Optimization on the Neutral Sulfite Semi-chemical (NSSC) Pulping of Birch

by

Xingzhi Jiang

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Supervisor(s): Yonghao Ni, Ph.D., Chemical Engineering

Examining Board: Brian Lowry, Ph.D., Chemical Engineering, Chair
Guida Bendrich, Ph.D., Chemical Engineering
Zhibin (Ben) He, Ph.D., Chemical Engineering
Xuejun Zou, Ph.D., Chemical Engineering

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Abstract

Neutral sulfite semi-chemical (NSSC) pulping is the dominant industrial process to produce corrugated medium. In this thesis, the NSSC cooking process was investigated in a lab-scale setup, and the effect of cooking conditions and chemical charges were studied to understand their effect on different properties of the produced pulp. During the first phase, the cooking data were collected to create models that can predict the pulp yield, degree of sulfonation, and delignification degree, as well as determining the activation energy of the birch delignification process. In the second phase, cooked wood chips were refined into pulps and then made into hand sheets to evaluate the strength properties. The study also included how the Na_2SO_3 charge and refining would impact the paper strength, as well as identifying the threshold of the Na_2SO_3 charge, which can help in improving the paper strength while minimizing the chemical dosage.

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Nomenclature

A	Pre-exponential factor
CMP	Chemi-mechanical pulping
CSF	Canadian Standard Freeness
CTMP	Chemi-thermomechanical pulping
E_a	Activation energy (kJ/mol)
H	H-factor (hours)
Holding time	Actual cooking time when desired temperature has been reached
k_L	Rate constant for the delignification reaction
k_T	Rate constant at temperature T
L	Residual lignin concentration (g/L)
n & m	constant used in the rate of reaction
NCG	Non-condensable gases
NSSC	Neutral sulfite semi chemical
o.d	Oven dried
R	gas constant (J/mol·K)
RH	Relative Humidity (%RH)
r_L	Rate of delignification
S	Residaul Na_2SO_3 concentration (g/L)
TMP	Thermo- mechanical pulping

Chapter 1
Introduction

1.1 Pulping Process

In the pulp and paper industry, various wood species or other lignocellulosic plants are used as raw materials to produce pulp fibers that will be further processed into paper, cardboard, and other paper products, which include magazine paper, tissue paper, cardboard, and even textile raw material (such as dissolving pulp for the production of rayon fibers).

Generally, pulping technology can be classified into mechanical, semi-chemical, and chemical pulping processes. Thermal mechanical pulping (TMP) is an example of a mechanical pulping process that utilizes refiners to physically break down wood chips into fibers. This method gives the highest pulp yield since it retains most of the lignin and can achieve approximately 91-95% of pulp yield (Bajpai, 2018a). The Semi-chemical process, such as chemi-thermomechanical pulping (CTMP) and neutral sulfite semi-chemical (NSSC) pulping has a chemical pretreatment stage prior to the mechanical refining of treated wood chips. The purpose of the chemical pre-treatment stage is to soften lignin and save energy for the refinery process (Kocurek & Stevens, 1983). Kraft pulping is the main chemical process that uses NaOH and Na_2S as cooking chemicals to achieve high lignin removal and lower fiber degradation, which gives the strongest pulp compared to other processes (P. Chandra & J. Ragauskas, 2002).

The NSSC process is used to produce corrugated medium, which will then be used for manufacturing packaging boxes. In Canada, wood species such as maple, poplar, and birch are important raw materials for the NSSC process. Extensive research has been conducted to investigate the delignification kinetics of various wood species to improve process control. However, the study on the delignification kinetics of birch wood species is insufficient and its activation energy is not available in the literature. Numerous studies had been conducted on the sulfonation of CTMP or CMP pulping, with the focus on the effect of cooking conditions on strength properties. However, no research had been conducted that is related to the influence of cooking conditions on the degree of sulfonation, which could then be utilized for process control. Therefore, A quantitative understanding of the delignification kinetics and degree of sulfonation of the birch wood species would be crucial for the optimization of the birch NSSC process.

1.2 Problem Statement & Significance of the Study

Even though the market for corrugated packaging boxes has shown an increasing trend, the global market for printing and writing paper products is declining. Canadian pulp and paper industry is facing strong competition from other countries in South America and Southeast Asia due to their low material and labor cost. Hence better product quality is essential to stay competitive in the market, which can be achieved through improving the process control and optimization of the chemical charges.

Early studies for CTMP had shown how refining intensity and sulfonation would improve the tensile strength of the paper (Heitner et al., 2005). However, the influence of cooking conditions or chemical charges on the change of sulfonation has not been investigated. In addition, since the NSSC pulping is different from CTMP, whether the same trend can be observed under extensive chemical treatment is still unidentified. A good understanding of how cooking parameters affect the sulfonation reaction and paper strength can give guidance to the NSSC or CTMP mills to optimize their cooking process.

The existence of sulfur-containing cooking chemical (Na_2SO_3) is hazardous to the biological treatment processes of the NSSC mills, which decreases the treatment efficiency. Either discovering the threshold of the Na_2SO_3 charge or finding its replacement can minimize or mitigate the related environmental issues.

Birch is an important wood species in Canada as raw material for pulp and paper processing. However, its kinetics information is not readily available. Therefore, a study on the fundamentals of birch cooking and its delignification kinetics can greatly help the process control in processes, such as birch NSSC pulping, potentially improving the product quality and economic performance.

1.3 Purpose and Objectives

The study aimed to help the control and optimization of the NSSC cooking process for the production of high-quality corrugated medium, an in-depth study on the fundamentals of the NSSC cooking of birch was required. This included the study on the delignification and sulfonation kinetics as well as the investigation of the optimal cooking conditions and chemical charges that produces pulp with high yield and mechanical strength.

NSSC pulp is considered as high yield pulping process, a thorough literature review of the related studies would give guidance on the experimental design as well as test methods. Cook experiments were designed and conducted to understand the relationship between cooking parameters or independent variables (Temperature, time, chemical charge) and the produced pulp or dependent variables (yield and sulfonation). Models were generated to demonstrate and predict how individual factors affect the dependent variables.

The H-factor is widely used as an indication of the degree of cooking or delignification, it combines the effect of cooking temperature and time into one parameter. The activation energy is a crucial parameter required for the determination of the H-factor, and it varies with wood species (Bajpai, 2018). This parameter for NSSC cooking of birch was determined with the cooking data to help with the process control.

The threshold of Na_2SO_3 charge was studied to minimize the chemical dosage while maintaining the mechanical strength of the paper. The effect of sulfite charge on refining energy consumption and other chemical options was also studied. In addition, the effect of refining on the pulp freeness and strength properties was evaluated.

Chapter 2

Literature Review

2.1 NSSC Pulping Process

The NSSC process is the traditional pulping method to produce corrugating medium with hardwood, which is the raw material for making packaging boxes. NSSC pulping is a two-stage process that starts with a chemical pre-treatment of wood chips, which is then followed by mechanical refining to produce pulp. The process typically has a yield between 70% to 85%, depending on the wood species as well as chemical dosage and cooking conditions (Kocurek & Stevens, 1983). Due to its high chemical and energy requirement, softwood would result in a higher material cost and energy requirement in the pre-treatment and refining stage. On the other hand, nearly all hardwoods are suitable for the NSSC pulping process; they are less expensive (than softwood) and readily available to produce pulp with high yield and strength properties. The blend cooking of softwood and hardwood is not recommended due to the high shive content in the resulting pulp (Kocurek & Stevens, 1983).

Similar to other thermomechanical processes (CTMP & CMP), NSSC pulping utilizes sodium sulfite as the main cooking chemical along with sodium carbonate or caustic soda to control the end pH (Area et al., 1998). The conventional NSSC pulping starts with chip handling just like other pulping processes. Wood chips are subjected to screening so that oversized wood chips and fines are removed. Pre-steaming is generally applied to the accepted chips to remove the air inside their void space for better liquor penetration. Wood chips are then mixed with prepared cooking liquors for the impregnation. The cooking process occurs inside a digester under designated cooking conditions. The most important parameters during the cooking stage are cooking temperature, retention time, and chemical charges (Bajpai, 2018). The Cooking temperature between 160 and 190 ℃ is desired to complete the process in a reasonable period, while the end pH should be neutral to protect the equipment and prevent carbohydrates from degradation (Kocurek & Stevens, 1983). In addition, Lower pH is favored for the other unit operations in the mill, like the paper machine due to its influence on water retention and its rheology, which could lead to drainage issues and a lower production rate (Lehmonen **et** al., 2009). Cooking liquor containing sodium sulfite and caustic soda is used for the sulfonation reaction to take place, with lignin dissolution and carbohydrate degradation also occurring. After chemical treatment, cooked wood chips are then subjected to mechanical refining to produce pulp fibers at the desired freeness. Mechanical refined pulps are then diluted to the desired consistency and sent to the paper machine for sheet formation and drying.

2.2 H-factor & Delignification Kinetics

H-factor is a typical parameter used for process control in the Kraft mills, it was proposed by Vroom (1964) which combines the effect of time and temperature to reflect the delignification of the wood chips (Pereira et al., 2011). Since the H-factor takes the influence of both time and temperature into account, pulp with similar yield and strength properties can be produced under consistent chemical charges and liquid to wood ratio in the ideal scenario (Bajpai, 2018). The development of the H-factor requires a two-stage process; it starts with obtaining the delignification kinetics model to calculate the rate constant at various temperatures. The Equation 1 is the delignification model of the NSSC process:

$$-r_L = -\frac{dL}{dt} = k_L L^n S^m \quad \textbf{Equation 1}$$

Where: r_L is the rate of delignification

k_L is rate constant

L is lignin concentration (g lignin/L liquor)

S is sodium sulfite concentration (g Na_2SO_3/L liquor)

n & m are constants

For the determination of the rate constant, large excess of sodium sulfite needs to be added to keep its concentration constant throughout the experiment. And Equation 1 can be simplified into the following form.

$$-r_L = -\frac{dL}{dt} = k_L{}'L^n$$ **Equation 2**

$$k_L{}' = k_L S^m$$

This will allow the observer to monitor the change in delignification rate and lignin concentration, and also give the value of constant n. Then, with the known value of n, sodium sulfite concentration can be varied to determine the constant m, and the rate constant will be calculated after. Once the rate constant is determined, activation energy and the H-factor are then calculated using the following equations (Keskin & Kubes, 1994):

$$k_T = Ae^{-E/(RT)}$$ **Equation 3**

Or

$$Ink_T = InA - E/RT$$ **Equation 4**

And

$$H = \int_0^t \frac{k_T}{k_{373}} dt$$ **Equation 5**

Where: k_T is rate constant at temperature T

k_{373} is rate constant at 373 K

A is a constant

E is experimental activation energy (kJ/mol)

R is gas constant (J/mol·K)

T is absolute temperature (K)

Equation 3 is the Arrhenius Equation that indicates the temperature dependence of the rate constant k_T. By plotting Ink_T against $\frac{1}{T}$, the slope gives $-\frac{E}{R}$. With R being the gas constant, the activation energy can be calculated.

H-factor can be calculated through a differential equation with the ratio between the rate constant at temperature T and 373 K as shown in Equation 5.

2.3 Delignification & Activation Energy

As discussed in Section 2.2, H-factor is created for the Kraft pulping process control to achieve a similar degree of delignification. The calculation of the H-factor depends not only on cooking time and temperature but also on the activation energy of the delignification reaction. There had been numerous studies on the delignification kinetics of various wood species under different cooking conditions.

An early study on the delignification found the activation energy was around 140 kJ/mol for the Softwood (Sjostrom, 1993). Later, Santos et al. did a study on the Kraft delignification behavior with 5 different wood species; including both hardwood and softwood (Pine, Sweetgum, Red oak, Maple, and Eucalyptus). The activation energy is between 131 – 139 kJ/mol for the 5 wood species (Santos et al., 2011). The result from these two studies demonstrated a minor variation of the activation energy from both hardwood and softwood.

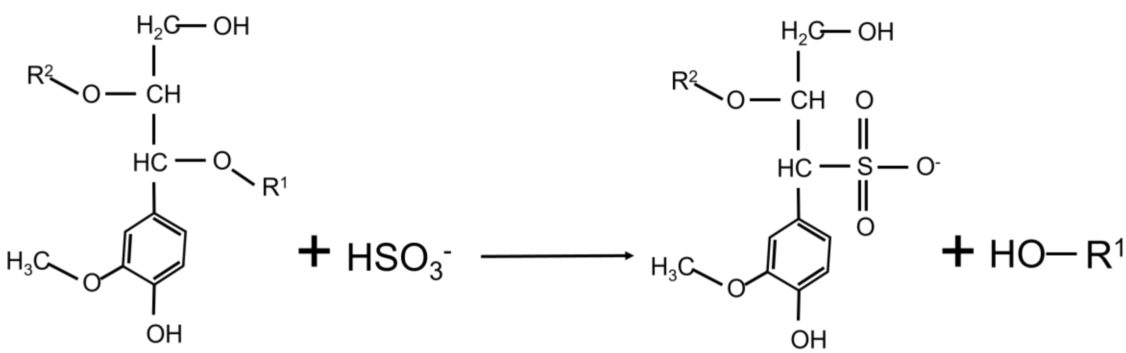
However, different results were obtained from other studies. For a study on the delignification of beech NSSC pulping, the temperature varied from 135℃ to 175℃ with final pulp yield in the range of 55% to 75%. The study found it to be first order corresponding to the residual lignin with an activation energy of 106 kJ/mol for the bulk delignification (Basu et al., 1974). In another NSSC cooking of tropical hardwood with a temperature between 140 to 180℃, 14% chemical charge was applied along with liquor to wood ratio of 4:1. The activation energy was found to be 126 kJ/mol (Kansal & Basu, 1986). The activation energy of aspen was found to be 233 kJ/mol in the temperature range of 170 and 196 ℃ from another NSSC cooking study. In addition, the delignification constant was found to be 2.2 and 0.4 for lignin and sulfite concentrations respectively (Chari, 1968).

Other research on NSSC pulping studied the addition of anthraquinone to the process. Anthraquinone is an additive that act as a catalyst; it improves pulp strength as well as reduced cooking times, refiner energy, and activation energy (Keskin & Kubes, 1994). For the NSSC cooking of loblolly, the temperature was adjusted between 160 to 180℃, at these conditions the activation energy was found to be 122 kJ/mol with anthraquinone, and 155 kJ/mol without anthraquinone (Eagle & Mcdonough, 1988). However, in a different study on black spruce, it was found that activation energy of 130 kJ/mol with anthraquinone and 181 kJ/mol without it. The experiment was conducted under similar temperature range of 165 and 180 ℃. Additionally, the study found the reaction order to be 1.7 with respect to residual lignin and 0.28 with respect to sodium sulfite (Keskin & Kubes, 1994).

Overall, these studies had shown similar activation energy for Kraft pulping even with different wood species. However, significant variation has been observed from the studies on NSSC pulping for both activation energy (varying from 106 to 233 kJ/mol) and reaction orders. The application of AQ also shows a big influence on activation energy.

2.4 Sulfonation & Strength Properties

The sulfonation reaction is the most important reaction in the NSSC pulping process. The lignin structure in the wood is water insoluble, and its hydrophilicity can be improved through the sulfonation reaction to form lignosulfonate (YanHua et al., 2004). With the addition of the sulfonate group, the structure of the lignosulfonate acts similarly to a surface-active agent (Heradewi, 2007). The reaction not only improves the hydrophilicity of the fibers but also promotes fiber swelling to achieve better fiber bonding and strength properties (Heitner & Hattula, 1988).



*R_1 & R_2 are hydrogen or different hydrocarbon side chains

Figure 1: Sulfation reaction of lignin (Lindholm, 2009)

Under neutral cooking conditions, approximately 30% of the lignin can be sulfonated, and the sulfonation of the phenylpropane units is favored as the reaction showed in Figure 1 (Ämmälä et al., 2019). The measurement of the sulfonate group within the pulp is usually conducted after the chemical treatment. The cooked chips are washed thoroughly and then mechanically refined into pulp fibers for the sulfonate analysis. The sulfonate group content of pulp fibers is generally determined based on the conductometric titration method (SCAN-CM 65:02).

The cooking conditions and chemical charge can have a significant influence on the pulp strength properties. In a study on NSSC pulping of hybrid poplar, cooking temperature was controlled between 154℃ and 186℃ with retention time varying in the range of 10 to 30 minutes. Sodium sulfite (4 – 12%) was used along with sodium carbonate (0 – 3%) as the cooking chemicals. The pulp yield was in the range of 79.9% to 93.9% with temperature showing the biggest influence. As for the strength properties (tensile, burst, tear), cooking temperature still showed the highest impact compared to other parameters (time, Chemical charge). In addition, the increase of Na_2CO_3 also showed a positive influence on mechanical strength. The optimal cooking conditions in terms of mechanical properties were at the cooking temperature of 186 ℃ with 30 minutes holding time, along with 11.6% sodium sulfite charge and 3.05% of sodium carbonate (Area et al., 1998). In a similar study for the NSSC cooking of birch, the temperature varied between 172℃ to 179℃, with 13 to 15.5 minutes of cooking time. At the same time, the liquor to wood ratio changed between 1.2 and 2.2. The chemical charge remained identical throughout all the cooks. The study found cooking temperature had a significant impact on CMT and burst strength. In addition, shorter cooking time was found to be beneficial for the CMT and SCT strength of the pulp (Bocianowski et al., 2013). In both studies, the temperature was found to be an important factor for the strength properties. However, the contribution of yield loss on strength improvement wasn’t recognized. The studies didn’t compare cooks at a similar yield to observe the influence of sulfite charge or sulfonation.

From some of the other studies on the effect of cooking conditions, it was recommended to have a cooking temperature above 165℃ to achieve the optimal economic benefit and pulp yield (Basu et al., 1974). For the NSSC cooking of Eucalyptus over the temperature range of 170 to 200 °C with two different liquors to wood ratios; 5:1 and 10:1. Higher pulp strength was observed with the increase of temperature up to 180℃, and it started to decrease after 190℃. However, pulp yield decreased with increasing temperature (Higgins et al., 2017).

In an early study on the sulfonation reaction and refining intensity of the CTMP or CMP process, the sodium sulfite concentration was changed in the range of 10 g/L to 140 g/L to observe the influence of sulfonation on the strength properties. Two different refining intensity (1200 rpm, and 1800 rpm) was applied along with the cooking temperature and time kept at 150℃ and 30 minutes respectively. The study demonstrates sulfonation has no influence on the refining energy, yet tensile strength increases with sulfite charge across the whole sulfonation range. The high intensity refining can provide better tensile strength as well (Heitner et al., 2005).

In another study that focused on the effect of sulfite charge, the cooking temperature was kept at 170°C with 90 minutes of cooking time. The sodium sulfite charge varied in a wide range from 5.9% to 35.4%. Overall, the study focused on the result of a pulp yield around 80%. It was observed that with high sodium sulfite charge, physical and mechanical properties largely improved. However, at an extremely high chemical charge (over 26%), no significant further improvement has been observed. In addition, the rate of sulfonation reaction was less dependent on sulfite concentration when the chemical dosage was beyond 16.5% (Pereira et al., 2011).

From the different literature studies, the temperature was claimed to have a large influence on not only pulp yield but also strength properties. At the same time, the increase of sulfite charge or degree of sulfonation continues to show the positive impact on the strength properties.

Chapter 3
Methodology

3.1 Wood Preparation

The birch wood chips were used throughout this study, which were provided by the Lake Utopia Paper mill.

Figure 2: Chip Class chips classification system

The wood chips were first fractionated using a Sensor & Simulation chip classification system (Figure 2). they passed through chip screens with various sizes of slots (2 mm, 4 mm, 6 mm, 8 mm, 10 mm) under vibration and got separated based on their thickness. all the collected chips were then air dried for easier storage. The weight of each fraction was measured to determine the weight composition of the mill chips so that the same composition can be simulated in the lab study. A sample was taken from each fraction of chips and heated in an oven to determine their moisture content.

Table 1 Wood chips thickness distribution and composition for each cooking trial

Chip Thickness	Composition (%)
10 mm	8.3%
8 mm	11.2%
6 mm	41.6%
4 mm	28.4%
2 mm	9.5%
Less than 2mm	0.9%

Wood chips were then collected and packed into sealed bags to avoid moisture change; each bag contained 200 grams of chips on an oven-dried basis with the determined composition shown in Table 1.

The initial acid-insoluble lignin or Klason lignin was determined with the method showed in GB/T747-1989. The acid-soluble lignin was detected using a spectrophotometer at 205 nm of wavelength. The total lignin content was determined through the combination of Klason lignin and acid soluble lignin.

3.2 Cooking Process

All the cooking experiments were carried out in a lab scale stainless steel reactor, as showed in Figure 3, it simulates the process that happens inside a pulp & paper mill reactor so called digester.

Figure 3: Lab scale batch reactor system

Prepared wood chips and cooking liquor can first be added to the reactor. The 2-liter reactor was then used to cook wood chips under high temperatures and pressure. The heating was provided through an electric heating jacket that was connected to a temperature control system. A circulation pump extracted cooking liquors from the bottom of the reactor and transfer them to the top to maintain the liquor recirculation during the cooking process. Liquor samples were taken from a sample port in the recirculation line for pH and residual chemical analysis. There was a pressure gauge installed at the top of the reactor to monitor the pressure change throughout the experiment, NCG generated during the cooking experiments was vented off through the pressure relief valve.

3.3 Blend & Yield Measurement

The cooked chips (Figure 4, left) were collected from the reactor after the initial washing and then transferred into a lab scale blender to break the cooked wood chips into pulp fibers (Figure 4, right). Further washing was applied through a pulp bag with 200 mesh screen to remove the lignin and fines that were adsorbed on the surface of the chips.

Figure 4: Cooked wood chips (left) and blended wood fibers (right)

Excessive amounts of water were squeezed out of the fibers through the pulp bag to reach approximately 20% dryness, and the total weight of the wet fibers was recorded for calculation purposes.

Figure 5: Mixer for fiber moisture balancing

A mixer (Figure 5) was used to balance the moisture content of the blended fibers. Approximately 5% of the total fibers on an o.d. basis was taken from three different levels of the mixer as the sample. All the samples were heated in the oven at 105℃ to determine the moisture content. The average moisture content of the three samples was utilized to back calculate the total yield from the original wood chips in each bag.

$$\%Yield = \frac{Total\ Fiber\ Mass\ (g) \times (1 - Average\ Moisture\ in\ fibers\ (\%))}{200\ g\ Wood\ Chips\ per\ Bag}$$ **Equation 6**

3.4 Spent Liquor Analyses

Liquor samples (Figure 6) were taken every five minutes from the sample port on the recirculation line. The residual sodium hydroxide, sodium sulfite, and dissolved lignin content in the samples were measured as well as the liquor pH to create a profile. All the titration procedures were provided by the Lake Utopia Mill, the dissolved lignin measurement followed the TAPPI standard (TAPPI T 222 OM-21).

Figure 6: Cooking liquor samples collected during the trial

For the determination of residual sodium hydroxide, 1 ml of spent liquor was first pipetted into a 250 ml beaker. 1 ml of 10% Barium Chloride was then added. The solution was then diluted with 100 ml of distilled water. Two drops of phenolphthalein indicator were added to change the solution color to pink before starting to titrate with 0.01N HCl. The residual NaOH in the spent liquor could be calculated with the following equation.

$$g/L \ of \ NaOH = ml \ of \ HCL \ \times 0.4$$ **Equation 7**

The determination of residual sodium sulfite started by adding 25 ml of 0.01N iodine into a beaker, followed by adding 2 ml of 37% (w/w) HCl to adjust the pH. 1 ml of liquor sample was then pipetted into the beaker and to be titrated with 0.01N sodium thiosulfate. Once the solution reached light-yellow color, 3 drops of starch indicator could be added to turn the solution into dark brown color. The titration continued until the solution reached a clear endpoint. The mechanism of this titration was for the residual sodium sulfite in the liquor first react with the iodine, then titrated the residual iodine with thiosulfate. and A blank sample was needed to determine the amount of thiosulfate to titrate 25 ml of 0.01N iodine. The residual sodium sulfite could be calculated with the following equations.

$$ml \ thiosulfate \ (blank) - ml \ thiosulfate \ (Actual)$$ **Equation 8**

$$= ml \ of \ thiosulfate \ (reacted)$$

$$g/L \ sodium \ sulfite = ml \ of \ thiosulfate \ (reacted) \times 0.63$$

The lignin content in the spent liquor was measured with a spectrophotometer, and the concentration of the soluble lignin was calculated with Equation 9.

$$Soluble \ Lignin \ (g/L) = A/110 \times D$$ **Equation 9**

Where: A is absorbance at 205 nm wavelength

D is the value of dilution (varies to keep A within 0.2-0.7)

3.5 Degree of Sulfonation

The sulfonate group content of pulp fibers is generally determined based on the conductometric titration method (SCAN-CM 65:02). Approximately 3 grams of o.d wood fibers need first get blended into small pulp. Then the pulp will be immersed into 100 ml of 0.1 M HCl for 45 minutes twice to remove the Na ion on the sulfonic acid. The pulp needs then be washed with deionized water until the conductivity goes below 5 μS/cm. After the preparation, the pulp was added into the 0.001 M sodium chloride solution to be titrated with 0.1 M sodium hydroxide solution. The conductivity of the solution was recorded to calculate the degree of sulfonation.

$$\begin{aligned} &Degree\ of\ Sulfonation\ (mmol/kg) \\ &\quad = Required\ NaOH\ (ml) \times 0.1M \\ &\quad \div o.d\ mass\ of\ pulp\ (g) \times 1000\ g/kg \end{aligned}$$

Equation 10

3.6 PFI Refining

The pulp refining was completed with a lab scale PFI refiner (Figure 7), the refining procedure followed the TAPPI standard (TAPPI/ANSI T 248 sp-15).

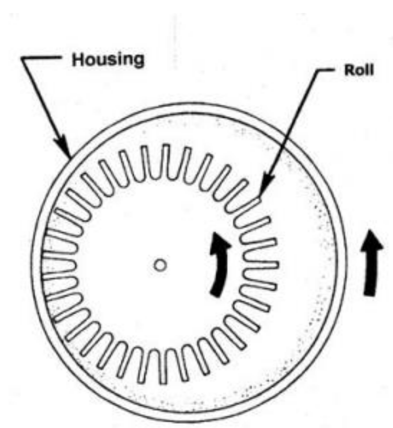


Figure 7: The PFI laboratory beater element (Technical Association of the Pulp and Paper Industry, 2015)

During each refining, 24.0 ± 0.25 g of oven dry (o.d.) pulp was taken as a sample to be diluted with distilled water to reach approximately 10% consistency. The diluted pulp samples were distributed evenly between the roll and the housing of the beater. The gap size between the roll and housing was maintained at 0.4 mm for all the refining. Pulp refining was performed after the desired number of PFI revolutions was set and the cover was sealed onto the beater.

3.7 Freeness Test

The measurement of pulp freeness followed TAPPI standard T 227 om-94. Approximately 3 g of pulp on an oven-dried basis was first mixed with distilled water in a 1000 ml graduate cylinder to reach 3% consistency. The pulp slurry was then filled into a freeness tester chamber.

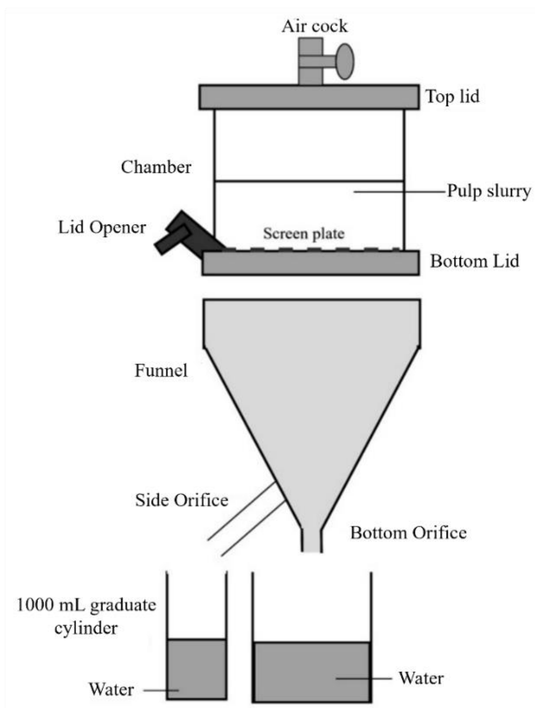


Figure 8: Apparatus of freeness tester (Umair et al., 2020)

The freeness tester (Figure 8) consists of a drainage chamber and a rate measuring funnel, as the pulp slurry stayed inside the chamber, the bottom lid could be unfolded to release the slurry. When the water drained through the screen plate, it entered the funnel. Depending on the degree of refining, water could pass through the bottom orifice and side orifice with different ratios. Recorded the reading from the 1000 ml graduate cylinder as the rectified pulp freeness. Temperature measurement and the actual consistency were required for the adjustment to get the rectified pulp freeness.

3.8 Handsheets Formation

The paper grammage was calculated by using the mass of a handsheet (g) divided by its area (m^2). Therefore, it had the unit of g/m^2. The handsheets made in this study were all at 60 grammage, which meant each sheet weight 1.2 g. The handsheets formation followed the TAPPI standard (T 205 sp-95).

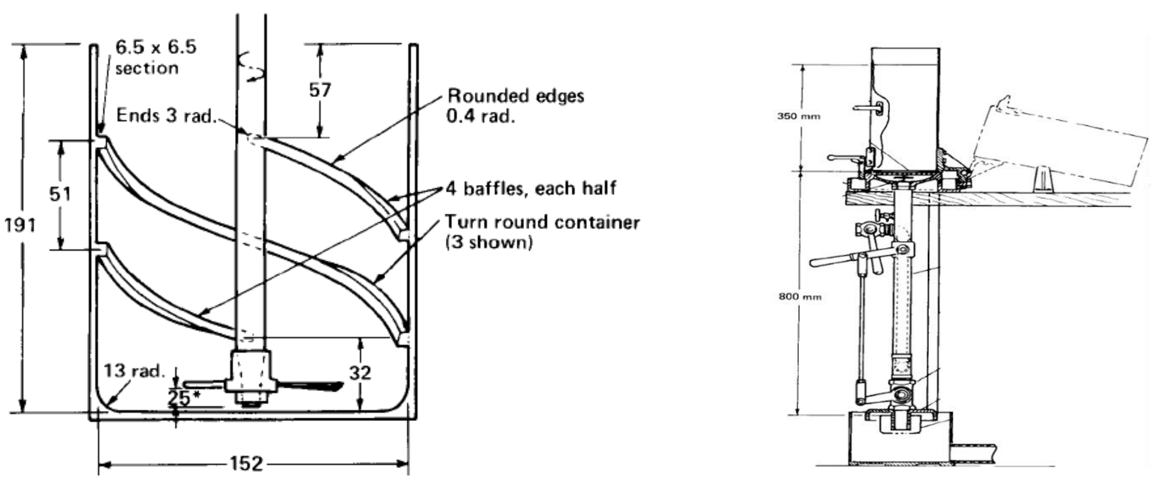


Figure 9: Apparatus of a disintegrator (left) and handsheet machine (right) (Technical Association of the Pulp and Paper Industry, 2006a)

Prior to the handsheets making, the refined pulp was first disintegrated (Figure 9, left) for better fiber separation. The pulp was then diluted to 0.3% consistency. For the handsheet formation, the estimated amount of pulp slurry for one handsheet was added into the handsheet former (Figure 9, right) along with water to fill to the top of the handsheet machine. The perforated stirrer was inserted to mix the pulp with water. The drain was then fully opened to let the water pass through the screen under the suction provided by the bottom water leg. The fibers retained on the screen would form a handsheet. A sample handsheet was made and oven dried to back calculate the required volume for a 1.2 g handsheet.

3.9 Strength Tests

3.9.1 Tensile Strength Test

Prior to the test, the handsheets needed to be conditioned in a controlled room with 50.0% ± 2.0% RH and 23.0℃ ± 1.0℃ for 24 hours. Each handsheet would then be measured with an analytical balance for their weight. The actual grammage of the sheet would be calculated as well.

Equation 11

$$Grammage\ (g/m^2) = mass\ of\ handsheet(g) \times moisture\ (\%) \div Area\ of\ the\ handsheet$$

Where: Area of the handsheet is 0.01981 m^2

As the most important mechanical property of a handsheet, the tensile strength test was completed through a Lorentzen & Wettre tensile strength tester (Figure 10). The testing procedure followed the TAPPI standard (T 494 om-01).

Figure 10: Lorentzen & Wettre tensile strength tester

Each test specimen was cut from a handsheet to form a strip with 15 cm length and 1.5 cm width.

Six handsheets were prepared for each cooking recipe with two paper strips from each handsheet, which would give a total number of 12 test specimens. The test specimen was aligned and clamped in the jaws of the tester, and constant load and rate were applied to the paper strip until it ruptured at the maximum force. The test force required to break the test specimen of 1.5 cm was given in the unit of kN/m, the tensile index could then be calculated.

$$Tensile\ index\ \left(N.\frac{m}{g}\right) = \text{Tensile strength}\ \left(\frac{\text{kN}}{\text{m}}\right) \times 1000 \left(\frac{\text{N}}{\text{kN}}\right) \div \text{grammage}\ (\text{g/m}^2) \qquad \textbf{Equation 12}$$

3.9.2 Burst Strength Test

Figure 11: Lorentzen & Wettre burst strength tester

Similar to tensile strength, the burst strength of the handsheets was determined with a Lorentzen & Wettre burst strength tester (Figure 11) following the TAPPI standard (T 403 om-91). The handsheet specimen would be clamped in between two annular stainless steel surfaces to secure the position and avoid slippage during the test. Air pressure was then applied through the bottom rubber diaphragm to break the clamped handsheet. The required pressure to break the sheet would be recorded with a unit of kPa.

$$Burst\ index\ (kPa.m^2/g) = Applied\ pressure\ (kPa) \div \text{grammage}\ (\text{g/m}^2) \quad \textbf{Equation 13}$$

3.9.3 Tear Strength Test

Figure 12: Lorentzen & Wettre Elmendorf-type tearing tester

The tear strength test was performed with an Elmendorf-type tearing tester (Figure 12) that followed TAPPI standard (T 414 om-88). The tester measured the energy used by the metal pendulum in tearing the specimen. The energy would divide by the total distance it tore through to give the tear strength. The test specimen would be clamped in a plane parallel to the axis of the pendulum. A cutting knife at the bottom would create a slit or breaking point at the bottom of the specimen. Then the pendulum needed to tear through 43.0 ± 0.2 mm distance to determine the required energy.

$$Tear\ index\ \left(mN.\frac{m^2}{g}\right) = \text{Tear strength } (mN) \div \text{grammage } (\text{g/m}^2\text{ }) \qquad \textbf{Equation 14}$$

Chapter 4
Delignification Kinetics & Effect of sulfonation

4.1 Introduction

In traditional NSSC and CTMP cooking, sodium sulfite is utilized for the sulfonation reaction of lignin. A high degree of sulfonation and its enhancement to the pulp strength properties were studied in many papers (Heitner et al., 2005; Pereira et al., 2011 Area et al., 1998;). Other parameters like cooking temperature and time can affect the rate of sulfonation reaction as well as the total sulfonated lignin in the pulp, which also reflect on the pulp strength.

The purpose of this study was to investigate the effect of each parameter on the degree of sulfonation. The experiment design was to build correlations between the degree of sulfonation and other parameters to identify their relationship and determine the optimal cooking conditions and chemical charges. Pulp yield and end pH as well as the residual chemicals in the spent liquor were measured to compare with those in the literature.

4.2 Experimental Design & Procedures

A total of four parameters was varied during the cooking experiments, and three of them are independent parameters. Sodium sulfite (Na_2SO_3) and caustic soda (NaOH) are the cooking chemicals that were applied for this NSSC cooking study. Temperature and time were also changed at three different levels to determine their influence on the degree of sulfonation. Table 2 below lists all the parameters, as well as the values, which were used during the cooking experiment.

Sodium sulfite initiates the sulfonation reactions with lignin in the wood chips to form sulfonated lignin, which improves fiber swelling and hydrophilicity that leads to better strength properties. Temperature and time can have a significant influence on the degree of sulfonation.

Table 2 Parameters for cooking trials

	Minimum	Mean	Maximum
Cooking Temperature (℃)	165	172	180
Cooking Time (min)	30	45	60
Sodium Sulfite (%)	4	7	10
Sodium Hydroxide (%)	——	——	——

* Cooking time is the holding time after the reactor reaches the desired cooking temperture

The experimental design followed a three-level factorial design. As listed in Table 2, the three independent variables were the cooking temperature, cooking time, and sodium sulfite charge; each variable was divided into three levels for a total number of 27 combinations or cooks. Based on the literature review and the data from an NSSC mill, cooking temperature and time were varied between 165-180℃ and 30-60 min respectively, with sodium sulfite dosage changed incrementally from 4% to 10%. Caustic soda was added accordingly to adjust the end pH. Therefore, the caustic soda dosage had to be estimated rather than decided since its sole purpose was to maintain a neutral end pH between 6.5 - 7.

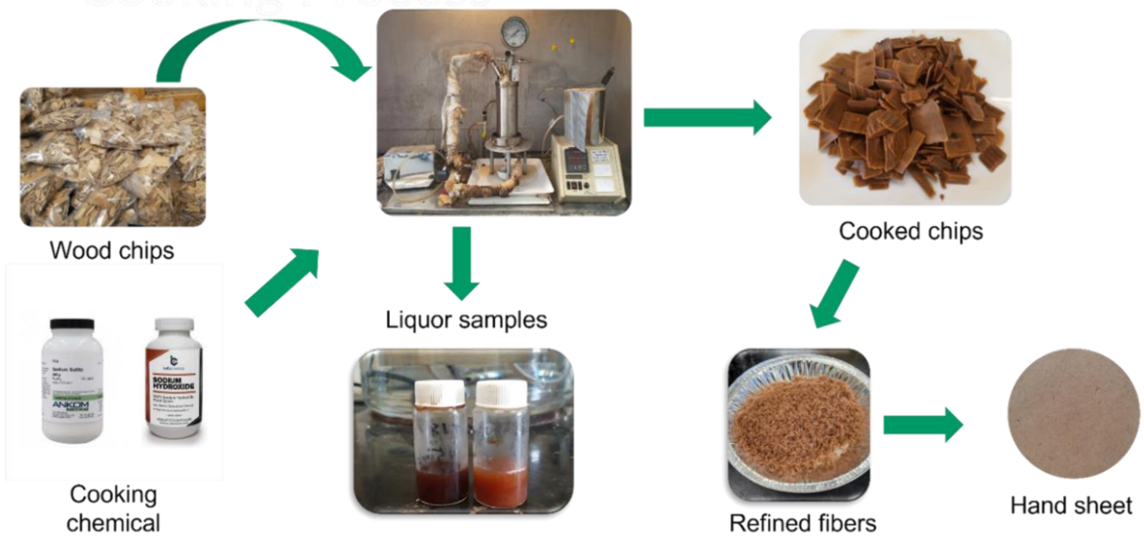


Figure 13: Detailed procedures for NSSC pulping trials

Figure 13 is detailed procedures. The cooking trial was conducted in a 2 liter stainless steel Parr batch reactor. For each cook, a bag of air-dried wood chips (200 g o.d.) was added to the reactor. A designated amount of cooking chemicals was dissolved into boiling distilled water to make up the lab cooking liquor. The liquor to wood ratio was maintained at 5:1 so that the liquor level can stay above the wood level throughout the experiment. An electric heating mantle (wrapping the reactor) was used, it would take approximately 40 minutes for the liquor and wood to reach the desired cooking temperature. The cooking temperature was recorded in a excel file throughout the cook to create a heating curve. Once the holding time started, a liquor sample was taken from the sample port every five minutes for future liquor analysis. When the cook was completed, cold water was sprayed onto the reactor to cool it down. The cooled wood chips were first taken out of the reactor and disintegrated into wood fibers. They were then collected to determine the overall pulp yield from each cook. The wood fibers were further refined into pulp at certain freeness before making hand sheets for the test of strength properties. The pH and residual chemcicals (NaOH,

Na_2SO_3), and lignin concentration in the liquor samples were measured. The sulfonation degree of each pulp sample was determined with the conductivity method.

4.3 Influence of Cooking Parameters on Pulp Yield

The pulp yield was determined from all 27 cooks under different cooking conditions. Cooking temperature, holding time and Na_2SO_3 charge are the three parameters that were analyzed to create a correlation with pulp yield. During the Kraft cooking process, NaOH is utilized for the delignification reaction, so it also contributes to the yield loss. However, in the present NSSC cooking, a much lower NaOH charge was applied, and its sole purpose was to control the end pH. Therefore, the effect of NaOH on yield loss was neglected.

Table 3: Yield change under identical cooking temperature and holding time but different chemical charges

Group	Temperature (°C)	Time (min)	Na_2SO_3 (wt%)	NaOH (wt%)	Yield (%)	Standard Deviation
	180	60	4	6	80.2%	
1	180	60	7	5	81.0%	0.5%
	180	60	10	4.2	79.8%	
	180	45	4	5.3	81.2%	
2	180	45	7	4.4	82.4%	1.2%
	180	45	10	3.3	79.4%	
	180	30	4	4.6	85.8%	
3	180	30	7	4	84.2%	0.8%
	180	30	10	2.6	84.2%	

As displayed in Table 3, the effect of Na_2SO_3 charge was studied. Cooks at 180℃ were used as an example. When looking at cooks with the same holding time, these 9 cooks can be divided into 3 groups, the chemical charge in each group varied from 4% to 10% with a maximum difference of 6%. The standard deviation of the yield was 0.5%, 1.2%, and

0.8% with respect to each group. The effect of sulfite charge on the yield was insignificant under these conditions.

Table 4: Yield change under identical cooking temperature and chemical charges but different holding times

Group	Temperature (℃)	Time (min)	Na_2SO_3 (wt%)	NaOH (wt%)	Yield (%)	Standard Deviation
	172	60	4	5	80.9%	
1	172	45	4	4.2	87.0%	4.3%
	172	30	4	3.3	91.3%	
	172	60	7	4	85.5%	
2	172	45	7	3.2	88.0%	1.8%
	172	30	7	2.5	89.9%	
	172	60	10	3	84.8%	
3	172	45	10	2.4	88.9%	4.6%
	172	30	10	1.6	96.0%	

When looking at cooks with different holding times (Table 4), the pulp yield was lower at a longer cooking time across all three groups. The biggest difference was from Group 3 where pulp yield dropped by 11.2% when cooking time increased from 30 minutes to 60 minutes. The standard deviation of yield among the three groups had a maximum value of 4.6%, which showed cooking time had a greater effect on yield compared to the sulfite charge.

Table 5: Yield change under identical holding time and chemical charges but different cooking temperatures

Group	Temperature (℃)	Time (min)	Na_2SO_3 (wt%)	NaOH (wt%)	Yield (%)	Standard Deviation
	165	45	4	3	93.5%	
1	172	45	4	4.2	87.0%	5.0%
	180	45	4	5.3	81.2%	
	165	45	7	2	94.3%	
2	172	45	7	3.2	88.0%	4.9%
	180	45	7	4.4	82.4%	
	165	45	10	1	94.4%	
3	172	45	10	2.4	88.9%	6.2%
	180	45	10	3.3	79.4%	

The cooking temperature was the last parameter of interest (Figure 5). The maximum yield difference came from the cook at 165℃ and 180℃ in group 3, and the pulp yield decreased by 15% when the temperature increased by 15℃. The maximum standard deviation was 6.2% from group 3 as well, which means cooking temperature had the most significant influence on the pulp yield among the three cooking parameters under the studied cooking conditions.

A correlation was built based on the three cooking parameters, and the linear model was the best fit.

Table 6: Linear model for the pulp yield prediction

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	753.43	3	251.4	70.63	<0.0001	Significant
A-Temp	564.39	1	564.39	158.73	<0.0001	
B-Time	187.53	1	187.53	52.74	<0.0001	
E-Na_2SO_3	1.50	1	1.50	0.4225	0.5221	
Residual	81.78	23	3.56			
Cor Total	835.21	26				

From Figure 14 the sulfite charge showed a p-value of 0.5221, which was the highest out of all three parameters. The high p-value indicated that the sulfite charge was statistically insignificant to the yield change, while both cooking temperature and time were significant. This observation matched those in Tables 4 & 5. As the sulfite charge was eliminated from the correlation, the best fit for the yield model only included time and temperature.

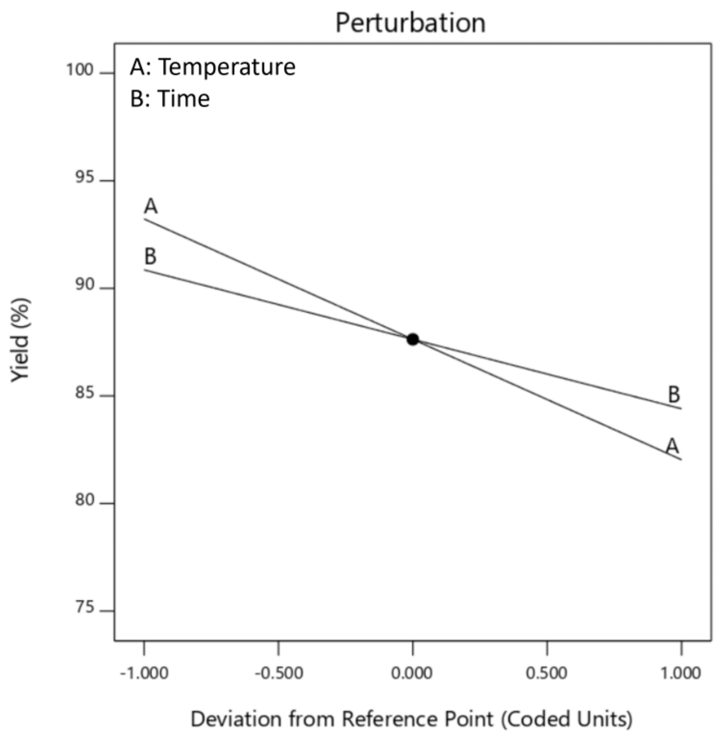


Figure 14: Perturbation plot for the effect of each parameter on the yield

The perturbation plot (Figure 15) was used to identify the influence of each parameter that was included in the model. The parameter with a positive slope had a positive influence on the dependent variable, and vice versa. The larger slope meant the parameter had a greater effect on the dependent variable. In this case, the cooking temperature was showing a greater impact on the pulp yield compared to the cooking time. This result from the perturbation plot matched the observation from Table 5.

$$Yield(\%) = 226.009 - 0.746\left(\frac{\%}{°C}\right) \times Temp - 0.215\left(\frac{\%}{Minute}\right) \times Time \qquad \textbf{Equation 15}$$

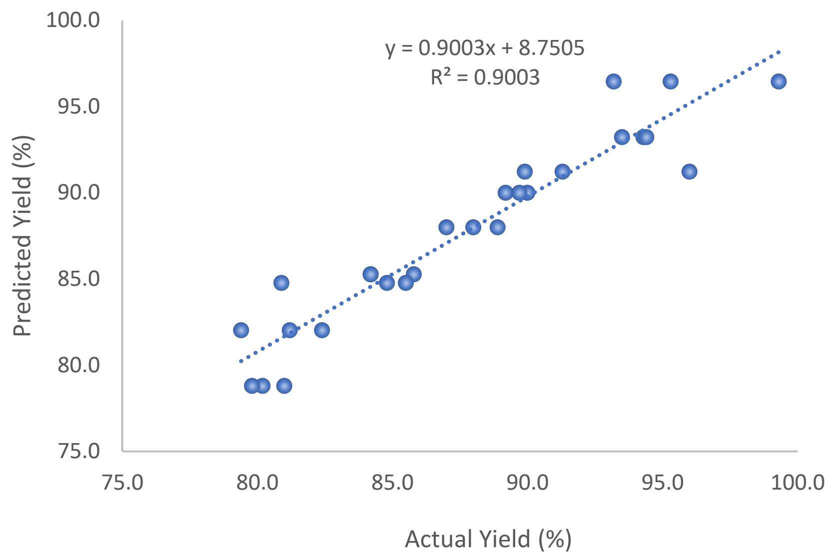


Figure 15: Actual yield vs the predicted yield from the linear model

The best fit correlation for pulp yield would have an R^2 of 0.9003 and a standard deviation of 1.8% (Figure 16). The influence of cooking temperature and time on yield can be explained by their contribution to the carbohydrates and lignin loss during the cooking process. As the holding time increased under the same cooking temperature, carbohydrates dissolution and lignin removal increased, leading to a lower yield. The influence of cooking temperature is tied to the reaction rate. Both delignification and carbohydrate degradation increased with temperature, leading to higher yield loss under higher cooking temperatures.

4.4 Delignification Kinetics: Activation Energy

As an important control parameter, H-factor is widely used in the pulp and paper mills for their cooking control. As explained in Section 2.2, this factor was calculated based on cooking temperature and time with a certain activation energy. The activation energy of the reaction varies with the wood species, and birch wood was used for this study.

In this study, the method of determining the activation energy of birch was based on the definition of the H-factor. H-factor was created to monitor the delignification degree under different combinations of temperature and time, which means cooks with the same H-factor would have the same percent of lignin removal. The determination of the activation energy consisted of two steps. In the first step, it was required to generate a model to predict the delignification degree based on the cooking parameters.

The liquor samples collected during each of the 27 cooks were used to determine the soluble lignin in the spent liquor. This was achieved by using a spectrophotometer to measure the absorption value at 205 nm wavelength, the detailed method was described in section 3.4. Since the total lignin (soluble and insoluble) was already determined, the delignification degree was then calculated.

Table 7: Linear model for the prediction of percent delignification

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	735.67	3	245.22	69.70	<0.0001	Significant
A-Temp	513.18	1	513.18	145.86	<0.0001	
B-Time	158.42	1	158.42	45.03	<0.0001	
E-Na_2SO_3	64.07	1	64.07	18.21	0.0003	
Residual	80.92	23	3.52			
Cor Total	816.59	26				

Std. Dev.	1.88		R^2	0.9009
Mean	19.03		Adjusted R^2	0.8880
C.V.%	9.86		Predicted R^2	0.8661
			Adeq Precision	28.2255

$$\%Delignification = -116.9 + 0.7 \times Temp + 0.2 \times Time + 0.6 \times Na_2SO_3$$ **Equation 16**

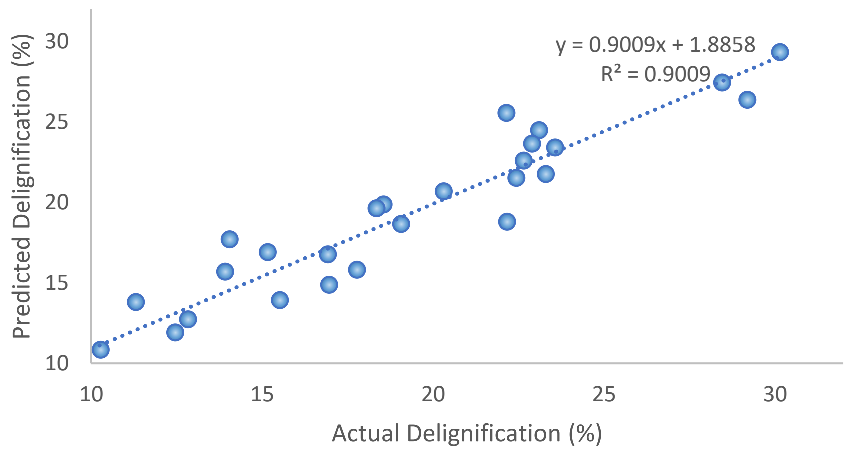


Figure 16: Actual delignification vs the predicted delignification from the linear model

The measured delignification results from the 27 cooks were analyzed to create the model that could predict percent lignin removal based on the applied cooking parameters (Figure 17). Cooking time, temperature, and sulfite charge generated a linear model with an R^2 of 0.9 (Figure 18) to estimate the delignification of the wood chips.

Table 8: Predicted cooking time under defined Na_2SO_3 charge and delignification target

Temperature (°C)	Time (min)	Na_2SO_3 (%)	Delignification (%)
165	**54.2**		
166	**50.9**		
167	**47.6**		
168	**44.3**	5%	15%
169	**40.8**		
170	**37.2**		
171	**33.5**		

In the second step, the activation energy was calculated with the delignification results from a series of combinations of cooking time and temperature. As listed in Table 6, the sulfite charge was fixed at 5% with 15% of delignification as the target. Both values were within the typical range of an NSSC mill. With the target lignin removal and a list of different cooking temperatures, the required cooking time was calculated with the delignification model. Since the same delignification result would give a similar H-factor, A universal activation energy should work out an identical H-factor with different combinations of cooking time and temperature.

Table 9: Activation energy based on controlled Na_2SO_3 and delignification

	Temperature	Time (min)	Na_2SO_3 (%)	Delignification (%)	H-factor
	165	54.2	5%	15%	**447**
	166	50.9			**455**
	167	47.6			**462**
	168	44.3			**466**
	169	40.8			**465**
	170	37.2			**459**
	171	33.5			**447**
Average					457
STDEV					7.1
Effective Time (168℃)					0.7 min

Calculating with Equation 5 would give the optimal activation energy of 128.4 kJ/mol. The H-factor calculated with the determined activation energy had an average value of 457-hour H-factor and standard a deviation of 7.1-hour H-factor. When cooking at 168℃, this represented 0.7 minutes of variation in cooking time. This activation energy was tested at different Na_2SO_3 and delignification targets, and it worked in all cases.

4.5 Effect of Cooking Parameters on Sulfonation

The degree of sulfonation in the pulp was known to have a significant improvement on the paper strength properties in many studies, especially the studies from Heitner and his co-workers (Heitner **et** al., 2005). This finding applies to both CTMP and NSSC cooking processes since they both used sodium sulfite for chemical pre-treatment to increase the paper strength.

As the degree of sulfonation from each cook was measured with the conductometric method, these results were compared and analyzed to find the relationship between the degree of sulfonation and cooking parameters.

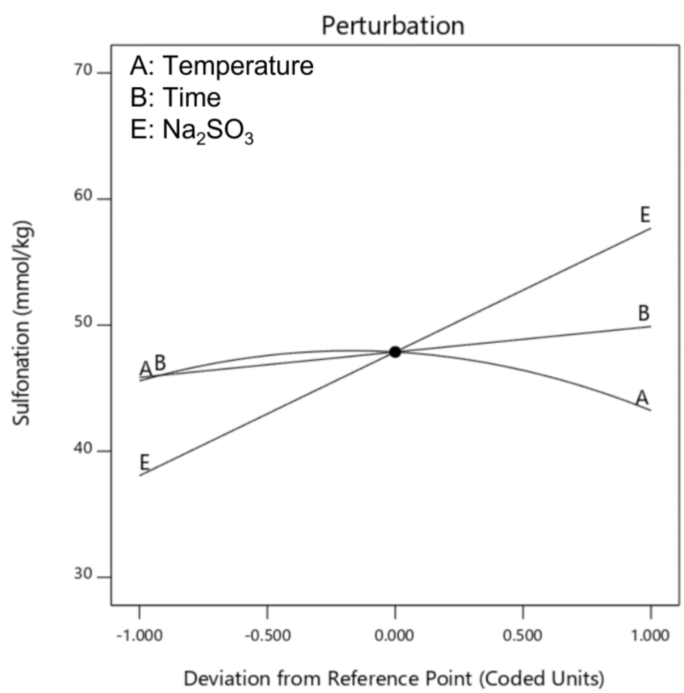


Figure 17: Perturbation plot for the effect of each parameter on the sulfonation degree

From the perturbation plot, the influence of the Na_2SO_3 charge showed the biggest positive impact on the sulfonation. This observation was expected since the purpose of add Na_2SO_3 was to induce the sulfonation reaction and adding sulfonic groups to the lignin. With more sulfite available in the cooking liquor the rate of sulfonation reaction will increase as well to reach a higher degree of sulfonation. Temperature and time showed a similar impact on sulfonation. However, the reaction didn't favor high cooking temperatures, it started showing a negative influence on the sulfonation at above 172℃. This may be caused by the loss of sulfonated lignin at elevated temperatures. While the sulfonic group attached to the lignin through the sulfonation reaction to make it more hydrophilic, sulfonated lignin would dissolute into the cooking liquor at the same time. The rate of lignin dissolution could be higher than the rate of sulfonation reaction at a higher temperature, causing an overall drop in the sulfonation in the resultant pulp fibers. This would indicate that there is a maximum point for the sulfonation degree during the NSSC cook. It would be crucial to end the cooking process when achieving the maximum sulfonation.

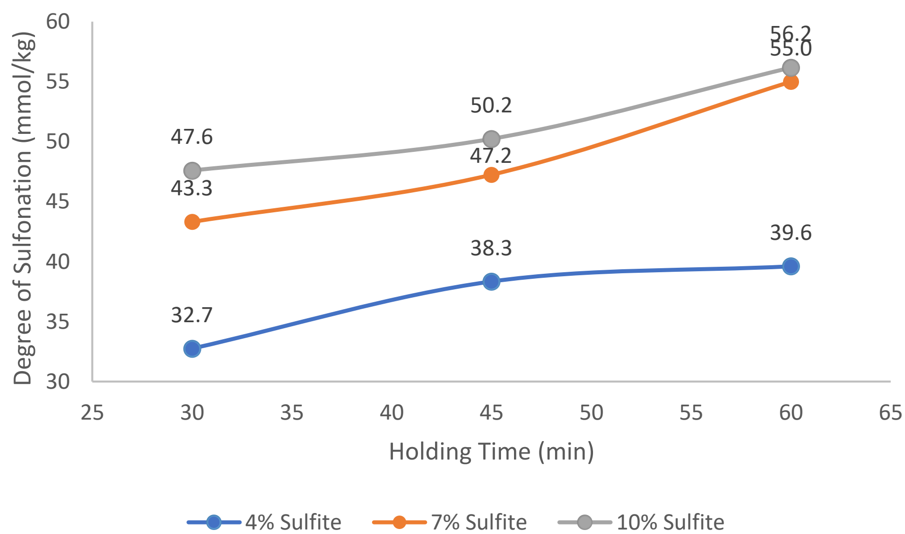


Figure 18: Sulfonation at 165 ℃ with different holding times and sulfite charges

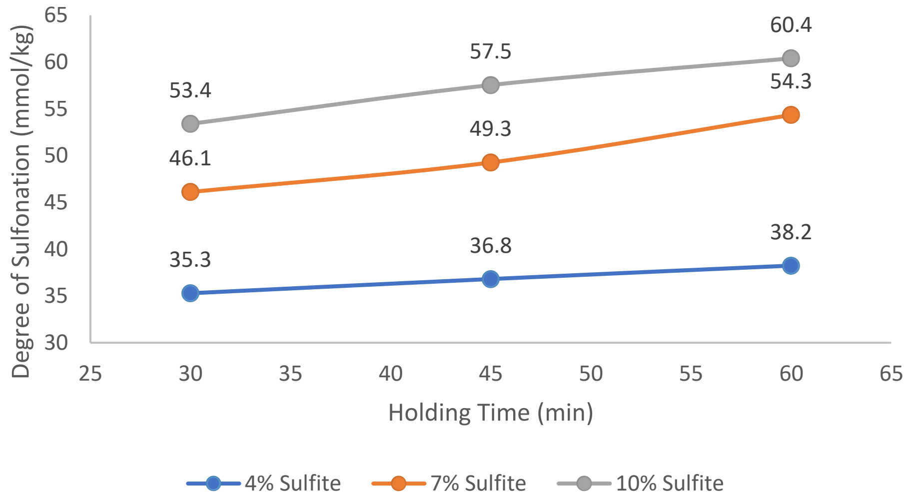


Figure 19: Sulfonation at 172 °C with different holding times and sulfite charges

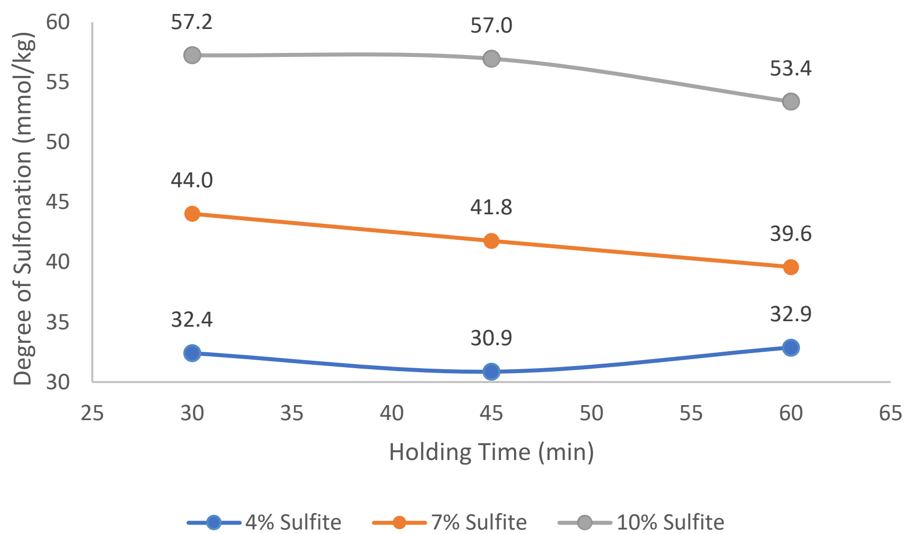


Figure 20: Sulfonation at 180 °C with different holding times and sulfite charges

Figures 20 and 21 display the change of sulfonation under 165℃ and 172 ℃ respectively. Both show a higher degree of sulfonation with increasing cooking time, and cooks with higher sulfite charge consistently gave better sulfonation results as well. However, the cooks at 180℃ (Figure 22) show a decreasing trend of sulfonation with time. The maximum degree of sulfonation appeared at 30 minutes across all three levels of chemical charges. The sulfonation results further support those from the perturbation plot. At a high cooking temperature (180℃), The sulfonated lignin dissolution and the sulfonation reached its peak before or at 30 minutes of holding time. As the concentration of sodium sulfite started to decrease in the cooking liquor, the rate of sulfonation reaction decreased as well, while excessive sulfonated lignin dissolves, causing the overall degree of sulfonation on the pulp started to drop with time. This wasn't observed with cooks at 165℃ and 172℃ since the degree of sulfonation only started to plateau around 60 minutes of holding time. Also, the highest degree of sulfonation at these two cooking temperatures was relatively similar under the same sulfite charge, with the biggest difference of 7%. Therefore, it is likely the maximum degree of sulfonation was mainly affected by the sulfite charge.

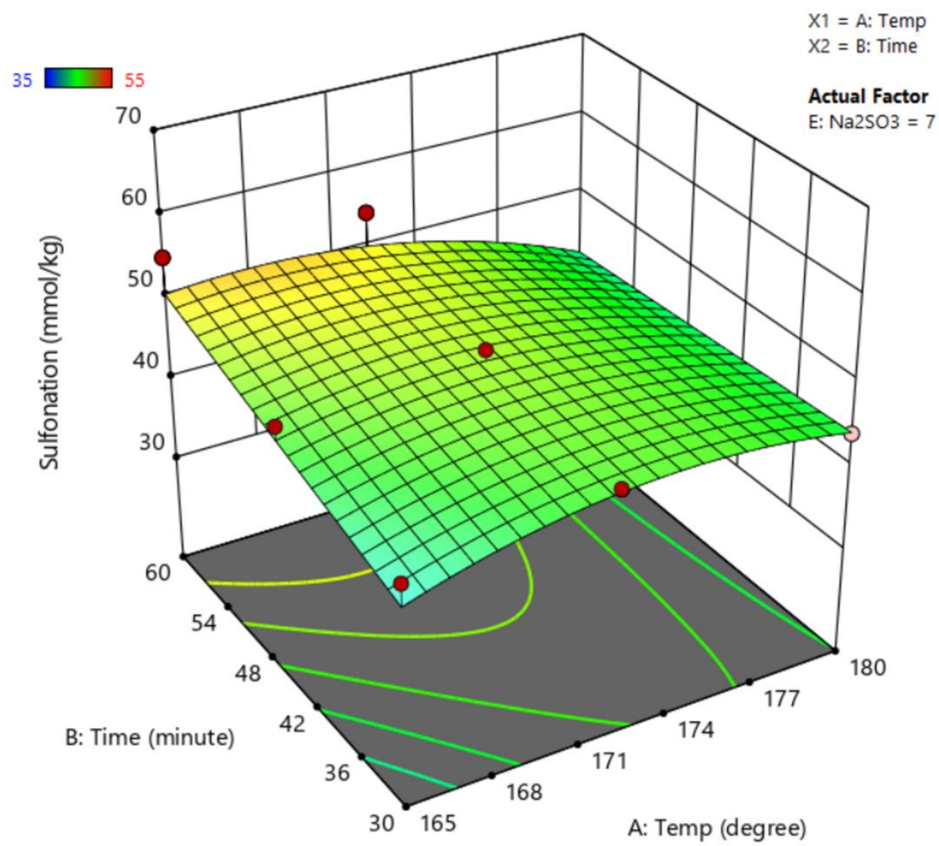


Figure 21: 3-D surface analysis of time and temperature effect on the sulfonation

The 3-D surface analysis (Figure 23) presents the combined effect of time and temperature on the sulfonation. When the sulfite charge was kept constant at 7%, cooks at 165℃ and 172℃ were showing an increasing trend with the highest sulfonation happening at 165℃ and 60 minutes, while the sulfonation at 180℃ with relatively consistent or even decreasing.

Table 10: Change of sulfonation under similar H-factor

Temperature (℃)	Time (min)	H-Factor	Na_2SO_3 (%)	Sulfonation (mmol/kg)	Difference (mmol/kg)
165	60	433	4	39.6	4.3
172	30	401	4	35.3	
172	60	737	4	38.2	5.8
180	30	730	4	32.4	
165	60	433	7	55.0	4.9
172	30	401	7	46.1	
172	60	729	7	54.3	10.3
180	30	730	7	44.0	
165	60	435	10	56.2	2.8
172	30	405	10	53.4	
172	60	737	10	60.4	3.2
180	30	730	10	57.2	

H-factor is the traditional control parameter used in the pulp and paper mills to evaluate the degree of cooking, and it's calculated from the combination of time and temperature. Whether cooks under identical H-factor could give a similar degree of sulfonation would be an interesting finding. This is due to its potential to give guidance to the cooking conditions in the mill.

The data in Table 8 could be divided into 6 groups, and each of them had a similar H-factor. However, when comparing the cooks from each group, the cook with a lower temperature showed a better degree of sulfonation, and this is consistent across all the groups. Therefore, it can be concluded sulfonation favors lower cooking temperature under the same H-factor.

Table 11: Quadratic model for the sulfonation prediction

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2062.16	6	343.69	64.3	<0.0001	Significant
A-Temp	24.79	1	24.79	4.64	0.0437	
B-Time	73.12	1	73.12	13.68	0.0014	
E-Na_2SO_3	1732.63	1	1732.63	324.15	<0.0001	
AB	103.85	1	103.85	19.43	0.0003	
AE	65.10	1	65.10	12.18	0.0023	
A^2	71.35	1	71.35	13.35	0.0016	
Residual	106.90	20	5.35			
Cor Total	2169.06	26				

Std. Dev.	2.31		R^2	0.9507
Mean	45.58		Adjusted R^2	0.9359
C.V.%	5.07		Predicted R^2	0.9075
			Adeq Precision	25.1785

$$\begin{aligned} Sulfonation\ (mmol/kg) &= -1865.8 + 21.6 \times Temp + 4.6 \times Time \\ &- 14.7 \times Na_2SO_3 - 0.03 \times Temp \times Time \\ &+ 0.1 \times Temp \times Na_2SO_3 - 0.03 \times Temp^2 \end{aligned}$$

Equation 17

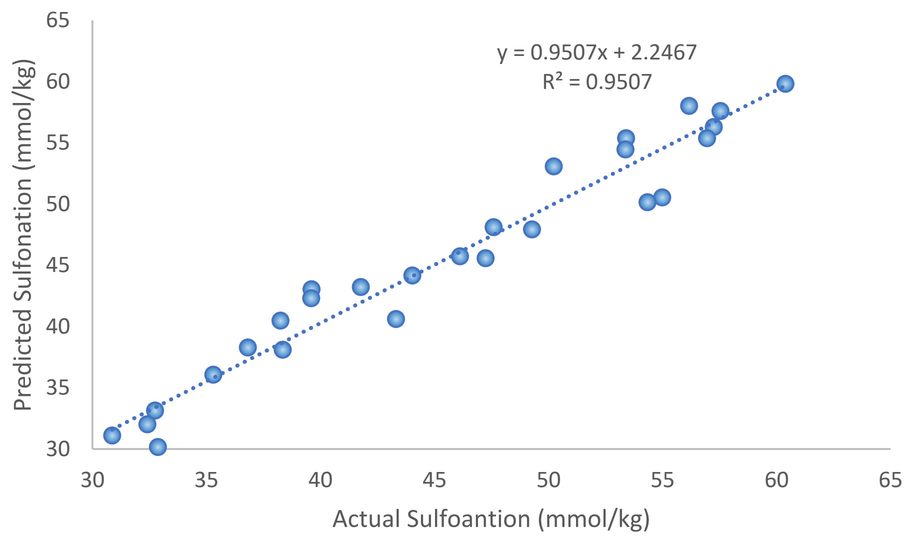


Figure 22: Actual sulfonation vs the predicted sulfonation from the quadratic model

Figure 24 displays the parameters included in the modified quadratic model for the sulfonation prediction. All the insignificant terms in the model were already removed. Figure 25 displays the comparison between predicted sulfonation and the measured value with an R^2 of 0.95.

4.6 Summary

The NSSC process is considered as high yield pulping process, it is important to maintain the strength properties while achieving high pulp yield. In the present study, a model was created based on the cooking results to predict the pulp yield. Out of the three cooking parameters, the change of sodium sulfite didn't show any influence on pulp yield, while temperature and time showed a significant impact on it. The model could be used as guidance to predict the final pulp yield for NSSC cooking.

With the spent liquor being tested for the dissolved lignin content, the percentage of lignin removal was calculated to generate the model that can predict the delignification with the three cooking parameters (Time, Temperature, Na_2SO_3 charge). H-factor was developed to predict the degree of delignification under different cooking temperatures and times. The delignification target and Na_2SO_3 charge were fixed with a list of cooking temperatures being set. The delignification model was utilized to back calculate the required time to achieve identical lignin removal. The activation energy of 128.4 kJ/mol was found for the birch NSSC cooking.

The degree of sulfonation has important effect on the paper strength properties. A relationship was developed between the sulfonation and the three cooking parameters. With both Na_2SO_3 charge and cooking time showing a positive influence on the degree of sulfonation, a very high cooking temperature did not favor high degree of sulfonation. At 180°C, the degree of sulfonation reached its maximum at or before 30 minutes, then started decreasing with cooking time. This could be due to the higher rate of sulfonated lignin dissolution compared to the rate of sulfonation reaction under these conditions, especially when the available Na_2SO_3 concentration became low in the cooking liquor. The maximum achievable sulfonation was mainly affected by the Na_2SO_3 charge, which in turn affected the available Na_2SO_3 concentration in the cooking liquor for the sulfonation reaction. At the same H-factor target and Na_2SO_3 charge, a lower cooking temperature is favorable to reach a higher degree of sulfonation.

Chapter 5

Strength Properties: Na_2SO_3, Freeness, and Refining

5.1 Introduction

The effect of the three cooking parameters (time, temperature, sulfite charge) on the degree of sulfonation has been evaluated. Furthermore, it would be interesting to understand whether there is a threshold for the sulfite charge to cause a significant change in the paper strength properties. A similar study was conducted by Pereira and his colleagues (Pereira et al., 2011) , but the applied sulfite charge in the paper was too high to be applicable in the industrial environment. The reason for finding the threshold was to potentially minimize the Na_2SO_3 dosage during the cooking process while maintaining the paper strength requirement. The existence of high sulfur content in the spent cooking liquor could create challenges in the wastewater treatment plant because it can negatively affect the efficiency of the biological treatment (anaerobic or aerobic) process.

At the same time, it would be interesting to understand how the change of sulfite charge can influence the pulp freeness. Some studies claimed high sulfite charge could help save the refining energy, which was also analyzed during this set of experiments.

5.2 Initial Determination of Na_2SO_3 Threshold & Influence on Refining Energy

In this set of experiments, all the cooks were carried out under 165℃ and 45 minutes of holding time, which gave a 300- hour H-factor. The cooking conditions were chosen based on the data from the Lake Utopia Paper mill.

Table 12: First experiment set for determining the threshold of sulfite charge

Cook	Na_2SO_3 (%)	NaOH (%)	Temperature (℃)	Time (min)
1	0%	6.1	165	45
2	1%	5.5		
3	2%	4.9		
4	3%	4.2		
5	4%	3.8		

The Na_2SO_3 charge was varied from 0% to 4% with an increment of 1%, the NaOH charge changed accordingly to maintain the neutral end pH.

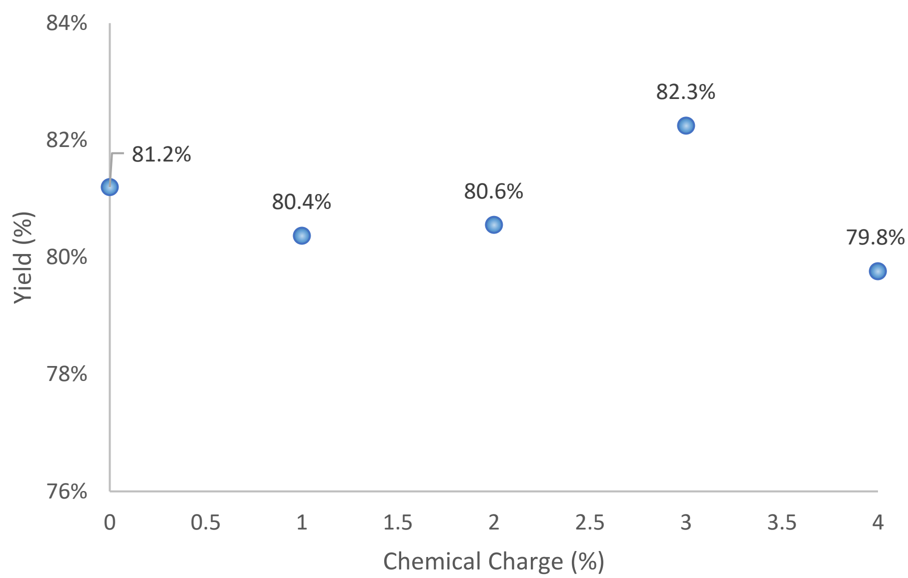


Figure 23: Pulp yield with different sulfite charges.

The average yield from the 5 cooks was 80.8% with a standard deviation of 0.8% (Figure 26). The change in sulfite charge didn't show a significant influence on the pulp yield, which agrees with the results in Table 3.

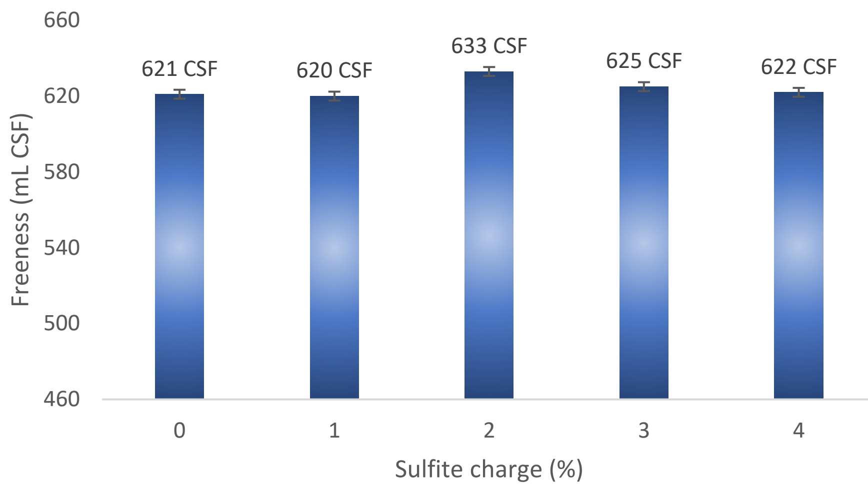


Figure 24: Pulp freeness at 3500 PFI revolutions and different sulfite charges

All 5 samples were first disintegrated, then refined with the PFI refiner for 3500 revolutions. and then tested for their freeness. The result showed an average value of 624 with 4.7 standard deviation. There wasn't enough evidence to prove the benefit of high sulfonation on the pulp refining.

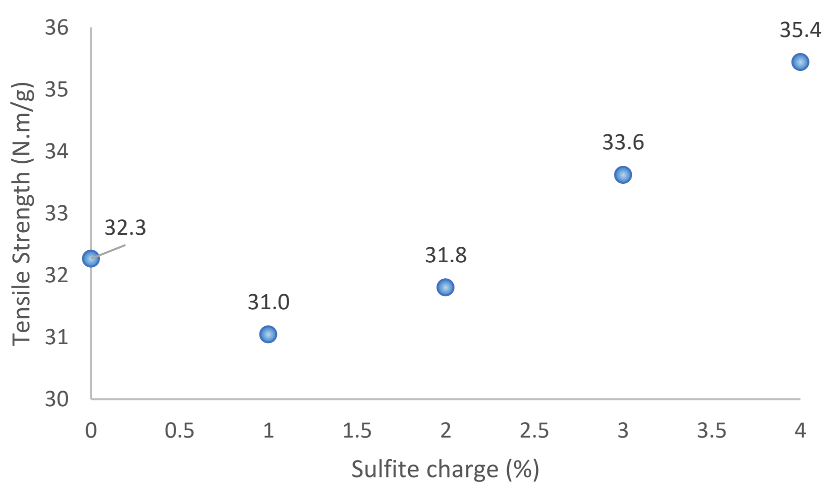


Figure 25: Set 1 Tensile strength at different sulfite charges

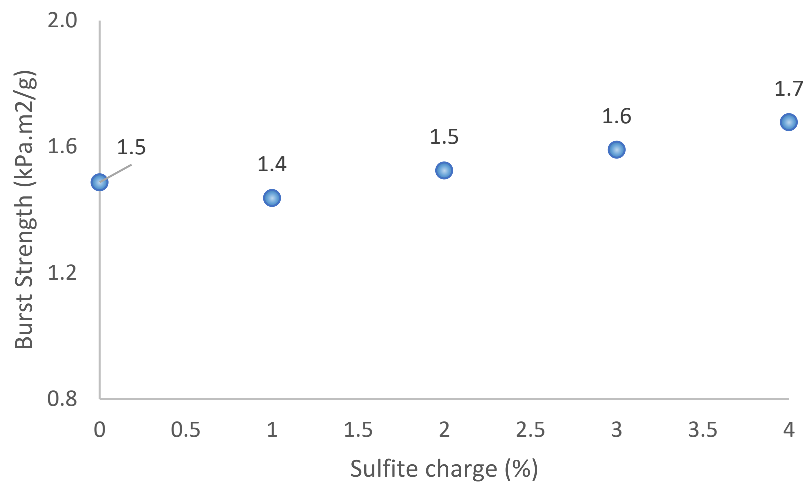


Figure 26: Set 1 Burst strength at different sulfite charges

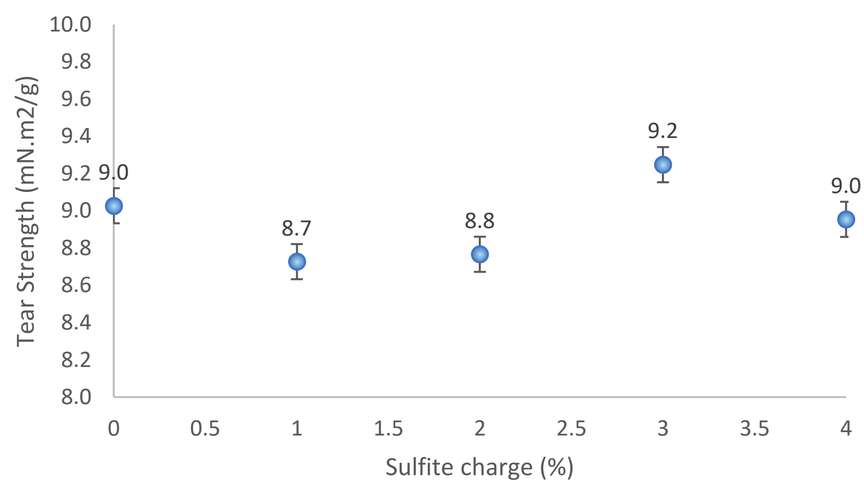


Figure 27: Set 1 Tear strength at different sulfite charges

The refined pulp from each cooking (different sulfite charges) was made into 6 hand sheets (60 gsm basis weight). These samples were tested for tensile, burst, and tear strength, and there were 12, 10, and 10 results for the respective test. All the test results were taken as the average and plotted to compare the differences under these conditions. Tensile strength is the most important test out of the three. As displayed in Figure 28, the tensile strength was relatively constant from 0% to 3% sulfite charge and showed 9% improvement at 4%

sulfite charge. A similar trend was observed with the burst strength test, the hand sheet at 4% sulfite charge showed an 11% improvement compared to the cook without the addition of Na_2SO_3. However, there was no information on how the strength properties would change at a 6% Na_2SO_3 charge. Whether the strength properties would keep increasing or remain the same with more Na_2SO_3 would be important evidence to prove the existence of the threshold Na_2SO_3 charge. As for the tear strength, it didn't show any trend with the change in the Na_2SO_3 charge.

5.3 Expended Chemical Charge on Determining Na_2SO_3 Threshold

The previous set of experiment did not show enough evidence to support the existence of the threshold of the sulfite charge. Therefore, the range of sulfite charge was expended to test if that would give a better indication.

Table 13: Second experiment set for determining the threshold of sulfite charge

Cook	Na_2SO_3 (%)	NaOH (%)	Temperature (℃)	Time (min)
1	0%	6	165	45
2	2%	4.9		
3	4%	4		
4	6%	3		
5	8%	2		
6	2%(Na_2CO_3)	2		

In the second set of experiments, all the cooks were still conducted at 165℃ and 45 minutes of holding time while the Na_2SO_3 charge varied from 0% to 8% with an increment of 2%. At the same time, a new trial with Na_2CO_3 instead of Na_2SO_3 was tested to see its effect on strength and other parameters. Na_2CO_3 and NaOH are the chemical compositions in green liquor, thus the cooking was called the green liquor cooking process, it was claimed in the literature that this green liquor cooking process would give a similar result as the NSSC cooking. Without the sulfur in the cooking process, green liquor cooking could be beneficial for the wastewater treatment process. A cook was conducted with 2% Na_2CO_3 instead of Na_2SO_3 as a comparison. Less NaOH was utilized for the green liquor cooking due to the excellent buffer effect from Na_2CO_3.

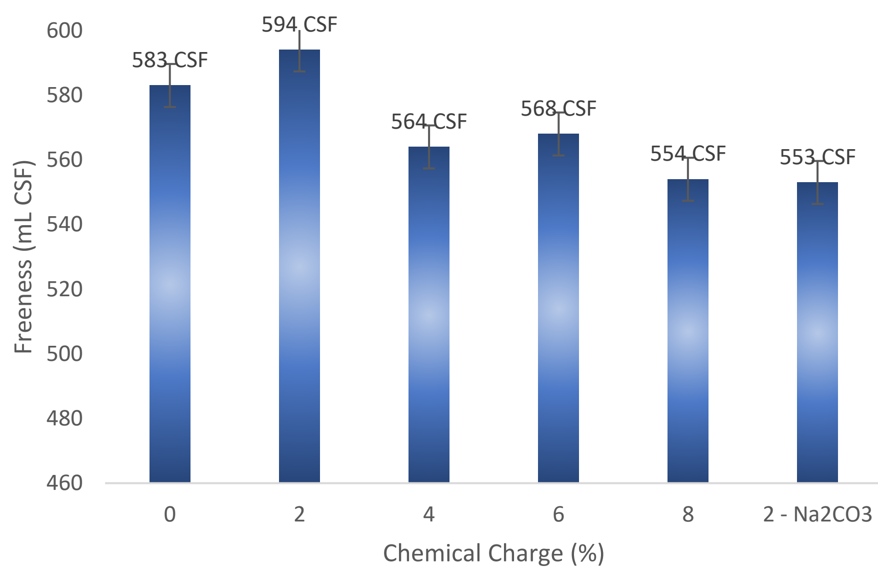


Figure 28: Pulp freeness at 3500 PFI revolutions and different chemical charges

Like the first set of experiments, all the pulp samples were refined with 3500 PFI revolutions, and there wasn't a significant difference among all these trials. The pulp freeness had an average of 569 ML CSF with a standard deviation of 15 ML. The addition of more Na_2SO_3 still did not show an improvement in the degree of refining, which also meant no refining energy saving.

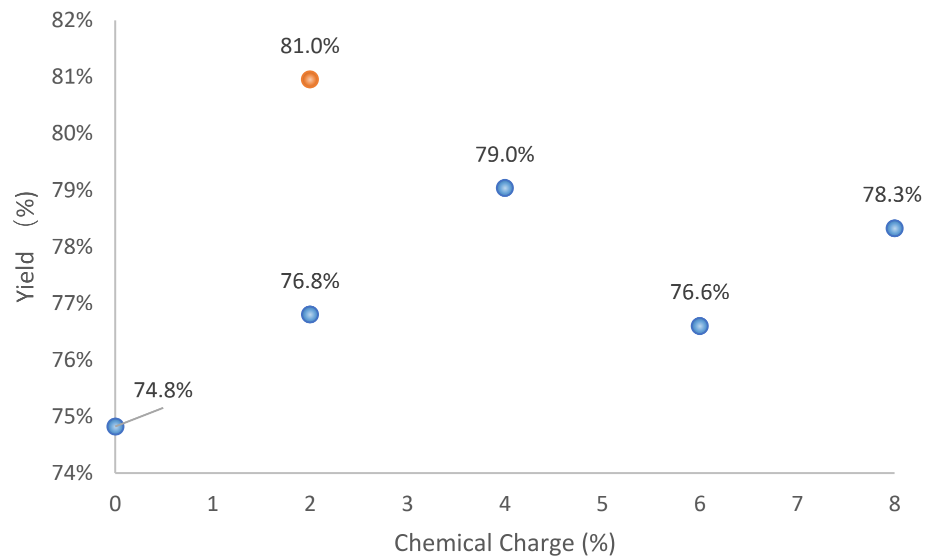


Figure 29: Pulp yield with different chemical or chemical charges

The blue points in Figure 32 were the cooks with Na_2SO_3. Aside from the cook with 0% sulfite charge, the other cooks still showed similar pulp yield. The lower yield observed from the first cook could be due to the extra bark in the wood chips. The orange point in Figure 32 indicated the cook with Na_2CO_3. When comparing cook 2 and 6, the cook with 2% Na_2CO_3 showed 4.2% extra pulp yield. This could mean Na_2CO_3 contributed to the preservation of carbohydrates to give a higher overall yield, but more cooks were required to confirm this finding.

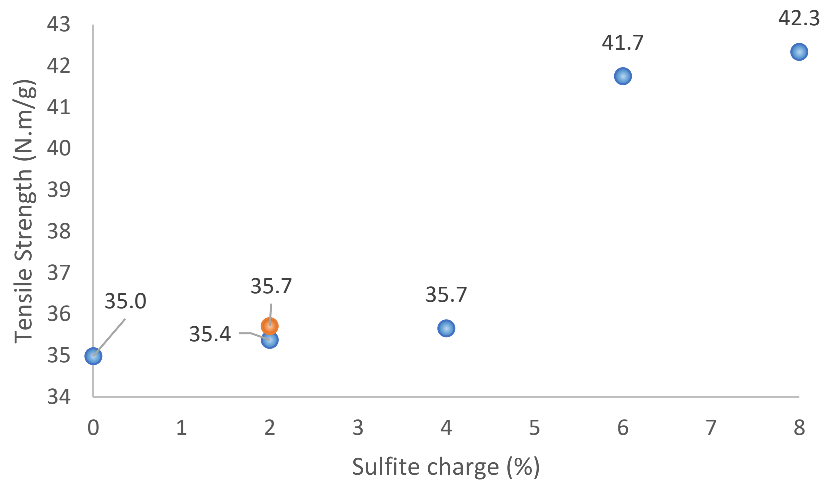


Figure 30: Set 2 tensile strength with different chemical and chemical charges

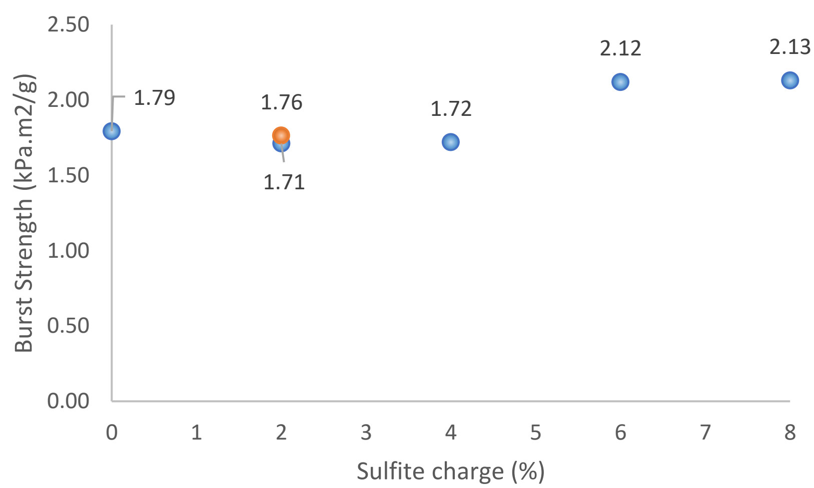


Figure 31: Set 2 burst strength with different chemical and chemical charges

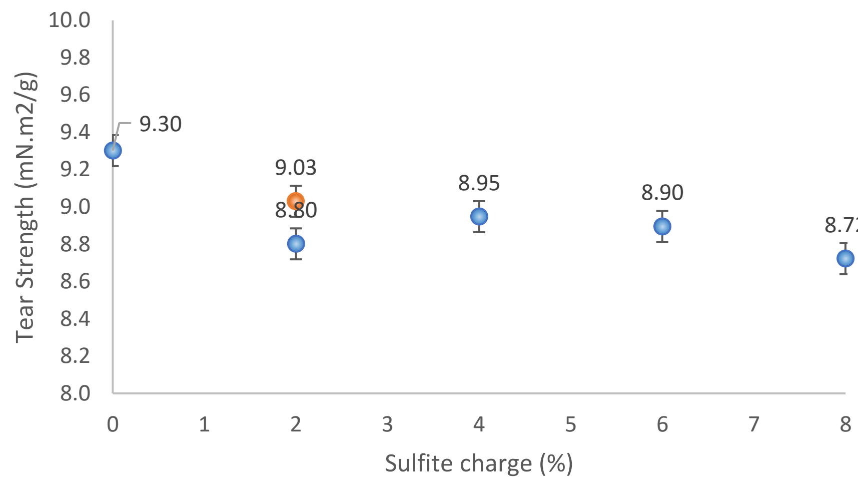


Figure 32: Set 2 Tear strength with different chemical and chemical charges

Unlike the first set of experiments, tensile strength at 0% sulfite charge increased from 32.3 N.m/g to 35.4N.m/g, and the same improvement appeared for the 2% sulfite charge. Therefore, the improvement from 0% to 4% sulfite charge showed in experiment set 1 no longer exists. However, from 4% to 6% sulfite charge, the tensile strength improved by 15%. At the same time, there was a 19% increase in burst strength. The improvement with a 2% of extra sulfite charge was significant, and the same change wasn't observed from 6% to 8% sulfite charge. It was suggesting the threshold of the sulfite charge existed within this range. Same as set 1, tear strength wasn't affected by the increase in the sulfite charge. Also, the cook with 2% Na_2CO_3 showed similar strength properties as cook 2, which uses 2% Na_2SO_3 during the cook. These results showed the potential of using Na_2CO_3 as the cooking chemical to reach similar paper quality as the NSSC cooking.

5.4 Impact of PFI Revolutions on Freeness and Strength Properties

To further confirm the results from Experiment set 1, the cooking trials with 4% and 6% sulfite charges were repeated under the same cooking conditions.

Table 14: Third experiment set for sulfite charge threshold and refining effect

Cook	Na_2SO_3 (%)	NaOH (%)	PFI revolutions	Temperature (°C)	Time (min)
1	4%	6	3500	165	45
2	6%	3	3500		
			4000		
			4500		
			5000		
			5500		

For the third set of experiments, not only to confirm the threshold of the sulfite charge but the effect of refining was also studied to understand its influence on the pulp freeness and strength properties. Cooks 1 and 2 were compared at 3500 PFI revolutions to confirm the finding from experiment set 2. At the same time, the pulp from Cook #2 was refined with different PFI revolutions from 3500 to 5500 before testing the pulp freeness and strength properties.

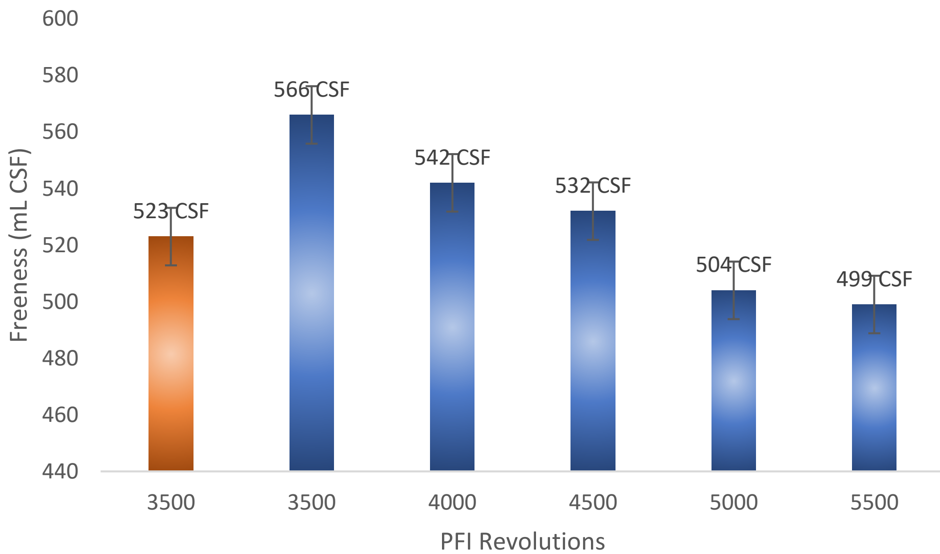


Figure 33: Pulp freeness with different chemical charges and refining revolutions

The yellow bar in Figure 36 was the cook with a 4% sulfite charge, while the rest were from the cook trials with a 6% sulfite charge and refined at different PFI revolutions. When comparing the two data points at 3500 PFI revolutions, there was a 43 CSF difference between them. The result from the 6% sulfite charge agreed with the cook from set 2, which also had 6% sulfite charge, while the one with the 4% sulfite charge got lower; it is an outlier. The pulp freeness was dropping gradually with increasing the number of PFI revolutions, but its change wasn't consistent, and it was barely dropping after 5000 revolutions. Unless changing the gap size between the housing and the bar roll, the pulp freeness would reach the plateau. The non-linear change of the freeness against the applied PFI revolutions could be due to the contact between the beater and the fibers. As the fibers bundles were developed during the refining process, it would be harder for the bars on the roll to further break down the smaller fibers, which led to a worse efficiency. Since the energy requirement would be different from each revolution, using the number of revolutions as an indication of the refining energy consumption is not accurate.

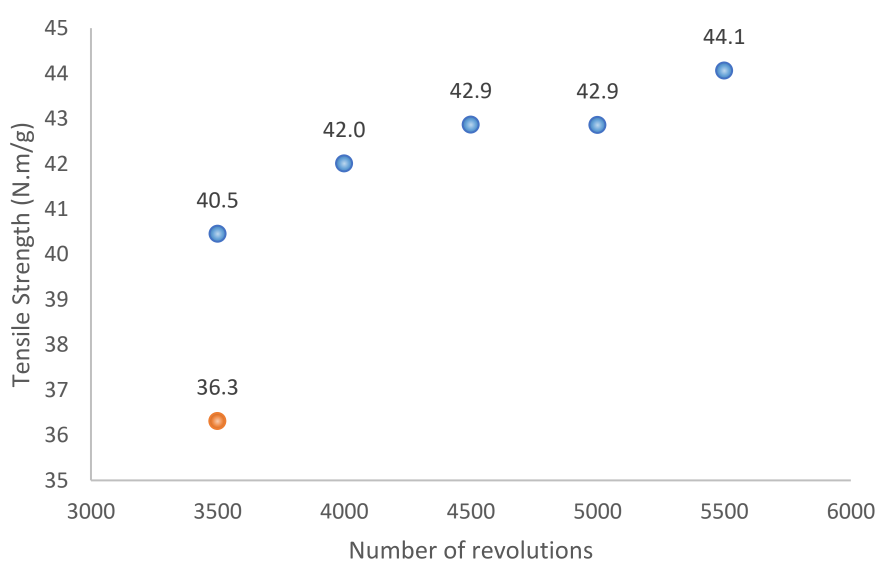


Figure 34: Tensile strength as different sulfite charges and freeness

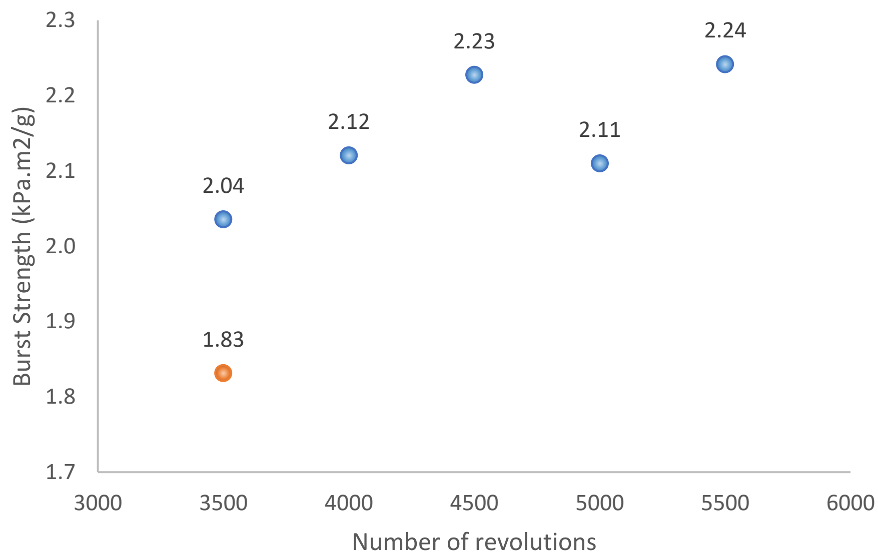


Figure 35: Burst strength as different sulfite charges and freeness

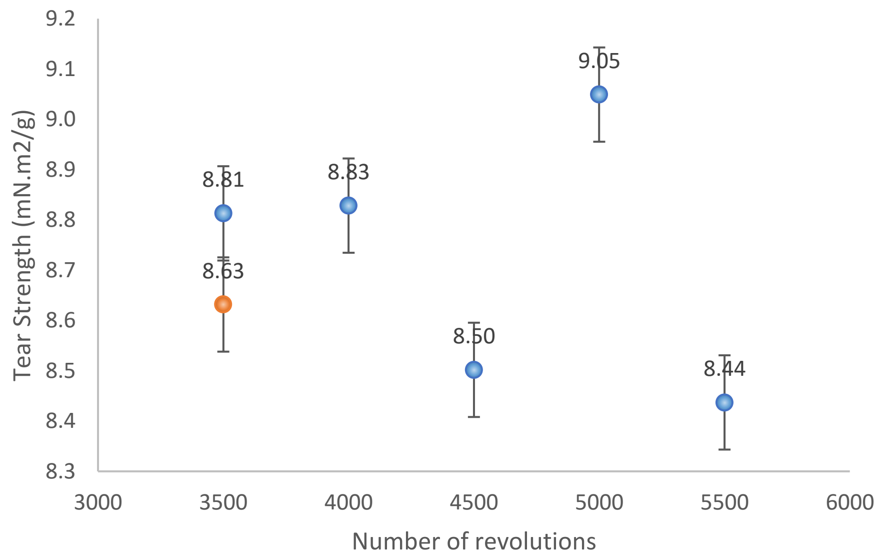


Figure 36: Tear strength as different sulfite charges and freeness

Similar to Experiment Set 2, both tensile and burst strength were showing an 11% increase by increasing the sulfite charge from 4% to 6%. Even though the improvement wasn't as significant as the previous cooking set, it still supports the existence of the sulfite charge threshold within this range. With the drop of 67 CSF with extra refining, the tensile and burst strength improved by 8.2% and 8.9% respectively. Same as before, tear strength didn't show any trend with the changing of PFI refining.

5.5 Summary

Three independent sets of experiments were designed to demonstrate the existence of the threshold for the Na_2SO_3 charge as well as to understand its effect on refining energy and strength properties.

In the first set, the pulp yield was once again approved not to be affected by the Na_2SO_3 charge, the influence of the addition of Na_2SO_3 on the refining energy consumption wasn't observed either. As the Na_2SO_3 charge was varied from 0% to 4%, there was an increase of 9% and 11% for the tensile and burst strength respectively. However, there was no confirmation that the strength properties would increase with the addition of more Na_2SO_3 to consolidate the existence of the threshold.

In the second set of experiments, the range of Na_2SO_3 charge was expanded from 0% to 8% . The strength properties with 0% and 2% Na_2SO_3 became higher than those in the first set under the same Na_2SO_3 charges, but no improvement was observed again as the Na_2SO_3 charge increased. However, when increasing from 4% to 6% Na_2SO_3 charge, a significant improvement of 15% and 19% appeared on both tensile and burst strength. The same degree of increase didn't happen at the 8% Na_2SO_3 charge case. The threshold of Na_2SO_3 charge could be within that range (4% to 6%). The cook with 2% Na_2CO_3 showed similar strength properties as the cook with 2% Na_2SO_3, with 4.2% higher in pulp yield, which is interesting.

In the third set of experiments, the cook trials at 4% and 6% Na_2SO_3 charges were repeated to confirm the finding of the Na_2SO_3 threshold. A similar degree of improvement was observed again. The pulp cooked at 6% Na_2SO_3 charge was refined with different PFI revolutions. The idea was to use PFI revolutions to indicate the refining energy consumption and determine how it would affect the pulp freeness and the strength properties. However, it wasn't a linear relationship between PFI revolutions and energy consumption (due to the limitation of the PFI itself), and this goal couldn't be achieved. The tensile and burst strength improved by 8.2% and 8.9% respectively with a drop of 67 ML CSF, which would be valuable data if the energy consumption could be practically measured. If so, then refining energy consumption, pulp freeness and corresponding strength properties could be tied to the energy cost to show whether it is economically beneficial.

Chapter 6

Conclusions & Future Works

6.1 Conclusions

This study was divided into two sections; the first section was to determine the effect of individual cooking parameters on the pulp yield and degree of sulfonation as well as find the activation energy for the birch delignification reaction. The main purpose of the second section was to evaluate the threshold of the Na_2SO_3 charge to minimize the chemical charge while maintaining the mechanical strength of the pulp. Cooks with different chemical ratios and chemical charges were conducted to determine their influence on the refining energy, pulp yield, and most importantly, the strength properties. Pulps were refined with different PFI revolutions to understand how energy consumption could affect pulp freeness and its mechanical strength. A cook with Na_2CO_3 instead of Na_2SO_3 was also completed to evaluate the potential of green liquor cooking.

Throughout the study, temperature demonstrated the biggest impact on the pulp yield followed by cooking time. Na_2SO_3 charge was proved to have no influence on the pulp yield in both sections of the study. In terms of the degree of sulfonation, Na_2SO_3 was found to be the dominant factor. In addition, the sulfonation reaction didn't favor high cooking temperatures (180°C), the highest degree of sulfonation was reached at an early stage of the cooking process and then decreased with cooking time. Also, the maximum achievable degree of sulfonation mainly depended on the Na_2SO_3 charge or its concentration in the cooking liquor. The activation energy of the birch delignification reaction was found to be 128.4 kJ/mol. When varying the Na_2SO_3 charge from 0% to 8% while maintaining a neutral end pH, the threshold of the chemical charge was determined to be between 4% and 6% Na_2SO_3. Under the same degree of refining, no difference in terms of the pulp freeness was observed. The cook with Na_2CO_3 showed similar strength properties as the cook with the same percentage of Na_2SO_3 charge, but with a 4.2% higher pulp yield. The effect of energy consumption on pulp freeness and mechanical strength couldn't be analyzed since each PFI revolution wouldn't consume the same amount of energy. Therefore, the impact of energy consumption and its economic benefit couldn't be determined.

6.2 Future Works

For future work, it would be interesting to further understand the sulfonation kinetics as well as the relationship between sulfonation and mechanical strength. With the development of the sulfonation kinetics for the birch wood, it had the potential to be used for process control purpose. Even though the relationship between cooking parameters and sulfonation was studied along with the connection between sulfite charge and strength properties. However, the degree of sulfonation and sulfite charge was not the same. It would be valuable to establish a correlation/model that can predict the pulp strength based on the degree of sulfonation and pulp yield. The cook with Na_2CO_3 showed potential to be used as a replacement for the Na_2SO_3. Further study should be conducted to understand its influence on pulp yield and mechanical strength. In future studies, the energy consumption during the refining stage should be monitored to compare with the economic benefit gained from better pulp strength or grade to optimize the refining parameters.

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Appendix I

Figure 37: Evolution 201 spectrophotometer

Figure 38: Labtech disintegrator

Figure 39: Canadian standard freeness tester

Figure 40: Lorentzen & Wettre PFI refine

Std	Run	Factor 1 A:Temp degree	Factor 2 B:Time minute	Factor 3 C:Effective time minute	Factor 4 D:H-factor	Factor 5 E:Na2SO3 g	Factor 6 F:NaOH %	Response 1 Yield %	Response 2 Sulfonation mmol/kg	Response 3 Residual Sulfite g/L	Response 4 Sulfur in dissol... mmol/kg lignin...	Response 5 Removed lignin %	Response 6 pH
15	1	165	30	34.3	239	4	2	95.3	32.7	2.5	139.4	10.2	6.68
3	2	165	45	49.3	334	4	3	93.5	38.3	2.4	174.8	12.5	6.9
8	3	165	60	64.9	433	4	4	90	39.6	0.5	175.7	17	6.19
10	4	172	30	35.5	401	4	3.3	91.3	35.3	1.2	152.8	15.5	6.47
6	5	172	45	50	567	4	4.2	87	36.8	0.6	146.5	15.2	6.83
9	6	172	60	65.3	742	4	5	80.9	38.2	0.3	152.2	18.6	6.7
16	7	180	30	35.7	755	4	4.6	85.8	32.4	0.7	136.5	18.4	6.85
2	8	180	45	50.5	1038	4	5.3	81.2	30.9	0.3	126.1	22.7	6.28
5	9	180	60	65	1344	4	6	80.2	32.9	0.95	135.8	22.2	6.73
11	10	165	30	35.3	229	7	1	99.3	43.3	6.7	192	10.3	6.39
17	11	165	45	49.9	329	7	2	94.3	47.2	6.2	221.8	11.3	6.7
13	12	165	60	64.5	436	7	3	89.2	55	4.4	236.6	16.9	6.87
7	13	172	30	34.8	401	7	2.5	89.9	46.1	5.8	202.1	17.8	6.89
12	14	172	45	48.6	587	7	3.2	88	49.3	3.9	221.2	22.2	6.59
4	15	172	60	64.6	729	7	4	85.5	54.3	3.3	242.8	23.3	6.85
14	16	180	30	36	730	7	4	84.2	44	2.9	191.5	22.4	7.12
1	17	180	45	52	992	7	4.4	82.4	41.8	1.8	173.8	23.1	6.7
23	18	180	60	64.7	1328	7	5	81	39.6	0.9	182	28.5	6.41
24	19	165	30	34.7	240	10	1	93.2	47.6	12	204	12.8	6.63
25	20	165	45	49.2	325	10	1	94.4	50.2	11.4	217.8	13.9	6.51
26	21	165	60	65.5	435	10	2.4	89.7	56.2	8.1	249.7	19.1	6.62
27	22	172	30	35.4	405	10	1.6	96	53.4	10.2	242.3	14.1	6.71
18	23	172	45	49.6	567	10	2.4	88.9	57.5	8.3	257.4	20.3	6.6
19	24	172	60	64.5	737	10	3	84.8	60.4	7.5	266.1	22.9	6.65
20	25	180	30	34.9	730	10	2.6	84.2	57.2	8.9	252.8	23.6	6.78
21	26	180	45	52.1	1045	10	3.3	79.4	57	4.7	257.2	29.2	6.65
22	27	180	60	67.7	1380	10	4.2	79.8	53.4	2.5	243.2	30.2	6.66

Figure 41: Raw data for the simulated cooks

CURRICULUM VITAE

Candidate’s full name: Xingzhi Jiang

University attended: University of New Brunswick, bachelor's degree, 2019.

Publications: “Advanced Polymer-Surfactant Systems via Self-Assembling” by Laura Romero-Zerón and Xingzhi Jiang

Conference Presentations: None