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Cold caustic extraction of spruce sulfite dissolving pulp

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Contents

Abstract ........................................................................................................................................... 2

Executive Summary .......................................................................................................................... 3

Abbreviations .................................................................................................................................. 5

1. Introduction ........................................................................................................................................ 6
   1.1 Objective ......................................................................................................................................... 6
   1.2 Wood constituents ........................................................................................................................... 6
   1.3 Softwood and Hardwood .............................................................................................................. 7
   1.4 Cellulose ......................................................................................................................................... 7
   1.5 Hemicellulose ............................................................................................................................... 9
      1.5.1 Dissolving pulp ....................................................................................................................... 9
   1.6 Lignin ............................................................................................................................................ 10
   1.7 Extractives ..................................................................................................................................... 11

2. Cold Caustic Extraction .................................................................................................................. 11

3. Material & Method .......................................................................................................................... 13
   3.1 R18 measurement ......................................................................................................................... 13
   3.2 Viscosity measurement .............................................................................................................. 14

4. Results & Discussion ...................................................................................................................... 14
   4.1 Effect of alkali extraction on yields ............................................................................................. 14
   4.2 Effect of alkali extraction on R18 Values .................................................................................... 16
   4.3 Effect of alkali extraction on limiting viscosities ....................................................................... 17
   4.4 Effect on yield with time ............................................................................................................ 18
   4.5 Effect on R18 with time .............................................................................................................. 19
   4.6 Effect on limiting viscosity with time ....................................................................................... 19

5. Conclusions ..................................................................................................................................... 20

6. Future work ..................................................................................................................................... 21

7. Acknowledgments .......................................................................................................................... 21

8. References ....................................................................................................................................... 22

9. Appendix ......................................................................................................................................... 24
Abstract

In this study, cold caustic extraction of a sulfite dissolving pulp was investigated. The cold caustic extraction effect was analyzed by measuring the yield, the R₁₈ and the limiting viscosity of the extracted pulp samples. Cold Alkali treatment was carried out at different alkali concentrations, different time intervals and between 3 - 60 ºC.

Dissolving pulps are used for the manufacturing of viscose fibers, rayon, methyl cellulose, carboxy-methyl-cellulose and other synthetic materials. These products require a high degree of pulp purity with respect to cellulose. Cold caustic extraction dissolves short chain carbohydrates and alkali dissolved pulp impurities which still remained in the pulp after cook. After the cold alkali extraction standard laboratory methods were used to measure the yield, the R₁₈ and the limiting viscosity. It was found that when the alkali concentration or the temperature or the time was increased, more xylan was removed. The increase in the R₁₈ value showed that this resulted in higher pulp purity.

Keywords: carbohydrates, cold caustic extraction, dissolving pulp, polysaccharides, xylan.

Sammanfattning

I denna studie undersöktes effekten av kall alkali extraktion av oblekt sulfitmassa. Kall alkali extraktion analyserades genom att mäta utbytet, R₁₈ och gränsviskositeten. Kall alkalibehandling utförs normalt vid 25ºC till 40 ºC men i denna studie utsträcktes intervallet till 3-60 ºC.

Dissolving massa användes för framställning av viskosfiber, rayon, metylcellulosa, karboxymethyl-cellulosa och andra syntetiska material, som kräver hög grad av renhet med avseende på cellulose. Standardiserade laboratoriemetoder användes för att mäta utbytet, R₁₈ och gränsviskositeten. Efter alkalibehandlingen visade det sig att när alkali och temperaturen ökade så blev också massan mer ren med avseende på cellulose vilket medförde att R₁₈ värden ökade.
Executive Summary

Almost after three decades of decline, dissolving pulp usage has turned upward sharply, especially during the last decade. It is estimated that almost 4.5 million tons of dissolving pulp was consumed in 2010. This turnaround was due to the strong viscose fiber market because the popularity of rayon and the similar materials has been boosted and increased the cotton prices. This massive demand for dissolving pulp has compelled some paper grade mills to convert into dissolving pulp production.

In the last decade the industry and the academia have joined forces to convert the some kraft mills into dissolving pulp mills as well as to improve the dissolving pulp qualities. Therefore many researchers have focused on this topic. As the global population is being increased day by day; consumer’s are increasing too and new technologies are being developed to meet the consumer’s demand. In view of these aspects an effort was made to optimize the dissolving pulp properties.

In this study, the purity of the sulfite pulp was in focus, for this reason the cold caustic extraction method was adopted to see the effect on the pulp. Pulp from the Lessebo Pulp Mill in Sweden was used. The Lessebo pulp mill uses spruce wood for sulfite pulping. Two batches of sulfite pulp from Lessebo mill were used during the study and also to see the difference in pulp properties after cooking.

The pulp (from Lessebo mill) was thoroughly washed with deionized water, to remove all the cooking chemicals in the pulp. The pulp consistency was 5% during the alkali extraction and it was performed in the plastic bags. The bags were put into water baths at a specific temperature for a specific time. When alkali extraction time was over, pulp was thoroughly washed with hot water to remove alkali and the pulp samples were dried at room temperature. ISO 5351 and ISO 699 standard methods were used to calculate the \( R_{18} \) and the limiting viscosity of the pulp respectively. This study was based on two sub cases, in the first case; sulfite pulp was treated with NaOH at different concentrations i.e. 5, 7 and 10 % sodium hydroxide for 10 minutes at different temperatures i.e. 3°C, room temperature, 40°C and 60°C. In the second case, the 5% pulp consistency samples were treated with 7% NaOH at a temperature of 3 °C and 40°C at different time intervals i.e. 10, 60 and 120 minutes.

After alkali extraction, three parameters i.e. the yield; the limiting viscosity and the \( R_{18} \) were measured to analyze the impact of alkali extraction. Increase in temperature, alkali concentration and time, dissolved more hemicelluloses and short chain carbohydrates. The pulp yield decreased with increasing temperature, alkali concentration and time, because when pulp was mixed with alkali, the pulp was swelled to release short chain carbohydrates and alkali soluble impurities dissolved into the alkali solution to make the pulp more pure. The high alkali concentration
might also degrade some of the cellulose but did not affect the cellulose reactivity. It was observed that a lower amount of short chain carbohydrates were separated from the pulp at low temperature as compared to the amount of short chain carbohydrates separated at high temperature. Time duration for alkali extraction affected the pulp quality. Less impurities and carbohydrates were separated at shorter alkali extraction as compared to a longer alkali extraction.

In the cold caustic extraction high concentration of sodium hydroxide were used and the used alkali filtrates could be utilized in the hot alkali extraction or in the kraft pulp cooking or it can be recycled after recovery plant.
<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
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<tbody>
<tr>
<td>CCE</td>
<td>Cold caustic extraction</td>
</tr>
<tr>
<td>CED</td>
<td>Cupri-ethylene-di-amine</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
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<tr>
<td>HCE</td>
<td>Hot caustic extraction</td>
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<td>NaOH</td>
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<td>Pc</td>
<td>Pulp consistency</td>
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<td>°C</td>
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<td>SD</td>
<td>Standard deviation</td>
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1. Introduction

Wood consists mainly of the three elements: carbon, hydrogen and oxygen. There are also traces of nitrogen and inert inorganic elements. Wood is highly organized in several hierarchical levels from parts of the tree down to molecular level. Differences in the hierarchical levels are a very important property of the raw material for pulp and paper industry. There are different wood species and each tree has different parts like top, stem, branches, leaves/needles and roots, these all are composed of cells. These are different cells with different chemical compositions and cell wall layers also vary in the different cells. As the tree has different parts, which has different chemical compositions, stem has highest proportion of cellulose greater than 50% among all of the tree’s part.

1.1 Objective

Dissolving pulp has high purity with respect to cellulose and for cellulosic derivative products high pulp purity is required, otherwise impurities in the pulp impair the cellulosic derivative product production process and a high chemical consumption will be required. The aim of this study was to investigate the effect of cold caustic extraction (CCE) on spruce sulfite dissolving pulp at variable sodium hydroxide concentrations, extraction time as well as temperatures. It has been observed, when sodium hydroxide concentration, extraction time and temperature conditions were varied, short chain carbohydrates were removed and pulp purity increased.

1.2 Wood constituents

Fundamentally wood is a complex biological structure having a porous material, however wood serves three main functions in plants; it conducts water from the roots to leaves, provide mechanical support to the plant body and store bio-materials. Chemically wood is a three dimensional biopolymer composite, composed of an interconnected network of cellulose, hemicelluloses and lignin with traces of extractives. Wood cell walls on a dry weight basis consist of sugar based polymers (carbohydrates 65-75%) along with lignin (18-35%). Elemental composition of dry wood is shown in below figure 1:

![Figure 1: Elemental composition of dry wood](image-url)
Wood has major portion of carbohydrates which is composed of cellulose and hemicellulose polymers with minor amounts of other sugar polymers such as starch and pectin. The combination of cellulose and hemicelluloses is called holo-cellulose and it is 65-75% present in a dry wood. Carbohydrates differentiate from each other by rather a very small structural difference which could be very important from a biological and mechanical point of view, therefore different monosaccharides could have the same molecular structure but different directions of hydroxyl group can give an important biological difference. Wood is mainly divided into two major groups; namely softwood and hardwood. The softwoods have a higher cellulose content of about 40-45% and relatively higher lignin 26-34% content, while hardwoods have 38-49% of cellulose and 23-30% of lignin [4].

1.3 Softwood and Hardwood

Botanically softwoods are those woods that come from gymnosperms (mostly conifers), and hardwoods are those that come from angiosperms (flowering plants). Softwoods and hardwoods differ in terms of tree types from which they are derived and they also differ in terms of their component cells. Most important difference between these two general kinds of wood is that hardwoods have a characteristic cell type called a vessel element, while softwoods do not posses that. An important cellular similarity between softwoods and hardwoods is that, most of the cells are dead when they reach maturity even in the sapwood [4]. Softwood has longitudinal fibers, tracheids with tubular structure of an average length of 3.5 millimeters [3]. Softwoods have long fibers as compared to hardwoods. Most softwood species are used for pulping, whereas a large number of hardwood species are also used for pulping [2].

1.4 Cellulose

Cellulose is the most abundant polymer in the world and the main component in plant cell wall. Presence of cellulose in the plant and it’s abundance makes the cellulose outstandingly most common bio-compound on the earth. Cellulose structure favors organization into bundles with the crystalline order held together by hydrogen bonds [2].

Cellulose has long homo-polysaccharide chain [6]. The cellulose chemical structure is very simple and it has very long unbranched chains of glucose. Cellulose has shown several special properties which makes it of great scientific and technical interest. In fact cellulose and different types of hemicelluloses belong to the large group of bio-molecules named carbohydrates, which play a major role in all forms of life [2]. Generally cellulose is an important and fascinating biopolymer, almost inexhaustible and renewable raw material. The new trend towards such kind of resources and tailoring of innovative products for science, medicine and technology has led to
a global renaissance of interdisciplinary cellulose research to increase the use of this abundant organic polymer \cite{7,8}.

Wood cell wall is mainly made up of cellulose, hemicelluloses and hydroxyl groups, these components make the cell wall very hygroscopic and lignin binds these cells together which act as a cementing agent. As cellulose consists of cellbiose and the number of glucose units in cellulose molecule is referred to as the degree of polymerization. The greater the length of polymeric chain and higher the degree of polymerization as well as greater the strength of the unit cell which contributes to the wood strength. Cellulose molecules have a tendency to form intermolecular and intramolecular hydrogen bonds because cellulose molecules are randomly oriented \cite{4}. An important feature of cellulosic material that it has both crystalline and amorphous regions as shown in figure 2 and these regions influence the accessibility and chemical reactivity of fibers. The cellulose chemical reactivity can be increased by making the cellulose crystalline region more accessible to the reactants by swelling and de-crystallization \cite{9}.

![Figure 2: Cellulose crystalline region ( ) and amorphous region ( )](image)

Cellulose contains polymeric crystals, linear cellulose molecules are interconnected by hydrogen bonds to form linear bundles hence increasing the crystalline structure. These crystalline regions are interrupted by noncrystalline amorphous regions. Crystalline region may contain some kinks in the polymer chain known as defects and these defects vary with the type of cellulose \cite{10}, if the amorphous region in the cellulose is degraded by chemicals, cellulose crystalinity increases \cite{11}.

Cellulose crystalline regions are formed when the packing density of cellulose increases. Most wood derived are cellulose is highly crystalline and they can contain 65% crystalline regions and the portion which has a lower packing density is characterized as amorphous cellulose. The surface of crystalline cellulose is accessible to water, chemicals, microorganisms, etc. but rest of the crystalline cellulose is nonaccessible to water, chemicals, etc., whereas most of the noncrystalline cellulose is accessible \cite{4}.
1.5 Hemicellulose

Plants cell walls are by far the largest pool of organic carbon, plant cell wall consist of a variety of different compounds. Hemicellulose belong to the family of carbohydrates and represents normally 20-35% of the mass. Thus hemicellulose are the second most abundant polysaccharide group in plants. Hemicelluloses are present in the matrix between cellulose fibrils in the cell wall. Hemicelluloses are short chain carbohydrates and they are easily soluble in alkali and hydrolyzed by acids. Hemicelluloses have a lower degree of polymerization than the cellulose. Most of the hemicellulose are present interspersed within or on the boundaries of the amorphous regions of the cellulose chains and they are very close to the lignin. Hemicelluloses can be the connecting material between cellulose and lignin. Chemical and thermal stability of hemicelluloses is lower than cellulose.

1.5.1 Dissolving pulp

The demands for dissolving pulp have boomed worldwide in the last few years and the pulping process used are the acid sulfite process and the alkaline prehydrolysis kraft process. Dissolving pulp is being produced from cotton linters (soda pulping) and from wood via the prehydrolysis kraft and the acid sulfite pulping processes. The main challenge is the selectively removal of hemicelluloses without degrading the cellulose molecules or the crystallinity of these as this will affect the pulp quality and it will have a negative influence on the chemical consumption in the following process stage.

The most common uses of pulp are in paper manufacturing but now this pulp is also used for the production of cellulose derivatives including viscose fiber, rayon, carboxy-methyl cellulose, cellulose acetate and cellulose esters due to these products, dissolving pulp production growth rate has significantly increased. To produce these products dissolving pulp is used because dissolving pulp has a very high purity with respect to cellulose and such pulps contain alpha-cellulose content (90-95 %) and hemicelluloses (5-10 %) and traces of lignin and resin. During cold alkali extraction of dissolving pulp, the alkali lye contains beta and gamma cellulose. Beta cellulose is that cellulose which forms precipitates upon acidification of an aqueous alkaline solution containing dissolved pulp constituents, while gamma cellulose consists of the dissolved carbohydrate residue in the solution and alpha cellulose is the highly refined, delignified woody insoluble material remaining when other soluble material has been removed.

Wood pulp specially obtained by sulfite process requires subsequent hemicelluloses removal steps, so these hemicelluloses are removed in bleaching steps. Dissolving pulp is a very clean pulp; due to its purity dissolving pulp is well suited as a raw material for different kinds of cellulose products like staple fibers, films and derivatives. Therefore low amount of
hemicellulose is one of the characteristics of dissolving pulp and it is necessary to remove hemicellulose from dissolving pulp otherwise it will impair subsequent conversion processes during cellulose derivatives, such as viscose fiber, lyocell fiber and cellulose acetate production, furthermore cellulose derivatives quality are also affected by the presence of short chain heteropolysaccharides[17].

The quality of dissolving pulp depends on both the raw material wood and the pulping process. Cellulose pulp reactivity could refer to its capacity to participate in diverse chemical reactions [16]. A good dissolving pulp should have special properties like a uniform molecular weight distribution[5, 16], viscosity and high level of brightness etc. [16]. Cold caustic extraction gives high purity dissolving pulp as well as a caustic lye which contains a high concentration of hemicelluloses molecules. High molecular weight of hemicellulose isolated by cold caustic extraction (CCE) may be utilized either as an additive for a pure carbohydrate source for the conversion into building block chemicals which improve yield and fiber-fiber bonding capability [18].

Undesirable carbohydrate components consist of residual hemicellulose left after cooking like glucomannan and glucuronoxylan. Some hemicelluloses components might be accepted in the pulp using dissolving process provided their physical and chemical characteristics are suitable for the particular process while some of the cellulose molecules might be too short to accept the properties of certain final products like rayon and high tenacity staple fibers, therefore short cellulose molecules have to be removed from the pulp. Hence pulp purification is adjusted to the need of the dissolving process; thereby a wide range of pulp purifies are available in the market. The most common way of expressing the degree of purification is to measure the R_{18} value[1].

1.6 Lignin

Lignin is the third main wood component, it occurs in the range of 20-35% of wood. Lignin is the less desirable component between the three main wood components and it has to be removed or bleached to an extent, according to the desired pulp grade. Moreover lignin has quite a high share in wood weight, lignin has long attracted interest for conversion into useful chemicals, due to this reason lignin chemistry has grown to a separate and important branch of organic and physical chemistry [19].

Lignin has an amorphous structure and does not contain a single repeating unit of the hemicellulose such as cellulose. Lignin is classified in different ways, but lignin is commonly divided according to their structural elements.

Lignin is distributed all over the secondary cell wall, but middle lamella contains the highest concentration of lignin. Almost 70% of lignin is located in the cell wall because of the difference
in volume of middle lamella to secondary cell wall [4]. Lignin distribution within the cell wall and the lignin contents of different parts of a tree are not uniform [3]. Lignin is a complex phenolic polymer formed by radical coupling reactions of p-coumaryl, coniferyl and sinapyl alcohol, these monomers are called monolignols [20].

1.7 Extractives

Wood extractives are defined as chemical compounds which can be extracted using various neutral solvents. Solvent and the extraction procedure used must be specified because these variables affect the yield and the composition of the obtained extract [2]. It is important for some cases that the extractives are classified by the solvent used to extract them. For instance [4], the composition of a water extract will be different from that of a hexane extract, since water soluble extractives like sugar lignin and other phenolic compounds have less importance during pulp production [2]. Many extractives have been identified and in few cases extractives role in the tree are well understood while in some cases it is not clear why they are present in the tree [4].

Wood resins are defined as components which are soluble in liquids of low polarity, e.g. hexane. Fats and resins are made up of fatty acids and resin acids respectively [2]. Extractives are a group of cell wall chemicals that mainly consist of fats, fatty acids, phenols and many other minor organic compounds, while all these chemicals exist as monomers, dimmers and polymers. Softwoods have higher extractive content than hardwoods, in which some are responsible for color, smell and durability of the wood [4].

2 Cold Caustic Extraction

Caustic extraction steps remove the short chain carbohydrates from pulp that resisted the pulping process [3]. The dissolution of short chain material by cold alkali purifies the pulp. The cold alkali purification is the most selective way of increasing the alphacellulose content of the pulp. It also gives the highest yield and the highest purity [1]. To get desired properties in the product like increased fiber strength, higher brightness and brightness stability, alkaline purification procedures are carried out. Alkaline purification procedures could be either cold or hot caustic extractions [3]. Cold alkali extraction takes place below 40ºC and at high sodium hydroxide concentration up to 18% [1]. This cold caustic extraction involves mainly physical changes. Yield losses are in the range of 1.2-1.5% per increase of 1% alpha cellulose content. During the cold alkali extraction recirculation of the lye (after pressing) deteriorates the results of the purification significantly because of the accumulation of impurities derived from short chain carbohydrate degradation products [3].

Carbohydrate removal in bleaching operations lies in the purification of dissolving pulp; sulfite pulps are more sensitive to alkaline treatment than alkaline cooked pulp. During alkaline
purification carbohydrates are removed especially hemicellulose. At some extent these losses of easily accessible cellulose is even desired in order to get a more homogeneous chain length distribution in the remaining pulp. Lignin and resin are removed during the alkali stage. More often alkali extraction stage is carried out on the unbleached pulp as the first bleaching stage, however in some rare cases viscosity control is a function of the alkaline extraction stage, either pulp purification is carried out at very high temperature or in cold alkali lye extraction using oxidants and possibly oxidation catalysts.

Alkaline purification of pulp is also carried out by cold alkali purification, which consists of a treatment of the pulp in concentrated lye at room temperature or slightly higher or lower, while intermicellar and some intramicellar swelling takes place, allowing short chain material and microfibril fragments to dissolve. Cold alkali purification specifically involves physical changes and little alkali is consumed in chemical reactions [3].

Cold alkali purification takes place below 40ºC and at lye concentrations below 18% NaOH. At such a low temperature no chemical reaction takes place and this stage is only dissolution of the hemicellulose. Further increase in temperature will decrease the alpha cellulose content [1]. Pre-hydrolysis-kraft pulp has high alpha cellulose content after cooking and only a limited extraction is required to remove the residual hemicelluloses content. In the case of sulfite pulp, if lye concentration is 10-12% NaOH, it gives maximal alpha cellulose content. However it should be noted that 100% of alpha cellulose cannot be achieved because some new fragmentation of microfibrils will always occur. Cold caustic extraction gives high purity dissolving pulp and high quality hemi-caustic-lye [21]. Cold alkali extraction purified pulps are easily bleached, whereby the alpha cellulose is further decreased. Time needed for the alkali treatment is short because as the sodium hydroxide comes in contact with the pulp, instantaneously pulp swelling takes place and cold alkali treatment removes more xylan and also more glucomannan as compared to hot caustic extraction or other pulp bleaching processes.

Hot caustic extraction (HCE) is also used to remove short chain hemicellulose for the production of reactive dissolving pulp based on acid sulfite cooking. Alkali concentration in hot caustic extraction is not as higher as in cold alkali extraction. Hot caustic extraction has a temperature range from 70ºC to 140ºC, and during HCE the degree of purification is regulated by alkali charge, temperature, time duration for extraction and pulp consistency. Pulp which is treated with hot caustic process has usually a $R_{18}$ value of 94-95% [3].
3 Material & Method

Pulp from Lessebo pulp mill was thoroughly washed to remove all the dissolved impurities in the pulp and dried at room temperature. 40g of dry pulp was weighed by Precisa scale and put into a plastic bag for alkali extraction. 800ml of 5% NaOH was added in the plastic bag, the bag was put into the water bath having a temperature of 40°C for 10 minutes. Pulp was thoroughly washed with hot water until the filtrate pH lied in the range of 6-8. The pulp samples were then weighed after which some pulp was taken in a plastic cup and put into the oven at a temperature of 105°C for overnight, to calculate the yield and rest of the pulp was dried at room temperature.

Same procedure of $R_{18}$ and viscosity measurement was done with the pulp treated with different sodium hydroxide concentrations like 5%, 7% and 10%, and at different temperatures; 3°C, room temperature, 40 °C and 60°C respectively. In second study the same procedure of cold caustic extraction, $R_{18}$ and viscosity was done by keeping 5% pulp consistency (g dry pulp/ml liquid), 7% sodium hydroxide concentration and at a temperature of 3°C and 40 °C while alkali extraction time was varied i.e. 10 minutes, 60 minutes and 120 minutes respectively.

Limiting viscosity and $R_{18}$ value was measured by ISO 5351 and ISO 699 respectively. The limiting viscosity and the $R_{18}$ value of two batches of pulp received from Lessebo mill were also measured and results are shown in table 1 in appendix, yield and $R_{18}$ formulas were also mentioned in appendix. All graphs are drawn with standard deviations having three times of repeated values however in some graphs error bars are too small to notice and all the values in table 1-6 in appendix are represented with standard deviation.

3.1 $R_{18}$ measurement

2.5 g of dry pulp was taken in a conical flask, 25ml of 18% NaOH was added and flask was placed in a water bath at 20°C for 3 minutes then pulp was mercerized for 3 minutes, another 25 ml of 18%NaOH was added, stirred the suspension then diluted by adding 100ml more of sodium hydroxide solution and the flask was covered with a lid. Again flask was placed in a water bath at 20°C. Sixty minutes time was given to the pulp from the first addition of sodium hydroxide then pulp was washed first with 200ml of 10% acetic acid then with hot water until the pulp filtrate becomes neutral. Pulp was taken in a plastic cup and put into oven at a temperature of 105°C for an overnight duration to be able to determine the dry weight needed for the calculation of $R_{18}$ value.
3.2 Viscosity measurement

0.25g of dry pulp was taken in a plastic bottle along with 3-4 pieces of copper wire and 25ml of deionized water was added and the bottle was placed on a shaker for 15 minutes then 25ml of CED (cupri-ethylene-di- amine) solution was added and again the bottle was placed on a shaker for 15 minutes. Pulp bottle was placed in a water bath having a temperature of 25ºC for 15 minutes. Pulp sample was drained out through the capillary tube viscometer and efflux time for the pulp sample was noted down to calculate the limiting viscosity of the sample.

4 Results & Discussion

In this study Lessebo mill sulfite pulp was used and this study is divided into two sub cases:

1) Alkali extraction carried out at 5% pulp consistency, 3ºC, room temperature, 40ºC and 60ºC alkali extraction temperatures, 10 minutes extraction time and 5,7 and 10% sodium hydroxide concentrations.

2) Alkali extraction carried out at 5% pulp consistency, 3ºC and 40ºC alkali extraction temperatures, 7% sodium hydroxide concentration and 10, 60 and 120 minutes extraction time.

After alkali extraction the yield, the $R_{18}$ and the limiting viscosity parameters of the alkali treated pulps were measured to analyze the treatment effects. Two pulp batches from Lessebo mill were received which were used during the study to analyze the effect on the results. During case 1, pulp from batch 1 was used however pulp taken for alkali extraction at 60ºC were from the pulp batch 2. During study 2, pulp from batch 2 were used.

Laboratory work was repeated several times to make the results more precise, three readings were taken to calculate the standard deviations, however in measuring the pulp received from Lessebo mill including pulp batch 1 and pulp batch 2, limiting viscosity and $R_{18}$ value two readings were taken to calculate the standard deviation.

4.1 Effect of alkali extraction on yields

In case 1: 5% pulp consistency was treated with different alkali concentrations at different temperatures for 10 minutes. Wood pulp obtained by sulfite process still contain considerable amount of low molecular weight carbohydrates and lignin. These impurities make the pulp less suitable for many purposes therefore strong solutions of sodium hydroxide at low temperatures were used to make the pulp suitable for many processes. It is quite clear from the fig. 3 that the extraction of wood pulp with highest concentration of sodium hydroxide solutions i.e. 10 % had the lowest pulp yield because more short chain carbohydrates and alkali soluble impurities were
dissolved. At a specific alkali concentration a lower temperature resulted in a lower yield as compared to higher temperature because pulp swelled more at low temperature which helped the pulp to release short chain carbohydrates.

Cold alkali extraction is a selective pulp purification process because it mainly involves physical changes in the corresponding pulp substrate. At these low temperatures when alkali comes in contact with the pulp fiber, pulp fiber starts swelling in no time, which helps in dissolving the lignin (which was not removed during pulping process) and hemicellulose (xylan) present in the fiber. When pulp fibers swelled too much, it caused difficulties in washing to get rid of all dissolved hemicelluloses and other impurities. 5% Pc was used, during this experiment and a higher alkali charge reduces the yield, since sodium hydroxide concentration had increased more sodium hydroxide molecules came in contact with the pulp fiber, caused the amorphous hemicellulose structure and traces of lignin to get rid off from the fiber structure. Minute amount of lignin was also removed to increase the alpha cellulose content in the pulp at a specific temperature.

Figure 3: Yield loss as a function of the amount of hemicellulose removed from unbleached sulfite pulp during CCE treatment

During cold caustic extraction stage short chain carbohydrates and other alkaline soluble impurities were dissolved in the alkali solution to give low pulp yield and higher alpha cellulose content. It is clear from figure 3 that the amount of hemicellulose and alkali soluble impurities were removed more at low temperature as compared to high temperature; provided the alkali concentration remained the same. One reason could be that some of hemicelluloses were reattached to the pulp at high temperature caused increase in yield at specific alkali
concentration. Higher the sodium hydroxide concentration and temperature, pulp purity was higher, to give optimum amount of alphacellulose.

4.2 Effect of alkali extraction on R_18 Values

To dissolve pulp impurities, 18% sodium hydroxide solution has become more widely used especially to characterize the dissolving pulp. Alkali solubility tests at room temperature give the information about the pulp quality like the amount of hemicellulose present in the pulp and extent of cellulose degradation in the pulp. During R_{18} test pulp samples were treated with 18% sodium hydroxide to dissolve the pulp impurities. The solubility of a sulfite pulp in 18% NaOH gives a fair indication of the hemicellulose content, though some degraded cellulose may go into solution and some hemicelluloses remained undissolved. In pulp which contained much degraded cellulose, this portion of degraded cellulose tends to dissolve in the lye. It is clear from figure 4 that the R_{18} value has a linear relation with increasing the sodium hydroxide concentration and removal of hemicellulose i.e. short chain carbohydrates and degraded carbohydrate chains, so when the pulp was washed these carbohydrates were also removed. The R_{18} value shows the alphacellulose content.

![R_{18} Value Graph](image)

Figure 4: Effect of alkali extraction of unbleached sulfite pulp on R_{18}

At specific sodium hydroxide concentration, temperature also has an effect. At lower temperature, pulp possess low amount of alphacellulose content as compared to amount of alphacellulose at higher temperature. The relationship between initial pulp purity R_{18} and final pulp purity R_{18} depends on alkali concentration, even xylan removal during alkali extraction increases with increasing initial hemicellulose content, initial pulp purity must exceed at a certain
level in order to achieve sufficient pulp purity without approaching a change in the super-
molecular structure.

4.3  Effect of alkali extraction on limiting viscosities

Viscosity measurement is one of the important methods for pulp analysis because viscosity
measures the average degree of polymerization of the pulp sample, mainly cellulose. Viscosity
test makes it possible to check the extent of degradation of polymer caused by cooking and
bleaching processes, which greatly influence the quality of the final product. During viscosity
measurement pulp samples were dissolved in a cupri-ethylene-di-amine (CED) solution at a
certain concentration.

During CCE, pulp encountered with strong alkali solutions which caused the cellulose and
hemicellulose DP to reduce. Viscosity is strictly a measure of the cellulose DP. During the CCE
process fibril formation also takes place on the fiber, when these fibrils removed DP also
reduced.

When alkali concentration was increased; limiting viscosity also increased because more and
more short chain carbohydrates were removed leaving the long chain carbohydrates behind,
having high DP and these long chain fibers indicated that high alkali concentration had great
effect on the pulp purity. Viscosity indicates only the fiber average chain length and as the
degradation is distinctly heterogeneous, considerable portion of the cellulose elements are also
likely to have become degraded (during process) to a critical DP and this could be an important
cause of fiber chain length reduction. But it is clear from figure 5 that temperature also played a vital role in reducing the hemicellulose amount which at higher temperature more hemicelluloses were removed to give a long cellulose chain length at a specific alkali concentration. It is also clear from figure 5 that more hemicelluloses were removed by increasing the temperature and alkali concentration, and figure 5 showed the practical resemblance with the literature. When short chain carbohydrates were removed, pulp viscosity increased because of availability of longer cellulose chains. Higher alkali concentration during extraction process increased depolymerization of the cellulose as compared to the lower alkali concentration resulting in lower viscosity.

4.4 Effect on yield with time

![Figure 6: Effect of alkali extraction on yield with respect to time]

In case 2: 5% pulp consistency and 7% NaOH were used at a temperature of 3°C and 40°C having different time intervals. For 10 minutes, pulp yield in both cases were found to be the same because alkali concentration was the same. When alkali came in contact with the pulp, pulp started swelling immediately leaving the short chain carbohydrates. It is shown in figure 6 that when time duration for CCE was increased; more and more hemicelluloses and short chain carbohydrates were separated from the fiber giving low pulp yield.
4.5 Effect on $R_{18}$ with time

In case 2: Time interval for alkali extraction was increased, short chain hemicellulose were separated from the fiber leaving more alphacellulose behind. Longer time separated higher amount of hemicellulose and dissolved degraded cellulose from the pulp in the solution along with removing traces of lignin. At high temperature i.e. 40 °C more shorter chain carbohydrates were separated from the pulp and degraded carbohydrates were also separated to give the high amount of alphacellulose which correlates with the literature. In $R_{18}$ test; pulp contents were dissolved other than the crystalline cellulose, so the pulp which had longer time for alkali extraction contained a higher percentage of cellulose content as compared to shorter time. Similarly the pulp which had higher temperature during alkali extraction contained a higher percentage of alphacellulose as compared to lower temperature.

![Figure 7: Effect of alkali extraction on $R_{18}$ with respect to time](image)

4.6 Effect on limiting viscosity with time

In case 2: Viscosity measurement is used to measure the degradation of the cellulose and fiber cellulose chain length during alkali extraction process when alkali came in contact with the fibers, fibers started swelling, due to this reason short chain hemicellulose or alkali dissolved impurities were separated from the fibers. As a result of this; pulp contained those polymers which had crystalline structure and longer cellulose chain. Alkali extraction at high temperature and longer time dissolved more short chain hemicellulose and already degraded amorphous cellulose while the one which extracted at low temperature and the same time. Pulp which had
lower temperature for alkali extraction had lower viscosity, and alkali extraction at higher temperature had higher viscosity and high degree of polymerization. Similarly it is also clear from figure 8 that pulp which was alkali extracted for longer time dissolved more hemicelluloses and short chain fibrils to give high viscosity having high degree of polymerization along with high crystallinity.

![Limiting Viscosity](image)

Figure 8: Effect of alkali extraction on limiting viscosities with respect to time

5 Conclusions

Case 1:

- Cold alkali extraction dissolved hemicelluloses and lignin of the sulfite pulp and thus the pulp yield decreased and it decreased more with lower temperature and higher alkali concentration.
- $R_{18}$ value increased with higher temperature and higher alkali concentration.
- At specific NaOH concentration; lower alkali treatment temperature dissolved lower amount of hemicelluloses resulting in lower $R_{18}$ value.
- Limiting viscosity of the pulp increased with higher temperature and alkali concentration.
- At specific NaOH concentration; limiting viscosity increased with temperature.

Case 2:

- Pulp yield decreased with increasing alkali treatment temperature and longer time.
• $R_{18}$ value increased with higher alkali treatment temperature and longer time.
• Limiting viscosity increased with higher alkali treatment temperature and time.

High consumption of sodium hydroxide is required for cold caustic extraction and after extraction pulp becomes gel like material and pulp washing becomes more difficult therefore to avoid these problems no pulp mill is using this process.

6 Future work

It could be of interest to analyze the effect of cold caustic extraction followed by hot caustic extraction, parameters which could be measured to make the work more interesting is the yield, the $R_{18}$, the limiting viscosities and the brightness.

7 Acknowledgments

I am thankful to Allah Almighty for providing such an excellent opportunity to accomplish my one more dream. I am obliged to Professor Ulf Germgård for his support and kind behavior to make this work fruitful and I am also thankful to Lessebo pulp mill for providing pulp.
8 References


5 Kordsachia, O., Robkopf, S., Patt, R. (2004) Production of spruce dissolving pulp with the prehydrolysis alkaline sulfite process (PH-ASA), Lenzinger Berichte Vol.83 (1) pp 24-34


9 Appendix

\[
Yield = \frac{weight\ of\ wet\ pulp \times dry\ content\ value \times 100}{weight\ of\ pulp\ taken}
\]

\[
R18 = \frac{m1 \times 100}{m2}
\]

m1 = oven dry mass of alkali insoluble fraction in grams
m2 = mass of the test portion calculated on an oven dry basis in grams

Table 1: \( R_{18} \) and viscosity values with standard deviation of received pulp from Lessebo mill

<table>
<thead>
<tr>
<th>Sample #</th>
<th>( R_{18} ) (%)</th>
<th>Viscosity (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lessebo pulp batch 1</td>
<td>89.7 ± 0.28</td>
<td>630 ± 15</td>
</tr>
<tr>
<td>Lessebo pulp batch 2</td>
<td>89.4 ± 0.42</td>
<td>579 ± 3</td>
</tr>
</tbody>
</table>

Case 1

Table 2: Effect on yield after cold alkali treatment at different temperatures and alkali concentrations

<table>
<thead>
<tr>
<th>Samples</th>
<th>3°C (SD)</th>
<th>R. Temp. (SD)</th>
<th>40°C (SD)</th>
<th>60°C (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % NaOH</td>
<td>96.6 ± 0.21</td>
<td>97.4 ± 0.14</td>
<td>97.7 ± 0.14</td>
<td>97.9 ± 0.05</td>
</tr>
<tr>
<td>7 % NaOH</td>
<td>93.8 ± 0.07</td>
<td>95.5 ± 0.30</td>
<td>95.8 ± 0.18</td>
<td>96.0 ± 0.16</td>
</tr>
<tr>
<td>10 % NaOH</td>
<td>91.0 ± 0.10</td>
<td>91.6 ± 0.35</td>
<td>91.7 ± 0.14</td>
<td>91.9 ± 0.18</td>
</tr>
</tbody>
</table>

Table 3: Effect on \( R_{18} \) after cold alkali treatment at different temperatures and alkali concentrations

<table>
<thead>
<tr>
<th>Samples</th>
<th>3°C (SD)</th>
<th>R. Temp. (SD)</th>
<th>40°C (SD)</th>
<th>60°C (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % NaOH</td>
<td>90.0 ± 0.24</td>
<td>90.3 ± 0.35</td>
<td>91.4 ± 0.53</td>
<td>93.2 ± 0.10</td>
</tr>
<tr>
<td>7 % NaOH</td>
<td>90.5 ± 0.20</td>
<td>92.4 ± 0.31</td>
<td>92.7 ± 1.50</td>
<td>95.4 ± 0.09</td>
</tr>
<tr>
<td>10 % NaOH</td>
<td>91.9 ± 0.27</td>
<td>94.6 ± 0.29</td>
<td>95.0 ± 1.66</td>
<td>98.0 ± 0.16</td>
</tr>
</tbody>
</table>
Table 4: Effect on Viscosity after cold alkali treatment at different temperatures and alkali concentrations

<table>
<thead>
<tr>
<th>Sample</th>
<th>3°C (SD)</th>
<th>R. Temp. (SD)</th>
<th>40°C (SD)</th>
<th>60°C (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% NaOH</td>
<td>585 ± 5</td>
<td>597 ± 5</td>
<td>603 ± 6</td>
<td>606 ± 3</td>
</tr>
<tr>
<td>7% NaOH</td>
<td>614 ± 4</td>
<td>618 ± 5</td>
<td>620 ± 6</td>
<td>623 ± 3</td>
</tr>
<tr>
<td>10% NaOH</td>
<td>626 ± 2</td>
<td>628 ± 3</td>
<td>633 ± 5</td>
<td>641 ± 5</td>
</tr>
</tbody>
</table>

Case 2

Table 5: Effect on Yield, Viscosity and R_{18} after cold alkali treatment at 3 ºC and 40 ºC and at different time intervals

<table>
<thead>
<tr>
<th>Samples</th>
<th>Yield (%)</th>
<th>Viscosity (ml/g)</th>
<th>R_{18} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min.)</td>
<td>3 °C (SD)</td>
<td>40 °C (SD)</td>
<td>3 °C (SD)</td>
</tr>
<tr>
<td>10</td>
<td>94.6 ± 0.31</td>
<td>94.6 ± 1.63</td>
<td>585 ± 6</td>
</tr>
<tr>
<td>60</td>
<td>93.0 ± 0.85</td>
<td>92.8 ± 0.92</td>
<td>592 ± 10</td>
</tr>
<tr>
<td>120</td>
<td>90.9 ± 0.99</td>
<td>91.2 ± 0.07</td>
<td>610 ± 4</td>
</tr>
</tbody>
</table>