EVALUATION AND PREDICTION OF WOOD PROPERTIES IN PULP AND PAPER PRODUCTION

Estimation of Wood chemical properties and pulping results using Near Infrared Spectroscopy: A case study in BillerudKorsnäs in Gävle

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ABSTRACT

In paper and pulp industries, the quality of pulp depends on many different parameters such as type of used wood, chemicals, beaters, etc. Those traits of raw materials which mostly affect the pulp quality are usually measured in the laboratory. Advancement in method of spectroscopy have proved that this technology could be applied in determination and prediction of both chemical and physical properties of forest plants and wood.

Near Infrared spectroscopy has been recently applied in predicting the different materials especially chemical properties of raw wood used in the pulp and paper mills. In this research, the main goal was to estimate wood chemical properties in the chemical pulping at BillerudKorsnäs mill in Gävle. In fact, the quantity of moisture and lignin was measured using a standard method in the laboratory. Then, with near infrared spectroscopy (NIR) data from solid wood, a model was developed to predict moisture and lignin content in the wood chips. Moreover, the yield of digesting process as well as pulp Kappa value were analyzed for the samples taken from the mill.

Good calibration models were separately created for Acid Insoluble Lignin (AIL), Total Lignin, Pulp Yield, and Kappa number of pulp using Orthogonal Signal Correction (OSC) treated NIR spectra with the R-Square values of 0.92, 0.89, 0.85, and 0.99, respectively. The model developed for moisture content showed low R-Square value of 0.52, which indicates some over or under estimation in prediction and high calibration errors. So, it cannot be reliably used for prediction. Moreover, Acid Soluble Lignin (ASL) calibration results with R-Square value of 0.077 were poorly correlated with the laboratory measured values.

Based on the results, the OSC treated NIR spectra from raw solid wood can be used to estimate AIL and total lignin content as well as pulp yield and Kappa number. These models could be applied to the fiber lines 1 and 2 at the mill to control the pulping process efficiently and increase the pulp quality. However, the reliability of them needs to be analyzed before application.

Keywords: NIR, Calibration, Lignin, moisture, pulp quality, Kappa number
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<thead>
<tr>
<th>Indication</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>A</td>
<td>Absorption at different wavelength</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Dilution factor</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>Volume of filtrate</td>
<td>liter</td>
</tr>
<tr>
<td>a</td>
<td>Extinction coefficient of lignin</td>
<td>gr/liter</td>
</tr>
<tr>
<td>b</td>
<td>Cuvette path length</td>
<td>cm</td>
</tr>
<tr>
<td>M</td>
<td>Weight of dry sample</td>
<td>gr</td>
</tr>
<tr>
<td>m</td>
<td>Weight of sample residue</td>
<td>gr</td>
</tr>
<tr>
<td>Rf</td>
<td>Reflectance</td>
<td>-</td>
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<tr>
<td>Ab</td>
<td>Absorption</td>
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### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>NIR</td>
<td>Near Infrared Reflectance</td>
</tr>
<tr>
<td>EA</td>
<td>Effective Alkaline</td>
</tr>
<tr>
<td>S</td>
<td>Sulfidity</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly Ethylene Glycol</td>
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<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>PCR</td>
<td>Principal Component Regression</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial Least Square regression</td>
</tr>
<tr>
<td>OSC</td>
<td>Orthogonal Signal Correction</td>
</tr>
<tr>
<td>MLR</td>
<td>Multiple Linear Regression</td>
</tr>
<tr>
<td>SNV</td>
<td>Standard Normal Variate</td>
</tr>
<tr>
<td>RMSEP</td>
<td>Root Mean Standard Error of Prediction</td>
</tr>
<tr>
<td>RMSEC</td>
<td>Root Mean Standard Error of Calibration</td>
</tr>
<tr>
<td>AIL</td>
<td>Acid Insoluble Lignin</td>
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<tr>
<td>ASL</td>
<td>Acid Soluble Lignin</td>
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1 INTRODUCTION

This part gives a short introduction about the woody biomass and also a background about the principles of chemical pulping. It is then followed by the problem formulation, purpose of this study and research questions, limitation and scopes of the work.

1.1 Background

Nowadays, sustainable development as a global criteria requires renewable, environmentally friendly resources for supplying industrial production. Many countries around the world heavily depend on non-renewable resources to meet the various needs of the growing population. Global warming and climate change, population and resources, and health issues are some of the global challenges caused by utilization of unsustainable resources. In order to address these issues, many industries have transformed their production strategies and started to use renewable resources as raw material in production lines.

Amongst different type of sustainable resources, biomass as a cellulosic material have become an attractive and commonly used source. Forest or agricultural materials -as examples of biomass- are considered suitable alternatives for non-renewable feedstock. In fact, biomass refers to non-fossilized and all organic material produced from plant through natural processes or gained from animal and microorganisms. In general, biomass is all dead or living biological materials.

Biomass mostly consists of cellulose, hemicellulose, lignin, extractives, and many other components. The portion of these materials in each plant depends on the type of the biomass. For instance, lignocellulosic biomass like wood contains mainly lignin, cellulose, and hemicellulose in the complex polymeric structure (B.Agbor, et al., 2011).

Cellulose is the abundant constituent available in the plants walls, which makes the plants structure stronger and strict. It is also available in fungi and algae (B.Agbor, et al., 2011). The second main polymer in a plant structure is hemicellulose, which is forming 20% to 50% of lignocellulosic plants. Unlike the cellulosic polymers, hemi cellulosic material is chemically homogenous and is sensitive to temperature (B.Agbor, et al., 2011) (Hendricks & G.Zeeman, 2009) (S.L & J.E, 1990).

The third key polymer in the plant building is the lignin, which is available in the wall of the plant cells and protect the plant from microbial attack. In fact, lignin refers as the ”glue” that attaches the individual cellulosic polymers together, which makes it insoluble in water (B.Agbor, et al., 2011). In the wood as an example, the fibrous material is bind together with lignin as the glue.
The amount of cellulose, hemicellulose, and lignin differs in the biomass depending on the type. This means that the grasses, herbaceous plants, crops, and woody plants have different amounts of the mentioned polymers. The content of polymers, especially lignin, in the biomass is important in order to determine its digestibility (B. Agbor, et al., 2011).

Considering the properties of biomass, mostly lignocellulosic types, many industries have recently become interested in using biomass as the raw material in processes for bio production. Amongst them, paper and pulp mills is a typical example using the woody biomass to produce different bioproducts and separate different polymers such as lignin, cellulose, and hemicellulose existing in the wood through the process called pulping.

The pulping is the process in which a cellulosic biomass, mostly wood, is transformed to fibrous substances like individual cellulososes through mechanical technique, chemical method, or through a combination of both methods (B. Agbor, et al., 2011). (In this project, the chemical pulping is studied). Before converting to fibrous pulp, both hardwood and softwood should be debarked and chipped into small pieces. The wood chips are then screened and become ready to be used in the pulping process (Gullichsen & Paulapuro, 1999).

By the chemical pulping, the lignin content in the wood, which binds the individual cellulose fibers together, is dissolved in aqueous solutions of acidic, alkaline, or neutral components (called “white liquor”) at high pressure and temperature during a cooking process. This is also called delignification process (Gullichsen & Paulapuro, 1999). Although the wood loses most of its lignin, wood structure does not change through chemical pulping process. The produced cellulosic fibers are separated from the cooking liquor and then washed and bleached. Used cooking liquor containing lignin (generally called “black liquor”) is too dilute. So, before reusing the liquor, it should be evaporated to lose the excess water (Gullichsen & Paulapuro, 1999).

The liquor could be burned in a recovery boiler with the aim of recovering the cooking solvent and energy production. Depending on the type of wood and the process, yield of cellulose fibers varies from 45% to 55%. Also, the removed lignin has some portion of cellulosic and hemicellulosic materials (B. Agbor, et al., 2011).

The quality of the produced pulp depends on different factors such as amount and type of applied chemical liquor, the quality of raw woods meaning that they should be free of barks as much as possible, and most importantly, the chemical properties of wood chips such as lignin and cellulosic materials.

In order to control the process of pulping in an efficient way and achieve pulps with high quality, various measures and techniques have been employed. Recently, Near Infrared (NIR) spectroscopy has become an attractive method in predicting both physical and chemical properties of different materials (Poke, et al., 2005). Based on the reflectance of molecules, each material has the unique spectra and absorption band, therefore, the content of materials could be estimated.

The main goal of this research was to estimate wood properties in the chemical pulping at BillerudKorsnäs mill in Gävle. In fact, the quantity of moisture and lignin was measured using
a standard method in the laboratory. Then, with NIR spectra from wood, a model was going to be created to predict the properties of wood chips. Moreover, the yield of the digesting process and pulp Kappa number as the indicators for pulp quality were analyzed for the samples taken from the mill.

Many types of research have been carried out on NIR and prediction model. For example, Poke and Raymond applied NIR spectroscopy on eucalyptus solid wood in order to estimate its lignin and cellulose contents (Poke, et al., 2005). In this project, the analysis was done on pine as the softwood used in BillerudKorsnäs pulping mill to create a suitable prediction model with relatively high accuracy.

1.1.1 BillerudKorsnäs background

BillerudKorsnäs Gävle is a pulp and paper mill which is a supplier of highly processed fiber-based packing materials from renewable sources in a sustainable way. In fact, this mill is the combination of two companies Billerud and Korsnäs, which are merged on November 2012. Billerud dates back to the 19th century and it is formed with the purpose of supply of forest and good communications (BillerudKorsnäs, 2015) (BillerudKorsnäs, 2014). Korsnäs established in 1855 and it was mostly like sawmill. In the 1960s, the company changed to high grade processing from low grade, such that in 1965, the company produced 15% of highly processed goods. After buying the second paper machine in 1976, the broad production began and the goods production reached 85%. In 2002, the saw mill was sold. The combination between the two companies contributed to a focused and strong player in packing solutions and production of packing material (BillerudKorsnäs, 2015) (BillerudKorsnäs, 2014).

Today, BillerudKorsnäs has 8 production units around ten different countries and around 4300 employees are working there. The annual sales of the company is approximately SEK 20 billion. The market is divided into four main segments: Food and beverages (59%), Industrial products (25%), Consumer and luxury goods (10%), and Medical and hygiene (6%) (BillerudKorsnäs, 2015).

BillerudKorsnäs considers the sustainability criteria and contributes to increased sustainability in future economic, environment, and social and wellbeing. The general goals of the company are listed as follow:

- Be innovative in the packing industry
- Using the renewable raw materials and good solutions
- Increase the communication and share knowledge
- Save more resources, contribute to a sustainable future, and increase the profit (BillerudKorsnäs, 2015) (BillerudKorsnäs, 2014).
1.2 Problem formulation

As a commonly used source, different types of biomass have various properties, which affect the end-use products from different aspects. This issue is mostly concerned in industries like paper and pulp mills, where directly use biomass as the raw material for processes. A combination of softwood or probably hardwood chips and wood flakes from saw mill are used in the chemical pulping in the mill. The properties of wood chips strongly vary depending on the type of tree and the thriving conditions (Gullichsen & Paulapuro, 1999). This variation can also be observed even in a single tree, such that barks and outer parts of trees (known as sapwood) are strong, hard, and in color black, while, heartwood which is the inner part of trees is soft and has a cream color. So, it is important to know the structure and properties of wood used for the process (Gullichsen & Paulapuro, 1999).

As it is mentioned, the constituent materials in the wood structure are cellulose, hemicellulose, and lignin, which are polymers. There are also small amount of extractives in the wood that can be dissolved in water. The quantity of each polymer in wood, especially lignin, can affect the process of pulping and the quality of products as well (Ásling, 2016). For instance, the amount of lignin needs to be measured since it affects the cook ability or digestibility of wood in the process. It is also important to find if the lignin can be solved in the cooking liquor. Some other factors such as microbiological particles and spores, foreign particle in both raw material and product, existence of bark in raw material have impacts on quality of pulp (Ásling, 2016).

The pulp quality depends on the Kappa value, which is measured by titration of pulp solved in sulfuric acid with Potassium Permanganate (KMnO₄). In fact, Kappa number is a measure of the residual lignin in the produced pulp. Variation in Kappa number affects the stock preparation, therefore it is needed to find a stable kappa number and remove the lignin content in the pulp as much as possible without changing the fibers structure. With this, the exchanges would increase and a reliable system can be found to control the process in the most efficient way (Ásling, 2016).

The process at fiber lines 1 and 2 in BillerudKorsnäs mill sometimes shows variation in Kappa number. Therefore, the company is trying to address this problem by controlling the amount of lignin in the produced pulp.
1.3 Research questions

The goal of this study is to predict the properties of wood chips and cooking results to have a better control on the pulping process and improve the products quality. For this purpose, the chemical properties of wood chips such as moisture content and lignin content need to be measured in the laboratory. Also, the quality of produced pulp needs to be analyzed by measuring the yield and pulp Kappa number. As the final step in this project, by calibrating the laboratory results and NIR spectra from wood, several models would be created with which the moisture and lignin content in the wood, and pulp yield and Kappa value could be predicted.

To carry out the analyses, two following questions have been formulated:

1- How can chemical properties of wood including moisture and lignin be predicted using NIR - Spectroscopy?
2- Is it possible to find a connection between NIR spectra of wood chips and the cooking results (pulp yield and Kappa number)? And how can the cooking process be controlled based on the NIR technique?

Therefore, the purpose of this project is to analyze the chemical properties wood chips moving to the digesters using spectral data from solid wood and a calibration model. Moreover, correlation between NIR spectra and pulping results is going to be evaluated to see whether it is possible to control the pulping process.

1.4 Delimitation and scope

The pulp and paper production is a broad industry, so that it starts with the raw material preparation and finishes by production of end-use products such as paper and cardboard. However, the focus of this study is mostly on digesting of wood chips and the produced pulp, which is the first stage in the paper production procedure. Moreover, this project was carried out for digester 1 and digester 2 in BillerudKorsnäs in Gävle, and they use the combination of softwood and saw mill chips as the feedstock for the pulping process. Therefore, all analyses are carried out on the wood samples that are taken from the mill.

The mill contains three digesters and three operation lines. Line three is followed by bleaching unit in which the process of whitening the pulp is done and the quality of the paper increases. In this project, it is dealt with operation lines 1 and 2 without bleaching unit.

As it mentioned in the purpose section, the goal is to analyze some properties of the raw materials used in digesting process in order to have high-quality pulp with stable Kappa number in the process. Many factors such as lignin and resin content, moisture, bacteria and fungi particles, foreign particles like plastic, etc. can affect the quality of the pulp. In addition,
the rate of digesting, cooking temperature and pressure, and digesting time are other important factor that needs to be considered in this process. Yet, the analyses are restricted to measuring only moisture content, amount of lignin and the digestibility (pulp yield and Kappa value) of the wood chips with different portions of softwood and wood chips from saw mill.

This study is limited to find the correlation between properties of wood chips and produced pulp with NIR spectroscopy to get the most qualified pulp. In fact, a model based on NIR spectroscopy was suggested for predicting the lignin content of further woods as well as moisture content, pulp yield and kappa value. Therefore, the implementation of suggested work is not performed during the limit time. Hence, these factors are the limitations in doing this project that need to be considered.

Due to some limitation in using the equipment, the digesting experiments were carried out at Karlstad University. A square net sieve was used in order to prepare the samples for cooking experiments, however, it is not a suitable sieve for wood particles. So, the separation of fine particles was done manually after primary filtering with available sieves. These limitation in doing the experiments might reduce the accuracy of the work.

Overall, the followings are the outlines of this study:

**Chapter1:** It gives an introduction about the topic of the research to the reader, and presents main aim of the research. Then, it is followed by the mill where the project is performed. The problem is formulated and the research questions and work limitations are also included in this section. The chapter is ended with the scopes of the work.

**Chapter2:** In this chapter the research methodology by which the thesis was carried out is presented. In the methodology section, all of the chosen methods are explained as well as how the analyses was carried out. The literature review and data collection conducted in this project is also described. At the end of this chapter the steps of experiments and analyses are discussed.

**Chapter3:** The literature which is necessary for analysis is reviewed to get insights of the project topic. The description of the pulping process, effective factors, energy use, and improvements to energy efficiency is included in this part.

**Chapter4:** This section presents the procedure of modeling followed by the explanation of used calibration method. The experiments and analyses carried out on the samples are also described in this chapter.

**Chapter5:** All measurements and NIR calibration results are presented in this chapter, as well as the identification of problems and performance assessment.

**Chapter6:** In this chapter the results and gathered data will be reviewed and analyzed. It is followed by the explanation of the issues and answering the research questions. Finally, the final proposal is clarified.

**Chapter7:** In the conclusion chapter as the last section, a summary of the outcomes of the work is presented and some recommendations and improvements to the work are suggested, which would be topics for further researches.
2 METHODOLOGY

The research procedure is presented in this part of the report. The used tools and methods, data gathering, reviewing the related literatures, and different experiments and observation used for analysis are explained in this section.

2.1 Research method

There are several types of investigations such as: modeling and experimental work, quantitative analysis, case study, and surveys. Modeling work is to find a pattern for a phenomenon. It is argued that the experimental method is the most difficult research method, which is to be “too accurate” (Shuttleworth, 2016). In quantitative analysis, the collected data from a large example of a studied phenomenon is investigated. The commonly used method is case study in which the researcher selects a specific case and wants to answer why, what or how research question. In fact, the case study contributes to find reasons for a complexity about a real case and select a good way to address the problem (Shuttleworth, 2016) (K.Yin, 2003).

According the research questions in this project, it is going to answer what question; what would be the properties of wood chips. During the analysis, it will be found, how the amount of chemical properties of wood could be predicted. It is also going to answer how predicting properties of wood chips can affect the quality of the pulp. This analysis and study have been exactly done on the process of digesting at Korsnäs mill.

The present project is designed a case study due to the following reason: The area of study is chemical pulping and the case of this study is analysis the properties of the wood chips used for pulping process in BillerudKorsnäs mill in Gävle. In order to find the properties of wood chips like lignin, to answer the research question: how to predict the properties of wood chips, and to assess how they affect the pulping process and pulp quality, it has been done the modeling and some experiments in the laboratory. Therefore, experimental work is also included in the case study. In fact, this research is a combination of these two research method.

2.2 Process of research

This project contained three main parts: the first task was to measure the spectra of the raw woods in the wavelength of NIR range. The next part of the project was to answer a “what question”: what is the chemical properties of wood chips and what are the important factors affecting the pulp quality. So, in this part, feedstock properties such as lignin, moisture, as well as the yield and Kappa number of the produced pulp were determined and assesse. Most of the experiments and measurements have been carried out in this step of research. Experimental works and literature study as well as direct observation were applied during the analysis.
The last step was to find a solution for observed results and find a correlation between NIR spectra and properties of wood chips and pulp by creating several models. In fact, a “How” concept was going to be answered to obtain a decision and conclusion approach: How the process can be controlled by NIR calibration models.

At the beginning of the research, literature review was done to get some basic knowledge about the project subject. This continued during the first month of the research. After taking samples, the experiments were begun for assessment. At the same time, I started with writing the draft report. As the procedure went on, reading scientific papers and writing the report continued together with gathering data and analyzing them. Some part of the experiments like digesting were done in Karlstad University. As the final step, the calibration and cross validation were done to find prediction PLS models for lignin content, moisture, pulp yield, and Kappa number. The process of the project has been shown in Figure 1.

2.2.1 Literature study

The prior step in any research is developing a good framework for the study subject. The goal of this development is to have some basic information for the case study which help the writer to become familiar with the processes, acts, thoughts and ideas. In order to have a good theoretical development, literatures with the similar concept to the case need to be reviewed. Then, the ideas should be discussed with others and the challenges and questions related to the area of study as well as possible results need to be considered (K.Yin, 2003).

At the early stage of doing this thesis, small literature review was completed in order to get familiar with paper and pulp industry, process of pulping, used raw material, structure of wood and so on. The steps in the procedure of literature review for this project can be followed in bellow:

- **Finding the key words:** from the title and the subject of the study the key words can be identified. Pulping, Chemical pulping, cellulosic biomass, wood chips, and lignin determination are some of the key words searched to find the literatures related to the study subject.
- **Searching in databases:** databases such as Scopus, ScienceDirect, and Google Scholar were mostly used to find literatures in books, journals, articles and PHD thesis.
- **Extracting relevant papers:** reading the title and the abstract of searched articles, those with the most relevancy are selected.
- **Reading the article which are within the project topic:** this step was to read the different section of the relevant articles such as introduction, results, and discussion. Around 15 articles were exactly central to the subject.
- **Taking notes and writing summaries:** a draft summary of all read papers is prepared at this step, which can help to design the process of writing the final report.
- **Reviewing the articles and literatures:** with writing the draft summary of the most important texts, the literatures and the primary concepts of them were reviewed.
Selection of project subject and setting the research questions

To answer What question
- Literature review
- Data collection
- Experimental work

To answer How question
- Data Analysis
- Calibration and Modeling

Discussion and Conclusion

Figure 1 Design of research procedure
2.2.2 Data collection

For each research, there are two different data: quantitative and qualitative. The first group of data represents information in numbers. However, the qualitative data are in the form of text, picture, conversation, etc. (K.Yin, 2003). For gathering different data there are many sources, while, direct and indirect observation and discussion with others were mostly used as sources for data collection in this thesis.

2.2.3 Experimental works

To measure some parameters and determine the content of some chemical properties, some observation, analysis, and laboratory experiments were conducted through the research procedure.

2.2.3.1 Wood chips

The raw wood chips were taken from the conveyor belt moving to digester 1 and 2 at the mill. The normal feed stock used for a continuous digesting process contains 50% saw mill chips and 50% softwood chips from pine wood. Pine wood is employed as the softwood chips in the pulping process in BillerudKorsnäs mill. The samples were collected every one hour with a reduced percentage of saw mill chips each time and in total, 29 unique samples were taken and packed in 68 different bags. The following table represents the specification of wood chips taken within 2 days:

Table 1 Information about samples collected from the mill in 26th and 27th of January

<table>
<thead>
<tr>
<th>Time</th>
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26-jan-16

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27-jan-16
2.2.3.2. Spectroscopy (NIR)

Near Infrared Reflectance (NIR) has become one of the quick and cheapest indirect method for determination of chemical properties of the wood such as cellulose content, lignin, and extractive content (Poke, et al., 2005). By NIR analysis, the spectra of the sample is measured in near infrared wavelength region, which is normally between 1200 nm and 2500 nm (Poke, et al., 2005).

In fact, in spectroscopy, the molecules in the sample absorbs the light with specific frequency and the energy of the molecule increases, which make vibration in molecule. Each molecule absorb a certain wavelength. There is a linear relation between the absorption and the concentration of absorbing species (Skvaril, 2016):

\[ A = a_\lambda \cdot b \cdot c \]

\textit{Equation 1}

Where:

\( A \): absorbance
\( a_\lambda \): absorptivity coefficient
\( b \): path length
\( c \): concentration

With the measured NIR spectra and then developing calibration and finding a correlation between the spectral data and lignin content, for example, a model can be set in order to predict the lignin content in the wood.

\[ \text{Figure 2 Collection of wood chips from conveyor belt} \]
In this thesis, the method of NIR spectra was used for 68 samples taken from the mill. The spectra were recorded over a wavelength range from 12000 cm\(^{-1}\) to 4000 cm\(^{-1}\) with the spectral resolution of 8 cm\(^{-1}\). Since the surface of the samples in the dish is not homogeneous, the experiment is carried out six times for each of the samples in both static mode and moving with the velocity of 1 m/s (or 181 rpm) with rotating the dish between each scans. The reason for repetition was to get the most representative result. Thirty two scans are accumulated for each NIR experiment and the average result is considered as the final result for each sample.

The NIR spectrometry was also done in the same way on the ground wood which was more homogenous compared with the wood chips. For this part of the experiment, the moving mode was skipped since it was not possible to be done on wood powder. The scans were replicated five times for this case. Then, an averaged spectra is considered as the representative result.

The analysis of the NIR result was done by developing a regression model which relates the spectra from NIR to the known amount of lignin and moisture in the wood determined by standard methods in the lab. With this model, the lignin and moisture contents of the further wood can be predicted (Poke, et al., 2005). The same procedure was done to create the model for pulp yield and Kappa number.

\subsection{Moisture content}

The moisture content is the amount of water in wood chips that is expressed as a percentage of water in wet wood. The moisture content can be defined in both volumetric and gravimetric content. Generally, the content of water in a substance is expressed by the weight of water in the unit mass of the sample using the formula in below:

\[ U = \frac{m_{\text{Wet sample}} - m_{\text{Dry sample}}}{m_{\text{Wet sample}}} \]

\textit{Equation 2}

All wood has some amount of moisture. The content of water in the wood can range from 0% (means completely dry) to 30% or it can be more like 50% depending on the conditions that the wood is placed or kept. In the presence of high quantity of water in wood, fungi and mold can be grown on the wood surface, which in our case reduce the quality of produced pulp and end-use paper. Moreover, the water in the wood increases its weight, however, the dry content of wood is the useful part. Therefore, it is important to measure the water content in the wood and decrease the moisture as much as possible.

In this thesis, the simplified method ISO 18134-2:2015 based on the Svensk Standard is used for doing the moisture content experiments. According to this method, wood chips were weighed, then were put in the drying oven at temperature in the range of 105 ± 2 °C for 24 hours. After measuring the weight of dried sample, the moisture content was calculated in percent using Equation 2.

\subsection{Lignin determination}

Lignin content is determined in the laboratory using the method according to the Protocol for round robin test of lignin content (COST FP0901). However some improvements and
modifications were implemented on the method. Based on this method, the following laboratory equipment are used for this experiment:

- Drying oven at the temperature of 105 °C
- Water bath at 30 °C
- An autoclave at its maximum temperature (121 °C)
- Laboratory scale
- Filters
- Spectrophotometer

In the procedure, approximately 1 ml of 72% Sulphoric acid (H$_2$SO$_4$) is added to each sample of 0.1 g of dry wood mill in the glass tube. Then, it is put in the water bath at 30 °C for 1 hour. In the next step, the sample and acid will react in the autoclave for one hour at 121 °C. After the hydrolysis is finished, the precipitate is filtered with 100 ml of water by the vacuum and weighed glass filter. The absorption of the filtrate is then measured at wavelengths of 205 nm, 250 nm, and at the maximum value of the peak. With this, the lignin content which is soluble in acid can be determined (Aldaeus, 2010):

$$\text{ASL} = \frac{A.D.V}{a.b.M} \times 1000 \frac{mg}{g}$$  \hspace{1cm} \text{Equation 3}

Where:

- ASL: Acid-Soluble Lignin
- A: Absorption at different wavelength
- D: Dilution factor
- V: Volume of filtrate (liter)
- a: Extinction coefficient of lignin (g/liter)
- b: Cuvette path length (cm)
- M: Weight of the dry sample before hydrolysis with acid (gr)

The glass filter with precipitate is weighed after being dried in the oven at 105 °C for 2 hours. By the following equation the acid-insoluble lignin content is calculated (Aldaeus, 2010):

$$\text{AIR} = \frac{m}{M} \times 1000 \frac{mg}{g}$$  \hspace{1cm} \text{Equation 4}

Where:

- AIR: Acid-Insoluble Residue
- m: weight of residue after drying
- M: Weight of the dry sample before hydrolysis with acid (gr)

So, total lignin content in the sample is:

Total lignin content = ASL + AIR
2.2.3.5. Preparation of wood chips for digesting

For digesting, the "Academic method" needed to be followed, in which the suitable size of the wood chips is \( 3 \times 5 \times 0.7 \) cm and the samples should be dry (this is used as the standard method in the laboratory at Karlstad University). In order to separate wood chips with mentioned dimensions, first the sieving was done for the dried samples. Sieves with the net size of 1.6 cm was selected to remove fine wood chips, then the separation was carried out manually to remove over-size and under-size particles and to achieve sample with the good size and condition. Finally, 200 g of dry and sieved samples with the certain dimensions were prepared for cooking experiments.

2.2.3.6. Ash content

After burning the wood, an inorganic and solid residue is remained called ash. The ash content in wood depends on the type of tree. Normally, the amount is within a range between 0.4% and 2 %. This value is higher for bark and it raises up to 5 %. Carbon, calcium, magnesium, potassium, sodium, and phosphorus are the elements which can be mainly found in the ash of wood (Goyal, 2016).

In this study, measuring the ash content of the wood is randomly carried out as the final step in the lignin determination experiments, so that, after weighing the dried filter containing residue, it is put in the furnace at temperature of 550 °C for about one hour. Then, it is weighed after being cooled down. The difference in the weight will give the ash content. This was done to assess the availability of barks in the milled wood.

2.2.3.7. Cooking

This part of experiments was accomplished in Karlstad University. The digesting experiment was conducted for 200 g of 18 dry wood chips. Since the homogeneity of is the most important factor in cooking process, wood chips with specified dimensions (roughly \( 3 \times 5 \times 0.7 \) cm) were separated using a square mesh sieve with the size of 1.6 cm. The cooking process was done at elevated temperature of 160 °C and using alkaline (a mixture of Sodium hydroxide and sodium sulfide) as the cooking liquor. After digesting, the produced pulp was washed with water and the content of refined and the Kappa number were determined. The percentage of refined pulp shows the yield of cooking (Fonseca, et al., 2014).

The procedure of cooking have been carried out following the steps below:

1. Dry wood chips were weighed in order to calculate the amount of sodium hydroxide (NaOH) and sodium sulphide (Na2S) needed to make the cooking liquor (Alkaline solvent). For calculation of chemical, the Effective Alkaline (EA) and the Sulfidity (S) were estimated 35% and 20% respectively. Each sample was roughly 200 gr.
2. After transferring wood chips into the digester, the steaming process was then done, in which recirculating water steam at a pressure of around 3 bars passes through the wood chips placed in the steam boiler. This step took around 10 minutes for each digester.

3. The next step after steaming is the cooking process. The chemical was added to the wood chips and placed in the Polyethylene glycol (PEG) bath. Then, the cooking
process was done at high pressure and temperature of 160 °C for 2 hours. The cooking was done with a ratio of 4:1 between liquor and the wood chips.

Figure 5 PEG bath (Cooking process)

4. After cooking is finished, the pulp was removed from the digester and was washed with water in order to remove remained chemical called “black liquor”.

5. The washed sample was then put into the defibrator device in order to disintegrate produced pulp and make it homogenous. This process took approximately 10 minutes for each pulp.
6. Some portion of water was removed from the wet pulp up to the dryness of roughly 30% using a centrifuging device.

7. The wet pulp was then weighed. Some portion of wet pulp was stored and the rest was dried in the dry-oven over night.

In order to determine the Kappa value, the Standard method ISO 302-2015 was applied. Based on the method, 1 gram of dry pulp is used for Kappa number determination. Due to time limitation, Kappa value of 6 samples were determined on wet basis, 1.5 gr of wet pulp was taken for doing the measurement. After calculation of dryness, Kappa number on dry basis were recalculated for those 6 samples.
Figure 7 Kappa value determination
3 LITERATURE STUDY

In this chapter, the literatures which are necessary to analyze data and give the insights of the work to the readers were reviewed and presented. The chapter starts with a brief description of wood structure and its constituents, then it continues with introduction to the process of chemical pulping, effective factors during the process, and energy use related to pulp and paper mills. It finally finishes with the explanation of lignin determination and the NIR spectroscopy method in order to make a model for predicting the properties of wood.

3.1 Wood structure

All tree species are generally divided into two different groups: gymnosperms and angiosperms. Softwoods are put in the first group, however hardwoods belongs to the second group. The fiber as the main cell in all trees of the both groups has a supportive task which provide the mechanical strength to the wood. The structure of the cells in the hardwoods have different arrangement compared to the softwoods, which are developed about 300 million years before hardwoods (Fahlen, 2005). In this work, we are dealing with the softwoods, so the focus is on the structure of these types.

The walls of the wood cells are basically built up of two main layers: first layer and secondary part. The primary part of the cell (P) which contains an open micro fibril network is thinner, however, the secondary layer (S) is thick and subdivides into three further layers: S1, S2, and S3 (Gullichsen & Paulapuro, 1999).

Wood fibers are in the shape of tubes with a hollow inside which is called lumen. The water moves through it and is transferred to the fiber (Fahlen, 2005). The middle lamella layer is the lignin rich part of the cell wall that bends cells together (Gullichsen & Paulapuro, 1999). The normal length and width of fiber in Scandinavian wood including Scots pine and Norwegian spruce is 2-4 mm and 0.02-0.04 mm respectively (Fahlen, 2005).

3.1.1 Wood fiber

Wood fiber is mainly made of three polymers of cellulose, hemicellulose, and lignin. It also contains some contents of extractives and inorganic compounds. In general, the most part of the dry wood consists of cellulose, which forms more than 40% of the wood. Distribution of main components of softwood in different layers of cell wall is illustrated in the figure below:
The structure of the cellulosic polymers is linear composition of glucose units (Figure 9). Most of the cellulosic molecules in the wood have approximately the same size (Goring & Timell, 1962) (Fahlen, 2005) and they can be found in both crystalline and amorphous form (Gullichsen & Paulapuro, 1999). The cellulosic fibers are also acid and alkaline resistant material.

The second group of the polymers in the wood fibers is hemicelluloses. Several monomers like mannose, xylone and galactan build this polymer (Fahlen, 2005). Since they have less resistance to chemicals than cellulose, hemicellulosic materials could be dissolved in both alkaline and acid (Gullichsen & Paulapuro, 1999). Around 15-25% of wood consists of hemicelluloses (PrintWiki, 2016).
3.1.2 Lignin

The most complex 3-dimensional polymer in the wood fibers is lignin. It is derived from a Latin term “Lignum” and is the wood constituent which is containing extractives and carbohydrates (Fahlen, 2005). In fact, this polymer is known as the glue in the wood structure and glues the cellulose fibers together. Therefore, it plays an important role in strengthening the wood. Unlike cellulosic and hemi cellulosic polymers, lignin are not stable to the attack of chemicals such as acid (Gullichsen & Paulapuro, 1999). Around 15% to 35% of the wood consists of lignin, however its content in the wood is somehow depending on the tree species (PrintWiki, 2016).

Different type of feedstock has different quantity of lignin that should be removed from the wood fibers in order to increase the digestibility of the biomass. The removal of lignin by the chemical liquor is called delignification by which the lignin structure is destroyed and the inner space increases. After delignification, the digestibly of the wood increases compared with the raw biomass (B.Agbor, et al., 2011).

Since the lignin bend the cellulosic fibers together, one of the main tasks in the pulping is to remove the lignin from the wood and separate fibrous materials (cellulose). In fact, this is the purpose of the chemical pulping, while in mechanical pulping process the attempt is to reach a high pulping yield instead of high lignin removal (PrintWiki, 2016).

3.1.2.1. Structure of lignin

Lignin as the main part of the lignocellulosic plants has a three dimensional polymer structure (Chakar & J.Ragauskas, 2004).

Due to the complexity in the structure based on the three monolignols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, see Figure 10(Fahlen, 2005), the exact structure of lignin is still unknown. This also causes some problems in finding the chemical compositions of wood (Fahlen, 2005). However, research on finding the products of the degradation of lignin and the method of spectroscopic analysis have clarified the building of lignin polymers (Chakar & J.Ragauskas, 2004). Lignin makes wood very strong and it makes difficult the penetration of water through cells of wood.
3.2 Pulping

Pulping is the process of cooking of wood chips and converting them into the pulp which is later used to produce paper and cardboard. Basically, pulping is to separate cellulosic fibers from other constituents in the wood and the goal is to make individual cellulosic components (Kramer, et al., 2009). Pulp can be also manufactured using waste papers or less commonly straw and linters as the feedstock (Kramer, et al., 2009).

In the structure of wood, or generally lignocellulosic biomass, cellulosic fibers are bind together by the lignin, which is the constituent non fibrous substances in the wood. The lignin make the structure of the wood stranger and reduce its flexibility. Therefore, the existence of lignin reduces the quality of produced paper. So, the main purpose in pulping process is to remove the lignin from pulp (Chakar & J.Ragauskas, 2004).

Main processes carried out in pulp and paper industries include pretreatments of feedstock (mainly wood chipping), pulping (using different methods), whitening and bleaching, chemical recovery, drying, and finally paper production. Pulp mills are usually unique units, meaning that they are separated from paper production house (Kramer, et al., 2009). The block diagram in Figure 11 illustrates a schematic of these processes in pulp and paper industries (Kramer, et al., 2009).
Figure 11 Schematic of main processes in pulp and paper production. (Diagram inspired by (Kramer, et al., 2009))
3.2.1 Feedstock preparation

As the major source for pulp and paper production, wood is typically transported to the plant in the shape of wood block or wood chips of both softwoods and hardwoods. At the primary step in the process, logs and wood blocks are converted to suitable size and form for pulping. This treatment includes cutting to suitable size, debarking, flaking or chipping, and screening (Kramer, et al., 2009) ((DOE), 2005). In the case of having logs in large size, they are sent to the saw mill for size reduction before delivery to pulp mill (Chakar & J.Ragauskas, 2004).

After size reduction, the bark is removed from wood blocks since it is an impurity in the process of pulping. Debarking is usually done by placing the logs in a large drum and by rubbing and friction, the bark is removed from wood blocks (Kramer, et al., 2009). Another method is using hydraulic debarkers in which bark is removed by high pressure water jets. The main disadvantage of this method is high energy consumption. The removed barks by this process also need to be pressed before using as the fuel. Therefore, hydraulic debarking method is not the dominant process in pulp industries (Martin, et al., 2000) (Kramer, et al., 2009).

Prior to screening, wood is chipped to small particles using a chipping machine. This makes the wood particles consistent in size and shape and increase the efficiency of pulping process. Depending on the employed pulping method and wood species, the optimum dimension of wood particles could be found (Kramer, et al., 2009) ((DOE), 2005).

At the final step, wood chips are screened by passing through some vibrating sieves in order to remove oversize and undersize particles. With this, too big chips go for further size reduction, while too small particles, known as “fine particles”, are used as hog fuels in boiler for steam generation. By passing over a conveyor belt, wood chips are then transferred to the digesters for pulping process (Kramer, et al., 2009) (Martin, et al., 2000).

3.2.2 Pulping Process

The main goal in the pulping process and paper production is to remove the lignin from the wood and to free the individual cellulosic fibers in the wood chips. So, cellulosic and hemicellulosic fibrous materials are the main papers ingredients (around 65%) and the rest of it consists of lignin and ash. Produced pulp is then refined and used to produce papers (Fahlen, 2005). By moving through a drainage wire, the pulp is oriented and converted in to paper in the paper machine (Fahlen, 2005). Pulp with lower lignin content and longer fibrous materials produces papers with higher quality and strength (Kramer, et al., 2009).

The process of pulp production is carried out in three different manners: mechanical pulping, chemical pulping, and semi-chemical pulping. It is also possible to produce pulp and paper from waste paper by recycling. The type of pulping depends on different factors such as type of wood (softwood or hardwood), desired properties of pulp and paper to be produced (Kramer, et al., 2009). The characteristics of each process are summarized in the Table 2.
As its name reveals, in the mechanical pulping, the cellulosic fibers is separated and converted to pulp using a mechanical energy and grinding at elevated temperature. The pulping yield in this method is above 90% since the waste material is very low or negligible (Chakar & J.Ragauskas, 2004). However, in this process the lignin would not be dissolved, therefore, the produced pulp has low strength and resistance (Kramer, et al., 2009). This process also needs more screening than chemical pulping in order to remove contaminants and knots ((DOE), 2005). As a result, mechanical pulping is used for production of newsprint and papers for magazines and catalogues.

Chemical pulping in contrast produces stronger pulp with better properties and stable fibers, however, the yield is lower (Fahlen, 2005). This process is the commonly used method for pulp production (Kramer, et al., 2009). And it has been seen as more leading pulping process today compared with mechanical pulping. For instance, around 85% of U.S. paper pulp is produced through chemical pulping, whereas, mechanical pulping shows roughly 8% of the production (Kramer, et al., 2009).

Addition of a chemical is the first step in chemical pulping to dissolve the lignin present in the lamella to separate the cellulosic fibers and secondly to remove lignin from the wood cell at high temperature and pressure to produce a pulp with high level of flexibility and strength (Fahlen, 2005). The produced pulp is then suitable for manufacturing different kind of papers. (Chakar & J.Ragauskas, 2004).

In the cooking stage in chemical pulping, the solvent which is called white liquor, moves through the wood chips. The process is done in a large vessel shape digester at elevated
temperature as well as high pressure for about two hours (Chakar & J.Ragauskas, 2004). During the process, the polymer structure of lignin is destroyed and turn into smaller fragments that is soluble in water or alkaline.

Factors such as fungi particles, temperature, moisture content, and pH of the wood can affect the process of delignification (Fonseca, et al., 2014) (Patel, et al., 2009).

By dissolving higher amount of lignin in the chemical liquor through chemical digesting, separation of the cellulosic fibers would be improved and would result in producing papers with high quality.

There are two types of chemical pulping based on the chemical used for delignification: sulphite pulping and kraft pulping (or sulfate). The primary product in sulphite pulping is calcium bisulfite. The combination of calcium bisulfite (CaHSO₃) and sulphurous acid (H₂SO₄) dissolve the lignin and produce individual cellulose. This method is flexible and strong and typically used in newsprint. The pulping chemical would be reused to regenerate solvent and energy recovery (Kramer, et al., 2009).

Problems with recovering the whole amount of chemicals used in the process, restrictions in using different types of tree, and pollutions issues are disadvantages of this process (Chakar & J.Ragauskas, 2004).

The widely used process in the chemical pulping is Kraft or sulfate process in which a stronger solvent is used in the digesting process. Kraft is a Swedish word which means “strength”. The chemical is a combination of an alkaline and sodium sulfate. With this process, a robust and strong pulp would be produced. Above the pulp strength, this process brings about many advantages such as, better chemical and heat recovery, a cost effective process, enganced digesting efficiency, added bleaching process which increases the pulp whiteness. Overall, with kraft chemical pulping, the produced pulp and papers have stronger structure than the pulp and papers generated by other methods (Chakar & J.Ragauskas, 2004).

The process of kraft pulping is firstly used in the 9th century. Kraft pulping is generally an alkaline pulping in which wood chips is digested in a liquor of combination of “hydroxide ions and hydrosulfide ions” like sodium hydroxide (NaOH) and sodium sulphide (Na₂S) (Chakar & J.Ragauskas, 2004).

The first step in kraft pulping is to steam wood chips and force out the trapped air. Then, the white liquor (a mixture of NaOH and Na₂S) is added to the wood. This combination is then cooked at elevated temperature of 160-170 °C in the digester for several hours until the liquor permeates the wood particles and dissolves non-fibrous materials in the wood such as lignin and extractives (Kramer, et al., 2009).

It is not possible to remove lignin selectively, so some other carbohydrates like hemicellulos is also degraded through the process. Normally, the removed carbohydrates and lignin in the pulping is approximately 50% (Fahlen, 2005).
In fact, the process of kraft pulping is divided into three main phases for dissolving lignin. In the first phase, the rate of lignin dissolution is slow while the carbohydrates loss is fast. The maximum temperature at this phase is around 150°C (Fahlen, 2005) Most of the lignin dissolution happens in the second phase. The carbohydrates loss is almost stable. Heating temperature is changed between 150-170 °C, however the digesting occurs at the max temperature (170°C). In the final phase which is known as residual phase, the delignification is slow (Fahlen, 2005). In fact, this phase starts when 90% of the lignin is dissolved. Selectivity in this phase is decreased, so continued pulping process can cause carbohydrates degradation. For example, the great quantity of xylene in the wood is dissolved in the white liquor (Fahlen, 2005). Still the remained amount of lignin which is typically around 5% is eliminated in the bleaching process (Smook, 1992).

![Figure 12 Different phases of delignification in kraft pulping (Fahlen, 2005)](image)

The reactions with respect to lignin in the chemical pulping can be divided into two groups: the first group of reactions which is desirable is degradation in which the lignin is broke into the fragments. The second reaction, on the contrast, causes the formation of substances which are alkali insoluble (Gierer, et al., 1987).

There are two types of digesters: batch digesters in which the cooking process is carried out on batch bases and continuous digesters where wood chips are cooked on continuous bases. Since the process steam is reused in continuous digesting, they are more energy efficient compared with batch digesting. They also require less labor force (Kramer, et al., 2009).
The hot pulp and used chemical is sent to low pressure blow tanks after cooking. The spent chemical which is called “black liquor” are washed from the pulp and sent to the recovery unit in order to be used as fuel in boilers. The produced pulp is brown in color and can be applied in cardboard production without bleaching process. However, for writing paper production, the next step would be the bleaching phase (Kramer, et al., 2009).

Different types of papers can be produced using both Kraft and sulphite pulping, while, kraft pulping has become the dominant process since it has some advantages over the other method. Application of different wood species in the process, stronger produced pulp, higher yield and high rates of lignin removal, and chemical recovery are some of these benefits. Because of inefficient chemical recovery and production of pulp with short fibers, sulphite pulping is mostly applied in production of special product like smooth papers (Kramer, et al., 2009) (Elaahi & Lowitt, 1988).

The combination of chemical and mechanical pulping creates another process which is called semi chemical pulping. In semi chemical pulping, that is mostly used for hardwoods, the wood undergoes a chemical digesting and then they changes into pulp by mechanical process (Kramer, et al., 2009) (Martin, et al., 2000).

**3.2.3 Chemical Recovery**

The main goal of this process is the recovery of white liquor from used cooking chemical or black liquor. The recovered chemicals is then reused in further pulping processes. The cooking liquor could be regenerated at a maximum rate of around 98% (Kramer, et al., 2009). With this, the cost of purchasing chemicals would be sharply reduced. Another advantages of chemical recovery is that the pulp waste which is removed from black liquor can be combusted in boilers in order to produce some portion of steam needed for pulping process (Kramer, et al., 2009).

The process of chemical recovery have four major stages: I) concentration of black liquor, II) combustion of used chemicals, III) re-causticizing, and IV) lime burning or calcining.

In the first step, the water is evaporated from the black liquor in order to increase its concentration and to enhance the solid content. This would increase the efficiency of recovery boiler burning. Due to the higher efficiency of multiple effect evaporators (for example seven effects), they are commonly employed to make concentrated black liquor (Kramer, et al., 2009). At this stage, the fuel value of the black liquor would increase to approximately 7000 Btu/lb (Biermann, 1996).

By combusting the concentrated black liquor, a great amount of steam requirement in pulping process is produced. For each increase of 5% in black liquor concentration above 65%, the thermal efficiency of boiler increases by 2%, so, the steam production grows (Kramer, et al., 2009) (Smook, 1992).
The third stage is re-causticizing process in which the molten smelt (predominantly is organic chemicals) removed from boiler is firstly combined with white liquor in order to make a weak solution called “green liquor” that consists of sodium sulfite (Na$_2$S) and sodium carbonate (Na$_2$CO$_3$). At the presence of calcium hydroxide, Na$_2$CO$_3$ available in the green liquor is converted to solid calcium carbonate- known as lime mud- and sodium hydroxide. Therefore, the green liquor is re-causticized.

In the final step, the lime mud is then heated in the kiln in order to produce CaO (lime) along with the liberation of Carbon dioxide. The produced lime can be dissolved in the water to generate calcium hydroxide which is used in other processes.

### 3.2.4 Bleaching

The bleaching process is to increase the brightness of the pulp. The kraft pulping generates pulp with color range from brown to cream. These pulps are usually employed in production of bags or cardboard boxes for groceries and other application that the color is not important. However, production of writing and printing paper require a bleaching process followed by the typical pulping before paper manufacturing process (Fahlen, 2005) (Kramer, et al., 2009).

In fact, the color of pulp depends on amount of lignin remained after pulping so that around 90 % of the color of pulp is affecting by the amount of residual lignin (Hartler & Norrström, 1969). Therefore, with bleaching the remained lignin in the pulp is removed through adding a non-fibrous substances to the pulp called fillers. The produced material which is mixture of pulp and fillers (called furnish) goes to the refining process unit (PrintWiki, 2016). As a widespread process, kraft pulping and the subsequent bleaching process consume chemicals like chloride a lot (Fonseca, et al., 2014). However, applied chemical in bleaching process varies based on some factors such as environmental regulations, desired properties of pulp, and cost.

Commonly used chemical in bleaching phase have been listed as follow:

<table>
<thead>
<tr>
<th>Bleaching chemical</th>
<th>Formula</th>
<th>Purpose of use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>O$_3$</td>
<td>This is an oxidizer used to eliminate lignin. Low selectivity to lignin. Must be used in low charges to prevent damaging pulp strength.</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>ClO$_2$</td>
<td>An oxidizer that destroys lignin with low impact on pulp strength.</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>NaOH</td>
<td>An alkali mixed with steam and oxidized pulp to transfer lignin such that the lignin can be extracted from the pulp.</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>Mixed with alkali and used under pressure to increase lignin extraction</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>HClO, NaOCl, Ca(OCl)$_2$</td>
<td>Typically used in sulfite pulping in order to destroy lignin. This chemical is phased out because of environmental concerns related to chloroform formation.</td>
</tr>
</tbody>
</table>

*Table 3 commonly used bleaching chemicals (Kramer, et al., 2009) ((DOE), 2005)*
The bleaching process is affected by the type of pulping process. For instance, semi chemical and mechanical pulping generates pulps with high amount of lignin. So, they require an intensive bleaching phase which the main focus is to decolorize the lignin. However, due to low lignin content in the pulp produced through chemical pulping, the remained lignin is totally removed in bleaching process.

The increasing demand for writing paper and packing material lead to strong expansion of pulping industries in different countries (Fonseca, et al., 2014). As one of the major industrial activities, pulp and paper production is the main consumer of lignocellulosic biomass resources, especially wood. This industry is also consuming great amount of electricity and water, therefore, it is main contributor to environmental pollution. The statistics for paper consumption in 2004 have shown that each person use approximately 52.45 kg of writing paper annually (Laftah & Rahaman, 2015).

### 3.2.5 Pulp drying and paper production

Before sending to paper manufacturing mills, the pulp should lose its water content to reach a dryness of 10%. Since pulp drying consumes significant amount of energy and it is not necessary to be done prior to paper production process, combination of pulping and paper manufacturing at one unique facility would decrease the energy consumption and increase energy saving. Such mill is called integrated pulp and paper industry (Kramer, et al., 2009).

Paper is produced through three main process; the first one is feedstock preparation in which the pulp is treated for paper making process (if it is needed). In the second stage known as “wet end”, paper sheets are formed. And in the “dry end” process as the final process, the papers are dried and the process finishes (Kramer, et al., 2009).

Papers produced from the pulp with uneven surface and low strength, have low quality. It means that paper would contain some gaps and it might be inflexible (Hartman & Higgins, 1983). In order to eliminate these undesirable properties and improve the quality of paper, a mechanical treatment or refining of chemical pulp is required (Fahlen, 2005).

### 3.3 Energy consumption in pulp and paper industry

In Pulp and paper industries, a great amount of money is typically spent on purchasing fuel and electricity. The electricity in pulp mill is usually used in motors, conveyor belts, and pumps along with other consumption such as ventilation and lighting systems. Boilers are the largest consumers of fuel in order to produce steam requirements. The main fuel in boiler is black liquor combined with natural gas and hog fuels. Natural gas and also oil are typical fuels used in the lime kiln (Kramer, et al., 2009) ((DOE), 2005). Around 45% of the purchased energy is consumed in paper and paperboard production units (Kramer, et al., 2009).
Hog fuel and black liquor are two by products which are mainly used as fuels in boiler in pulp and paper industries. More than 50% of the energy needs in pulp mill can be met by these by products. By this, the mill's dependency on purchased fuel and electricity is reduces. The added benefit is that cooking liquor can be reused, therefore, the need to purchasing raw material reduces and the lower waste is produced (Kramer, et al., 2009).

As it mentioned before, the recovered black liquor and hog fuel along with oil and natural gas are used in boilers for power and steam generation (Jacobs & IPST, 2006). In fact, the black liquor is burnt in recovery boiler which is used to generate steam for recovering white liquor for further pulping processes. Due to low heating value of these fuels, the efficiency of boiler is low around 65% ((DOE), 2005). Energy efficiency improvement by reducing losses and improving equipment is an initiative in order to reap great energy savings. For example, increasing electrical efficiency targeted at fans, pumps, and improvements to equipment using electricity (like boilers) can lead to lower energy demand (Kramer, et al., 2009).

It has been seen that the amount of energy consumption in pulp and paper industries depends on the type of pulping process. For instance, kraft pulping requires great quantity of steam and some fuels in the process of chemical recovery. Jacobs and IPST (2006) have estimated that production of kraft pulp consumes approximately 10-12 million Btu per ton in total. The consumption for mechanical pulp is estimated a bit lower around 11 million Btu per ton (Jacobs & IPST, 2006). Around two-thirds of energy needs for paper manufacturing is used in drying stage (Kramer, et al., 2009).

### 3.3.1 Greenhouse gas emissions

The associated greenhouse gas emissions with pulping processes can be found in: on-site fuel combustions, steam and electricity generated in the mill or transferred to it, and carbon dioxide emission released from chemical reactions occurred in kiln.

Energy efficiency improvements and reduction in fuel and generally energy consumption in pulp industry can significantly reduce the mill’s GHG emissions (Kramer, et al., 2009).

### 3.3.2 Improvements to energy efficiency in chemical pulping

Since chemical pulping processes use a vast majority of electricity, steam, and fuels especially at chemical recovery stage, improvements to energy efficiency in chemical pulping can lead to great saving in energy in the industry. The followings discuss the most effective measures for energy saving in kraft pulping and subsequent processes of bleaching and chemical recovery.
3.3.2.1. **Kraft Pulping**

Higher pulping yield is one factor in energy use reduction and energy efficiency improvement. Some aids can be added to the pulping process in order to make a better liquor penetration and improve the cooking procedure. By producing more pulp in such an efficient way, the energy consumption is significantly reduced per ton of produced pulp. This will also reduce the need for raw material such as chemical liquor and increase the productivity.

A suitable chemical penetration can reduce the cooking time. This will consequently lead to lower energy utilization and higher energy savings up to 125000 Btu per ton of feedstock. It is also reported that shorter cooking time increase the yield and reduce the reject factor and the bleaching chemical (Kramer, et al., 2009) ((DOE), 2005).

Another effective factor in energy saving is controlling the dilution factor. In fact, the used chemical solvent can be washed from the produced pulp. This will increase the chemical recovery level and at the same time minimize the black liquor dilution. Studies have been shown that optimizing black liquor dilution (by considering the cost of steam and controlling the amount of used water for washing at an optimum level in the last step of washing) reduces the amount of water to be evaporated from black liquor and consequently decrease the steam consumption in evaporators ((NCASI), 2001).

Digester performance is another factor which improving and controlling can lead to reduction in losses, environmental effects, and cost of process, whereas, the productivity and quality of pulp increase ((DOE), 2005). The performance can be improved by optimizing the chemical and thermal parameters in the process.

3.3.2.2. **Bleaching**

Conventional washing system in bleaching phase consists of four washing drums where water is sprayed on the fibers under vacuum pressure in order to wash out solids. In the improved system of washing, the vacuum pressure is replaced with wash or diffusion presses. Since this system needs less steam, power, and chemical for bleaching, it is more efficient compared to vacuum unit and results in higher solid removal (Kramer, et al., 2009) (Martin, et al., 2000).

3.3.2.3. **Chemical recovery**

Increase the concentration of black liquor is one action which is carried out during the chemical recovery process. The concentrator is designed to enhance the amount of solid in the liquor before it is combusted in the boiler (Kramer, et al., 2009). It is obvious that with higher solid
content in black liquor, less water is required to be evaporated in recovery boiler. Therefore, steam production efficiency will increase.

There are two commonly used types of concentrators: one is "submerged tube" in which the black liquor is heated by circulating through submerged tubes and the evaporation is done after flashing the liquor to the concentrator. Another type is falling film which is more stable to fouling and this will allow the evaporator to produce highly concentrated liquor (Kramer, et al., 2009) (NCASI, 2001).

3.3.3 Emerging technologies in energy saving in pulp and paper industries

New technologies related to pulp and paper industries are cumulatively developed and evaluated. With some of these technologies it is possible to provide energy saving as well as water saving, high reliability, higher product quality, and improved efficiency.

For example, gasification of black liquor is one the recently emerged technologies which refers to syngas production from black liquor through converting the bio material content available in the liquor. Syngas and also produced energy carriers can be then used in steam processes. Still this technology is under research and development (Kramer, et al., 2009).

Removed lignin in the modern kraft pulping mill can be used as a source of energy. Production of biofuels through lignin conversion has become an attractive action among pulp and paper industries (Kramer, et al., 2009). Still, researchers is trying to re-engineer the current pulping process in the future into the biorefiner. In fact, a biorefiner is a modern paper mill where energy and chemical feedstock as basis for bio materials will be produced together with paper (Enari, 1994). In such modern mills, lignin as a bio resource is utilized for the combining renewable, bio polymer complex, and biofuels (Chakar & J.Ragauskas, 2004).

Another new technology is the utilization of green liquor in wood chips pre-treatment. Since the amount of hydrosulfide ions in the green liquor is high, it can be used to accelerate the pulping process. Therefore, the pulping yield and the pulp quality increase using lower energy. This technology is applied in pulp mills in Finland (Kramer, et al., 2009) ((DOE), 2005).

Near infrared spectroscopy is a recently emerged technology with which the properties of wood chips as well as properties of pulp could be analyzed. This technology is currently employed in different industries and it has become an attractive technology among researchers.

Prediction of wood properties contributes to higher control on process of chemical pulping and will result in more consistent result (for example, lower variation in Kappa number). This will consequently reduce the energy use especially in chemical recovery. In the next section, principals of this method is briefly presented.
3.3.4 Near Infrared spectroscopy (NIR)

In order to utilize the lignocellulosic materials such as wood, corn stover, wheat, and other forest and agricultural materials in the production of cellulosic bio products like paper, it is important to analyze their chemical compositions. Lignin is one of the abundant renewable sources and around 15% to 25% of the lignocellulosic material is lignin (Kline, et al., 2010).

In paper and pulp industries, the quality of pulp depends on many different parameters such as type of wood used, chemicals, beaters, etc. It is sometimes impossible to measure all these parameters in the laboratories (Metrohm NIR System, 2016), however, those factors which would affect the pulp quality is mostly measured.

Advancement in method of spectroscopy and analysis of pulp with reflectance spectrometry have proved that this method is the most reliable and rapid technology in determination and estimation of biochemical properties of forest plants and foliage (McLellan, et al., 1991). With this method, it is possible to get insights of different processes like chemical pulping. Indeed, predicting the composition of biochemical in forest foliar can contribute to increase the knowledge about different processes at small to big scales by providing remote identifying techniques (Soukupova, et al., 2002) (Peterson, et al., 1988).

The basis of spectroscopy is to rise the vibration of the molecules of the substance at the specific wavelength. The absorption band of many plant compounds occur in the mid- infrared region. However, the overtone of each constituents are different and it is sensitive to changes in environmental conditions of absorbing molecules (Soukupova, et al., 2002). According to (Zwiggelaar, 1998), the overtone normally happens in the near infrared wavelength. As a result, the near infrared region is generally accepted as the most useful absorption band to determine the chemical compositions of different substances (Soukupova, et al., 2002).

The near infrared (NIR) reflectance is generated by doing 1 or 32 or 50 separate scans and the final spectra represents an average of all scans per sample. Then, the absorption statistics are converted to the reflectance data using the following equation\(^1\) (Soukupova, et al., 2002):

\[
R_f = 10^{Ab}
\]

Where:

\(R_f\) : reflectance

\(Ab\) : absorption

\(^1\) This conversion was not done in this project and results kept in absorbance. The measure in this study is called relative absorbance.
The amount of lignin, proteins, sugars, cellulose (McLellan, et al., 1991) and composition of some elements like nitrogen can be determined from spectroscopy in the near infrared spectral region. The calculations and equations for predicting the composition are usually done according to the empirical experiments or setting (linear) regression model (Soukupova, et al., 2002) (Fourty & Baret, 1998).

The process of pulping of wood involves digesting of the wood particles in the presence of chemical liquor like alkaline solution at high temperature and pressure. The lignin is dissolved and the cellulosic fibers are released and form the pulp. The yield in the pulping process represents the amount of removed lignin through pulping. So, the goal is to achieve a high yield in the process (Raymond, et al., 2001).

The presence of lignin in the produced pulp can affect the quality and flexibility of the end-use products, therefore, determining the quantity of lignin in the feedstock as well as the final produced paper is of importance. In this study, the focus is on finding the lignin content in the wood used as feedstock for pulp production. Due the complex structure of lignin polymers, it is difficult to measure the exact amount of lignin (Metrohm NIR System, 2016).

There are some methods like wet chemistry but it is time consuming and sometimes erroneous. It is also restricting the number of samples that should be analyzed. As a result, the method of near infrared (NIR) spectroscopy is one of the most useful, cost effective, and accurate alternate techniques which is recently developed in determining the lignin content in the wood (Metrohm NIR System, 2016). The absorption of spectra by lignin is stronger than cellulose and hemicellulose, so the spectroscopy is an attractive method for specifying the lignin content of biomass (Kline, et al., 2010). By the spectroscopy, the lignin concentration can be found using the absorbance peaks in the specific wavelength (Metrohm NIR System, 2016).

In order to analyze the data from NIR method, a calibration model should be built based on the result of NIR spectroscopy on a great number of samples and the known lignin content in the wood obtained by doing the chemical experiments. In fact the model relates the NIR results and the measured lignin content. Then, with the model based on the wavelength, the lignin content of further new and similar samples can be predicted (Raymond, et al., 2001).

It is also possible to analyze other parameters such as the kappa number and the yield of pulping process using the same procedure. With all this information and predicting different parameters, the production capacity would increase; moreover, the pulp quality would be improved (Avelin, et al., 2009). This subsequently contributes to have a good control on the pulping process.

In order to quantify the lignin content in the lignocellulosic materials, a laboratory instruction has been developed by National Renewable Energy Laboratory (NREL). This method is commonly used as a standard for determination of lignin in woody biomass (National Renewable Energy Lab NREL, 2008). (The method was explained in 2.2.3.4). Using this protocol have some issues like safety issues of working with concentrated acid and error driven by transferring biomass particles between dishes.
Therefore, NIR spectroscopy is a safe method which is recently used to assess the biochemical properties of different type of biomass. This method have been mostly used as the most rapid and safe approaches to determine the amount of lignin in lignocellulosic biomass (Kline, et al., 2010) (Hatfield & Fukusshima, 2005). However, it is also applicable in evaluating different material in forest products, bioenergy plants, pulp and paper industries, and heat treatment units (K.Via, et al., 2014).

4 MODELING

The quality of produced pulp and paper is mostly controlled in laboratories, where majority of tests like wet-chemistry experiments are complicated to find chemical properties of products. Some of lab experiments consume time and require more technicians’ attention. This will probably increase the experimental errors that can subsequently affect the measured quality of end-products (H.Bharati, et al., 2002).

In the wet chemistry method, as one of the quality control tests, pulp and paper samples are dissolved in an acidic or alkaline liquor before analysis. Therefore, this method could be destructive to the samples. As a result, to determine the chemical properties of the pulp and paper end-products, multiple samples need to be experimented in the lab (H.Bharati, et al., 2002).

Due to the mentioned problem with the wet-chemistry method, pulp and paper industries is searching for a reliable technology with which the quality of pulp and paper could be rapidly tested and at the same time, they provide the properties of products from one unique sample without destructive reflects (H.Bharati, et al., 2002).

Among various introduced technologies, application of NIR spectroscopy along with using chemometrics methods have shown a satisfactory result in characterization of different samples and products in different industries including food, chemical, pulp and paper, and pharmaceutical industries (H.Bharati, et al., 2002).

Many pulp and paper mills in many countries have invested a great amount of money on employment of NIR technology in order to analyze pulp and paper quality. All samples in the different phases of vapor, liquid, semi soil, and solid can be analyzed through NIR technology with no special preparation (Wold, et al., 1998). The speed and flexibility provided by this method, contributes to rapidly analysis of end-products with no destructive effects on samples. This features have made NIR technology quite attractive among researchers and industries especially in the forest products manufacturing industries (H.Bharati, et al., 2002).

Different regression models can be used in multivariate analysis of NIR. Principal Component Regression (PCR) and Partial Least Square regression (PLS) are two commonly used techniques in multivariate data analysis such as data from NIR spectroscopy and it finds an strong covariance between spectra and the reference values. In PCR method, the model is
developed based on the X data matrices and Y data matrix is not considered in interpretation. However, both X and Y data matrices are considered in PLS technique in order to find the covariance between them. This contributes to higher value of $R^2$ in calibration model and improved covariance between X and Y matrices (K.Via, et al., 2014).

PLS regression model is majorly chosen for developing a prediction model for the empirical data. The reason is that this method is able to analyze large sets of correlated NIR spectral data (H.Bharati, et al., 2002). After the PLS model is built, it can be used to predict the constituents of wood or pulp from new NIR spectral data of further samples (H.Bharati, et al., 2002).

Antti et al. showed the application of NIR spectroscopy in prediction of Kappa value in the pulping process. Many other researchers have developed NIR calibrations used together with chemometrics methods in order to estimate the pulp yield, lignin content, cellulose content, etc. (Antti, et al., 2000). Almost all developed predictive model by NIR calibrations have resulted in successful estimation (S.Poke & A.Raymond, 2009). Yet et al., for instance, measured the lignin content and hardwood content in bleached and unbleached pulp respectively (Yet, et al., 1990) (H.Bharati, et al., 2002).

Over the recent decades, NIR calibration methods have been used as a suitable substitute to traditional costly methods like wet-chemistry and it has become such a cost-effective and rapid tool that can reliably predict the important wood chemical properties (S.Poke & A.Raymond, 2009).

As is mentioned earlier, in this research, a predictive model was developed using NIR spectra of wood chips attempts to estimate the lignin content, moisture content, and the pulp yield. The analysis is done using PLS regression model. All spectral data have been measured from the wet wood chips surfaces and then, the correlation between NIR and wood chemistry has been developed using a multivariate data analysis in Unscrambler ®. Thickness, shape, and craggy surface of wood are some factors that affect the spectroscopy resulting in prediction errors. In order to control the variation and improve the prediction, data pre-processing is required prior to the modeling. Pre-treatment of raw NIR spectral data results in increasing the R-squared in calibration, however, it probably changes the accuracy of the modeling (K.Via, et al., 2014).

4.1 Data preparation

The first step in the multivariate calibration is data pre-treatment. NIR data pre-processing prior to developing the regression model is vital in order to smooth the noises in the spectral data and remove the undesired variation. This variation could be due to differences in the path length in spectroscopy and light scattering especially for solid samples (Wold, et al., 1998). It also happens as a result of absorption in small spectral part. NIR data pre-treatment is known as “spectral filtering techniques”. Multiplicative Signal Correction (MSC), Standard Normal Variate (SNV), Savitzky-Golay technique, and Orthogonal Signal Correction (OSC) are some of the commonly used spectral filtering methods (H.Bharati, et al., 2002). The main approach in all of these techniques is to filter the NIR data to increase the predictive potential of Spectral
data used in developing the regression model (H.Bharati, et al., 2002). This may also remove some information of measured reference variables (Wold, et al., 1998). In fact, improvements in covariance between X and Y could shift the wavenumbers and consequently cause inflation in the “Peak”. Therefore, the model implemented by PLS method might be suitable for prediction but it may has low accuracy (K.Via, et al., 2014). Looking at the score plot after developing the model, the undesired variations in data can be somehow figured out.

The spectral data from solid wood chips which were collected from the conveyor belt from the mill and also ground wood were used in calibration. Wood chips were scanned six times over the Near Infrared wavelength ranging from 12000 cm⁻¹ – 4000 cm⁻¹ for 32 scans in a single operation. The average value is then calculated in the process. For calibration, one of the recorded NIR spectra out of six was randomly selected. The model developed using the NIR for the ground wood did not provide good predictive results, therefore, all models were developed using the spectral data recorded for solid wood chips.

The lignin content is measured in laboratory using the standard protocol mentioned earlier in methodology section. All samples are tested for moisture content, also pulping yield of 18 samples is determined by delignification treatment conducted at Karlstad University. All these measurements were used as the reference data for calibration.

The common applied pre-processing method is first and second order derivative using Savitzky- Golay smoothing technique which eliminate the band overlapping. The offset variance between data and independent points to the wavelength is removed in the first derivative, while, in the second order derivative wavelength dependent data and any slope effect on the data is furthermore removed (Kong, et al., 2015) (Rinnan, 2014).

In this study, several filtering techniques including Savitzky Golay first and second order derivative with 25 smoothing points and second order polynomial approach, MSC, SNV, and OSC were applied to the NIR data. The subsequent PLS models showed that OSC approach gives the best predictive model with high correlated X and Y data and provides higher regression coefficient value than ones developed based on MSC or Savitzky-Golay basis data. All results are presented in detail in the result section.

4.1.1 Orthogonal Signal Correction (OSC)

One technique of data pre-processing is to remove some of the spectral data from matrix X which is not related to the response matrix (Y) and is irrelevant to the analysis. However, it should be guaranteed that the filtered data from matrix X is orthogonal to Y or close to it as much as possible. This approach is called orthogonal signal correction or OSC and it is proposed by Wold et al. (Wold, et al., 1998) (H.Bharati, et al., 2002). It is mostly possible to apply the OSC approach when the number of calibrating samples is lower than number of variables in Matrix X. So, an orthogonal solution could be found (Wold, et al., 1998).

In this filtering technique, the unrelated components to Y is removed from matrix X, therefore, the model Y will be developed better using the remained related components (Wold, et al., 1998). In fact, X variables are filtered to minimize the covariance between X and Y such that
the OSC components are orthogonal to Y. By this, OSC components contains data with undesired X variations and filtered matrix contains all spectral data with variations of importance related to the response matrix Y (H.Bharati, et al., 2002).

When the Matrix X has no information about response matrix Y, it might result in a good treated data sets, however, the subsequent PLS model converges towards multiple linear regression (MLR). MLR solution has shown an over-fit with multivariate X data, so it is not recommended to apply OSC and PLS method if many OSC components are selected (Wold, et al., 1998). According to Wold et al. the number of allowed OSC components should be a small fraction of minimum of X variables and number of training samples. This will reduce the risk of spurious relation between filtered X and Y (Wold, et al., 1998).

Evaluation of spectral data treated by OSC method reveals that this technique gives lower Root Mean Standard Error of Prediction (RMSEP) values in the developed PLS model compared with the model developed using raw NIR or MSC data. This will result in providing a simpler model (Wold, et al., 1998).

All unwanted noises in the spectral data is removed though OSC filtering and the information about wood chemical properties which are mostly relevant to the pulp quality are increased.

The removal OSC components was set to maximum 3 components in order to avoid removing too much systematic important variations. It is possible to improve the correlation between matrices X and Y by removing more OSC components, but those components might be the most correlated with Y, however, they are noisy. Therefore, it is recommended to remove at most two OSC components from matrix X (H.Bharati, et al., 2002).

Using the NIR spectra without pre-treatment would include the information which is not useful in the calibration or it is not related to the response variables. In fact, noises and undesired variations in NIR spectra cause systematic errors or provide some information which is not of importance in analysis (Rinnan, 2014). This would result in developing an unreliable model for predicting the properties of further samples (Wold, et al., 1998).

4.2 Chemometrics on spectral data

Data pre-processing and the PLS models were constructed in Unscrambler® V10.3. Five spectral data sets related to Acid Insoluble lignin (AIL), Acid Soluble Lignin (ASL), Total Lignin content, moisture content, pulp yield, and Kappa number are pre-treated using OSC method which resulted in the lowest RMSEC value.

Several models were executed based on raw NIR, first derivative, MSC, SNV and treated data by Orthogonal Signal Corrections (OSC). Data pre-processing was conducted prior to PLS modeling.
All 68 samples were used in model construction for moisture. Fifty samples were used for building the model and the rest was used for model validation.

Since some samples were destroyed during grinding and/or lignin determination in laboratory, some spectral data were excluded from the dataset used for lignin calibration. Moreover, due to some overestimations in lignin content, nine samples out of 55 samples were also removed from dataset. Therefore, 46 samples were analyzed for lignin model construction. Then, forty samples out of 46 were considered for calibration and 6 samples were applied for validation. The calibration and validation datasets were selected randomly.

For NIR calibration regarding pulp yield, 18 samples, which their yield was measured in the lab, were considered as the response dataset in analysis with 12 samples for calibration and 6 samples for validation. Laboratory measured values are available in appendix in this report.

A model was also developed for pulping Kappa value, which was measured for 18 samples after digesting experiments. Due to the experimental errors, 6 samples with overestimated Kappa number were excluded to get a better calibration model. Therefore, 12 samples were used for Kappa value calibration with the testing set of 9 samples and validation of 3 samples.

All spectral data used in calibration was collected 6 times from each of the samples, while, in modeling, only one of them is used as employment of replicate data did not correlated with the reference values.

After modeling, the predictive performance of the model was assessed considering the regression coefficient ($R^2$), Root Mean Square Error for calibration set (RMSEC), and the Root Mean Square Error of Prediction (RMSEP).
5 RESULTS

Prediction results of different developed models are presented in this section. Several filtering methods were applied in order to correct spectral signals. Each of these techniques improved the model by filtering out the undesired variations and noises in the spectra information, however, the OSC approach provided the best correction in data. To illustrate, Figure 13 shows the difference between raw NIR and OSC treated data regarding moisture content. By employment of OSC method, all variation in spectra which was independent to the reference value was removed such that NIR (matrix X) is orthogonal to matrix Y as much as possible.

![Figure 13 Comparison between raw NIR and OSC treated spectra regarding moisture content](image)

5.1 Calibration results

The results of all calibrations illustrated in this section.

5.1.1 Moisture

Moisture calibration was primarily done including 40 samples in calibration set and 28 samples in validation set (Models not included). Due to very poor prediction results, a larger calibration data was applied to improve the model. Prediction of moisture content using first derivative of spectral data for 50 samples was poorly correlated with the laboratory measured values with an R-square of 0.059 and root mean error of 3.04, see Figure 14.
Using data processed with SNV technique has given approximately the same model as 1st derivative calibration with a slightly higher R-square of 0.092, as it is shown in Figure 15. The only difference between these two models is that the sample 1076 (containing 10% saw mill wood) is excluded from the calibration since it was outlier. With this the prediction was slightly improved, however, still it is poorly correlated with the reference value.

The best prediction of moisture obtained doing the calibration of OSC treated spectra of 50 samples. The prediction of moisture through this trait is moderately correlated with R-square
of 0.529 and RMSE of 1.619. As the graph shows, the predicted moisture values were well fitted with the reference values. Yet again, Sample 1076 was excluded from the calibration set as it was outlier. Despite the roughly good correlation coefficient for moisture OSC model, regression showed the lack accuracy in prediction due to the low value of X multiplier (0.538). For the accurate prediction the multiplier of X should be 1 or close to 1.

![Graph](image)

**Figure 16** Relationship between measured and predicted moisture content based on the OSC filtered NIR

Evaluating the graph for regression coefficient reveals the wavelength of interest in calibration the moisture content. The important absorption band regarding moisture could be seen in Figure 17.
Figure 17 Regression coefficient with specified wavelength of interest for moisture calibration

5.1.2 AIL

The model was developed for prediction of acid insoluble lignin content using first derivative treated data reveals such a good correlation between predicted and laboratory lignin content that the regression is 0.731 with the RMSE of 1.711, see Figure 18. However, lignin content predictions were either over or under estimated for some samples. Moreover, some samples including 1060, 1077, 1073, 1054, 1084, 1075, 1086, 1063, 1070, 1068 (see Appendix 3, quick identification column) were excluded from the calibration set since they outliers and their performance in calibration was not satisfactory. Removing spectral data for 11 samples from calibration could destroy relevant data which would be important for calibration. Therefore, the accuracy of the model may decrease.
As Figure 19 shows, prediction of acid insoluble lignin content was highly correlated with OSC treated spectra with R-square value of 0.92 and RMSE of 0.965. The X multiplier is 0.913 and it shows the high accuracy of the model. To improve the calibration 2 samples (1070 and 1086, see Appendix 2) should have been excluded as they were not performed like other samples (The reason is discussed in detail in the following section). For some samples, the prediction was not fitted the reference value and it showed over or under estimated results. However, the accuracy of the model outweighs the small overfitting results, so, the AIL model based on the OSC treated spectra is the best developed calibration indicating that the majority of lignin content predictions were almost close to the reference values. This can be obviously seen in the graph in which the regression lines for calibration and validation sets are shown as well as the target line.

Figure 18 Relationship between observed and predicted AIL based on the 1st derivative filtered NIR
5.1.3 ASL

Calibration regarding acid soluble lignin using raw NIR did not show any relationship between the predicted lignin contents and the laboratory values. Although, application of MSC, second order derivative, and OSC treated NIR in calibration slightly improved the model, still the prediction for acid soluble lignin content were over/under-estimated (Figure 20). Different employed filtering techniques on NIR spectra regarding moisture content resulted in roughly the same calibration models with R-square values of 0.082, 0.08, and 0.077 for second derivative, MSC, and OSC models, respectively.
Figure 20 Relationship between observed and predicted ASL content a) based on the 2nd derivative treated NIR, b) MSC treated NIR, and c) OSC treated NIR data
5.1.4 Total Lignin content

Prediction of total lignin content for 40 samples using MSC treated spectra was poorly correlated with R-square value of 0.053 which indicates that the accuracy of model is very poor and lignin contents were generally under-estimated.

![Figure 21 Relationship between measured and predicted total lignin content based on the MSC filtered NIR](image)

Treating data using second derivative basis spectra along with excluding outliers, samples 1058, 1075, 1086, 1077, 1083, 1063, 1094, 1060 provided a better model with R-squared value of 0.389 and x multiplier of 0.49. Still the prediction is over fitted, however, the correlation was improved compared to MSC model.
Employment of OSC de-noising method slightly improved the prediction and resulted in an increased regression coefficient of 0.89. To improve the model, some samples (1069, 1077, and 1086) which the calibration and validation values significantly differed were removed from the data set. The predicted results versus the reference value for Total lignin content is illustrated in Figure 23. The target regression line is also shown in the figure.
Pulp yield was also calibrated with the OSC treated spectral data from solid wood NIR spectroscopy. Prediction of pulp yield for 18 samples showed a good correlation with the laboratory measured data. The predicted value of pulp yield was quite close to the corresponding value. A high value of 0.85 for R-square and RMSE of 1.82 were obtained for the calibration of pulp yield.

![Graph showing relationship between measured and predicted pulp yield](image)

**Figure 24 Relationship between Measured and the predicted value of pulping yield based on the OSC treated NIR**

A calibration model was also executed for pulping Kappa number in which the prediction of kappa values of 9 samples was exactly fitted the laboratory measured data with R-square value of 0.998 and the RMSE of 0.195, see Figure 25. Prior to PLS modeling, data was treated using OSC approach. As it is mentioned earlier, samples with undesirable results were excluded from data set. In fact, removing the overestimated kappa numbers significantly increased the accuracy and R-square value of the calibration model.
Figure 25 Relationship between Measured and the predicted Kappa number based on the OSC treated NIR

Statistics for all calibration model except ASL have been generally summarized in Table 4. The best NIR calibration model achieved for Kappa number of pulp with high R-Square value of 0.998 and low calibration error of 0.196.

Table 4 Summary of cross validation for different wood traits

<table>
<thead>
<tr>
<th>Component</th>
<th>Number of factor</th>
<th>$R^2$</th>
<th>SEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>2</td>
<td>0.52</td>
<td>1.636</td>
</tr>
<tr>
<td>AIL</td>
<td>5</td>
<td>0.92</td>
<td>0.977</td>
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<tr>
<td>Total Lignin</td>
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<td>2.128</td>
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<tr>
<td>Yield</td>
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</tr>
<tr>
<td>Kappa number</td>
<td>7</td>
<td>0.998</td>
<td>0.196</td>
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</table>
6 DISCUSSION

The evaluation of results of this research is done in this section. First, the structure of raw wood chips and the process of NIR calibration were analyzed. Then, the research questions were answered to present the correlation between NIR spectra of wood and pulping results as well as the possibility of controlling the pulp quality using NIR information.

6.1 Evaluation of feedstock structure

Samples collected from the BillerudKorsnäs mill in Gävle were used in this study to find the connection between chemical properties of wood and its spectra in NIR range of wavelength. The aim was also to develop several models with which the lignin and moisture content of wood chips, as well as pulping yield and pulp Kappa value would be predicted. By this, the process of pulping is probably controlled.

As is explained earlier, a mixture of raw wood chips and wood chips from saw mill with ratio of 50-50 is used as the feedstock for pulping process in the mill. Wood logs in saw mill are also from the same tree type as the raw wood used in the mill. In other words, both are softwoods from pine tree, so, the mixture of them would have the similar properties as when they are used separately. The only difference between them is the size of wood particles, such that, the size of saw mill wood chips is smaller than the chips provided in the mill, as it is expected.

The results of cooking in the mill sometimes show variations in Kappa number of produced pulp. One possible reason would be the existence of bark particles in wood flakes coming from saw mill. Another reason may be the difference in size of wood chips, since it is obvious that smaller particles would have efficient pulping results. Therefore, the wood chips contained different percentage of saw mill wood flakes from 50 to 0 percent were collected from the conveyor belt. The samples were collected every one hour with reduced percentage of saw mill chips each time, in order to see if wood chips from saw mill could affect the cooking process.

Evaluation of experiment results reveals that the increasing or decreasing the portion of saw mill wood flakes in the feedstock did not change the amount of lignin in raw material. Considering models developed for lignin and the pulp yield, neither saw mill wood chips nor time of collection considerably influence the process of pulping. For instance, lignin content for wood chips including 50% saw mill flakes and sample with 0% saw mill wood chips were calculated 33.865% and 34.58%, respectively. This indicates that wood chips from saw mill mixed with raw woods have similar structure, meaning that they are both softwoods. So, saw mill wood chips could not be the cause for rarely fluctuations in the pulp Kappa value.

6.2 Analysis of NIR spectroscopy for solid and ground wood

As is explained in the methodology section, spectra of all samples were recorded over the NIR wavelength range from 12000 cm\(^{-1}\) to 4000 cm\(^{-1}\) in both static mode and moving with the
velocity of $1 \text{ m/s (or 181 rpm)}$ with rotating the dish between each scans. This was repeated six times for each of unique samples in both types of solid and ground wood. Indeed, the reason for recording the spectra of ground wood was that it was expected spectroscopy on the fine wood mill can reduce the variations observed in the spectra of solid wood. As a results, the needs for baseline shift in the spectra prior to building model development would be reduced. However, employment of NIR from ground wood in calibration resulted in a model that was poorly correlated with the reference value.

The spectral data from solid and ground samples are different since cell wall polymers at different angles is involved in the spectra taken from the wood mill. While, in the spectra of solid wood, the cell wall polymers are at the consistent angle (S.Poke & A.Raymond, 2009). Moreover, it seems that the spectra from wood chips is more representative for determination of moisture content in the wood rather than the ground wood NIR. Therefore, the NIR spectra collected from solid wood was employed in all calibration models in this research. Calibration of solid wood NIR suitably worked for predicting different parameters, especially lignin content.

The NIR spectroscopy on solid wood is also known as the cost effective and rapid predicting tool (S.Poke & A.Raymond, 2009). Despite the advantages of the calibration using solid wood spectroscopy, there are types of research about application of NIR on solid wood for calibration model development. As Poke et al. claimed in their research this may be because of the non-homogeneity of solid wood. This limits the use of reflectance measurement on the wood due to restricted penetration depth to the solid wood (S.Poke & A.Raymond, 2009). Non homogeneity in wood causes significant variation in the collected spectra and increase the dependency of spectroscopy on sample preparation and its size (S.Poke & A.Raymond, 2009).

Due to good performance of NIR spectra in predicting physical and chemical properties of both hardwood and softwood, this method is still used especially for solid wood in order to develop the calibration model for prediction (S.Poke & A.Raymond, 2009).

### 6.3 NIR Calibration

This study represented that calibration of NIR spectral data can be developed for prediction of moisture and lignin content of solid wood chips with relatively high accuracy. The goal in calibration is too achieve a model with low error and high regression coefficient.

Different data treatments were done on the NIR data prior to the main calibration in order to eliminate the unwanted variations or noises, which reduce the accuracy of the model. Pre-treating the NIR data using first derivative method through Savitzky Golay technique resulted in a better PLS model that the model developed based on raw NIR. To illustrate, the score plot of the PLS model developed for total lignin from raw NIR spectra and the model after pre-treating (with second derivative and OSC method) is compared in Figure 26.

According to the figure, the model created with raw NIR shows poor stability (plot a), while the stability of model has been significantly improved by treating NIR data using Savitzky Golay
method (plot b). The last model (plot c) developed using OSC treated spectra indicates the highest stability.

Figure 26 comparison between the stability of models developed using a) Raw NIR, b) Second derivative basis NIR, c) OSC treated NIR
The models developed on the basis of first derivative NIR data indicates a better calibration results compared with the case that raw spectra were applied in analysis. In fact, pre-processing using the 1st derivative resulted in a better predictive model with higher value of regression coefficient and lower standard error of calibration. First derivative pre-processing method contributes to the removal of unwanted baseline shifts, so, the PLS coefficient graph is intensively improved (K.Via, et al., 2014).

Although the score plot of samples indicates a good stability, this method is not suitable for prediction because of the low value of regression coefficient.

The second order derivative correlation was also better than the correlation resulted from the raw data. However, the value of R-square was not satisfactory. The model for total lignin was developed using second derivative based NIR spectra, but the results showed no significant changes neither in prediction error nor R-square value, see Figure 22.

Both MSC an SNV pre-treating methods improved the spectra repeatability, however, they have impacts on the distribution of spectral data and cause interference on NIR information. Calibration regarding acid soluble lignin and total lignin content developed using MSC treated spectra information indicates a good correlation between predicted and response data, while the regression coefficient and the calibration error was not acceptable for a predictive trait.

Generally, the best calibrations for all traits except ASL were developed using OSC treated NIR data, which subsequently provided a good PLS model with lower calibration error and higher R-square value compared to other filtering technique applied in this study. A comparison between filtering techniques applied to each model has been illustrated in Figure 27.
According to the figure above, OSC method resulted in lower calibration error and higher R-Square value rather than other techniques. In fact, the OSC method gives significant improvements to all models developed based on the original NIR spectra, except ASL. There is almost no difference between the ASL models developed using various de-noising techniques.

Score plot of the OSC model showed a good stability of data as well as a relatively high prediction capacity of the model such that the validation data sets is generally well fitted with the calibration set. However, the comparison between the predicted value and the
reference measured value represents over-fitting for some samples; the high R-square value and also model’s accuracy outweigh the negative effect of the over-fitted results.

6.4 Prediction of chemical properties of wood chips using NIR calibration

The results of this study prove that the NIR spectroscopy of solid wood and its further calibration could provide a model with which the chemical properties of wood chips such as lignin and moisture would be predicted with remarkable accuracy. This technology is being used in different industries with different purposes. Of all, NIR calibration is the most feasible technology used in pulp and paper industries in order to estimate the lignin content of raw wood chips moving to the digesters.

In this study, models for prediction of several properties of wood chips including Acid Soluble Lignin (ASL), Acid Insoluble Lignin (AIL), Total Lignin, Moisture content, and pulping yield were developed using NIR spectra of solid wood. Developed calibration models showed different calibration errors and accuracy. In other words, the pre-processing data using different techniques resulted in calibration with various prediction capacity and accuracy. This indicates that NIR calibration is unreliable method for estimation.

6.4.1 NIR calibration for lignin content

As the results revealed, models could be developed for predicting the lignin content using the OSC treated NIR information. In order to increase the accuracy of the model, nine samples out of 54 samples were removed from the calibration set because of the over-estimation in their laboratory measured lignin contents.

The model developed for AIL (Figure 19) represents that the prediction of lignin content using OSC treated NIR is highly correlated with the reference values with high value for R-Square.

As it discussed earlier, lignin polymer has very complex structure, so, it is difficult to determine the exact amount of lignin in the wood. As a result, the error in the built model might be due to errors in lignin determination in the laboratory as well as the experimental errors. To increase the regression coefficient of the model, two samples with undesirable results (1070 and 1086) were excluded from modeling. In fact, the predicted AIL for these two samples were poorly correlated with the real measured value.

Still, there are over estimation or under estimation for some samples, however, the slopes of the regression lines for calibration and validation are close to the slope of the target line. The stability of model is also high compared with other developed model. Therefore, AIL content of softwood can be predicted by the developed model below:

\[ Y = 0.913X + 3.093 \]
Where X is the wavelength at which the carbon-oxygen and carbon-hydrogen connection in lignin polymer stretch and the molecule vibrates. According to the results of this study, the important wavelength range for prediction of lignin is from 5500 cm\(^{-1}\) to 4200 cm\(^{-1}\).

ASL calibration represented unsatisfactory results since the correlation between NIR and measures data is poor.

Unsuccessful calibration regarding ASL may be because of small variations in laboratory measured values of ASL. Also, response dataset contains small numbers, such that the maximum value of measured ASL is 2.462. The complexity of lignin polymer is another possible reason for not getting the satisfactory results for ASL model. Samples may contained 2 or 3 different types of lignin polymers. It is possible to improve the calibration results by grouping data with similar laboratory results and calibrating each groups of data separately; however, this could not be possible in this work due to small number of sample.

Incorrect measured laboratory values could be another reason that a reliable model was not achieved for ASL prediction. According to the results for this trait, different filtering techniques provided similar models with approximately the same prediction error and R-Square value, see Figure 27. It indicates that the reference method is probably in correct, therefore, this calibration could not be dependably used to predict the acid soluble lignin content of different samples.

The same procedure was done for total lignin. The model was developed using OSC processed spectra. By excluding samples 1069, 1077, and 1086, which their results were outlier in the calibration model, the prediction error reduced and a relatively good model was achieved with high value of R-Square f 0.89. As a results, the following relation could be used for total lignin prediction:

\[ Y = 0.913X + 3.049 \]

Where X is ranging from 5500 cm\(^{-1}\) to 4000 cm\(^{-1}\).

Models developed for AIL and total lignin shows the same X multiplier and approximately same offset values. This means that the great part of the lignin available in the wood structure is acid insoluble lignin and acid soluble lignin content forms small portion of lignin content in the wood. This can be also found from the laboratory determined lignin content.

### 6.4.2 NIR calibration for moisture

Three model for moisture were developed using MSC, SNV, and OSC treated spectral information. Although the OSC model resulted in better prediction and correlation of all, still the accuracy of the model is poor and the R-Square value is not satisfactory. The following relation obtained for moisture content prediction:

\[ Y = 0.538X + 25.483 \]

Low value of X multiplier indicates that the regression line of calibration is not on the target regression line, therefore, predicted values by the constructed model is over-fitted the response.
moisture values and it subsequently shows that the model is not reliable for predicting the moisture content.

The reason might be the low amount of data or the high moisture content of wood chips. Generally, softwoods contain up to 35% of moisture in their structure, however, the mean value for moisture content found in this research is 55%. The calculated moisture content of sample 1076 was 42% which was very low compared with other determined values. So, this sample was not considered in the process of modeling.

In all developed models for moisture, the important wavelength in determination of moisture were 5300-5200 cm\(^{-1}\), 7300-7100 cm\(^{-1}\), and 8800 cm\(^{-1}\).

6.5 Correlation between NIR information from wood chips and cooking results as a contributor for controlling the pulping process

As it is mentioned earlier, the amount of lignin in the raw wood significantly affect the cooking process. Such impact can be also seen in this study that the sample with low lignin content would result in high yield and low Kappa value, which is the desirable condition for produced pulp. The Kappa value and pulp yield of 18 samples were measured in the laboratory, however, data for 6 of these samples were excluded in modeling since their undesired values. The over estimation in Kappa number determination might be due to experimental error or lack of precision in doing the test. Results of Kappa value for other samples were in a stable range from 33 to 39. The same results happened for pulp yield with an average value of 52%.

NIR spectroscopy has provided a tool with which a predictive model is developed to estimate the value of a parameter based on spectral data of a specific material. So, calibration models for Kappa and the pulping yield using the spectra from raw wood chips were also developed in this work.

According to the results, a good correlation could obtain between prediction of yield and the real value. The calibration was done for 18 samples including 6 samples for validation. OSC treated NIR provided the best model with almost all predicted yields close to the laboratory measured values. So, the relation between yield and NIR wavelength is shown in the equation below:

\[ Y = 0.939X + 3.258 \]

The best model developed in this study is the calibration model for Kappa number of pulp. According to the results, prediction of pulp Kappa value is possible using OSC processed NIR information of raw solid wood chips. The model is highly correlated with the response values with the relation below:

\[ Y = 0.978X + 0.792 \]
It should be mentioned that the 6 samples with undesired Kappa results were removed from the calibration set and the modeling was done using NIR information of 12 samples and the corresponding measured Kappa number.

In fact, errors in the Kappa values of those 6 samples was due to the change in experiment procedure. According to the standard oxidation method (ES ISO 302:2012) used for Kappa determination in this study, the oven-dry pulp is used in titration. Because of time limitation, the last 6 samples were not dried in the oven, so, wet samples were applied in the experiment with an estimated moisture content. Then, after drying and calculating the exact moisture, the Kappa numbers were recalculated. By this, the final Kappa values were overestimated for those 6 samples since oxidation method is too sensitive to the way that the experiment is done. Therefore, the overestimated results were excluded from the calibration set and the model was created using those Kappa values which were found exactly based on the standard method.

The developed model and its accuracy generally show that it is possible to predict the yield of pulping process using wood chips spectroscopy. Moreover, the calibration model for Kappa number as highly correlated with the NIR data. This means that having spectral data of feedstock contributes to estimate the cooking results.

Prediction of pulping yield and Kappa number as the pulping results contributes to control the process of pulping. In other words, spectroscopy on the raw wood used in pulping process provides such a good information that the yield and Kappa value of the produced pulp could be estimated. With this, the quality of pulp would be predicted. Having an overview of the end products properties contributes to control the pulping process efficiently.

Moreover, properties of raw material would be estimated using its spectral data. Chemical properties of wood chips especially lignin is a factor of interest in pulping process. Knowledge about the lignin content of wood helps finding out the approximate amount of lignin needs to be removed from the wood. Therefore, the adequate amount of cooking chemical could be identified efficiently. Controlling the amount of chemical used in cooking process helps to save energy and increase the pulping efficiency.

All models developed in this study are based on the properties of raw materials used for fiber lines 1 and 2 in BillerudKorsnäs mill. So, they can be used to predict the AIL, Total lignin content, pulping yield, and Kappa number. Calibration regarding moisture content needs improvement, while it seems impossible to use the ASL model for prediction.
7 CONCLUSION AND RECOMMENDATION FOR FURTHER WORK

NIR spectroscopy has become one the commonly used method in pulp and paper industries to predict the chemical properties of wood chips. Properties such as lignin content in the wood could significantly affect the pulping process and the end-products quality. Therefore, knowing the approximate amount of lignin present in the raw wood chips will enable better control of the pulping process and achieve high-quality end use products.

The aim of this study was to develop a model using the NIR spectra of solid wood chips in order to predict their chemical properties such as lignin and moisture content and also calibration for pulp yield and Kappa value. Since these parameters are the quality indicators in pulping process, with prediction models, the process would be controlled efficiently and the energy use in the mill could be saved.

The results of the study show that the NIR calibration model can be developed for lignin content of softwood chips used in the pulp and paper mill with considerable accuracy and high correlation coefficient. In other words, using NIR spectra from solid wood as the multivariate data and laboratory measured lignin content as the reference data set, a PLS model could be created to be used for prediction of lignin content in the wood. The created model for moisture content also represent an acceptable correlation coefficient of 0.52, however, it might not be good enough for reliable prediction.

Results also reveal that it is possible to find a correlation between the cooking results including pulp yield and Kappa number and NIR spectra from raw wood chips. This means that having spectral information of wood chips, the pulp yield and Kappa number would be predicted. With this, the pulping process could be controlled to achieve the products with high quality.

The OSC de-noising technique was applied to the spectra prior to calibration provided optimal data corrections and consequently, good PLS model with relatively high accuracy. Therefore, all models created using OSC treated data led to good prediction results; except for the ASL model in which the prediction error was high and the correlation between the predicted ASL and the reference values was poor.

The best calibrations were created for AIL and Kappa number with high correlation coefficient of 0.92 and 0.99, respectively. So, they can be reliably used for prediction. Knowledge about the lignin content of wood and prediction of pulping results contribute to providing an overview of the end products properties such as yield and Kappa number. This consequently leads to control the pulping process in an efficient way.

All models developed in this study used NIR information from the wood chips moving to the fiber line 1 and 2 at the BillerudKorsnäs mill. Different portions of saw mill wood chips added to the raw softwood did not make significant changes neither in chemical properties of feedstock nor in the value of yield and Kappa number. So, it is concluded that the properties of sawmill wood flakes are similar to the raw wood chips used in the mill. Therefore, all calibration models could be reliably applied to fiber lines 1 and 2 in the mill with the aim of controlling the pulping process.
OSC is not commonly used filtering technique in NIR calibration. To see if all important variations in spectra (related to the target trait) are used in the calibration, the reliability of OSC method needs to be assessed. In fact, validation and reliability of the developed models based on OSC treated data could be assessed in the future work. Moreover, application of larger number of samples and data in further NIR calibration research may reduce the prediction errors of developed models in this study and provide a better calibration for ASL.
REFERENCES


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Fahlen, J., 2005. The cell wall ultrastructure of wood fibers effects of the chemical pulp fiber line, Stockholm: KTH University.


APPENDIX 1

Measured moisture content of samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture</th>
<th>Sample</th>
<th>Moisture</th>
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APPENDIX 2

Laboratory measured Lignin Content for samples used in calibration

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## APPENDIX 3

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<th>Sulfidity Factor [%S]</th>
<th>Pulp weight including moisture</th>
<th>Pulp for drying</th>
<th>Oven dry weight of pulp</th>
<th>Pulp moisture content (%)</th>
<th>Yield [%]</th>
<th>Kappa number (mL/gr)</th>
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