROXYMONOSULPHATE PULPING OF ASPEN (MINOR AND SPRINGER, 1993)

Pretreatment	Pulping Time (h)	Extent Fiberized (%)	Lignin Content (%)	Yield (%)
NaOH	15	0	>15.5	75
	24	54	6.2 (core) 3.6 (fiber)	68
	39	100	4.6	63
	48	100	2.9	62
Water Soak (Control)	48	20	12.0 (inner core) 7.7 1.1 (fiber)	77

TABLE 2 EFFECT OF PRETREATMENT ON PEROXYMONOSULPHATE PULPING OF VARIOUS SPECIES (MINOR AND SPRINGER, 1993)

Species	Pulping Time (h)	Pretreatment Effect (%)						
		NaOH Pretreatment			Water Soak			
		Yield	Extent Fiberized	Lignin Content	Yield	Extent Fiberized	Lignin Content	
							Core	Fiber
Red Oak	48	55.1	100	7.1	69.3	23	20	9.4
	140	53.7	100	-	64.1	55	-	-
Honey Locust	24	-	100	7.5	-	0	16.7	-
Slash Pine	164	59	100	3.1	60	100	-	5.3
White Pine	72	-	-	15.5	-	0	19.9	-
	100	-	-	13.7	-	0	18.3	-

2.5 THE ROLE OF CHIP COMPRESSION AND CHIP CRUSHING ON IMPREGNATION

In CMP pulping, prex-impregnation (pressing the wood chips after presteaming using pressure by either a piston or a screw) with cooking liquor enhances the distribution of chemical into the wood chip structure when compared to that obtained by soaking alone. In consequence, higher strength properties are observed (28).

Although compression ratios used in industrial screw feeders and chemical impregnators are usually in the range of 2 to 2.7:1 (29), it was found that impregnation of *Gmelina Arborea* using a compression ratio of 4.3:1 produces pulps with higher scattering coefficients than pulps produced using a compression ratio of 2.5:1 (30).

Heitner et al. (31) used high compression ratio prex-impregnation of black spruce chips with sulphite and recommend compression ratios in the range of 4:1 to 8:1 followed by liquid phase cooking and disc refining to improve tear index and wet web properties. High compression can have adverse affects on physical properties, in particular tear index, as shown by Michalowicz (32). However, using photomicrographs of cross-sections of black spruce chips that were either soak impregnated or press-impregnated, Heitner et al. (31) showed that even at the extreme compression ratio of 8:1, the fibre wall was deformed considerably and the fibres partially separated, but no evidence of fibre cutting was observed (see Figures 5 and 6).

FIGURE 5

SOAK-IMPREGNATED CHIPS

Heitner et al., 1985

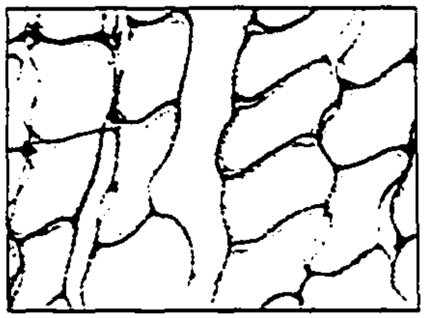


FIGURE 6

HIGH COMPRESSION PREX-IMPREGNATED CHIPS

Heitner et al., 1985

Wood chip thickness is the critical dimension in producing uniform penetration into chips in alkaline pulping (26). Fissures and micro-cracks present in the wood structure improve penetration by increasing the available surface area of wood in contact with the cooking liquor (33). Colombo et al. (34) passed wood chips through compression rolls prior to kraft pulping. This improved alkali penetration, increased screened pulp yield, and reduced cooking time, without affecting physical pulp properties.

2.6 THE ROLE OF CHIP STEAMING AND EVACUATION ON IMPREGNATION

Wood is generally in a three-phase state: wood substance, water, and air. Air is the most difficult phase to penetrate with cooking liquor. Air, a non-condensable gas, will be compressed as the cooking liquor proceeds inside the chip and will create an increasing back-pressure during impregnation until mass penetration ceases altogether (35). It is therefore vital to remove or displace the air as completely as possible in order to achieve complete penetration. This is most commonly accomplished by either steaming the wood chips or by wood chip evacuation (35).

Presteaming is defined as a flow of saturated steam, either at atmospheric or superatmospheric pressure, through the vessel containing the chips (35). Steaming the wood chips is the most common method of air removal (1). This causes thermal expansion of the air in the wood chips, removing about 25 percent of it. The increased vapour pressure will further aid in expelling air from the chips. The increased temperature also helps in the outward diffusion of air and the inward diffusion of water vapour. Additionally, presteaming facilitates liquid flow and diffusion through the wood structure by opening pit membrane pores (35).

A practical presteaming temperature is about 105 or 110 degrees Celsius. Higher temperatures (above 120°C) would be beneficial for penetration, but leads to hydrolysis of carbohydrates and condensation of lignin, both undesirable effects to pulp quality (36).

Alm and Stockman (37) and Aurell et al. (38) used spruce heartwood chips in sulphite pulping and found that a suitable combination of steaming and pressure impregnation gives the best penetration and will allow a shorter cooking time and more uniform pulping.

Experiments have shown that evacuation greatly increases penetration velocity. This is because, as the wood chips become void of air, back-pressure of the entrapped air is eliminated. Also, a resulting pressure differential causes forced liquid flow. Numerous studies have indicated that evacuation is the most efficient method for removing air from wood chip voids (2,39,40). However, very low pressures (i.e. below 40 mmHg) must be used to achieve almost complete penetration. Many impregnators and digesters are not built to withstand vacuum, and therefore this method has remained at the laboratory stage.

2.7 THE ROLE OF CHEMICALS ON IMPROVING PULP PROPERTIES

Impregnating wood chips with sulphite improves physical properties of refiner mechanical pulps (41). Atack et al. (42) found that when black spruce is treated with different types of sulphite liquor, its softening temperature is reduced. Therefore, at a given refiner energy input, pulps produced from sulphonated black spruce should have superior characteristics to those of corresponding unchemically treated black spruce.

Heitner and Hattula (43) pulped Norway spruce wood chips in sodium sulphite solution at concentrations in the range of 63-126g/L for 30 minutes at temperatures between 130 and 160 degrees Celsius. They concluded that the softening temperature and irreversible softening of lignin increased the extent of fibre collapse and interfibre bonded area (see Figures 7 and 8).

Heitner and Hattula concluded that when the sulphonate content is increased to 325mmol/kg, the handsheet density and breaking length double. These results were due to the fivefold increase in breaking length of the long fibre fractions.

FIGURE 7 LOW SULPHONATION CMP HANDSHEET EXHIBITS LARGE AMOUNT OF UNCOLLAPSED AND PARTIALLY COLLAPSED FIBRES

Heitner and Hattula, 1988

FIGURE 8 HIGH SULPHONATION CMP HANDSHEET EXHIBITS MOSTLY FULLY COLLAPSED FIBRES

Heitner and Hattula, 1988

2.8 THE ROLE OF SOAKING TIME ON IMPROVING IMPREGNATION

After presteamed wood chips are compressed and submerged into the impregnating liquor, chemicals can impregnate the wood structure by penetration and diffusion. Penetration is a fast process and it takes place first, followed by a much slower diffusion process.

Morin (25) showed that more than 50% of the overall impregnation was reached after only two seconds of liquor soaking. After the rapid mass penetration was completed, chemical intake slowed and diffusion dominated. Therefore, after the initial 2 seconds, the impregnation rate slowed substantially.

However, increasing the soaking time improved the average AHQ and sulphite penetration. Morin found that this improvement was the result of a longer time allowed for diffusion but that after 20 minutes, the soaking time effect was no longer significant.

CHAPTER III
MATERIALS AND METHODS

3.1 EXPERIMENTAL PARAMETERS

3.1.1 WOOD

Black spruce wood containing 29.3% lignin was used in this study. It arrived at the Pulp and Paper Research Institute of Canada (PAPRICAN) and had been harvested from one single geographical location. This limited the variations in the species due to different growth soils or growth climates. The wood was debarked, chipped and screened to remove over-sized chips (greater than 8mm thick), under-sized chips (less than 2mm thick) and knots. Wafer wood chips (less than 1mm thick were also made from this supply.

A portion of the wood chips was classified using a Domtar chip classifier into four categories: less than 1mm thick chips (wafers, screened for pin chips and sawdust), 2-4mm thick chips, 4-6mm thick chips and 6-8mm thick chips. These four denominations were used to observe the effects of chip thickness in the CMP-AQ pulping process. For all other experiments, 2-8mm thick wood chips were used, which is typical of industrial chip thickness ranges.

3.1.2 PULPING LIQUOR

Most articles have reported sodium sulphite concentrations in the range of 63g/L to 126g/L (8,12,13,14,43,46) during CMP pulping. In this study, impregnation and cooking liquor concentration was maintained constant at 80g/L $NaHSO_3$ (for all experiments except when the effect of liquor concentration was investigated with concentrations of 60g/L $NaHSO_3$ and 10g/L $NaHSO_3$). When analyzed for sulphite, the composition of the pulping liquor was 80.23g/L Na_2SO_3. This liquor concentration would ensure a high driving force for diffusion and almost complete sulphonation, in agreement with the work of Heitner and Hattula (43).

The pH of pulping liquor was adjusted to 7.9 with laboratory grade caustic (NaOH) pellets. It has been observed in a previous study (14) that AQ does not behave as a catalyst in CMP pulping below pH 7. For this reason, the neutral pH was chosen. Most importantly, sulphite/quinone pulping at pH 7 to 8 reveals promise for producing a better quality chemi-mechanical pulp with respect to sulphonation of wood and brightness of pulp (14). For experiments where caustic and borol pretreatment agents were used, the liquor pH after impregnation rose to 10.6 and 10.9, respectively.

Soluble anthraquinone was used in the form of alkaline solution of disodium salt of 1,4-dihydro-9,10-dihydroxyanthracene (DDA) and its concentration was set at a 0.07% charge on oven-dried wood (for all experiments except when the effect of AQ dosage was investigated with charges of 0.2% and 0%). Nomura and Nakamura (17) showed beneficial effects of AQ catalyst on CMP with 0.02% charge on oven-dried wood, and Wang (14) proved the catalytic effect of AQ with as little as 0.01% charge on oven-dried wood when pulping CMP black spruce wafers. However, when investigating the effects on regular spruce chips (2-8mm) the higher AQ dose of 0.07% on wood was chosen to observe its catalytic effect on the pulping process. The liquor-to-wood ratio was chosen to be 6:1 on oven-dried wood. This approaches the higher extreme of typical industrial ratios (4:1 to 6:1) (8,12,13,17,42,43,45), but ensured that the volume of cooking chemicals would not be a limiting factor with respect to wood penetration and diffusion.

3.1.3 COOKING TIME AND TEMPERATURE

The literature (8,12,13,14, 31,42,43,44,45) indicates typical CMP pulping temperatures in the range from 135°C to 175°C. The pulping temperature and time in this study were maintained constant at 170 degrees Celsius and 30 minutes respectively. Wang (14) found that decreasing the cooking temperature from 170°C to 150°C produced a similar quality of pulp. However, this resulted in a slower reaction rate. Therefore, this higher temperature was chosen to favour the chemical reaction rate and to shorten the cooking time since low temperatures require longer cooking times which results in a low productivity of the digester.

3.1.4 CHIP PRETREATMENT AGENTS

Pretreating wood chips with alkali or alcoholic solutions should increase the permeability of the wood and hence improve the penetration of water soluble chemicals into the wood structure. Black spruce wood chips of thicknesses ranging from 2mm to 8mm were soaked overnight in a 10% caustic charge on oven-dried wood, or a 10% caustic charge contained in borol solution. Borol solution is a proprietary mixture containing sodium hydroxide and sodium borohydride ($NaBH_4$), a reducing agent which may increase the catalytic effect of AQ. Sodium borohydride was also proven to produce strong, bright chemi-mechanical pulps from both hardwood and softwood by Ruffini (46).

Above stated conditions were chosen based on the work of Minor and Springer (26). They found that changing the sodium hydroxide pretreatment charge between 1% and 10% did not influence the results for peroxymonosulphate pulping of aspen. Since they also found that softwoods (slash pine and white pine) experienced penetration problems in the dense latewood of the species, the stronger extreme of the sodium hydroxide pretreatment charge (10%) was chosen for black spruce pretreatment.

3.1.5 COMPRESSION RATIO

The extent of compression is usually measured as a compression ratio. For example, a compression ratio of 2:1 means that the final volume of wood chips after compression is half that of the initial volume. Compression ratios used in industrial pulping systems are usually in the range of 2:1 to 2.7:1 (31). However, Heitner et al. (31) found that impregnation of black spruce chips by sodium sulphite at compression ratios in the range of 4:1 to 8:1 improved wet web properties and tear index without any fibre damage. A compression ratio of 4:1 was maintained throughout the experiments except when the effect of compression ratio was investigated and a control with 1:1 compression was tested along with very high compression using a hydraulic press.

3.1.6 HYDRAULIC PRESSING OF THE WOOD CHIPS

It has been shown that any method which would purposely introduce cracks and fissures into a normal chip supply would be beneficial to enhance liquor penetration (33,34). To improve penetration, crushing the wood chips using a hydraulic press (See Figure 9) which would open up the wood chip structures by compression should be proven to be effective. Pre-steamed wood chips were placed in the press and after compression, the chips absorbed the cooking liquor as the pressure was released. A 41400 kPa hydraulic pressure was used (9729 kPa on wood) and using a micrometer, the corresponding compression ratio of 9:1 was noted.

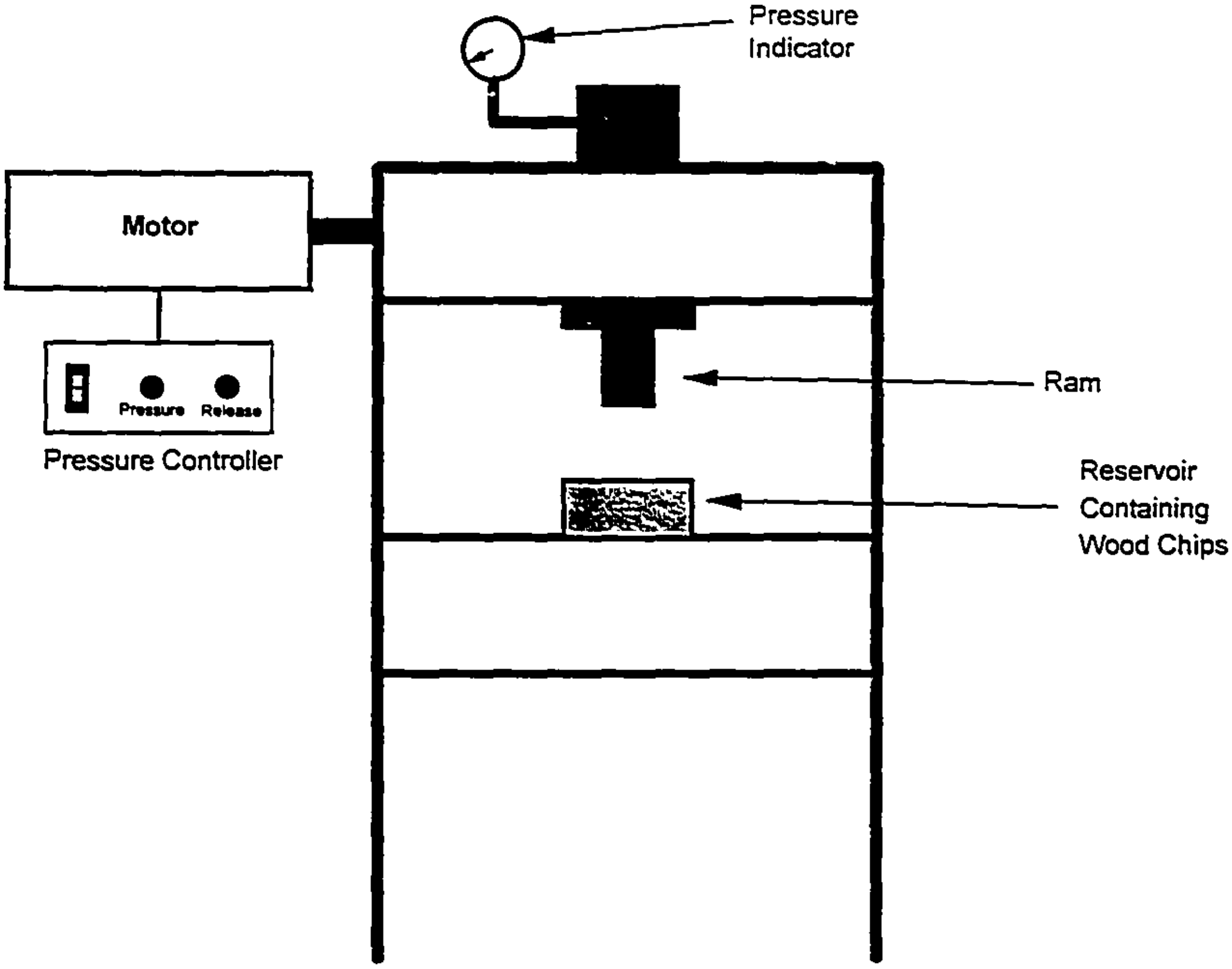


FIGURE 9 HYDRAULIC PRESS

3.1.7 PRESTEAMING AND EVACUATION

Wood chip steaming and evacuation have been studied as pretreatment methods to remove non-condensable gases from the wood chip structure (35-40).

It is of interest to compare the action of steaming the wood chips to the action of evacuating them for chemi-mechanical-anthraquinone pulping. A ten minute steaming time at 138 kPa was maintained throughout all experiments except when the effect of steaming time was investigated where no steaming and a 30 minute steaming time were compared. Tay et al. (13) used 10 minutes steaming when investigating sulphite/quinone chemi-mechanical pulping of jack pine. Heitner et al. (31) used 20 minutes steaming at atmospheric pressure when investigating high compression chemi-mechanical sulphite liquor impregnation of black spruce. Heitner and Hattula (43) steamed Norway spruce chips three times at 300 kPa for 3 minute durations. Alm and Stockman (38) varied steaming time from 5 minutes to 45 minutes when investigating the penetration of sulphite cooking liquor into industrial spruce chips and found an increase in screened pulp yield with increasing the steaming time.

Studies have shown that evacuation (below 40 mmHg) is the most efficient method of air removal from wood chip voids (2,39,40). Alm and Stockman (37) investigated evacuation times between 5 minutes and 45 minutes but found that evacuation had little effect when using moist chips. Therefore, evacuation experiments of air-dried black spruce chips with evacuation times varying from 0 to 30 minutes were carried out. Air-dried spruce chips were placed in a filtering flask and vacuum was applied. Upon reaching the desired evacuation time, the liquor was forced in under the vacuum, and soaked for 30 minutes prior to cooking.

3.1.8 SOAKING TIME AND TEMPERATURE

After presteamed wood chips are compressed and submerged into the impregnating liquor. two distinct mechanisms occur: The first one is a rapid penetration of liquor through voids and capillaries. while the other is much slower diffusion of the chemicals through the cell walls. Penetration takes place first. and diffusion then takes over in the liquid penetrated areas.

To avoid diffusion as a limiting factor in the impregnation process. a lengthy soaking time of 30 minutes was used throughout the course of experiments. Since this is an infeasible duration for industrial purposes. soaking times of 15 and 5 minutes were also investigated to observe the effect of this variable on optimizing the pulping process. The soaking temperature was set at 90 degrees Celsius. Woods (35) showed that under similar presteaming conditions and using distilled water as a penetrant. the rate of penetration was greater at 90°C than at 60°C or 30°C.

3.2 IMPREGNATION AND PULPING EQUIPMENT

3.2.1 THE SPROUT-BAUER LAB IMPREGNATOR

The Sprout-Bauer Laboratory Impregnator (See Figure 10) has a liquor pre-heater and a thermostat which can be operated at the desired temperature. Wood chips are charged into the compression chamber and the compression piston is advanced until the piston closes the charging opening. The wood chips are now pre-steamed by opening the pre-heat steam valve. Steam at this location softens and moistens the wood chips to prevent their brittle fracture during compression. The moisture and elevated temperature also enhance diffusion of liquor during impregnation.

After pre-steaming, the compression piston is operated until the desired compression ratio is achieved. Then the valves from the liquor pre-heater to the impregnator are opened to fill the impregnator to the desired liquor-to-wood ratio. The compression piston is then advanced to the left and this pushes the compressed chips into the impregnating liquor. When the chips are immersed in liquor, the penetration of liquor through the wood voids and capillaries, and diffusion of the chemicals through the cell walls occur.

After the chips have been impregnated for the desired time, the impregnator is depressurized and the wood chips and liquor are collected.

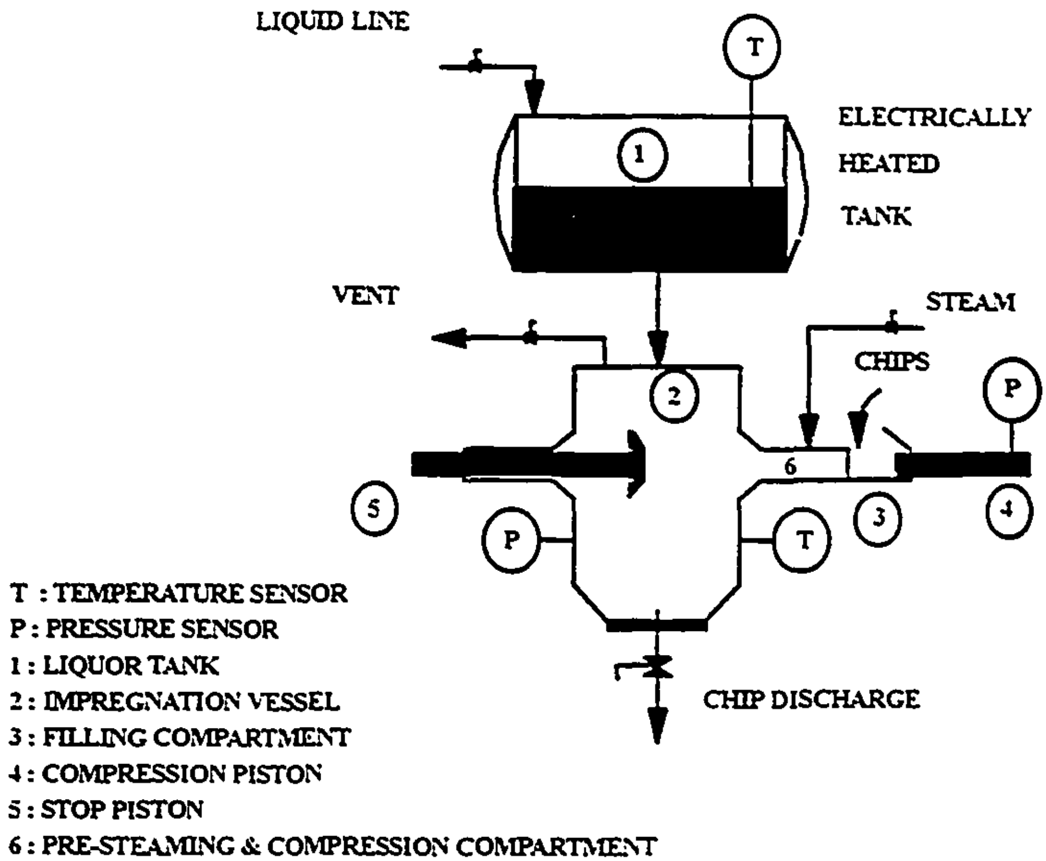


FIGURE 10: THE SPROUT-BAUER LABORATORY IMPREGNATOR

(Morin, 1993)

3.2.2 THE LABORATORY DIGESTER

The cooking of the wood chips was carried out in a pilot scale batch digester (See Figure 11). The digester consists of six 2.0 litre autoclaves mounted on a rotating drum and immersed in an electrically-heated glycol bath. The drum rotates at 3.5 revolutions per minute which provides homogeneous cooking and optimum heat transfer. A computer controls the temperature of the digester and cooking time. Cooks may be performed in two ways: with a heat-up period (where time-to-cooking temperature is an important factor), or isothermally (where the glycol bath is preheated to the desired cooking temperature and the autoclaves are inserted into the digester).

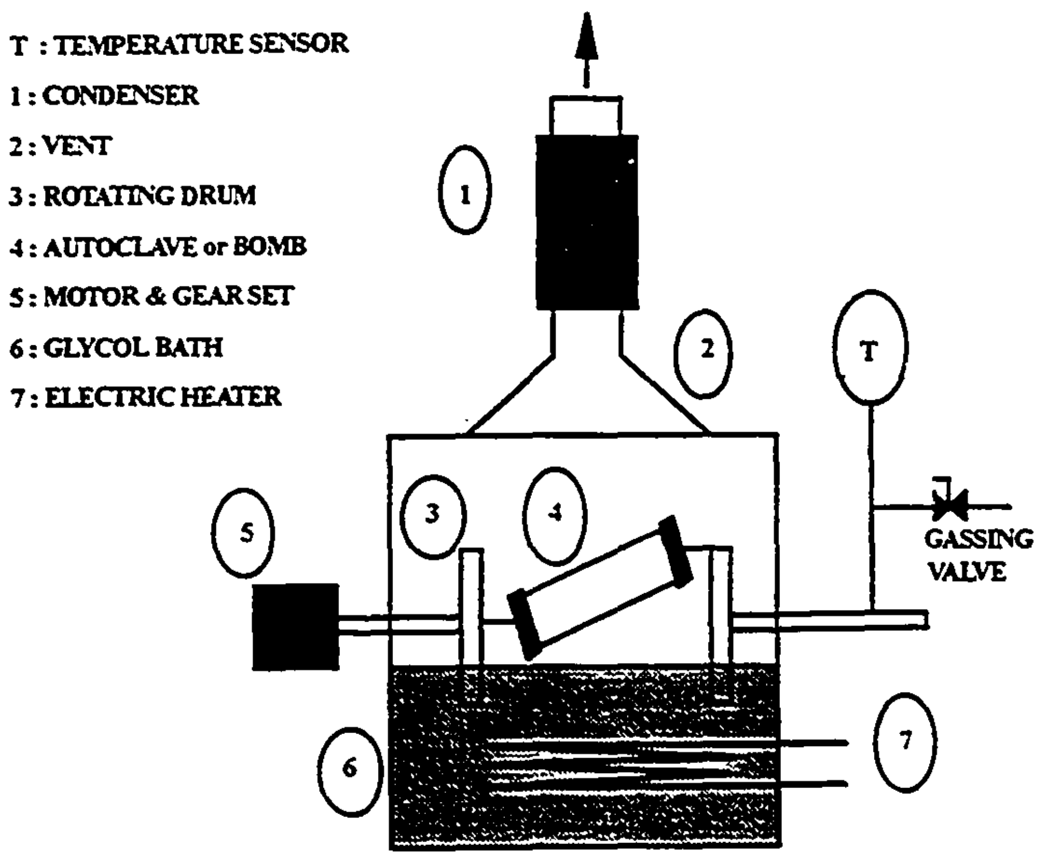


FIGURE 11: THE LABORATORY DIGESTER

(Morin, 1993)

Experiments in this thesis were performed under isothermal conditions, since pulp and paper mills normally send impregnated wood chips straight to the heated digester. The absorption of heat from the glycol bath by the autoclaves lowered the digester temperature slightly, but this was corrected by pre-heating the digester a few degrees higher than the operating temperature. Within 3 minutes, the digester temperature was brought to the operating temperature.

3.2.3 THE SPROUT-WALDRON LABORATORY REFINER

In mechanical pulping, disc refiners convert wood chips to pulp using removable, rotating plates that have pronounced radial bar and groove patterns. The Sprout-Waldron Lab Refiner is a single-rotating, 12-inch disc refiner operating under atmospheric conditions where the rotor disc rotates against a fixed stator disc (See Figure 12). Plate clearance is of critical importance in refiner control. A screwfeeder introduces wood into the open eye of the refiner. As the material moves through the refining zone towards the periphery, it is separated into its individual tracheids and the outer wall layers (lamellae) of the fibres are removed. The fibre wall structure is now made flexible.

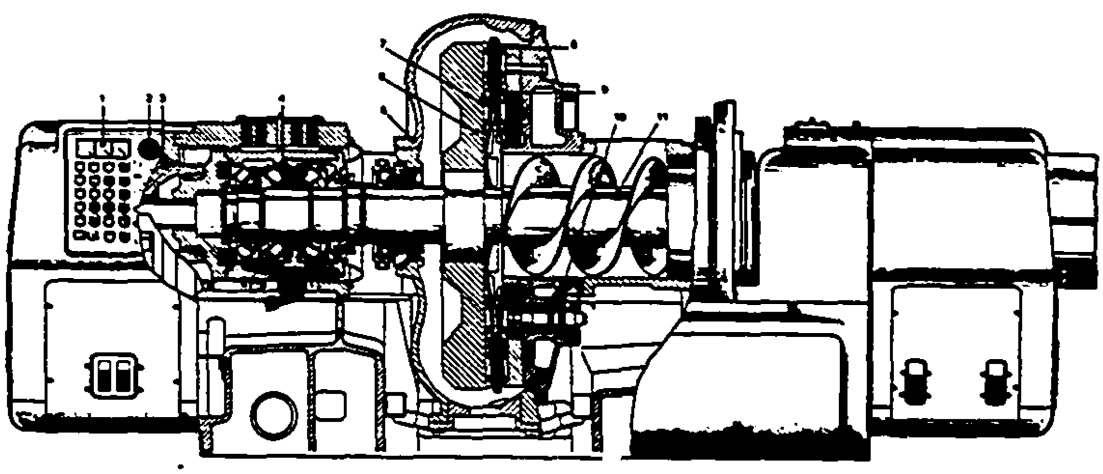


FIGURE 12: THE SPROUT-WALDRON LABORATORY REFINER

(Smook, 1992)

Chemical pulps are normally beaten in a PFI mill (Norwegian Paper Industry Institute) which is a laboratory pulp beating device. The purpose of beating is to mechanically condition the fibres for papermaking in order to produce the greatest change in pulp properties for a given change in freeness. However, mechanical pulps are stiff and do not respond to the PFI mill beating. It was for this reason that the pulps were mechanically conditioned by refining.

The refining process in this study consisted of two steps, or passes, with the disc plate clearance set at 0.023 and 0.004 inches, respectively, and three additional passes where the disc plate clearance was set at 0.003 inches. Pulp yield was measured after the second pass. The subsequent three passes were used to prepare the pulp at three different freeness levels for physical testing.

3.2.4 THE WARING BLENDER

Refiner rejects are considered to be a good measure of chip impregnation if the refiner operation can be precisely controlled. However, a reliable operation of a laboratory (12 inch diameter) refiner, available for this study, was affected by man factors, such as fluctuations in water temperature, refiner plate clearance, flow of chips into refiner and therefore also the pulp consistency during refining. Instead, the method using a laboratory Waring blender for screen rejects determination has been adopted. The cooked wood chips were blended at a known consistency for a known period of time and resulting pulp was then passed over a flat vibrating screen, and the amount of rejected pulp was measured.

The conditions of blending were chosen such that the worst-case impregnation experiments (chip thickness of 6-8mm) should give about 50% rejects. A consistency of 15.3 grams of oven-dried, impregnated and cooked wood chips in 1 litre of distilled water, and a blending time of 2 minutes on the blender "medium setting was used. This gave the 6-8mm chip thickness experiment 49.9% rejects and set precedence for all other experiments. From these results, "percent screen rejects" could be determined and used as a basis of comparison for extent impregnation from experiment to experiment. This test for extent of fiberization as a measure of impregnation was relative, but was appropriate for this study because of the considerable difference obtained between the results of wafer wood chips and 6-8mm thick wood chips.

3.3 ANALYTICAL METHODS

3.3.1 YIELD

Pulp yield was determined by collecting all pulp from the digester and measuring the moisture content according to CPPA Standard A.9. The amount of oven-dried pulp obtained from the initial oven-dried wood charge gave the total yield.

3.3.2 SCREEN REJECTS

To measure the rejects from the Waring Blender, the sample was placed in a reservoir whose screen base contained slots ten one-thousandths of an inch thick. The vibrating motion of the screen and constant flow of water into the reservoir ensured proper mixing of the pulp slurry. The fibres that passed through the screen and the fibres that remained on the screen were oven-dried and weighed. This determined the percentage of screen rejects.

3.3.3 LIGNIN ANALYSIS

The analytical method for determining lignin in this study was carried out in accordance with the CPPA Standard G.9.

3.4 PHYSICAL TESTING OF THE PULP

To characterize the pulp samples in terms of strength, the traditional technique is to compare strength test results at specified reference freeness levels, typical levels being between 500 and 300 Canadian Standard Freeness (CSF). Physical testing of the pulp was performed on test handsheets prepared in accordance to CPPA Standard C.4.

3.4.1 BREAKING LENGTH

Breaking length is the maximum (or ultimate) tensile force required to rupture the paper test strip in terms of a fictitious length. Breaking length is defined as the length of a strip of the paper sample that, when suspended under gravitational forces, would break under its own weight. That is, the weight of the sample is equivalent to the force that would break it. This length is reported in kilometres. Breaking length analysis was carried out in accordance to CPPA Standard D.6.

3.4.2 TEARING STRENGTH

Tearing strength uses a falling pendulum to continue a tear in the paper sample. The force of the pendulum acts perpendicular to the plane of the sheet. The loss in energy of the pendulum is related to the force required to continue the tear. Tearing strength analysis was carried out in accordance to CPPA Standard D.9.

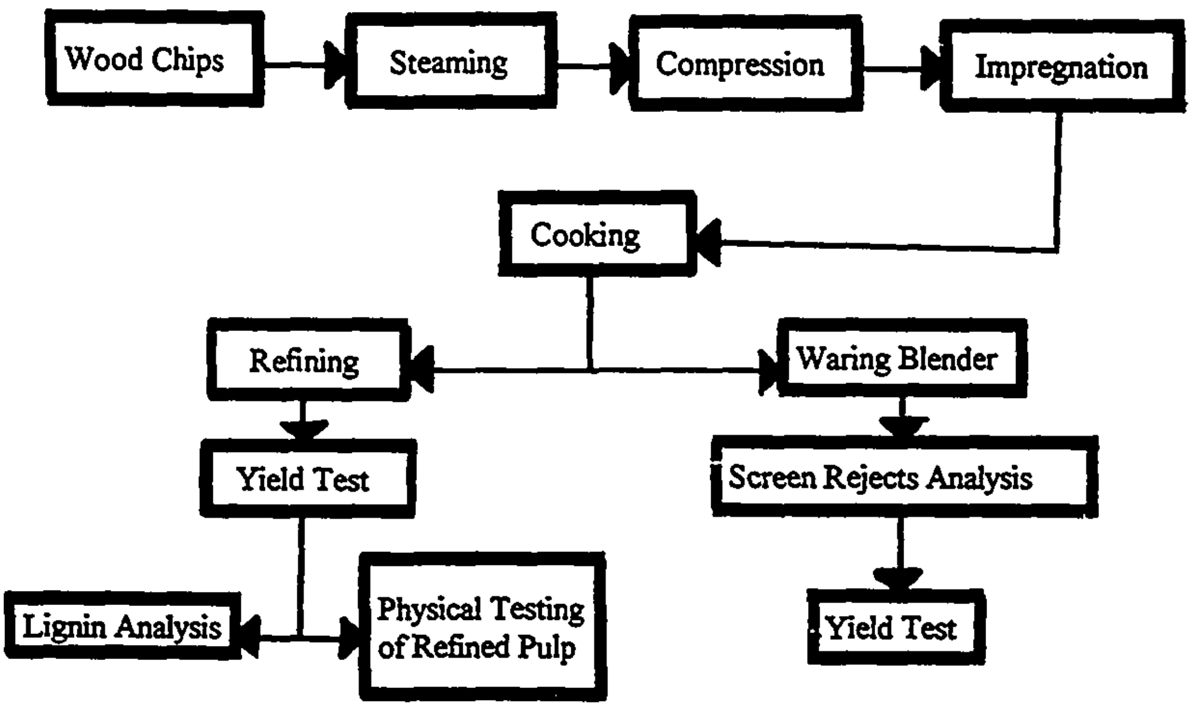
3.4.3 BURSTING STRENGTH

The principal function of the bursting test is to measure the resistance of a paper sample to rupture. Bursting strength is determined by clamping the sample over a rubber diaphragm through which pressure is applied at a gradually increasing rate until rupture. The pressure at rupture is noted. Bursting strength analysis was carried out in accordance to CPPA Standard D.8.

3.4.4 BRIGHTNESS

Brightness is the reflectance value of blue light with a specified spectral distribution peaking at a wave-length of 457nm compared to that of a perfectly reflecting, perfectly diffusing surface. Since no physical material has such a surface, a reference material thus calibrated establishes the scale of Absolute Brightness. Brightness analysis was carried out in accordance to CPPA Standard E.1.

A general flowsheet outlining the experimental procedure is presented below.



CHAPTER IV
RESULTS AND DISCUSSION

4.1 INTRODUCTION

The purpose of this chapter is to present the results from the experiments carried out in this project. and to discuss the resulting pulp characteristics when process variables are changed. Tables 3 and 4 presented below indicate the constant pulping conditions and pulping variables. respectively. Following these tables are the graphical results for the pulping variables and a discussion of these results in attempts to investigate facilitation of AQ penetration into wood chips and to study the parameters affecting CMP-AQ pulping conditions in order to obtain a high yield and better quality of pulp. It should be noted here that when a pulping variable produced little change in yield. lignin content. and rejects. strength properties were not investigated. For this reason. strength properties were not reported for replicates and experiments when the following variables changed: presteaming time. concentration of pulping chemicals. and soaking time.

TABLE 3: CONSTANT PULPING CONDITIONS

Parameter	Condition
pH of Cooking Liquor	7.9
Liquor to Wood Ratio	6:1
Presteaming Pressure	138 kPa
Soaking Temperature	90° Celsius
Cooking Time	30 minutes
Cooking Temperature	170° Celsius

TABLE 4: PULPING VARIABLES

Parameter	Constant Parameters	Variables
Wood Chip Thickness, mm	2-8	<1, 2-4, 4-6, 6-8
Pretreatment Agents	-	caustic, borol
Compression Ratio	4:1	1:1, 4:1, 9:1
Hydraulic Pressing, kPa	-	40 900
Presteaming Time, minutes	10	0, 10, 30
Evacuation Time, minutes	-	0, 15, 30
$NaHSO_3$ Concentration, g/L	80	10, 60, 80
AQ Dose, % on o.d. wood	0.07%	0.2%, 0.07%, 0%
Soaking Time, minutes	30	5, 15, 30

4.2 REPRODUCIBILITY OF RESULTS

When several steps are involved in any process, it is important to determine the repeatability of results. Three experiments were carried out under identical conditions on different dates. The agreement between these results is vital before any conclusions may be drawn from all other experiments. According to Figures 13a to 13d, agreement between replicate experiments is quite good with respect to total yield, total lignin content, and percent screen rejects.

A statistical evaluation of these replicates is in Appendix B. The results of this analysis show that for a 90% Confidence Limit (limits with a given degree of probability), the total yield is accurate to within ±0.96%, the total lignin content is accurate to within ±0.23%, and the percent screen rejects is accurate to within ±2.81%. Using this statistical evaluation, a basis of comparison between experiments may be drawn to determine whether the various pulping variables produce effects on the results.

Reproducibility of Results

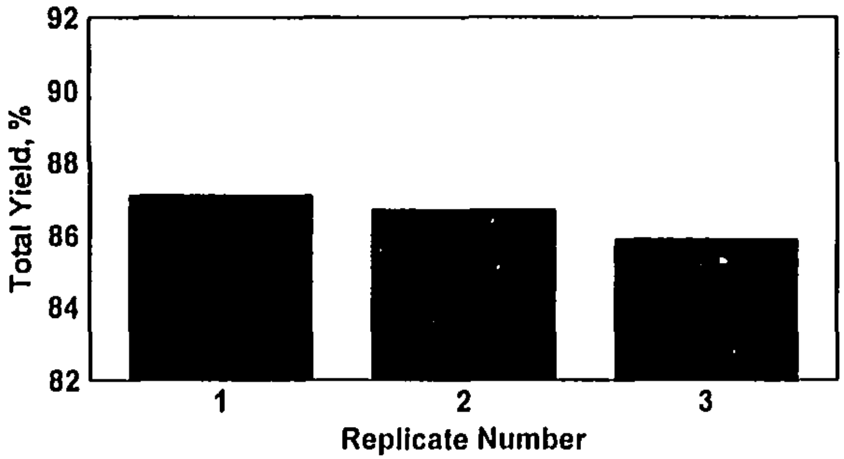


Figure 13a Reproducibility of Results for Total Yield

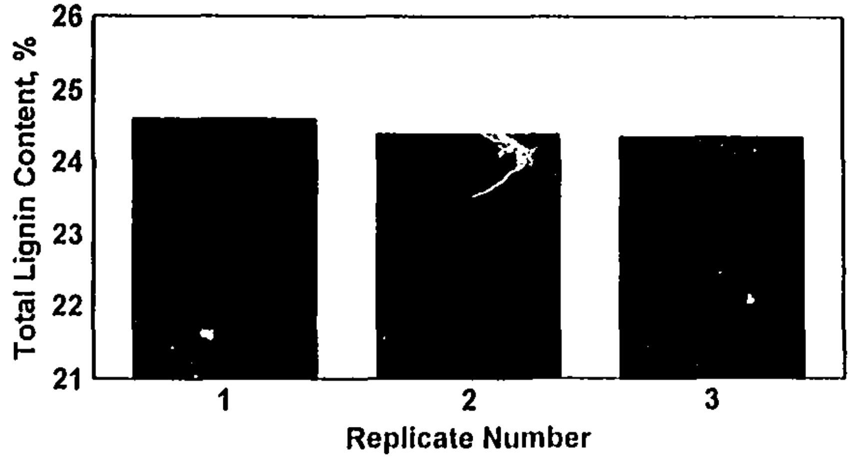


Figure 13b Reproducibility of Results for Total Lignin Content

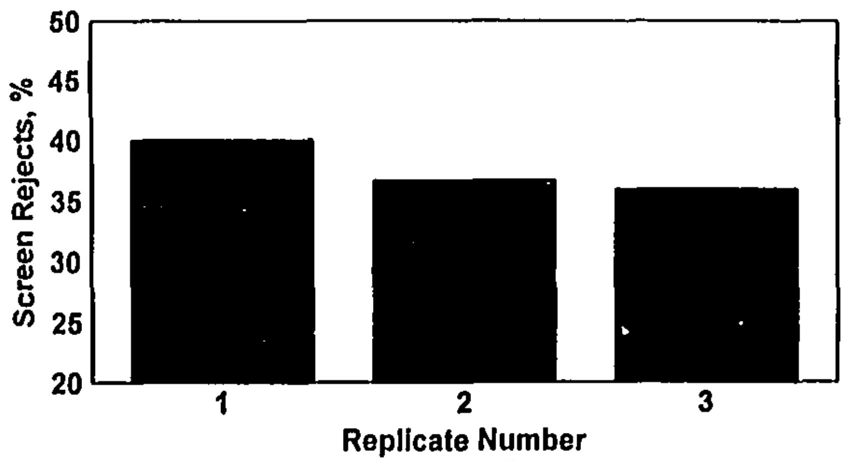


Figure 13c: Reproducibility of Results for Percent Screen Rejects

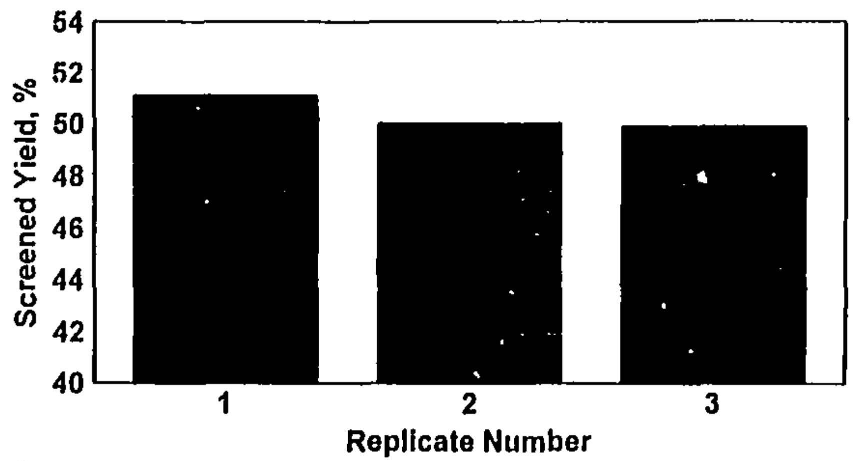


Figure 13d: Reproducibility of Results for Screened Yield

4.3 EFFECT OF WOOD CHIP THICKNESS

The total yield and the total lignin content of the pulps both show a direct relationship to wood chip thickness: as wood chip thickness increases, so do the yield and lignin content when treated under identical conditions (see Figures 14a and 14b). The percent of screen rejects also follows this direct relationship. Good impregnation is a function of wood chip thickness: better chemical impregnation occurs with thinner wood chips.

It is evident from Figure 14c that the thickest wood chips (6-8mm) were poorly impregnated. Figure 14d shows screened yield (total yield minus percent screen rejects) versus wood chip thickness. As expected, the wafer wood chips produced the greatest screened yield. They were almost completely fiberized under the blending conditions outlined in Chapter III. It appears from the results demonstrated in Figures 14a to 14d that screen rejects are controlled by wood chip dimensions which confirms the findings of Hatton (24).

If controlling the levels of total lignin and percent screen rejects were the only concerns, then it would appear that the thinner wood chips produce the best pulp. However, this advantage does not adhere to pulp strength properties. Thinner wood chips (less than 1mm thick) receive greater fibre damage and cutting when being made. Furthermore, when these wood chips are treated chemically and are refined into separate fibres, the pulp contains mostly short, cut fibres. Such fibres negatively affect breaking length, tear and burst indices, as evidenced in Figures 14e, 14f, 14g, and 14h. Wood chip thicknesses of 2mm to 6mm produce the strongest pulp because of the longer fibres and the acceptable level of chemical impregnation. The larger wood chips (6mm to 8mm) produce weaker pulp because, although long fibres are present, the benefit from chemical impregnation is lost.

Brightness decreases as chip thickness increases, as shown in Figure 14i. It may be concluded, then, that brightness corresponds to rejects: as the rejects level increases, the brightness decreases, or, the brighter pulps characteristic of the thinner wood chips presumably resulted from better chemical penetration.

The results from these experiments show that impregnation is enhanced greatly when thinner wood chips are used, but wafer wood chips, although very well impregnated, produce weaker pulp when compared to the slightly thicker denominations, most likely as a result of fibre damage when being made and pulp that contains mostly short, cut fibres. For best overall results, wood chip thicknesses of 2mm to 6mm should be used since an acceptable level of chemical impregnation is achieved and the long fiber content maintains pulp strength.

Effect of Wood Chip Thickness

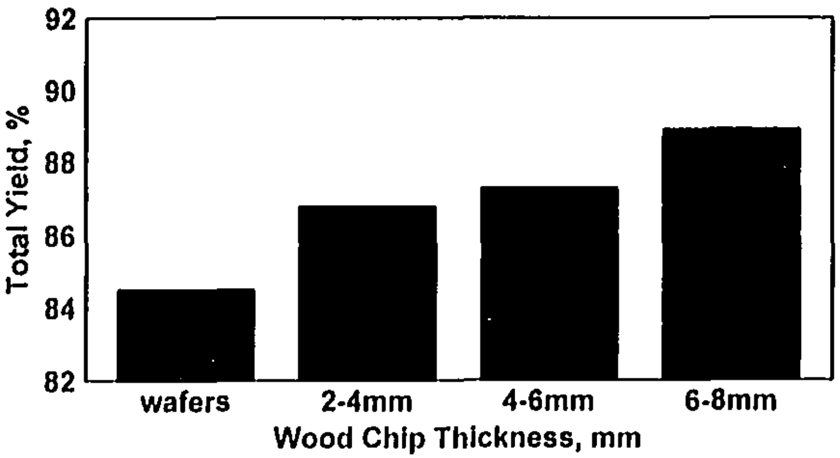


Figure 14a Effect of Wood Chip Thickness on Total Yield

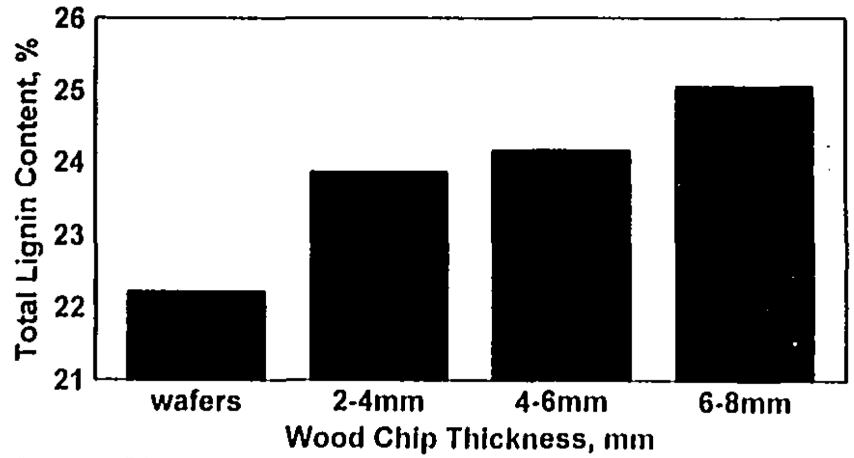


Figure 14b Effect of Wood Chip Thickness on Total Lignin Content

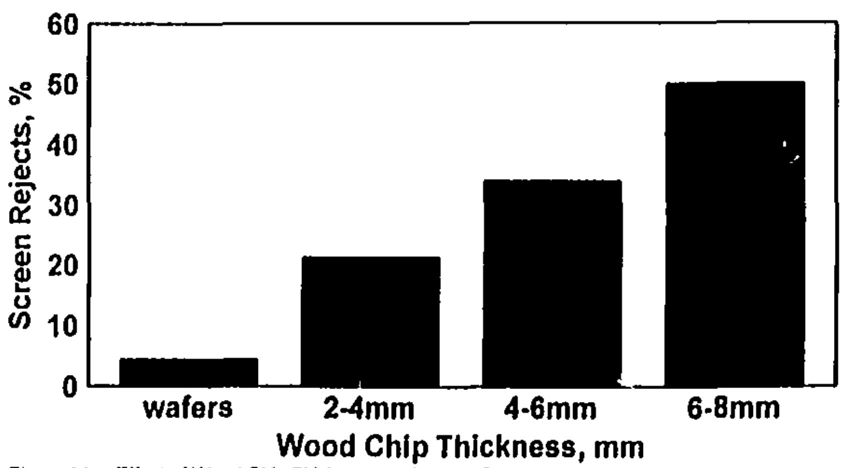


Figure 14c: Effect of Wood Chip Thickness on Percent Screen Rejects

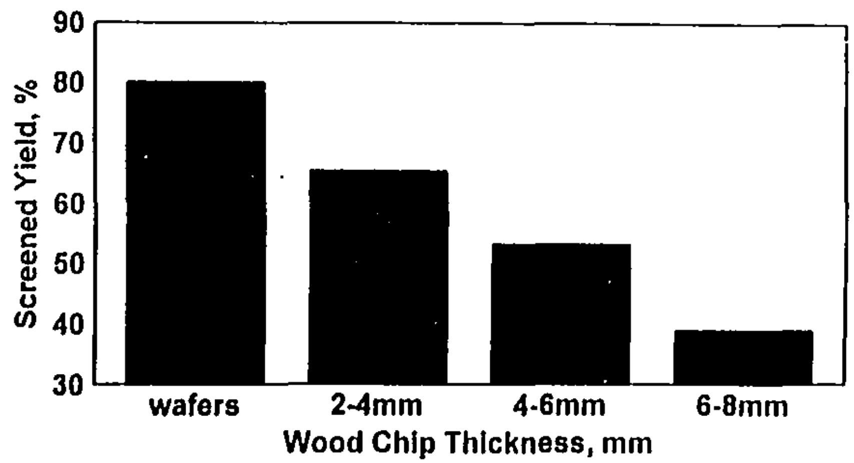


Figure 14d Effect of Wood Chip Thickness on Screened Yield

Effect of Wood Chip Thickness

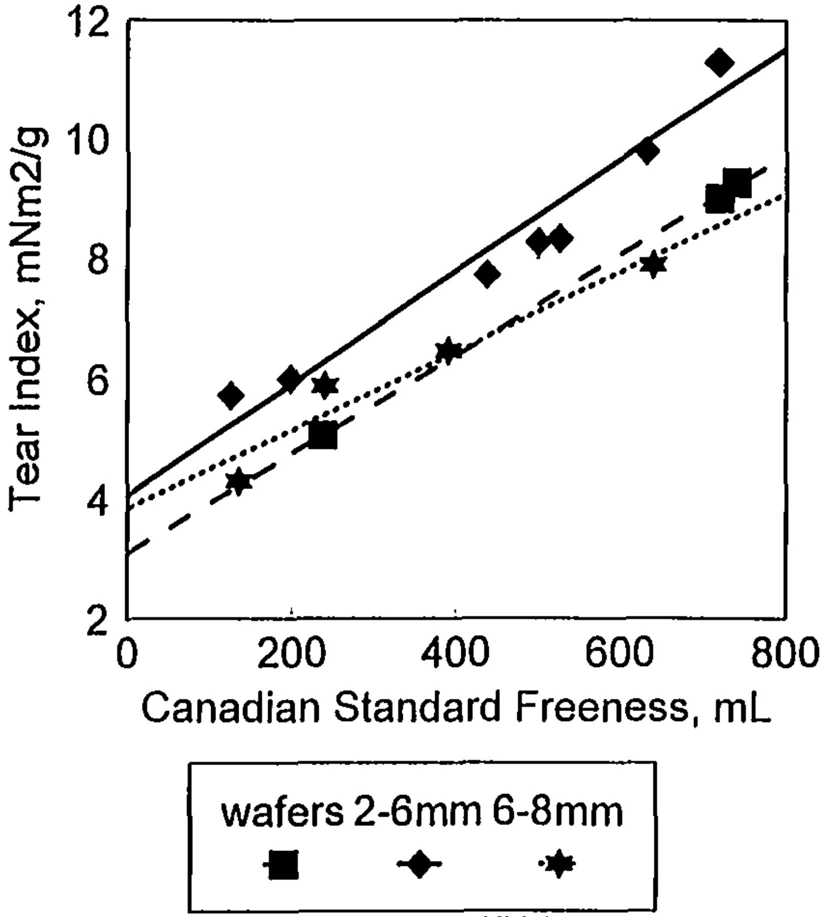


Figure 14e: Effect of Wood Chip Thickness on Tear Index
Tear Index vs Canadian Standard Freeness

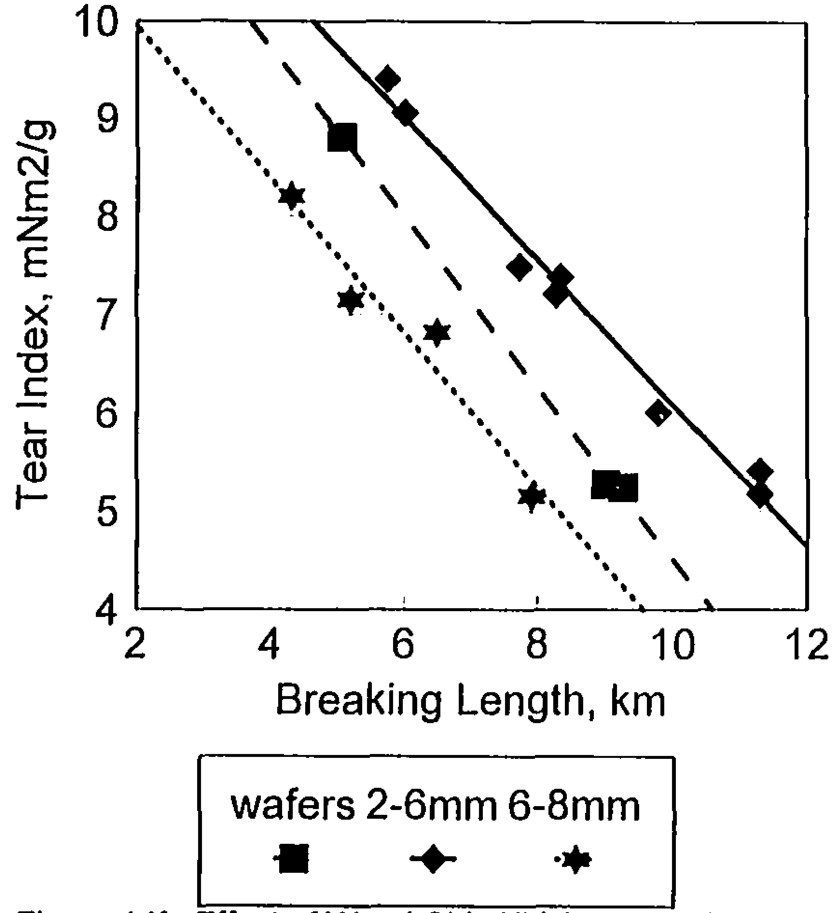


Figure 14f: Effect of Wood Chip Thickness on Tear Index
Tear Index vs Breaking Length

Effect of Wood Chip Thickness

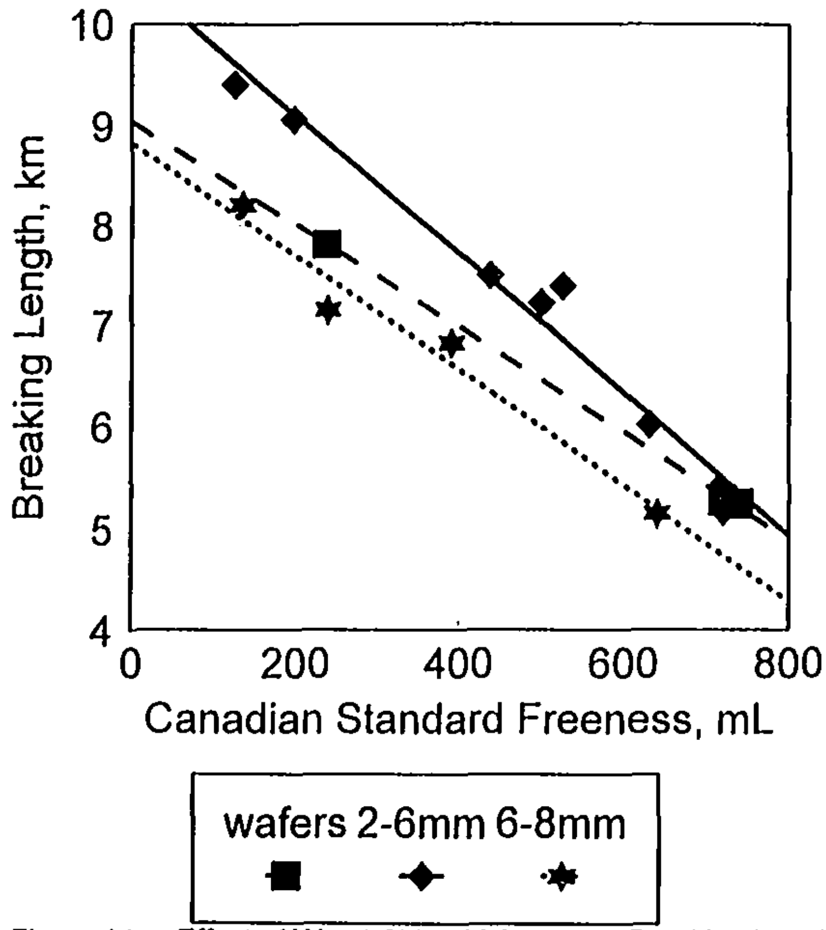


Figure 14g: Effect of Wood Chip Thickness on Breaking Length
Breaking Length vs Canadian Standard Freeness

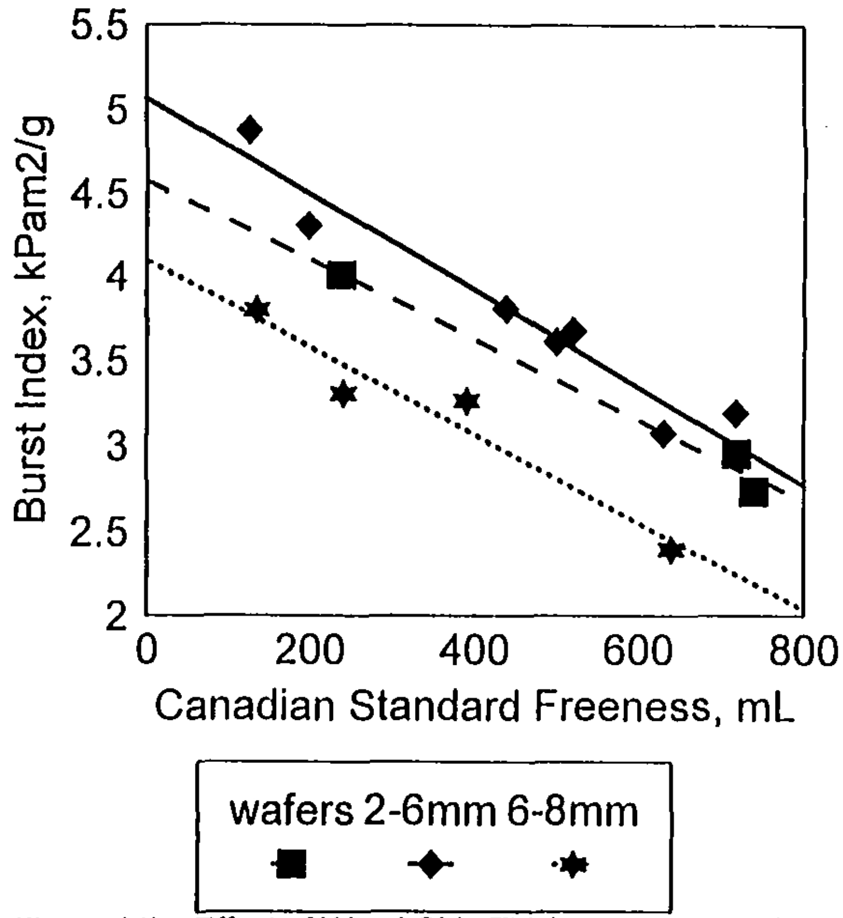


Figure 14h: Effect of Wood Chip Thickness on Burst Index
Burst Index vs Canadian Standard Freeness

Effect of Wood Chip Thickness

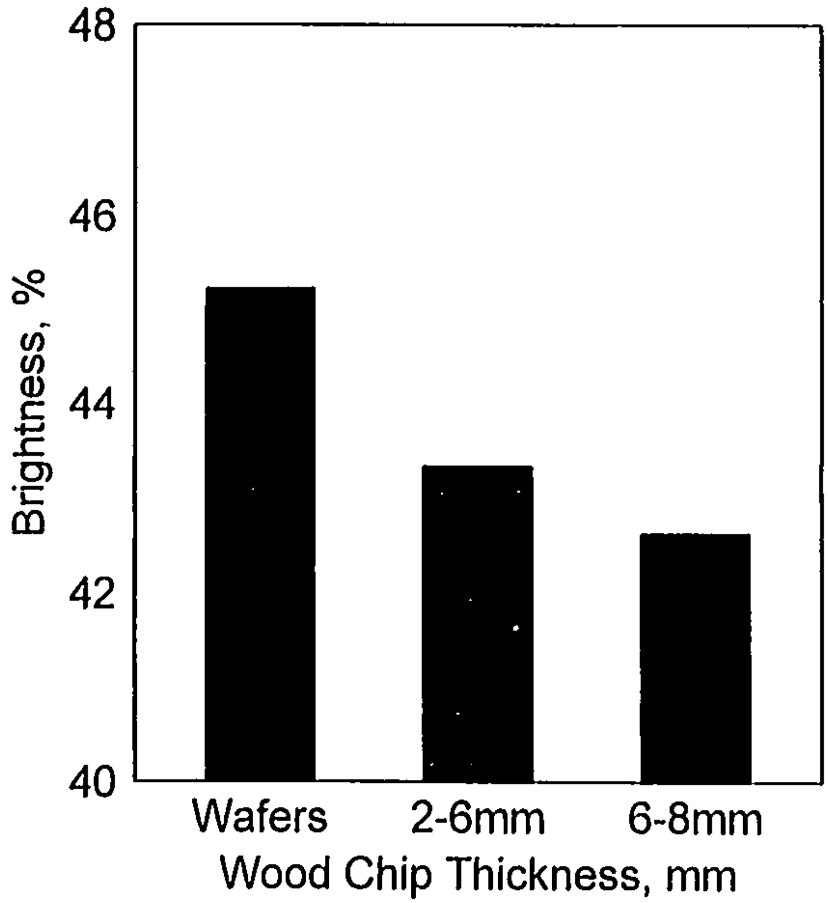


Figure 14i: Effect of Wood Chip Thickness on Brightness at 400mL Canadian Sta

4.4 EFFECT OF PRETREATMENT AGENTS

Pretreating black spruce with caustic significantly improved the rate and uniformity of CMP pulping when compared to that under identical pulping conditions with no pretreatment. Figures 15a to 15d clearly show that caustic pretreatment produces pulps that are easily defiberized in the Waring Blender, with a significantly higher screened yield and lower lignin content.

Pretreating wood chips with caustic undoubtedly swelled the wood structure and increased the permeability of pulping chemicals into the wood chips. This may be due to a facilitated passage of the pulping chemicals to the individual wood fibres and increased permeability of the individual fibre walls.

Borol pretreatment had little effect on pulp properties. This is surprising since it was expected to increase the catalytic effect of anthraquinone due to the high reducing power of sodium borohydride. Perhaps such a strong reducing agent did not allow anthraquinone to become oxidized and terminated the reduction-oxidation cycle for anthraquinone.

Tear index, burst index, and breaking length are also improved due to the caustic pretreatment (Figures 15e to 15h). This is expected since the enhanced penetration effect produced homogeneously impregnated wood chips and pulp with relatively low lignin content.

Unfortunately, Figure 15i demonstrates that when pre-treatment agents are used (particularly pure caustic) the brightness decreases significantly, compared to the same pulp with no pre-treatment. Sodium hydroxide reacts with lignin and produces chromophores which darkens the pulp. Though the alkaline pretreated pulps suffer in terms of brightness, the pulps could be bleached with sodium hydrosulphite (27).

The results from these experiments show that caustic pretreatment greatly improves the homogeneity of pulping by improving the diffusion of the pulping chemicals to the reaction sites. When this pretreatment agent is used, pulps with lower percent screen rejects, lower lignin content, and considerably higher strength properties are produced.

Effect of Pretreatment Agents

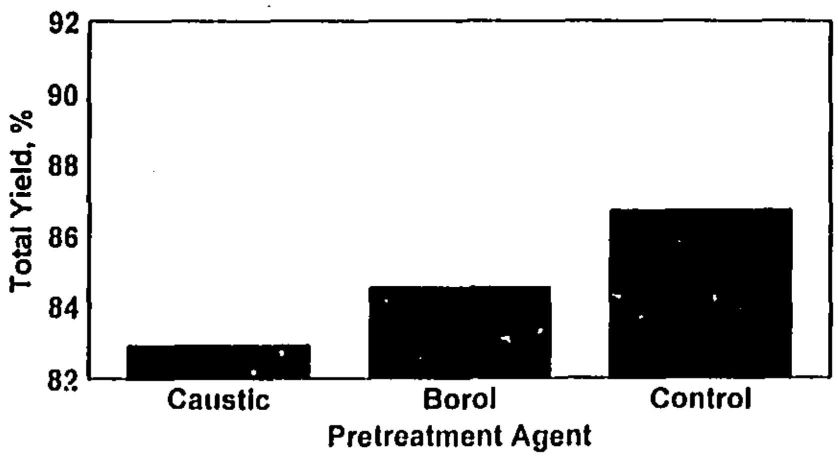


Figure 15a Effect of Pretreatment Agents on Total Yield

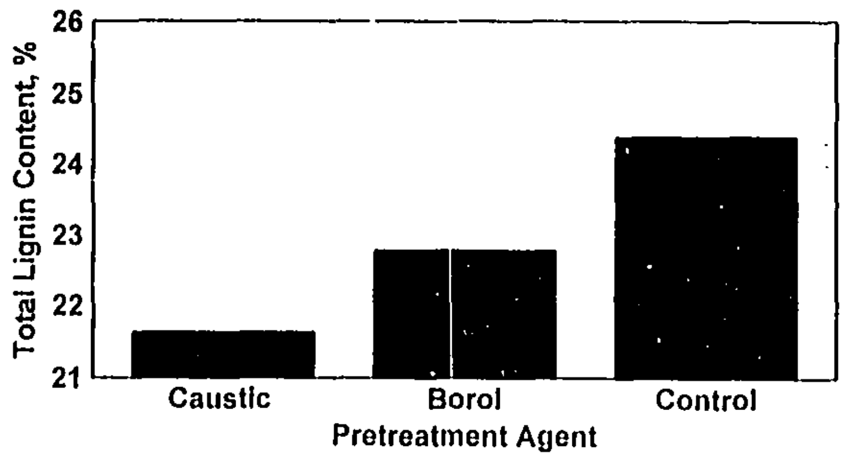


Figure 15b Effect of Pretreatment Agents on Total Lignin Content

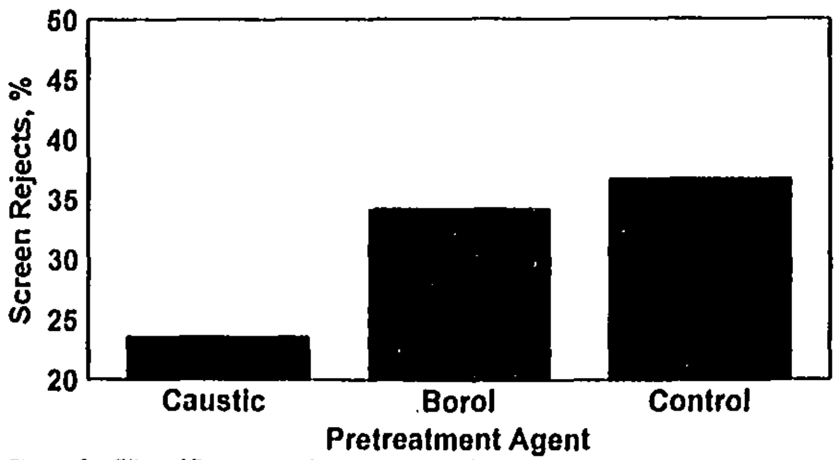


Figure 15c: Effect of Pretreatment Agents on Percent Screen Rejects

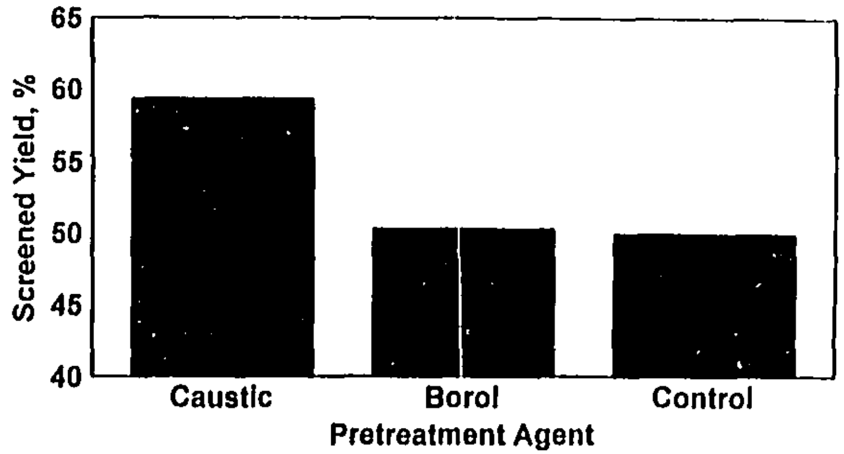


Figure 15d: Effect of Pretreatment Agents on Screened Yield

Effect of Pretreatment Agents

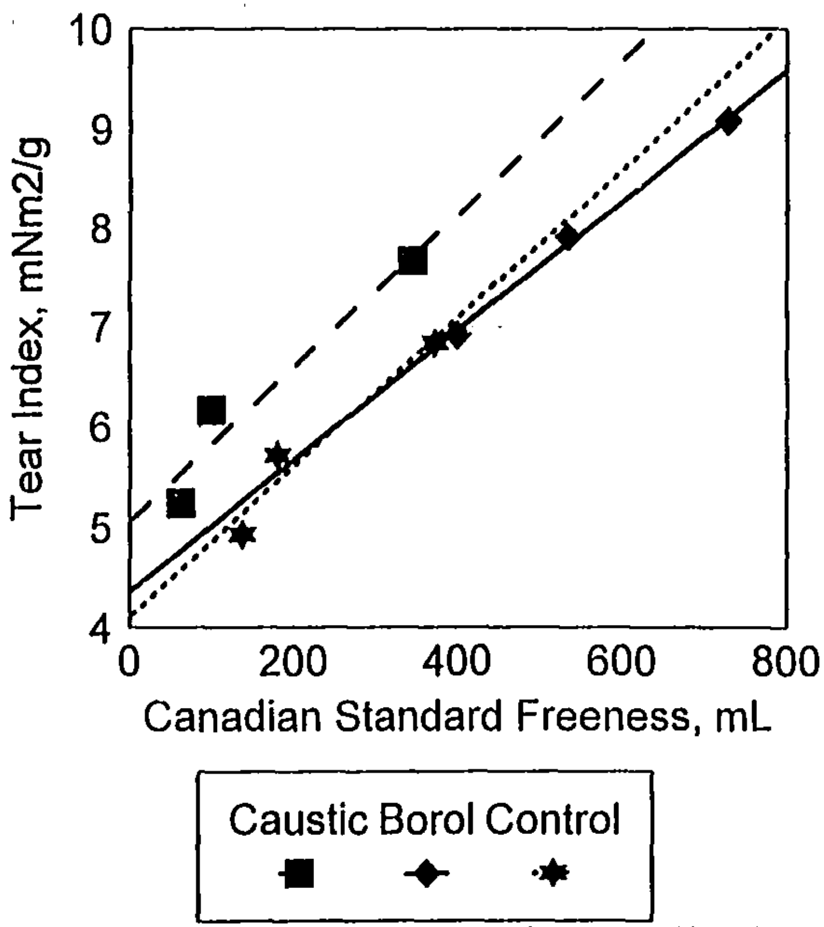


Figure 15e: Effect of Pretreatment Agents on Tear Index
Tear Index vs Canadian Standard Freeness

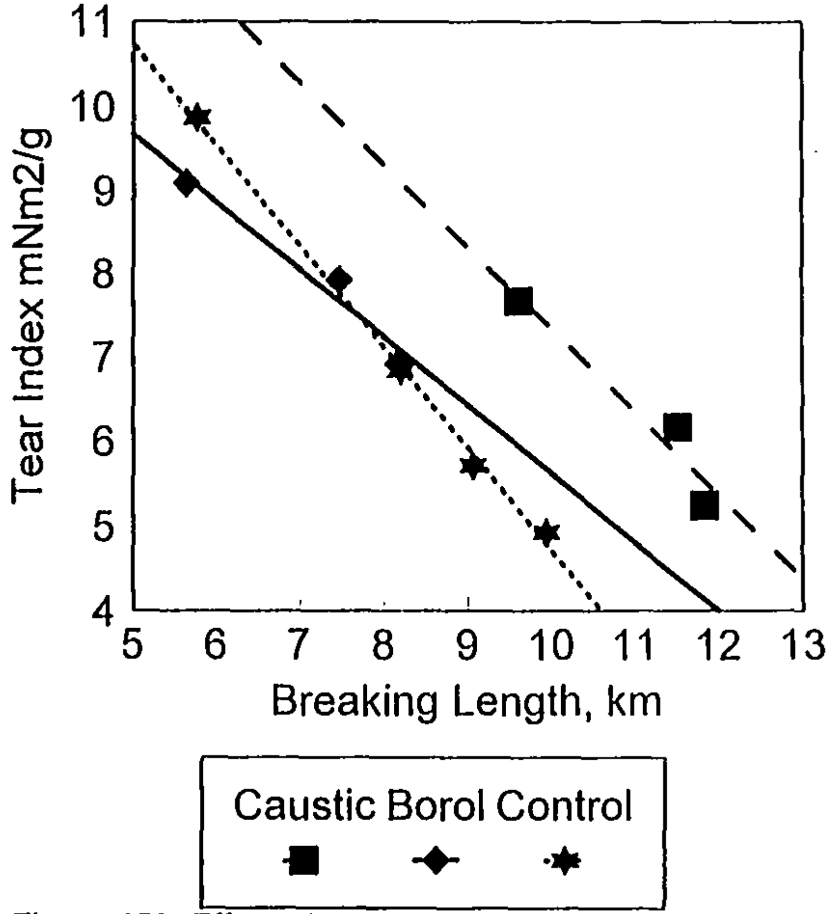


Figure 15f: Effect of Pretreatment Agents on Tear Index
Tear Index vs Breaking Length

Effect of Pretreatment Agents

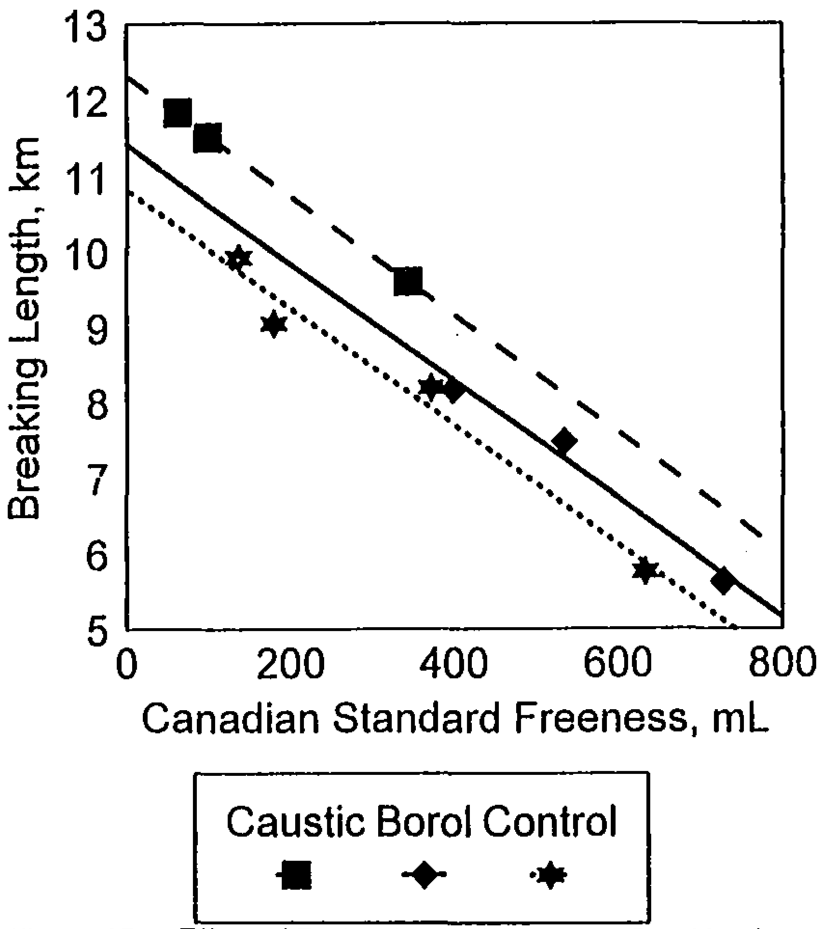


Figure 15g: Effect of Pretreatment Agentst on Breaking Length
Breaking Length vs Canadian Standard Freeness

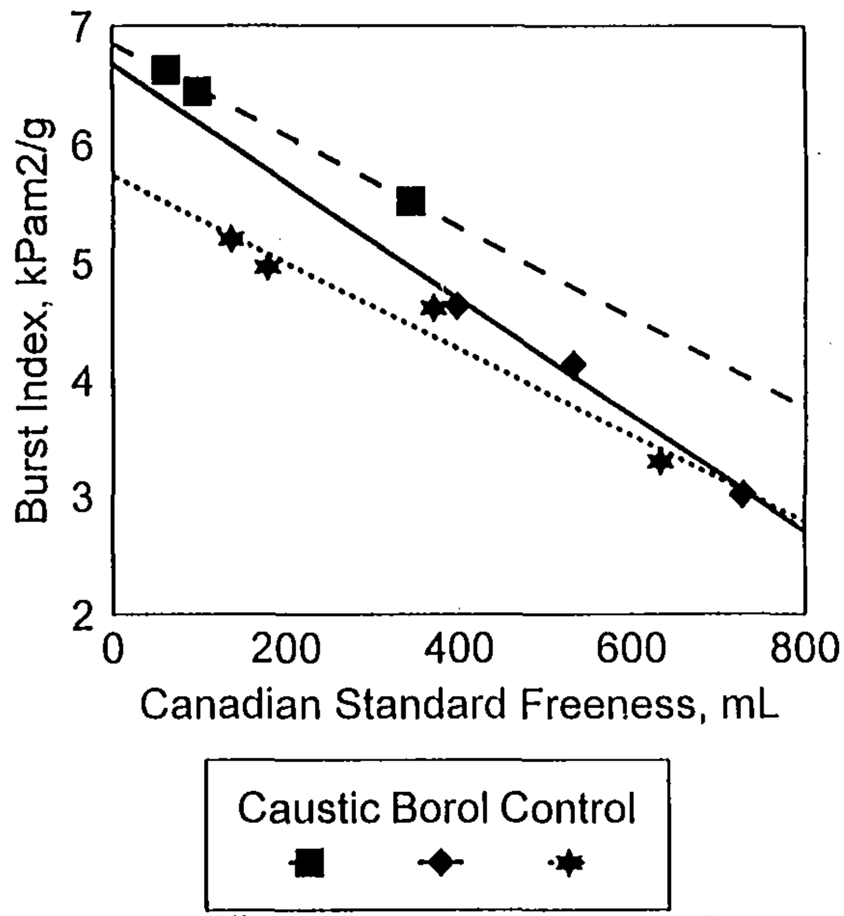
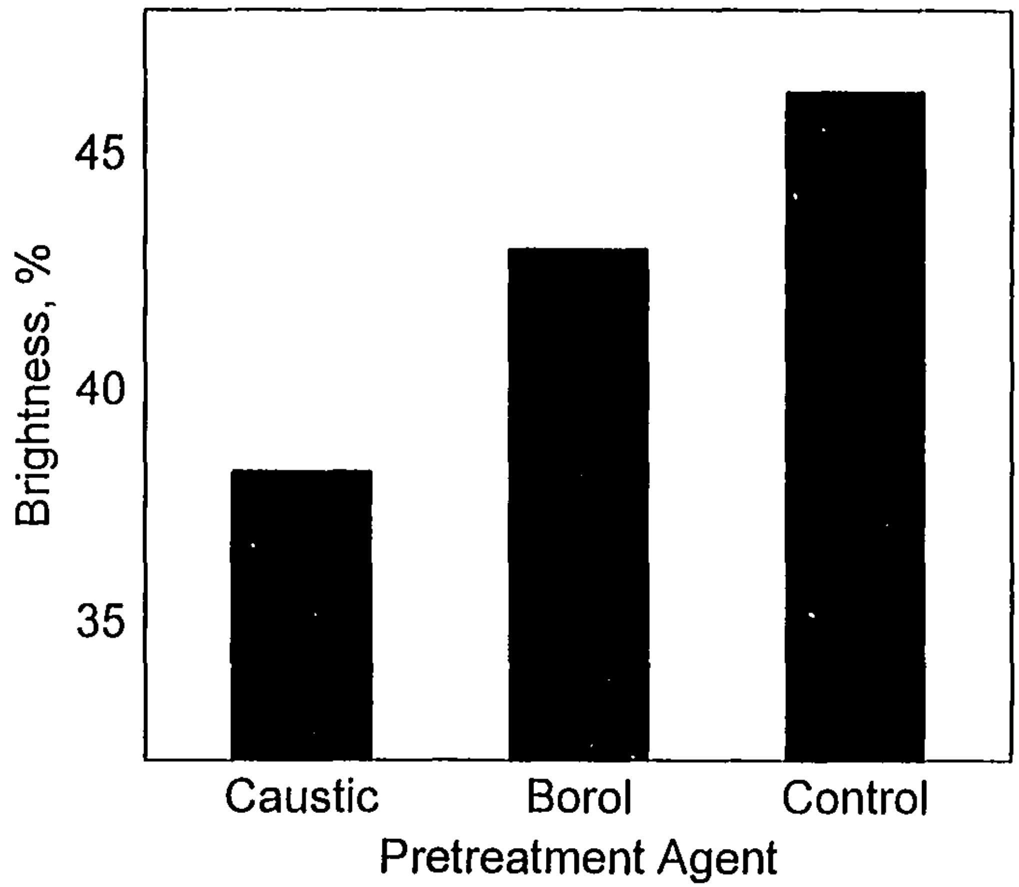


Figure 15h: Effect of Pretreatment Agenst on Burst Index
Burst Index vs Canadian Standard Freeness

Effect of Pretreatment Agents



Fsigure 15i: Effect of Pretreatment Agents on Brightnessat 400mL Canadian Stan

4.5 EFFECT OF COMPRESSION RATIO AND HYDRAULIC CRUSHING

Increasing compression ratio during impregnation from 1:1 to 4:1 to hydraulic pressing at 9:1 improved the rate and uniformity of CMP pulping, and hence pulp properties. Total lignin content and percent screen rejects decrease with increasing compression as evidenced by Figures 16b and 16c. Although Figure 16a shows a reduction in total yield with higher compression prex-impregnation, the benefits of compression are more clearly seen by Figure 16d where screened yield is plotted against total lignin content. It is obvious from this graph that a better quality of pulp is produced when high compression is used since a higher screened yield is obtained with a lower total lignin content. It should also be noted here that the compression ratio of 9:1 was obtained using the hydraulic press and the isothermal soaking temperature of 90°C could not be maintained with this device. Woods (35) showed that the rate of penetration of cooking liquor during impregnation is greater at 90°C than at 60°C or 30°C.

To observe whether fibre damage had occurred with high compression impregnation (which would negatively affect strength properties), scanning electron microscope photographs of both the surface and cross-section of a crushed wood chip and a soak-impregnated wood chip are presented (Figures 17 to 20). When compared to the soak-impregnated wood chip (compression ratio 1:1), it is obvious that the crushed wood chip exhibits partial separation of fibres and fibre wall deformation. Some fibre cutting and damage is observed.

Heitner et al. (31) state that there are two distinct regimes of impregnation which may be defined as the low and high compression regimes. Compression ratio of 2:1 is a low compression prex-impregnation whereas high compression prex-impregnation is achieved at compression ratios in the range of 4:1 to 8:1. They discovered that pulps produced within the high compression regime (4:1 to 8:1) have improved tear index and breaking length compared to pulps produced within the low compression regime (2:1 or soak-impregnated). In addition, they showed that no loss in strength occurred as the compression ratio increased from 4:1 to 8:1 (31).

Figures 16e to 16h compare strength properties for compression ratios of 4:1 and 9:1. No observable improvement in strength properties is noticed within this high compression prex-impregnation regime. However, the benefits of a higher screened yield pulp with a lower lignin content is achieved with partial crushing of the wood chips.

It may be concluded from these experiments that compression ratios in the range of 4:1 to 9:1 improve the penetration of impregnating chemicals when compared to soak impregnated experiments. Scanning electron microscopic photographs of hydraulically crushed wood chips to a 9:1 compression ratio show fibre deformation and partial separation with some fibre damage. A 9:1 compression ratio produced a better quality of pulp, with a higher screened yield for a given lignin content, but without improvement in strength properties.

Effect of Compression Ratio and Hydraulic Crushing

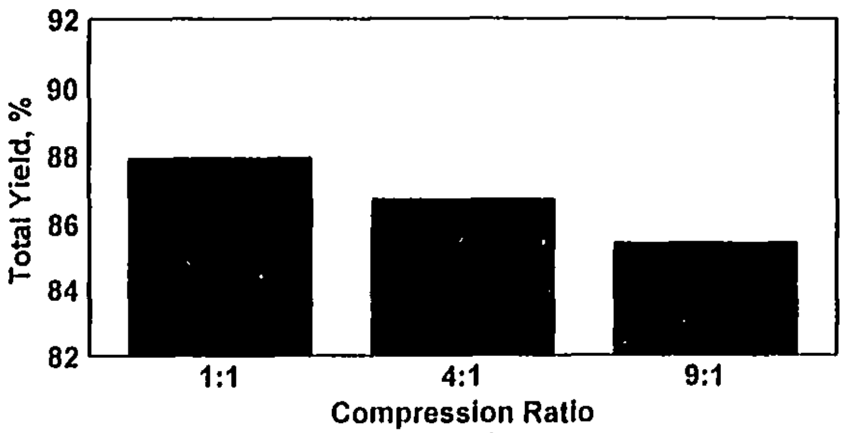


Figure 16a Effect of Compression Ratio and Hydraulic Crushing on Total Yield

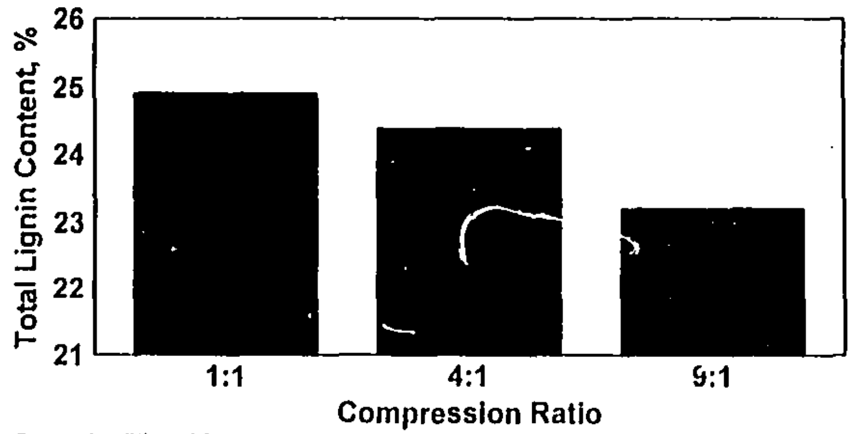


Figure 16b Effect of Compression Ratio and Hydraulic Crushing on Total Lignin Content

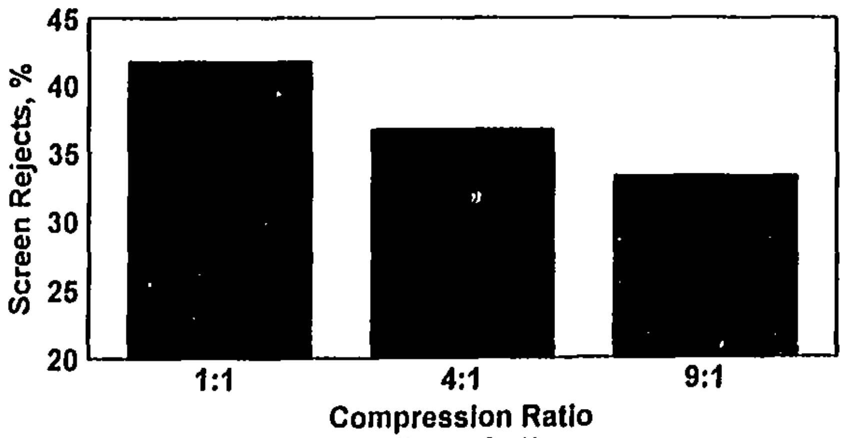


Figure 16c: Effect of Compression Ratio and Hydraulic Crushing on Percent Screen Rejects

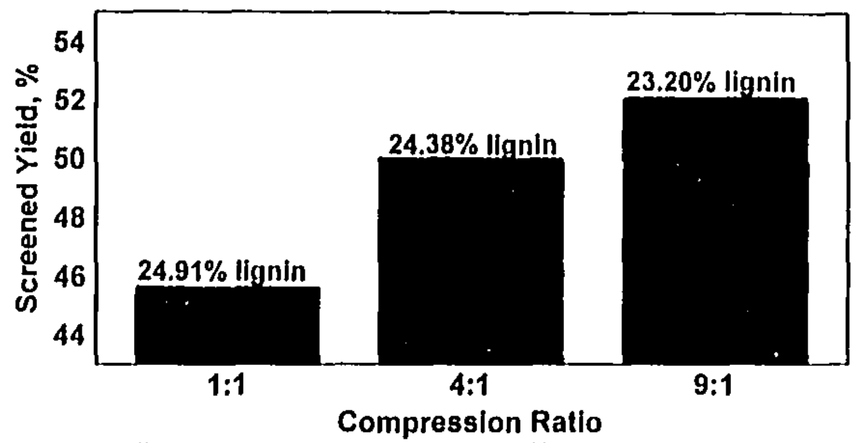


Figure 16d. Effect of Compression Ratio and Hydraulic Crushing on Screened Yield and Total Lignin Content

Effect of Compression Ratio and Hydraulic Crushing

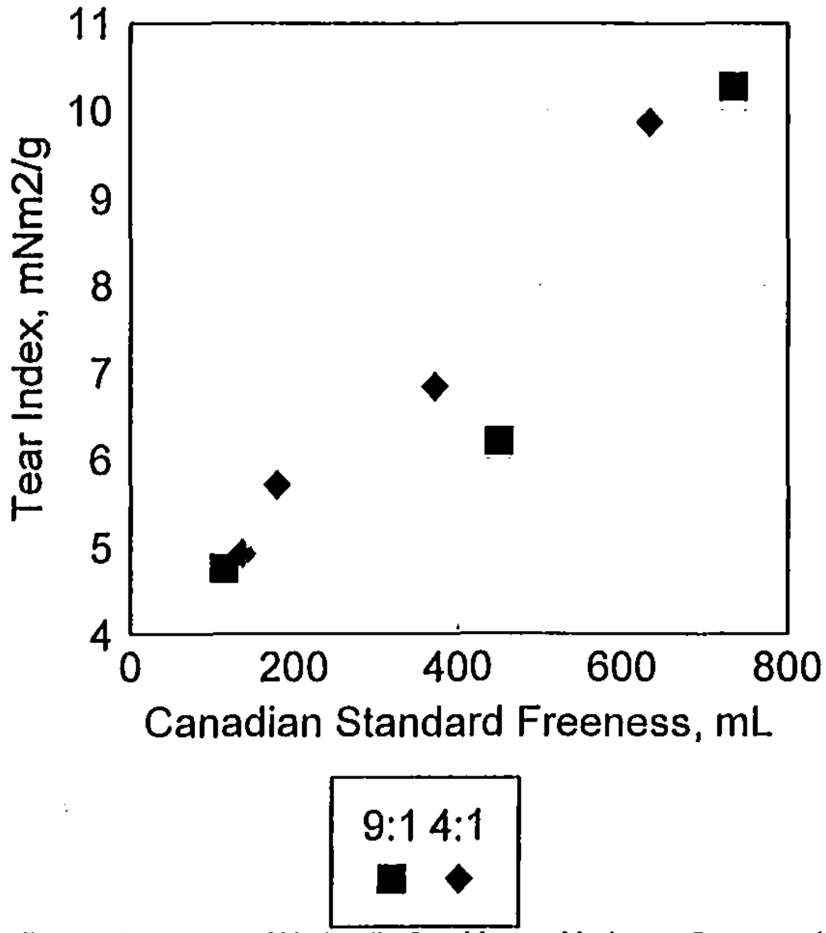


Figure 16e: Effect of Hydraulic Crushing vs Moderate Compression
Tear Index vs Canadian Standard Freeness

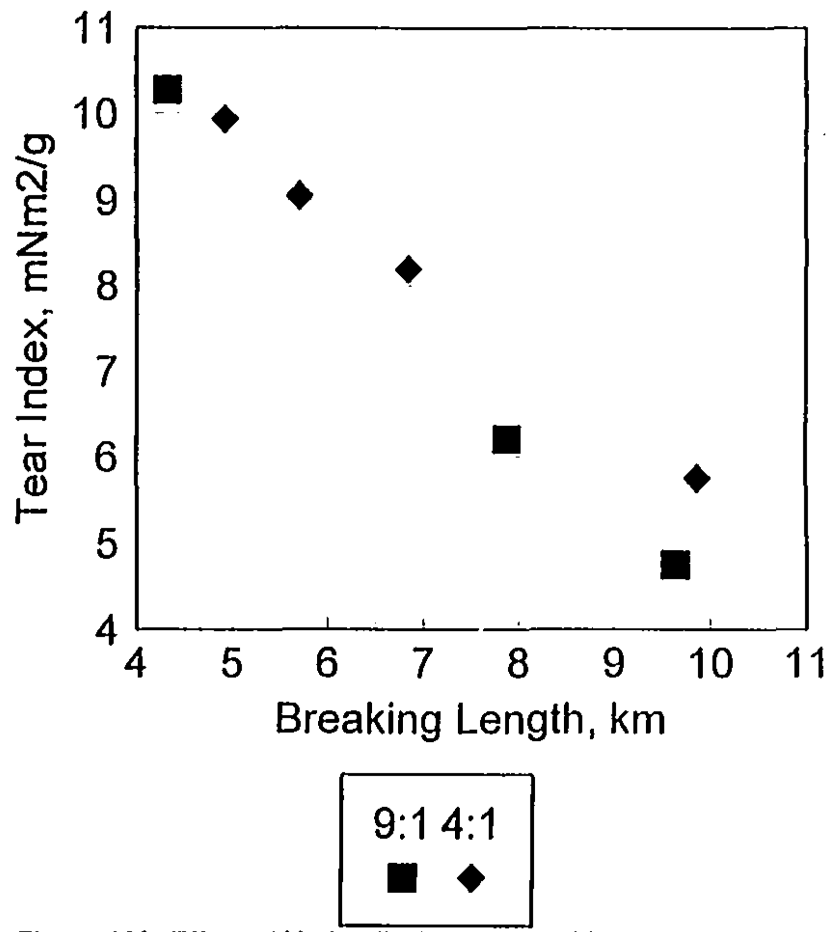


Figure 16f: Effect of Hydraulic Crushing vs Moderate Compression
Tear Index vs Breaking Length

Effect of Compression Ratio and Hydraulic Crushing

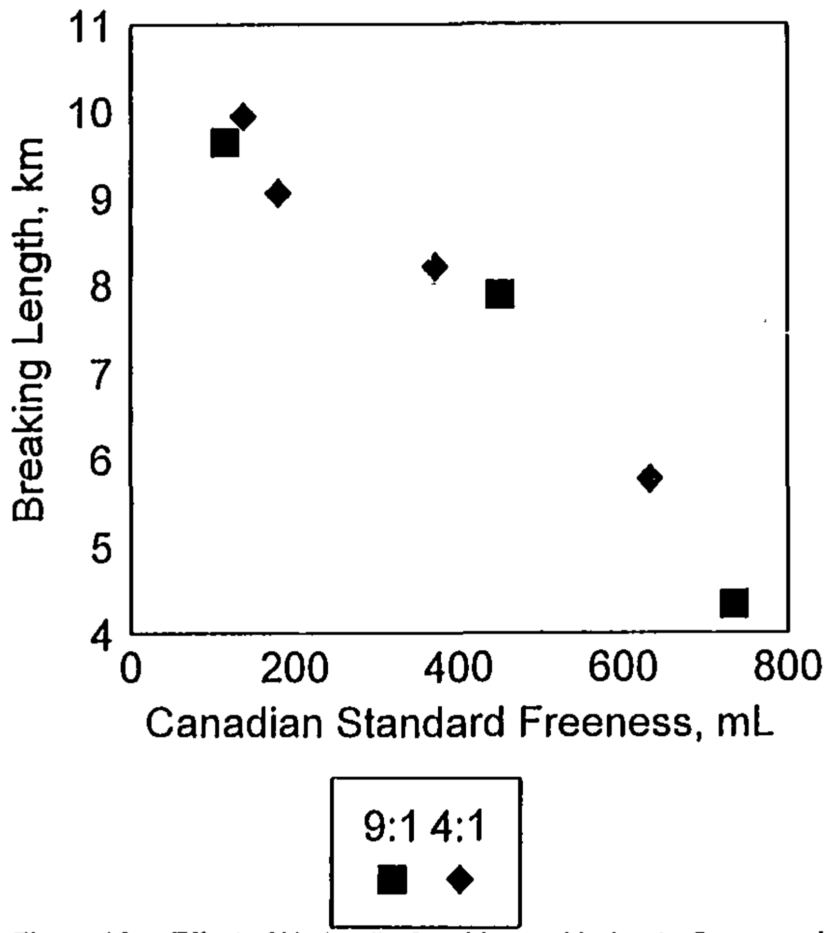


Figure 16g: Effect of Hydraulic Crushing vs Moderate Compression
Breaking Length vs Canadian Standard Freeness

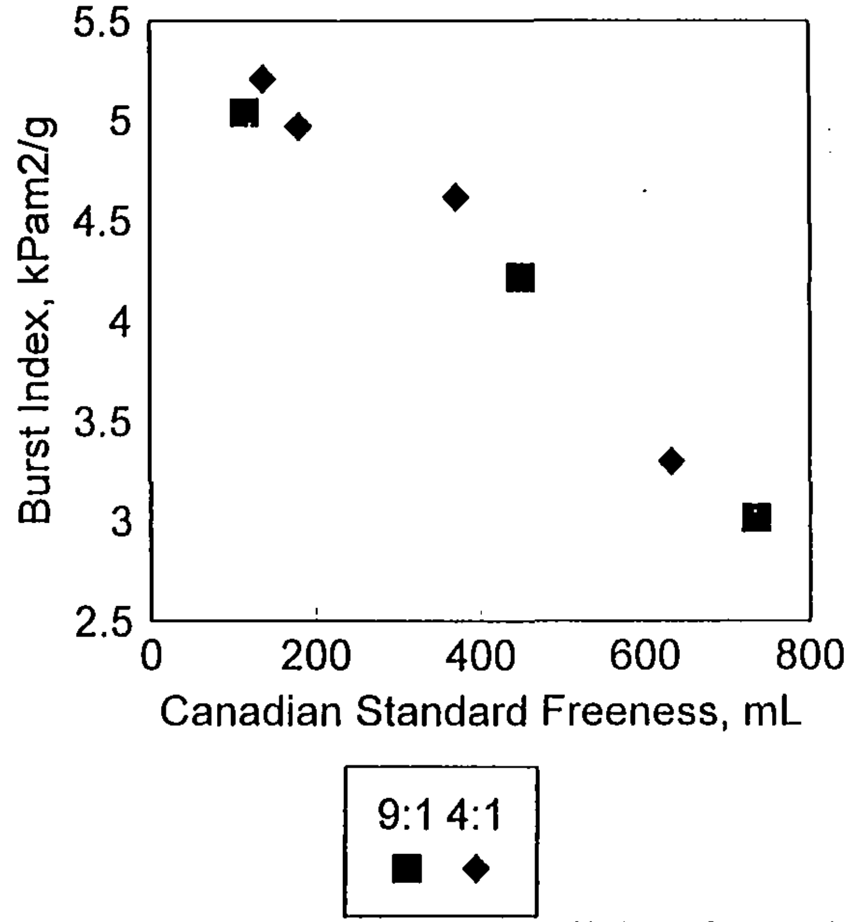


Figure 16h: Effect of Hydraulic Crushing vs Moderate Compression
Burst Index vs Canadian Standard Freeness

FIGURE 17: SURFACE SEM PHOTOGRAPH FOR CRUSHED WOOD CHIP

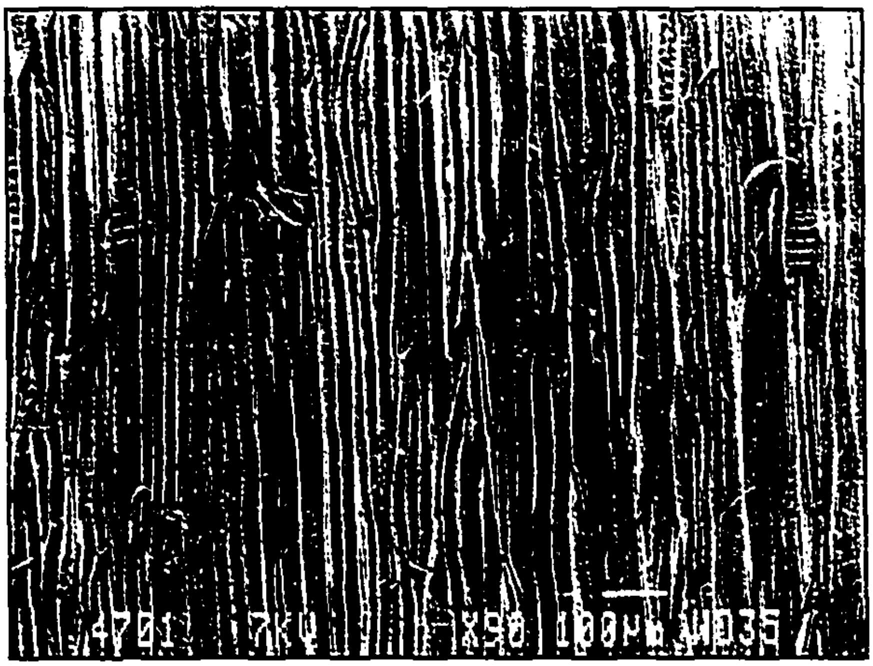


FIGURE 18: SURFACE SEM PHOTOGRAPH FOR SOAK IMPREGNATED WOOD CHIP

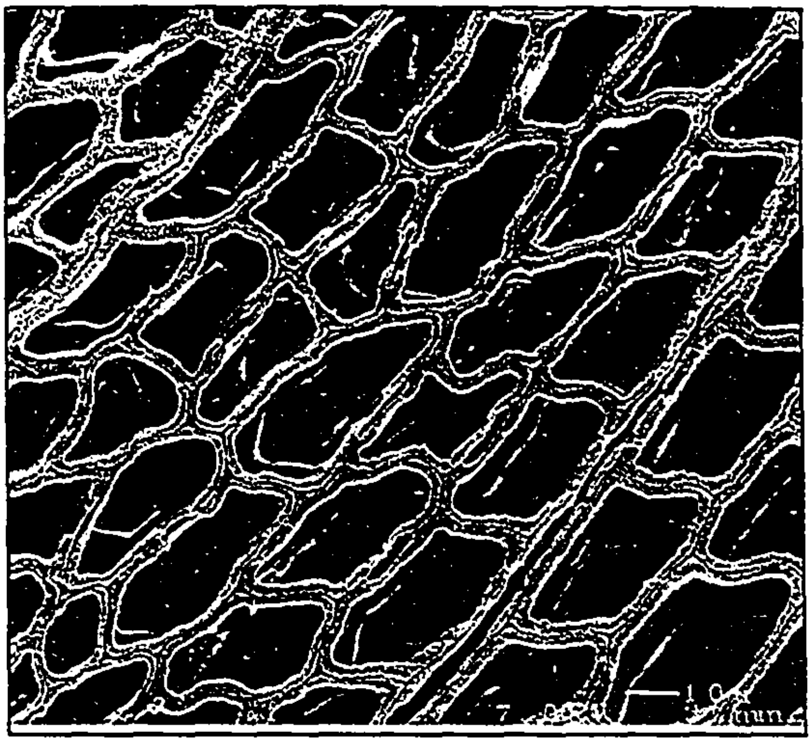


FIGURE 19: CROSS-SECTIONAL SEM PHOTOGRAPH FOR CRUSHED WOOD CHIP

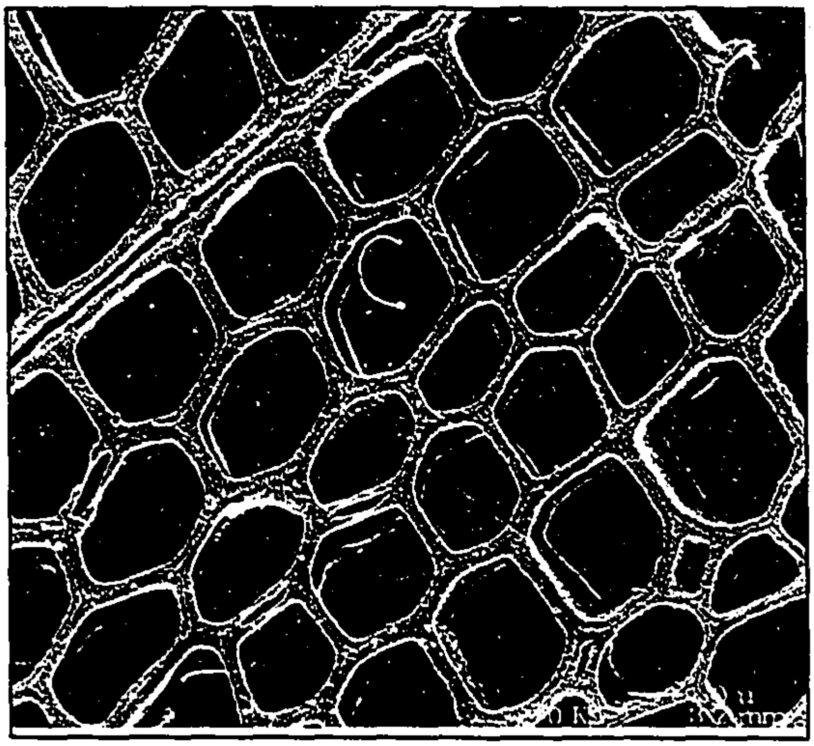


FIGURE 20: CROSS-SECTIONAL SEM PHOTOGRAPH FOR SOAK-IMPREGNATED WOOD CHIP

4.6 EFFECT OF PRESTEAMING TIME

When the presteaming time was varied from 10 to 30 minutes, pulp properties remained the same, as seen in Figures 21a to 21d. However, when pulp was produced under identical conditions with no presteaming, rejects content increased, as did lignin content. Therefore, presteaming does enhance the impregnation of cooking chemicals, but benefits of extended presteaming were not observed in the 10 to 30 minute presteaming interval. This is in agreement with the findings of Alm and Stockman (37). They discovered that percent screenings on wood was reduced significantly when presteaming increased from 5 minutes to 20 minutes. However, increasing presteaming from 20 minutes to 45 minutes had very little effect on percent screen rejects and screened yield.

One possible explanation for these results would arise from the mechanisms involved in air removal from the capillary structure of the wood chips during presteaming. Entrapped air expands during heating which creates an internal pressure in the capillary structures, opening up some closed pit membrane pores and some air is expelled. Air also becomes displaced by evaporated water, and undergoes diffusion, either through steam or through water. The diffusion coefficients through steam and through water are $3.7 \cdot 10^{-5}$ m^2/s and $13 \cdot 10^{-9}$ m^2/s, respectively, at 115°C. Therefore, diffusion through steam would dominate. However, only part of the air can be removed by diffusion through steam because condensing steam immediately forms a water film on the surface of the wood chip.

From these experiments it may be concluded that presteaming is beneficial in improving penetration of cooking liquor into black spruce wood chips during CMP-AQ pulping, but that presteaming seems only beneficial during the heating-up of the chips where air expansion and displacement occur. A 10 minute presteaming time seems to be adequate.

Effect of Presteaming Time

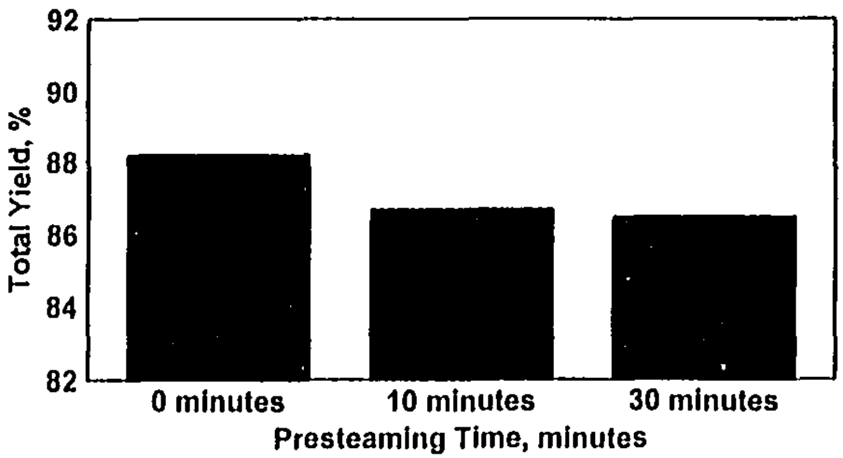


Figure 21a. Effect of Presteaming Time on Total Yield

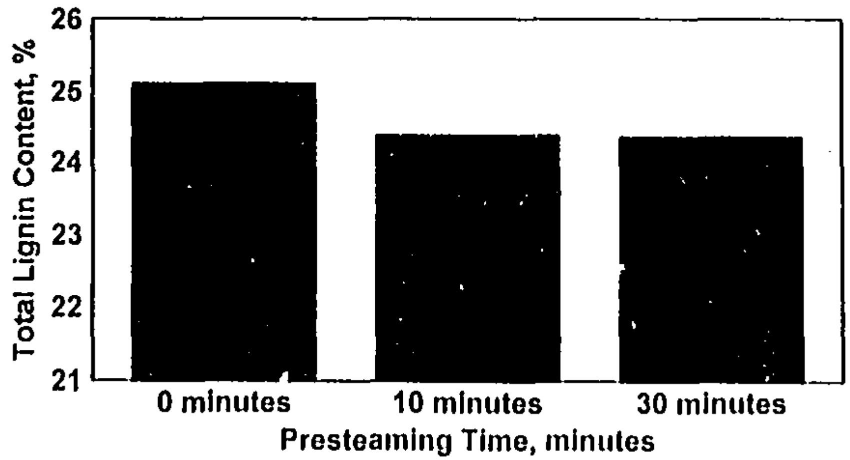


Figure 21b Effect of Presteaming Time on Total Lignin Content

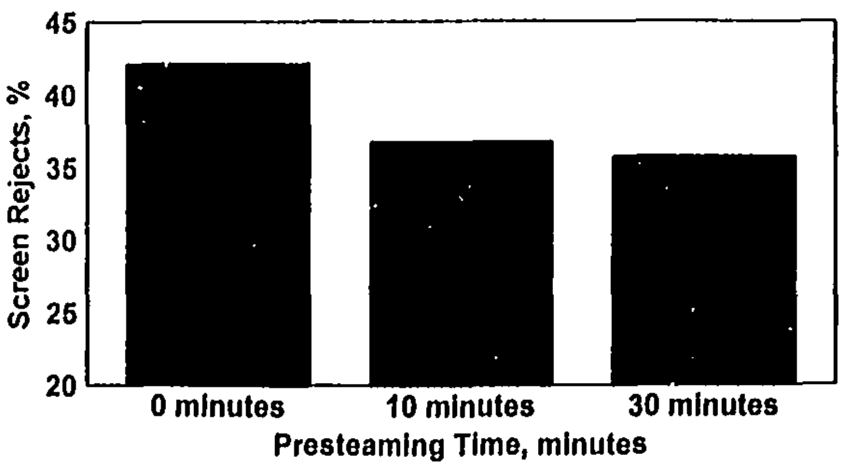


Figure 21c Effect of Presteaming Time on Percent Rejects

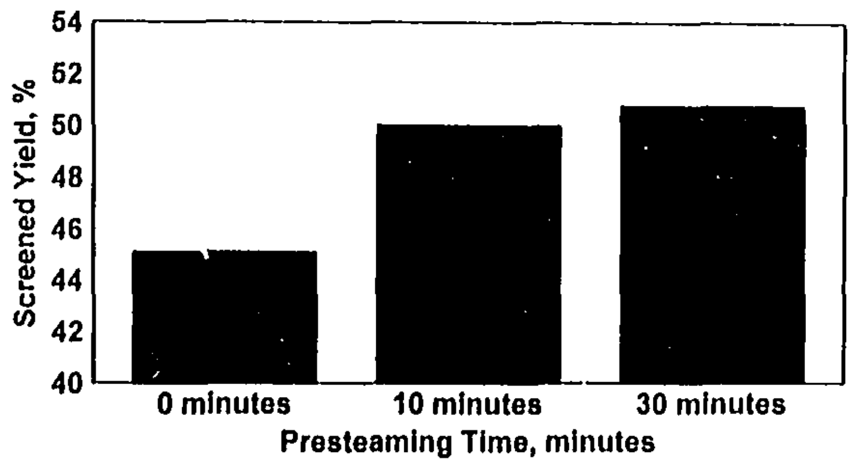


Figure 21d Effect of Presteaming Time on Screened Yield

4.7 EFFECT OF EVACUATION TIME

Improvements in CMP-anthraquinone pulping of black spruce are observed with increasing evacuation time as seen by Figures 22a to 22d. A 30 minute evacuation period significantly reduces percent screen rejects, thereby increasing the screened pulp yield. This suggests that as evacuation time increases, back-pressure of the entrapped air is reduced and the pressure differential causes a greater forced liquid flow of impregnation chemicals into the wood chips.

It is surprising that, when analyzed for pulp strength properties, significant improvements in tear, burst, and breaking length were not observed, as shown in Figures 22e to 22h. A possible explanation for these results may pertain to the use of air-dried wood chips since evacuation is most effective in removing entrapped air when the wood chips are dry (37). It has been found that moisture content of wood chips is considered important in sulphite pulping. Most mill experience indicates that inferior quality pulp is obtained with dry wood (47). When wood chips lose moisture, the fibres collapse which is an irreversible process. For best pulp strength properties, wood chips of 30 to 40 percent moisture or more should be used (47). Perhaps the use of air-dried chips for the evacuation experiments was detrimental to pulp strength.

It may be concluded that evacuating black spruce wood chips for 30 minutes is an effective method to improve the extent impregnation. However, since evacuation has little effect when using moist chips (37), and very low pressures must be used, significant modifications to existing pulping equipment would be required to implement this air-removal technique in industry. Pulp strength properties appear to be negatively affected with the use of air-dried wood chips.

Effect of Evacuation Time

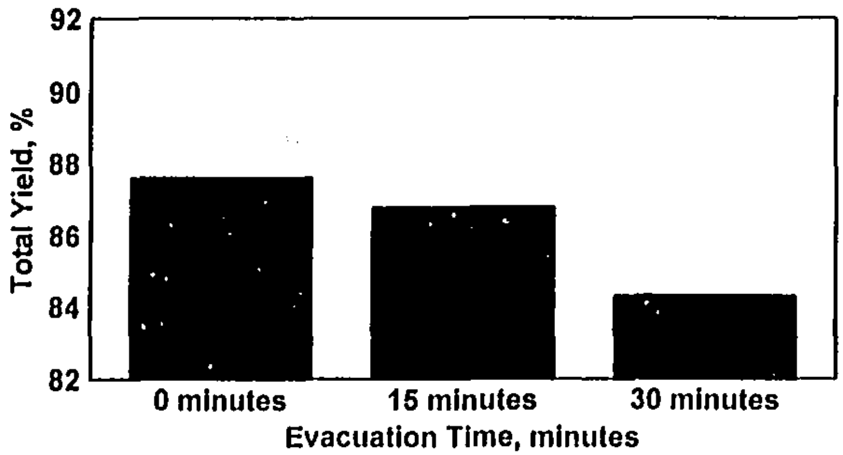


Figure 22a. Effect of Evacuation Time on Total Yield

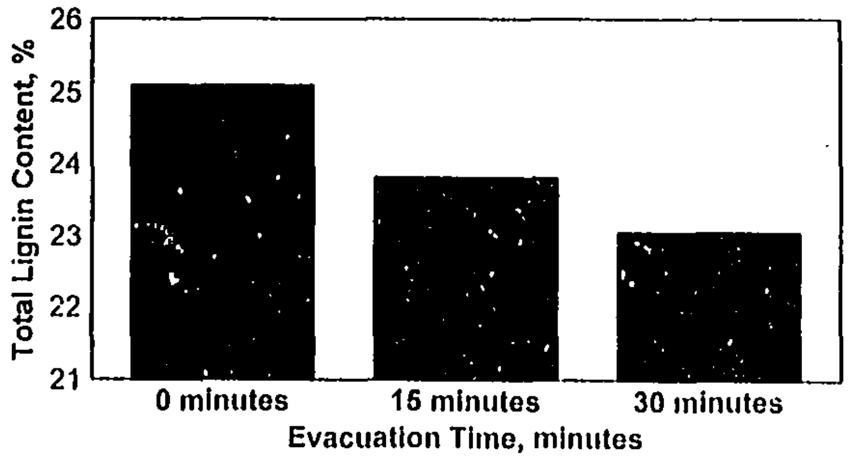


Figure 22b Effect of Evacuation Time on Total Lignin Content

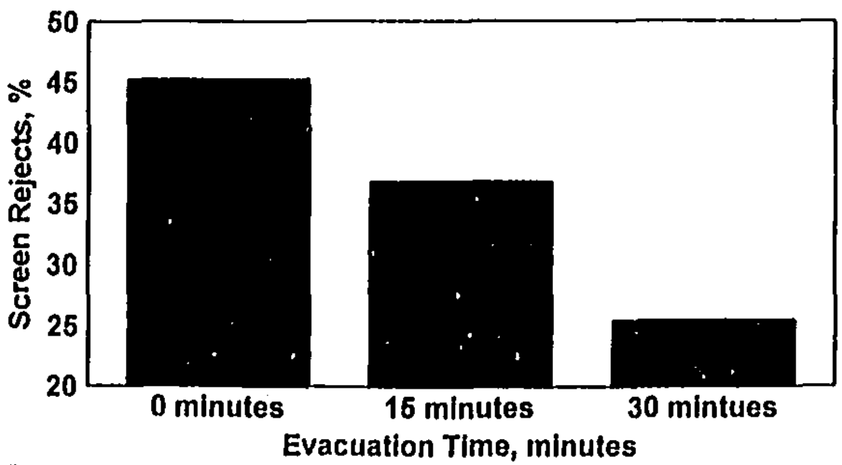


Figure 22c: Effect of Evacuation Time on Percent Screen Rejects

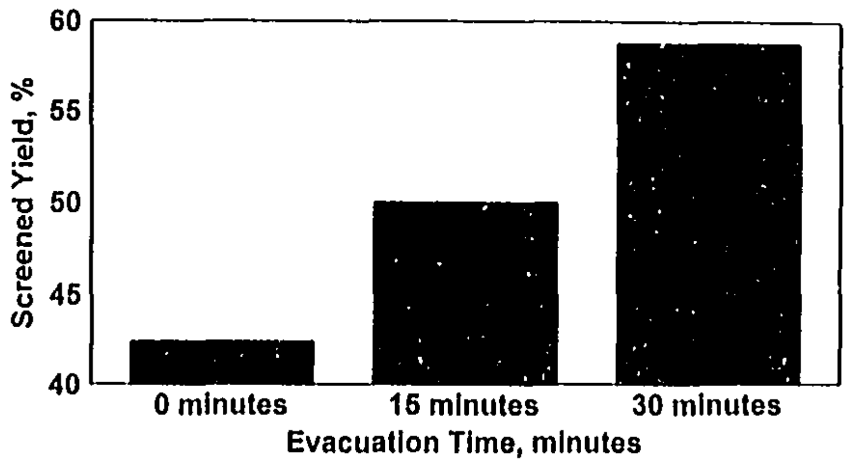


Figure 22d. Effect of Evacuation Time on Screened Yield

Effect of Evacuation Time

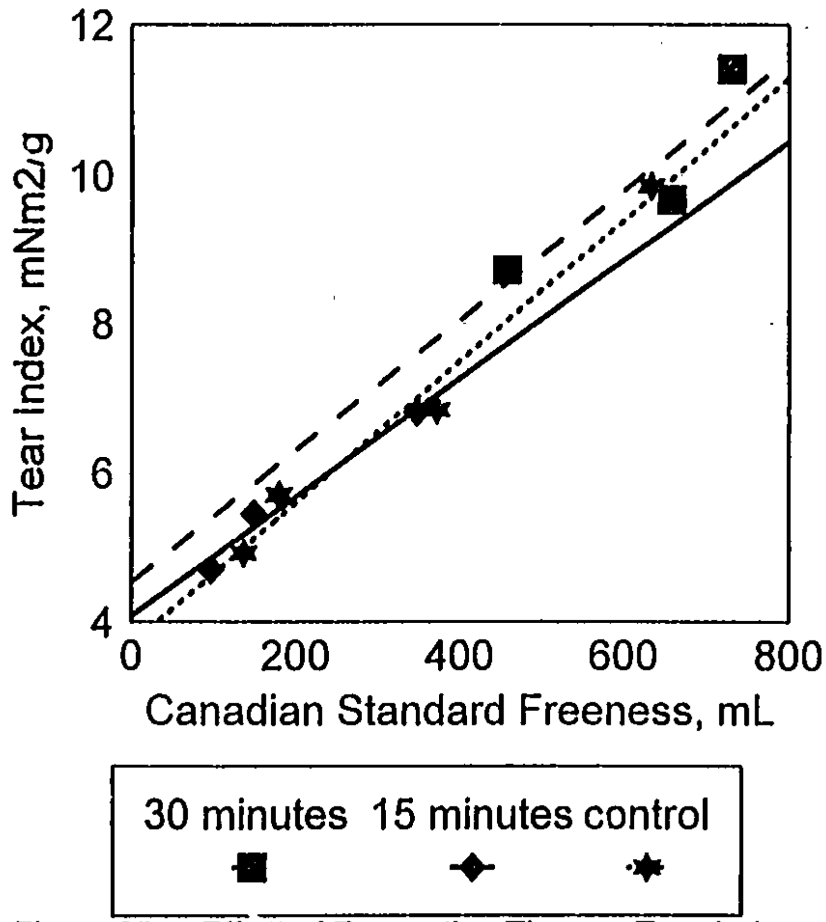


Figure 22e: Effect of Evacuation Time on Tear Index
Tear Index vs Canadian Standard Freeness

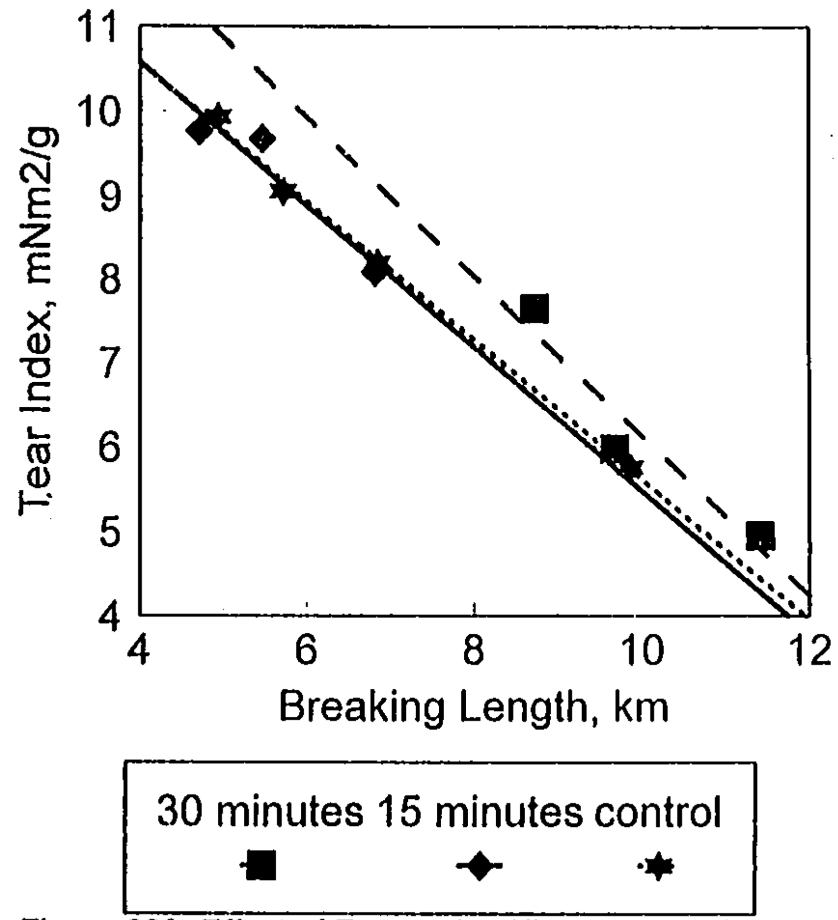


Figure 22f: Effect of Evacuation Time on Tear Index
Tear Index vs Breaking Length

Effect of Evacuation Time

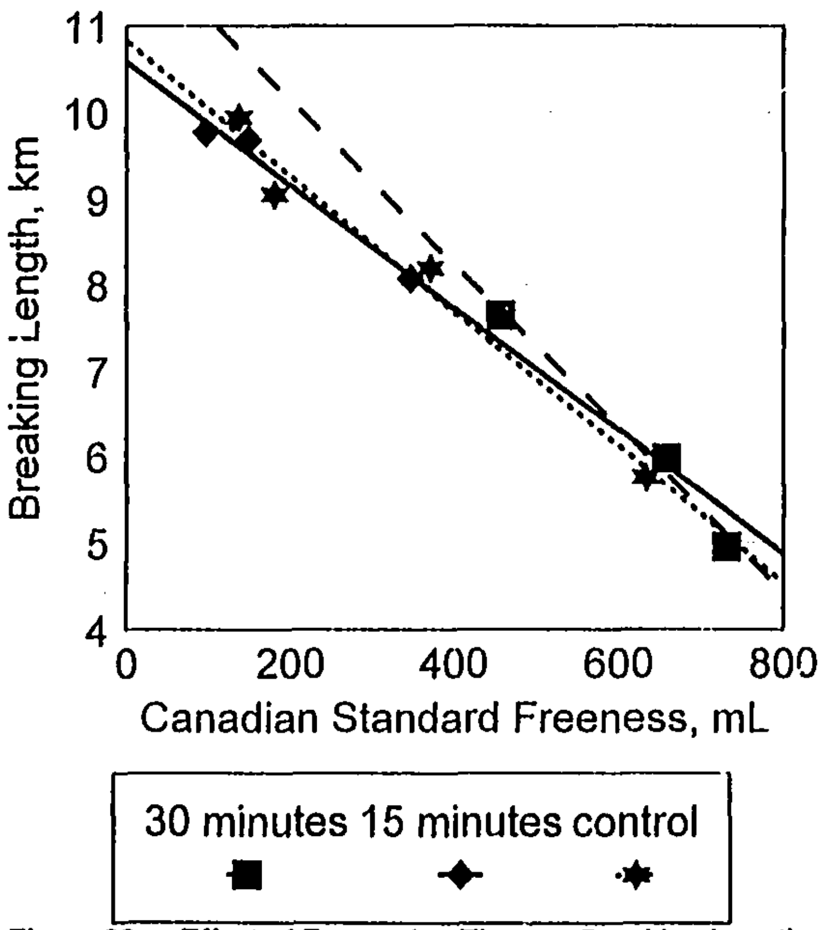


Figure 22g: Effect of Evacuation Time on Breaking Length
Breaking Length vs Canadian Standard Freeness

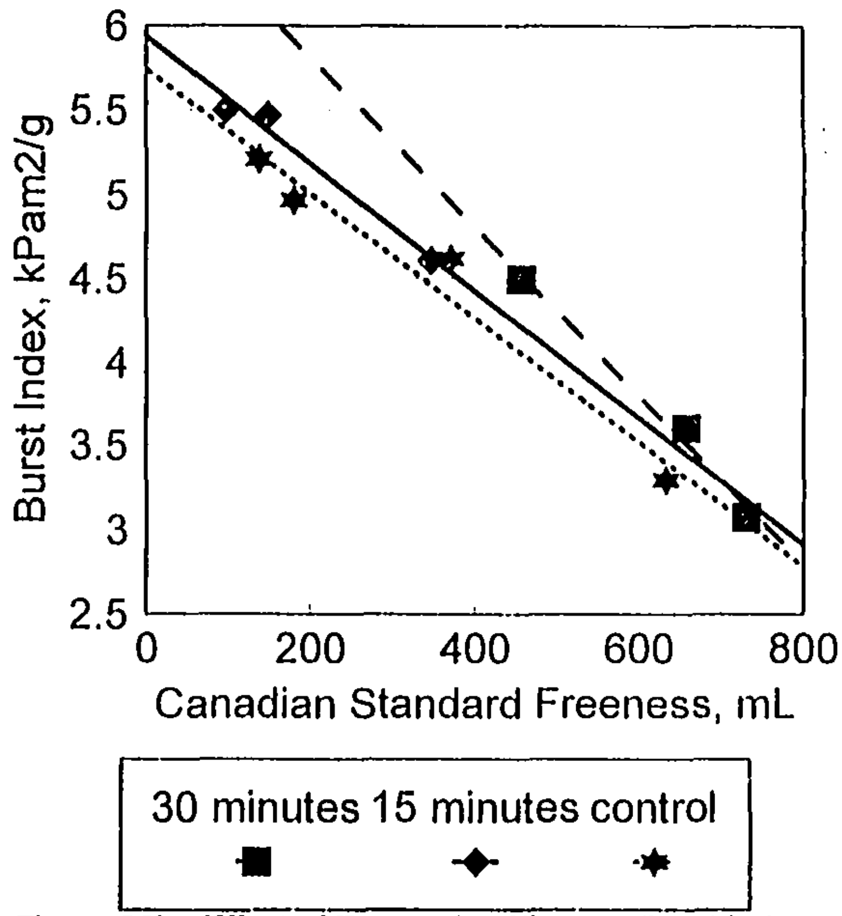


Figure 22h: Effect of Evacuation Time on Burst Index
Burst Index vs Canadian Standard Freeness

4.8 EFFECT OF PULPING CHEMICALS CONCENTRATION

The bisulphite ions (HSO_3^-) contained in the cooking liquor combine with lignin to soften it and to render it more hydrophilic. However, a portion of sulphonated lignin cleaves into smaller and more soluble molecular fragments (lignosulphonates). Bisulphite ions also hydrolyse hemicellulose into soluble sugars. It would therefore appear that increasing the chemical charge would also increase all of these reactions. Figure 23a to 23d show that a 10g/L sodium bisulphite concentration produces pulp high in screen rejects and lignin content, and low in screened yield when compared to pulps produced by impregnation with 60g/L or 80g/L sodium bisulphite concentrations. This mild sulphonation undoubtedly produced very weak pulp with a large amount of stiff, poorly collapsed fibres which contributed to the excessively large rejects content.

Increasing the sodium bisulphite concentration from 60g/L to 80g/L had very little effect on yield, rejects content and lignin content. Heitner and Hattula (42) reported that with high pulping temperatures, almost complete sulphonation is achieved in the 63g/L to 126g/L sulphite concentration range. The yield of moderate to highly (275mmol/kg to 325mmol/kg) sulphonated softwood fibres depends primarily on the temperature and pH of the sulphite treatment and is virtually independent of sulphite concentration.

From these experiments it may be concluded that impregnating wood chips with 60g/L sodium bisulphite produces pulp with significantly fewer rejects and lignin content when compared to impregnation under identical conditions with 10g/L. Little improvement in pulp properties are observed when this concentration increases to 80g/L.

Effect of $NaHSO_3$ Concentration

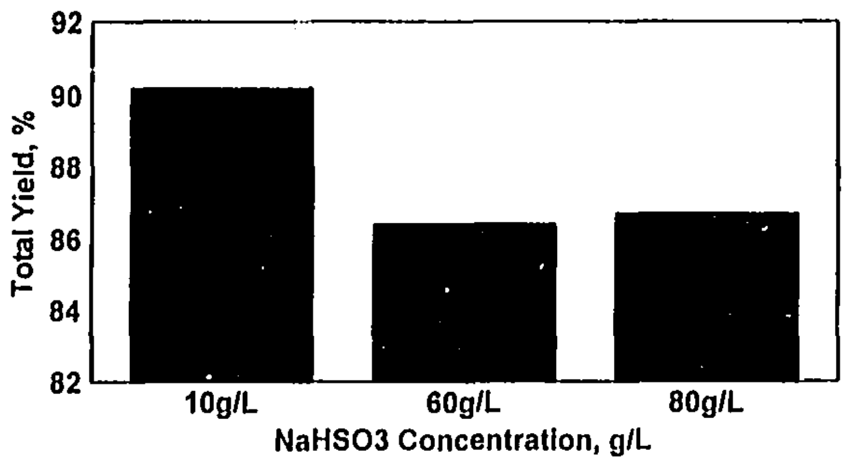


Figure 23a: Effect of NaHSO3 Concentration on Total Yield

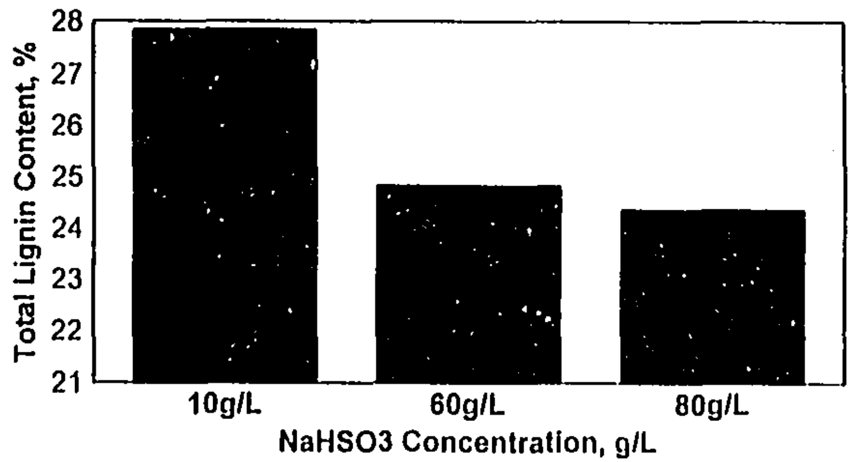


Figure 23b: Effect of NaHSO3 Concentration on Total Lignin Content

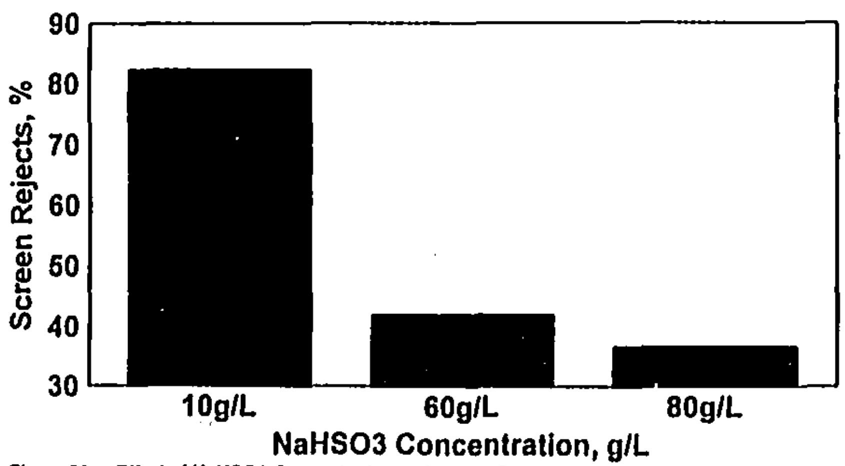


Figure 23c: Effect of NaHSO3 Concentration on Percent Screen Rejects

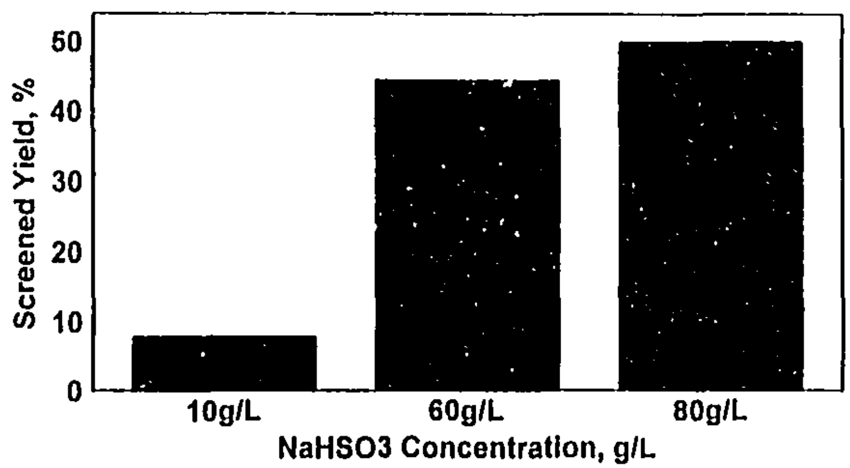


Figure 23d: Effect of NaHSO3 Concentration on Screened Yield

4.9 EFFECT OF SAQ DOSE

Total pulp yield is dependent on SAQ addition as shown in Figure 24a. Yield loss with SAQ addition is in part related to preferential delignification (see Figure 24b). Percent screen rejects (Figure 24c) also decreases with SAQ addition. Figure 24d clearly shows the benefits of SAQ with respect to screened yield and total lignin content. As SAQ dose increases, a pulp of unusually high screened yield was obtained for a given lignin content which agrees with the results of Wang (14), Keskin (23) and Morin (25).

Although the FDA restricts the amount of SAQ used in the pulp and paper industry (6), 0.2% SAQ charge on oven-dried wood was tested as a maximum extreme. The pulp produced was tested only for yield, lignin, and percent screen rejects for comparison with 0.07% SAQ charge and control. As expected, the results showed a dramatic improvement in these pulp properties with this large dose.

Strength properties at 0.07% on oven-dried wood show improvements in burst index, breaking length, and tear index for a given freeness and for a given breaking length (Figures 24e to 24h) compared to the control cook where no SAQ was used. Addition of SAQ produces stronger pulps. This is because lignin, which interferes with hydrogen bonding of the fibres, is preferentially removed (13).

A 0.07% SAQ dose on oven-dried wood had a negligible effect on pulp brightness. Brightness results at 400mL Canadian Standard Freeness were reported at 46.49% and 46.96% for pulps treated with and without SAQ, respectively. This agrees with the work of Wang (14) who found that neither the treatment temperature nor presence of AQ had any effects on pulp brightness and that only increased alkalinity of the pulping liquor darkens the pulp.

There are several ways these results may be exploited in industry, depending on the product being produced. SAQ addition benefits include shortened cooking times, improved pulp strength properties through preferential delignification, and increased screened yield.

Effect of SAQ Dose

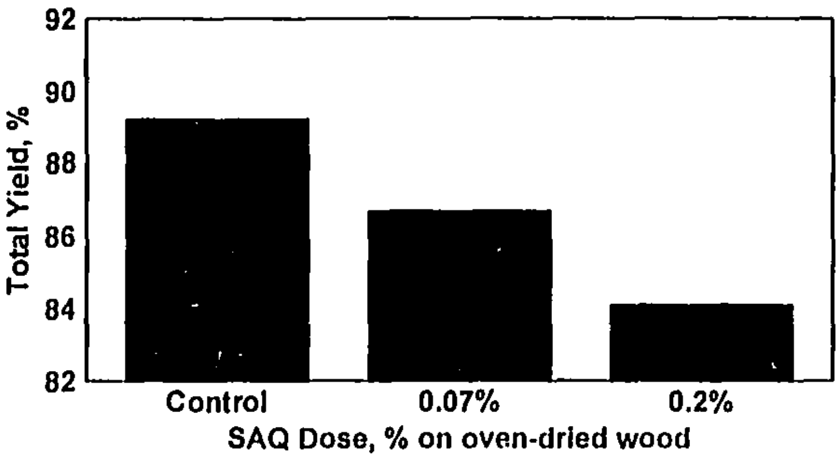


Figure 24a. Effect of SAQ Dose on Total Yield

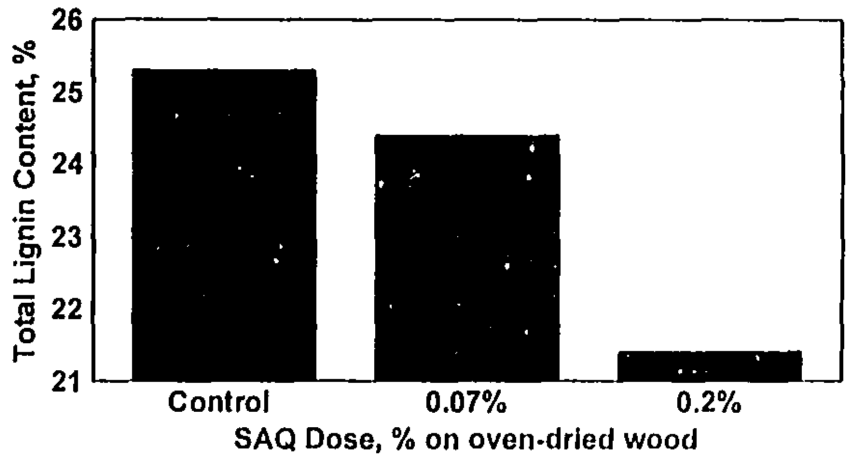


Figure 24b. Effect of SAQ Dose on Total Lignin Content

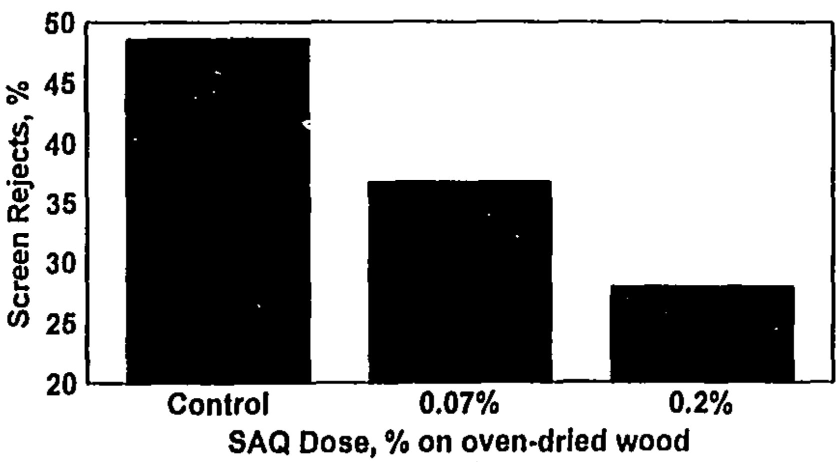


Figure 24c: Effect of SAQ Dose on Percent Screen Rejects

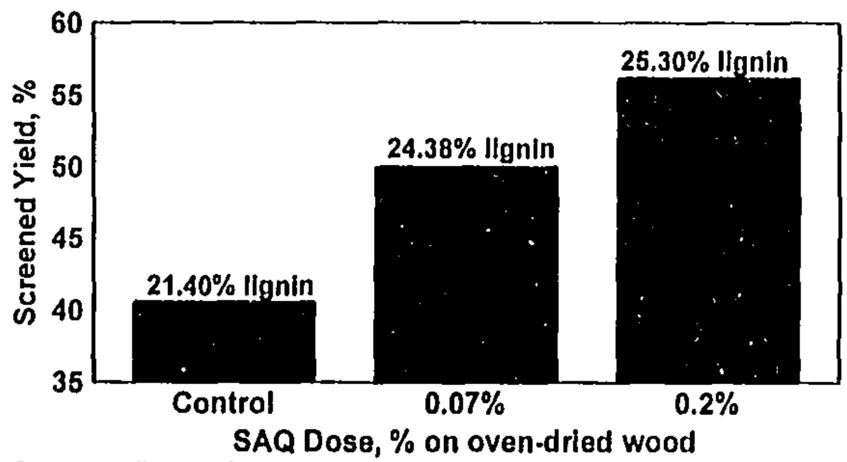


Figure 24d: Effect of SAQ Dose on Screened Yield and Total Lignin Content

Effect of SAQ Dose

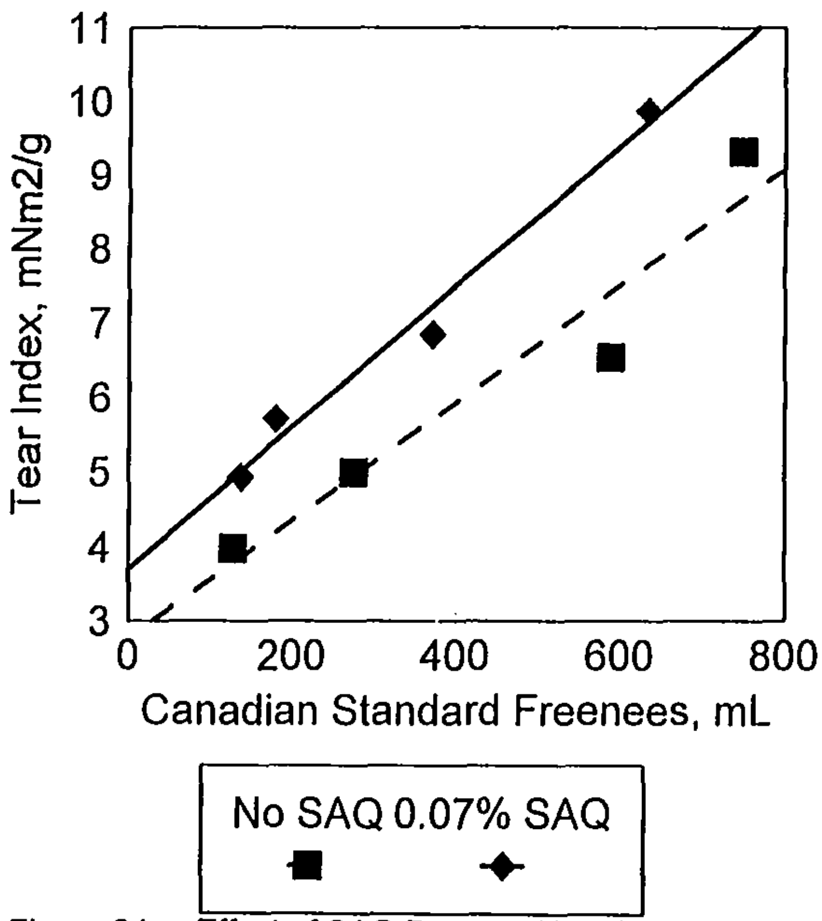


Figure 24e: Effect of SAQ Dose on Tear Index
Tear Index vs Canadian Standard Freeness

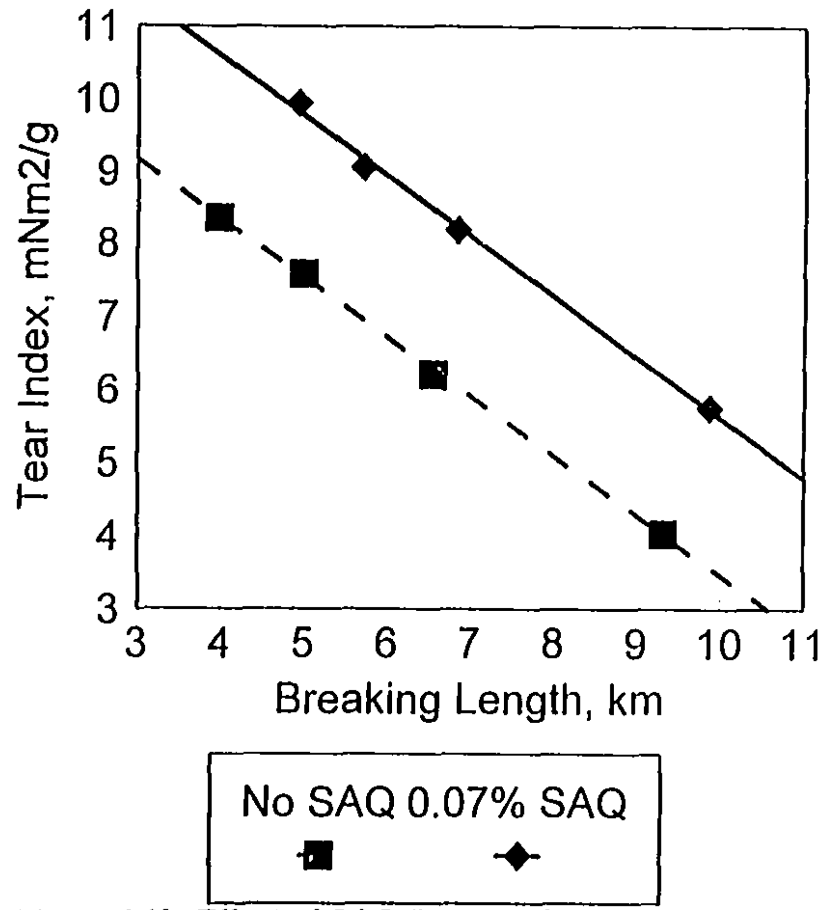


Figure 24f: Effect of SAQ Dose on Tear Index
Tear Index vs Breaking Length

Effect of SAQ Dose

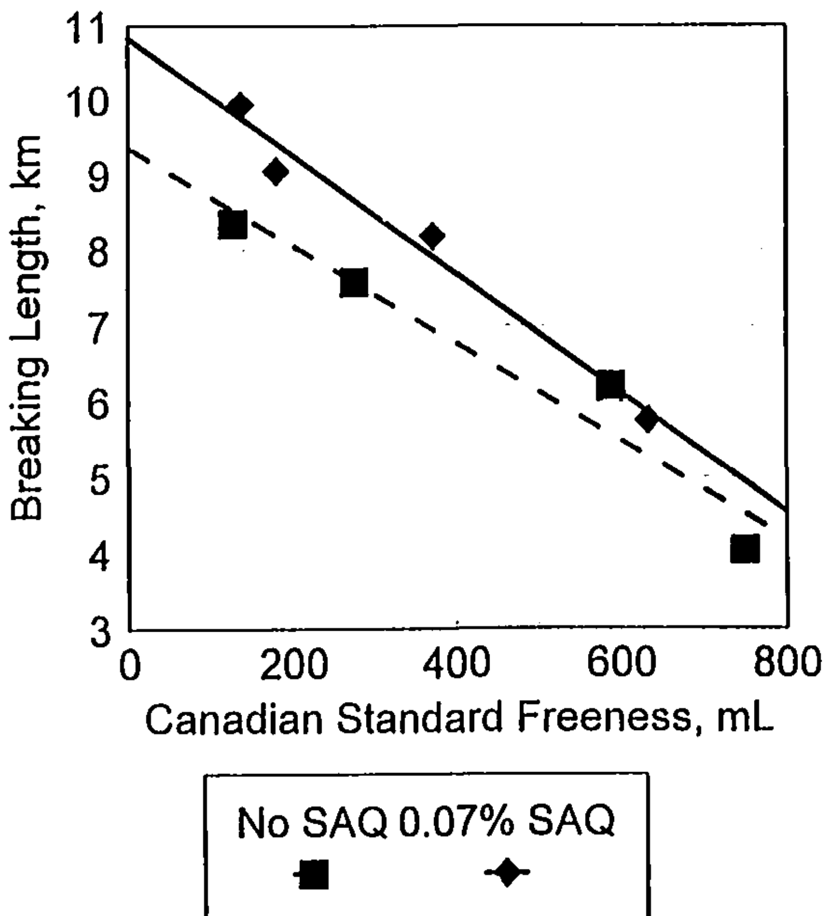


Figure 24g: Effect of SAQ Dose on Breaking Length
Breaking Length vs Canadian Standard Freeness

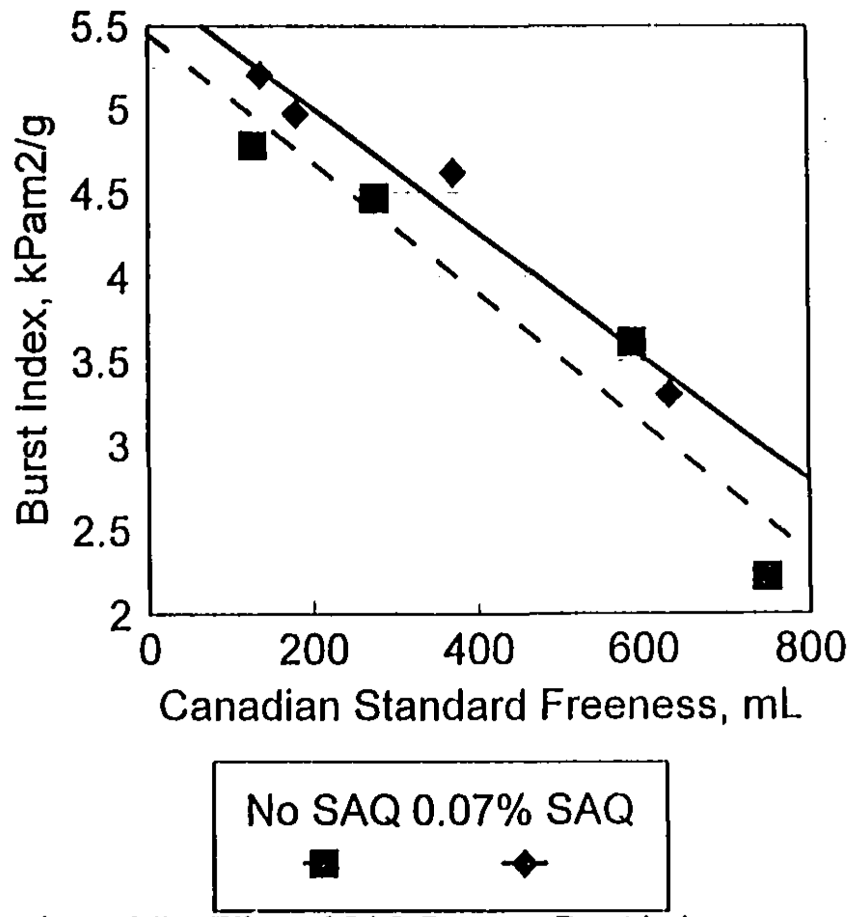


Figure 24h: Effect of SAQ Dose on Burst Index
Burst Index vs Canadian Standard Freeness

4.10 EFFECT OF SOAKING TIME

After submerging presteamed and compressed wood chips into the cooking liquor, two mechanisms occur: penetration of liquor through voids and capillaries, and diffusion of the chemicals through the cell walls. Since diffusion occurs in a liquid saturated environment, penetration must take place initially. The residence time of the wood chips in the soaking liquor prior to cooking is significant. A 5 minute soaking time produced pulp high in percent rejects and lignin content. Soaking times of 15 and 30 minutes produced similar results with respect to total yield, total lignin content, percent screen rejects and therefore, screened yield.

Morin (43) showed that over 50% of the overall impregnation was achieved after the initial two seconds of liquor soaking. After the penetration was completed, chemical intake slowed and diffusion dominated. Therefore , after the initial 2 seconds, the impregnation rate slowed substantially. Morin found that after 20 minutes, the soaking time effect was no longer significant. Figures 25a to 25d show that a 15 minute soaking time is adequate, allowing ample time for the cooking liquor to diffuse through the cell walls.

These results confirm the work performed by N.I. Woods (1956), where he investigated percent penetration for varying presteaming time and varying soaking time. For 10 minutes presteaming at 138 kPa and 90°C impregnation with distilled water, 90 percent penetration was reached after 15 minutes soaking. Additionally he found that the last 10 percent of penetration may be achieved with higher presteaming pressures.

In conclusion, percent penetration consists of mass penetration, which is completed in the initial seconds of soaking, and diffusion which takes place subsequently. The benefits of extending soaking time is significant in the first 15 minutes. After this time, diffusion slows dramatically and is no longer significant.

Effect of Soaking Time

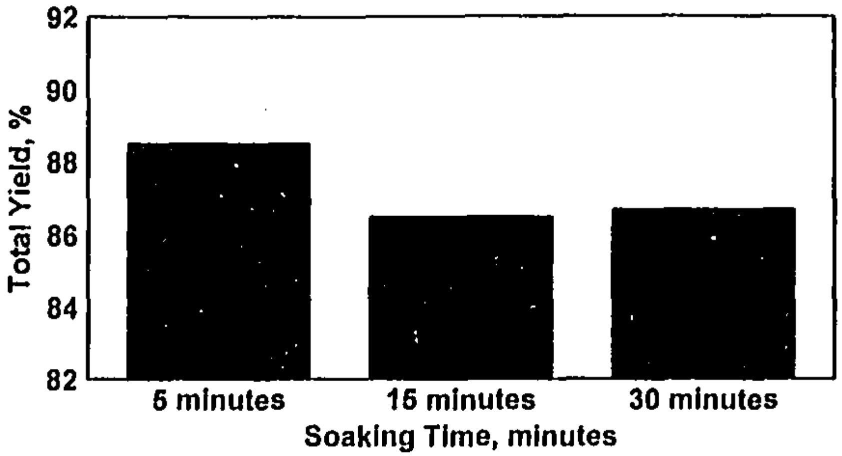


Figure 25a Effect of Soaking Time on Total Yield

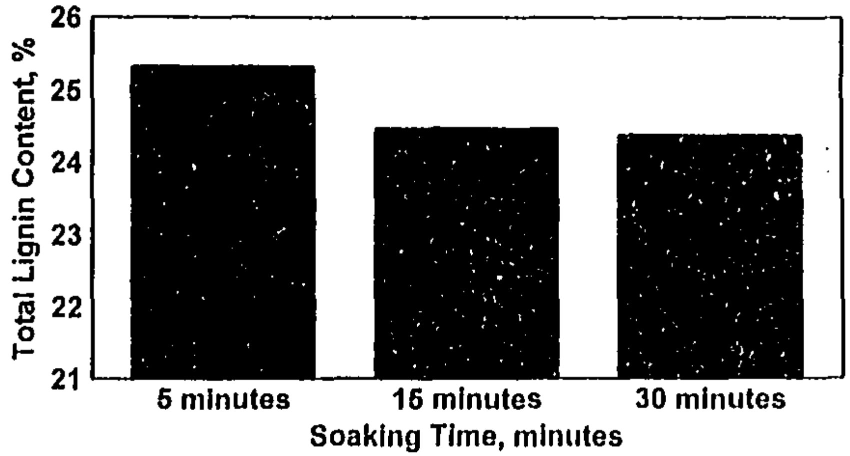


Figure 25b Effect of Soaking Time on Total Lignin Content

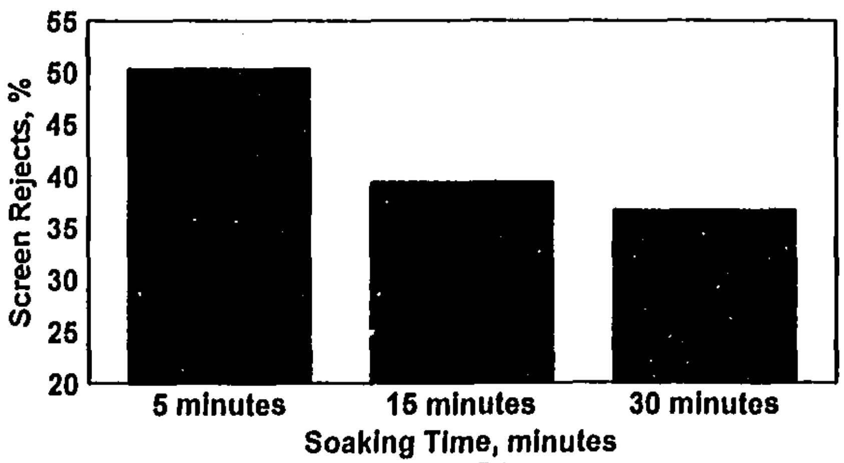


Figure 25c: Effect of Soaking Time on Percent Screen Rejects

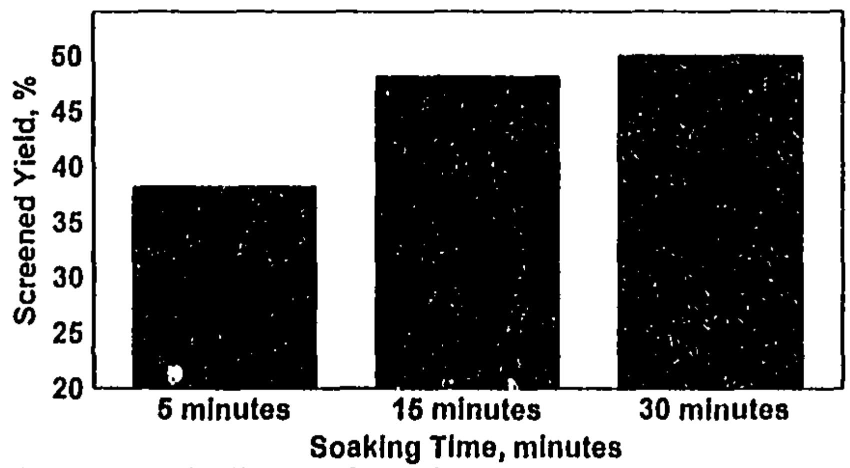


Figure 25d: Effect of Soaking Time on Screened Yield

CHAPTER V
CONCLUSIONS

5.1 CONCLUSIONS

The effects of some pulping variables were investigated to improve the penetration of chemicals during CMP-AQ pulping. The conclusions of this study may be summarized as follows:

1) Impregnation is enhanced greatly when thinner wood chips are used, but wafer wood chips, although very well impregnated, produce weaker pulp when compared to the slightly thicker denominations, most likely as a result of fibre damage when being made and pulp that contains mostly short, cut fibres. For best overall results, wood chip thicknesses of 2mm to 6mm should be used since an acceptable level of chemical impregnation is achieved and the long fiber content maintains pulp strength.

2) Caustic pretreatment greatly improves the homogeneity of pulping by improving the diffusion of the pulping chemicals to the reaction sites. When this pretreatment agent is used, pulps with lower percent screen rejects, lower lignin content, and considerably higher strength properties are produced. Borol pretreatment had little effect on pulp properties. Perhaps the strong reducing agent sodium borohydride in borol solution did not allow anthraquinone to become oxidized and terminated the reduction-oxidation cycle for anthraquinone.

3) Compression ratios in the range of 4:1 to 9:1 improve the penetration of impregnating chemicals when compared to soak impregnated experiments. Scanning electron microscopic photographs of hydraulically crushed wood chips to a 9:1 compression ratio show fibre deformation and partial separation with some fibre damage. A 9:1 compression ratio produced a better quality of pulp in terms of screened yield and total lignin content, but no improvement in stregnth properties was observed.

4) Presteaming is beneficial in improving penetration of cooking liquor into black spruce wood chips during CMP-AQ pulping, but presteaming seems only beneficial during the heating-up of the chips where air expansion and displacement occur. A 10 minute presteaming time seems to be adequate.

5) Evacuating black spruce wood chips for 30 minutes is an effective method to improve the extent impregnation. However, since evacuation has little effect when using moist chips, and very low pressures must be used, significant modifications to existing pulping equipment would be required to implement this air-removal technique in industry. Pulp strength properties appear to be negatively affected with the use of air-dried wood chips.

6) Impregnating wood chips with 60g/L sodium bisulphite produces pulp with significantly fewer rejects and lignin content when compared to impregnation under identical conditions with 10g/L. Little improvement in pulp properties are observed when this concentration increases to 80g/L.

7) Yield loss with SAQ addition is in part related to preferential delignification. As SAQ dose increases, a pulp of unusually high screened yield is obtained for a given lignin content. Improvements are apparent in burst index, breaking length, and tear index compared to the control cook where no SAQ was used. Pulps treated with SAQ showed very little change in brightness.

8) The benefits of extending soaking time is significant in the first 15 minutes. After this time. diffusion slows dramatically and is no longer significant.

5.2 CONTRIBUTIONS TO KNOWLEDGE

The effects of wood chip thickness. pretreatment agents. compression ratio. pre-steaming and evacuation. sulphite charge. SAQ dose. and soaking time on CMP pulp properties were measured. Optimal conditions for liquor penetration into black spruce wood chips. from the results of this study. would involve the following:

- the use of thinner wood chips
- pretreatment with caustic solution
- prex-impregnation in the high compression regime
- presteaming for a 10 minute duration
- sulphite impregnation with 60g/L sulphite solution for a 15 minute soaking period at 90°C.

The use of SAQ catalyst may be exploited several ways in industry. depending on the product being produced. SAQ addition benefits have included reduced refiner energy requirements. shortened cooking times. improved pulp strength properties through preferential delignification. and increased screened yield.

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APPENDICES

APPENDIX A: EXPERIMENTAL RAW DATA

Effect of Wood Chip Thickness

Chip Thickness	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
wafers	20.73+1.49=22.22%	84.5%	4.4%	80.1%
2-4mm	21.39+2.48=23.87%	86.8%	21.3%	65.5%
4-6mm	21.53+2.63=24.16%	87.3%	34.0%.	53.3%
6-8mm	22.53+2.53=25.06%	88.9%	49.9%	39.0%

Effect of Pre-Treatment Agents

Pretreatment Agent	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
Caustic	19.52+2.11=21.63%	82.9%	23.6%	59.3%
Borol	21.35+1.43=22.78%	84.5%	34.2%	50.3%
No Pre-Treatment	22.36+2.02=24.38%	86.7%	36.7%	50.0%

Effect of Compression Ratio

Compression Ratio	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
1:1	23.04+1.87=24.91%	87.9%	41.7%	45.6%
4:1	22.36+2.02=24.38%	86.7%	36.7%	50.0%
9:1	21.14+2.06=23.20%	85.4%	33.3%	52.1%

Effect of Presteaming Time

Pre-Steaming Time	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
30 minutes	21.49+2.87=24.36%	86.5%	35.7%	50.8%
10 minutes	22.36+2.02=24.38%	86.7%	36.7%	50.0%
0 minutes	23.25+1.86=25.11%	88.2%	42.1%	45.6%

Effect of Evacuation Time

Evacuation Time	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
30 minutes	20.84+2.22=23.06%	84.3%	25.6%	58.8%
15 minutes	21.26+2.55=23.81%	86.8%	32.8%	50.0%
0 minutes	23.02+2.08=25.10%	87.6%	44.1%	42.4%

Effect of $NaHSO_3$ Concentration

$NaHSO_3$ Concentration	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
10 g/L	25.43+2.41=27.84%	90.2%	82.3%	7.98%
60 g/L	22.88+1.95=24.83%	86.4%	42.0%	44.4%
80 g/L	22.36+2.02=24.38%	86.7%	36.7%	50.0%

Effect of AQ Dosage

AQ Dosage % on od wood	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
0.2%	19.61+1.79=21.40%	84.1%	27.9%	56.2%
0.07%	22.36+2.02=24.38%	86.7%	36.7%	50.0%
0.0%	23.21+2.09=25.30%	89.2%	48.6%	40.6%

Effect of Soaking Time

Soaking Time	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
30 minutes	22.36+2.02=24.38%	86.7%	36.7%	50.0%
15 minutes	22.15+2.32=24.47%	86.5%	39.4%	48.1%
5 minutes	22.32+3.01=25.33%	88.5%	50.3%	38.2%

Replicates

Replicate Number	Lignin: Klasen+UV=Total	Yield %	Rejects %	Screened Yield %
1	22.36+2.02=24.38%	86,7%	36.7%	50.0%
2	20.76+3.84=24.60%	87.1%	40.0%	51.1%
3	21.67+2.68=24.35%	85.9%	36.0%	49.9%

APPENDIX B: STATISTICAL ANALYSIS OF REPLICATES (49)

When making a statistical evaluation for replicates, one must assume that the few replicate experimental results gathered are a tiny, but representative fraction of an infinite number of results that could be collected if one had infinite time. This small set is a SAMPLE and is viewed as a subset of a population of data.

Nomenclature for Statistical Analysis:

$\bar{x}$ = sample mean

μ = population mean

s = sample standard deviation

σ = population standard deviation

N = number of experiments

z = statistical parameter for population confidence limits

t = statistical parameter for sample confidence limits

One can only talk about the sample mean ($\bar{x}$) since the population mean would be taken from this infinite number of experiments (population mean = μ).

$$\text{sample standard deviation, } s = \sqrt{\sum_{i=1}^{N}(x_i - x)^2/(N-1)}$$

For yield, $s=0.5683$ and $\bar{x}=86.07$

For lignin results, $s=0.1366$ and $\bar{x}=24.44$

For rejects results, $s=1.6703$ and $\bar{x}=38.50$

Statistical theory allows one to set limits around an experimentally determined mean x and the true mean μ lies within these limits with a given degree of probability. These are known as CONFIDENCE LIMITS (CL).

CL for $\mu = \bar{x} \pm (z\sigma)/\sqrt{N}$ (for 95% Confidence, $z=1.96$)

For yield, $\mu=86.07\pm(1.96\cdot 0.5683)/\sqrt{3} = 86.07\pm 0.64$

For lignin results, $\mu=24.44\pm(1.96\cdot 0.1366)/\sqrt{3} = 24.44\pm 0.155$

For rejects results, $\mu = 38.50 \pm (1.96 \cdot 1.6703)/\sqrt{3} = 38.50 \pm 1.89$

This means that the chances are 95 in 100 that the population yield mean is located between 85.43% and 86.71%, the population lignin mean is located between 24.285% and 24.595%, and the population rejects mean is located between 36.61% and 40.39%. Note that this was calculated assuming the sample standard deviation, s, is equal to the population standard deviation, σ. To be more precise, where one assumes that σ is not accurately known, CL for $\mu = \bar{x} \pm ts/\sqrt{N}$ where the parameter t is similar to the statistical z parameter, but with broader boundaries.

Then for 95% Confidence Limit, t=4.30 and:

$$\text{yield} = 86.07 \pm 1.41\%$$

$$\text{lignin results} = 24.44 \pm 0.339\%$$

$$\text{rejects results} = 38.50 \pm 4.14\%$$

(A sure knowledge of σ (population deviation) significantly decreases the Confidence Interval).

Similarly, for a 90% Confidence Interval:

$$\text{yield} = 86.07 \pm (2.92 \cdot 0.5683)/\sqrt{3} = 86.07 \pm 0.96\%$$

$$\text{lignin results} = 24.44 \pm (2.92 \cdot 0.1366)/\sqrt{3} = 24.44 \pm 0.23\%$$

$$\text{rejects results} = 38.50 \pm (2.92 \cdot 1.670)/\sqrt{3} = 38.50 \pm 2.81\%$$

The chances here are 90 in 100 that the population yield mean is located between 85.11% and 87.03%, the population lignin mean is located between 24.21% and 24.67% and the population rejects mean is located between 35.69% and 41.31%.