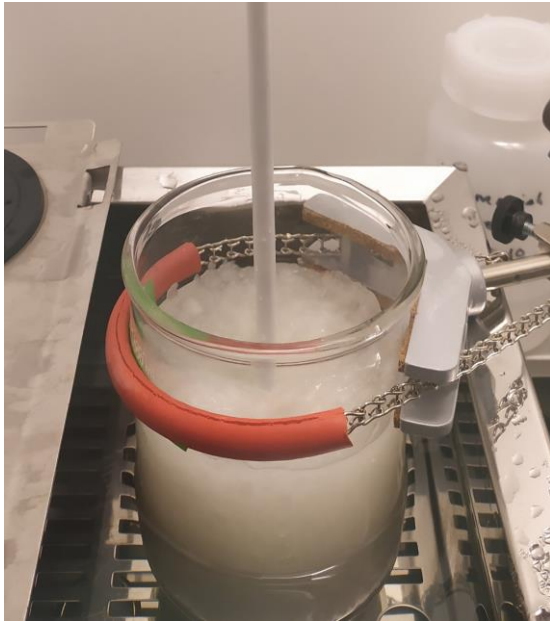




CHALMERS
UNIVERSITY OF TECHNOLOGY



Aging model of a dissolving market pulp

Master's thesis in Innovative and Sustainable Chemical Engineering

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CHALMERS UNIVERSITY OF TECHNOLOGY
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Cover:
Photograph of the alkalization step. Dissolving pulp is mixed with sodium hydroxide (aq) forming a thick slurry.

Acknowledgement

This thesis work was performed at Södra Innovation & Nya Affärer in Väröbacka. During the time at Södra all people I've interacted with have been friendly, helpful and knowledgeable and I feel grateful to have gotten the opportunity to work in this environment. I would especially like to thank my supervisors Anna Palme and Catharina Fechter. While the ongoing covid-19 pandemic stopped most face-to-face discussions this was compensated by regular online meetings, always leading to new ideas, perspectives and a few laughs.

Finally, I would also like to thank my examiner Merima Hasani for giving helpful feedback in finalizing the report. During graduate courses Merima introduced me to the subjects of biorefinery and cellulose derivatives, leading me to actively look for a master thesis within this area of research.

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Gothenburg
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Abstract

In a world where circular economy and sustainability is becoming more and more significant one important sector to look at is the clothing and textile industry and the problems and possibilities this sector entails. One possible route the textile industry could take to increase sustainability is to focus more on regenerated cellulose fibers like viscose. In the viscose process cellulose found in wood and plants are extracted, dissolved and then regenerated into textile fiber. A process using renewable material, in contrast to the most common textile fiber polyester, which is an oil-based material.

In this thesis the aging step in the viscose process is investigated, an important part in the process of producing viscose fiber. Aging in the viscose process is used to control the degree of polymerization (DP) of the pulp, the length of the cellulose polymer. This is a process where dissolving pulp first goes through a step in which the cellulose fibers chemically change form to alkaline cellulose through steeping in sodium hydroxide. After the NaOH steeping step, also called alkalization, excess NaOH liquid is removed which exposes the pulp to air/oxygen. This starts an oxidative reaction that will randomly cut the cellulose polymers somewhere along its length. As an indicator for the DP intrinsic viscosity was used as it strongly correlates with DP. During aging it is not possible to measure either DP or intrinsic viscosity of the pulp. The resulting DP can only be evaluated after aging is done, creating the need for a mathematical model predicting DP.

The key question under investigation was whether it was possible to predict the intrinsic viscosity of a hardwood dissolving pulp as a function of the aging time and temperature and initial viscosity.

Based on experimental work, it was possible to create a mathematical model describing the intrinsic viscosity after aging of a commercial dissolving pulp. The model predicts intrinsic viscosity with a residual standard deviation of 3,50 ml/g. To estimate the variance of the method a series of experimental repeats were used, yielding a pooled standard deviation of 1,88 ml/g. Both model and method exceeded expectations.

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1. Introduction

1.1 Background

Increasing focus is put on the source of raw materials for commercial products. Products like building material, packaging and textiles all have negative impact on the environment with plenty of room for improvement. In all of these areas the timber as well as pulp and paper industries are making progress in creating products with lower levels of greenhouse gas emissions (D'Amico, et al., 2021). These industrial sectors work very close to each other, and often in the same company, creating synergistic effects good for both economy and environmental impact (emissions and pollution).

While there are great opportunities in products like cross-laminated timber and paper packaging (D'Amico, et al., 2021) this thesis focuses on the textile industry. It's possible to point out several big negative impacts the clothing and textile industry have (like water use, human rights, pesticide use and carbon dioxide emissions). One possible route the textile industry could take to decrease these negative effects is to focus more on regenerated cellulose fibers like viscose and lyocell - processes in which cellulose found in wood and plants are extracted, dissolved and then regenerated into textile fibers (The Fiber Year GmbH, 2020).

Regenerated cellulose textile fibers (mainly viscose and lyocell) is the third largest textile fiber after polyester and cotton (Freitas, A.; Mathews, R., 2017). The production rate of viscose fibers increases yearly, 7,5% during 2019, the biggest increase of any staple fiber. Investments done in industry indicate this rate will increase even further the upcoming years (The Fiber Year GmbH, 2020).

While viscose fibers have many positive properties, a big disadvantage is the use of the poisonous and flammable chemical carbon disulfide, CS_2 during the viscose production. What makes CS_2 especially dangerous is that it is highly volatile, which makes exposure through inhalation likely. The use of CS_2 is highly controlled by legislation. Today, CS_2 in the viscose process is recovered to be reused, but historically this has been a big problem for workers and the environment near these plants. The plants are designed to minimize the human interference in the process steps involving CS_2 , and the part of the process that make use of it is under negative pressure (ensuring no CS_2 leaves the room). If human interference is unavoidable heavy use of protective equipment combined with high air exchange rates is used. Guidelines like these are enough to make viscose mills safe for workers (and thereby ethical to consume viscose textiles), but to what extent these rules actually are enforced are difficult to determine (Gelbke, et al., 2009).

The raw material in the viscose process is dissolving pulp, which is produced from wood in a pulp mill. Dissolving pulp is a special quality of pulp with high cellulose content which is used for production of regenerated fibers, cellulose esters and cellulose ethers (Woodings, 2001).

The first step in the viscose process is alkalization of the dissolving pulp. The purpose of this step is to transform the cellulose structure to alkali-cellulose, which increases the reactivity. The alkalization of the pulp is followed by a process called aging during which both oxidation and peeling of the cellulose take place. Oxidation is however the dominant reaction during typical aging conditions and will make random scission to the cellulose polymer. During aging the aim is to decrease the degree of polymerization in a controlled way. The kinetics of the oxidation reaction is determined by the conditions during alkalization and the characteristics of the specific pulp. The actual reaction rate and DP will then be a function of elapsed time and temperature during aging.

After aging the alkalized pulp goes through xanthation, in which the pulp is converted to cellulose xanthate. The cellulose xanthate is dissolved in dilute sodium hydroxide which creates a thick, orange liquid called the viscose dope. The cellulose xanthate is finally regenerated to cellulose by extruding the viscose dope into a bath of sulfuric acid (Woodings, 2001).

This master thesis will focus on modelling of the aging process of a dissolving pulp. For evaluation of experiments there will be a strong focus on the DP, mainly evaluated by measuring intrinsic viscosity. Further unit operations in the viscose process are outside the scope of this thesis.

The aim of this study:

- Create a mathematical model describing aging of an alkalized Kraft dissolving pulp as a function of initial viscosity, temperature and time.

2 Theory

This chapter will introduce the process of producing viscose textiles starting from the raw material wood as well as some background to the chemical analysis methods relevant to the alkalization and aging step in the viscose process. The dissolving pulp and viscose fiber industries run these processing steps efficiently but there is still a lot unknown about the chemical reactions behind and how to control them. Finally, there is a short chapter about mathematical modelling in general followed by a derivation of a model applied to aging of dissolving pulp.

2.1 Wood morphology

Trees are classically divided into softwoods and hardwoods. Softwood are coniferous trees like pine and spruce, while hardwoods are broad-leaved trees like birch, beech and eucalyptus. The macrostructure of softwood and hardwood differs a lot. Softwood consists mostly of a cell type called tracheids, which have the function of conducting liquids and providing support. The macrostructure of hardwood is more diversified and consists of the four different cell types: vessels, fibres, tracheids and parenchyma, each having a specific function in the tree. For both softwood and hardwood, the wood cells/fibers are long hollow tubes/fiber, see figure below showing transverse section of both softwood and hardwood. The cells of softwood ranges from 2.5-4.5 mm in length and hardwood 0.7-1.6 mm. See Table 1 below:

Table 1: Fiber lengths for common wood types (Ek, et al., 2009)

Wood type	Fibre length, mm
Temperate softwood	2.5-4.5
Temperate hardwood	0.7-1.6
Eucalyptus	0.7-1.5

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The walls of the cells/tubes consist of several different layers all made from the three main components of wood: cellulose, hemicellulose and lignin. Within each cell wall layer cellulose is oriented in one direction (apart from the outer, so called primary cell wall, with random orientation of cellulose fibrils), but in comparing different cell wall layers the orientation differs. This alternating orientation of the cellulose gives sturdiness to the wood cell and support for the tree trunk. Hemicellulose is found usually closely associated to cellulose. The amorphous lignin cover the hemicellulose and cellulose, it also fills the space between cells (middle lamella) (Sjöström, 1993).

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The cellulose content of softwoods and hardwoods are both in the range of 40-50 %, hemicellulose 20-30% and lignin about 20-30%. Besides the main constituents there is also a small amount of extractives and other polysaccharides, see Table 2 below (Ek, et al., 2009).

Table 2: Chemical composition of common wood, wt% (Ek, et al., 2009).

Species	Extractives	Lignin	Cellulose	Glucosmannan	Xylan	Other polysacch.	others
Softwoods							
Norway Spruce (<i>Picea abies</i>)	1.7	27.4	41.7	16.3	8.6	3.4	0.9
Scots Pine (<i>Pinus sylvestris</i>)	3.5	27.7	40.0	16.0	8.9	3.6	0.3
Hardwoods							
Birch (<i>Betula verrucosa</i>)	3.2	22.0	41.0	2.3	27.5	2.6	1.4
Beech (<i>Fagus sylvatica</i>)	1.2	24.8	39.4	1.3	27.8	4.2	1.3
River red gum (<i>Eucalyptus calmdulensis</i>)	2.8	31.3	45.0	3.1	14.1	2.0	1.7
Red maple (<i>Acer rubrum</i>)	3.2	25.4	42.0	3.1	22.1	3.7	0.5

2.1.1 Cellulose

Cellulose is the most abundantly available biopolymer in nature. It's present in all vegetative matter and contributes to 40-50% of the dry mass for most wood species (Sjöström, 1993). It's the main component giving support to the wood cell/tree.

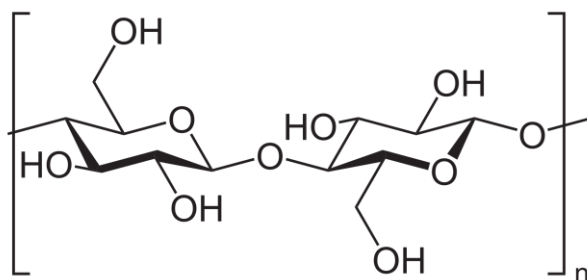


Figure 1: Cellulose structure.

The cellulose polymer is linear made of glucose units, see Figure 1 above linked together by β -(1,4) glycosidic bonds. The length of the cellulose polymer, the degree of polymerization (DP), can be up to about 12000 units as found in nature.

In the wood structure the cellulose chains form strong hydrogen bonds between chains. Bundles of cellulose chains, connected to each other by hydrogen bonds, create microfibrils. The microfibrils have both amorphous and ordered crystalline parts. Assemblies of microfibrils form macrofibrils (Sjöström, 1993). The cellulose structure is physically very strong, inaccessible and well-stabilized by intermolecular interactions. Cellulose is very difficult to dissolve without chemical derivatization.

2.1.2 Hemicellulose

Hemicelluloses are heterogenous polymers found mostly inside the cell wall layers. Their role in the wood structure is not completely understood but has likely some regulating functions. The different types of hemicellulose are made from different mono sugars, including xylose, arabinose, mannose, and galactose. The major type of hemicellulose in hardwood is xylan and in softwood glucomannan, see Table 2 above for typical proportions. Hemicelluloses are compared to cellulose much shorter polymers, about 50-200 units long (Sjöström, 1993).

2.1.3 Lignin

Lignin is a complex heterogenous polymer often described as the “glue” holding the tree together. Much of lignin in wood is found together with hemicellulose in the cell wall layers, but also in the middle lamella (the region between wood cells). The lignin molecule is made from three different monolignols *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Of these only two, coniferyl and sinapyl alcohol are found in wood lignin. The monolignols are linked together by either carbon-carbon or carbon-oxygen bonds.

Contrary to the hydrophilic cellulose and hemicellulose lignin is hydrophobic, an important property for the function of the cell wall as it enable wood cells to transport water and nutrients (Ek, et al., 2009).

2.2 Wood Pulping

Pulping refers to the process in which the macroscopic structure of wood is broken down to fibers. There are several different common methods of pulping, generally divided into the categories chemical pulping and mechanical pulping. Chemical pulping uses chemicals to chemically convert and separate specific components (primarily lignin) of the wood, while mechanical pulping is performed in a process where wood is grinded in the presence of water. The resulting pulp from chemical and mechanical pulping differs a lot, the chemical pulps are often very pure from lignin and hemicellulose while mechanical pulping does not remove much material at all.

In the world of chemical pulping there are mainly two different processes: the Kraft process and the sulfite process. Both processes involve taking wood chips and cooking them in a chemical to dissolve the lignin and thereby breaking down the wood to its fibers/cells. Delignification chemistry in the Kraft process relies on the action of sodium hydroxide and sodium sulfide while in the sulfite

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Commented [MH5]: Bytte plats på dessa två, då denna mening är mer generell.

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Commented [MH8]: Det är inte så att cellulosa är mer robust, utan snarare så att delignifieringskemien är sådan att den är mycket mer selektiv mot lignin. Det säger du redan på sätt och viss i den föregående meningen (att det är lignin som i första hand reagerar, löses upp och extraheras).

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process the cooking chemicals are salts of sulfites (SO_3^{2-}) or bisulfites (HSO_3^{2-}). The cooking step is followed by bleaching that takes pulp from cooking to further delignify the cellulose.

There are several different types of wood pulp produced in these processes, the work done in this thesis focuses on dissolving pulp (the material used in producing viscose fibers) produced using the Kraft process. Dissolving pulp has a higher cellulose content than most paper pulps. The high purity of dissolving pulp is important for applications where it is used (for instance regenerated cellulose fibers), but this comes at a cost of lower yield compared to paper pulp (Sjöström, 1993).

Both the Kraft process and sulfite process are used to produce dissolving pulp and have quite similar performance regarding chemical composition of the pulp and cellulose yield. One important difference is the shape of the molecular weight distribution, with the Kraft process producing more uniform pulp than the sulfite process, which might affect performance in further processing toward textile fibers or cellulose derivatives (Sixta, 2006).

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2.3 Textile fibers

For long time all textiles were made from naturally occurring fibers like cotton, wool and linen. This era was broken toward the end of the 19th century as manmade regenerated cellulose fibers were discovered and started being produced. In the 1940s the oil-based fibers were invented and entered the market (Woodings, 2001).

The change in world consumption of different textile fibers from 1960 to 2014 can be seen in Figure 2 below. From the 1960s to this day the production of manmade non-cellulosic fibers has steadily grown, both in absolute number and market share. The production capacity of cotton has also increased during this period, but not close to the rate of non-cellulosic fibers, making the market share for cotton to shrink from about 70 to 30 %. From this figure it becomes clear that regenerated cellulose fibers (manmade cellulosic in Figure 2) has grown slightly, but it is still only a very small part of the total textile fiber production (Kriifa & Stevens, 2016). A shift towards cellulose-based fibers is expected and big investments in the regenerated textile fiber industry has been made in recent years (The Fiber Year GmbH, 2020).

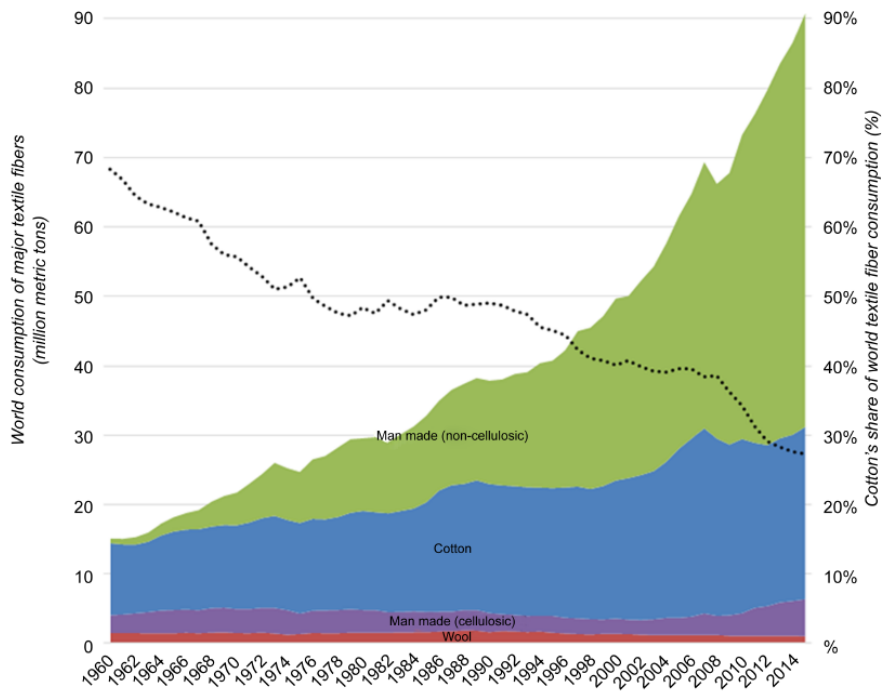


Figure 2: The world consumption of major textile fiber and cotton market share (Krifa & Stevens, 2016).

2.3.1 Regenerated cellulose fibers

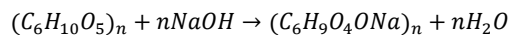
The idea of using cellulosic material that don't naturally form long textile fibers (like cotton) is the key to regenerated cellulose fibers. This is however not that simple to do as cellulose from wood is strong and difficult to dissolve. In the viscose process this is solved by introducing an intermediate step where the cellulose is converted into a soluble cellulose derivative. The solution of the dissolved cellulose derivative can then be regenerated into cellulose in a controlled way. This enables industrial production of customizable textile fibers from renewable materials (Woodings, 2001). There are several different types of regenerated cellulose textile fibers (not only relying on derivatization mediated dissolution), but this thesis focuses only on viscose.

2.3.2 Viscose process

The viscose process starts off by making a slurry of dissolving pulp and sodium hydroxide, in the literature this step goes by several different names; steeping, alkalization and mercerizing is common (Woodings, 2001). This step converts the cellulose to alkali cellulose, Na-Cell, which is sensitive to oxidative degradation if exposed to oxygen. Besides transforming cellulose to Na-Cell the alkalization step removes short chained cellulose and hemicellulose (Fechter, et al., 2020). The chemical reaction for alkalization can be seen below:

Commented [MH12]: Spelar inte så stor roll för löslighet eller applikation i textila fibrer. Robust, resistent?

Commented [MH13]: För det här är ingen universal lösning. Tänk på Lyocell.



cellulose + sodium hydroxide → alkali cellulose + water

The concentration of the sodium hydroxide in the slurry is standardized to about 18 wt% and the slurry temperature is about 50°C. The cellulose will reach maximum swelling at a concentration of 10 wt.% NaOH, enabling good transport of the NaOH in the whole fiber, but a higher concentration is needed to fully transform the cellulose to Na-Cell. The concentration of 18 wt% NaOH is a compromise, which swells the cellulose while still being strong enough to fully convert the cellulose to Na-Cell. The duration of the alkalization is in industrial applications around 30 minutes (Woodings, 2001). Consistency (the weight percentage wood fiber) for the slurry is normally under 6% (Sixta, 2006).

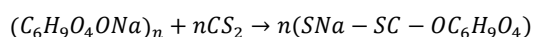
After the alkalization step excess sodium hydroxide is removed from the Na-Cell by pressing. This is performed to optimize the ratio cellulose/NaOH/H₂O for the coming process step: aging. The pressed Na-Cell contains about 30-36% cellulose and 13-17% NaOH (Woodings, 2001). In industrial application the excess NaOH from the alkalization step is recirculated. This is essential from a financial standpoint (Sixta, 2006).

After pressing the alkali cellulose is shredded. Shredding enables good access to oxygen and will lower the density of the pulp. The volume of alkali cellulose pulp will about triple during this step. Shredding is followed by aging, in which an oxidative process will cause random scission of the Na-Cell polymer and thereby lower the DP. Peeling, end-wise scission of monomers, of the Na-Cell also occurs but at a much slower rate (Ahmad, et al., 2015).

The target DP for the alkali cellulose after aging is about 300, this is a tradeoff between fiber- and spinning properties (Woodings, 2001). Aging is industrially performed at temperatures between 30-60°C. A duration of 0.5-5 hours is normal (Woodings, 2001), but it is not uncommon to take much longer (up to 3 days) (Ahmad, et al., 2015).

What causes the increased reactivity of cellulose when transformed to Na-Cell is breakage of hydrogen bonds and swelling of fibers. The breakage of hydrogen bonds enables easier access to the hydroxyl groups on the glucose molecule and swelling makes molecular diffusion of reagents easier. Swelling of the cellulose means also that the supramolecular structure of the cellulose web changes, specifically that the distance between cellulose lattice planes in the crystalline regions increases (Sixta, 2006).

After the alkalization and aging phase, the next step is xanthation. In the xanthation step the alkali cellulose is mixed with carbon disulfide vapor to create cellulose xanthate. To ensure the carbon disulfide is in vapor phase the process occurs under vacuum. This is industrially performed both as a batch and a continuous process at temperatures about 28-35°C. The main chemical reaction can be seen below:



alkali cellulose + carbon disulfide → sodium cellulose xanthate

While the chemical reaction described above is the key reaction involved in xanthation, it should be noted that there are side reactions producing the unwanted products Na₂CS₃, Na₂S and Na₂CO₃.

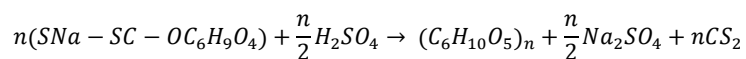
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Unfortunately, the selectivity for these by-products are favored by higher temperature, forcing a tradeoff between speed of reaction and the efficient use of chemicals (Woodings, 2001).

After xanthation the sodium cellulose xanthate is a solid. To dissolve it, it is mixed with dilute sodium hydroxide (typically 1-2%) to a specific concentration, depending on the viscose fiber produced. The solubility of the sodium cellulose xanthate is best at low temperatures and is normally performed with cooling at 8-12°C. The resulting liquid is called the viscose dope. To avoid problems later in the process the viscose dope is filtered and deaired, these steps ensure the viscose dope is free from particles and bubbles, important in the spinning step.

Spinning is performed by extruding viscose dope at high speed through very small holes (through a spinning jet) into a bath containing sulfuric acid, sodium sulfate and zinc sulfate. The chemical reaction in the spin bath is very complex but for the sodium cellulose xanthate the important reaction is:



sodium cellulose xanthate + sulfuric acid → cellulose + sodium sulfate + carbon disulfide

The sodium cellulose xanthate reacts with sulfuric acid to form cellulose (the textile fiber), sodium sulfate and carbon disulfide. Most chemicals are recovered in the process, but the sodium sulfate formed in the spinning bath is purged as it has no use in the process. Unfortunately, the economic value of sodium sulfate is very low. It would be possible to chemically close the process even further if electrochemical splitting of the sodium sulfate to sodium hydroxide and sulfuric acid was applied, two chemicals essential in the process (Öhman, et al., 2014).

2.3.3 More on aging of alkaline cellulose

Aging in the viscose process is used to control the degree of polymerization (DP) of the pulp, the length of the cellulose polymer. When the excess NaOH is removed from the alkalinized pulp in the viscose process an autooxidation (a oxidation reaction at, or near, room temperature sustained without input of heat (Foote, 1995)) of the cellulose polymers starts. This oxidation reaction will randomly cut the cellulose polymer. The exact reaction mechanism is not completely understood, but there have been quite a few different attempts made.

An early description of this mechanism was presented by Entwistle et al. (Entwistle, et al., 1949). The mechanism is built on the idea of a chain mechanism in which the removal of active hydrogen from an aldehyde end-group of the cellulose polymer would cause the formation of a hydroperoxide radical and a cellulose radical. This would lead to a series of reactions involving the cellulose radical and unmodified cellulose causing the random scission. Mattor (Mattor, 1963) describes an ionic mechanism in which oxygen reacts with the end groups of cellulose, creating cellulose ions. The cellulose ions would then further react with oxygen forming hydrogen peroxide. The hydrogen peroxide would finally react with the cellulose chain and cause the scission.

Entwistle et al. (Entwistle, et al., 1949) might not have conclusively described the mechanism, but in the experimental work a lot of knowledge was gained. As an indicator of the reaction rate during aging the oxygen consumption is commonly used and is strongly correlated with the carbonyl content of the pulp. For dissolving pulp with low carbonyl content, the oxygen consumption of the reaction will initially be low. As aging progresses the carbonyl content and oxygen consumption

increase together. For pulps of high carbonyl content, the oxygen consumption starts out high, but will decrease in parallel with the carbonyl content as reaction progresses. In both the case of high- and low initial carbonyl content there is a close relation between carbonyl content and reaction rate, where carbonyls acts as a catalyst for the reaction (Entwistle, et al., 1949). There appears to be a non-zero equilibrium for the carbonyl content during aging, where new carbonyl groups are created at the same rate as they are consumed. This equilibrium depends on the conditions of aging (Samuelsson, 1967).

There are several examples of metals that works either as catalysts or inhibitors for the reaction rate. Some metals, like tin, nickel and chromium, have been identified as catalysts, but lacks importance for this evaluation as they are not naturally occurring in the wood raw material or the pulping process in high enough concentrations to have practical importance. Samuelsson (1967) identified manganese as very important in the context of aging of alkaline cellulose. It can act both as a catalyst and inhibitor depending on its concentration. Small concentrations, about 5-10 ppm, catalyzes the reaction, while high concentrations, about 150 ppm, it instead inhibits the reaction.

As indicated in the previous chapter, the purity of the sodium hydroxide solution used in the alkalization step is very important regarding the presence of non-process elements. The metallic content of the sodium hydroxide solution is possibly more rate determining than the metallic content of the pulp itself (Samuelsson, 1967).

2.4 Measuring DP and MWD to assess dissolving pulp properties

2.4.1 Intrinsic viscosity

By dissolving cellulose fibers into individual polymers, the viscosity of the resulting solution can be measured to determine the DP of a pulp. In comparing the viscosity of such an solution with molecular weight distribution (MWD) data (which gives DP) it's been found that viscosity and DP for cellulose pulps strongly correlate (Evans & Wallis, 1989). Viscosity is the most common industrial method for determining average molecular weights for pulps (Oberlerchner, et al., 2015).

There are several different standards of measuring the viscosity of a pulp, the most common methods are Tappi viscosity (T 230) and intrinsic viscosity (ISO 5351:2010). Both methods use cupri-ethylenediamine (CED) as solvent and measures the effluent time for the solution to flow through a standardized capillary. In the Tappi viscosity standard the concentration of pulp in the CED solution is always 0,5 %, giving different effluent times for pulps of different viscosity. Intrinsic viscosity on the other hand aims to keep effluent times constant, meaning that the concentration of pulp in the CED solution is different for pulps of different viscosity. While similar methods there is no generally used correlation between the two types of viscosity. In this thesis intrinsic viscosity following the ISO 5351:2010 standard is used (Swedish Standards Insitute, 2010).

Commented [MH16]: Om standardmetod ange nummer. Hur skiljer den sig från intrinsic?

2.4.2 Molecular weight distribution

In evaluating and comparing the properties of paper- and dissolving pulp the molecular weight distribution (MWD) is a powerful tool giving a lot of information. A common experimental method to obtain a molecular weight distribution analysis is size exclusion chromatography (SEC), specifically gel permeation chromatography (GPC) in combination with multi angle light scattering (MALLS) (Oberlerchner, et al., 2015).

One important information from the MWD is the degree of polymerization. The degree of polymerization is calculated from the molecular weight of the cellulose polymer, but this can be calculated in several ways taking different types of averages of the molecular weight. The three most common can be seen below (Oberlerchner, et al., 2015):

$$\text{The number average } M_n \text{ is given by: } M_n = \frac{\sum n_i M_i}{\sum n_i} \quad \text{Equation 1}$$

$$\text{The weight average } M_w \text{ is given by: } M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad \text{Equation 2}$$

$$\text{The Z average } M_z \text{ is given by: } M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \quad \text{Equation 3}$$

In these equation M_i is the molecular weight of a specific size of cellulose molecule, n_i is the total number of molecules of this size. The term $\sum n_i M_i$ corresponds to the total number of a specific cellulose molecule size times the molecular weight of this molecule, summed over all molecule sizes. This would be the same as the total weight of the analyzed sample. The term $\sum n_i$ is the total number of molecules. These different average molecular weights always fulfill:

$$M_n < M_w < M_z$$

Of these average molecular weights M_z is seldomly used (but has some applications, not relevant for this thesis). For the purpose of correlating intrinsic viscosity and degree of polymerization both M_n and M_w have been used in literature, but the weight-weighted M_w correlates better (Evans & Wallis, 1989) (Oberlerchner, et al., 2015). DP is calculated by dividing the weight average molecular mass by the mass of one glucose unit.

Another important number for molecular weight distributions is the dispersity, \mathfrak{D}_M , of the distribution:

$$\mathfrak{D}_M = \frac{M_w}{M_n} \quad \text{Equation 4}$$

\mathfrak{D}_M shows how heterogenous the sample is regarding polymer length. If all polymers are of the same length, then $\mathfrak{D}_M = 1$. The closer \mathfrak{D}_M is to one, the narrower is the distribution (Oberlerchner, et al., 2015).

Molecular weight distributions are usually visualized by plotting the logarithmic M_w against the differential weight fraction, see Figure 3 below for example (Ahmad 2015):

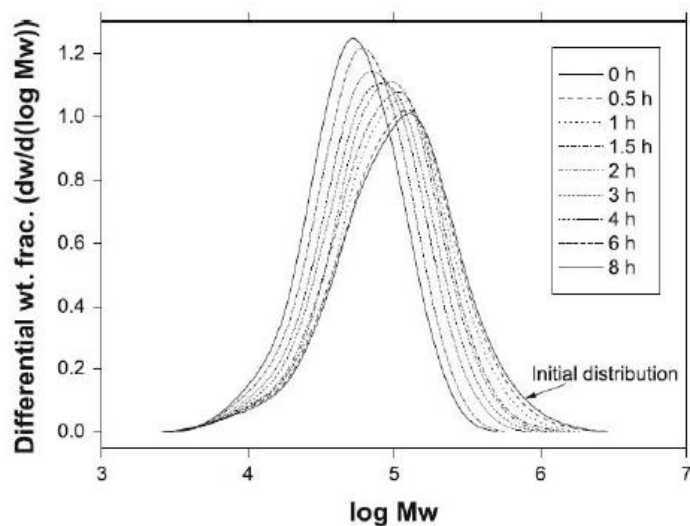


Figure 3: Example of weight distribution curves. This is from Ahmad et al 2015 showing an example of how the distribution of an alkalinized pulp changed during aging.

While it can be very useful to do a MWD analysis of a dissolving pulp to estimate the DP, its compared to intrinsic viscosity an expensive and sometimes time-consuming method (Oberlerchner, et al., 2015).

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2.4.3 Correlating DP and intrinsic viscosity

As previous chapter indicates the average molecular mass of a pulp correlates to its intrinsic viscosity. The correlations found in literature between DP and intrinsic viscosity almost always follows the structure according to:

$$DP^a = b \cdot [\eta] \quad \text{Equation 5}$$

Where DP is the degree of polymerization and $[\eta]$ is the intrinsic viscosity. a and b are constants that varies between correlations.

The two most common correlations for the intrinsic viscosity and degree of polymerization for dissolving pulps are Immergut (Immergut, et al., 1953) $DP_n^{0.905} = 0.75 \cdot [\eta]$ and Evans & Wallis (Evans & Wallis, 1989) $DP_n^{0.9} = 1.65 \cdot [\eta]$.

The correlations from Immergut and Evans & Wallis are created using molecular weight distribution data. The historically often used correlation from Immergut only uses the number average molecular weight, in practice assuming polydispersity to be one. There is no doubt the correlation from Immergut works well on some data, but it often significantly underestimates DP. Evans & Wallis,

on the other hand, did take polydispersity into consideration and correlated the intrinsic viscosity with the weight-weighted degree of polymerization instead, which appears to have a much better universal use (Evans & Wallis, 1989).

2.5 Modelling of alkaline cellulose aging

The main objective of this thesis is the mathematical modelling of the aging step in the viscose process, this problem can be approached in several different ways. Either the process of alkalization and aging is considered to be a “black box”, in which there are no knowledge about the process (at least not any knowledge used in the model). In the black box case, the output is only described using the input data in the mathematical model. The opposite is a “white box” model, in which there is a complete knowledge about the process (Glanville, 1982).

To solve a black box model simple linear regression suggesting linear terms capturing main effects and interactions is a useful tool. An example of such an equation can be seen below:

$$\hat{y} = b_0 + b_1 \cdot X_1 + b_2 \cdot X_2 + b_3 \cdot X_1 \cdot X_2 + b_4 \cdot X_1^2 + b_5 \cdot X_2^2 \quad \text{Equation 6}$$

Where \hat{y} is the prediction, X_1 and X_2 are the variables in the model (for aging of dissolving pulp this could correspond to time and temperature) and b_i are the linear contributions to the prediction optimized in regression to minimize the sum of square error. This is a simple straight forward method, but it does not give any real physical understanding of the reaction (Glanville, 1982) (Rasmuson, et al., 2014). Black box models are frequently used as they can perform very well with almost no effort.

From an academic point of view the black box model is unsatisfying, as it doesn't describe the real mechanism of the process. The white box model however is much more demanding and might be impossible to reach even for simple processes (depending on what it means to know a process it can be argued the white box doesn't exist). For the case of aging alkalized cellulose, the white box is not realistic. The complexity of completely describing the process is too high.

However, there are some things known about alkalization and aging, and it is possible to shed some light into the black box.

2.5.1 The derivation of the empirical aging model

In this chapter one mathematical model of how DP declines during alkalization and aging is presented. The variables of the model are the intrinsic viscosity of the dissolving pulp and the temperature and duration of aging.

Sixta (Sixta, 2006) suggests an approach to the modelling of how intrinsic viscosity declines during oxygen delignification of pulp. Oxygen delignification is different than the alkali autooxidation during aging, but the approach has shown promise in earlier unpublished experiments.

The starting point of this approach is Equation 7 below, calculating m_n , the number of cellulose chains per ton dry pulp:

$$m_n = \frac{10^6}{162 \cdot DP} \quad \text{Equation 7}$$

Where 10^6 is grams per ton, 162 is the molar mass of a single cellulose unit and DP is the average degree of polymerization.

The DP of the pulp is the factor of main importance for aging, but as the theory chapter suggests the strong correlation between intrinsic viscosity and DP , making it reasonable to substitute DP in Equation 7 with a correlation to intrinsic viscosity instead. From the general form of these correlations, $DP^a = b \cdot [\eta]$, the DP can be solved for:

$$DP = \sqrt[a]{b \cdot [\eta]} \quad \text{Equation 8}$$

Equation 7 and Equation 8 combined gives Equation 9.

$$m_n = \frac{10^6}{162 \cdot \sqrt[a]{b \cdot [\eta]}} \quad \text{Equation 9}$$

Now the intrinsic viscosity, $[\eta]$, is solved for.

$$[\eta] = \frac{\frac{1}{b} \left(\frac{10^6}{162} \right)^a}{m_n^a} \quad \text{Equation 10}$$

At the start of the aging process the number of cellulose chains per ton dry pulp as a function of intrinsic viscosity can be calculated according to Equation 7 or Equation 9. It is known that the number of cellulose chains per ton dry pulp will increase as the pulp goes through aging, an expression describing the number of cellulose chains per ton dry pulp as a function of time and temperature is needed.

Assuming a zero-order reaction and a non-linear time contribution the number of cellulose molecules per ton dry pulp can be described as a function:

$$m_{n(t)} = m_{n(o)} + k \cdot t^p \quad \text{Equation 11}$$

From Sixta (Sixta, 2006) the reaction rate constant k can be described as:

$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot [OH^-]^m \cdot [O_2]^n \quad \text{Equation 12}$$

In this thesis the concentration of hydroxide ions and oxygen will be constant in all experiments, making it possible to simplify k to:

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$$k = A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \quad \text{Equation 13}$$

The time dependent $m_{n(t)}$, Equation 11, can be applied to Equation 10:

$$[\eta] = \frac{\frac{1}{b} \left(\frac{10^6}{162}\right)^a}{(m_{n(o)} + k \cdot t^p)^a} \quad \text{Equation 14}$$

Finally, combining Equation 9, Equation 13 and Equation 14, this results in Equation 15.

$$[\eta] = \frac{\frac{1}{b} \left(\frac{10^6}{162}\right)^a}{\left(A \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot t^p + \frac{10^6}{162 \cdot a \cdot b \cdot [\eta]}\right)^a} \quad \text{Equation 15}$$

In this form, a and b are the correlation dependent constants, A, E_a and p are the coefficient to be optimized in regression. Using this final form of the solution it is easy to try different correlations between DP and $[\eta]$ as only constants a and b need to be changed. While not very common, there are $DP \leftrightarrow [\eta]$ correlations following other structures than Equation 5. For these cases the general approach to the solution is still valid, but the final form of the solution would look different.

Equation 15 creates a non-linear mathematical model. What makes the regression model linear or non-linear depends on which way the parameters optimized in a least square solution contribute to the predictor. For instance, in the linear example in Equation 6, the parameters b_i all make linear contribution to the prediction \hat{y} , even if the terms themselves might be quadratic. Non-linear regression optimizes parameters that does not give a linear contribution to the prediction.

3 Materials and Methods

3.1 Materials

For the purpose of this trial six different pulps were available, from these four were selected for the purpose of creating data for modelling. All the investigated pulps are short fiber (hardwood) kraft pulps from the same commercial dissolving pulp producer. The full list of available pulps and purpose in the study is presented in Table 3 below. The pulps are named after their starting intrinsic viscosity. Pulp 282 was only alkalinized, not aged.

Table 3: List of available dissolving pulp, their intrinsic viscosity and what they were used for in the project.

Pulp ID:	Intrinsic viscosity [ml/g]:	Use:		
		Modelling:	Validation:	Other:
Pulp 282	282			X
Pulp 349	349	X		
Pulp 403	403	X	X	
Pulp 463	463	X		
Pulp 532	532	X		
Pulp 544	544		X	

Intrinsic viscosity was measured on all samples, for other chemical analysis methods only a subset of samples was analyzed, see Table 4. Pulp ### refers to the starting material, Pulp ### AC0 refers to the zero-sample (after alkalization, before aging) and Pulp ### AC250 refers to a sample close to viscosity 250 ml/g.

Table 4: Selection of samples chosen for carbohydrate-, molecular weight distribution (MWD)- and carbonyl group analysis.

Sample:	Carbohydrates:	MWD:	Carbonyl groups:
Pulp 349	x	x	
Pulp 349 AC0	x	x	
Pulp 403	x	x	x
Pulp 403 AC0	x	x	x
Pulp 403 AC250	x	x	x
Pulp 463	x	x	
Pulp 463 AC0	x	x	
Pulp 532	x	x	x
Pulp 532 AC0	x	x	
Pulp 532 AC250	x	x	
Pulp 282	x		
Pulp 544	x		

3.2 Experimental design

While the aim of this thesis is to create a mathematical model describing aging as a function of initial viscosity, temperature and time of aging, all time and temperature combinations are not of interest. A target viscosity of 250 ml/g is used (Woodings, 2001), and this target viscosity should be reached in a time that allows for normal, daytime, working hours. In practice this means that from a starting viscosity of 349-532 ml/g it should reach 250 ml/g in about 18-24 hours at temperatures around 25-35°C.

Each of the four pulps used intended for creating the mathematical model, see Table 3, were put through the plan seen in Table 5. The pulps were divided into two batches, alkalized separately. Alkalization 1 gave samples early in the aging process, and alkalization 2 gave samples late in the process. This meant that all pulps gave duplicate zero samples (testing the repeatability of the alkalization and viscosity measurements) and duplicate 23,5 hours samples (testing the repeatability of the alkalization, aging process and viscosity measurements).

Table 5: The experimental plan all the pulps for modelling went through.

Alkalization:	Temperature [°C]:	Aging time [h]:					
		0	3.5	7.5	-	-	23.5
1	25	0	3.5	7.5	-	-	23.5
2	25	0	-	-	15.5	19.5	23.5
1	30	0	3.5	7.5	-	-	23.5
2	30	0	-	-	15.5	19.5	23.5
1	35	0	3.5	7.5	-	-	23.5
2	35	0	-	-	15.5	19.5	23.5

3.3 Alkalization

30 grams (on dry basis) of dissolving pulp was divided into roughly 2x2 cm pieces by hand. 900 grams of NaOH 18wt% (producer: Labservice AB) was heated to 50°C in a beaker placed in a temperature-controlled water bath.

The pulp pieces were placed in the NaOH(aq) where they were kept under constant stirring for 30 minutes ensuring homogenous swelling and alkalization of the pulp (this is seen on the front page of the thesis). After the 30-minute alkalization the pulp slurry was moved to a Buchner funnel with a nylon filter in the bottom. Vacuum was applied, which exposes the alkalized pulp to air/oxygen and starts the autoxidative degradation of the cellulose polymer.

Vacuum filtration removes most of the NaOH(aq). To get the correct concentration of NaOH(aq) in the alkalized pulp it was further pressed at 20 bars in a hydraulic press. After pressing, the final filter cake was weighed as a final control of the NaOH(aq) to cellulose ratio, the ratio between the dry dissolving pulp to the weight of the alkalized and pressed pulp must be between 2,6-3. Next, the alkalized pulp was shredded using a kitchen blender at full effect for 30 seconds. Directly after shredding a 5-gram zero sample was placed in a glass beaker, the rest of the pulp (in 5-gram portions) was placed in 50 ml plastic bottles. During pressing, shredding and bottle preparation the work pace was adjusted for it to take another 30 minutes (total 60 minutes since alkalization started). At this point 250 ml of deionized water was poured on the zero-sample (stopping reaction) and the prepared plastic bottles were placed into three different ovens, preheated to 25°C, 30°C and 35°C respectively.

To the zero sample 0,5 M sulfuric acid was added until pH 6 was reached. The liquid of the neutralized sample was then removed using vacuum filtration. The filtrate was recycled one time before the sample was rinsed with 800 ml deionized water (portioned 2x400ml). Most of the water in the sample was removed using vacuum, then left to completely dry in ambient conditions.

3.4 Aging of alkaline cellulose

Three ovens were preheated to 25°C, 30°C and 35°C, controlled before and after each experiment. From ovens samples were removed according to experimental plan and were neutralized with water and 0,5 M sulfuric acid, then rinsed with deionized water (same procedure as for the zero sample for alkalization).

3.5 Molecular weight distribution using GPC-MALLS

The molecular weight distribution was analyzed using GPC-MALLS (Gel Permeation Chromatography – Multi Angle Light Scattering) by a method described by Henniges et al (2011). The solvent used to dissolve the cellulose sample was a mixture of dimethylacetamine (DMAc) and lithium chloride (LiCl).

3.6 Analysis of carbonyl groups using fluorescence labeling

The carbonyl content of the selected pulps was determined by using fluorescence labeling of carbonyl groups together with the above described GPC-MALLS methodology combined with UV-detection. The method is described by Röhrling et al. (Röhrling, et al., 2002). For labeling of carbonyl groups carbazole-0-carboxylic acid was used.

3.7 Intrinsic viscosity

The intrinsic viscosity of the samples was analyzed following the ISO5351:2010 standard, a method using copper ethylene diamine (CED) as solution agent for the pulp sample. The ISO5351:2010 standard also specifies that duplicates of samples must be prepared, and the intrinsic viscosity analyzed, this was not done for the purpose of this thesis.

While there were no duplicate samples, the samples were analyzed using three capillaries, the measurement was repeated until the result between repetitions did not change within a 0.5% tolerance.

3.8 Carbohydrates

The analysis of the carbohydrate composition was performed according to the TAPPI-T 249 cm-85 standard, a standard using 72 wt% H₂SO₄. A method based on the acid hydrolysis of the pulp sample followed by quantification of the carbohydrate constituents using ion chromatography. Equipment used was HPAE ICS-3000 from Dionex with Pulsed Amperometric Detection. The results from carbohydrate analysis include arabinose, galactose, glucose, xylose and mannose.

4 Results and discussion

4.1 Aging study

The primary experimental results in this thesis are the intrinsic viscosity measurements done on the aging experiment samples, this will be presented first followed by the chemical analysis results. Finally, the mathematical model will be presented followed by a general discussion.

4.1.1 Viscosity after alkalization

In Figure 4 below the starting viscosity versus viscosity after alkalization is presented for all pulps included in this thesis. A linear regression line has been added to the data with a coefficient of determination, R^2 , of over 0,99. For Pulp 544, seen furthest to the right in Figure 4, the viscosity after alkalization is the same as for Pulp 532. Whether this would be true for even higher starting viscosities was not evaluated.

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Determination/correlation?

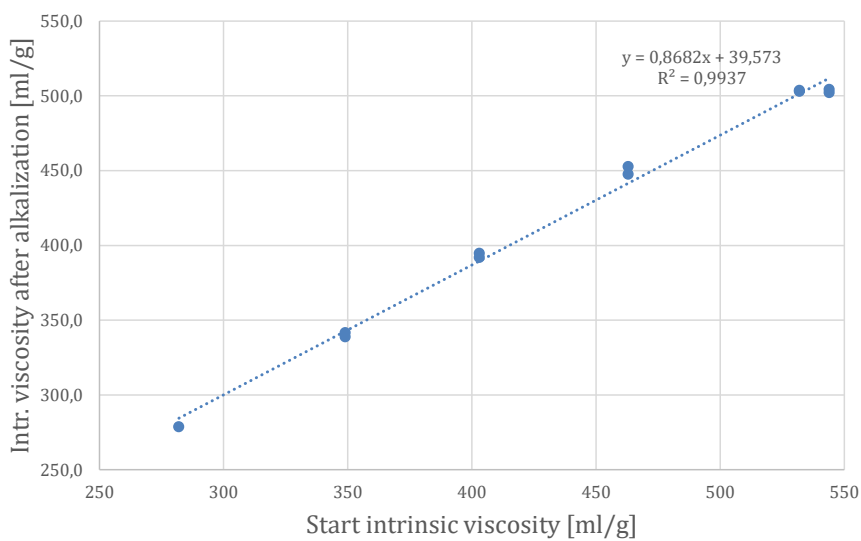


Figure 4: Intrinsic viscosity before and after alkalization with linear regression line.

4.1.2 Viscosity after aging

In Figure 5, Figure 6, Figure 7 and Figure 8 below the results from the viscosity measurements for the aging study can be seen for Pulp 349, Pulp 403, Pulp 463 and Pulp 532. All four figures show the decline of viscosity during aging. Samuelsson (1967) describes the viscosity drop being the fastest in the beginning, this can also be observed in the figures. The slope between samples taken during the first ten hours are steeper than between samples taken between 15-24 hours. At 0 hours and 23,5 hours there are duplicate data in all figures, but as repeatability was very good this is often not visible in the figures below.

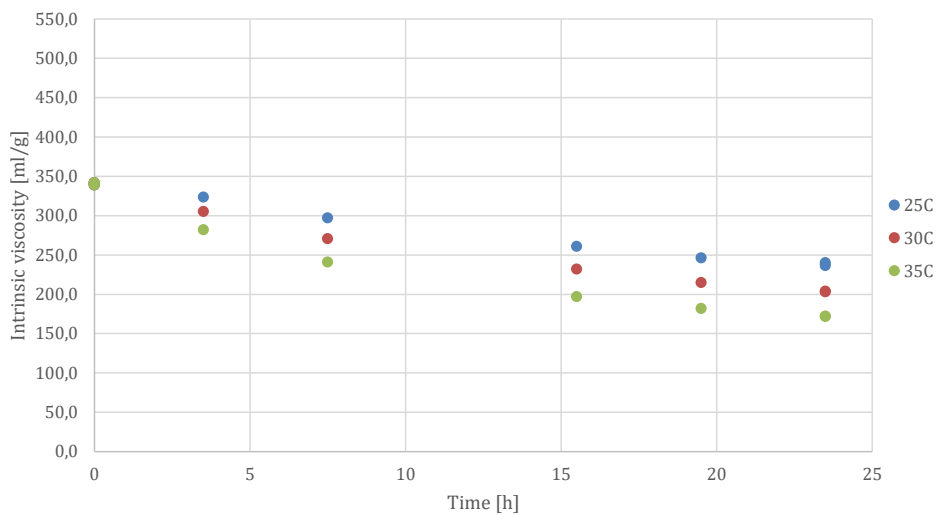


Figure 5: Pulp 349, viscosity as function of time and temperature of aging.

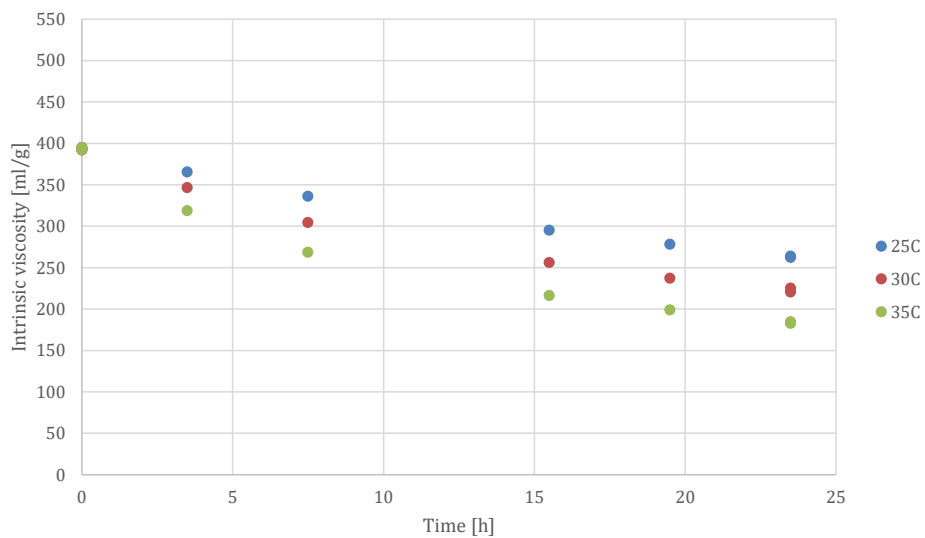


Figure 6: Pulp 403, viscosity as function of time and temperature of aging.

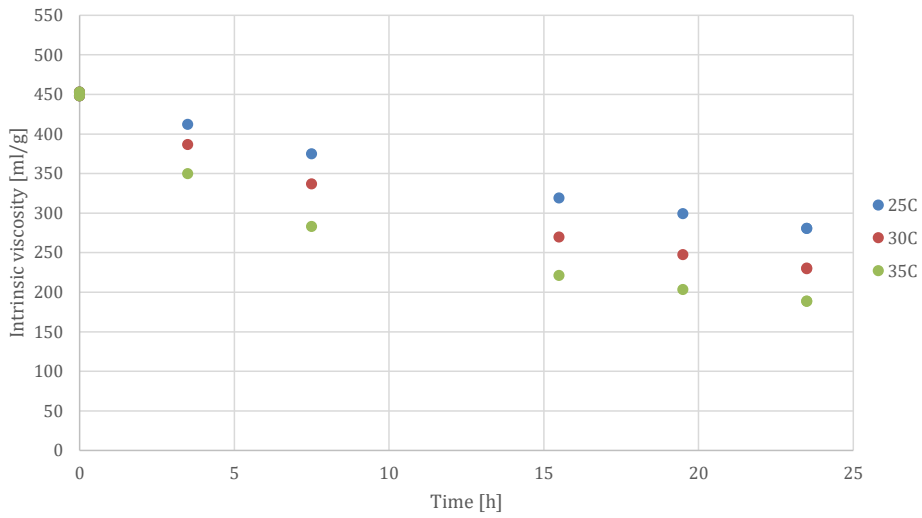


Figure 7: Pulp 463, viscosity as function of time and temperature of aging.

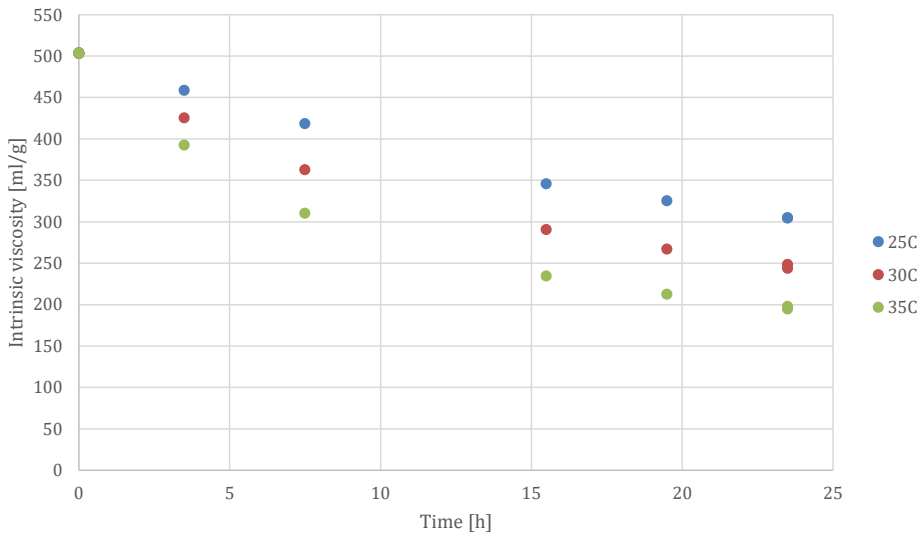


Figure 8: Pulp 532, viscosity as function of time and temperature of aging.

If instead the temperature is fixed but all four pulps are included in the same figure it appears that the intrinsic viscosity for the different pulps converges with time, likely due to a declining reaction rate, see Figure 9 (in this case at 35°C).

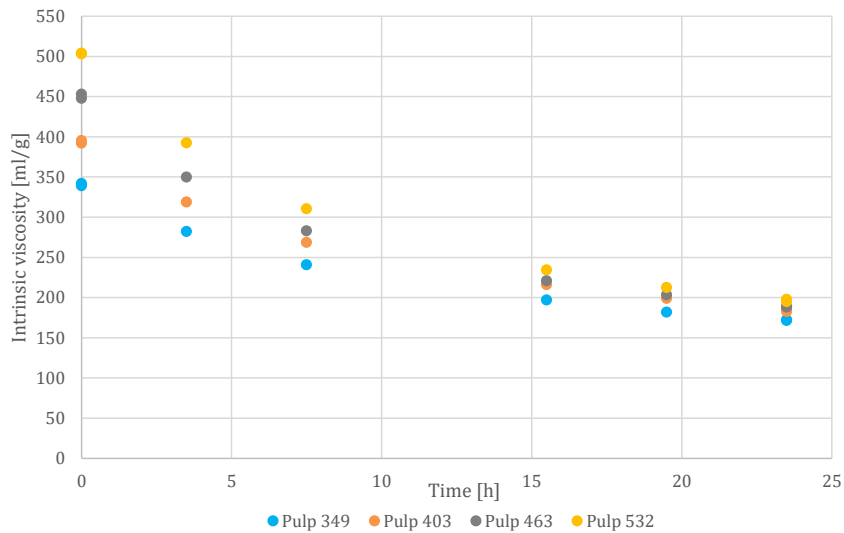


Figure 9: Intrinsic viscosity as function of aging time for pulps aged at 35°C.

4.2 Carbohydrates

The carbohydrate composition of the studied samples can be seen in Table 6 below. It can be observed the xylose content is between 3,1-3,9 wt% for all pulps before alkalization but drops to between 1-1.3 wt% after.

Table 6: Carbohydrate analysis results.

Anhydrous sugar calculated to 100% yield, mg/g dry pulp						
Sample ID:	Sample type:	Arabinose	Galactose	Glucose	Xylose	Mannose
Pulp 349	Untreated	0	0	962	33	4
Pulp 349 AC0	Alkalized	0	0	988	10	2
Pulp 403	Untreated	0	0	956	39	4
Pulp 403 AC0	Alkalized	0	0	986	12	2
Pulp 403 AC250	Alkalized and aged	0	0	986	12	2
Pulp 463	Untreated	0	0	957	38	4
Pulp 463 AC0	Alkalized	0	0	984	13	2
Pulp 532	Untreated	0	0	958	38	4
Pulp 532 AC0	Alkalized	0	0	984	14	2
Pulp 532 AC250	Alkalized and aged	0	0	985	13	2
Pulp 544	Untreated	0	0	958	37	5
Pulp 282	Untreated	0	0	964	31	5

The mannose content in the pulps is much lower than for xylose but follows the same general trend of dropping during the alkalization step. The low levels of arabinose and galactose was expected as the raw material used in producing these dissolving pulps was hardwood (naturally low in these sugars). The observed drop in hemicellulose in the alkalization step corresponds well to the literature (Budtova & Navard, 2016) (Fechter, et al., 2020).

4.3 Analysis of carbonyl groups using fluorescence labeling

The results for the carbonyl analysis can be seen in Table 7 below. Normal carbonyl content for pulps is within the range of about 3-40 $\mu\text{mol/g}$ (Röhring, et al., 2002), in this evaluation the results ranged from 3,26-5,08 $\mu\text{mol/g}$.

The data presented in Table 7 follow Pulp 403 before alkalization, after alkalization and after aging. The carbonyl content for Pulp 403 increases during alkalization, to then decrease during aging. Potthast et al. (Potthast, et al., 2003) showed how the carbonyl group content reduced by almost 50% during the alkalization for a bleached sulfite pulp. It is possible that the difference in pulping process explains the discrepancy between the results.

Table 7: Results from carbonyl group analysis.

Pulp:	Intrinsic viscosity [ml/g]:	Carbonyl content [$\mu\text{mol/g}$]:
Pulp 403	403	4,73
Pulp 403 AC0	392	5,08
Pulp 403 AC250	244	4,87
Pulp 532	532	3,26

Notable is the difference between Pulp 403 and Pulp 532. If taking DP from the MWD analysis into consideration (presented in the next chapter) and applying Equation 7 it is found that the number of chains per ton dry pulp is very different. If comparing carbonyl group content per cellulose chain (relevant since carbonyl groups are, apart from infrequent occurrence along the chain, found always in the ends of the cellulose polymer) instead of per gram pulp the difference disappears. Samuelsson (Samuelsson, 1967) indicated the carbonyl group content was important for the reaction rate during aging, this is likely true, but for the low-carbonyl pulps studied in this thesis it does not appear to be an important factor.

4.4 Molecular weight distribution

The molecular weight distributions were measured for a selected number of samples. For each pulp sample two SEC/GPC-MALLS analysis was performed. In Table 8 the average value of the two analysis can be seen for all evaluated samples.

Table 8: Molecular weight distribution results.

Sample name:	Intrinsic viscosity [ml/g]:	DPw:	Mn [kDa]:	Mw [kDa]:	Mz [kDa]:	Polydispersity:
Pulp 349	349	844	69	137	232	1,99
Pulp 349 AC0	339	842	75	136	224	1,83
Pulp 403	403	1056	70	171	331	2,47
Pulp 403 AC0	392	989	85	160	273	1,88
Pulp 403 AC250	244	526	56	85	121	1,53
Pulp 463	463	1272	89	206	383	2,31
Pulp 463 AC0	453	1188	94	192	335	2,05
Pulp 532	532	1552	91	251	502	2,78
Pulp 532 AC0	503	1347	107	218	390	2,04
Pulp 532 AC250	248	547	59	89	124	1,51

In this table a few different observations can be made: Polydispersity always decreases in the alkalization step; it decreases even further during aging. The number average molecular weight, Mn, always increases after alkalization. The Mn increase after alkalization indicates removal of hemi cellulose and low Mw cellulose (Oberlerchner, et al., 2015).

In comparing Pulp 403 AC250 and Pulp 532 AC250, it appears like the MWD for Pulp 403 and Pulp 532 converge during aging, also reported in literature by Samuelsson (Samuelsson, 1967).

The graphical representation of the MWDs can be seen in Figure 10, Figure 11, Figure 12, Figure 13, Figure 14 and Figure 15. The distribution for the different starting pulps (only one of the two analysis per pulp shown) can be seen in Figure 10. It's visible that the average molecular weight increases as the intrinsic viscosity of the pulp increases.

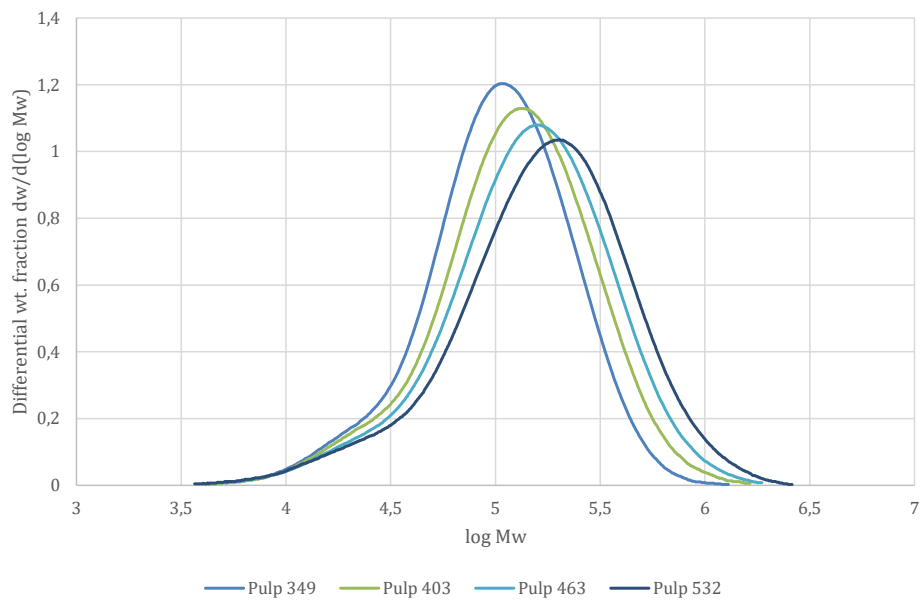


Figure 10: Molecular weight distribution for four different pulps, before alkalization.

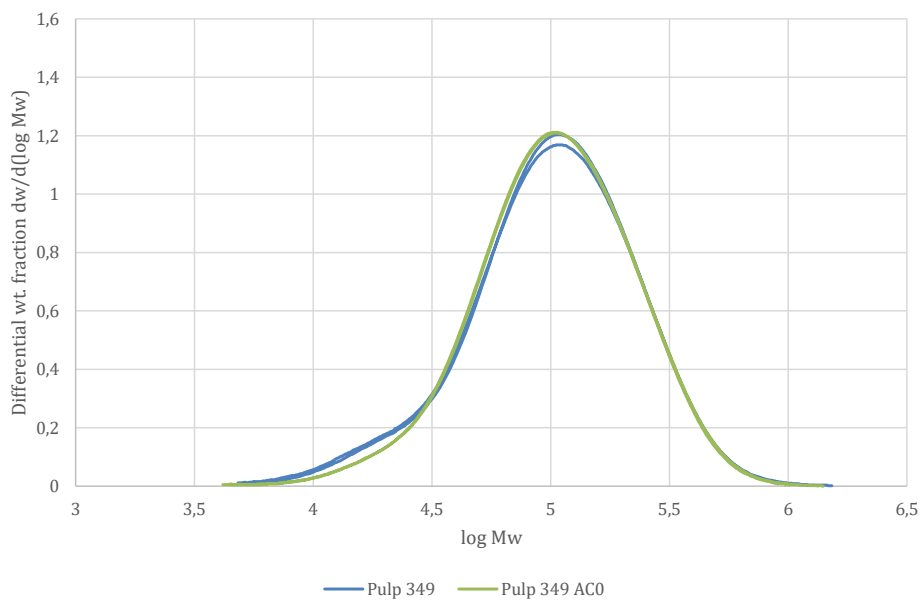


Figure 11: Molecular weight distribution for Pulp 349 before and after alkalization.

The results for Pulp 349 before and after alkalization can be seen in Figure 11, the repeated analysis included creating two lines for each series. There is very little difference between the curves. This is mirrored by the results presented in Table 8.

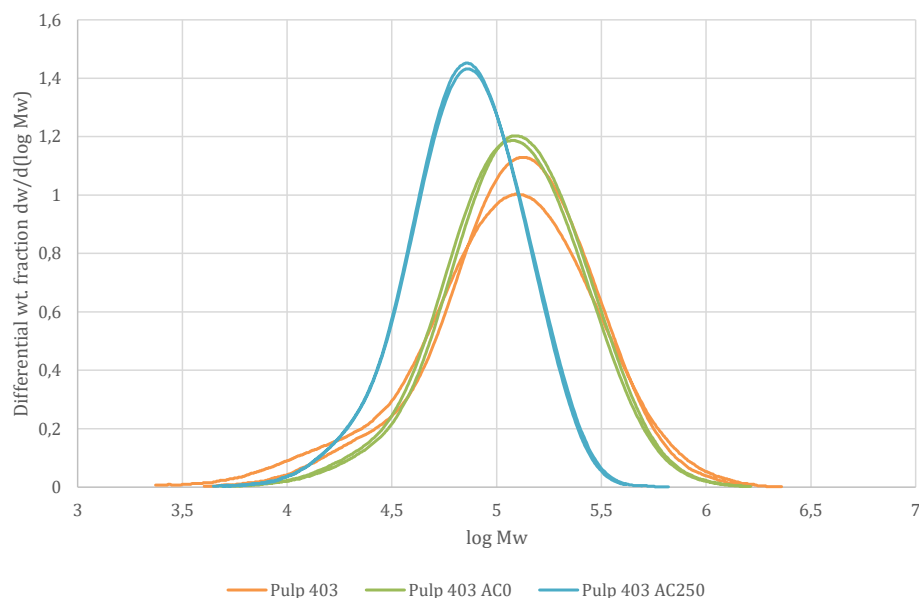


Figure 12: Molecular weight distribution for Pulp 403 before/after alkalization and after aging.

How the MWD changes during alkalization and aging for Pulp 403 is presented in Figure 12, the repeated analysis included creating two lines for each series. In comparing Pulp 403 and Pulp 403 AC0, there is a clear difference in the range log Mw 3,5-4,5, indicating the removal of short chained hemicellulose and cellulose during alkalization. The two samples for Pulp 403 differ quite a lot (the two orange lines should coincide better). In comparing with the other starting pulps (see Figure 10), the line with the highest maximum follows the trend better and is considered being more accurate.

The results of Pulp 463 is presented in Figure 13 below, the repeated analysis included creating two lines for each series. The difference before and after alkalization is not big but like for Pulp 403 there is some differences. Most interesting is once again the loss of low molecular polymers.

In Figure 14 below the results for Pulp 532 are presented, the repeated analysis included creating two lines for each series. The difference, especially the average molecular weight, before and after alkalization, is very clear. The sample after aging, Pulp 532 AC250, differs quite a lot between the two analysis done. It is difficult to tell which one is more accurate. This is not considered a problem in this thesis, as they both show the same trend compared to the other samples for Pulp 532.

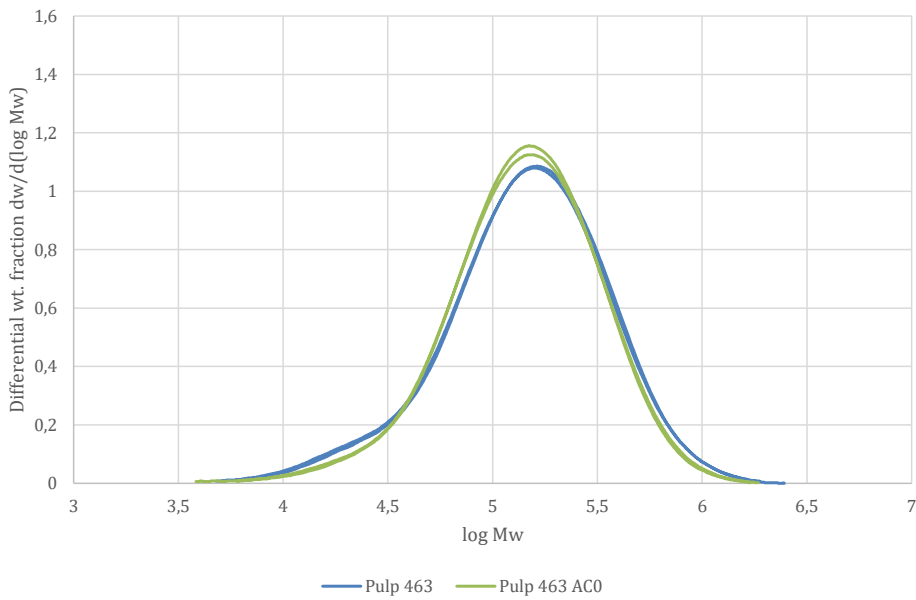


Figure 13: Molecular weight distribution for Pulp 463 before and after alkalization.

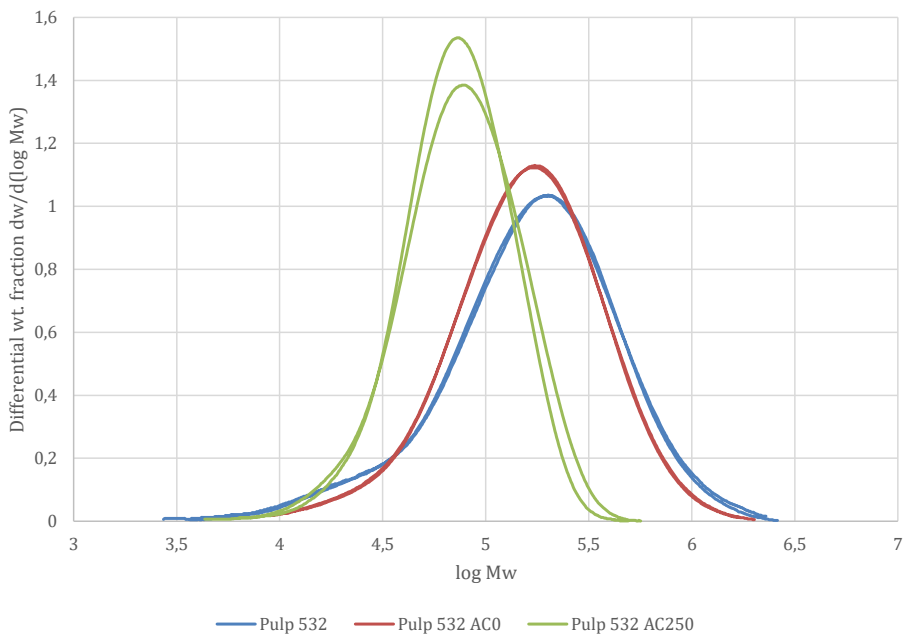


Figure 14: Molecular weight distribution for Pulp 532 before/after alkalization and after aging.

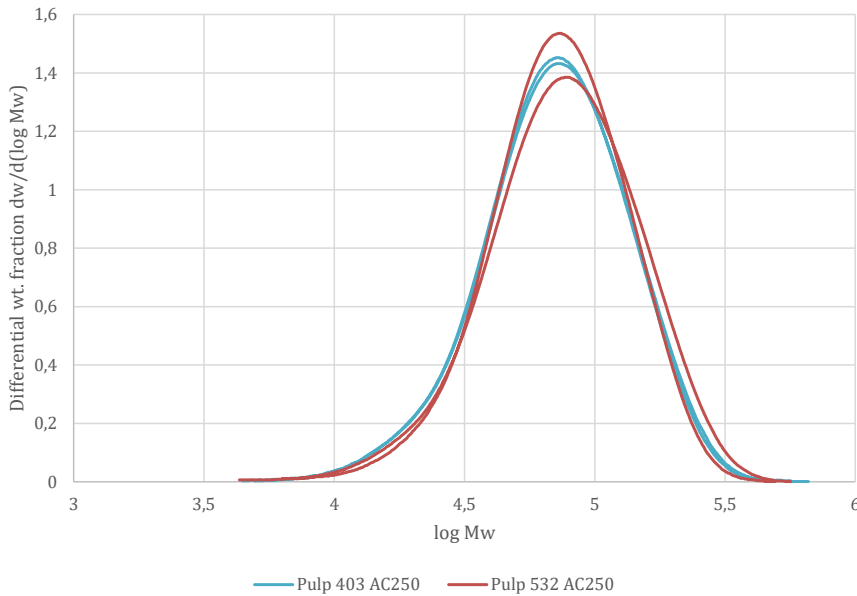


Figure 15: Molecular weight distribution for Pulp 403 and Pulp 532, both close to target viscosity.

Finally, Figure 15 shows a graphical comparison between the two pulps analyzed at target viscosity, the repeated analysis included creating two lines for each series. Again, it is difficult to determine which of the lines for Pulp 532 AC250 are more accurate. Either way, the results are similar to Pulp 403 AC250.

4.5 Modelling

With the model described in the theory chapter, again shown in Equation 16 below, a few different $DP \leftrightarrow [\eta]$ correlations were tested. The starting viscosity, η_0 , is the intrinsic viscosity after alkalization. This was calculated from a simple linear regression model from the data comparing viscosity before and after alkalization, as shown in Figure 4.

$$[\eta] = \frac{\frac{1}{b} \left(\frac{10^6}{162} \right)^a}{\left(A \cdot \exp\left(-\frac{Ea}{R \cdot T} \right) \cdot t^p + \frac{10^6}{162 \cdot a \sqrt{b \cdot [\eta_0]}} \right)^a} \quad \text{Equation 16}$$

The tested correlations can be seen in Table 9 below. Besides the commonly used correlations from Evans & Wallis (1989) and Immergut (1953) three other correlations found in literature were tried. Two from Marx-Figini (Marx-Figini, 1978), and one from Palme (Palme, 2017). The correlation Eklund was created from the MWD data presented in a previous chapter, see Table 8.

Table 9: Different correlation for DP <-> viscosity with their recommended DP range.

Correlation	Defined DP range	a	b
Eklund	500-1500	0,75	0,42
Evans & Wallis (1989)	700-7000	0,9	1,65
Immergut (1953)	-	0,905	0,75
Marx-Figini (1978)	<950	1	1/0,42
Marx-Figini (1978)	950-3000	0,76	1/2,28
Palme (2017)	400-5000	0,85	0,85

For all six correlations above the parameters A , Ea and p were optimized using the `nlinfit` command in MATLAB and results evaluated. The `nlinfit` command needs four things to perform a non-linear regression: an output vector of the experimental responses (intrinsic viscosity), a matrix of experimental variables (start viscosity, aging temperature and aging time), the function predicting the output (in this case Equation 16) and finally a guess for the parameters to be optimized (A , Ea and p). MATLAB iteratively changes parameter A , Ea and p to find the best least square solution.

4.5.1 Model evaluation

Unlike linear regression, the coefficient of determination R^2 , is not a good way of judging the performance of a non-linear model. For linear models R^2 ranges from zero to one, for non-linear models R^2 can be even larger and optimizing a model to get close to $R^2 = 1$ will often lead to a non-optimal solution (Ogee, et al., 2014). Looking in the literature there is no straight forward approach in evaluating and comparing non-linear models. A suggested approach is to simply look at the residuals of the model, where the average size of the residual is a good performance indicator (Ogee, et al., 2014). But this must be combined with further reasoning, for instance by looking at trends in the residuals.

Table 10 below a summary of the results of the six different models is presented. It appears that all correlations perform very well in the model applied to the training data. Independently of correlation used the intrinsic viscosity can be predicted with a mean residual of less than 4 ml/g (average of the absolute value of the residual).

Table 10: Results of model applied on training data using the different correlations.

Correlation:	A	Ea	p	Residual standard deviation [ml/g]:	Mean absolute residual [ml/g]:
Eklund	5,5141e+10	7,4385e+04	0,9337	3,5138	2,8277
Evan & Wallis (1989)	7,8418e+09	6,9980e+04	0,8870	3,9511	3,1611
Immergut (1953)	1,8690e+10	6,9869e+04	0,8858	3,9788	3,1865
Marx-Figini (1978) (DP <950)	5,8163e+09	6,7999e+04	0,8661	4,5631	3,7963
Marx-Figini (1978) (DP 950-3000)	4,9161e+10	7,3717e+04	0,9266	3,4982	2,7949
Palme (2017)	1,7611e+10	7,1161e+04	0,8995	3,7055	2,9360

The Marx-Figini correlation for DP 950-3000 performs best giving the smallest standard deviation and mean residual, but Eklund performs almost as good.

For the best performing model above, Marx-Figini (1978) DP 950-3000, a further evaluation focusing on residuals and validation is presented below. The residual error in these plots is calculated by: $e_{residual} = y - \hat{y}$. Where \hat{y} is the prediction of the model and y is the experimental result.

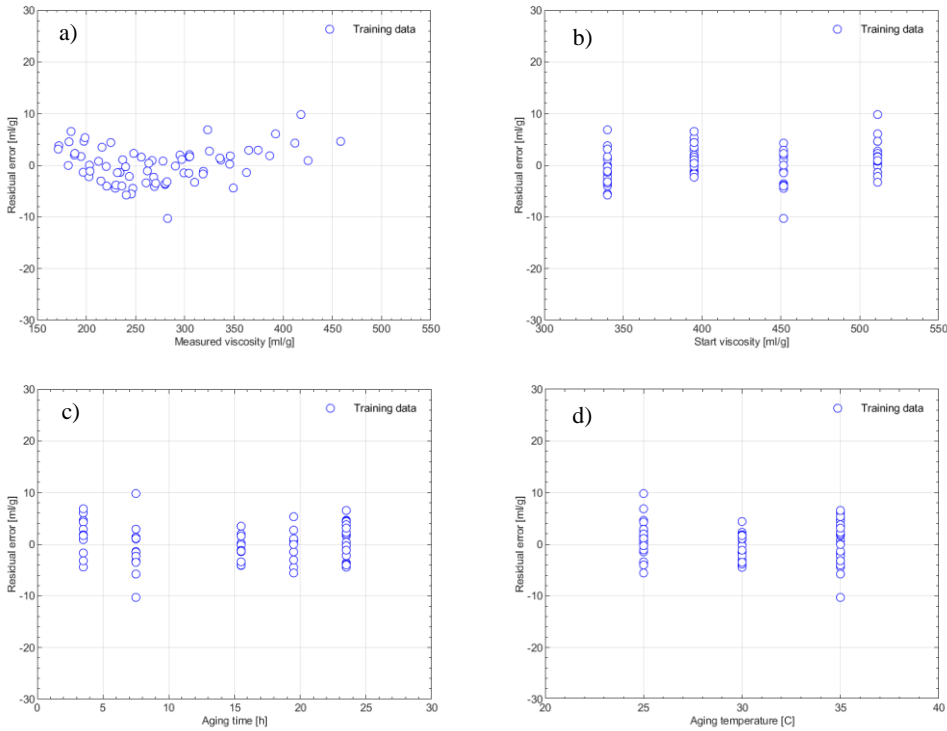


Figure 16: Residual error plots for model using Marx-Figini correlation as function of measured viscosity, start viscosity, aging time and aging temperature.

Looking at the residual plots in Figure 16 above there are no strong trends observed. Plot a) appears to have some curvature, slightly underestimating the prediction for low and high measured viscosities, and overestimate for viscosities around 250-300 ml/g. For plot d) it can be observed that the residual distribution at 25°C and 35°C are wider than samples aged at 30°C.

4.5.2 Modell validation

To validate the model a few different experiments were performed, and some data from experimental work performed outside of this thesis using the same method and type of dissolving pulp. These results can be seen in Figure 17 below:

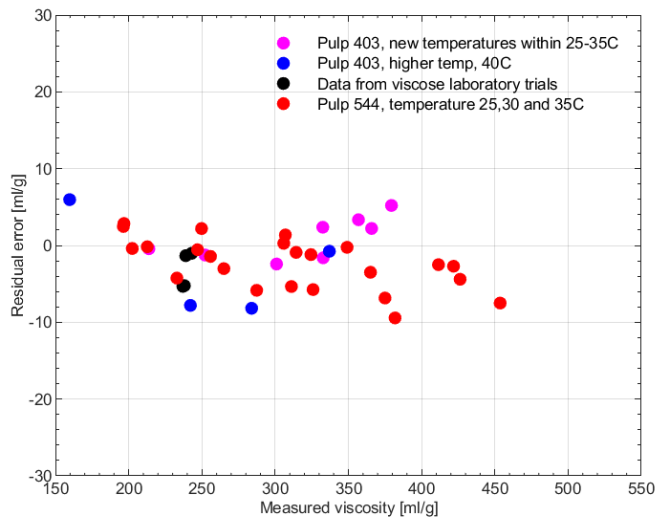


Figure 17: Residual error on validation data. Model created using Marx-Figini (1978) correlation.

In the validation data residual plot above four data series can be seen. Two of these were performed using Pulp 403, one of the four pulps used in the experimental design, but here in a new experimental series at new temperatures. The new temperatures for this Pulp 403 experimental series was 27,4°C, 32°C and 40°C. The four data points from 40°C are the only experiments performed outside of the temperature range used in the experimental plan.

The red data series was for Pulp 544, with a starting intrinsic viscosity higher than the ones used in the experimental plan. Pulp 544 was evaluated in the same way as the pulps used for the model (alkalized two times, aged for 24 hours at temperatures 25, 30 and 35°C). The residual for these data points tends to be negative, seen in Figure 17, indicating that the model typically overestimates the viscosity of this pulp.

Finally, there are four black data points (grouped together two and two in the figure above, the lower black dot is two different dots almost completely overlapping). These data fit the model with residual errors within 6 ml/g.

In Figure 18 below the results for Pulp 544 can be seen in a new perspective, where intrinsic viscosity is plotted against aging time for the three different temperatures including both experimental data and the model prediction. The prediction of the model slightly misses the experimental data in some regions, but generally performs very well. Even if the model tends to overestimate intrinsic viscosity for pulp 544 it is not considered a problem.

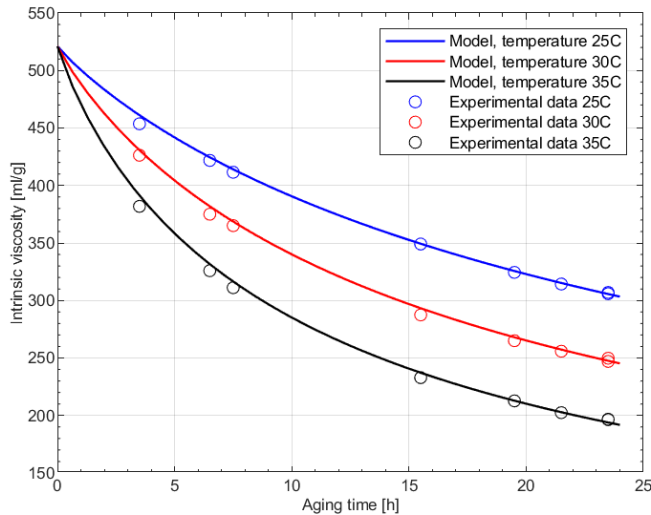


Figure 18: Pulp 544 performance plot. Plot visually showing the performance of the model on experimental data.

4.6 Model and method robustness

One important part in evaluating the performance of the model is to compare the model residuals with the variance of the experimental data. The variance of experimental data is estimated using pooled standard deviation. This makes it possible to combine several different sample populations with different means, but the variance of the populations is assumed to be identical. This is calculated as:

$$s_p^2 = \frac{(n_1-1) \cdot s_1^2 + (n_2-1) \cdot s_2^2 + \dots + (n_k-1) \cdot s_k^2}{n_1 + n_2 + \dots + n_k - k} \quad \text{Equation 17}$$

Where s_p^2 is the pooled standard deviation, n_i is the number of samples in population i , s_i^2 is the standard deviation of the samples in population i and k is the number of populations (McNaught & Wilkinson, 1997). In experimental plan there were several repeats. Each of the four pulps used in the model was alkalized and aged at three different temperatures for 23,5 hours twice. This gave 16 unique experimental conditions that were repeated once. From this data the pooled standard deviation could be calculated to 1,88 ml/g.

If looking at the standard deviation of the residuals for all models, the lowest number was 3,50 ml/g. The fact that this is a higher value than the pooled standard deviation of 1,88 ml/g is a good sanity check. If a model performs better than the errors in the method something is wrong, possibly overfitting of the model in which the natural variance in the data is explained. But it is also an indication that there might be room to improve the model. The question however is if this discrepancy is a real problem, and for the purpose of this evaluation it is not considered to be that.

Commented [MH20]: ? menar du the lowest standard deviation här?

Commented [MH21]: Något ord saknas. Dela upp i två meningar?

It was not completely clear how good a model like this could perform when the thesis work started, but the results were better than expected.

Early in the work of modelling the black box approach using a linear regression model was successfully tried but soon abandoned. The results looked promising, but the model was very long with ten or more terms to reach residual errors in the range of 10 ml/g and the model lacked any physical significance.

More validation data would be interesting to have but the validation data shown in the result chapter makes a really strong case. This model could be greatly useful for the specific case of this specific dissolving pulp.

4.7 General discussion

One important question is how general the aging model is. If only applied to the hardwood kraft pulp used in the evaluation it will most certainly perform very good in the experimental range, and there would likely not be any problems slightly outside the experimental range. But if applied to other pulps it would likely not be useful without modification.

The results for the molecular weight distribution might not be used in the actual mathematical model created but are useful in understanding what really happens to the pulps. If further experimental work would be done, possibly on other types of pulp, this data would be very interesting to compare and possibly explain why the model presented in this thesis does/doesn't work on a specific pulp.

The model performance indicates that the starting pulps are chemically homogenous, this is supported by the carbohydrate analysis.

A sample around 11-13 hours was not taken. This creates a big gap between samples taken at 7,5 hours and 15,5 hours. This is not considered to be a problem regarding the model. There is no indication it would add important information.

In the comparison of the different correlations it is important to be aware of the difficulty of measuring the molecular weight distributions of pulps. In a report by Potthast, et al. (Potthast, et al., 2015) this problem becomes very clear, where different laboratories using more or less similar methods report widely different results for the same samples. This does not mean that size exclusion chromatography lacks use, but it is difficult to generalize results. The lack of consistency between MWD analysis leads to the question to how useful the DP <-> intrinsic viscosity correlations earlier described really are, as they are based on MWD data.

If all assumptions made in the model and the MWD data was correct, then the best correlation for the purpose of modelling should have been the Eklund correlation, this was not the case. But the form of the mathematical model does not seem to be sensitive to the parameters a and b, the optimization in the non-linear regression seems quite forgiving when it comes to different correlations.

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5 Future work

It was deemed to be outside the scope of this investigation but testing aging temperatures outside 25°C-35°C would be very interesting. A short series was done at 40°C, but the results were not conclusive. A hypothesis could be that the same reactions happens outside the experimental range, and that the suggested model in this thesis captures the kinetics of the reaction. This needs to be proven and could for industrial applications be of high importance.

Something not conclusively shown in this thesis is whether the chemical properties of a pulp at target viscosity after aging depends on the way it got there. This would particularly be interesting to evaluate in the context of adding catalytic metals to the pulp before aging compared to no addition of metals.

If considering other dissolving pulps, the specific mathematical model created in this thesis would likely not be useful, but the general approach might be. This would be an interesting area to put further research into. Maybe even more interesting would be to model mixtures of pulps (for instance a Kraft- and a sulfite pulp with very different MWD). This is a common practice among viscose producers and would bring both academic and industrial value.

6 Conclusions

The main objective of this thesis was to create a mathematical model predicting the degree of polymerization (via intrinsic viscosity) of a dissolving pulp as function of the starting viscosity, time and temperature of aging. This was possible to do with good results.

Due to the good repeatability of the intrinsic viscosity measurements a few different conclusions can be made. The starting dissolving pulps is homogenous within the samples provided by the mill; the alkalization is even time to time, aging conditions replicable and the process of measuring the intrinsic viscosity is also reliable.

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