The effects of kneading and enzymatic treatments on properties of viscose-grade dissolving wood pulp

DJ Sandham

orcid.org/0000-0003-2596-1548

Dissertation accepted in fulfilment of the requirements for the degree *Master of Engineering in Chemical Engineering* at the North-West University

Supervisor: Prof S Marx

Co-Supervisors: Dr B Coetzee and Mr R Fischer

Graduation: May 2022

Student number: 36563234

Abstract

Dissolving wood pulp (DWP) is a high-purity form of cellulose that is produced by pulping and bleaching lignocellulosic biomass to obtain a cellulose content greater than 90%. DWP is used as the feedstock for many applications with viscose production being the most dominant. DWP of high purity and quality can be produced through chemical, mechanical, and enzyme treatments. Mechanical and enzymatic treatments are currently of interest as they lower the environmental impact by limiting the volume of chemicals used in the production of viscose.

This study aims to improve the critical properties of DWP through a combination of mechanical (kneading) and endoglucanase enzyme treatments. The critical properties of DWP for viscose production are reactivity and viscosity. The study was divided into three distinct phases. In the first phase, two different formulations of endoglucanase enzyme were investigated at a bench-scale level, using a range of incubation times and enzyme concentrations. In the second phase, the scale was, firstly, increased to pilot plant level using the most effective enzyme concentration, formulation, and incubation time. And then, secondly, the most effective sequence of mechanical kneading and enzymatic treatments was investigated to further enhance the pulp properties. In the final phase, viscose was produced using the treated pulp from the previous phase to validate the results and conclude whether the treatments could be effective to improve the quality of DWP.

The bench-scale investigation showed that endoglucanase could be used to reduce the viscosity by up to 50 mL/g (8.8%) with the most effective overall incubation time of 2 hours. The Ecopulp R formulation did not significantly increase the reactivity, but the NS 51179 did. It was thus concluded that the Ecopulp R formulation was the most effective of the two.

The second phase of investigation found kneading to be a harsh mechanical treatment that resulted in increased amounts of degraded cellulose without decreasing the viscosity or improving the reactivity of the pulp. Additionally, kneading also caused compression of the pulp fibres that resulted in decreased enzyme and chemical efficiency by reducing the available surface area of the pulp fibres. This was demonstrated when the combination of kneading followed by enzyme treatment resulted in a lower pulp reactivity compared to the control, while the viscosity was not reduced as much as the enzyme-treated pulp. Both enzyme treatment alone and enzyme treatment followed by kneading resulted in similar viscosity changes, with the key difference being that the combination of enzyme treatment and kneading resulted in lower reactivity, indicating that chemical accessibility was hindered by introducing kneading. It was therefore concluded that using enzyme treatment alone, without kneading, was the most effective way to decrease viscosity and improve reactivity.

The final phase of the investigation found that all viscose results were highly variable with no significant improvement of viscose quality being observed. Therefore, the combination of kneading and enzymatic treatments was not effective in producing DWP of higher quality.

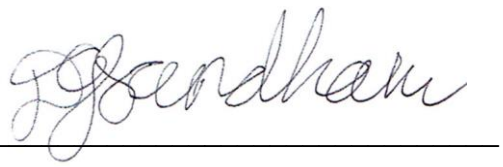
Declaration of authorship

I declare that this report is a presentation of my own original work.

Whenever contributions of others were involved, every effort was made to indicate this clearly, with due reference to the literature.

No part of this work has been submitted in the past, or is being submitted, for a degree or examination at any other university or course.

Signed on this 14th day of October 2021 in Roodepoort.



INITIALS AND SURNAME

Acknowledgements

I would like to acknowledge the following individuals for their continuous support and guidance throughout this study and during the completion of the dissertation; your assistance and guidance proved invaluable and are duly appreciated:

- First and foremost, Our Heavenly Father, who provided the required strength to overcome all hurdles and who has always had a larger plan with my life up to this point and into eternity.
- My family for their unconditional love and support throughout this study.
- My supervisors, Prof Sanette Marx, Dr Berdine Coetzee and Mr Robin Fischer for their knowledgeable guidance and overall kindly and friendly manner.
- Ms Nicolette Kerr and Mr Craig Pearcey, from Sappi Technology Centre, for their help and guidance during certain sections of this study.
- Mr Mazibuko Velenkosini for managing and assisting during viscose making and testing.
- All other personnel at Sappi Technology Centre for their support and guidance.

Table of contents

Abstract i

Declaration of authorship 2

Acknowledgements 1

Table of contents 1

List of figures 4

List of tables 6

Chapter 1: Introduction 7

1.1 Background and motivation 7

1.2 Problem statement and hypothesis 8

1.3 Aim and objectives 8

1.4 Scope of the investigation 8

Reference list 10

Chapter 2: Literature review – application of kneading and cellulase for the modification of cellulose 12

2.1 Introduction 12

2.2 Lignocellulose composition and characteristics 15

2.3 Dissolving wood pulp treatment techniques 17

2.3.1 Chemical treatments 17

2.3.2 Enzymatic treatment of dissolving wood pulp 18

2.3.3 Mechanical treatment of dissolving wood pulp 20

2.4 Critical parameters of dissolving wood pulp 23

2.4.1 Reactivity 23

2.4.2 Viscosity 24

2.4.3 Crystallinity 25

2.4.4 Alkali solubility 25

2.5 Concluding remarks 26

Reference list 27

Chapter 3: Modification of fully bleached dissolving wood pulp through endoglucanase treatment 37
3.1 Introduction 37
3.2 Materials and methods 38
3.2.1 Enzyme characterisation 38
3.2.2 Enzyme treatments 39
3.2.3 Handsheet analysis 40
3.3 Results and discussion 41
3.3.1 Enzyme characterisation 41
3.3.2 Intrinsic viscosity of dissolving wood pulp 43
3.3.3 Alkali solubility 45
3.3.4 Quick reactivity results 49
3.4 Conclusions and recommendations 51
References 52
Chapter 4: A combination of enzymatic and kneading treatments of dissolving wood pulp for viscose production 55
4.1 Introduction 55
4.2 Materials and methods 56
4.2.1 Kneading treatments 56
4.2.2 Enzymatic treatments 56
4.2.3 Handsheet formation and sample preparation 57
4.2.4 Steeping of dissolving wood pulp 57
4.2.5 Ageing kinetics of alkali cellulose 57
4.2.6 Determination of chemical charges for viscose making 58
4.2.7 Bulk density of alkali cellulose 58
4.2.8 Viscose production 59
4.2.9 Analysis of viscose solution 59
4.3 Results and discussions 60
4.3.1 Determination of number of passes for kneading 60
4.3.2 Intrinsic viscosity of dissolving wood pulp 61

4.3.3 Alkali solubility results 62
4.3.5 Quick reactivity results 63
4.3.6 Ageing kinetics for alkali cellulose 64
4.3.7 Degree of polymerisation of alkali cellulose after ageing 67
4.3.8 Bulk density of alkali cellulose 67
4.3.9 Hottenroth ripening index 68
4.3.10 Filterability of viscose solution 69
4.4 Conclusions and recommendations 70
References 72
Chapter 5: Conclusions and recommendations 76
5.1 Conclusions 76
5.2 Recommendations 77
Appendix i
Raw data of enzyme assay i
Viscosity data for phase 1 ii
Alkaline solubility for phase 1 iv
Quick reactivity results for phase 1 viii
Preliminary data for pilot plant viii
Viscosity data for phase 2 ix
Alkaline solubility results for phase 2 x
Quick reactivity results for phase 2 xi
Ageing kinetics results in phase 3 xii
Viscose data xxiv

List of figures

Figure 2.1: Structural differences between cellulose (left) and hemicellulose (right) as described by Eriksson *et al*. (2014) 16
Figure 2.2: Hierarchical structure of lignocellulose, adapted from Dufresne (2013) and Yang *et al.*(2019)..... 16
Figure 2.3: Illustration of the mechanism to improve cellulase adsorption onto the cellulose fibre with the use of CPAM, adapted from Yang *et al.* (2019) 20
Figure 2.4: Diagram of a PFI mill, adapted from Chakraborty *et al.* (2007) 21
Figure 3.1: Effect of the enzyme treatment of pulp on free sugar concentration at different incubation times. Primary axis: ● - Ecopulp R, ● - NS 51179. Secondary axis: ● - Ecopulp R ● - NS 51179. 42
Figure 3.2: Effect of dosage of the Ecopulp R enzyme on the intrinsic viscosity of the DWP at incubation times of 1 h (A) and 2 h (B) 43
Figure 3.3: Effect of dosage of the NS 51179 enzyme on the intrinsic viscosity of the DWP at incubation times of 1 h (A) and 2 h (B) 44
Figure 3.4: Effect of dosage of the Ecopulp R enzyme on the degraded cellulose of the DWP at incubation times of 1 h (A) and 2 h (B) 47
Figure 3.5: Effect of dosage of the NS 51179 enzyme on the degraded cellulose of the DWP at incubation times of 1 h (A) and 2 h (B) 48
Figure 3.6: Effect of viscosity reduction on the increase of degraded cellulose content (R^2=0.6) 49
Figure 3.7: Comparison of reactivity as a percentage of undissolved fibre at an enzyme dosage of 300 g/t and 2 h incubation time..... 50
Figure 4.1: Dispersion of DWP in NaOH after the first pass in the kneader 60
Figure 4.2: Undissolved lumps of DWP after steeping and two passes in the kneader..... 61
Figure 4.3: Intrinsic viscosity of untreated pulp and different combinations of enzyme and kneading treatments 62
Figure 4.4: Degraded cellulose content of untreated pulp and different combinations of enzyme and kneading treatments..... 63
Figure 4.5: Quick reactivity of untreated pulp and different combinations of enzyme and kneading treatments 64
Figure 4.6: Ageing curve for untreated DWP used to determine the ageing time to reduce the alkali cellulose intrinsic viscosity to 240 g/L..... 65
Figure 4.7: Degree of polymerisation of different samples after ageing 67
Figure 4.8: Bulk densities of various alkali cellulose samples after ageing 68
Figure 4.9: Hottenroth ripening index of various viscose samples after ripening..... 69

Figure 4.10: Filterability index before and after viscosity adjustment (blue and orange respectively) of various treatments. Primary axis: ■ – K_w after ripening, ■ – K_w corrected for ball fall. 70

List of tables

Table 3.1: Commercial EG preparations that were used to treat fully bleached industrial DWP 40
Table 4.1: Required ageing times for different samples in the viscose process 66

Chapter 1: Introduction

1.1 Background and motivation

Dissolving wood pulp (DWP) is composed of high-purity cellulose (90%–95%) and can be used in the production of a wide variety of specialised compounds. These compounds include cellulose ester, cellulose ethers, nanocellulose and viscose (Kumar & Christopher, 2017). DWP can be obtained through pulping and bleaching of lignocellulosic biomass resulting in a high-purity cellulose (Friebel *et al.*, 2019; Sixta *et al.*, 2013; Wang *et al.*, 2020). Besides the required specification of cellulose content within the DWP, both viscosity and reactivity are critical specifications that need to be met. Viscosity relates to the filterability and homogeneity for mercerisation and xanthation reactions (Chen *et al.*, 2016). Reactivity influences the chemical demand in subsequent production processes.

A wide variety of processes and treatments has been developed specifically to improve the purity of DWP along with its properties. Of these treatments, enzymatic treatments are currently of great interest as they are biodegradable and environmentally friendly (Wang *et al.*, 2020). Although enzymatic treatments have been shown to be effective in producing high-purity, quality cellulose, some factors limit enzyme efficiency. These factors include electrostatic repulsion between the enzyme and cellulose fibres and substrate surface area that inhibits the performance of the enzyme (Ju *et al.*, 2013; Miao *et al.*, 2015; Sun *et al.*, 2016).

Electrostatic repulsion exists between the cellulose fibres and cellulase as both carry a negative charge thereby limiting interaction. To improve the efficiency of the enzymes, additives, such as cationic polyacrylamide (CPAM), are used to reduce the electrostatic repulsion between the enzyme and the substrate (Reye *et al.*, 2011; Wang *et al.*, 2015).

Mechanical refining can also be used as it results in fibrillation, thereby increasing the surface area of the cellulose fibres as an increase in surface area is associated with an increase in enzymatic hydrolysis of the substrate (Sun *et al.*, 2016; Yang *et al.*, 2019). Mechanical refining can be achieved using a PFI mill, sonication, and kneading. Previous reports investigating the effect of PFI mill refining and enzymatic saccharification indicated that a combination of the treatments could improve enzyme efficiency (Gao *et al.*, 2015; Miao *et al.*, 2015; Wang *et al.*, 2020). However, there are currently no reports on the use of kneading for fibre modification but rather for facilitating even distribution of the enzyme in industrial processes (Engström *et al.*, 2006; Ibarra *et al.*, 2009).

1.2 Problem statement and hypothesis

There is currently limited information on the combinatorial effect of kneading and enzymatic treatments on DWP. It is hypothesised that there will be a synergetic effect when combining kneading and enzymatic treatments, as seen with other mechanical activation techniques (Miao *et al.*, 2015; Yang *et al.*, 2019). This synergetic effect is expected to reduce the chemical demand during the production of viscose.

1.3 Aim and objectives

This study aims to modify DWP properties, such as reactivity and viscosity, through the combination of the above-mentioned treatments, thereby reducing the chemical demand of the viscose process.

The primary objectives of this study are:

1.3.1 To determine the optimum enzyme dosage conditions required to improve pulp reactivity and/or viscosity.

1.3.2 To determine the optimal kneading intensity required to improve pulp reactivity and/or viscosity.

1.3.3 To determine the combinatorial effect of enzymatic and kneading treatment on pulp reactivity and/or viscosity.

1.3.4 To investigate the potential impact of treatment order on these properties of DWP.

1.3.5 To determine the combinatorial effect of enzymatic treatment and kneading on the chemical demand for viscose production.

1.4 Scope of the investigation

This dissertation consists of the following sections:

- An introduction (Chapter 1):
    - The background and motivation, aim and objectives, and the scope of the investigation are discussed in this chapter.
- A literature review (Chapter 2):
    - The composition and structure of lignocellulose, DWP treatment techniques, and the critical parameters of DWP are discussed in this chapter.
- Experimental phase one (Chapter 3):

  - In this chapter all experiments conducted at bench scale level to determine which combination of enzyme formulation, enzyme dosage, and enzyme incubation time was the most effective, are presented and discussed. The properties measured were alkali solubility (S10 and S18), reactivity, and viscosity. Only key samples were tested for reactivity to get an idea of how enzyme treatments affected this parameter.
- Experimental phase two (Chapter 4):
  - This chapter reports on how the findings from the previous chapter combined with a kneading treatment affected the measured variables, i.e., alkali solubility, reactivity, and viscosity. The experiments were done using a pilot plant. Viscose was produced from the treated pulp to analyse the quality and to determine if the treatments were effective in reducing the chemical demand.
- Conclusions and recommendations (Chapter 5):
  - The conclusions and recommendations found in the previous chapters are discussed.

Reference list

Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., … Ni, Y. 2016. Cellulose (dissolving pulp) manufacturing processes and properties: a mini-review. *Bioresources*, 11(2):5553-5564.

Engström, A.-C., Ek, M., & Henriksson, G. 2006. Improved accessibility and reactivity of dissolving pulp for the viscose process: pretreatment with monocomponent endoglucanase. *Biomacromolecules*, 7(6):2027-2031. doi:10.1021/bm0509725

Friebel, C., Bischof, R.H., Schild, G., Fackler, K., & Gebauer, I. 2019. Effects of caustic extraction on properties of viscose grade dissolving pulp. *Processes*, 7(3):122. doi:10.3390/pr7030122

Gao, W., Xiang, Z., Chen, K., Yang, R., & Yang, F. 2015. Effect of depth beating on the fiber properties and enzymatic saccharification efficiency of softwood kraft pulp. *Carbohydrate Polymers*, 127:400-406. doi:10.1016/j.carbpol.2015.04.005

Ibarra, D., Köpcke, V., & Ek, M. 2009. Exploring enzymatic treatments for the production of dissolving grade pulp from different wood and non-wood paper grade pulps. *Holzforschung*, 63(6):721-730. doi:10.1515/HF.2009.102

Ju, X., Grego, C., & Zhang, X. 2013. Specific effects of fiber size and fiber swelling on biomass substrate surface area and enzymatic digestibility. *Bioresource Technology*, 144:232-239. doi:10.1016/j.biortech.2013.06.100

Kumar, H. & Christopher, L.P. 2017. Recent trends and developments in dissolving pulp production and application. *Cellulose*, 24(6):2347-2365. doi:10.1007/s10570-017-1285-y

Miao, Q., Tian, C., Chen, L., Huang, L., Zheng, L., & Ni, Y. 2015. Combined mechanical and enzymatic treatments for improving the Fock reactivity of hardwood kraft-based dissolving pulp. *Cellulose*, 22(1):803-809. doi:10.1007/s10570-014-0495-9

Reye, J.T., Maxwell, K.E., & Banerjee, S. 2011. Cationic polyacrylamides promote binding of cellulase and amylase. *Journal of Biotechnology*, 154(4):269-273.

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., … Schottenberger, H. 2013. Novel concepts of dissolving pulp production. *Cellulose*, 20(4):1547-1561.

Sun, S., Sun, S., Cao, X., & Sun, R. 2016. The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials. *Bioresource Technology*, 199:49-58. doi:10.1016/j.biortech.2015.08.061

Wang, Q., Fu, X., Liu, S., Ji, X., Wang, Y., He, H., Yang, G., & Chen, J. 2020. Understanding the effect of depth refining on upgrading of dissolving pulp during cellulase treatment. *Industrial Crops and Products*, 144:112032.

Wang, Q., Liu, S., Yang, G., Chen, J., & Ni, Y. 2015. Cationic polyacrylamide enhancing cellulase treatment efficiency of hardwood kraft-based dissolving pulp. *Bioresource Technology*, 183:42-46. doi:10.1016/j.biortech.2015.02.011

Yang, S., Yang, B., Duan, C., Fuller, D.A., Wang, X., Chowdhury, S.P., … Ni, Y. 2019. Applications of enzymatic technologies to the production of high-quality dissolving pulp: a review. *Bioresource Technology*, 281:440-448. doi:10.1016/j.biortech.2019.02.132

Chapter 2: Literature review – application of kneading and cellulase for the modification of cellulose

2.1 Introduction

DWP is a high-purity form of cellulose that is obtained by subjecting raw lignocellulosic biomass to various pulping and bleaching sequences (Behin & Zeyghami, 2009; Kumar & Christopher, 2017). Through the utilisation of these various processes, the final product consists of cellulose (90% to 95%), hemicellulose (<4%), and trace amounts of lignin (Sixta, 2006; Yang *et al.*, 2018). This pure form of cellulose has a variety of applications in a range of industries to produce products such as viscose, cellulose ethers, cellulose esters, and speciality products, such as nanocellulose (Bajpai, 2015; Ek *et al.*, 2009; Kumar & Christopher, 2017; Sixta, 2006).

Viscose production uses more than 70% of the global DWP produced annually (Chen *et al.*, 2016; Kumar & Christopher, 2017). Cellulose derivatives, such as cellulose ethers, can be used in the manufacture of paints and pharmaceuticals. Other cellulose derivatives, like cellulose esters, can be used in the production of plastics (Kumar & Christopher, 2017; Sixta *et al.*, 2013).

The application of cellulose in the production of value-added products requires its initial separation from other lignocellulosic constituents, hemicellulose and lignin (Dong *et al.*, 2020). Pulping and bleaching sequences are primarily used to achieve this hemicellulose dissolution and delignification (Benjamin *et al.*, 1969; Dong *et al.*, 2020; Kumar & Christopher, 2017)

Pulping describes the process used to treat lignocellulosic materials through chemical and mechanical processes allowing the liberation of a fibrous mass, denoted as pulp (Bajpai, 2018). Chemical, semi-chemical, chemical-mechanical and mechanical pulping are the four categories of pulping processes that are used in the pulp and paper industry (Biermann, 1996).

Chemical pulping relies solely on chemicals to separate fibres while mechanical pulping relies on physical actions (Bajpai, 2015; 2018). Chemical pulps often have lower yields than mechanical pulps as the chemicals tend to degrade the biomass components. However, chemical pulps are often of higher purity as hemicellulose and lignin are removed to a larger extent. The removal of hemicellulose and lignin makes chemical pulps ideal for DWP production.

There are currently two main chemical processes used to produce DWP, namely acid sulphite (AS) pulping and prehydrolysis kraft pulping (PHK), both of which were developed in the 1950s (Sixta *et al.*, 2013; Wang *et al.*, 2020; Yang *et al.*, 2019).

The PHK process is a modification of the kraft process where a prehydrolysis stage is added to remove hemicellulose (Bajpai, 2018). A neutralisation step is required after prehydrolysis as it is performed under acidic conditions (Bi *et al.*, 2021). Once neutralisation is achieved kraft cooking is done using alkali conditions to remove the majority of the lignin (Chen *et al.*, 2016). The PHK process has gone through several adaptions to improve the quality of the DWP while lowering the energy demands of the process (Sixta *et al.*, 2013). An example is the combination of displacement technology with steam prehydrolysis (Wizani *et al.*, 1994).

During AS pulping, hemicellulose, lignin, and other minor constituents are removed from the wood chips. The components are then dissolved in sulphite liquor which can be used as a feedstock for the production of other value-added products like lignosulfonates (Chen *et al.*, 2016). The AS process is currently the more frequently used process, accounting for 65% of the total DWP production (Kumar & Christopher, 2017). The primary reason for this is that it has a higher reactivity as measured by the Fock reactivity test (Eriksson *et al.*, 2014); however, PHK pulp also have lower yields with higher associated capital and running costs (Gehmayr *et al.*, 2011; Mateos-Espejel *et al.*, 2013). Once the biomass has been pulped it can be sent to the bleaching step which is the next phase of the process.

Bleaching treats lignocellulosic pulp with chemicals to increase the brightness and remove any residual lignin and hemicellulose (Friebel *et al.*, 2019). The bleaching procedure depends on the type of pulp that is being treated. The main objectives of bleaching are lignin removal, resulting in an increased brightness of the DWP and viscosity control. The brightness is typically controlled through chemicals such as chlorine dioxide (D-stage) and peroxide, while the viscosity is typically controlled through chemicals such as hypochlorite (H-stage) and ozone (Z-stage) (Bajpai, 2018; Suess, 2010).

Enzymatic bleaching was developed in the 1990s, making the process more environmentally friendly (Ek *et al.*, 2009). The lignin in the pulp before bleaching gives the pulp a brownish colour but once it is removed the pulp turns white. Removal of lignin in mechanical pulps is counterproductive; therefore, the lignin is dyed, while in chemical pulps the lignin is completely removed (Sjöström, 1993). Brightness is an important variable in DWP which generally has a brightness of 90% relative to a MgO standard, although other brightness measures also exist (Sappi North America, 2017).

Bleaching not only adjusts the brightness of the DWP to the required specifications but is also crucial in adjusting viscosity, molecular weight distribution (MWD), and reactivity (Bajpai, 2018; Suess, 2010). Viscosity refers to the intrinsic viscosity, which is important for filterability and homogeneity which allows mercerisation and xanthation reactions within the viscose process

can take place effectively (Chen *et al.*, 2016). After pulping and bleaching to the required specifications, DWP can be sold to produce various value-added products.

The demand for DWP has increased in recent years due to the wide variety of applications. Global production of DWP has increased from 4.2 million tonnes to 5.6 million tonnes to 7.5 million tonnes from 2011 to 2013 to 2015, respectively (Kumar & Christopher, 2017; Sixta *et al.*, 2013). China's DWP output is believed to increase by 10% annually (Chen *et al.*, 2016). Furthermore, Sixta *et al.* (2013) indicated that the market share of DWP will continue to increase during the next decades. Additionally, global production of DWP is expected to increase to 19 million tons by 2030 (Shen & Patel, 2010). Sappi is one of the largest global manufacturers and sellers of DWP, producing 16% of the global supply from three mills in South Africa and North America (Sappi, 2020).

The growth of the DWP market can also be attributed to the renewable nature of lignocellulosic material. Natural and environmentally friendly methods have been explored in the DWP industry to further reduce the carbon footprint of the process. One such method is the application of various hydrolytic enzymes.

The use of enzymes for DWP production has experienced an increase in popularity as they can effectively modify pulp properties, such as viscosity and reactivity, while reducing waste. Cellulases are used typically to achieve improved pulp fibre properties. Cellulases hydrolyse the glycosidic bonds of the cellulose chain (Okal *et al.*, 2020; Yang *et al.*, 2019). There are three types of cellulases that hydrolyse distinct regions on the cellulose chain, namely endoglucanase (1,4-β-D-glucan 4-glucanohydrolase), exoglucanase (1,4-β-D-glucan cellobiohydrolase) and β-glucosidases (Hildén & Johansson, 2004; Yang *et al.*, 2019). While enzymatic treatments are ideal to achieve the desired modification of the cellulose chain, they are often slow-acting due to limiting factors, such as adsorption onto the cellulose fibre through electrostatic repulsion (Yang *et al.*, 2019). By combining enzymatic treatments with mechanical refining the efficiency can be greatly improved (Wang *et al.*, 2020).

Mechanical treatment is the process that is used to refine or repeatedly beat pulp to achieve modification of the fibres. Some of the mechanical treatments to modify DWP include PFI mill refining and sonication. The extent of these modifications depends on the refining instrument. The modification of the fibres can be achieved in several ways including cutting of fibres, increasing external fibrillation, and production of fines (Lumiainen, 2000). Fibrillation allows for larger surface areas to be exposed for hydrolysis via chemical or enzymatic treatments (Miao *et al.*, 2015; Yang *et al.*, 2019). Mechanical treatment techniques are very seldomly operated in isolation but are rather used in conjunction with other technologies such as chemical or enzymatic treatments (Lin *et al.*, 2018; Wang *et al.*, 2020; Yang *et al.*, 2019). Wang *et al.*

(2020) reported that mechanical refining of DWP before enzymatic treatment can improve cellulase efficiency by increasing accessibility to the cellulose fibres. However, it has also been reported that enzymatic treatment before mechanical refining can reduce the energy required for refining (Lin *et al.*, 2018; Tejado *et al.*, 2012; Yang *et al.*, 2019). A variety of mechanical treatments have been used to modify the properties of DWP.

Kneading is a rare type of mechanical treatment that could potentially modify DWP fibres. However, previous research involving the kneading of DWP was on facilitating the mixing of enzymes to better distribute them through the pulp rather than using mechanical refining (Engström *et al.*, 2006; Ibarra *et al.*, 2009). Therefore, kneading done to mechanically modify the pulp has largely gone unexplored.

2.2 Lignocellulose composition and characteristics

Lignocellulose is the most abundant naturally occurring polymer on earth (Dufresne, 2013). Lignocellulose consists of carbohydrate polymers, cellulose and hemicellulose, and an aromatic polymer, lignin (Sun *et al.*, 2016). Furthermore, an estimated 2 x 10^{11} tonnes of lignocellulose is produced annually through plants undergoing photosynthesis (Chen, 2015). Generally, lignocellulose is composed of 30% to 50% cellulose, 20% to 35% hemicellulose and the remaining 15% to 30% is lignin (Lu *et al.*, 2017). The structures and chemical composition of these three polymers differ widely. Lignin is a three-dimensional, branched phenolic polymer and its chemical structure varies appreciably (Lu *et al.*, 2017; Shigeto *et al.*, 2016; Sun *et al.*, 2016) depending on the plant tissue and the age of the tissue (Healey *et al.*, 2016). Some of the functional groups contributing to the complex nature of the polymer are methoxy, hydroxyl, and carbonyl groups (Kai *et al.*, 2016).

Hemicellulose is a predominantly branched heteropolymer with a low degree of polymerisation composed of several monosaccharides, namely, xylose, mannose, and glucose (Behin & Zeyghami, 2009; Zhao *et al.*, 2017). Hemicellulose interacts with cellulose by forming a matrix that encloses the cellulose fibres (Sadhu & Maiti, 2013; Sun *et al.*, 2016). The composition of hemicellulose differs substantially from softwood to hardwood plant species. Hardwood hemicellulose is mostly comprised of xylans, whereas softwood hemicellulose contains mainly glucomannans (Adav & Sze, 2014).

Unlike hemicellulose, cellulose is a linear, homopolymer of repeating D-glucose units (Figure 2.1). The units are linked with β-1,4-glycosidic bonds while each molecule is oriented 180° to the previous molecule, thereby forming a linear polymer (Granström, 2009). Two repeating units of glucose form the basic building block of cellulose known as cellobiose. Each glucose contains three hydroxyl groups (C2, C3, and C6). However, terminal groups of the cellulose

chain are slightly different in structure from the non-terminal groups. One terminal is known as the reducing end and the other terminal is known as the non-reducing end due to the presence of an aldehyde functional group (Granström, 2009).

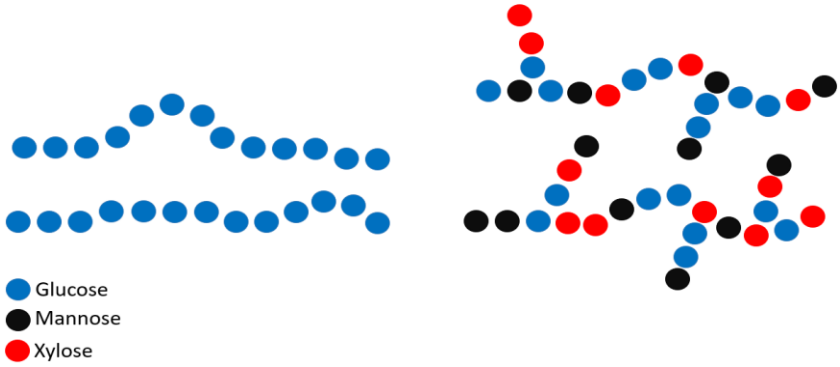


Figure 2.1: Structural differences between cellulose (left) and hemicellulose (right) as described by Eriksson *et al*. (2014)

The repeating units of cellobiose interact with one another through hydrogen intermolecular forces to form complex formations within the polymer. These forces lead to complex supramolecular structures, where the individual cellulose chains interact with one another forming cellulose microfibrils (Granström, 2009). These microfibrils then group and form fibrils that are suspended in a hemicellulose and lignin matrix (Dufresne, 2013; Ek *et al.*, 2009). Figure 2.2 illustrates how cellulose chains are encased in hemicellulose and lignin to form the fibril matrix. The morphology is further complicated through the presence of both amorphous and crystalline structures in the microfibrils (Dufresne, 2013; Heinze & Liebert, 2001). The chemical behaviour and characteristics of cellulose can be attributed to the hydrogen bonding within the cellulose matrix and to the crystallinity of the cellulose microfibrils (Heinze & Liebert, 2001).

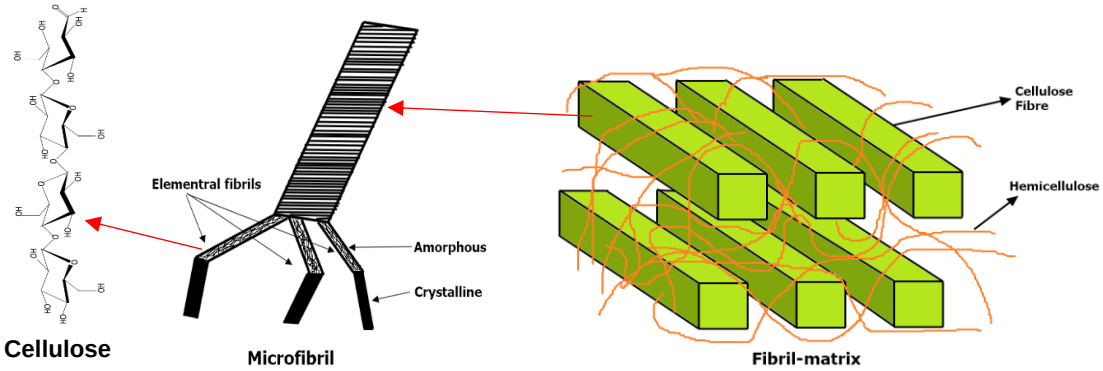


Figure 2.2: Hierarchical structure of lignocellulose, adapted from Dufresne (2013) and Yang *et al.*(2019)

Crystalline structures are normally described as using lattice parameters to distinguish between different unit cells. The lattice parameters are interaxial angles: α, β, γ and axial relationships: a, b, c. Cellulose has six different polymorphs: I, II, III_I, III_{II}, IV_I, IV_{II}, while cellulose I has two different allomorphs which are denoted as I_α and I_β (O'Sullivan, 1997; VanderHart & Atalla, 1984). Cellulose I or native cellulose is a naturally occurring cellulose structure. Cellulose I_α is found in primitive organisms such as algae and bacteria, while cellulose I_β is found in more complex organisms such as plants (Rongpipi *et al.*, 2019). The difference between the two allomorphs is that cellulose I_α has a triclinic crystal lattice while I_β has a monoclinic lattice structure (Rongpipi *et al.*, 2019). The other forms of cellulose, namely, II, III, and IV are formed through chemically treating cellulose I and are collectively called regenerated cellulose (Wang *et al.*, 2016).

2.3 Dissolving wood pulp treatment techniques

As the demand for DWP with high-purity cellulose has grown over the past decade, innovative processes and concepts needed to be developed to facilitate this need (Sixta *et al.*, 2013). DWP treatment techniques are currently utilised to improve the quality of the pulp while also attempting to minimise any yield losses that may occur. These treatment techniques include chemical treatments, enzymatic treatments, and mechanical activation of pulp.

2.3. Chemical treatments

Chemical treatments have been used to remove hemicellulose and lignin while improving the brightness, reactivity, and viscosity of the DWP (Yang *et al.*, 2019). Chemical treatments can be used prior to bleaching, or form part of the bleaching sequence, or be done post-bleaching. Oxidative treatments are used to improve the DWP characteristics and purity, and include the use of hypochlorite and ozone, which form part of the bleaching sequence. Acid extraction and alkali extraction are the chemical treatments that can be used to improve the purity of DWP (Bajpai, 2018). These extractive techniques are used to improve the purity of the DWP by removing the unwanted hemicellulose (Kumar & Christopher, 2017).

2.3.1.1 Alkali extraction and acid extraction

Alkali treatments are classified as cold caustic extraction (CCE) or hot caustic extraction (HCE). CCE is performed between 25°C and 45°C while HCE is performed between 70°C and 120°C (Friebel *et al.*, 2019). CCE is typically performed at sodium hydroxide (NaOH) concentrations of 8% to 10% while HCE is performed at lower concentrations of 0.4%–1.5% (Arnoul-Jarriault *et al.*, 2015; Bajpai, 2018; Li, Zhang, *et al.*, 2018). Generally, CCE is preferred as higher temperatures can lead to cellulose degradation and will consequently lower the yield of the DWP (Li *et al.*, 2015). Caustic extraction can form part of the pretreatment process as

indicated by Sixta *et al.* (2013) or it can be done within the bleaching sequence as done by Friebel *et al.* (2019). Furthermore, Friebel *et al.* (2019) specified that caustic extraction is mostly done on PHK pulp, while very seldomly being used on AS pulp.

Acid extraction serves the same purpose as alkali extraction but specifically targets the alkali-resistant fraction of hemicellulose (Jiang *et al.*, 2020). Acid extraction is conducted at temperatures of 95°C to 145°C for 1 hour to 2.5 hours while maintaining a pH of 2.5 to 3.5. Acid extraction is also best suited for PHK pulps (Bajpai, 2018). Both acid and alkali extractions are primarily used to remove hemicellulose; and thus, improving the purity of the DWP. Other chemical treatments, such as oxidative treatments, can be used to modify the DWP characteristics.

2.3.1.2 Oxidative treatments to modify the properties of dissolving wood pulp

Oxidative treatments are frequently used to control the viscosity or improve the reactivity of DWP (Arce *et al.*, 2020; Sharma *et al.*, 2020). Oxidative treatments are performed during the bleaching sequence, using hypochlorite (H) or ozone (Z). Hypochlorite is used to oxidise the pulp, thereby modifying the MWD and adjusting the viscosity. However, hypochlorite is being phased out of many mills due to environmental concerns associated with its use (Bajpai, 2018; Sharma *et al.*, 2020). Ozone treatment has been used to move towards elemental chlorine-free (ECF) and total chlorine-free (TCF) processes (Shatalov & Pereira, 2007; Zhang *et al.*, 2020). The development of new industrial systems that can produce ozone in bulk has made ozone treatment more economically viable in recent years (Bajpai, 2018).

2.3.2 Enzymatic treatment of dissolving wood pulp

Enzymatic treatment first became a key interest in the pulp and paper industry during the 1950s when their potential to produce valuable products were realised (Kvarnlöf, 2007). However, the large costs and difficulty in maintaining specified operating conditions associated with the use of enzymes proved that it would be unfeasible (Kvarnlöf, 2007). This led to continuous research into the field of using cellulase as a treatment technique (Bhat, 2000). Cellulases are a group of enzymes that hydrolyse the 1,4-α-D-glycosidic bonds of the cellulose chain (Yang *et al.*, 2019). There are three types of cellulases (Hildén & Johansson, 2004), namely endoglucanase (1,4-β-D-glucan 4-glucanohydrolase) (EG), exoglucanase or cellobiohydrolase (1,4-β-D-glucan cellobiohydrolase) (CBH), and β-glucosidase (β-G). Each of these enzymes targets distinct regions in the cellulose chain (Kvarnlöf, 2007; Yang *et al.*, 2019).

EG randomly acts on the internal segments of the cellulose chain, thereby decreasing the degree of polymerisation (Lynd *et al.*, 2002). EG also targets amorphous regions of the cellulose chain more readily than crystalline regions (Cao & Tan, 2005; Rahikainen *et al.*,

2019). Moreover, EGs may have secondary catalytic effects on hemicelluloses, such as mannans and xylans, thereby improving the quality of DWP (Rahikainen *et al.*, 2019). EGs have been used to replace bleaching chemicals, such as hypochlorite, to reduce environmental concerns while at the same time improving the Fock reactivity (Duan *et al.*, 2016). Furthermore, it has been shown that EG can increase reactivity by improving the porosity of the fibre wall (Ibarra *et al.*, 2009; Rahikainen *et al.*, 2019). CBH can act on both the reducing and non-reducing ends of cellulose – CBH-I specifically targets the reducing end while CBH-II targets the non-reducing end (Yang *et al.*, 2020). β-G acts on the cellobiose units thereby forming glucose monomers (Juhász *et al.*, 2005).

Cellulase typically has two distinct regions that potentiate and facilitate hydrolysis of the cellulose chain. These regions are known as the carbohydrate-binding module (CBM) and the catalytic domain. However, it is possible for enzymes to only contain the catalytic domain (Rahikainen *et al.*, 2019). The CBM forms interactions with the cellulose chain so that the catalytic domain is allowed to operate more efficiently (Rahikainen *et al.*, 2019; Yan & Wu, 2020). Like all proteins, enzymes also require careful selection of physicochemical conditions to further enhance their efficiency and prevent denaturation (Britannica, 2019).

The pH and temperature are the key operating conditions that need to be considered when enzymes are involved (Rosdee *et al.*, 2020; Britannica, 2019). If the temperature is too low, enzymatic activity is significantly reduced, while if it is too high the enzyme is denatured (Rosdee *et al.*, 2020). Cellulase prepared for commercial use perform optimally between 50°C and 70°C (Lu *et al.*, 2010). A similar effect happens with pH. The optimum pH for EG is in the range of 4.8 to 7 (Rahikainen *et al.*, 2019). While both temperature and pH are critical to improve efficiency in enzyme applications, additives have also been used for this purpose.

Cationic polyacrylamides (CPAMs) have been investigated for improving enzyme efficiency by facilitating cellulase binding onto cellulose, thereby improving the rate of hydrolysis (Figure 2.3) (Yang *et al.*, 2018). Both cellulase and cellulose have negative charges, and therefore adding a CPAM reduces the electrostatic repulsion force and increases cellulose adsorption onto the cellulose fibres (Wang *et al.*, 2015). Yang *et al.* (2018) used polydiallyldimethylammonium chloride to improve Fock reactivity from 41.5% to 88.7% while reducing enzyme dosage.

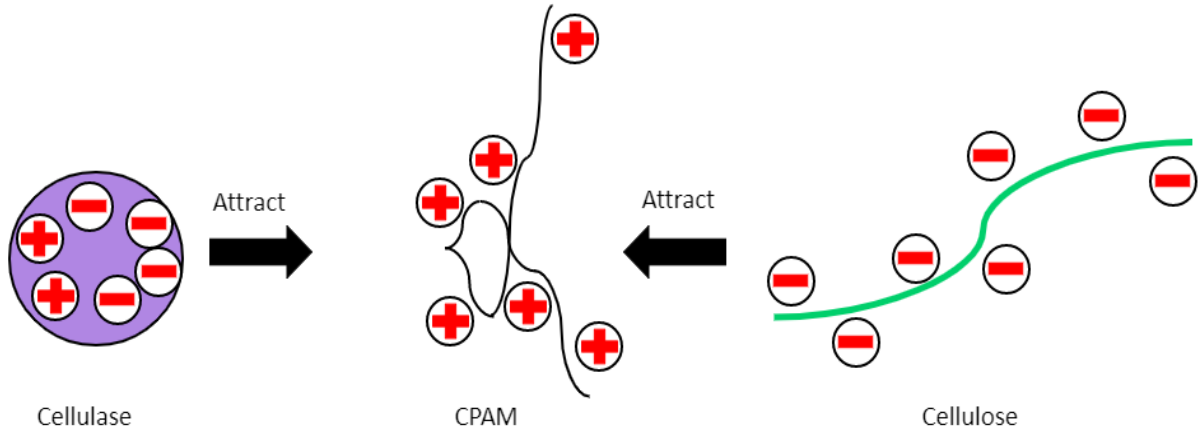


Figure 2.3: Illustration of the mechanism to improve cellulase adsorption onto the cellulose fibre with the use of CPAM, adapted from Yang *et al.* (2019)

2.3.3 Mechanical treatment of dissolving wood pulp

Mechanical treatment is a process that is used to refine pulp by repeatedly beating it to achieve modification of the fibres. This allows desired properties of the fibres to be expressed. Mechanical treatment is often simply referred to as refining (Lumiainen, 2000). Mechanical treatments are used to cut or grind the fibres, thereby exposing larger surface areas for chemical or enzymatic action (Liu *et al.*, 2016; Miao *et al.*, 2015; Yang *et al.*, 2019). The modification of the fibres can be achieved by cutting them, increasing external fibrillation and producing fines (Lumiainen, 2000). The extent of these modifications depends on the refining instrument. Tian *et al.* (2014) reported that mechanical treatments increase accessibility to the pulp fibres through fibrillation, thereby increasing the Fock reactivity. Wang *et al.* (2020) reported that mechanical refining of DWP prior to enzymatic treatment can improve cellulase efficiency by increasing accessibility to the cellulose fibres. However, it has also been reported that enzymatic treatment before mechanical refining can reduce the energy required for refining (Lin *et al.*, 2018; Tejado *et al.*, 2012; Yang *et al.*, 2019). Several instruments have been used to achieve mechanical modification of DWP. These mechanical instruments include the PFI mill, the sonotrode, microwaving, and the ball mill.

2.3.3.1 PFI mill refining

A PFI mill is an instrument that refines the pulp so that fibrillation of the fibres can occur (Tian *et al.*, 2014). Fibrillation is a term used when fibres are cut, peeled and delaminated, thereby exposing fibrils (Wang *et al.*, 2020; Yang *et al.*, 2018). The PFI mill refines the pulp by using a roll and housing that both rotate in the same direction, but at different peripheral speeds (Figure 2.4). The roller rotates faster than the housing (bedplate). The roller has bars while the housing is smooth (TAPPI, 2000a).

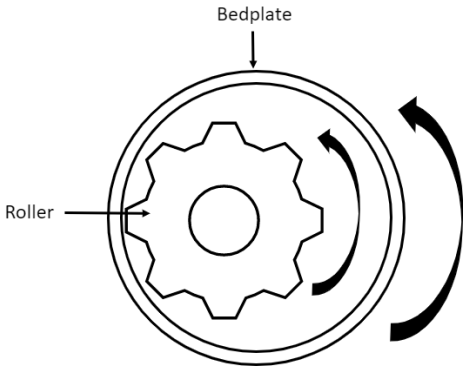


Figure 2.4: Diagram of a PFI mill, adapted from Chakraborty *et al.* (2007)

Pre-treating pulp with PFI refining increases the number of pores on the substrate, thereby improving enzymatic hydrolysis of DWP (Jones *et al.*, 2014; Liu *et al.*, 2020; Yang *et al.*, 2018). Several studies have been conducted by combining a PFI mill along with other treatment techniques to improve Fock reactivity of the DWP. Wang *et al* (2020) reported that Fock reactivity could be improved from 75.8% to 89.2% by combining enzymatic and PFI refining treatments. This result was concluded to be due to the increase of hydroxyl groups and cellulase adsorption ratio. Yang *et al* (2018) combined PFI and polydiallyldimethylammonium chloride-assisted cellulase (PDADMAC) treatment, which improved Fock reactivity from 41.5% to 88.7%, while also decreasing the viscosity of the pulp from 628.8 mL/g to 407.8 mL/g. PFI mill refining has also been used as the sole treatment to improve the properties of DWP. Tian *et al.*, (2014) found that Fock reactivity increased as the PFI revolutions increased but also that the viscosity decreased slightly. The increased reactivity was attributed to the fibrillation of the fibres.

2.3.3.2 Ultrasonication

Ultrasonication is a physicochemical process in which energy is transferred through high-frequency sound waves (Bonto *et al.*, 2021; Rehman *et al.*, 2013). These frequencies are greater than 20 kHz and thus out of the range of human hearing (Mohd Ishak *et al.*, 2020; Rehman *et al.*, 2013). Ultrasound can be divided into different categories depending on the frequency of transmission (Stander, 2015). Power ultrasound ranges between 16 kHz to 100 kHz, and high-frequency ultrasound ranges between 100 kHz and 1 MHz (Bonto *et al.*, 2021). Lastly, frequencies between 1 MHz and 10 MHz are low energy diagnostic ultrasound. Of these categories, only power ultrasound is of key interest in treating lignocellulosic biomass as it operates at the required energy levels for pretreatment (Kardos & Luche, 2001; Patist & Bates, 2008).

To transfer the energy for effective pretreatment, a sonotrode is required. The sonotrode is a solid rod that oscillates in the vertical direction at the frequency of ultrasound, thereby

transferring the energy to the fluid medium (Mohd Ishak *et al.*, 2020; Rehman *et al.*, 2013). Direct sonication is when the sonotrode is in direct contact with the fluid being sonicated and is best suited for the treatment of lignocellulosic biomass (Chisti, 2003). The sonotrode oscillation induces oscillation of the molecules in the fluid around their neutral position, resulting in altering regions of compression and rarefaction. The rarefaction results in localised regions of low pressure allowing the formation and growth of cavitation microbubbles (Suslick, 1989). Subsequently, the compression phase results in the implosion of the microbubbles which releases energy through shock waves that propagate through the fluid (Bonto *et al.*, 2021; Rehman *et al.*, 2013). Imploding microbubbles result in high local temperatures (10 000 K) and high local pressures (5 000 bar) (Chisti, 2003; Gogate & Pandit, 2008). When the microbubbles collapse, they generate liquid jets that fragment the biomass particles at the solid-liquid interface (Iskalieva *et al.*, 2012). This fragmentation then allows for an increased biomass surface area (Iskalieva *et al.*, 2012; Shewale & Pandit, 2009). Imai *et al.* (2004) ascertained that sonication increased the cellulose surface area for enzymatic hydrolysis. Sonication fragments the amorphous regions of the cellulose chain more readily than the crystalline regions (Huang *et al.*, 2007).

Modification of the morphology of the lignocellulosic biomass is dependent on a variety of process conditions. Some of the key variables that affect the biomass are the duration of sonication, sonication power, amplitude, frequency, properties of biomass and suspension fluid, and temperature (Rehman *et al.*, 2013). Treatment duration, amplitude and power are the three variables that have the greatest influence on biomass modification. The treatment duration directly correlates with the amount of energy transferred to the biomass being treated. The longer the duration of the treatment the greater the energy transferred into the system. By increasing the energy for biomass treatment, more modification occurs. However, there is a sonication length of time where no further modification will occur (Rehman *et al.*, 2013). This time length is crucial in industrial systems as going past this point will translate into energy wastage.

The power transmitted to the biomass is the second important variable that influences the treatment of lignocellulosic biomass. Imai *et al.* (2004) found that the power and the treatment duration are inversely proportional; therefore, by increasing the power transmitted to the biomass, the treatment duration can be reduced. Power also has a point at which extending the duration of the biomass treatment will have no further effect on the modification (Rehman *et al.*, 2013). Therefore, it is not solely power or duration that influence the biomass modification but rather their combined effect translating into the total energy that influences the modification process. Rehman *et al.* (2013) indicated that both the duration and the power need to be optimised for effective modification of the biomass. The power level of sonication

influences the phenomena of cavitation. The number of cavitation bubbles, the lifetime of the bubbles and implosion pressure are all influenced by the power level (Gogate *et al.*, 2011). However, Gogate *et al.* (2011) found that increasing the power level may decrease the efficiency of sonication. By increasing the power, the number of bubbles formed increases thereby impeding the transfer of energy from the sonotrode to the fluid. Therefore, care should be taken when choosing a power level.

2.3.3.3 Kneading and dispersion of pulp

Dispersion and kneading have been extensively industrialised since the 1960s (Van Guelpen, 1960). Dispersion and kneading do their work by homogenising the feedstock but can also alter the fibre properties depending on the operating conditions (Fabry & Carré, 2007; Kumar *et al.*, 2007). Currently, there are two principal methods for dispersion, namely high-speed dispersion, and low-speed dispersion. Low-speed dispersion is also called low speed kneading, and will thus be the main focus of the two principals (Kumar *et al.*, 2007).

Low-speed kneading relies on fibre-to-fibre friction with consistencies of 25% to 30%. A high operating temperature of 80°C can be reached without the need to inject steam due to the intense friction between the fibres (Patrick, 2017). At low speed (100 rpm) and high consistencies, no fibre cutting or fibrillation occurs (Patrick, 2017). However, other fibre modifications occur, such as increased tear strength, dimensional stability, fibre curl and bulk (Kumar *et al.*, 2007).

Previous research on the kneading of DWP was on using it to facilitate the mixing of enzymes to better distribute them through the pulp (Engström *et al.*, 2006; Ibarra *et al.*, 2009). Therefore, kneading done to mechanically modify the pulp has largely gone unexplored.

2.4 Critical parameters of dissolving wood pulp

DWP requires certain characteristics so that its processability and filterability in later processes can be optimised (Yang *et al.*, 2019). Some of the key variables for DWP are reactivity, viscosity, and crystallinity.

2.4.1 Reactivity

Reactivity is perhaps the most crucial property of DWP as it improves the quality and homogeneity of the cellulose-based end products and reduces the chemical demand for the synthesis of these products (Ibarra *et al.*, 2010; Quintana *et al.*, 2015; Schild & Sixta, 2011). The reactivity of DWP for viscose use specifically refers to its ability to participate in derivatisation and dissolution processes (Elg Christoffersson, 2005). The reactivity of DWP is influenced by the accessibility of the hydroxyl groups on the cellulose chain to various reagents (Filpponen & Argyropoulos, 2008). Indirect methods have also been used to correlate various

properties like the water retention value (WRV), specific surface area, and fibre saturation point with reactivity (Khanjani *et al.*, 2017). Certain mechanisms such as hornification may reduce reactivity (Elg Christoffersson, 2005; Khanjani *et al.*, 2017). Hornification is a term used to refer to a permanent decrease in WRV through drying; however, its use is not limited to dehydration but also to certain chemical treatments (Khanjani *et al.*, 2017; Pönni *et al.*, 2014).

The definition of reactivity is flexible and depends on the intended final application of the cellulose product (Khanjani *et al.*, 2017). Viscose rayon production from DWP uses a test known as Fock reactivity (Yang *et al.*, 2018). By improving the Fock reactivity of the DWP, higher quality products can be produced, while lowering the carbon disulphide (CS_2) demand of the viscose process. This lowers the environmental implications while improving the cost-effectiveness of the process (Yang *et al.*, 2018).

Other reactivity tests, such as the 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation (4-AcNH-TEMPO$^+$) test, that oxidise the hydroxymethyl groups on the cellulose, can also be used to assess the chemical reactivity of DWP. This test has been shown to complement other indirect methods, such as the WRV test (Khanjani *et al.*, 2017). The Treiber viscose filterability test is also regularly used in industrial applications (He & Chai, 2015).

A current issue with reactivity tests, such as the Fock and Treiber methods, is that they are complicated and time-consuming (He & Chai, 2015). A rapid reactivity test has been developed by He & Chai (2015) that allows for the detection of small amounts of particles in a solution by measuring light scattering. By using this principle, a strong linear correlation between the absorbance at 600 nm of a cellulose suspension and the Fock reactivity method was developed (He & Chai, 2015).

2.4.2 Viscosity

The viscosity of DWP should be carefully adjusted within acceptable limits as it affects the processability of the pulp (Yang *et al.*, 2019). Appropriate viscosity is generally in the range of 400–600 mL/g (Yang *et al.*, 2019). Having viscosities within the specified range is beneficial for both downstream processabilities and final product quality. However, decreasing the viscosity below acceptable tolerances can have a negative impact on the final product (Yang *et al.*, 2018). Generally, bleaching sequences are used to adjust the viscosity of the pulp (Bodhlyera *et al.*, 2015). However, enzymes, in particular, are effective in controlling the intrinsic viscosity (Duan *et al.*, 2016a).

Viscosity testing can indicate the degree of polymerisation and degree of degradation of the pulp due to bleaching (Bodhlyera *et al.*, 2015). Intrinsic viscosity is measured using the TAPPI standard, T 230 om-99 (TAPPI, 2004). This procedure involves dissolving a weighed pulp

sample into a solution containing 25 mL of deionised water and 25 mL of cupriethylenediamine (CED), and then measuring the efflux time in a capillary viscometer (Wang *et al.*, 2020).

2.4.3 Crystallinity

The supermolecular structure of cellulose is complex with ordered (crystalline) and non-ordered (amorphous) domains along the fibrils (Ioelovich *et al.*, 2010). The cellulose chains pass through these domains and bond with them through 1,4-β-glycoside bonds (Ioelovich *et al.*, 2010). The crystallinity of cellulose can be determined by X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy (Pönni *et al.*, 2012). Crystallinity is not absolute as these different analytical techniques yield different degrees of crystallinity (Pönni *et al.*, 2012). As such, most crystallinity results are reported using an index of crystallinity which shows the comparative amount of crystalline fraction of several cellulose samples (Ioelovich & Veveris, 1987).

The crystallinity of cellulose can be closely linked to the reactivity of the pulp (Ciolacu, 2007). Tejado *et al.* (2012) indicated that the reactivity is limited with high crystallinity. Furthermore, to increase the reactivity of the cellulose, the crystalline regions need to be made more accessible to reagents through de-crystallisation and swelling (Ciolacu, 2007).

Lastly, to improve enzymatic efficiency and reactivity the cellulose crystalline regions should be disrupted and loosened thereby increasing the surface area for hydrolysis to take place (Arantes & Saddler, 2010).

2.4.4 Alkali solubility

Alkali solubility indicates the amount of degraded cellulose and the amount of hemicellulose within the pulp (Bodhlyera *et al.*, 2015; Sango *et al.*, 2018). Degraded cellulose refers to the low molecular weight cellulose that will be lost during subsequent phases, thereby reducing the yield. S10 (10%) alkali solubility refers to a 10% NaOH solution that is used to dissolve the short-chain glucan polymers along with the hemicellulose. S18 (18%) alkali solubility refers to an 18% NaOH solution which only dissolves hemicellulose. The difference between the two methods is then used to indicate the amount of degraded cellulose also known as percentage beta (β%). Equation (2.1) is used to calculate the amount of degraded cellulose (Bodhlyera *et al.*, 2015).

$$S_{10} - S_{18} = Degraded\ cellulose\ percentage \quad (2.1)$$

The procedure that is used for both the S10 and S18 alkali solubilities is the TAPPI T235 om-60 standard (TAPPI, 2000b). The principal procedure is that cellulose and hemicellulose are extracted using the specified sodium hydroxide solutions.

2.5 Concluding remarks

DWP is a highly pure form of cellulose that can be used in a variety of applications such as viscose (Bajpai, 2015; Kumar & Christopher, 2017). Typically, DWP is produced through either the AS process or PHK pulping. The pulp is then bleached using a variety of bleaching agents, such as ozone and chlorine dioxide (Bajpai, 2018). This process allows the lignocellulose components to be separated leaving a highly pure form of cellulose.

These processes also produce DWP with the correct parameters. The most crucial parameters that need to be controlled are reactivity, viscosity, and alkali solubility. Reactivity is important as it reduces the chemical demand during the production of the relevant cellulose-based products (Ibarra *et al.*, 2010). The viscosity of DWP should be controlled as it affects the processability of the pulp and gives an indication of the degree of polymerisation (Bodhlyera *et al.*, 2015; Yang *et al.*, 2019). Alkali solubility gives an indication of the amount of degraded cellulose and hemicellulose within the pulp (Bodhlyera *et al.*, 2015; Sango *et al.*, 2018).

To further improve these characteristics of DWP, the use of cellulase has been evaluated. Cellulases are a group of enzymes that hydrolyses the 1,4-α-D-glycosidic bonds of the cellulose chain (Yang *et al.*, 2019). These enzymes include EG, CBH and β-G. EG, specifically, has been shown to improve the reactivity of DWP (Ibarra *et al.*, 2009).

Mechanical treatments to improve the efficiency of enzymes and their activity on DWP have also been investigated. Mechanical refining prior to enzymatic treatment increases the pulp reactivity by increasing accessibility to the cellulose fibres (Wang *et al.*, 2020). Furthermore, enzymatic treatment before mechanical refining can reduce the energy required for refining (Lin *et al.*, 2018).

Reference list

Adav, S.S. & Sze, S.K. 2014. Trichoderma secretome: an overview. In: Gupta, V.K., Schmoll, M., Herrera-Estrella, A., Upadhyay, R.S., Druzhinina, I., Tuohy, M.G., eds. *Biotechnology and biology of Trichoderma*. Amsterdam: Elsevier. pp. 103-114.

Arantes, V. & Saddler, J.N. 2010. Access to cellulose limits the efficiency of enzymatic hydrolysis: the role of amorphogenesis. *Biotechnology for Biofuels*, 3(1):4. doi:10.1186/1754-6834-3-4

Arce, C., Llano, T., García, P., & Coz, A. 2020. Technical and environmental improvement of the bleaching sequence of dissolving pulp for fibre production. *Cellulose*, 27(7):4079-4090.

Arnoul-Jarriault, B., Lachenal, D., Chirat, C., & Heux, L. 2015. Upgrading softwood bleached kraft pulp to dissolving pulp by cold caustic treatment and acid-hot caustic treatment. *Industrial Crops and Products*, 65:565–571.

Bajpai, P. 2015. *Green chemistry and sustainability in pulp and paper industry*. Switzerland: Springer.

Bajpai, P. 2018. Biermann's handbook of pulp and paper. 3rd ed. Vol. 1, *Raw material and pulp making*. Amsterdam: Elsevier.

Behin, J. & Zeyghami, M. 2009. Dissolving pulp from corn stalk residue and waste water of *Merox* unit. *Chemical Engineering Journal*, 152(1):26-35. doi:10.1016/j.cej.2009.03.024

Benjamin, M., Douglass, I.B., Hansen, G.A., Major, W.D., Navarre, A.J., & Yerger, H.J. 1969. A general description of commercial wood pulping and bleaching processes. *Journal of the Air Pollution Control Association*, 19(3):155-161. doi:10.1080/00022470.1969.10466471

Bhat, M.K. 2000. Cellulases and related enzymes in biotechnology. *Biotechnology Advances*, 18(5):355-383.

Bi, R., Khatri, V., Chandra, R., Takada, M., Figueroa, D.V., Zhou, H., … Saddler, J. 2021. Enhancing Kraft based dissolving pulp production by integrating green liquor neutralization. *Carbohydrate Polymer Technologies and Applications*, 2:100034. doi:10.1016/j.carpta.2021.100034

Biermann, C.J. 1996. Pulping fundamentals. In: Biermann, C., ed. *Handbook of pulping and papermaking*. 2nd ed. San Diego: Academic Press. pp. 55-100.

Bodhlyera, O., Zewotir, T., Ramroop, S., & Chunilall, V. 2015. Analysis of the changes in chemical properties of dissolving pulp during the bleaching process using piecewise linear regression models. *Cellulose Chemistry and Technology*, 49(3-4):317-332.

Bonto, A.P., Tiozon, R.N., Sreenivasulu, N., & Camacho, D.H. 2021. Impact of ultrasonic treatment on rice starch and grain functional properties: a review. *Ultrasonics Sonochemistry*, 71:105383. doi:10.1016/j.ultsonch.2020.105383

Britannica. 2019. *Enzyme*. In: *Britannica.* https://www.britannica.com/science/enzyme Date of access: 9 Sep. 2021.

Cao, Y. & Tan, H. 2005. Study on crystal structures of enzyme-hydrolyzed cellulosic materials by x-ray diffraction. *Enzyme and Microbial Technology*, 36(2):314-317.

Chakraborty, A., Sain, M., Kortschot, M., & Ghosh, S. 2007. Modeling energy consumption for the generation of microfibres from bleached kraft pulp fibres in a PFI mill. *BioResources*, 2(2):210-222. doi:10.15376/biores.210-222

Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., … & Ni, Y. 2016. Cellulose (dissolving pulp) manufacturing processes and properties: a mini-review. *BioResources*, 11(2):5553-5564

Chen, H. 2015. *Lignocellulose biorefinery engineering: principles and applications*. 1st ed. Cambridge: Woodhead Publishing.

Chisti, Y. 2003. Sonobioreactors: using ultrasound for enhanced microbial productivity. *Trends in Biotechnology*, 21(2):89-93. doi:10.1016/s0167-7799(02)00033-1

Ciolacu, D. 2007. On the supramolecular structure of cellulose allomorphs after enzymatic degradation. *Journal of Optoelectronics and Advanced Materials*, 9(4):1033.

Dong, Y., Ji, H., Dong, C., Zhu, W., Long, Z., & Pang, Z. 2019. Preparation of high-grade dissolving pulp from radiata pine. *Industrial Crops and Products*, 143:111880. doi:10.1016/j.indcrop.2019.111880

Duan, C., Verma, S.K., Li, J., Ma, X., & Ni, Y. 2016. Viscosity control and reactivity improvements of cellulose fibers by cellulase treatment. *Cellulose*, 23(1):269-276.

Dufresne, A. 2013. Nanocellulose: a new ageless bionanomaterial. *MaterialsToday*, 16(6):220-227. doi:10.1016/j.mattod.2013.06.004

Ek, M., Gellerstedt, G., & Henriksson, G. 2009. Pulp and paper chemistry and technology. Vol. 1, *Wood chemistry and wood biotechnology*. Berlin: De Gruyter.

Elg Christoffersson, K. 2005. *Dissolving pulp: multivariate characterisation and analysis of reactivity and spectroscopic properties*. https://www.diva-portal.org/smash/get/diva2:143367/FULLTEXT01.pdf Date of access: 19 Nov. 2021.

Engström, A.-C., Ek, M., & Henriksson, G. 2006. Improved accessibility and reactivity of dissolving pulp for the viscose process: pretreatment with monocomponent endoglucanase. *Biomacromolecules*, 7:2027-2031.

Eriksson, H. 2014. *Cellulose reactivity: difference between sulfite and PHK dissolving pulps*. https://www.diva-portal.org/smash/get/diva2:752051/FULLTEXT01.pdf Date of access: 19 Nov. 2021.

Fabry, B. & Carré, B. 2007. High-speed dispersing between two deinking loops: are there optimisation possibilities? https://www.tappi.org/content/events/07recycle/papers/carre.pdf Date of access: 19 Nov. 2021.

Filpponen, I. & Argyropoulos, D.S. 2008. Determination of cellulose reactivity by using phosphitylation and quantitative P NMR spectroscopy. *Industrial Engineering Chemistry Research,* 47(22):8906-8910.

Friebel, C., Bischof, R.H., Schild, G., Fackler, K., & Gebauer, I. 2019. Effects of caustic extraction on properties of viscose grade dissolving pulp. *Processes*, 7(3):122. doi:10.3390/pr7030122.

Gehmayr, V., Schild, G., & Sixta, H. 2011. A precise study on the feasibility of enzyme treatments of a kraft pulp for viscose application. *Cellulose*. 18(2):479-491.

Gogate, P., Sutkar, V., & Pandit, A. 2011. Sonochemical reactors: important design and scale up considerations with a special emphasis on heterogeneous systems. *Chemical Engineering Journal*, 166(3):1066-1082. doi:10.1016/j.cej.2010.11.069

Gogate, P.R. & Pandit, A.B. 2008. Application of cavitational reactors for cell disruption for recovery of intracellular enzymes. *Journal of Chemical Technology & Biotechnology*, 83(8):1083-1093.

Granström, M. 2009. *Cellulose derivatives: synthesis, properties and applications*. https://core.ac.uk/download/pdf/14916693.pdf Date of access: 19 Nov. 2021.

He, L. & Chai, X.-S. 2015. A rapid method for determining the reactivity of dissolving pulps by visible spectroscopy. *Cellulose*, 22(5):2851-2857.

Healey, A.L., Lupoi, J.S., Lee, D.J., Sykes, R.W., Guenther, J.M., Tran, K., Decker, S.R., Singh, S., Simmons, B.A., & Henry, R.J. 2016. Effect of aging on lignin content,

composition and enzymatic saccharification in Corymbia hybrids and parental taxa between years 9 and 12. *Biomass and Bioenergy*, 93:50–59.

Heinze, T. & Liebert, T. 2001. Unconventional methods in cellulose functionalization. *Progress in Polymer Science*, 26(9):1689-1762.

Hildén, L. & Johansson, G. 2004. Recent developments on cellulases and carbohydrate-binding modules with cellulose affinity. *Biotechnology Letters*, 26(22):1683-1693.

Huang, Q., Li, L., & Fu, X. 2007. Ultrasound effects on the structure and chemical reactivity of cornstarch granules. *Starch - Stärke*, 59(8):371-378. doi:10.1002/star.200700614

Ibarra, D., Köpcke, V., & Ek, M. 2009. Exploring enzymatic treatments for the production of dissolving grade pulp from different wood and non-wood paper grade pulps. *Holzforschung*, 63(6):721-730. doi:10.1515/HF.2009.102

Ibarra, D., Köpcke, V., Larsson, P.T., Jääskeläinen, A.-S., & Ek, M. 2010. Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp. *Bioresource Technology*, 101(19):7416-7423.

Imai, M., Ikari, K., & Suzuki, I. 2004. High-performance hydrolysis of cellulose using mixed cellulase species and ultrasonication pretreatment. *Biochemical Engineering Journal*, 17(2):79-83.

Ioelovich, M., Leykin, A., & Figovsky, O. 2010. Study of cellulose paracrystallinity. *Bioresources*, 5(3):1393-1407.

Ioelovich, M. & Veveris, G.P. 1987. Determination of cellulose crystallinity by x-ray diffraction method. *Journal of Wood Chemistry and Technology*, 5:72-80.

Iskalieva, A., Yimmou, B.M., Gogate, P.R., Horvath, M., Horvath, P.G., & Csoka, L. 2012. Cavitation assisted delignification of wheat straw: a review. *Ultrasonics Sonochemistry*, 19(5):984-993.

Jiang, X., Bai, Y., Chen, X., & Liu, W. 2020. A review on raw materials, commercial production and properties of lyocell fiber. *Journal of Bioresources and Bioproducts*, 5(1):16-25.

Jones, B.W., Venditti, R., Park, S., & Jameel, H. 2014. Comparison of lab, pilot, and industrial scale low consistency mechanical refining for improvements in enzymatic digestibility of pretreated hardwood. *Bioresource Technology*, 167:514-520.

Juhász, T., Szengyel, Z., Réczey, K., Siika-Aho, M., & Viikari, L. 2005. Characterization of cellulases and hemicellulases produced by Trichoderma reesei on various carbon sources. *Process Biochemistry*, 40(11):3519-3525.

Kai, D., Tan, M., Chee, P.L., Chua, Y., Yap, Y., & Loh, X.J. 2016. Towards lignin-based functional materials in a sustainable world. *Green Chemistry*, 18(5):1175-1200.

Kardos, N. & Luche, J.-L. 2001. Sonochemistry of carbohydrate compounds. *Carbohydrate Research*, 332(2):115-131.

Khanjani, P., Väisänen, S., Lovikka, V., Nieminen, K., Maloney, T., & Vuorinen, T. 2017. Assessing the reactivity of cellulose by oxidation with 4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxo-piperidinium cation under mild conditions. *Carbohydrate Polymers*, 176:293-298.

Kumar, H. & Christopher, L.P. 2017. Recent trends and developments in dissolving pulp production and application. *Cellulose*, 24(6):2347-2365.

Kumar, S., Fabry, B., Carré, B., Cochaux, A., Julien Saint Amand, F., & Galland, G. 2007. *Past, present and future of dispersion and kneading*. https://www.researchgate.net/profile/Alain-Cochaux/publication/242208234_Past_present_and_future_of_dispersion_and_kneading/links/5440f7cd0cf228087b6a2ba6/Past-present-and-future-of-dispersion-and-kneading.pdf Date of access: 19 Nov. 2021.

Kvarnlöf, N. 2007. *Activation of dissolving pulps prior to viscose preparation*. http://www.diva-portal.org/smash/get/diva2:5128/FULLTEXT01.pdf Date of access: 15 Nov. 2021.

Li, J., Zhang, H., Duan, C., Liu, Y., & Ni, Y. 2015. Enhancing hemicelluloses removal from a softwood sulfite pulp. *Bioresource Technology*, 192:11-16.

Li, J., Zhang, S., Li, H., Ouyang, X., Huang, L., Ni, Y., & Chen, L. 2018. Cellulase pretreatment for enhancing cold caustic extraction-based separation of hemicelluloses and cellulose from cellulosic fibers. *Bioresource Technology*, 251:1-6.

Lin, X., Wu, Z., Zhang, C., Liu, S., & Nie, S. 2018. Enzymatic pulping of lignocellulosic biomass. *Industrial Crops and Products*, 120:16-24.

Liu, W., Wang, B., Hou, Q., Chen, W., & Wu, M. 2016. Effects of fibrillation on the wood fibers' enzymatic hydrolysis enhanced by mechanical refining. *Bioresource Technology*, 206:99-103.

Liu, W., Wu, R., Wang, B., Hu, Y., Hou, Q., Zhang, P., & Wu, R. 2020. Comparative study on different pretreatment on enzymatic hydrolysis of corncob residues. *Bioresource Technology*. 295:122244.

Lu, J., Reye, J., & Banerjee, S. 2010. Temperature dependence of cellulase hydrolysis of paper fiber. *Biomass and Bioenergy*, 34(12):1973-1977.

Lu, Y., Lu, Y.-C., Hu, H.-Q., Xie, F.-J., Wei, X.-Y., & Fan, X. 2017. Structural characterization of lignin and its degradation products with spectroscopic methods. Journal of Spectroscopy, Article # 8951658. doi:10.1155/2017/8951658

Lumiainen, J. 2000. *Refining of chemical pulp*. https://turbulence-initiated.sites.olt.ubc.ca/files/2013/01/1998-Lumiainen-Ch4.pdf Date of access: 15 Nov. 2021.

Lynd, L.R., Weimer, P.J., van Zyl, W.H., & Pretorius, I.S. 2002. Microbial cellulose utilization: fundamentals and biotechnology. *Microbiology and Molecular Biology Reviews*, 66(3):506-577.

Mateos-Espejel, E., Radiotis, T., & Jemaa, N. 2013. Implication of converting a converting a kraft pulp mill to a dissolving pulp operation with a hemicellulose extraction stage. *TAPPI Journal*, 12:29-38.

Metais, A. & Germer, E. 2020. *Review of industrial ozone bleaching practices*. https://paper360.tappi.org/2018/09/24/review-of-industrial-ozone-bleaching-practices/ Date of access: 9 Sep. 2021.

Miao, Q., Tian, C., Chen, L., Huang, L., Zheng, L., & Ni, Y. 2015. Combined mechanical and enzymatic treatments for improving the Fock reactivity of hardwood kraft-based dissolving pulp. *Cellulose*. 22(1). doi:10.1007/s10570-014-0495-9

Mohd Ishak, N.A., Khalil, I., Abdullah, F.Z., & Muhd Julkapli, N. 2020. A correlation on ultrasonication with nanocrystalline cellulose characteristics. *Carbohydrate Polymers*, 246(1):116553. doi:10.1016/j.carbpol.2020.116553

O'Sullivan, A.C. 1997. Cellulose: The structure slowly unravels. *Cellulose*. 4(3):173-207.

Okal, E.J., Aslam, M.M., Karanja, J.K., & Nyimbo, W.J. 2020. Mini review: advances in understanding regulation of cellulase enzyme in white-rot basidiomycetes. *Microbial Pathogenesis*, 147:104410. doi:10.1016/j.micpath.2020.104410

Patist, A. & Bates, D. 2008. Ultrasonic innovations in the food industry: from the laboratory to commercial production. *Innovative Food Science and Emerging Technologies*, 9(2):147-154.

Patrick, K. 2017. *New kneading, washing technologies open door to advanced fiber recycling for tissue industry*. https://tissue360.tappi.org/2017/12/28/new-kneading-washing-technologies-open-door-to-advanced-fiber-recycling-for-tissue-industry/ Date of access: 9 Sep. 2021.

Pönni, R., Galvis, L., & Vuorinen, T. 2014. Changes in accessibility of cellulose during kraft pulping of wood in deuterium oxide. *Carbohydrate Polymers*, 101:792-797.

Pönni, R., Vuorinen, T., & Kontturi, E. 2012. Proposed nano-scale coalescence of cellulose in chemical pulp fibers during technical treatments. *Bioresources*, 7:6077-6108.

Quintana, E., Valls, C., Barneto, A.G., Vidal, T., Ariza, J., & Roncero, M.B. 2015. Studying the effects of laccase treatment in a softwood dissolving pulp: cellulose reactivity and crystallinity. *Carbohydrate Polymers*, 119:53-61.

Rahikainen, J., Ceccherini, S., Molinier, M., Holopainen-Mantila, U., Reza, M., Väisänen, S., Puranen, T., Kruus, K., Vuorinen, T., Maloney, T., Suurnäkki, A., & Grönqvist, S. 2019. Effect of cellulase family and structure on modification of wood fibres at high consistency. *Cellulose*, 26(8):5085-5103.

Rehman, M.S.U., Kim, I., Chisti, Y., & Han, J.-I. 2013. Use of ultrasound in the production of bioethanol from lignocellulosic biomass. *Energy Education Science and Technology Part A: Energy Science and Research*, 30(2):1410-1931.

Rongpipi, S., Ye, D., Gomez, E.D., & Gomez, E.W. 2019. Progress and opportunities in the characterization of cellulose – an important regulator of cell wall growth and mechanics. *Frontiers in Plant Science*, 1(9):1894. doi:10.3389/fpls.2018.01894

Rosdee, N.A.S.M., Masngut, N., Shaarani, S.M., Jamek, S., & Sueb, M.S.M. 2020. Enzymatic hydrolysis of lignocellulosic biomass from pineapple leaves by using endo-1,4-xylanase: effect of pH, temperature, enzyme loading and reaction time. *IOP Conference Series: Materials Science and Engineering*, 736:22095.

Sadhu, S. & Maiti, T.K. 2013. Cellulase production by bacteria: a review. *British Microbiology Research Journal*, 3(3):235-258.

Sango, C., Kaur, P., Bhardwaj, N.K., & Sharma, J. 2018. Bacterial cellulase treatment for enhancing reactivity of pre-hydrolysed kraft dissolving pulp for viscose. *3 Biotech*. 8(6):271.

Sappi. 2020. *Dissolving pulp: sustainable fibre for a thriving world*. https://www.sappi.com/dissolving-pulp Date of access 9 Sep. 2021.

Sappi North America. 2017. *Understanding paper brightness*. https://cdn-3.sappi.com/s3fs-public/sappietc/Understanding Paper Brightness.pdf Date of access: 9 Sep. 2021.

Schild, G. & Sixta, H. 2011. Sulfur-free dissolving pulps and their application for viscose and lyocell. *Cellulose*, 18:1113-1128.

Sharma, N., Bhardwaj, N.K., & Singh, R.B.P. 2020. Environmental issues of pulp bleaching and prospects of peracetic acid pulp bleaching: a review. *Journal of Cleaner Production*, 256:120338.

Shatalov, A.A. & Pereira, H. 2007. Polysaccharide degradation during ozone-based TCF bleaching of non-wood organosolv pulps. *Carbohydrate Polymers*, 67(3):275-281.

Shen, L. & Patel, M. 2010. Life cycle assessment of man-made cellulose fibres. *Lenzinger Berichte*, 88: 1-59.

Shewale, S.D. & Pandit, A.B. 2009. Enzymatic production of glucose from different qualities of grain sorghum and application of ultrasound to enhance the yield. *Carbohydrate Research*, 344(1):52-60.

Shigeto, J., Ueda, Y., Sasaki, S., Fujita, K., & Tsutsumi, Y. 2016. Enzymatic activities for lignin monomer intermediates highlight the biosynthetic pathway of syringyl monomers in Robinia pseudoacacia. *Journal of Plant Research*, 130(1):203-210.

Sixta H., Potthast A., Krotschek AW. 2006. Chemical pulping processes. In: Sixta H (ed) Handbook of pulp. Weinheim: Wiley, pp 325–366

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., van Heiningen, A., Froschauer, C., & Schottenberger, H. 2013. Novel concepts of dissolving pulp production. *Cellulose*, 20(4):1547-1561.

Sjöström, E. 1993. *Wood chemistry: fundamentals and applications*. 2nd ed. New York: Academic Press.

Stander, W.H. 2015. *Assessment of enzymatic treatment and ultrasonication of wood and old corrugated container pulp as an alternative to refining*. Potchefstroom: North-West University. (Dissertation – MEng (Chemical)).

Suess, H.U. 2010. *Pulp bleaching today*. Berlin: De Gruyter.

Sun, S., Sun, S., Cao, X., & Sun, R. 2016. The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials. *Bioresource Technology*, 199:49-58. doi:10.1016/j.biortech.2015.08.061

Suslick, K.S. 1989. The chemical effects of ultrasound. *Scientific American*, 260(2):80-86.

TAPPI. 2000a. *T248 sp-00 Laboratory beating of pulp (PFI mill method)*. Atlanta: TAPPI Press.

TAPPI. 2000b. *Alkali solubility of pulp, TAPPI T235 om-60*. Atlanta: TAPPI Press.

TAPPI. 2004. *Viscosity of pulp (capillary viscometer method)*. Atlanta: TAPPI Press.

Tejado, A., Alam, M.N., Antal, M., Yang, H., & van de Ven, T.G.M. 2012. Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers. *Cellulose*, 19(3):831-842.

Tian, C., Zheng, L., Miao, Q., Cao, C., & Ni, Y. 2014. Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments. *Cellulose*, 21(5). doi:10.1007/s10570-014-0332-1

Van Guelpen, L.C. 1960. Dispersion of asphalt materials in paper stocks. *TAPPI Journal*, 43(11):162A-165A.

VanderHart, D.L. & Atalla, R.H. 1984. Studies of microstructure in native celluloses using solid-state carbon-13 NMR. *Macromolecules*, 17(8):1465-1472. doi:10.1021/ma00138a009

Wang, Q., Fu, X., Liu, S., Ji, X., Wang, Y., He, H., Yang, G., & Chen, J. 2020. Understanding the effect of depth refining on upgrading of dissolving pulp during cellulase treatment. *Industrial Crops Production*, 144:112032.

Wang, Q., Liu, S., Yang, G., Chen, J., & Ni, Y. 2015. Cationic polyacrylamide enhancing cellulase treatment efficiency of hardwood kraft-based dissolving pulp. *Bioresource Technology*, 183:42-46.

Wang, S., Lu, A., & Zhang, L. 2016. Recent advances in regenerated cellulose materials. *Progress in Polymer Science*, 53:169-206.

Wizani, W., Krotscheck, A., Schuster, J., & Lackner, K. 1994. *Viscose production process*. (Patent: EP0672207B1). https://patentimages.storage.googleapis.com/03/94/90/f10364b5373c4c/EP0672207B1.pdf Date of access: 19 Nov. 2021.

Yan, S. & Wu, G. 2020. Implications of carbohydrate binding modules of cellulases summarized from visualization. In: Jaworski, M. & Marciniak, .M eds. *Conference Proceedings.* 22nd International Conference on Transparent Optical Networks (ICTON 2020), Bari, Italy, pp. 1-7.

Yang, S., Wen, Y., Zhang, H., Li, J., & Ni, Y. 2018. Enhancing the Fock reactivity of dissolving pulp by the combined prerefining and poly dimethyl diallyl ammonium chloride-assisted cellulase treatment. *Bioresource Technology*, 260:135-140.

Yang, S., Yang, B., Duan, C., Fuller, D.A., Wang, X., Chowdhury, S.P., … Ni, Y. 2019. Applications of enzymatic technologies to the production of high-quality dissolving pulp: a review. *Bioresource Technology*, 281:440-448.

Yang, T., Guo, Y., Gao, N., Li, X., & Zhao, J. 2020. Modification of a cellulase system by engineering Penicillium oxalicum to produce cellulose nanocrystal. *Carbohydrate Polymers*, 234:115862.

Zhang, X., Li, J., Gong, J., Kuang, Y., He, S., Xu, J., … Song, T. 2020. Cleaner approach for medium consistency eucalyptus slab pulp production using ozone bleaching under turbulent mixing. *Journal of Cleaner Production*, 276:124201.

Zhao, C., Jiang, E., & Chen, A. 2017. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *Journal of the Energy Institute*, 90(6):902-913.

Chapter 3: Modification of fully bleached dissolving wood pulp through endoglucanase treatment

3.1 Introduction

DWP has seen an increased demand in recent years due to its use in value-added products, particularly viscose (Kumar & Christopher, 2017; Sixta *et al.*, 2013). Currently, there are two main processes used to produce DWP, namely AS pulping and PHK pulping, both of which are followed by a bleaching sequence (Bajpai, 2018; Wang *et al.*, 2020).

Pulping and bleaching are paramount in the production of high-purity, high-quality DWP. Pulping is the process whereby lignocellulosic components are separated from one another; more specifically, the separation of cellulose from both lignin and hemicellulose (Bajpai, 2018). Bleaching is the process used to further increase DWP-purity by removing any residual lignin and hemicellulose, while increasing the pulp brightness (Friebel *et al.*, 2019). Bleaching is imperative in adjusting DWP properties, such as viscosity and reactivity. Brightness is typically controlled using chemicals such as chlorine dioxide (D-stage) and peroxide, while viscosity is controlled using chemicals such as hypochlorite (H-stage) and ozone (Z-stage) (Bajpai, 2018).

Improving reactivity, and controlling viscosity are perhaps the two most important parameters of high-quality DWP. Reactivity improves the quality and homogeneity of the cellulose-based end products and reduces the chemical demand in their production (Ibarra *et al.*, 2010; Quintana *et al.*, 2015). Viscosity of DWP should be adjusted carefully within acceptable limits as it affects the processibility of the pulp (Yang *et al.*, 2019). Many studies have been conducted to improve these parameters by using enzymes, namely cellulases (Ibarra *et al.*, 2010; Kumar & Christopher, 2017; Lin *et al.*, 2018; Wang *et al.*, 2020; Yang *et al.*, 2018; 2019).

Cellulases are a group of enzymes that hydrolyses the 1,4-α-D-glycosidic bonds of the cellulose chain (Yang *et al.*, 2019). There are three types of cellulases, namely endoglucanase (EG), cellobiohydrolase (CBH) and β-glycosidase (β-G), with each targeting distinct regions of the cellulose chain (Hildén & Johansson, 2004; Kvarnlöf, 2007; Yang *et al.*, 2019). EG acts randomly on the internal segments of the cellulose chain, thereby decreasing the degree of polymerisation (Lynd *et al.*, 2002). CBH can act on the both the reducing (CHB I) and non-reducing ends of cellulose (CBH-II) (Yang *et al.*, 2020). β-G acts on the cellobiose units, thereby releasing glucose monomers (Juhász *et al.*, 2005).

In this study, two commercially available formulations of EG were used to treat fully bleached AS pulp to measure their effect on the properties of DWP. The properties that were tested were reactivity, viscosity, and alkali solubility. The aim was to compare the enzymes based on

performance and to quantify how certain DWP properties were altered, thereby improving the final product for viscose application.

3.2 Materials and methods

3.2.1 Enzyme characterisation

The EG activity of two commercial enzyme preparations (Table 3.1) was determined using the modified filter paper assay (Chu *et al.*, 2012) to obtain information regarding expected activities at mill operating conditions. The thermostability of the preparations was also determined to establish the period of incubation. The assay was conducted using test tubes containing 50 mg (6 x 1 cm) Whatman grade 1 filter paper strips as substrate in 1 mL Britton-Robinson buffer (pH 6) solution (Mongay & Cerdà, 1974). The solutions were pre-incubated for 5 min at 60°C, after which 0.5 mL of 5 mg/mL diluted enzyme was added. The reaction mixtures were incubated for 10 min at the specified temperature. Both a control (no filter paper) and a blank (0.5 mL diluted enzyme replaced with 0.5 mL buffer) were also incubated. The enzyme reaction was stopped after 10 min by placing the test tubes into boiling water for 10 min. The solutions were centrifuged using an Eppendorf 5804R centrifuge (Eppendorf AG, Germany) at 4°C and 166.67 Hz for 5 min. The supernatants were transferred into clean Eppendorf tubes, kept cooled at 4°C, and analysed using high-performance liquid chromatography (HPLC).

The thermostability analysis was conducted by incubating diluted enzyme at 60°C for 2 h. After 1 h, a portion of the diluted enzyme was removed, and the enzyme assay as described above was conducted using the diluted enzyme. Similarly, after 2 h enzyme was removed, and an enzyme assay was repeated. This was done to see if the enzyme activities changed during the two incubation times.

HPLC analysis (Sigma-Aldrich) was conducted on the supernatants to determine the amount of cellobiose, and glucose released during the enzyme treatments. Standard solutions containing glucose and cellobiose at eight concentrations were prepared from analytical grade powders to construct calibration curves to quantify concentrations in the supernatants. The supernatants and standards were filtered through 0.45 µm polytetrafluoroethylene (PFTE) syringe filters. High-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was used to determine the amount of cellobiose and glucose within the supernatants. Sugar separation was conducted using a Dionex Ultimate 3000 system (Thermo Fischer Scientific) with a CarboPac PA1 column (240 x 4 mm) in combination with a CarboPac PA1 guard column (50 x 4 mm). Before injection, the samples were kept at 5°C, after which the analysis was conducted at 30°C. HPLC grade water was used as the eluent to

separate the components at a flow rate of 1 mL/min. Thereafter, a supporting electrolyte was added post-column using sodium hydroxide (132 mM) at a flow rate of 1 mL/min. The PAD settings that were used were: E_1 = 200 mV, E_2 = -1000 mV, E_3 = 600 mV and E_4 = -100 mV for 500, 10, 10 and 40 ms respectively. The time delay was 360 ms at a cell guard potential of 0 mV. The output of the detector was analysed using Chromeleon® software (Thermo Fischer Scientific). By integrating the peak areas, the cellobiose and glucose content could be quantified.

3.2.2 Enzyme treatments

All enzyme treatments were carried out on fully bleached DWP obtained from a local pulping mill (-30.182609, 30.775008). The pulp was received from the mill as high consistency (>30%) filter cakes at a pH value of 8. Consistency refers to the amount of solids in the slurry. The filter cakes were broken up to produce fluffed pulp. Before the enzyme treatments were done, the pH and the consistency of the pulp were corrected. The consistency was reduced to 10% by adding deionised (DI) water to this pulp, which allowed the enzymes to move freely. The pH of the pulp was then adjusted to a value of 6 using 98% analytical grade sulfuric acid (H_2SO_4). Aliquots of the diluted pulp slurry, that represented 50 g bone-dry pulp, was transferred to heavy-duty plastic bags.

The enzymatic treatments were done using two different formulations of EG, namely Ecopulp R and Novozyme (Table 3.1). The dosages were varied from 0 g/ton to 300 g/ton in increments of 50 g/ton. Two incubation periods were tested, namely 1 h and 2 h. All treatments were carried out in a water bath at 60°C. Before incubation, the enzyme was injected into the plastic bags and mixed. After the specified incubation times, the bags were opened and 2 L of boiling DI water was added to the pulp and allowed to stand for 5 min to ensure that the enzyme was denatured, thus stopping the enzyme reaction. The pulp was then washed with a further 2 L of boiling DI water in a Büchner funnel (240 mm diameter), using filter paper (Munktell Grade 1288). The filter cakes were then used to form handsheets to preserve the samples until testing.

Table 3.1: Commercial EG preparations that were used to treat fully bleached industrial DWP

Enzyme formulation	Supplier	Temperature (°C)	pH range	Reference
Ecopulp R	AB Enzymes (Darmstadt, Germany)	30–65	4.5–7.5	(AB Enzymes-Ecopulp R, 2009)
NS 51179	Novozymes (Bagsværd, Denmark)	50–70	5–7	(Reichel, 2020)

The handsheets were made by splitting the pulp samples into smaller masses to avoid excessively thick sheets and DI water was added to the samples to break up large lumps. These slurries were then added to a Rapid Köthen sheet former to form the handsheets.

3.2.3 Handsheet analysis

3.2.3.1 Viscosity

The CED viscosity test according to TAPPI standard T230 om-04 and the ISO 5351 standard, was used to determine the intrinsic viscosity of the pulps after enzymatic treatments (ISO, 2010; TAPPI, 2004). The treated pulp samples were accurately weighed to specified amounts based on an estimation of what the viscosity could potentially be. The pulp was then added to plastic bottles along with 6 to 8 pieces of copper wire, followed by the addition of 25 mL of DI water. The pulp mixtures were shaken for 30 min to allow the pulp to disperse in the water. Once the pulp has been dispersed, 25 mL of CED solution was added. The bottles were then squeezed while being closed, to remove the air within the bottles. The samples were then shaken for 30 min to allow the pulp to completely dissolve in the solution. The reaction mixtures were then placed into a water bath at 25 ± 0.1°C for 1 h. Each solution was placed into a capillary viscometer and the efflux time was measured. All measurements were repeated in duplicate, and the average efflux time was reported. The pulp consistency was also determined.

3.2.3.2 Alkali solubility

Alkali solubility was tested using the method described in the TAPPI standard T235 om-60 and the ISO 692 standard to determine the amount of degraded cellulose and hemicellulose content within the pulp samples (ISO, 1982; TAPPI, 2000b). The test procedure involved dissolving the pulp sample (1.6 g) in a 100 mL standardised 10 wt% (S10) or 18 wt% (S18) sodium hydroxide (NaOH) solution. 10 wt% NaOH solution is used to dissolve the short-chain glucan polymers along with the hemicellulose, while 18 wt% NaOH solution dissolves only the

hemicellulose (Bodhlyera *et al.*, 2015). The solution was then kept at 20°C for 1 h, after which it was filtered. The filtrate (10 mL) was added to 10 mL of 0.4 N potassium dichromate ($K_2Cr_2O_7$) and 30 mL concentrated (98%) H_2SO_4. After 10 min, 250 mL of DI water was added, and the sample was cooled for 1 h on the bench. Thereafter, 20 mL of 10 wt% potassium iodide (KI) was added to the solution. The solution was then titrated using a Dosimat 776 (Metrohm) with 0.1 N sodium thiosulphate ($Na_2S_2O_3$).

3.2.3.3 Quick reactivity

The reactivity of the pulp was determined using a reactivity test that was similar to the viscose filterability test (the method was developed in-house). This test was conducted by Sappi Saiccor (Umkomaas, South Africa). The test involved dissolving the pulp sample in NaOH, after which carbon disulphide (CS_2) was added. The CS_2 reacted with the cellulose fibres to produce dissolved cellulose fibres, which is commonly known as viscose dope. The undissolved fibres and viscose dope were separated with a centrifuge. The undissolved fibres were weighed, as their reactivity is indirectly proportional to the amount of undissolved fibres. A higher reactivity correlated with less undissolved fibres.

3.3 Results and discussion

3.3.1 Enzyme characterisation

Cellulases hydrolyse the 1,4-α-D-glycosidic bonds of the cellulose chain resulting in free sugars present as either glucose or cellobiose. The free glucose and cellobiose concentrations after enzyme treatment can thus be used to compare the activity of different enzymes. Figure 3.1 gives the free sugar concentrations obtained after treatment of the pulp with either the Ecopulp R or NS 51179 enzyme formulation. The standard deviation in the measurements is indicated by vertical error bars.

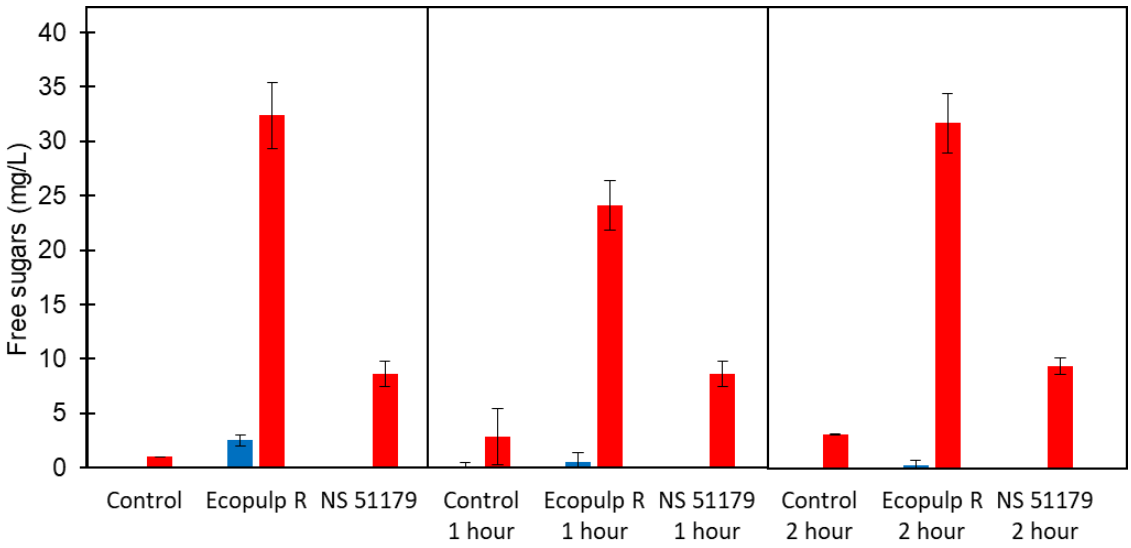


Figure 3.1: Enzyme assays for hydrolysis of filter paper and thermostability analysis for two commercially available enzymes at 0 h, 1 h and 2 h. ● - Glucose ● - Cellobiose.

The highest cellobiose and glucose concentrations were obtained with the Ecopulp R enzyme formulation and cellobiose was the main free sugar observed for both enzymes. This result was expected for EG as reported by Zhang *et al*. (2018). The first assay without prior enzyme incubation showed that Ecopulp R release significantly more cellobiose compared to NS 51179 formulation (32.4 mg/L compared to 8.6 mg/L). It can be deduced from the results in Figure 3.1 that the activity of the Ecopulp R formulation is about three times higher than that of the NS 51179 enzyme formulation even though the treatment conditions of 60°C and pH of 6 were well within the suppliers temperature and pH range for high enzyme activity (Table 3.1). Similar trends can be seen in both the 1 hour and 2 hour enzyme incubations prior to conducting the assay. Incubation time did not have a significant effect on the cellobiose concentration obtained with either of the enzyme formulations. The glucose concentration obtained with the Ecopulp R formulation was higher; however, this result was significantly influenced by the incubation time with a drop in concentration from almost 2.5 mg/L to below 0.5 mg/L during the first incubation hour. A further increase in incubation time did not, however, have a significant effect on either glucose or cellobiose concentration. Thus, the enzymes remained thermally stable for the duration of the treatments as cellobiose concentrations remained high.

Ecopulp R performed better than the NS 51179 as the cellulase composition was different. Additionally, Ecopulp R formulation most likely had higher concentrations of EG, as an increased enzyme concentration would result in better sugar conversion, and thus the sugar concentration was higher than in the NS 51179 formulation.

3.3.2 Intrinsic viscosity of dissolving wood pulp

DWP viscosity is an important parameter that needs to be carefully controlled, especially for viscose application, as it affects drainability of the viscose fibres (Lin *et al.*, 2018). Incubation times and enzyme dosages were identified as the two variables that need to be controlled, so that the viscosity of the pulp could be appropriately adjusted within acceptable limits. The effect of enzyme dosage on the intrinsic viscosity of the DWP is given in Figures, Figure 3.2 and Figure 3.3 for the Ecopulp R and NS 51170 enzyme formulations, respectively. The standard deviations of the measured values are indicated by error bars in the figures.

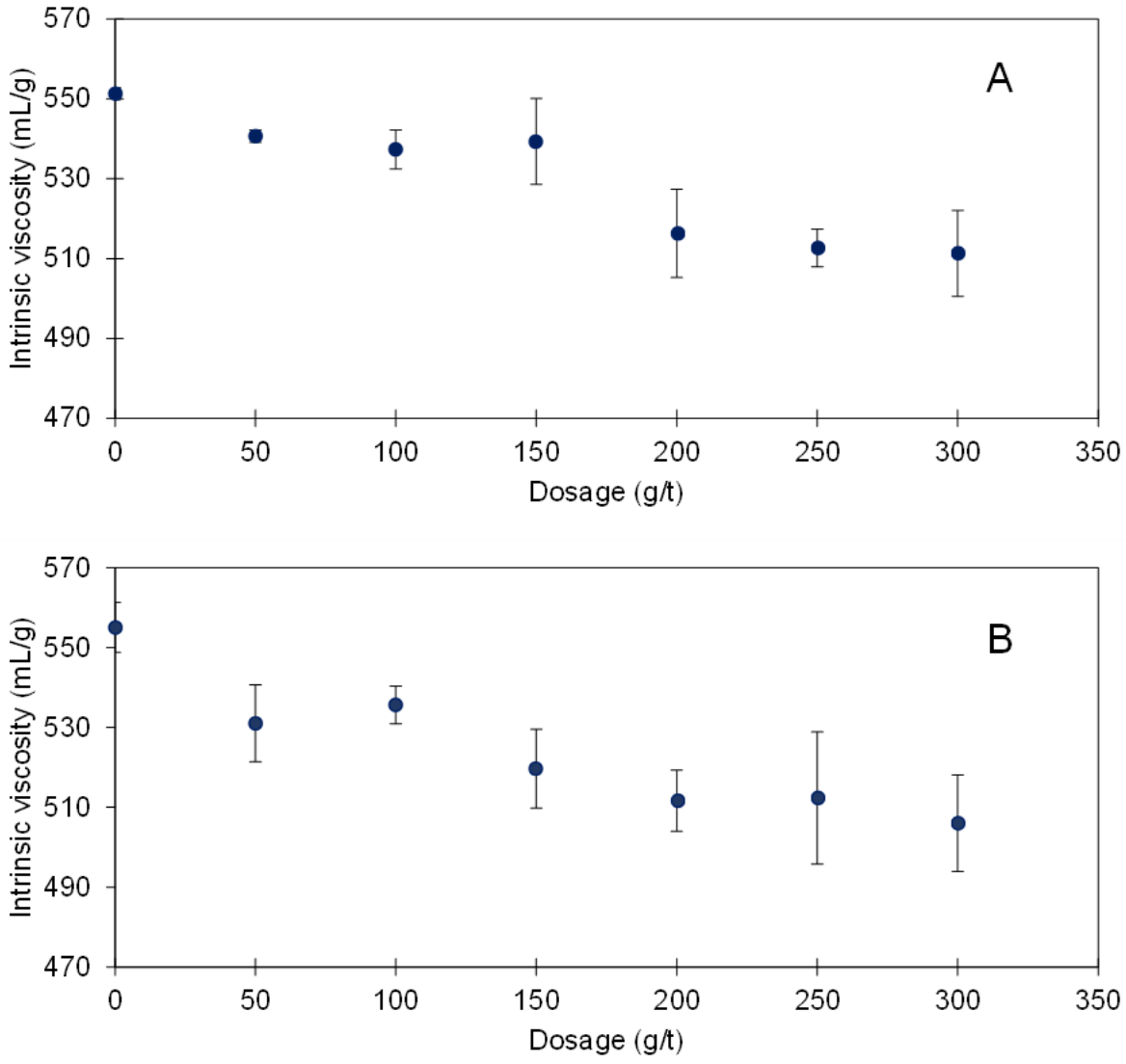


Figure 3.2: Effect of dosage of the Ecopulp R enzyme on the intrinsic viscosity of the DWP at incubation times of 1 h (A) and 2 h (B)

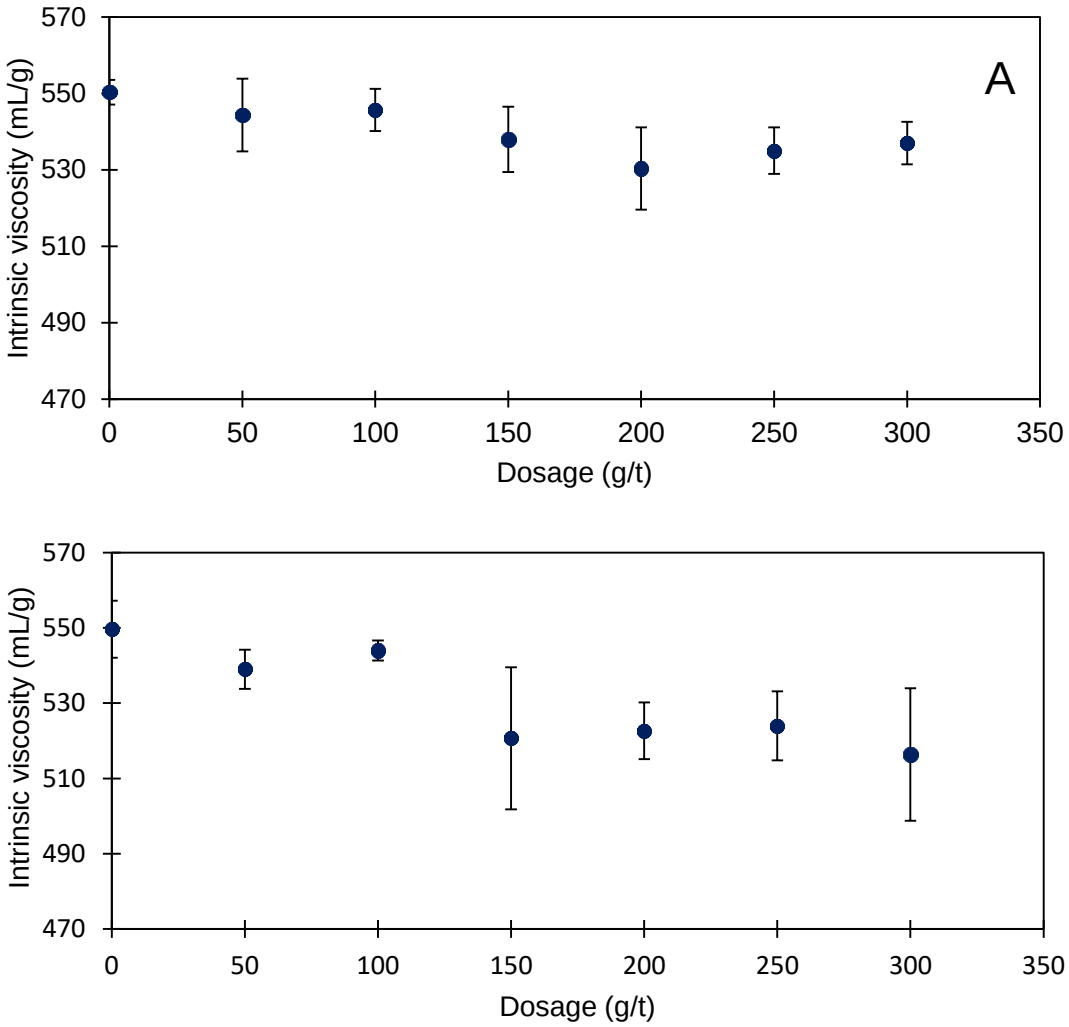


Figure 3.3: Effect of dosage of the NS 51179 enzyme on the intrinsic viscosity of the DWP at incubation times of 1 h (A) and 2 h (B)

The Ecopulp R formulation lowered the viscosity from 551 mL/g to 511 mL/g which was a significant reduction compared to the viscosity of the control sample. Lowering of the viscosity occurred through two stages as also observed by Liu *et al.* (2015). The 1 h incubation time was divided into two plateaus where they were separated by a sharp drop at 200 g/t dosage. This was because enzyme efficiency was optimal at 200 g/t. By further increasing the dosage no notable change was observed as enzyme inhibition started to affect the efficiency.

Similarly, the viscosity for an incubation time of 2 h was lowered from 555 mL/g to 506 mL/g, which correlates with an 8.8% decrease in viscosity when compared with the control sample. The 2 h incubation time also moved the sharp drop between the two plateaus to 150 g/t after which enzyme inhibition became less efficient. The difference in final viscosity obtained at the highest enzyme dosage was not significantly different for the two incubation times investigated, and for this reason, an incubation time of 1 h was chosen as the best incubation time to be used for lowering the intrinsic viscosity of the DWP.

Figure 3.3 shows that treatments with the NS 51179 formulation did not decrease the viscosity of the pulp to the same extent as with the Ecopulp R formulation, only achieving a reduction in viscosity of approximately 3.6% from 550 mL/g to 530 mL/g for an incubation time of 1 h. There was also no notable drop in viscosity as seen with both incubation times for Ecopulp R. The 2 h incubation time for NS 51179 did decrease pulp viscosity by 6.2% from 555 mL/g to 506 mL/g and this notable decrease occurred at 150 g/t after which enzyme inhibition became less efficient.

Ecopulp R performed better compared to the NS 51179 enzyme formulation; this is validated by Figure 3.1 as it shows that Ecopulp R released more sugars which related to higher activity. Therefore, with a higher activity, more pulp fibres could be reached and degraded; thus, lowering the viscosity.

3.3.3 Alkali solubility

The viscosity and the degraded cellulose content of pulp are closely related. The intrinsic viscosity is a measure of the molecular weight of the cellulose fibres. As the length of cellulose fibres is reduced, the viscosity decreases, and the content of short-chain cellulose molecules typically increases. The extent to which cellulose and hemicellulose were degraded by the enzyme treatment can be quantified by alkali solubility using the S10 and S18 tests. Degraded cellulose can be obtained by subtracting S18 from S10. The effect of enzyme dosage on the cellulose degradation at different incubation times is given in Figures Figure 3.4 and Figure 3.5, respectively. The vertical error bars for the degraded cellulose were obtained by using the errors from S10 and S18 data and adding them in quadrature (3.1).

$$\delta C = \sqrt{(\delta S10)^2 + (\delta S18)^2} \tag{3.1}$$

where δC is the uncertainty for degraded cellulose and $\delta S10$ and $\delta S18$ are the errors for S10 and S18, respectively.

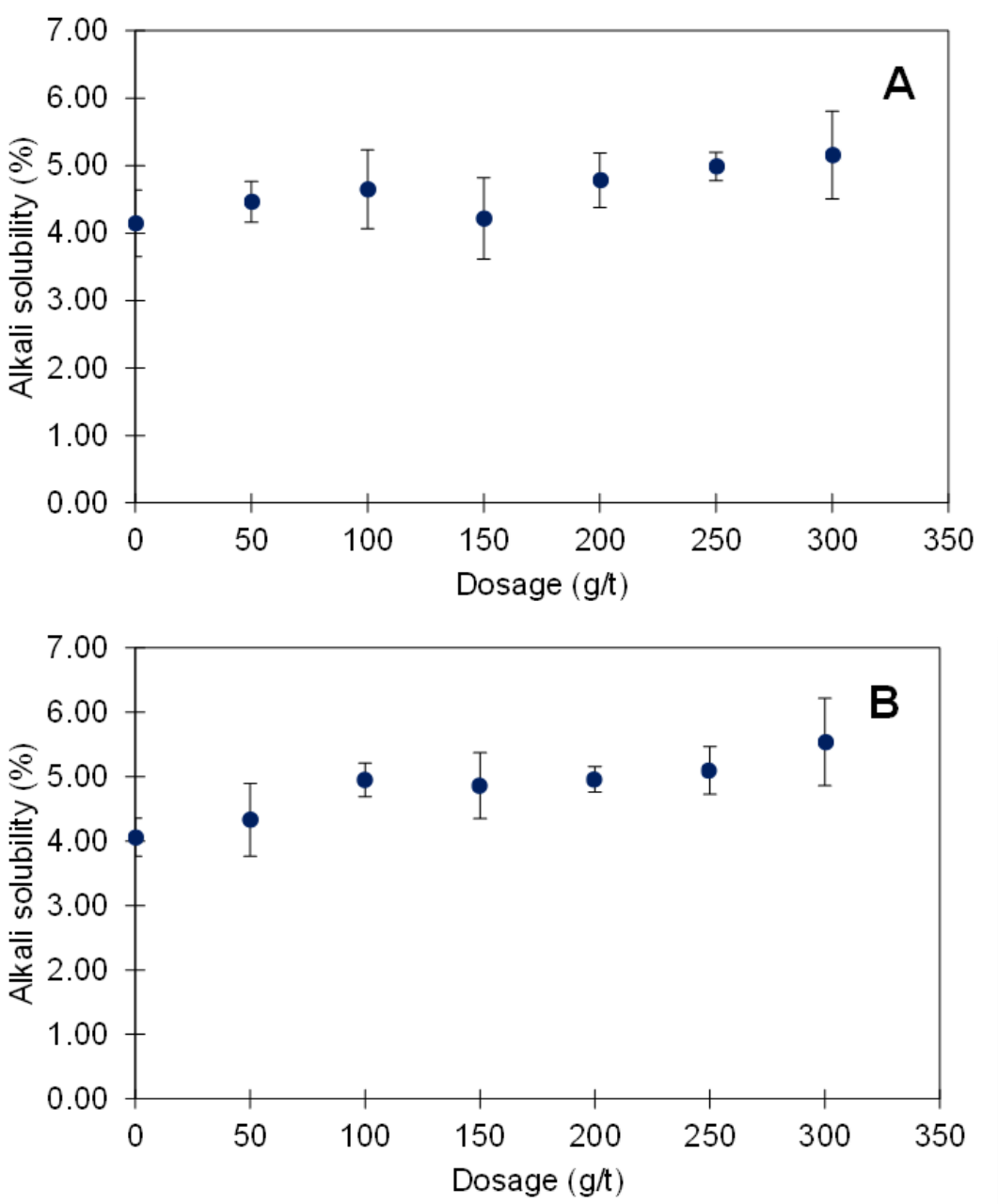


Figure 3.4: Effect of dosage of the Ecopulp R enzyme on the degraded cellulose of the DWP at incubation times of 1 h (A) and 2 h (B)

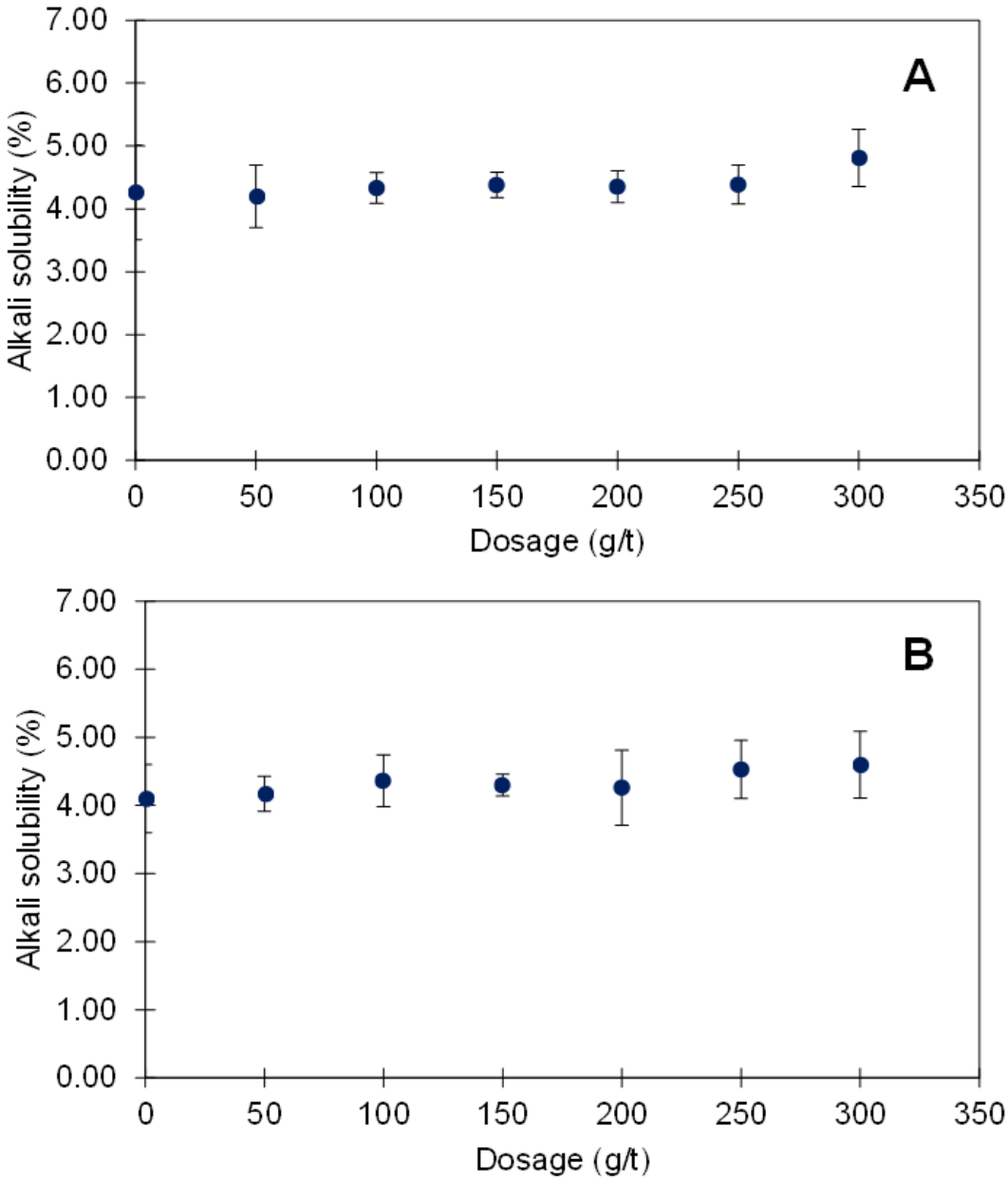


Figure 3.5: Effect of dosage of the NS 51179 enzyme on the degraded cellulose of the DWP at incubation times of 1 h (A) and 2 h (B)

Neither Ecopulp R nor NS 51179 enzyme formulations significantly increased the degraded cellulose content at any dosage at the 1 h incubation time. However, there was a slight increase in degraded cellulose for Ecopulp R at 300 g/t but no increase for the NS 51179 formulation at 2 h incubation time. Although there was a statistical increase in degraded cellulose at high enzyme dosages and at 2 h incubation time, this increase was not large enough to change the yield of the pulp after treatment. Figure 3.6 shows how the reduction in viscosity increased the degraded cellulose.

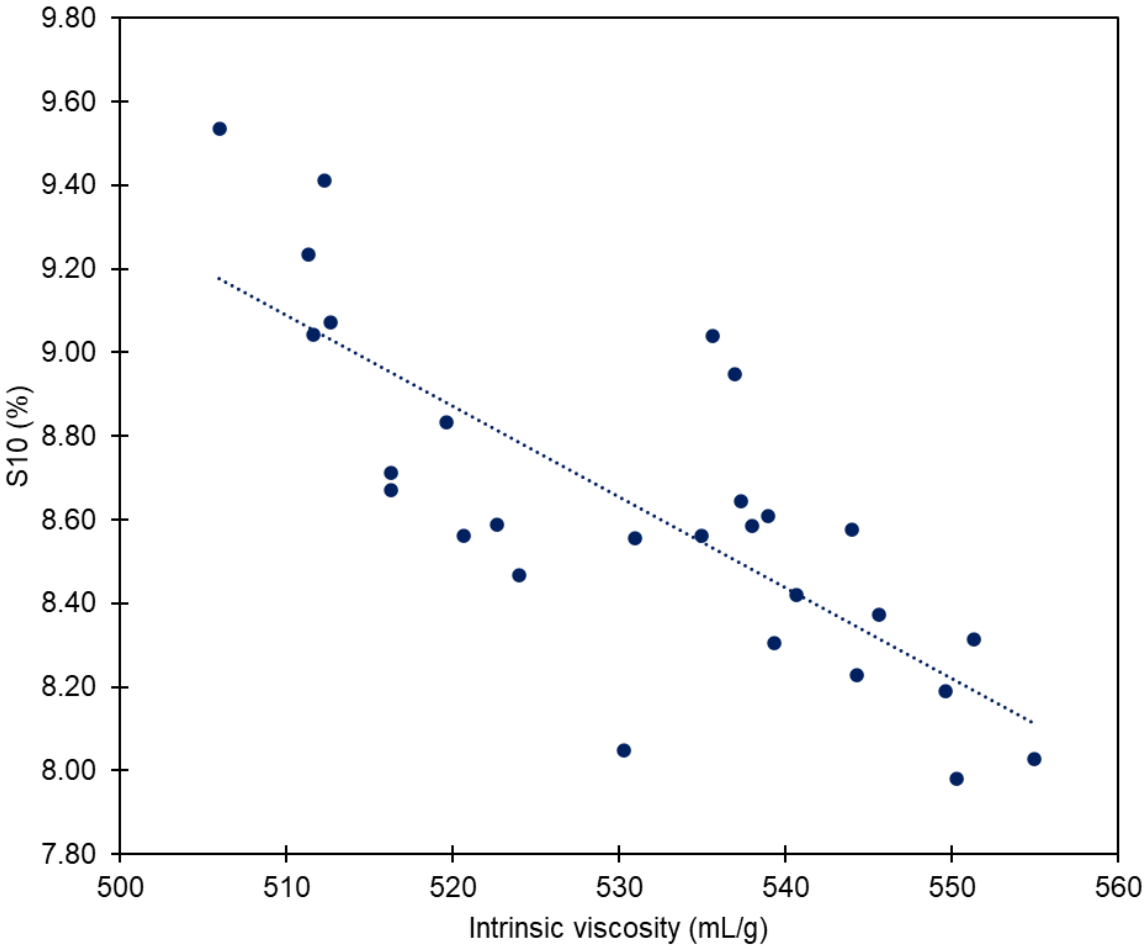


Figure 3.6: Effect of viscosity reduction on the increase of degraded cellulose content (R^2=0.6)

The increase in degraded cellulose was weakly related to the decrease in viscosity. This is attributed to a decrease in cellulose fibre length. While the correlation is weak, it does give an indication of how closely the variables were related but it could be influenced by outliers. The weak trend can be attributed to NS 51179 enzyme formulation not increasing the degraded cellulose content to the same extent as the Ecopulp R formulation. If the NS 51179 data is ignored the R^2 value increases to 0.77 indicating a much stronger correlation between the two variables. This shows that the increase in viscosity drop comes at a trade-off of increased degraded cellulose for Ecopulp R.

3.3.4 Quick reactivity results

High reactivity is an essential requirement in producing DWP (Wu *et al.*, 2015; Yang *et al.*, 2019). Quick reactivity testing was performed on several pulp samples and the amount of undissolved fibres was measured. The samples that were selected were the control pulp and the pulps that were treated with 300 g/t Ecopulp R and NS 51179 at 2 h incubation time. This was primarily done to determine if the enzyme formulations were significantly different under

extreme conditions. Figure 3.7 compares the undissolved fibre content obtained for each enzyme treatment to the control sample. The standard deviations of the data are shown by the vertical error bars.

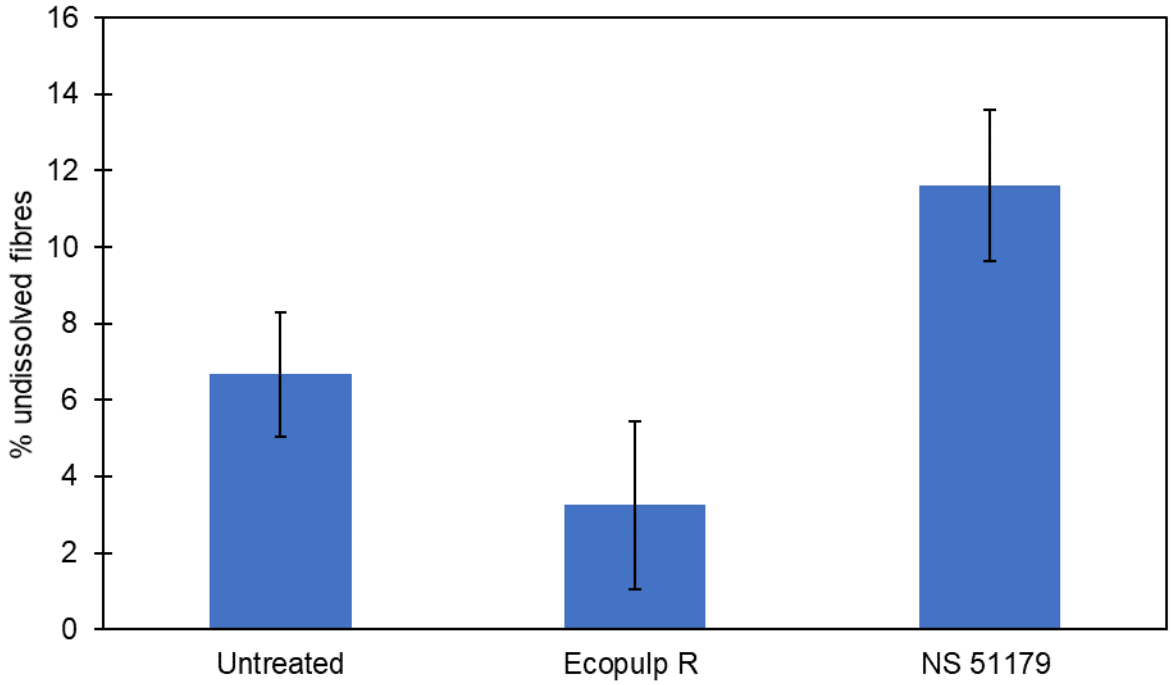


Figure 3.7: Comparison of reactivity as a percentage of undissolved fibre at an enzyme dosage of 300 g/t and 2 h incubation time

The Ecopulp R enzyme treatment had no significant effect on the reactivity of the pulp as seen by having a similar percentage of undissolved fibres as the untreated sample in Figure 3.7. The NS 51119 treatment, however, had a negative effect on pulp reactivity as the amount of undissolved fibres increased after treatment compared to the untreated control sample.

While Ecopulp R and NS 51179 EG formulations did have similar results for both viscosity and alkali solubility, it was in the reactivity results where there was a significant difference between them. This difference could potentially be due to the mechanism of how each of the formulations acted on the cellulose fibre. Ecopulp R formulation acts in such a way that viscosity is decreased without limiting chemical access to the cellulose fibre; however, NS 51179 appears to do the opposite. By decreasing the pulp's viscosity its structure is altered, thereby limiting chemical access. As such Ecopulp R is the better enzyme formulation to achieve the viscosity and reactivity adjustment required.

3.4 Conclusions and recommendations

Characterisation of the two enzyme formulations proved that both contained notable EG activity, as the main product released during the filter paper assay by both, was cellobiose. When fully bleached DWP was treated with these formulations, the EG action reduced the viscosity, with the highest drop in viscosity obtained with the Ecopulp R formulation. Treatment with Ecopulp R also resulted in a slightly higher degradation of the cellulose fibres compared to the NS 51179; and as expected, this was supported by a larger reduction in viscosity. However, the amount of undissolved fibres in pulp that was treated with Ecopulp R was significantly lower than that treated with NS 51179, thus indicating a higher pulp reactivity when comparing the two different formulations. Ecopulp R was, therefore, identified as the better enzyme formulation compared to NS 51179, as pulp treatment resulted in improved viscosity and unchanged reactivity. Only the Ecopulp R formulation was thus used in further experiments.

References

AB Enzymes. 2009. *Ecopulp R description and specifications*. Darmstadt: AB Enzymes.

Bajpai, P. 2018. Biermann's handbook of pulp and paper. 3rd ed. Vol. 1, *Raw material and pulp making*. Amsterdam: Elsevier.

Bodhlyera, O., Zewotir, T., Ramroop, S., & Chunilall, V. 2015. Analysis of the changes in chemical properties of dissolving pulp during the bleaching process using piecewise linear regression models. *Cellulose Chemistry and Technology*, 49(3-4):317-332.

Chu, D., Deng, H., Zhang, X., Zhang, J., & Bao, J. 2012. A simplified filter paper assay method of cellulase enzymes based on HPLC analysis. *Applied Biochemistry and Biotechnology*, 167(1):190-196. doi:10.1007/s12010-012-9673-0

Friebel, C., Bischof, R.H., Schild, G., Fackler, K., & Gebauer, I. 2019. Effects of caustic extraction on properties of viscose grade dissolving pulp. *Processes*, 7(3):122. doi:10.3390/pr7030122.

Hildén, L. & Johansson, G. 2004. Recent developments on cellulases and carbohydrate-binding modules with cellulose affinity. *Biotechnology Letters*, 26(22):1683-1693.

Ibarra, D., Köpcke, V., Larsson, P.T., Jääskeläinen, A.-S., & Ek, M. 2010. Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp. *Bioresource Technology*, 101(19):7416-7423

ISO. 1982. *ISO 692:1982: Pulps: determination of alkali solubility*.

ISO. 2010. *ISO 5351:2010: Pulps: determination of limiting viscosity number in cupri-ethylenediamine (CED) solution*.

Juhász, T., Szengyel, Z., Réczey, K., Siika-Aho, M., & Viikari, L. 2005. Characterization of cellulases and hemicellulases produced by Trichoderma reesei on various carbon sources. *Process Biochemistry*, 40(11):3519-3525.

Kumar, H. & Christopher, L.P. 2017. Recent trends and developments in dissolving pulp production and application. *Cellulose*, 24(6):2347-2365. doi:10.1007/s10570-017-1285-y

Kvarnlöf, N. 2007. *Activation of dissolving pulps prior to viscose preparation*. http://www.diva-portal.org/smash/get/diva2:5128/FULLTEXT01.pdf Date of access: 19 Nov. 2021.

Lin, X., Wu, Z., Zhang, C., Liu, S., & Nie, S. 2018. Enzymatic pulping of lignocellulosic biomass. *Industrial Crops and Products*, 120:16-24.

Liu, S., Wang, Q., Yang, G., Chen, J., Ni, Y., & Ji, X. 2015. Kinetics of viscosity decrease by cellulase treatment of bleached hardwood kraft-based dissolving pulp. *BioResources*, 10(2):2418-2424.

Lynd, L.R., Weimer, P.J., van Zyl, W.H., & Pretorius, I.S. 2002. Microbial cellulose utilization: fundamentals and biotechnology. *Microbiology and Molecular Biology Reviews*, 66(3):506-577.

Mongay, C. & Cerdà, V. 1974. A Britton-Robinson buffer of known ionic strength. *Annales de Chimie*, 64:409-412.

Quintana, E., Valls, C., Barneto, A.G., Vidal, T., Ariza, J., & Roncero, M.B. 2015. Studying the effects of laccase treatment in a softwood dissolving pulp: cellulose reactivity and crystallinity. *Carbohydrate Polymers*, 119:53-61.

Reichel, C. 2020. *Modification of dissolving wood pulp using endoglucanase*. Potchefstroom: University of North-West. (Dissertation – MEng (Chem)).

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., … Schottenberger, H. 2013. Novel concepts of dissolving pulp production. *Cellulose*, 20(4):1547-1561.

TAPPI. 2000. *Alkali solubility of pulp, TAPPI T235 om-60*. Atlanta: TAPPI Press.

TAPPI. 2004. *Viscosity of pulp (capillary viscometer method)*. Atlanta: TAPPI Press.

Wang, Q., Fu, X., Liu, S., Ji, X., Wang, Y., He, H., Yang, G., & Chen, J. 2020. Understanding the effect of depth refining on upgrading of dissolving pulp during cellulase treatment. *Industrial Crops and Products*, 144:112032.

Wu, C., Zhou, S., Li, R., Wang, D., & Zhao, C. 2015. Reactivity improvement of bamboo dissolving pulp by xylanase modification. *BioResources*, 10(3):4970-4977.

Yang, S., Wen, Y., Zhang, H., Li, J., & Ni, Y. 2018. Enhancing the Fock reactivity of dissolving pulp by the combined prerefining and poly dimethyl diallyl ammonium chloride-assisted cellulase treatment. *Bioresource Technology*, 260:135-140.

Yang, S., Yang, B., Duan, C., Fuller, D.A., Wang, X., Chowdhury, S.P., … Ni, Y. 2019. Applications of enzymatic technologies to the production of high-quality dissolving pulp: a review. *Bioresource Technology*, 281:440-448. doi:10.1016/j.biortech.2019.02.132

Yang, T., Guo, Y., Gao, N., Li, X., & Zhao, J. 2020. Modification of a cellulase system by engineering Penicillium oxalicum to produce cellulose nanocrystal. *Carbohydrate Polymers*, 234:115862.

Zhang, P., Chen, M., Duan, Y., Huang, R., Su, R., Qi, W., Thielemans, W., & He, Z. 2018. Real-time adsorption of exo- and endoglucanases on cellulose: effect of pH, temperature, and inhibitors. *Langmuir*, 34(45):13514–13522. doi:10.1021/acs.langmuir.8b02260

Chapter 4: A combination of enzymatic and kneading treatments of dissolving wood pulp for viscose production

4.1 Introduction

Many studies have investigated various methods to improve the quality of DWP (Kumar & Christopher, 2017; Yang *et al.*, 2019). The methods include chemical treatments (Ambjörnsson *et al.*, 2014; Wang *et al.*, 2015), enzyme treatments (Duan *et al.*, 2016b; Lin *et al.*, 2018), mechanical refining (Gao *et al.*, 2015; Liu *et al.*, 2020; Tian *et al.*, 2014), and a combination of these treatments. Enzymes are of particular interest as they can be used as green alternatives to improve pulp quality (Li, Zhang, *et al.*, 2018).

Enzymatic hydrolysis of cellulose fibres can, however, be limited by the accessibility of the enzyme to the fibres (Gao *et al.*, 2015; Leu & Zhu, 2013). By mechanically activating the pulp fibres before enzyme treatment, the efficiency of the enzyme can be greatly improved (Wang *et al.*, 2020). Kneading has been largely overlooked as a mechanical activation technique. Previous research involving the kneading of DWP was aimed at facilitating the mixing of enzymes to better distribute them through the pulp (Engström *et al.*, 2006; Ibarra *et al.*, 2009). By using a combination of kneading and enzyme treatments it is hypothesised that the quality of the DWP can be improved.

DWP is used as the precursor in the viscose process (Spörl *et al*., 2016). The DWP is first steeped in an 18 wt% sodium hydroxide (NaOH) solution causing the pulp fibres to swell. It is then known as alkali cellulose, which is highly reactive and used as an intermediate for cellulose-based derivatives (Ciolacu & Popa, 2010; Gondhalekar *et al*., 2019; Kotek, 2007). The alkali cellulose is pressed to remove excess NaOH and then shredded to increase the surface area for subsequent chemical reactions (Kotek, 2007). The alkali cellulose is then aged to reduce the degree of polymerisation (Kotek, 2007; Miao et al., 2014). This process is also known as mercerisation. The aged pulp is then allowed to react with carbon disulphide (CS_2) in a xanthation reaction, followed by mixing with dilute NaOH to form viscose (Kotek, 2007).

Viscose fibre is an important regenerated cellulose fibre that can be manufactured from DWP (Kumar & Christopher, 2017; Xu *et al*., 2021). Increased interest in viscose fibre has been seen in the chemical and textile industries because of its biodegradable properties (Xu *et al.*, 2021).

4.2 Materials and methods

Before treatment, the maximum number of required kneading passes was determined, since previous internal studies at Sappi indicated that excessive kneading could alter the fibre structure, thereby limiting dispersion in the steeping of DWP in the viscose process. Different treatment regimens were conducted and compared to the control (no treatments). These regimes included enzyme treatment only, kneading only, enzyme treatment followed by kneading, and kneading followed by enzyme treatment.

All resulting pulps were tested for viscosity, alkali solubility and reactivity (Sandham, 2021:40-41).

4.2.1 Kneading treatments

The kneading treatments were conducted using an industrial screw feed kneader. High pulp consistency (>30%) was used to allow sufficient fibre-to-fibre friction. The final temperature of the pulp exiting the kneader was measured as 75°C. If multiple passes through the kneader were required, the pulp was first mixed after the total sample passed through the kneader, then kneaded again for the next pass.

4.2.2 Enzymatic treatments

Enzyme treatments were carried out on fully bleached pulp (H-stage) obtained from Sappi Saiccor mill, KwaZulu-Natal, South Africa. The pulp was collected at a consistency of 10%, after which it was filter-pressed to high consistency filter cakes (>30%) to preserve the pulp between treatments. Consistency refers to the amount of solid fibre in a slurry. The pulp was sent to the Sappi Technology Centre in Pretoria, Gauteng, South Africa for the enzyme treatments.

The consistency of the pulp was determined prior to treatment and the pulp was added into the pilot plant reactor using a dry mass of 3 kg pulp. DI water was added into the reactor to reduce the consistency to 10%. The reactor was equipped with a pH probe and the pH of the slurry was adjusted from 8 to a value of 6 by adding 5 mL of a 98% analytical grade sulfuric acid solution (H_2SO_4) before enzyme treatments. The pilot plant reactor operated as a jacketed reactor and the temperature within was maintained at 60°C. This was done through feedback control. A control unit would receive the temperature input from a thermocouple sensor in the reactor and the unit would change the flow rate of boiling water to the jacket of the reactor by manipulating the inlet valve. Once the required consistency, temperature and pH were reached, Ecopulp R enzyme formulation (AB Enzymes-Ecopulp R, 2009) was added in a dosage of 300 g/t based on dry pulp mass. The pulp slurry was continuously mixed at an initial

speed of 2 Hz for the first 5 min after which the mixing speed was lowered to 1 Hz for the remainder of the 2 h treatment time.

After 2 h, the pH was increased to 10 using sodium hydroxide (NaOH) for 30 min to denature the enzyme. The pulp was then rinsed using DI water and placed into a Rousselet Robatel (France) centrifuge. The pulp was rinsed a further two times and the water removed. The final pulp consistency was measured as 35% after centrifuge dewatering.

4.2.3 Handsheet formation and sample preparation

After all enzymatic and kneading treatments were completed, the pulp was preserved as handsheets. This was done to mimic the process at Saiccor mill, where sheets are sold to customers after drying. The handsheets were made by weighing approximately 80 g (dry basis) of pulp and adding it to the custom-built handsheet former. Water was added to evenly disperse the pulp fibres and then drained to form a sheet. The sheet was pressed to remove most of the water and placed into an oven at 80°C for 2 h to dry. After the sheet was dried in the oven, it was further dried for 24 h in a ventilated room. The final consistency of the sheet was approximately 90%. The sheets were then shredded by hand to roughly 1 cm x 2 cm pieces.

4.2.4 Steeping of dissolving wood pulp

Steeping is a crucial step in the production of viscose as it enables the pulp fibres to swell, thereby promoting the accessibility of chemical reagents to the cellulose fibres so that reactions can take place (Gondhalekar *et al.*, 2019). Steeping was performed using 18.5 wt% sodium hydroxide (NaOH). The mass of the NaOH solution used was determined so that a final slurry consistency of 5% could be reached when the pulp was added. The 18.5 wt% NaOH solution was preheated in a 5 L vessel at 53°C (±1°C) for 30 min. The pulp was then added and mixed within the reaction vessel for a further 30 min. After steeping, the pulp was removed from the reaction vessel and placed in a hydraulic press to remove excess NaOH and to reach the correct percentage range of cellulose in steeped pulp (alkali cellulose) percentage (%CiA). The alkali cellulose was then removed from the press and placed into a shredder to increase the surface area. This step was important for mercerisation.

4.2.5 Ageing kinetics of alkali cellulose

Between 45 g and 50 g portions of the shredded alkali cellulose were weighed and placed into 500 mL glass containers. The sealed containers were placed in a preheated oven at 53°C to age. Six glass containers were used so that a container with an alkali cellulose sample could be removed from the oven for analysis every hour. The samples were neutralised with 400 mL

of a 10 wt% acetic acid solution and 400 mL of a 10 wt% sodium bicarbonate solution, followed by washing with demineralised water so that the final pH of the filter cake was 7. This system acted like a buffer solution thereby reaching a final pH of 7. The acetic acid solution was prepared from 99% glacial acetic acid and the sodium bicarbonate solution was prepared from 99% sodium bicarbonate powder. The pulp sample was then filtered into filter cakes and dried in an oven at 70°C for 8 h. The viscosity of each pulp sample was then measured using the CED viscosity test (ISO, 2010; TAPPI, 2004). The results for these samples were used to generate a curve to determine the correct ageing time for viscose. The ageing times of the pulps were important as it reduced the pulp viscosity before xanthation.

4.2.6 Determination of chemical charges for viscose making

The chemical charges used for viscose making were determined using the %CiA and percentage soda in alkali cellulose (%SiA). The %SiA was determined by using 4 g ± 0.005 g of shredded alkali cellulose and adding 50 mL demineralised water, followed by the addition of 1 N hydrochloric acid (HCl). The solution was then titrated with 1 N NaOH. The percentage SiA was calculated using Equation (4.1).

$$\%SiA = \frac{(20 - T) \times 4}{W} \tag{4.1}$$

where *T* is the titration volume of NaOH used and *W* is the mass of alkali cellulose taken

A volume of 5 mL of 1 N HCl was added to the titrated sample, followed by filtration, and washing. The resulting filter cake was then dried in an oven at 125°C for 2 h. The %CiA was calculated using Equation (4.2).

$$\%CiA = \frac{Weight\ of\ filter\ cake\ \times 100}{W} \tag{4.2}$$

4.2.7 Bulk density of alkali cellulose

Bulk density of the alkali cellulose was measured to ensure homogenous chemical accessibility and uniform xanthation. The bulk density was measured by adding alkali cellulose up to the 700 mL mark of a large volumetric cylinder and then measuring the mass. Bulk density was then calculated using Equation (4.3).

$$Bulk\ density = \frac{Alkalised\ cellulose\ mass\ \times 1000}{Settled\ volume} \tag{4.3}$$

4.2.8 Viscose production

After the alkali cellulose was aged to reduce the viscosity through oxidation, it could be used for xanthation. An aliquot of 250 g of aged, alkali cellulose was weighed and placed in a bottle and sealed. The air was removed from the bottle using a vacuum source and carbon disulphide (CS_2) was added to the alkali cellulose. The amount of CS_2 added was determined from the calculated %CiA. The required CS_2 mass percentage was 33% cellulose basis for the normal viscose recipe and 28% cellulose basis for the reduced chemical recipe (Equation (4.4) and (4.5).

$$W_c = \%CiA \times W_A \tag{4.4}$$

$$W_{CS_2} = M \times W_C \tag{4.5}$$

where W_C is the mass of cellulose in alkali cellulose, W_A is *the mass of alkali cellulose mercerised,* W_{CS2} is *the mass of* CS_2 *required, M* is *the required mass percentage of* CS_2 *on a cellulose basis*

After xanthation was completed, 18.5 wt% NaOH was added to the xanthate crumbs based on the %SiA and the target percentage soda in viscose (%SiV). The xanthate slurry was mixed for 5.5 h at 18°C to ensure adequate ripening.

4.2.9 Analysis of viscose solution

4.2.9.1 Determination of ripening index

The ripening index indicates the coagulability of the viscose solution. It was determined by measuring the quantity of 10 wt% ammonium chloride (NH_4Cl) required to cause coagulation of 20 g of viscose solution diluted in 30 mL of water. The NH_4Cl solution was prepared from 99.8% analytical grade ammonium chloride powder. This procedure was based on the method described by Hottenroth (1915).

4.2.9.2 Determination of filterability index

The filterability (K_w) of the viscose solution was measured as described by Treiber *et al.* (1962) using a filter apparatus. The procedure involved filling a steel cylinder of a known area with viscose solution and passing compressed air at 207 kPa through the cylinder. The cylinder contained filters of varying mesh sizes. The mesh sizes were swansdown filter cloth, Calico filter cloth, Whatman No.54 filter paper, stainless steel gauge 24 mesh 29 SWG, and perforated plate with 45 1/8-inch holes. The filterability was then calculated using Equation (4.6) (Gondhalekar *et al.*, 2019).

$$K_w = \frac{2 \times [\frac{t_2}{m_2} - \frac{t_1}{m_1}] \times 10^5}{t_2 - t_1} \quad (4.6)$$

where t_1 and t_2 are the filtration times in minutes (20 min and 40 min, respectively) and m_1 and m_2 are the masses of solution in grams filtered at 20 min and 40 min, respectively

The filterability index was then adjusted for viscosity. The corrected filterability index (cK_W) was obtained by using Equation (4.7) (Gondhalekar *et al.*, 2019).

$$cK_W = K_W \times (1 - \frac{\eta - 55}{100}) \quad (4.7)$$

where η is the ball fall time in seconds

The ball fall time was obtained by dropping a small iron ball of known mass into a solution of ripened viscose and measuring the time it took to travel a set distance.

4.3 Results and discussions

4.3.1 Determination of number of passes for kneading

Before kneading and enzymatic treatments on DWP were conducted, the number of required passes was determined. Previous internal studies done at Sappi found that excess kneading could alter the fibre structure, thereby limiting dispersion in the steeping of DWP in the viscose process. Thus, the number of passes was selected to be the maximum without limiting dispersion.

During the first pass in the kneader, the DWP dissolved well in the NaOH solution, and no notable lumps were detected (Figure 4.1).

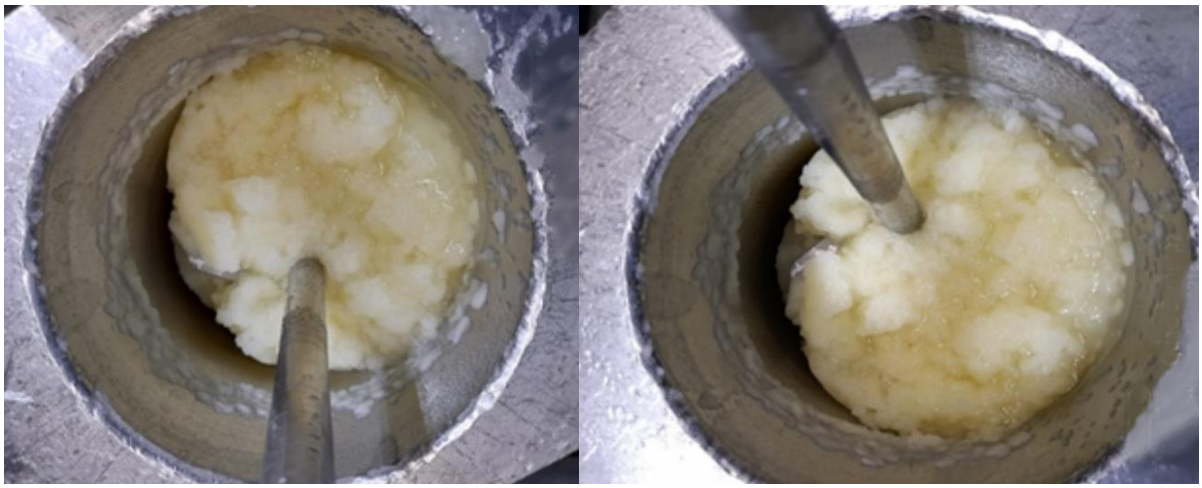


Figure 4.1: Dispersion of DWP in NaOH after the first pass in the kneader

During the second pass in the kneader, the pulp dispersed well; however, some lumps of undissolved fibre were detected (Figure 4.2). Two passes were thus found to be the maximum number of passes in the kneader as any further treatments would increase the number of undissolved fibres.

Figure 4.2: Undissolved lumps of DWP after steeping and two passes in the kneader

4.3.2 Intrinsic viscosity of dissolving wood pulp

Viscosity is an important parameter especially for viscose production as it relates to the degree of polymerisation (Sixta, 2006). The degree of polymerisation affects the processability in the production of viscose (Ibarra *et al.*, 2010). The untreated pulp had an intrinsic viscosity of 530 mL/g (Figure 4.3) and was used as the reference sample for all analyses. The standard deviations of the data are represented by the vertical error bars.

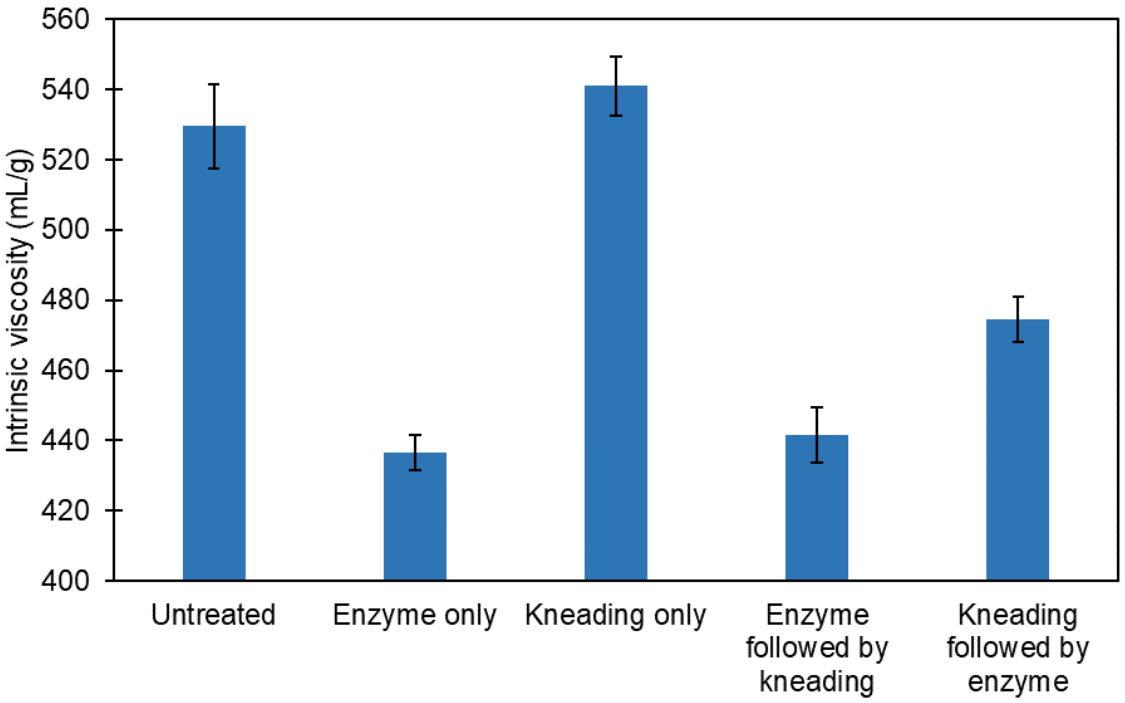


Figure 4.3: Intrinsic viscosity of untreated pulp and different combinations of enzyme and kneading treatments

Both treatments with the enzyme only and enzyme followed by kneading resulted in pulp with significantly lower viscosities (437 mL/g and 442 mL/g, respectively), compared to the control. While there was no significant difference between the two primary enzyme treatments, there was a large difference compared to the control. Kneading only did not have a significant effect on the viscosity (540 mL/g). However, the kneading followed by enzyme treatment did significantly decrease the viscosity to 475 mL/g, but not to the same extent as the two primary enzyme treatments. These results indicated that kneading was not effective at controlling viscosity. This was most likely due to the harsh mechanical treatment resulting in compression of the pulp fibres that decreased the available surface area for the enzyme to act on.

4.3.3 Alkali solubility results

The viscosity of the pulp and the amount of degraded cellulose content are closely related. The intrinsic viscosity is a measure of the molecular weight of the cellulose fibres (Ahn *et al.*, 2019), and as the cellulose lengths are reduced so is the viscosity. As a result, the amount of short-chain cellulose typically increases with a decrease in viscosity (Cao & Tan, 2006). The amount of degraded cellulose is obtained by subtracting S18 from S10. The degraded cellulose content of the various treatments is shown in Figure 4.4. The vertical error bars are obtained from (3.1).

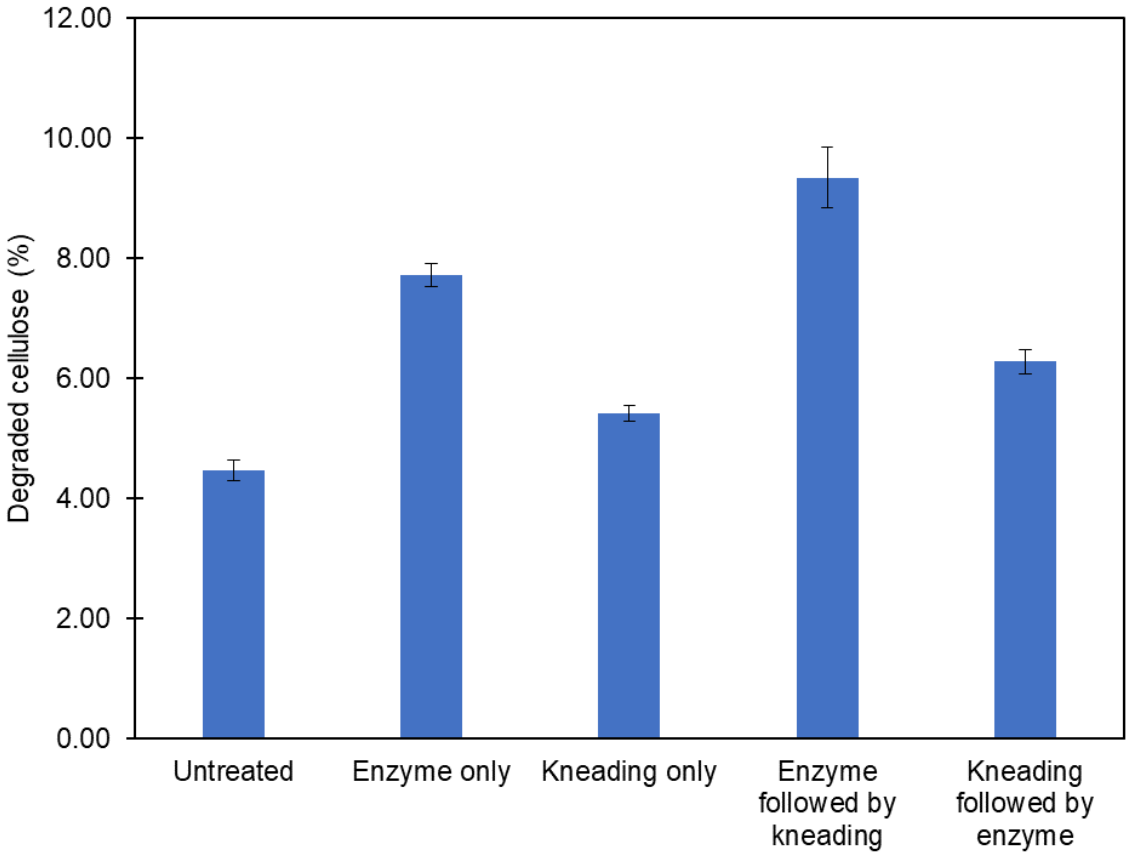


Figure 4.4: Degraded cellulose content of untreated pulp and different combinations of enzyme and kneading treatments

Both the enzyme only and enzyme followed by kneading treatments had significantly higher degraded cellulose content (7.7% and 9.3% respectively) compared to the untreated sample (4.5%). Kneading only and kneading followed by enzyme treatments also had significantly higher degraded cellulose content (5.5% and 6.3% respectively) compared to the control, although not as significant as the primary enzyme treatments. This trend is validated by Figure 4.3 as the primary enzyme treatments had the highest viscosity drop as did kneading followed by enzyme treatment. However, the kneading only treatment did not reduce the viscosity but increased the degraded cellulose content. This can be attributed to the harsh nature of the mechanical treatment.

4.3.5 Quick reactivity results

Reactivity is one of the most crucial parameters of DWP (Wu *et al.*, 2015; Yang *et al.*, 2019). The undissolved fibre percentage is shown in Figure 4.5 which gives an indication of the pulp's reactivity. The standard deviation is shown by the vertical error bars.

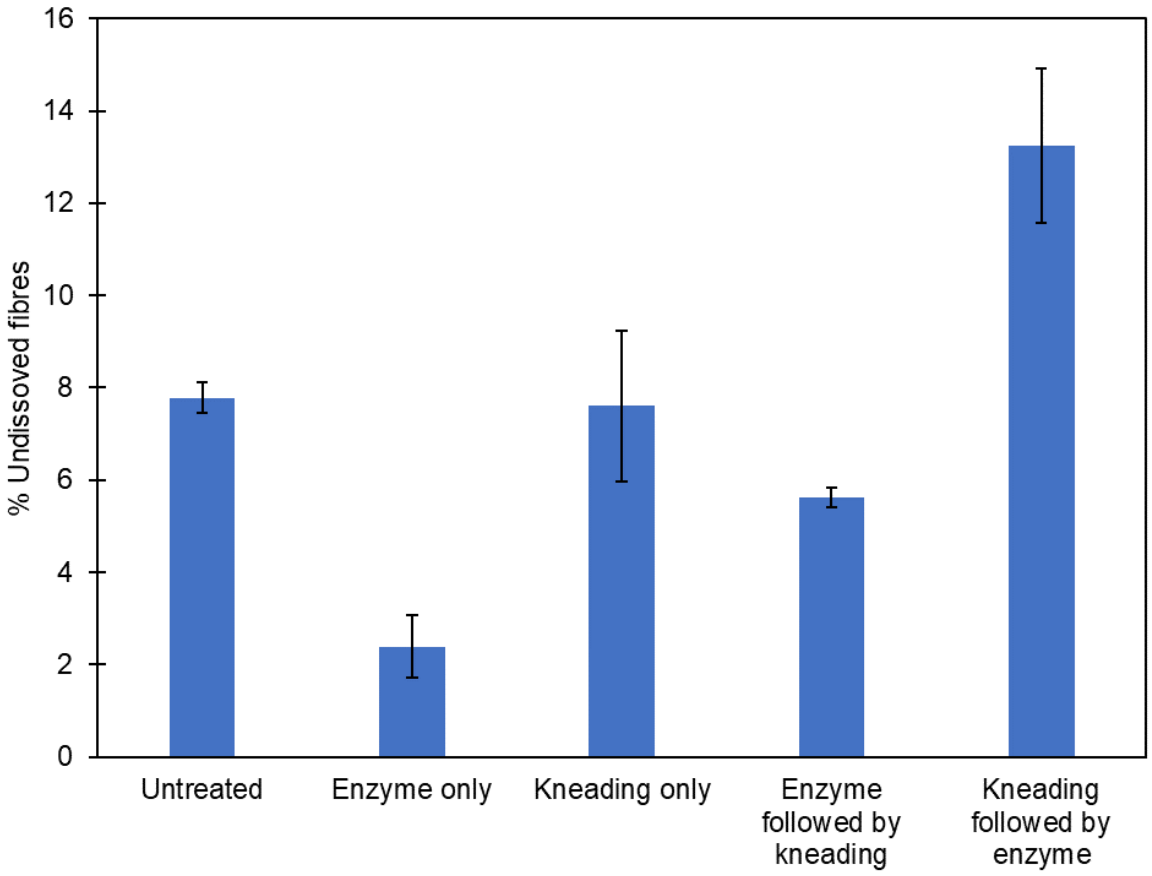


Figure 4.5: Quick reactivity of untreated pulp and different combinations of enzyme and kneading treatments

The enzyme only treatment was the most effective in significantly improving the pulp reactivity by decreasing the undissolved fibre content to 2.4% compared to 7.8% for the untreated sample (Figure 4.5). Kneading only did not have any significant effect on the reactivity (7.6%), although the variability increased. Kneading followed by enzyme treatment performed the worst with an undissolved fibre content of 13.2%. Enzyme treatment followed by kneading did have a lower undissolved fibre content (5.6%) compared to the control.

The primary reason why kneading seems to lower the reactivity of the pulp, is due to the harsh mechanical action. Kneading compresses the fibre that reduces the accessibility of the fibre to both the enzyme as well as the chemicals used in the reactivity testing. Enzymes have shown to improve reactivity which is in line with this data (Duan *et al*., 2016b; Lin *et al*., 2018).

4.3.6 Ageing kinetics for alkali cellulose

In the manufacturing of viscose, viscosity is an important factor as it allows the viscose dope to be processed (Javaid *et al*., 2014). The viscosity is directly correlated with the degree of polymerisation (DP), which is an important variable for viscose (Javaid *et al*., 2014). The

average DP during the steeping ageing process is reduced to about 350 (Coley, 1953). Sappi reduces their DP to about 300, which is in line with what their customers require. A DP of 300 correlates with a viscosity of 240 mL/g. Therefore, an ageing curve was constructed by measuring the viscosity at different ageing times. From this curve, the ageing time required to reduce the viscosity of the alkali cellulose to 240 mL/g could be determined.

The ageing curve of the untreated sample is shown in Figure 4.6. The ageing time required to achieve the target viscosity was 4 h and 30 min. This value corresponded to the typical ageing time that Sappi achieves at Saiccor mill.

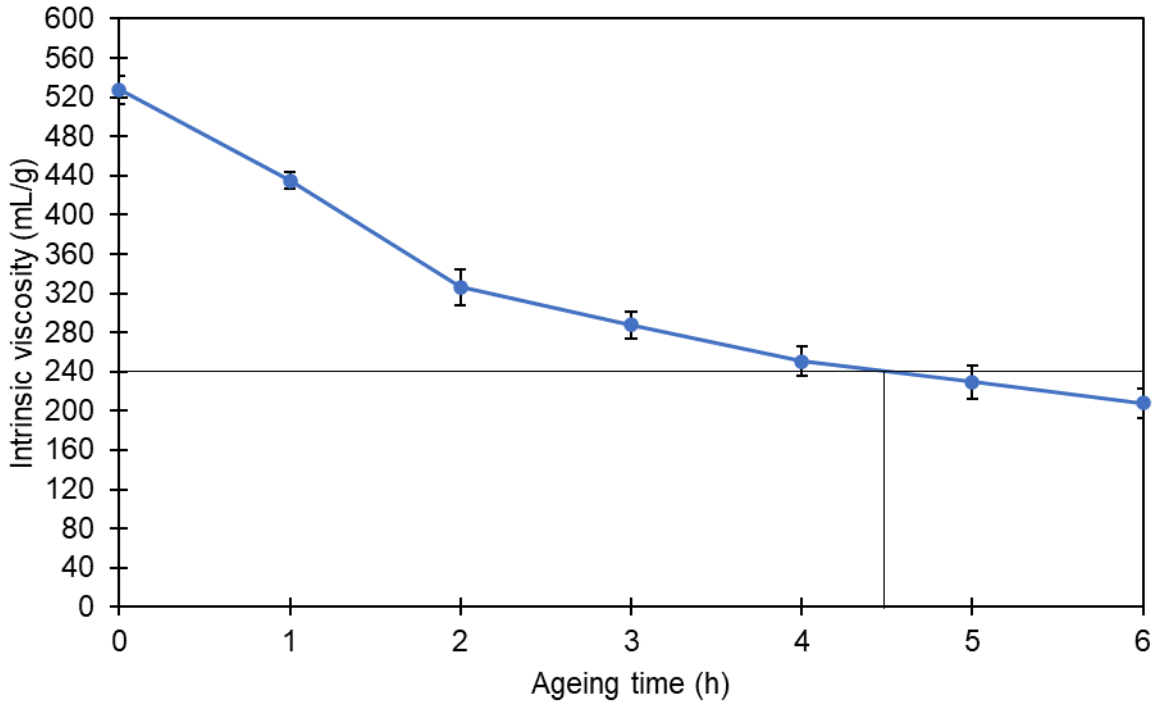


Figure 4.6: Ageing curve for untreated DWP used to determine the ageing time to reduce the alkali cellulose intrinsic viscosity to 240 g/L

The ageing times for the other treatments were obtained in a similar manner as shown in Figure 4.6. Table 4.1 summarises the ageing times obtained for these treatments.

Table 4.1: Required ageing times for different samples in the viscose process

Sample	Ageing time
Untreated	4h30min
Enzyme treatment	3h40min
Kneading treatment	3h50min
Enzyme followed by kneading treatment	3h00min
Kneading followed by enzyme treatment	3h45min

The enzyme-treated pulp required a shorter ageing time of 3 h and 40 min, compared to the untreated sample (Table 4.1). This was expected since the enzyme-treated sample had a higher reactivity compared to the untreated pulp (Figure 4.5).

The pulp treated with kneading also had a lower ageing time (3 h and 50 min) compared to the untreated sample (Table 4.1). This was unexpected as the reactivity was similar to that of the untreated pulp. It was, therefore, possible that the mechanical action assisted with the absorption of the chemicals during the steeping and ageing processes.

Enzyme treatment followed by kneading resulted in a reduced ageing time (3 h) (Table 4.1). This combination of treatments, however, resulted in the presence of significant amounts of undispersed fibres after steeping. The excessive amount of undispersed fibres resulted in too little available pulp for viscose; and for this reason, pulp treated with enzyme followed by kneading was not tested for viscose application. This is an important observation as the enzyme treatment followed by kneading resulted in improved reactivity compared to the control (Figure 4.5). Many studies similarly reported improved reactivity when pulps were treated with enzymes (Engström *et al*., 2006; Wang *et al*., 2020; Yang *et al*., 2018; 2019). However, even with improved reactivity, the sample was not of sufficient quality for viscose production due to ineffective dispersion during steeping. As such, reactivity testing should only be an indication of a chemical reduction in the viscose process. For accurate measurements, the complete viscose process should be used, since pulps could have improved reactivity, but steeping might yield a high amount of undissolved fibres leading to significant yield losses.

Kneading followed by enzyme treatment did have a lower ageing time of 3 h and 45 min compared to the untreated sample (Table 4.1).

4.3.7 Degree of polymerisation of alkali cellulose after ageing

The DP of the samples after ageing was obtained through a correlation with previous internal experiments conducted by Sappi. The DP values shown in Figure 4.7 represent the aged, alkali cellulose used to make viscose. The standard deviations of the samples are given by the corresponding vertical error bars.

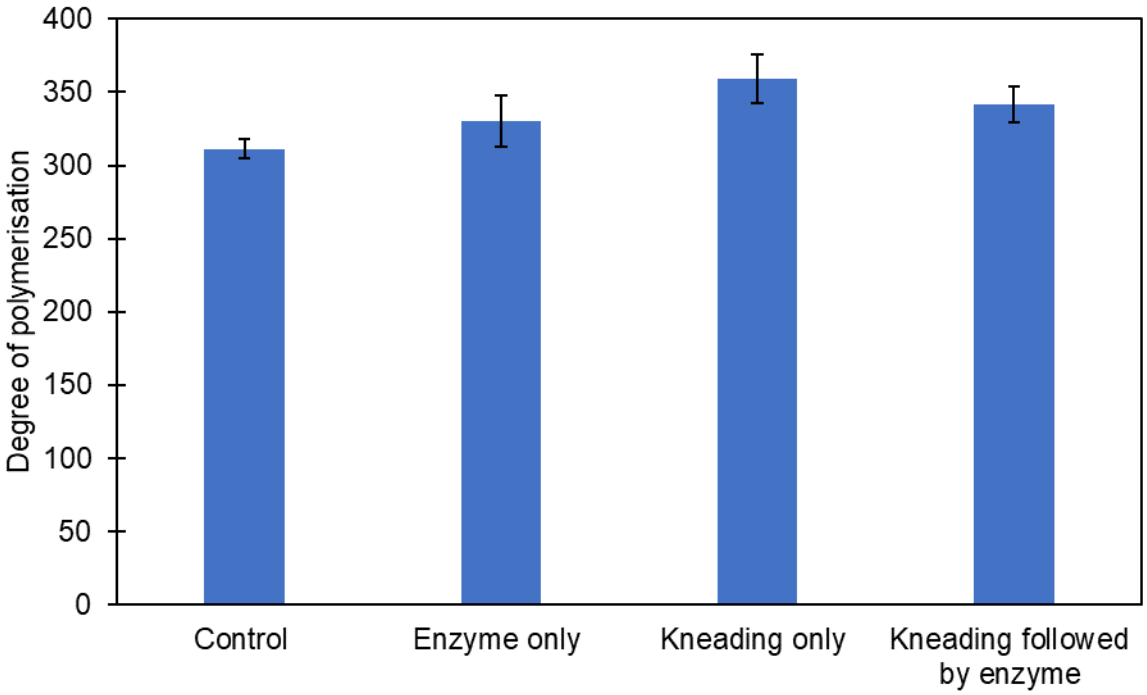


Figure 4.7: Degree of polymerisation of different samples after ageing

The DP illustrates that the pulp has aged appropriately and that the ageing curves were effective in determining the correct ageing time. Although there were some variances among the samples, they were all within the specifications used by Sappi.

4.3.8 Bulk density of alkali cellulose

Bulk density of the pulp is used as an indication of good and homogenous chemical accessibility of the pulp and that uniform xanthation will occur. A typical range for Sappi pulps is from 130 g/L to 165 g/L. If the bulk density is too high, it could lead to poor physical accessibility for chemical reagents during xanthation. The bulk densities for the various samples are shown in Figure 4.8. The vertical error bars are the standard deviations of the samples.

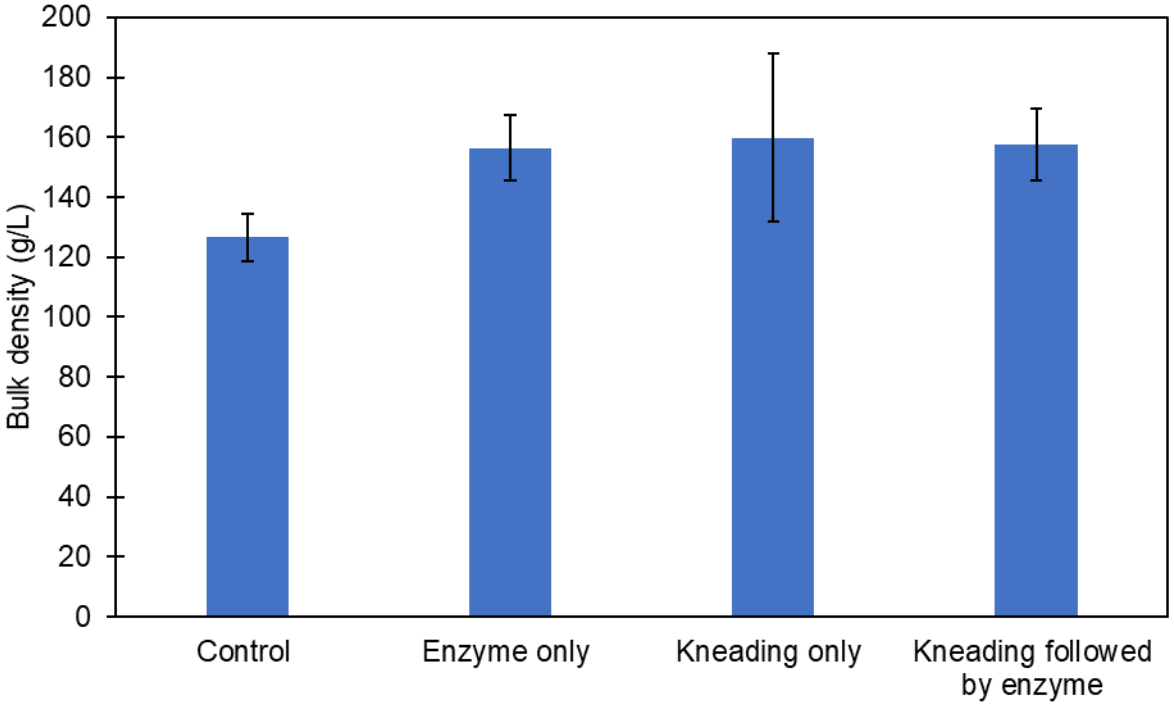


Figure 4.8: Bulk densities of various alkali cellulose samples after ageing

The control sample performed as expected with a bulk density of 127 g/L, which was in line with typical Sappi pulps (Figure 4.8). The bulk densities of the three treated samples were slightly higher than the control, but these differences were not significant, and the bulk densities were still within specifications.

4.3.9 Hottenroth ripening index

The Hottenroth ripening index for the different samples did not show any significant changes between the samples (Figure 4.9). All the samples displayed a high degree of variance; however, all treated samples were comparable to the control, indicating that treatments did not change the coagulability of the viscose solution. The Hottenroth values obtained were also similar to those found in the literature (Gondhalekar *et al*., 2019).

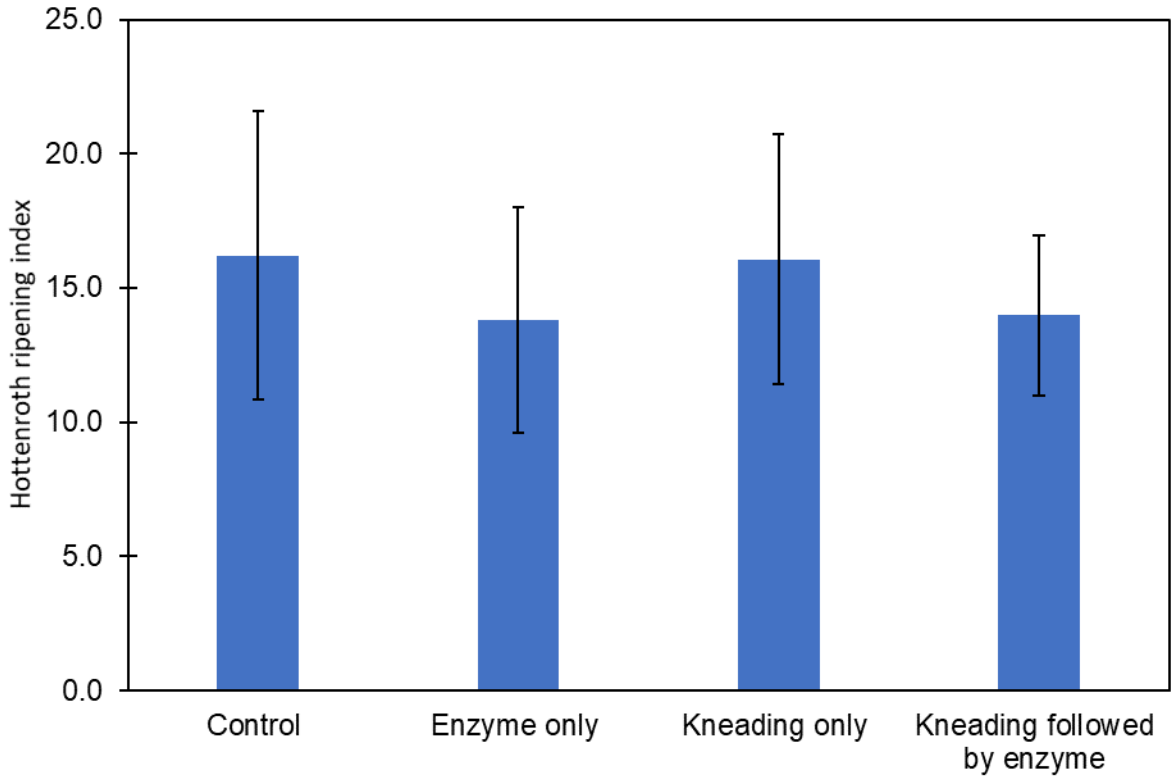


Figure 4.9: Hottenroth ripening index of various viscose samples after ripening

4.3.10 Filterability of viscose solution

The filterability of the viscose solution was highly variable when compared to the control (Figure 4.10), and thus no significant differences between the treated samples and the control could be observed. This indicated that the treatments did not impact on the quality of viscose. However, from a reliability point, treatments made the viscose solution too unpredictable and variable. Thus, the treatments of the DWP were not effective in producing a viscose of better quality. Due to the normal chemical recipe for viscose not being effective, reducing the chemicals would only make the results worse.

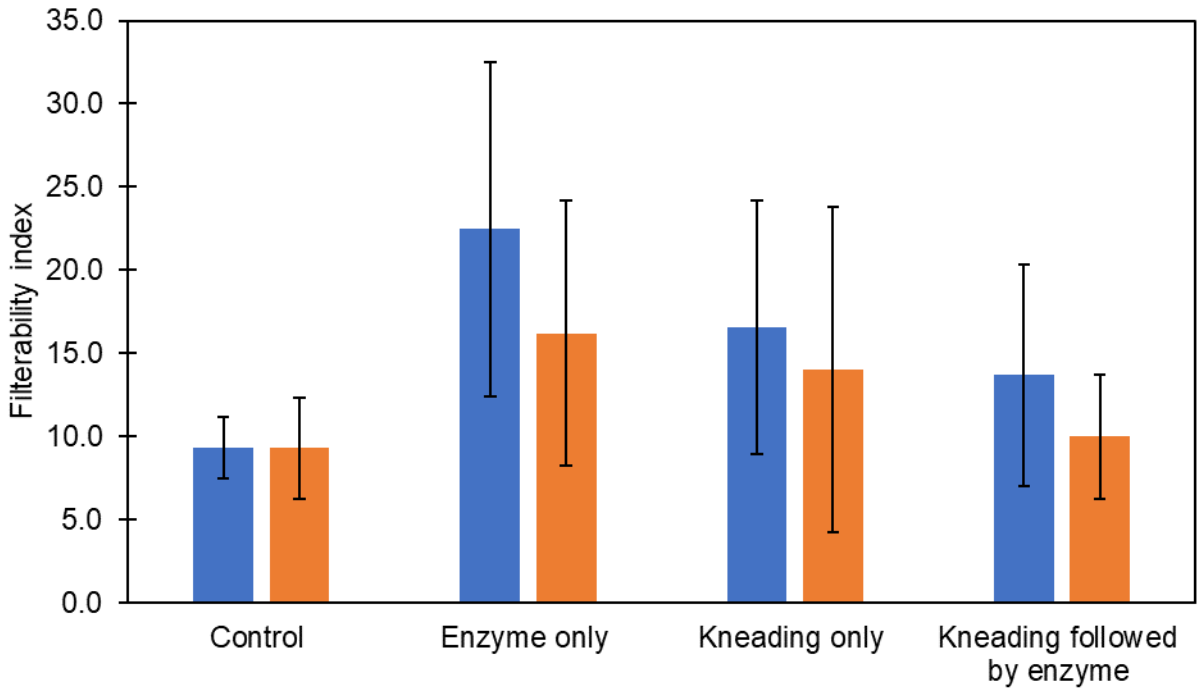


Figure 4.10: Filterability index before and after viscosity adjustment (blue and orange respectively) of various treatments. Primary axis: ■ – K_w after ripening, ■ – K_w corrected for ball fall.

4.4 Conclusions and recommendations

The effect of different treatments (kneading and enzyme treatments) and combinations of treatments (enzyme treatment followed by kneading and kneading followed by enzyme treatment) on key DWP characteristic; viscosity, alkali solubility and reactivity were evaluated. Firstly, kneading was found to be a harsh mechanical treatment that resulted in increased amounts of degraded cellulose without decreasing the viscosity or improving the reactivity of the pulp. Secondly, kneading also caused compression of fibres that resulted in decreased enzyme and chemical efficiency by reducing the available surface area of the pulp fibres. This was demonstrated when the combination of kneading followed by enzyme treatment resulted in a lower pulp reactivity compared to the control, while the viscosity was not reduced as much as the enzyme-treated pulp. Both the enzyme treatment and enzyme treatment followed by kneading resulted in similar viscosity changes, with the key difference being that the combination of enzyme treatment and kneading resulted in lower reactivity, indicating that chemical accessibility was hindered by introducing kneading. Therefore, enzyme only treatment was the most effective to decrease viscosity and improve reactivity.

All treatments and their different combinations were effective in reducing the ageing times after steeping, when compared to the control. Treatment of the pulp with enzyme only was

most effective in reducing the ageing time, followed by kneading treatment only. Enzyme treatment followed by kneading was not suitable for viscose making, since a large fraction of the sample's fibres was undispersed after steeping, which would translate into yield losses. The DP validated that the ageing times were correct to produce viscose. The bulk densities of all the treated samples were higher than the control, but still within specifications.

The coagulability of all samples including the control was highly variable and no significant differences were observed between them. Similarly, all treated samples were highly variable and showed no significant differences compared to the control. As such, treatments were not effective in producing better-quality viscose; however, the treatments could potentially be used to reduce the ageing times during viscose making thereby saving valuable time. This should be considered by comparing the time saved and the cost of treatment.

References

AB Enzymes. 2009. *Ecopulp R description and specifications*. Darmstadt: AB Enzymes.

Ahn, K., Zaccaron, S., Rosenau, T., & Potthast, A. 2019. How alkaline solvents in viscosity measurements affect data for oxidatively damaged celluloses: cupri-ethylenediamine. *Biomacromolecules*, 20(11):4117-4125.

Ambjörnsson, H.A., Östberg, L., Schenzel, K., Larsson, P.T., & Germgard, U. 2014. Enzyme pretreatment of dissolving pulp as a way to improve the following dissolution in NaOH/ZnO. *Holzforschung*, 68(4):385-391.

Cao, Y. & Tan, H. 2006. Improvement of alkali solubility of cellulose with enzymatic treatment. *Applied Microbiology and Biotechnology*, 70(2):176-182. doi:10.1007/s00253-005-0069-8

Ciolacu, D. & Popa, V.I. 2010. *Cellulose allomorphs: structure, accessibility and reactivity. polymer science and technology*. New York: Nova Science Publishers.

Coley, J.R. 1953. The effect of the degree of polymerization on the serimetric properties of regenerated cellulose fibers. *Textile Research Journal*, 23(1):34-36. doi:10.1177%2F004051755302300105

Duan, C., Verma, S.K., Li, J., Ma, X., & Ni, Y. 2016. Combination of mechanical, alkaline and enzymatic treatments to upgrade paper-grade pulp to dissolving pulp with high reactivity. *Bioresource Technology*, 200:458-463.

Engström, A.-C., Ek, M., & Henriksson, G. 2006. Improved accessibility and reactivity of dissolving pulp for the viscose process: pretreatment with monocomponent endoglucanase. *Biomacromolecules*, 7:2027-2031.

Gao, W., Xiang, Z., Chen, K., Yang, R., & Yang, F. 2015. Effect of depth beating on the fiber properties and enzymatic saccharification efficiency of softwood kraft pulp. *Carbohydrate Polymers*, 127:400-406. doi:10.1016/j.carbpol.2015.04.005.

Gondhalekar, S., Mohite, L., Pawar, P., Datta, S., & Naik-Nimbalkar, V. 2019. A study of viscose quality by reduction of knots in slurry and alkali cellulose. *Cellulose Chemistry and Technology*, 53:219-226.

Gondhalekar, S.C., Pawar, P.J., Dhumal, S.S., & Thakre, S.S. 2019. Mechanism of xanthation reaction in viscose process. *Cellulose*, 26(3):1595-1604.

Hottenroth, V. 1915. Bestimmung des reifegrades der viscose. *Chemiker Zeitung*, 39:119.

Ibarra, D., Köpcke, V., & Ek, M. 2009. Exploring enzymatic treatments for the production of dissolving grade pulp from different wood and non-wood paper grade pulps. *Holzforschung*, 63(6):721-730. doi:10.1515/HF.2009.102

Ibarra, D., Köpcke, V., Larsson, P.T., Jääskeläinen, A.-S., & Ek, M. 2010. Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp. *Bioresource Technology*, 101(19):7416-7423.

ISO. 1982. *ISO 692:1982: Pulps: determination of alkali solubility*.

ISO. 2010. *ISO 5351:2010: Pulps: determination of limiting viscosity number in cupri-ethylenediamine (CED) solution*.

Javaid, U., Ahmad, Z., Iqbal, S., & Naeem, S. 2014. *Viscose fiber strength and degree of polymerization*. http://www.diva-portal.org/smash/get/diva2:1312795/FULLTEXT01.pdf Date of access: 19 Nov. 2021.

Kotek, R. 2007. Regenerated cellulose fibers. In: Lewin, M., ed. *Handbook of fiber chemistry*. 3rd ed. Boca Raton: CRC Press. 667-772.

Kumar, H. & Christopher, L.P. 2017. Recent trends and developments in dissolving pulp production and application. *Cellulose*, 24(6):2347-2365. doi:10.1007/s10570-017-1285-y

Leu, S.-Y. & Zhu, J.Y. 2013. Substrate-related factors affecting enzymatic saccharification of lignocelluloses: our recent understanding. *BioEnergy Research*, 6(2):405-415.

Li, H., Legere, S., He, Z., Zhang, H., Li, J., Yang, B., Zhang, S., Zhang, L., Zheng, L., & Ni, Y. 2018. Methods to increase the reactivity of dissolving pulp in the viscose rayon production process: a review. *Cellulose*, 25(7):3733-3753.

Li, J., Zhang, S., Li, H., Ouyang, X., Huang, L., Ni, Y., & Chen, L. 2018. Cellulase pretreatment for enhancing cold caustic extraction-based separation of hemicelluloses and cellulose from cellulosic fibers. *Bioresource Technology*, 251:1-6.

Lin, X., Wu, Z., Zhang, C., Liu, S., & Nie, S. 2018. Enzymatic pulping of lignocellulosic biomass. *Industrial Crops Production*, 120:16-24.

Liu, W., Wu, R., Wang, B., Hu, Y., Hou, Q., Zhang, P., & Wu, R. 2020. Comparative study on different pretreatment on enzymatic hydrolysis of corncob residues. *Bioresource Technology*, 295:122244.

Miao, Q., Chen, L., Huang, L., Tian, C., Zheng, L., & Ni, Y. 2014. A process for enhancing the accessibility and reactivity of hardwood kraft-based dissolving pulp for viscose rayon production by cellulase treatment. *Bioresource Technology*, 154:109-113.

Qin, X., Duan, C., Feng, X., Zhang, Y., Dai, L., Xu, Y., & Ni, Y. 2021. Integrating phosphotungstic acid-assisted prerefining with cellulase treatment for enhancing the reactivity of kraft-based dissolving pulp. *Bioresource Technology*, 320:124283.

Quintana, E., Valls, C., Barneto, A.G., Vidal, T., Ariza, J., & Roncero, M.B. 2015. Studying the effects of laccase treatment in a softwood dissolving pulp: cellulose reactivity and crystallinity. *Carbohydrate Polymers*, 119:53–61.

Sandham, D., 2021. *Chapter 3: Modification of fully bleached dissolving wood pulp through endoglucanase treatment*. Potchefstroom: North-West University. pp. 38-53

Sixta H., Potthast A., Krotschek AW. 2006. Chemical pulping processes. In: Sixta H (ed) Handbook of pulp. Weinheim: Wiley, pp 325–366

Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., … Schottenberger, H. 2013. Novel concepts of dissolving pulp production. *Cellulose*, 20(4):1547-1561.

Spörl, J.M., Ota, A., Son, S., Massonne, K., Hermanutz, F., & Buchmeiser, M.R. 2016. Carbon fibers prepared from ionic liquid-derived cellulose precursors. *Materials Today Communication*, 7:1-10.

TAPPI. 2000. *Alkali solubility of pulp, TAPPI T235 om-60*. Atlanta: TAPPI Press.

TAPPI. 2004. *Viscosity of pulp (capillary viscometer method)*. Atlanta: TAPPI Press.

Tian, C., Zheng, L., Miao, Q., Cao, C., & Ni, Y. 2014. Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments. *Cellulose*, 21(5). doi:10.1007/s10570-014-0332-1

Treiber, E., Rehnström, J., Ameen, C., & Kolos, F. 1962. Using a laboratory viscose small-scale plant to test chemical conversion pulps. *Das Papier*, 16(3):85-94.

Wang, Q., Fu, X., Liu, S., Ji, X., Wang, Y., He, H., Yang, G., & Chen, J. 2020. Understanding the effect of depth refining on upgrading of dissolving pulp during cellulase treatment. *Industrial Crops and Products*, 144:112032.

Wang, Q., Liu, S., Yang, G., Chen, J., & Ni, Y. 2015. Cationic polyacrylamide enhancing cellulase treatment efficiency of hardwood kraft-based dissolving pulp. *Bioresource Technology*, 183:42-46.

Wu, C., Zhou, S., Li, R., Wang, D., & Zhao, C. 2015. Reactivity improvement of bamboo dissolving pulp by xylanase modification. *BioResources*, 10(3):4970-4977.

Xu, S., Qi, L., & Ma, C. 2021. Viscose fiber hybrid composites with high strength and practicality via cross-linking with modified melamine formaldehyde resin. *Materials Today Communications*, 26:102093.

Yang, S., Wen, Y., Zhang, H., Li, J., & Ni, Y. 2018. Enhancing the Fock reactivity of dissolving pulp by the combined prerefining and poly dimethyl diallyl ammonium chloride-assisted cellulase treatment. *Bioresource Technology*, 260:135-140.

Yang, S., Yang, B., Duan, C., Fuller, D.A., Wang, X., Chowdhury, S.P., … Ni, Y. 2019. Applications of enzymatic technologies to the production of high-quality dissolving pulp: a review. *Bioresource Technology*, 281:440-448. doi:10.1016/j.biortech.2019.02.132

Chapter 5: Conclusions and recommendations

5.1 Conclusions

The first phase of results showed that both Ecopulp R and NS 51179 enzyme formulations resulted in notable EG activities based on the cellobiose formation. The enzyme assays also showed that Ecopulp R formulation resulted in a higher enzyme activity compared to NS 51179 formulation. This was further validated as Ecopulp R was more effective at reducing the viscosity and increasing the reactivity of fully bleached pulp compared to NS 51179 enzyme formulation. Although the Ecopulp R degraded the cellulose structure when measuring alkali solubility, it was acceptable due to the improved reactivity results. Therefore, Ecopulp R enzyme formulation was deemed to be the most effective to improve DWP's properties.

During the second phase of investigation, mechanical kneading was introduced to see what effect it had on DWP properties but also how the sequence of enzymatic and kneading treatments influenced the pulp properties. It was observed that kneading was a harsh mechanical treatment as the amount of degraded cellulose increased without improving reactivity or viscosity. Furthermore, both kneading followed by enzyme treatment and enzyme treatment followed by kneading improved viscosity; however, reactivity improvement was limited compared to the enzyme only treatment. This showed that kneading compressed the fibres thereby limiting the effectiveness of enzyme and chemical treatments as the fibre surface area was reduced. The enzyme only treatment showed the highest reactivity and viscosity reduction and therefore was the most effective DWP treatment.

In the final phase of investigation, DWPs from the previous phase of treatments were used to produce viscose to validate that the treatments could be used to reduce the chemical demand within the viscose process. All treatments were effective in reducing the ageing time after steeping. The viscose results, however, were highly variable, and no treatment significantly improved the viscose properties. Therefore, since no improvements were seen with the normal viscose recipe, no improvements would be possible by reducing the chemical demand. One critical observation in this phase of investigation was that pulps with improved reactivity did not necessarily lead to better-quality viscose. This was observed when enzyme treatment followed by kneading did not result in dispersed fibres during steeping leading to significant yield losses. Therefore, improved reactivity results need to be verified by producing viscose.

5.2 Recommendations

During the first phase of investigation, which focused on bench-scale enzymatic treatments only, the 300 g/t enzyme dosages were tested. The primary reason for this was to see if the highest dosages could lead to improved reactivity thereby possibly reducing chemical demand in the viscose process, which was the primary aim of this project. If the highest dosages of the two formulations did not show improved reactivity, then neither would lower dosages. The NS 51179 EG formulation is evidence to this as a lower reactivity was produced at 300 g/t dosage. Therefore, future research could test the reactivity of a wider range of enzyme dosages which could better optimise the results.

In similar manner, phase two of the investigation used the highest enzyme dosage used in the previous phase, which was not necessarily the most optimal dosage. Again, this was done to see if combined mechanical and enzymatic treatments could be used to improve reactivity and reduce chemical demand within the viscose process. If a more optimal dosage from the previous phase was found and used, it could potentially lead to better results and save cost as a lower dosage was used.

In the last phase of the investigation, no significant evidence was obtained that proved that treating the DWP with a combination of mechanical and enzymatic treatments could reduce the chemical demand within the viscose process. The primary reason why no improvement was seen is that the DWP used within this project already met the specifications for the DWP that Sappi uses to make viscose since the pulp was taken directly from the hypochlorite bleaching stage. Therefore, by replacing the hypochlorite bleaching stage (which has negative environmental implications) with enzymatic and kneading treatments it is possible to achieve similar or better-quality DWP and still lower the environmental impact and possibly save on chemical costs.

Appendix

Raw data of enzyme assay

Table 1: Raw data of the peak areas of the enzyme assay for incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Sample name	Incubation time (h)	Peak areas	
		Glucose concentration (mg/l)	Cellobiose concentration (mg/l)
Control R1	1	0.5	3.5
Control R2	1	0	0
Control R3	1	0	5.1
Ecopulp R R1	1	0	24.2
Ecopulp R R2	1	0	21.8
Ecopulp R R3	1	1.5	26.4
NS 51179 R1	1	0	7.7
NS 51179 R2	1	0	8.2
NS 51179 R3	1	0	9.9
Control R1	2	0	3.1
Control R2	2	0	3
Control R3	2	0	3.1
Ecopulp R R1	2	0	34.5
Ecopulp R R2	2	0.8	29.1
Ecopulp R R3	2	0	31.4
NS 51179 R1	2	0	8.8
NS 51179 R2	2	0	10.2
NS 51179 R3	2	0	9
Control R1	-	0	3.1
Control R2	-	0	0
Control R3	-	0	0
Ecopulp R control R1	-	2.1	29.2
Ecopulp R control R2	-	3.1	35.2
Ecopulp R control R3	-	2.4	32.7

NS 51179 control R1	-	0	7.6
NS 51179 control R2	-	0	8.4
NS 51179 control R3	-	0	9.9

Viscosity data for phase 1

Table 2: Viscosity data for Ecopulp R at 1-hour incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Enzyme dosage (g/t)	**Viscosity (ml/g)**		
	R1	**R2**	**R3**
0	550	553	551
50	541	539	542
100	535	534	543
150	544	527	547
200	515	506	528
250	511	509	518
300	499	519	516

Table 3: Viscosity data for Ecopulp R at 2-hour incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Enzyme dosage (g/t)	Viscosity (ml/g)		
	R1	R2	R3
0	557	560	548
50	527	524	542
100	534	541	532
150	513	515	531
200	505	510	520
250	514	495	528
300	508	493	517

Table 4: Viscosity data for NS 51179 at 1-hour incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Enzyme dosage (g/t)	Viscosity (ml/g)		
	R1	R2	R3
0	554	549	548
50	554	544	535
100	542	552	543
150	530	537	547
200	518	535	538
250	538	528	539
300	542	531	538

Table 5: Viscosity data for NS 51179 at 2-hour incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Enzyme dosage (g/t)	Viscosity (ml/g)		
	R1	R2	R3
0	555	541	553
50	533	542	542
100	542	547	543
150	506	514	542
200	527	514	527
250	514	532	526
300	502	511	536

Alkaline solubility for phase 1

Table 6: Alkaline solubility data for various enzyme dosages and incubation time for Ecopulp R and NS 51179 enzymes (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Sample name	Enzyme dosage (g/t)	Incubation time (h)	S10 (%)	S18 (%)
Ecopulp R 300/2H R1	300	2	9.9	4.5
Ecopulp R 300/1H R1	300	1	9.8	3.8
Ecopulp R 250/1H R2	250	1	9.2	4.0
NS 51179 100/2H R3	100	2	8.2	3.9
NS 51179 0/1H R1	0	1	7.3	3.8
NS 51179 0/1H R2	0	1	8.6	3.3
Ecopulp R 300/2H R2	300	2	9.7	3.6
Ecopulp R 200/1H R3	200	1	8.7	3.4

Ecopulp R 250/2H R1	250	2	9.5	4.5
NS 51179 150/2H R2	250	2	8.7	4.3
NS 51179 50/1H R2	50	1	8.7	4.2
NS 51179 100/1H R2	100	1	8.4	4.0
NS 51179 100/1H R1	100	1	8.5	4.3
NS 51179 0/2H R2	0	2	8.7	4.1
NS 51179 300/1H R3	300	1	9.4	4.3
NS 51179 50/2H R3	50	2	8.7	4.3
NS 51179 150/2H R3	150	2	8.4	4.2
NS 51179 300/2H R3	300	2	8.6	4.2
Ecopulp R 100/2H R3	100	2	9.0	4.2
Ecopulp R 250/2H R3	250	2	9.1	4.1
NS 51179 100/2H R2	100	2	8.8	4.4
NS 51179 250/1H R1	250	1	8.9	4.3
Ecopulp R 100/1H R2	100	1	9.0	4.2
Ecopulp R 50/1H R2	50	1	8.3	4.0
NS 51179 150/1H R3	150	1	8.5	4.0
NS 51179 250/1H R3	250	1	8.5	4.0
NS 51179 300/2H R2	300	2	8.4	3.8
Ecopulp R 50/2H R2	50	2	9.0	3.9
Ecopulp R 50/1H R1	50	1	8.7	4.0
Ecopulp R 100/2H R1	100	2	9.3	4.1
Ecopulp R 150/2H R1	150	2	9.0	4.1
Ecopulp R 250/1H R1	250	1	9.1	4.2
Ecopulp R 50/1H R3	50	1	8.2	3.8

NS 51179 200/2H R2	200	2	8.9	4.8
NS 51179 50/2H R2	50	2	8.5	4.7
NS 51179 250/2H R3	250	2	8.9	4.0
Ecopulp R 0/1H R3	0	1	8.6	4.5
Ecopulp R 50/2H R1	50	2	8.6	4.5
Ecopulp R 0/2H R2	0	2	8.1	4.3
Ecopulp R 100/2H R2	100	2	8.8	4.0
Ecopulp R 200/1H R2	200	1	8.8	4.1
Ecopulp R 0/1H R2	0	1	8.5	4.1
NS 51179 250/2H R2	250	2	8.1	4.0
Ecopulp R 150/1H R1	150	1	8.3	4.3
Ecopulp R 200/1H R1	200	1	8.5	4.1
Ecopulp R 0/1H R1	0	1	7.9	3.9
Ecopulp R 0/2H R1	0	2	8.0	3.8
Ecopulp R 150/2H R2	150	2	8.3	3.9
Ecopulp R 300/1H R2	300	1	8.7	4.0
Ecopulp R 300/2H R3	300	2	8.9	3.9
NS 51179 300/1H R1	300	1	8.9	4.1
NS 51179 300/2H R1	300	2	9.2	4.3
Ecopulp R 100/1H R1	100	1	8.9	4.0
Ecopulp R 150/1H R3	150	1	7.7	4.0
NS 51179 0/2H R3	0	2	7.7	4.0
NS 51179 200/1H R3	200	1	8.1	4.0
NS 51179 50/1H R3	50	1	7.9	4.2
Ecopulp R 50/2H R3	50	2	8.1	4.2

NS 51179 200/2H R3	200	2	8.5	3.9
Ecopulp R 0/2H R3	0	2	7.9	3.8
Ecopulp R 100/1H R3	100	1	8.0	3.8
Ecopulp R 150/2H R3	150	2	9.2	3.9
Ecopulp R 300/1H R3	300	1	9.2	4.4
NS 51179 0/1H R3	0	1	8.0	4.1
NS 51179 300/1H R2	300	1	8.6	4.0
Ecopulp R 150/1H R2	150	1	8.9	4.0
NS 51179 100/1H R3	100	1	8.3	3.8
Ecopulp R 250/1H R3	250	1	8.9	4.0
Ecopulp R 200/2H R3	200	2	9.0	4.1
NS 51179 250/2H R1	250	2	8.4	3.8
NS 51179 200/1H R2	200	1	8.0	3.6
NS 51179 200/1H R1	200	1	8.1	3.6
NS 51179 50/1H R1	50	1	8.0	3.7
Ecopulp R 200/2H R2	200	2	9.3	4.0
NS 51179 200/2H R1	200	2	8.4	4.2
NS 51179 150/2H R1	150	2	8.6	4.3
Ecopulp R 200/2H R1	200	2	8.9	4.2
NS 51179 0/2H R1	0	2	8.2	4.2
NS 51179 250/1H R2	250	1	8.3	4.2

Quick reactivity results for phase 1

Table 7: Quick reactivity data for phase 1 at 300g/t enzyme dosage and 2-hour incubation time (R1 is the first replicate, R2 is the second replicate and R3 is the third replicate)

Sample name	Undissolved fibres (%)		
	R1	R2	R3
Untreated	6.17	5.35	8.49
Ecopulp R	2.34	1.65	5.75
NS 51179	9.38	13.17	12.3

Preliminary data for pilot plant

Table 8: Un-replicated preliminary data for pilot plant with continuous mixing and no mixing bench-scale

Sample name	**S10 (%)**	**S18 (%)**	**Viscosity (ml/g)**
Ecopulp R 300/1H	9.24	4.08	511
Ecopulp R 300/2H	9.53	3.99	506
Ecopulp R 300/2H Pilot	11.73	4.87	452
NS 51179 300/1H	8.95	4.14	537
NS 51179 300/2H	8.71	4.12	516

Viscosity data for phase 2

Table 9: Intrinsic viscosity for various treatments in the second phase of experiment (R1 is the first replicate and R2 is the second replicate)

Sample name	**Viscosity (ml/g)**
Kneading followed by enzyme treatment R1	479
Kneading followed by enzyme treatment R2	470
Kneading only R1	547
Kneading only R2	535
Enzyme only R1	440
Enzyme only R1	433
Untreated R1	538
Untreated R2	521
Enzyme followed by kneading treatment R1	447
Enzyme followed by kneading treatment R2	436

Alkaline solubility results for phase 2

Table 10: Alkaline solubility for various treatments in the second phase of experiment (R1 is the first replicate and R2 is the second replicate)

Sample name	**Enzyme dosage (g/t)**	**Incubation time (h)**	**S10 (%)**	**S18 (%)**
Untreated R2	300	2	8.5	3.9
Kneading only R1	300	2	9.3	3.8
Enzyme only R2	300	2	13.0	5.2
Kneading followed by enzyme treatment R2	300	2	10.6	4.3
Enzyme followed by kneading treatment R1	300	2	12.7	4.0
Kneading only R2	300	2	9.1	3.8
Kneading followed by enzyme treatment R1	300	2	10.4	4.1
Untreated R1	300	2	8.2	3.9
Enzyme followed by kneading treatment R2	300	2	13.4	3.4
Enzyme only R1	300	2	12.7	5.1

Quick reactivity results for phase 2

Table 11: Quick reactivity for various treatments in the second phase of experiment (R1 is the first replicate and R2 is the second replicate)

Sample name	**Undissolved fibres R1 (%)**	**Undissolved fibres R2 (%)**
Untreated	7.54	8.01
Kneading only batch 1	6.05	9.01
Kneading only batch 2	6.34	9.03
Enzyme only batch 1	2.68	3.03
Enzyme only batch 2	1.45	2.38
Kneading followed enzyme batch 1	15.49	13.13
Kneading followed enzyme batch 2	11.48	12.87
Enzyme followed kneading batch 1	5.77	5.72
Enzyme followed kneading batch 2	5.3	5.7

Ageing kinetics results in phase 3

Table 12: Ageing kinetics for untreated pulp

Untreated Hypo Pulp						
	Time (hr)	**Run 1**	**Run 2**	**Run 1 Mini Scale**	**Run 2 Mini Scale**	**Average**
Viscosity of FS pulp	FS					
Viscosity of AC going into xanthation (ml/g)	0	526	555	524	531	528
Viscosity of AC going into xanthation (ml/g)	1	452	445	431	439	435
Viscosity of AC going into xanthation (ml/g)	2	352	362	331	321	326
Viscosity of AC going into xanthation (ml/g)	3	314	310	289	286	288
Viscosity of AC going into xanthation (ml/g)	4	278	275	249	252	251
Viscosity of AC going into xanthation (ml/g)	5	261	255	231	228	230
Viscosity of AC going into xanthation (ml/g)	6	237	230	207	209	208

Table 13: Ageing kinetics for enzyme only treated pulp batch 1

Enzyme-Treated Only Batch 1									
	Time (hr)	**Run 1 Normal**	**Run 2 Normal**	**Run 1 Mini Scale**	**Run 2 Mini Scale**	**Run 2 Normal**	**Run 1 Mini Scale**	**Run 2 Mini Scale**	**Average**
Viscosity of FS pulp	FS								
Viscosity of AC going into xanthation (ml/g)	0	467	464	449	445	442	437	445	450
Viscosity of AC going into xanthation (ml/g)	1	383	378	362	358	373	375	380	373
Viscosity of AC going into xanthation (ml/g)	2	313	308	286	283	306	290	304	299
Viscosity of AC going into xanthation (ml/g)	3	273	269	250	244	266	261	273	262
Viscosity of AC going into xanthation (ml/g)	4	240	244	223	219	239	224	235	232
Viscosity of AC going into xanthation (ml/g)	5	222	221	204	199	219	206	217	213
Viscosity of AC going into xanthation (ml/g)	6	205	203	186	184	203	187	200	195

Table 14: Ageing kinetics for enzyme only treated pulp batch 2

Enzyme-Treated Only Batch 2						
	Time (hr)	**Run 1 Normal**	**Run 2 Normal**	**Run 1 Mini Scale**	**Run 2 Mini Scale**	**Average**
Viscosity of FS pulp	FS					
Viscosity of AC going into xanthation (ml/g)	0	Scrapped	442	437	445	441
Viscosity of AC going into xanthation (ml/g)	1	Scrapped	373	375	380	376
Viscosity of AC going into xanthation (ml/g)	2	Scrapped	306	290	304	300
Viscosity of AC going into xanthation (ml/g)	3	Scrapped	266	261	273	267
Viscosity of AC going into xanthation (ml/g)	4	Scrapped	239	224	235	233
Viscosity of AC going into xanthation (ml/g)	5	Scrapped	219	206	217	214
Viscosity of AC going into xanthation (ml/g)	6	Scrapped	203	187	200	197

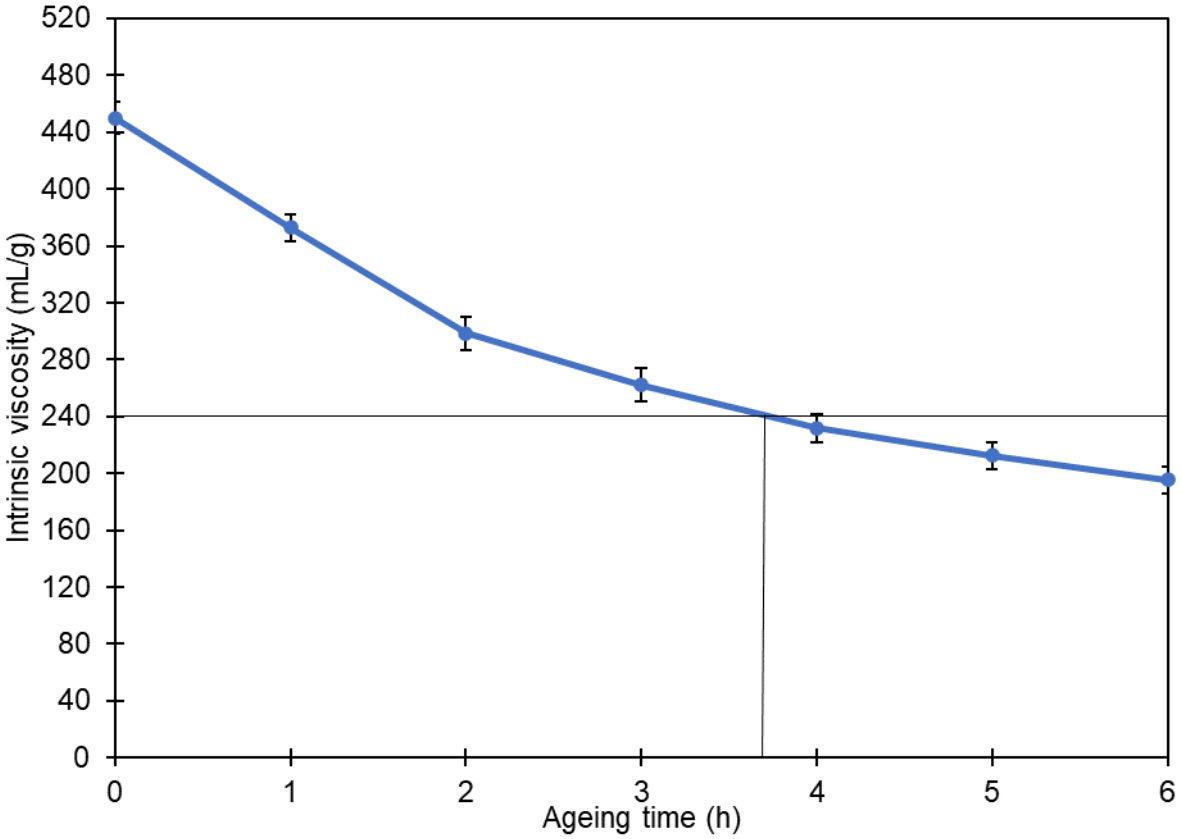


Figure 1: Ageing curve for enzyme-treated DWP used to determine the ageing time required to reduce the intrinsic viscosity to 240 g/L

Table 15: Ageing kinetics for kneaded only treated pulp batch 1

Kneaded only Batch 1						
	Time (hr)	**Run 1 Mini Scale**	**Run 2 Mini Scale**	**Run 1**	**Run 2**	**Average**
Viscosity of FS pulp	FS					
Viscosity of AC going into xanthation (ml/g)	0	538	522	544	511	529
Viscosity of AC going into xanthation (ml/g)	1	400	406	404	383	398
Viscosity of AC going into xanthation (ml/g)	2	313	307	334	272	307
Viscosity of AC going into xanthation (ml/g)	3	260	258	294	263	269
Viscosity of AC going into xanthation (ml/g)	4	230	225	251	230	234
Viscosity of AC going into xanthation (ml/g)	5	208	208	241	210	217
Viscosity of AC going into xanthation (ml/g)	6	190	188	215	192	196

Table 16: Ageing kinetics for kneaded only treated pulp batch 2

Kneaded only Batch 2				
	Time (hr)	**Run 1**	**Run 2**	**Average**
Viscosity of FS pulp	FS			
Viscosity of AC going into xanthation (ml/g)	0	544	511	528
Viscosity of AC going into xanthation (ml/g)	1	404	383	394
Viscosity of AC going into xanthation (ml/g)	2	334	272	303
Viscosity of AC going into xanthation (ml/g)	3	294	263	279
Viscosity of AC going into xanthation (ml/g)	4	251	230	241
Viscosity of AC going into xanthation (ml/g)	5	241	210	226
Viscosity of AC going into xanthation (ml/g)	6	215	192	204

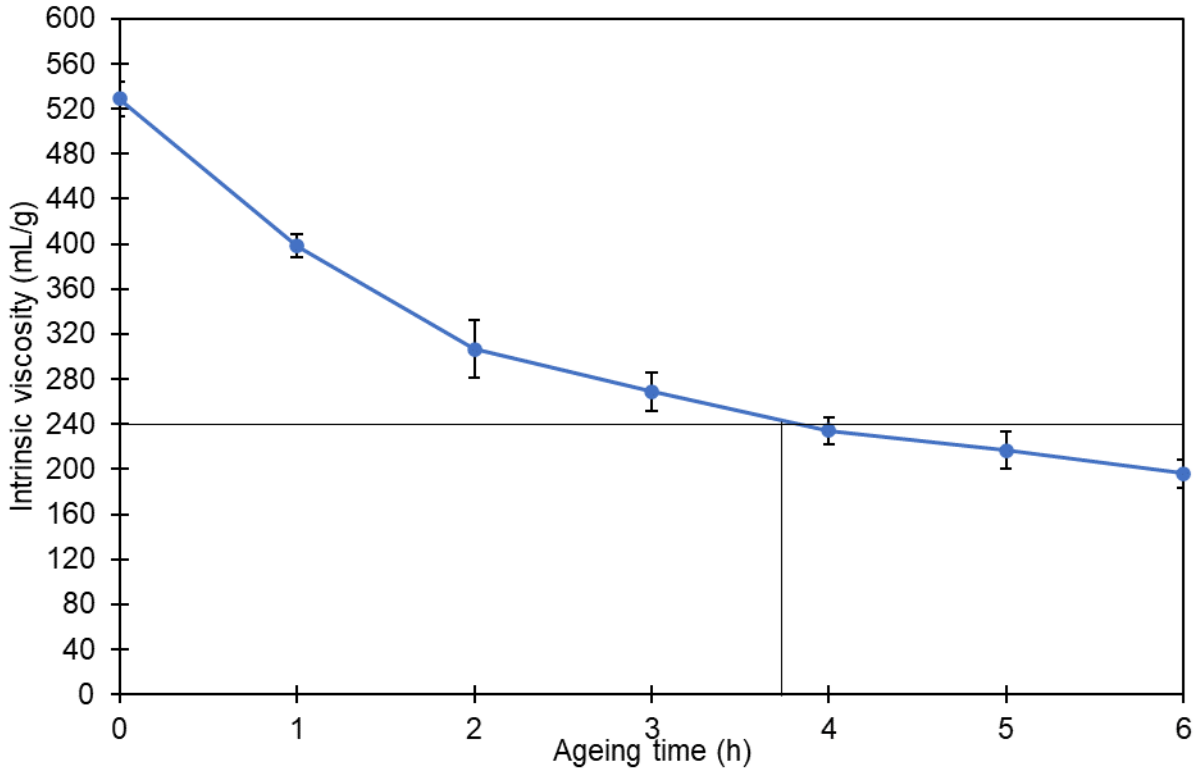


Figure 2: Ageing curve for kneaded DWP used to determine the ageing time to reduce the alkalised cellulose intrinsic viscosity to 240 g/L.

Table 17: Ageing kinetics for enzyme followed by kneading batch 1

Enzyme followed Kneading Treated Batch 1				
	Time (hr)	**Run 1**	**Run 2**	**Average**
Viscosity of FS pulp	**FS**			
Viscosity of AC going into xanthation (ml/g)	0	433	420	427
Viscosity of AC going into xanthation (ml/g)	1	353	320	337
Viscosity of AC going into xanthation (ml/g)	2	291	271	281
Viscosity of AC going into xanthation (ml/g)	3	251	227	239
Viscosity of AC going into xanthation (ml/g)	4	215	201	208
Viscosity of AC going into xanthation (ml/g)	5	205	186	196
Viscosity of AC going into xanthation (ml/g)	6	186	230	208

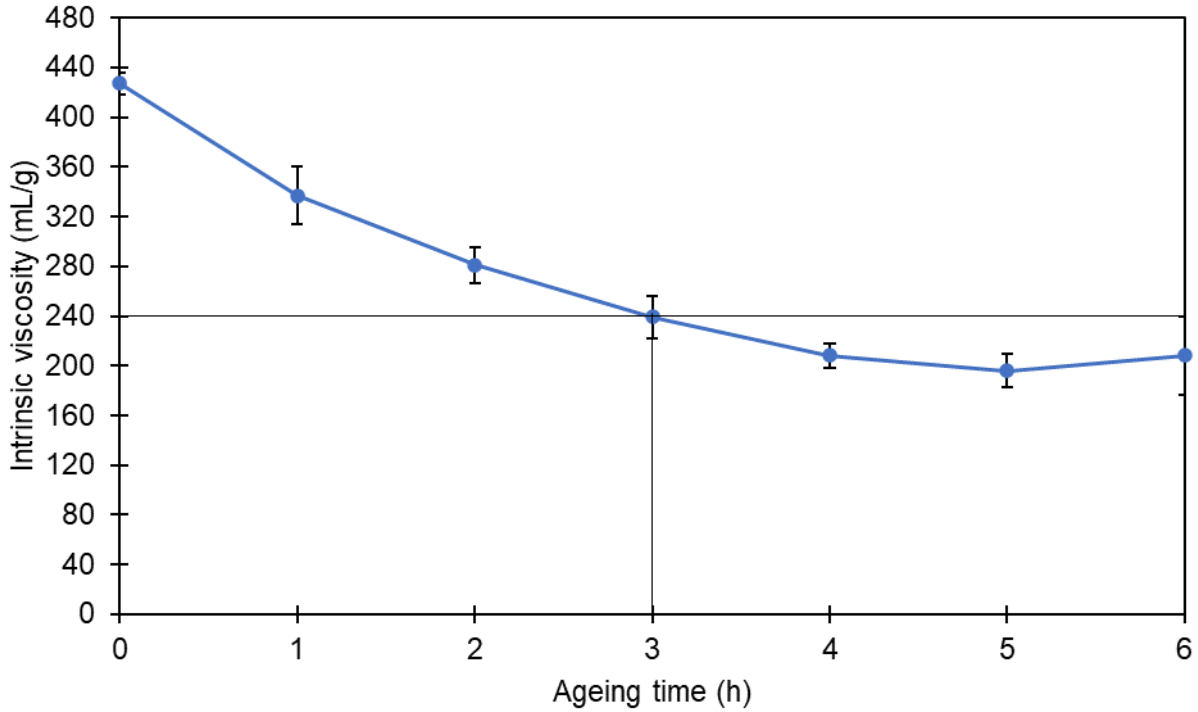


Figure 3: Ageing curve for enzyme followed by kneading treated DWP used to determine the ageing time to reduce the alkalised cellulose intrinsic viscosity to 240 g/L.

Table 18: Ageing kinetics for kneading followed by enzyme batch 1

Kneaded and Enzyme-Treated Batch 1				
	Time (hr)	**Run 1**	**Run 2**	**Average**
Viscosity of FS pulp	FS			
Viscosity of AC going into xanthation (ml/g)	0	469	478	474
Viscosity of AC going into xanthation (ml/g)	1	374	390	382
Viscosity of AC going into xanthation (ml/g)	2	311	312	312
Viscosity of AC going into xanthation (ml/g)	3	279	274	277
Viscosity of AC going into xanthation (ml/g)	4	244	232	238
Viscosity of AC going into xanthation (ml/g)	5	211	230	221
Viscosity of AC going into xanthation (ml/g)	6	210	205	208

Table 19: Ageing kinetics for kneading followed by enzyme batch 2

Kneaded and Enzyme-Treated Batch 2						
	Time (hr)	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Average**
Viscosity of FS pulp	**FS**					
Viscosity of AC going into xanthation (ml/g)	**0**	405	408	469	478	440
Viscosity of AC going into xanthation (ml/g)	**1**	358	354	374	390	369
Viscosity of AC going into xanthation (ml/g)	**2**	290	292	311	312	301
Viscosity of AC going into xanthation (ml/g)	**3**	254	260	279	274	267
Viscosity of AC going into xanthation (ml/g)	**4**	221	233	244	232	233
Viscosity of AC going into xanthation (ml/g)	**5**	204	219	211	230	216
Viscosity of AC going into xanthation (ml/g)	**6**	193	202	210	205	203

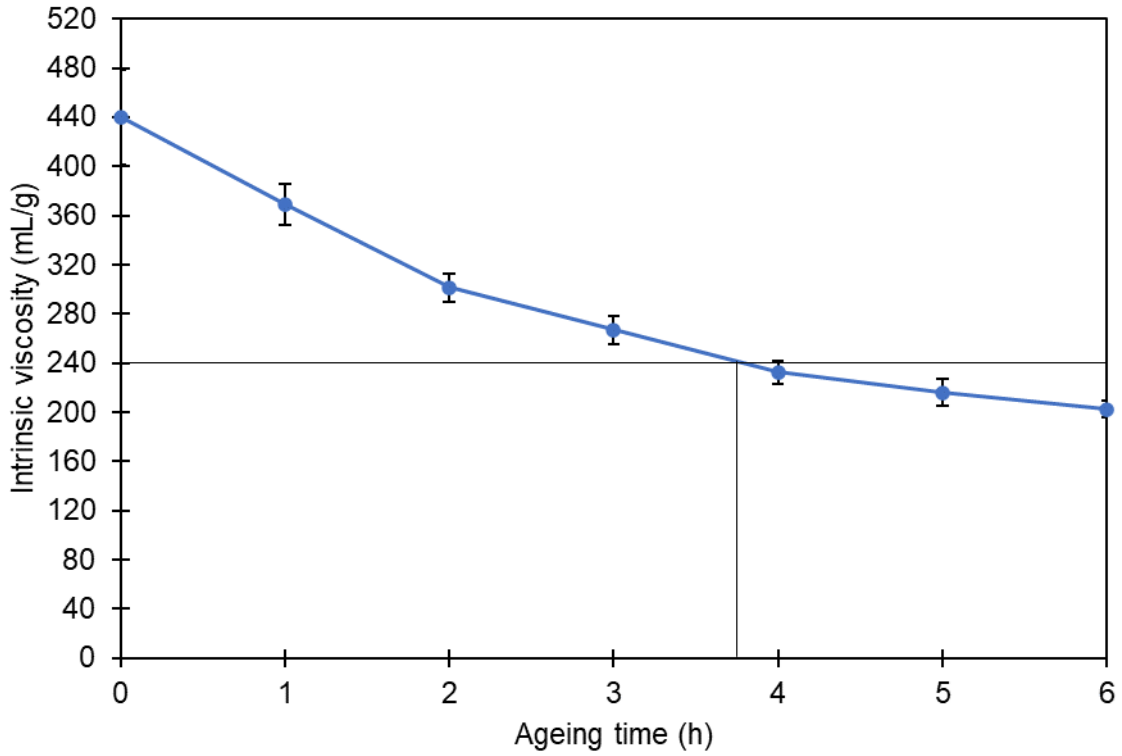


Figure 4: Ageing curve for kneaded followed by enzyme-treated DWP used to determine the ageing time to reduce the alkali cellulose intrinsic viscosity to 240 g/L.

Viscose data

Table 20: Viscose data for untreated pulp

Pulp Type	**Untreated Hypo Pulp**	
Run	**1**	**2**
STEP 1: STEEPING PULP BLEND		
PULP 1		
Soda source	18.50	18.50
Moisture of pulp 1 (%)	7.30	7.30
Blend Percentage 1	100.00	100.00
Total Vol Soda Required (ml)	2960.00	2960.00
Vol required (ml)	2960.00	2960.00
Density of Soda Source	1.2006	1.2006
Mass (g)	3553.78	3553.78
Required consistency (%)	5.00	5.00
Mass of bone-dry pulp (g)	187.04	187.04
Mass of air-dry pulp required (g)	201.8	201.8
PEG DOSAGE		
Target Press Range (g)	5510 - 5515	5510 - 5515
Press Range (g)	5511.20	5511.20
STEP 2: SHREDDING		
Shredding (min)	1 hr	1 hr
Shredding Temp (°C)	25	25

ALKALISED CELLULOSE & PRESS SODA ANALYSIS				
% SiA	A	B	A	B
Mass of alkali cellulose (g)	4.0041	4.0047	4.0010	4.0008
Vol of NaOH (ml)	4.49	4.68	4.51	4.51
% Soda in alkalised cellulose	15.49	15.30	15.49	15.49
Average % SiA	15.40		15.49	
% CiA	A	B	A	Enzyme
Mass of filter paper before drying (g)	51.8267	76.7669	51.8307	53.4774
Mass of alkalised cellulose + F/P after drying (g)	53.1429	78.0705	53.1342	54.7751
Mass of cellulose (g)	1.3162	1.3036	1.3035	1.2977
% CiA	32.87	32.55	32.58	32.44
Average % CiA	32.71		32.51	
Total HemiCell in steep soda				
Bulk Density				
Time (min)	6.00		6.00	
Weight of Cylinder (g)	550.30		551.10	
Weight of Cylinder + Alkalised cellulose (g)	642.90		635.70	
Weight of Alkalised cellulose (g)	92.60		84.60	
Cylinder Volume (ml)	700.00		700.00	
Bulk Density (g/l)	132.29		120.86	
STEP 3: AGEING				

STEP 4: XANTHATION		
Xanthation time (min)	75	75
Xanthation temp. (ºC)	30	30
Dissolving temp. (ºC)	18	18
Dissolving time (hr)	5.5	5.5
Ripening at 18 ºC (hr)	12	12
Viscose Composition		
Target CiV (%)	9.40	9.40
Target SiV (%)	5.60	5.60
Target AR	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50
S.G of NaOH used	1.2006	1.2006
Alkalised cellulose Analysis		
% CiA	32.71	32.51
% SiA	15.40	15.49
% weight CS_2	33.00	33.00
Mass of Alkalised cellulose mercerised (g)	250.00	250.00
Mass of cell in Alkalised cellulose (g)	81.78	81.27
Mass of CS_2 required (g)	26.99	26.82
Volume of CS_2 required (ml)	21.40	21.27

Total mass of viscose to be made (g)	869.99		864.57	
Mass of Soda solution to be added (g)	593.00		587.75	
Mass of Soda for given mass of viscose (g)	48.72		48.42	
Mass of Soda in Alkalised cellulose (g)	38.50		38.72	
Mass of Soda to be added (g)	10.22		9.70	
Mass of % w/w NaOH required (g)	55.27		52.43	
Volume of % w/w NaOH required (ml)	46.03		43.67	
Total volume of water required (ml)	537.73		535.32	
CHARGES REQUIRED FOR VISCOSE MAKING				
Alkali Cellulose (g)	250.00		250.00	
18.5% NaOH (ml)	46.0		43.7	
CS2 (ml)	21.4		21.3	
Water (ml)	537.7		535.3	
STEP 5: RIPENING				
Viscose Analysis:				
% CiV	A	B	A	B
Wet mass of viscose (g)	1.2035		1.2000	
Dry mass of viscose (g)	0.1168		0.1097	
% CiV	9.71		9.14	
% SiV	A	B	A	B
Mass of sample (g)	4.0019		4.0022	

Vol of NaOH (ml)	9.71		9.52	
% SiV	5.29		5.48	
Ball Fall	A	B	A	B
12 Hours	62.00	62.00	52.00	50.00
Average time (seconds)	62.00		51.00	
Hottenroth Number	A	B	A	B
Volume of Ammonium Chloride (ml)	12.40	12.40	20.00	20.00
Average Hottenroth No After Ripening (cc)	12.40		20.00	
Viscose Blockage Constant (Kw)				
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v
30	22.00	1.36	24.00	1.25
40	28.00	1.43	29.00	1.38
50	33.00	1.52	34.00	1.47
60	37.00	1.62	38.00	1.58
70	41.00	1.71	42.00	1.67
80	45.00	1.78	45.00	1.78
90	49.00	1.84	48.00	1.88
K	6.6234		13.1897	
	8.8312		9.3103	
	10.8600		11.0526	
	8.7409		8.9474	
	7.1870		11.3333	

	6.0136		9.9167	
Average Kw	8.04		10.63	
Coulter Count Before Filtration	1	2	1	2
Zero - Shear Viscosity (Carreau-model)				
Zero - Shear Viscosity (cP)	10093		7705	
Zero - Shear Viscosity (cP)	10100		7749	
Zero - Shear Viscosity (cP)	10083		7793	
Average Zero - Shear Viscosity (cP)	10092		7749	
Alkalised cellulose & Press Soda Analysis:				
Hemi in Press Soda g/l	0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00	
Gamma Cellulose g/l*5	0.00		0.00	
Beta Cellulose g/l*5	0.00		0.00	
Bulk Density g/l	132.29		120.86	
Viscosity of AC before ageing (cps)	12.69		18.73	
Viscosity of AC going into xanthation (cps)	4.98		4.87	
DP of AC going into xanthation	316		306	
Hemi in Aged AC				
Hemi in Aged AC*2.5				
CiA %	32.71		32.51	
SiA %	15.40		15.49	
Ageing time	4h30mins		4h30mins	
Viscose Analysis:				

CiV (%)	9.71	9.14
SiV (%)	5.29	5.48
Actual AR	0.54	0.60
Kw after ripening	8.04	10.63
Ball Fall after ripening (s)	62.00	51.00
Zero - Shear Viscosity (Carreau-model) (cps)	10092	7749
Kw corrected for Ball Fall	7.13	11.46
Hottenroth after ripening (cc)	12.40	20.00

Table 21: Viscose data for enzyme only pulp batch 1

Pulp Type	Enzyme-Treated Batch 1			
Run	1	2	3	4
STEP 1: STEEPING PULP BLEND				
PULP 1				
Soda source	18.50	18.50	18.50	18.50
Moisture of pulp 1 (%)	7.84	7.84	7.84	7.84
Blend Percentage 1	100.00	100.00	100.00	100.00
Total Vol Soda Required (ml)	2960.00	2960.00	2960.00	2960.00
Vol required (ml)	2960.00	2960.00	2960.00	2960.00
Density of Soda Source	1.2006	1.2006	1.2006	1.2006
Mass (g)	3553.78	3553.78	3553.78	3553.78
Required consistency (%)	5.00	5.00	5.00	5.00
Mass of bone-dry pulp (g)	187.04	187.04	187.04	187.04

Mass of air-dry pulp required (g)	203.0		203.0		203.0		203.0	
PEG DOSAGE								
Target Press Range (g)	5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515	
Press Range (g)	5509.70		5512.60				5502.40	
STEP 2: SHREDDING								
Shredding (min)	1 hr		1 hr		1 hr		1 hr	
Shredding Temp (^oC)	25		25		25		25	
Type of shredder								
ALKALISED CELLULOSE & PRESS SODA ANALYSIS								
% SiA	A	B	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0011	4.0020	4.0053	4.0034	4.0027	4.0042	4.0008	4.0062
Vol of NaOH (ml)	4.82	4.80	4.65	4.43	4.58	4.56	4.47	4.37
% Soda in alkalised cellulose	15.18	15.19	15.33	15.56	15.41	15.42	15.53	15.61
Average % SiA	15.18		15.44		15.42		15.57	
% CiA	A	B	A	B	A	B	A	B
Mass of filter paper before drying (g)	76.2372	76.5995	76.6470	53.4732	51.8332	53.4944	75.0188	75.8209
Mass of alkalised cellulose + F/P after drying (g)	77.5227	77.8871	77.8886	54.7146	53.1172	54.7692	76.2541	77.0624
Mass of cellulose (g)	1.2855	1.2876	1.2416	1.2414	1.2840	1.2748	1.2353	1.2415

% CiA	32.13	32.17	31.00	31.01	32.08	31.84	30.88	30.99
Average % CiA	32.15		31.00		31.96		30.93	
Total HemiCell in steep soda								
Bulk Density								
Time (min)	6.00		6.00		6.00		6.00	
Weight of Cylinder (g)	550.60		550.50		551.00		550.70	
Weight of Cylinder + Alkalised cellulose (g)	651.00		662.80		666.50		658.20	
Weight of Alkalised cellulose (g)	100.40		112.30		115.50		107.50	
Cylinder Volume (ml)	700.00		700.00		700.00		700.00	
Bulk Density (g/l)	143.43		160.43		165.00		153.57	
STEP 3: AGEING								
STEP 4: XANTHATION								
Xanthation time (min)	75		75		75		75	
Xanthation temp. (^oC)	30		30		30		30	
Dissolving temp. (^oC)	18		18		18		18	
Dissolving time (hr)	5.5		5.5		5.5		5.5	
Ripening at 18 ^oC (hr)	12		12		12		12	
Viscose Composition								
Target CiV (%)	9.40		9.40		9.40		9.40	
Target SiV (%)	5.60		5.60		5.60		5.60	

Target AR	0.60	0.60	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50	18.50	18.50
S.G of NaOH used	1.2006	1.2006	1.2006	1.2006
Alkalised cellulose Analysis				
% CiA	32.15	31.00	31.96	30.93
% SiA	15.18	15.44	15.42	15.57
% weight CS_2	33.00	33.00	33.00	33.00
Mass of Alkalised cellulose mercerised (g)	250.00	250.00	250.00	250.00
Mass of cell in Alkalised cellulose (g)	80.38	77.51	79.89	77.33
Mass of CS_2 required (g)	26.52	25.58	26.36	25.52
Volume of CS_2 required (ml)	21.03	20.28	20.91	20.24
Total mass of viscose to be made (g)	855.09	824.57	849.93	822.68
Mass of Soda solution to be added (g)	578.56	548.99	573.57	547.16
Mass of Soda for given mass of viscose (g)	47.88	46.18	47.60	46.07
Mass of Soda in Alkalised cellulose (g)	37.96	38.61	38.54	38.92
Mass of Soda to be added (g)	9.92	7.57	9.05	7.15

Mass of % w/w NaOH required (g)	53.65		40.91		48.94		38.67	
Volume of % w/w NaOH required (ml)	44.68		34.07		40.77		32.21	
Total volume of water required (ml)	524.92		508.08		524.62		508.49	
CHARGES REQUIRED FOR VISCOSE MAKING								
Alkali Cellulose (g)	250.00		250.00		250.00		250.00	
18.5% NaOH (ml)	44.7		34.1		40.8		32.2	
CS2 (ml)	21.0		20.3		20.9		20.2	
Water (ml)	524.9		508.1		524.6		508.5	
STEP 5: RIPENING								
Viscose Analysis:								
% CiV	A	B	A	B	A	B	A	B
Wet mass of viscose (g)	1.2037		1.2032		1.2080		1.2024	
Dry mass of viscose (g)	0.1110		0.1154		0.1115		0.1150	
% CiV	9.22		9.59		9.23		9.56	
% SiV	A	B	A	B	A	B	A	B
Mass of sample (g)	4.0037		4.0045		4.0014		4.0056	
Vol of NaOH (ml)	10.13		9.63		9.26		9.65	
% SiV	4.87		5.36		5.74		5.34	

Ball Fall	A	B	A	B	A	B	A	B
12 Hours	94.00	93.00	63.00	62.00	81.00	81.00	112.00	112.00
Average time (seconds)	93.50		62.50		81.00		112.00	
Hottenroth Number	A	B	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	11.50	11.50	14.30	14.30	17.50	17.60	9.20	9.10
Average Hottenroth No After Ripening (cc)	11.50		14.30		17.55		9.15	
Viscose Blockage Constant (Kw)								
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	4.00	7.50	10.00	3.00	10.00	3.00	8.00	3.75
40	5.00	8.00	12.00	3.33	12.00	3.33	10.00	4.00
50	6.00	8.33	13.00	3.85	14.00	3.57	11.00	4.55
60	7.00	8.57	14.00	4.29	16.00	3.75	12.00	5.00
70	8.00	8.75	15.00	4.67	17.00	4.12	14.00	5.00
80	9.00	8.89	17.00	4.71	18.00	4.44	15.00	5.33
90	10.00	9.00	18.00	5.00	19.00	4.74	16.00	5.63
K	51.0000		34.0000		34.0000		25.5000	
	34.0000		52.3077		24.2857		55.6364	
	24.2857		44.8352		18.2143		46.3636	

	18.2143		38.8571		37.5000		0.0000	
	14.1667		4.0000		33.3333		34.0000	
	11.3333		30.0000		29.8246		29.7500	
Average Kw	25.50		34.00		29.53		31.88	
Coulter Count Before Filtration	1	2	1	2	1	2	1	2
Zero - Shear Viscosity (Carreau-model)								
Zero - Shear Viscosity (cP)	15012		10251		13041		21636	
Zero - Shear Viscosity (cP)	15020		10078		13063		21347	
Zero - Shear Viscosity (cP)	15086		10112		13098		21085	
Average Zero - Shear Viscosity (cP)	15039		10147		13067		21356	
Alkalised cellulose & Press Soda Analysis:								
Hemi in Press Soda g/l	0.00		0.00		0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00		0.00		0.00	
Gamma Cellulose g/l*5	0.00		0.00		0.00		0.00	
Beta Cellulose g/l*5	0.00		0.00		0.00		0.00	
Bulk Density g/l	143.43		160.43		165.00		153.57	
Viscosity of AC before ageing (cps)	13.10		13.90		9.91		12.80	
Viscosity of AC going into xanthation (cps)	5.08		5.15		4.92		5.46	
DP of AC going into xanthation	324		329		311		353	

Hemi in Aged AC				
Hemi in Aged AC*2.5				
CiA %	32.15	31.00	31.96	30.93
SiA %	15.18	15.44	15.42	15.57
Ageing time	3h22mins	3h22mins	3h22mins	3h22mins
Viscose Analysis:				
CiV (%)	9.22	9.59	9.23	9.56
SiV (%)	4.87	5.36	5.74	5.34
Actual AR	0.53	0.56	0.62	0.56
Kw after ripening	25.50	34.00	29.53	31.88
Ball Fall after ripening (s)	93.50	62.50	81.00	112.00
Zero - Shear Viscosity (Carreau-model) (cps)	15039	10147	13067	21356
Kw corrected for Ball Fall	15.00	29.92	20.05	15.65
Hottenroth after ripening (cc)	11.50	14.30	17.55	9.15

Table 22: Viscose data for enzyme only pulp batch 2

Pulp Type	Enzyme-Treated Batch 2									
Run	1		2		3		5		6	
STEP 1: STEEPING PULP BLEND										
PULP 1										
Soda source	18.50		18.50		18.50		18.50		18.50	
Moisture of pulp 1 (%)	8.01		8.01		8.01		8.01		8.01	

Blend Percentage 1	100.00		100.00		100.00		100.00		100.00	
Total Vol Soda Required (ml)	2960.00		2960.00		2960.00		2960.00		2960.00	
Vol required (ml)	2960.00		2960.00		2960.00		2960.00		2960.00	
Density of Soda Source	1.2006		1.2006		1.2006		1.2006		1.2006	
Mass (g)	3553.78		3553.78		3553.78		3553.78		3553.78	
Required consistency (%)	5.00		5.00		5.00		5.00		5.00	
Mass of bone-dry pulp (g)	187.04		187.04		187.04		187.04		187.04	
Mass of air-dry pulp required (g)	203.3		203.3		203.3		203.3		203.3	
PEG DOSAGE										
Target Press Range (g)	5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515	
Press Range (g)	5514.40		5514.00		5514.00		5502.70		5511.20	
STEP 2: SHREDDING										
Shredding (min)	1 hr		1 hr		1 hr		1 hr		1 hr	
Shredding Temp (oC)	25		25		25		25		25	

Type of shredder										
ALKALISED CELLULOSE & PRESS SODA ANALYSIS										
% SiA	A	B	A	B	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0012	4.0049	4.0021	4.0008	4.0009	4.0019	4.0064	4.0073	4.0078	4.0026
Vol of NaOH (ml)	4.50	4.34	4.77	4.73	4.19	4.23	4.67	4.92	4.96	4.89
% Soda in alkalised cellulose	15.50	15.64	15.22	15.27	15.81	15.76	15.31	15.05	15.01	15.10
Average % SiA	15.57		15.24		15.78		15.18		15.06	
% CiA	A	B	A	B	A	B	A	B	A	B
Mass of filter paper before drying (g)	76.2338	76.5966	51.8183	53.4853	53.9703	75.8613	75.0540	75.8372	76.1205	76.6189
Mass of alkalised cellulose + F/P after drying (g)	77.5327	77.9002	53.1673	54.8306	55.2944	77.1886	76.3342	77.1364	77.4375	77.9315
Mass of cellulose (g)	1.2989	1.3036	1.3490	1.3453	1.3241	1.3273	1.2802	1.2992	1.3170	1.3126
% CiA	32.46	32.55	33.71	33.63	33.10	33.17	31.95	32.42	32.86	32.79
Average % CiA	32.51		33.67		33.13		32.19		32.83	

Total HemiCell in steep soda										
Bulk Density										
Time (min)	6.00		6.00		6.00		6.00		6.00	
Weight of Cylinder (g)	550.60		551.10		550.50		550.60		550.50	
Weight of Cylinder + Alkalised cellulose (g)	648.90		654.70		669.40		660.80		669.10	
Weight of Alkalised cellulose (g)	98.30		103.60		118.90		110.20		118.60	
Cylinder Volume (ml)	700.00		700.00		700.00		700.00		700.00	
Bulk Density (g/l)	140.43		148.00		169.86		157.43		169.43	
STEP 3: AGEING										
STEP 4: XANTHATION										
Xanthation time (min)	75		75		75		75		75	
Xanthation temp. (oC)	30		30		30		30		30	
Dissolving temp. (oC)	18		18		18		18		18	
Dissolving time (hr)	5.5		5.5		5.5		5.5		5.5	

Ripening at 18 oC (hr)	12		12		12		12		12	
Viscose Composition										
Target CiV (%)	9.40		9.40		9.40		9.40		9.40	
Target SiV (%)	5.60		5.60		5.60		5.60		5.60	
Target AR	0.60		0.60		0.60		0.60		0.60	
Concentration of NaOH in lab (% W/W)	18.50		18.50		18.50		18.50		18.50	
S.G of NaOH used	1.2006		1.2006		1.2006		1.2006		1.2006	
Alkalised cellulose Analysis										
% CiA	32.51		33.67		33.13		32.19		32.83	
% SiA	15.57		15.24		15.78		15.18		15.06	
% weight CS2	33.00		33.00		33.00		33.00		33.00	
Mass of Alkalised cellulose mercerised (g)	250.00		250.00		250.00		250.00		250.00	
Mass of cell in Alkalised cellulose (g)	81.27		84.17		82.83		80.47		82.07	

Mass of CS2 required (g)	26.82		27.77		27.33		26.55		27.08	
Volume of CS2 required (ml)	21.27		22.03		21.68		21.06		21.48	
Total mass of viscose to be made (g)	864.53		895.39		881.14		856.05		873.07	
Mass of Soda solution to be added (g)	587.72		617.61		603.81		579.49		595.98	
Mass of Soda for given mass of viscose (g)	48.41		50.14		49.34		47.94		48.89	
Mass of Soda in Alkalised cellulose (g)	38.92		38.11		39.46		37.95		37.64	
Mass of Soda to be added (g)	9.49		12.03		9.88		9.99		11.25	
Mass of % w/w NaOH required (g)	51.32		65.03		53.42		54.01		60.83	
Volume of % w/w NaOH required (ml)	42.74		54.16		44.49		44.98		50.66	
Total volume of water required (ml)	536.40		552.58		550.39		525.49		535.16	
CHARGES REQUIRED FOR VISCOSE MAKING										

Alkali Cellulose (g)	250.00		250.00		250.00		250.00		250.00	
18.5% NaOH (ml)	42.7		54.2		44.5		45.0		50.7	
CS2 (ml)	21.3		22.0		21.7		21.1		21.5	
Water (ml)	536.4		552.6		550.4		525.5		535.2	
STEP 5: RIPENING										
Viscose Analysis:										
% CiV	A	B	A	B	A	B	A	B	A	B
Wet mass of viscose (g)	1.2059		1.2033		1.2023		1.2051		1.2020	
Dry mass of viscose (g)	0.1145		0.1152		0.1061		0.1156		0.1124	
% CiV	9.49		9.57		8.82		9.59		9.35	
% SiV	A	B	A	B	A	B	A	B	A	B
Mass of sample (g)	4.0055		4.0047		4.0065		4.0057		4.0019	
Vol of NaOH (ml)	9.52		9.71		9.59		9.65		9.70	
% SiV	5.47		5.28		5.40		5.34		5.30	
Ball Fall	A	B	A	B	A	B	A	B	A	B
12 Hours	94.00	94.00	98.00	98.00	53.00	52.00	78.00	79.00	58.00	59.00
Average time (seconds)	94.00		98.00		52.50		78.50		58.50	

Hottenroth Number	A	B	A	B	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	11.10	11.10	12.30	12.30	21.20	21.20	9.20	9.30	17.70	17.70
Average Hottenroth No After Ripening (cc)	11.10		12.30		21.20		9.25		17.70	
Viscose Blockage Constant (Kw)										
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	10.00	3.00	14.00	2.14	14.00	2.14	11.00	2.73	18.00	1.67
40	13.00	3.08	18.00	2.22	17.00	2.35	13.00	3.08	22.00	1.82
50	16.00	3.13	22.00	2.27	20.00	2.50	15.00	3.33	25.00	2.00
60	19.00	3.16	26.00	2.31	22.00	2.73	17.00	3.53	28.00	2.14
70	21.00	3.33	30.00	2.33	24.00	2.92	18.00	3.89	30.00	2.33
80	23.00	3.48	33.00	2.42	26.00	3.08	19.00	4.21	32.00	2.50
90	25.00	3.60	36.00	2.50	28.00	3.21	20.00	4.50	34.00	2.65
K	7.8462		8.0952		21.4286		35.643		15.4545	

	4.9038		5.1515		15.0000		26.1538		18.5455	
	3.3553		3.5664		23.1818		20.0000		14.5714	
	17.8947		2.6154		19.3182		36.6667		19.4286	
	14.7826		9.2727		16.3462		32.8070		17.0000	
	12.4174		7.7273		14.0110		29.5263		15.0000	
Average Kw	10.20		6.07		18.21		30.14		16.67	
Coulter Count Before Filtration	1	2	1	2	1	2	1	2	1	2
Zero - Shear Viscosity (Carreau-model)										
Zero - Shear Viscosity (cP)	14236		17179		8383		13793		10643	
Zero - Shear Viscosity (cP)	14355		17117		8365		13272		10483	
Zero - Shear Viscosity (cP)	14417		17036		8364		13270		10442	
Average Zero - Shear Viscosity (cP)	14336		17111		8371		13445		10523	
Alkalised cellulose & Press Soda Analysis:										

Hemi in Press Soda g/l	0.00		0.00		0.00		0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00		0.00		0.00		0.00	
Gamma Cellulose g/l*5	0.00		0.00		0.00		0.00		0.00	
Beta Cellulose g/l*5	0.00		0.00		0.00		0.00		0.00	
Bulk Density g/l	140.43		148.00		169.86		157.43		169.43	
Viscosity of AC before ageing (cps)	13.04		13.90		12.80		13.59		12.63	
Viscosity of AC going into xanthation (cps)	5.27		5.51		4.96		4.94		5.17	
DP of AC going into xanthation	339		357		314		312		331	
Hemi in Aged AC										
Hemi in Aged AC*2.5										
CiA %	32.51		33.67		33.13		32.19		32.83	
SiA %	15.57		15.24		15.78		15.18		15.06	
Ageing time	3h40 mins		3h40 mins		3h40 mins		4hrs		4hrs	
Viscose Analysis:										
CiV (%)	9.49		9.57		8.82		9.59		9.35	

SiV (%)	5.47		5.28		5.40		5.34		5.30	
Actual AR	0.58		0.55		0.61		0.56		0.57	
Kw after ripening	10.20		6.07		18.21		30.14		16.67	
Ball Fall after ripening (s)	94.00		98.00		52.50		78.50		58.50	
Zero - Shear Viscosity (Carreau-model) (cps)	14336		17111		8371		13445		10523	
Kw corrected for Ball Fall	5.97		3.41		19.08		21.11		15.67	
Hottenroth after ripening (cc)	11.10		12.30		21.20		9.25		17.70	

Table 23: Viscose data for kneading only pulp batch 1

Pulp Type	Kneaded Treated Batch 1				
Run	1	2	3	4	5
STEP 1: STEEPING PULP BLEND					
PULP 1					
Soda source	18.50	18.50	18.50	18.50	18.50
Moisture of pulp 1 (%)	8.01	8.01	8.01	8.01	8.01
Blend Percentage 1	100.00	100.00	100.00	100.00	100.00
Total Vol Soda Required (ml)	2960.00	2960.00	2960.00	2960.00	2960.00

Vol required (ml)	2960.00		2960.00		2960.00		2960.00		2960.00	
Density of Soda Source	1.2006		1.2006		1.2006		1.2006		1.2006	
Mass (g)	3553.78		3553.78		3553.78		3553.78		3553.78	
Required consistency (%)	5.00		5.00		5.00		5.00		5.00	
Mass of bone-dry pulp (g)	187.04		187.04		187.04		187.04		187.04	
Mass of air-dry pulp required (g)	203.3		203.3		203.3		203.3		203.3	
PEG DOSAGE										
Target Press Range (g)	5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515	
Press Range (g)	5514.40		5514.00		5513.90		5513.90			
STEP 2: SHREDDING										
Shredding (min)	1 hr		1 hr		1 hr		1 hr		1 hr	
Shredding Temp (^{o}C)	25		25		25		25		25	
Type of shredder										
ALKALISED CELLULOSE & PRESS SODA ANALYSIS										
% SiA	A	B	A	B	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0036	4.0034	4.0052	4.0085	4.0006	4.0032	4.0055	4.0010	4.0012	4.0025
Vol of NaOH (ml)	4.63	4.61	4.56	4.62	4.77	4.89	4.49	4.38	4.69	4.57
% Soda in alkalised cellulose	15.36	15.38	15.42	15.35	15.23	15.10	15.49	15.62	15.31	15.42

Average % SiA	15.37		15.38		15.16		15.55		15.36	
% CiA	A	B	A	B	A	B	A	B	A	B
Mass of filter paper before drying (g)	51.8260	53.5015	75.6680	56.2124	53.9806	75.8698	76.6344	67.7083	54.4265	76.4582
Mass of alkalised cellulose + F/P after drying (g)	53.1219	54.7870	76.9903	57.5386	55.2915	77.1831	77.9295	68.9983	55.7632	77.7958
Mass of cellulose (g)	1.2959	1.2855	1.3223	1.3262	1.3109	1.3133	1.2951	1.2900	1.3367	1.3376
% CiA	32.37	32.11	33.01	33.08	32.77	32.81	32.33	32.24	33.41	33.42
Average % CiA	32.24		33.05		32.79		32.29		33.41	
Total HemiCell in steep soda										
Bulk Density										
Time (min)	6.00		6.00		6.00		6.00		6.00	
Weight of Cylinder (g)	550.90		550.50		550.50		550.50		550.70	
Weight of Cylinder + Alkalised cellulose (g)	706.90		670.50		668.80		669.40		658.70	
Weight of Alkalised cellulose (g)	156.00		120.00		118.30		118.90		108.00	
Cylinder Volume (ml)	700.00		700.00		700.00		700.00		700.00	
Bulk Density (g/l)	222.86		171.43		169.00		169.86		154.29	

STEP 3: AGEING					
STEP 4: XANTHATION					
Xanthation time (min)	75	75	75	75	75
Xanthation temp. (^oC)	30	30	30	30	30
Dissolving temp. (^oC)	18	18	18	18	18
Dissolving time (hr)	5.5	5.5	5.5	5.5	5.5
Ripening at 18 ^oC (hr)	12	12	12	12	12
Viscose Composition					
Target CiV (%)	9.40	9.40	9.40	9.40	9.40
Target SiV (%)	5.60	5.60	5.60	5.60	5.60
Target AR	0.60	0.60	0.60	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50	18.50	18.50	18.50
S.G of NaOH used	1.2006	1.2006	1.2006	1.2006	1.2006
Alkalised cellulose Analysis					
% CiA	32.24	33.05	32.79	32.29	33.41
% SiA	15.37	15.38	15.16	15.55	15.36
% weight CS_2	33.00	33.00	33.00	33.00	33.00
Mass of Alkalised cellulose mercerised (g)	250.00	250.00	250.00	250.00	250.00

Mass of cell in Alkalised cellulose (g)	80.60	82.62	81.97	80.72	83.53
Mass of CS_2 required (g)	26.60	27.27	27.05	26.64	27.57
Volume of CS_2 required (ml)	21.09	21.62	21.45	21.12	21.86
Total mass of viscose to be made (g)	857.43	878.98	871.99	858.71	888.65
Mass of Soda solution to be added (g)	580.83	601.71	594.94	582.07	611.09
Mass of Soda for given mass of viscose (g)	48.02	49.22	48.83	48.09	49.76
Mass of Soda in Alkalised cellulose (g)	38.42	38.46	37.91	38.88	38.41
Mass of Soda to be added (g)	9.60	10.76	10.92	9.21	11.36
Mass of % w/w NaOH required (g)	51.89	58.18	59.05	49.77	61.39
Volume of % w/w NaOH required (ml)	43.22	48.46	49.19	41.45	51.13
Total volume of water required (ml)	528.94	543.53	535.89	532.31	549.69
CHARGES REQUIRED FOR VISCOSE MAKING					
Alkali Cellulose (g)	250.00	250.00	250.00	250.00	250.00
18.5% NaOH (ml)	43.2	48.5	49.2	41.5	51.1
CS2 (ml)	21.1	21.6	21.5	21.1	21.9
Water (ml)	528.9	543.5	535.9	532.3	549.7

STEP 5: RIPENING									
Viscose Analysis:									
% CiV	A	B	A	B	A	B	A	B	A	B
Wet mass of viscose (g)	1.2042		1.2016		1.2042		1.2026		1.2051	
Dry mass of viscose (g)	0.1129		0.1132		0.1140		0.1134		0.1133	
% CiV	9.38		9.42		9.47		9.43		9.40	
% SiV	A	B	A	B	A	B	A	B	A	B
Mass of sample (g)	4.0016		4.0009		4.0000		4.0022		4.0081	
Vol of NaOH (ml)	9.49		9.35		9.72		9.79		9.57	
% SiV	5.51		5.65		5.28		5.21		5.42	
Ball Fall	A	B	A	B	A	B	A	B	A	B
12 Hours	108.00	108.00	74.00	73.00	46.00	45.00	49.00	49.00	85.00	84.00
Average time (seconds)	108.00		73.50		45.50		49.00		84.50	
Hottenroth Number	A	B	A	B	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	21.00	21.00	24.00	24.00	13.80	13.80	11.60	11.70	16.90	16.80
Average Hottenroth No After Ripening (cc)	21.00		24.00		13.80		11.65		16.85	
Viscose Blockage Constant (Kw)										

Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	15.00	2.00	14.00	2.14	14.00	2.14	20.00	1.50	12.00	2.50
40	19.00	2.11	17.00	2.35	17.00	2.35	23.00	1.74	15.00	2.67
50	22.00	2.27	20.00	2.50	19.00	2.63	26.00	1.92	17.00	2.94
60	25.00	2.40	23.00	2.61	20.00	3.00	29.00	2.07	19.00	3.16
70	28.00	2.50	25.00	2.80	21.00	3.33	31.00	2.26	21.00	3.33
80	32.00	2.50	27.00	2.96	22.00	3.64	34.00	2.35	23.00	3.48
90	35.00	2.57	29.00	3.10	23.00	3.91	36.00	2.50	25.00	3.60
K	10.7368		21.4286		21.4286		24.3913		17.0000	
	17.0813		15.0000		28.4211		18.7625		28.0000	
	12.9818		11.0870		37.5789		14.8806		22.1053	
	10.2000		19.5130		34.0000		19.2881		17.8947	
	0.0000		16.6222		30.9091		9.6774		14.7826	
	7.2857		14.3295		28.2213		15.0000		12.4174	
Average Kw	9.71		16.33		30.09		17.00		18.70	
Coulter Count Before Filtration	1	2	1	2	1	2	1	2	1	2

Zero - Shear Viscosity (Carreau-model)					
Zero - Shear Viscosity (cP)	17113	12502	7667	8963	15442
Zero - Shear Viscosity (cP)	17144	12282	7351	8901	15330
Zero - Shear Viscosity (cP)	17168	12254	7508	8898	15342
Average Zero - Shear Viscosity (cP)	17142	12346	7509	8921	15371
Alkalised cellulose & Press Soda Analysis:					
Hemi in Press Soda g/l	0.00	0.00	0.00	0.00	0.00
Hemi in Press Soda g/l*5	0.00	0.00	0.00	0.00	0.00
Gamma Cellulose g/l*5	0.00	0.00	0.00	0.00	0.00
Beta Cellulose g/l*5	0.00	0.00	0.00	0.00	0.00
Bulk Density g/l	222.86	171.43	169.00	169.86	154.29
Viscosity of AC before ageing (cps)	22.39	18.39	17.45	20.52	19.16
Viscosity of AC going into xanthation (cps)	5.44	5.39	5.44	5.96	5.67
DP of AC going into xanthation	352	348	352	389	369
Hemi in Aged AC					
Hemi in Aged AC*2.5					
CiA %	32.24	33.05	32.79	32.29	33.41
SiA %	15.37	15.38	15.16	15.55	15.36

Ageing time	3h38mins	3h38mins	4hrs	4hrs	4hrs
Viscose Analysis:					
CiV (%)	9.38	9.42	9.47	9.43	9.40
SiV (%)	5.51	5.65	5.28	5.21	5.42
Actual AR	0.59	0.60	0.56	0.55	0.58
Kw after ripening	9.71	16.33	30.09	17.00	18.70
Ball Fall after ripening (s)	108.00	73.50	45.50	49.00	84.50
Zero - Shear Viscosity (Carreau-model) (cps)	17142	12346	7509	8921	15371
Kw corrected for Ball Fall	4.95	12.22	36.38	19.08	12.17
Hottenroth after ripening (cc)	21.00	24.00	13.80	11.65	16.85

Table 24: Viscose data for kneading only pulp batch 2

Pulp Type	**Kneaded Treated Batch 2**			
Run	**1**	**2**	**3**	**4**
STEP 1: STEEPING PULP BLEND				
PULP 1				
Soda source	18.50	18.50	18.50	18.50
Moisture of pulp 1 (%)	7.85	8.01	8.01	8.01

Blend Percentage 1	100.00		100.00		100.00		100.00	
Total Vol Soda Required (ml)	2960.00		2960.00		2960.00		2960.00	
Vol required (ml)	2960.00		2960.00		2960.00		2960.00	
Density of Soda Source	1.2006		1.2006		1.2006		1.2006	
Mass (g)	3553.78		3553.78		3553.78		3553.78	
Required consistency (%)	5.00		5.00		5.00		5.00	
Mass of bone-dry pulp (g)	187.04		187.04		187.04		187.04	
Mass of air-dry pulp required (g)	203.0		203.3		203.3		203.3	
PEG DOSAGE								
Target Press Range (g)	5510 - 5515		5510 - 5515		5510 - 5515		5510 - 5515	
Press Range (g)	5515.00		5515.00		5507.20		5510.50	
STEP 2: SHREDDING								
Shredding (min)	1 hr		1 hr		1 hr		1 hr	
Shredding Temp (^{o}C)	25		25		25		25	
Type of shredder								
ALKALISED CELLULOSE & PRESS SODA ANALYSIS								
% SiA	A	B	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0049	4.0073	4.0067	4.0029	4.0026	4.0038	4.0029	4.0054
Vol of NaOH (ml)	4.66	5.10	4.58	4.70	4.63	4.81	4.79	4.65
% Soda in alkalised cellulose	15.32	14.87	15.39	15.29	15.36	15.18	15.20	15.33
Average % SiA	15.10		15.34		15.27		15.26	

% CiA	A	B	A	B	A	B	A	B
Mass of filter paper before drying (g)	77.1105	73.2537	76.8556	76.5949	75.0141	75.8263	75.6516	74.8527
Mass of alkalised cellulose + F/P after drying (g)	78.4664	74.5860	78.1878	77.9331	76.3042	77.1210	76.9615	76.1679
Mass of cellulose (g)	1.3559	1.3323	1.3322	1.3382	1.2901	1.2947	1.3099	1.3152
% CiA	33.86	33.25	33.25	33.43	32.23	32.34	32.72	32.84
Average % CiA	33.55		33.34		32.28		32.78	
Total HemiCell in steep soda								
Bulk Density								
Time (min)	6.00		6.00		6.00		6.00	
Weight of Cylinder (g)	550.80		550.70		550.70		550.50	
Weight of Cylinder + Alkalised cellulose (g)	644.40		646.40		650.40		647.60	
Weight of Alkalised cellulose (g)	93.60		95.70		99.70		97.10	
Cylinder Volume (ml)	700.00		700.00		700.00		700.00	
Bulk Density (g/l)	133.71		136.71		142.43		138.71	
STEP 3: AGEING								
STEP 4: XANTHATION								

Xanthation time (min)	75	75	75	75
Xanthation temp. (°C)	30	30	30	30
Dissolving temp. (°C)	18	18	18	18
Dissolving time (hr)	5.5	5.5	5.5	5.5
Ripening at 18 °C (hr)	12	12	12	12
Viscose Composition				
Target CiV (%)	9.40	9.40	9.40	9.40
Target SiV (%)	5.60	5.60	5.60	5.60
Target AR	0.60	0.60	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50	18.50	18.50
S.G of NaOH used	1.2006	1.2006	1.2006	1.2006
Alkalised cellulose Analysis				
% CiA	33.55	33.34	32.28	32.78
% SiA	15.10	15.34	15.27	15.26
% weight CS_2	33.00	33.00	33.00	33.00
Mass of Alkalised cellulose mercerised (g)	250.00	250.00	250.00	250.00
Mass of cell in Alkalised cellulose (g)	83.88	83.35	80.71	81.95
Mass of CS_2 required (g)	27.68	27.51	26.63	27.04
Volume of CS_2 required (ml)	21.95	21.81	21.12	21.45

Total mass of viscose to be made (g)	892.33		886.70		858.62		871.80	
Mass of Soda solution to be added (g)	614.65		609.20		581.99		594.76	
Mass of Soda for given mass of viscose (g)	49.97		49.66		48.08		48.82	
Mass of Soda in Alkalised cellulose (g)	37.74		38.35		38.17		38.16	
Mass of Soda to be added (g)	12.23		11.30		9.91		10.66	
Mass of % w/w NaOH required (g)	66.10		61.09		53.59		57.62	
Volume of % w/w NaOH required (ml)	55.05		50.88		44.63		48.00	
Total volume of water required (ml)	548.55		548.11		528.40		537.13	
CHARGES REQUIRED FOR VISCOSE MAKING								
Alkali Cellulose (g)	250.00		250.00		250.00		250.00	
18.5% NaOH (ml)	55.1		50.9		44.6		48.0	
CS2 (ml)	22.0		21.8		21.1		21.4	
Water (ml)	548.6		548.1		528.4		537.1	
STEP 5: RIPENING								
Viscose Analysis:								
% CiV	A	B	A	B	A	B	A	B
Wet mass of viscose (g)	1.2035		1.2067		1.2013		1.2030	

Dry mass of viscose (g)	0.1154		0.1152		0.1123		0.1135	
% CiV	9.59		9.55		9.35		9.43	
% SiV	A	B	A	B	A	B	A	B
Mass of sample (g)	4.0050		4.0000		4.0020		4.0078	
Vol of NaOH (ml)	9.68		9.43		9.62		9.69	
% SiV	5.31		5.57		5.38		5.30	
Ball Fall	A	B	A	B	A	B	A	B
12 Hours	81.00	81.00	70.00	69.00	79.00	79.00	73.00	74.00
Average time (seconds)	81.00		69.50		79.00		73.50	
Hottenroth Number	A	B	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	18.50	18.20	9.50	9.70	12.50	12.40	16.80	16.90
Average Hottenroth No After Ripening (cc)	18.35		9.60		12.45		16.85	
Viscose Blockage Constant (Kw)								
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	18.00	1.67	15.00	2.00	11.00	2.73	20.00	1.50
40	23.00	1.74	19.00	2.11	13.00	3.08	25.00	1.60
50	27.00	1.85	22.00	2.27	15.00	3.33	30.00	1.67
60	30.00	2.00	25.00	2.40	17.00	3.53	33.00	1.82

70	34.00	2.06	28.00	2.50	18.00	3.89	37.00	1.89
80	38.00	2.11	30.00	2.67	20.00	4.00	41.00	1.95
90	41.00	2.20	33.00	2.73	21.00	4.29	44.00	2.05
K	7.3913		10.7368		35.6643		10.2000	
	11.4976		17.0813		26.1538		6.8000	
	15.1111		12.9818		20.0000		15.4545	
	6.0000		10.2000		36.6667		7.5184	
	4.7368		17.0000		11.3333		6.0514	
	9.1656		6.1818		29.1429		9.6120	
Average Kw	8.98		12.36		26.49		9.27	
Coulter Count Before Filtration	1	2	1	2	1	2	1	2
Zero - Shear Viscosity (Carreau-model)								
Zero - Shear Viscosity (cP)	12234		12761		13269		12407	
Zero - Shear Viscosity (cP)	12303		12690		13304		12497	
Zero - Shear Viscosity (cP)	12188		12670		13399		12508	
Average Zero - Shear Viscosity (cP)	12242		12707		13324		12471	
Alkalised cellulose & Press Soda Analysis:								
Hemi in Press Soda g/l	0.00		0.00		0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00		0.00		0.00	

Gamma Cellulose g/l*5	0.00	0.00	0.00	0.00
Beta Cellulose g/l*5	0.00	0.00	0.00	0.00
Bulk Density g/l	133.71	136.71	142.43	138.71
Viscosity of AC before ageing (cps)	16.85	16.10	19.42	19.25
Viscosity of AC going into xanthation (cps)	5.54	5.80	5.36	5.27
DP of AC going into xanthation	359	378	346	339
Hemi in Aged AC				
Hemi in Aged AC*2.5				
CiA %	33.55	33.34	32.28	32.78
SiA %	15.10	15.34	15.27	15.26
Ageing time	4hrs	4hrs	4h20mins	4h20mins
Viscose Analysis:				
CiV (%)	9.59	9.55	9.35	9.43
SiV (%)	5.31	5.57	5.38	5.30
Actual AR	0.55	0.58	0.58	0.56
Kw after ripening	8.98	12.36	26.49	9.27
Ball Fall after ripening (s)	81.00	69.50	79.00	73.50
Zero - Shear Viscosity (Carreau-model) (cps)	12242	12707	13324	12471
Kw corrected for Ball Fall	6.10	9.78	18.44	6.94
Hottenroth after ripening (cc)	18.35	9.60	12.45	16.85

Table 25: Viscose data for kneaded followed by enzyme batch 1

Pulp Type	**Kneaded and Enzyme-Treated Batch 1**		
Run	**1**	**2**	**3**
STEP 1: STEEPING PULP BLEND			
PULP 1			
Soda source	18.50	18.50	18.50
Moisture of pulp 1 (%)	7.75	7.75	7.75
Blend Percentage 1	100.00	100.00	100.00
Total Vol Soda Required (ml)	2960.00	2960.00	2960.00
Vol required (ml)	2960.00	2960.00	2960.00
Density of Soda Source	1.2006	1.2006	1.2006
Mass (g)	3553.78	3553.78	3553.78
Required consistency (%)	5.00	5.00	5.00
Mass of bone-dry pulp (g)	187.04	187.04	187.04
Mass of air-dry pulp required (g)	202.8	202.8	202.8
PEG DOSAGE			
Target Press Range (g)	5510 - 5515	5510 - 5515	5510 - 5515
Press Range (g)	5508.50	5511.20	5500.40
STEP 2: SHREDDING			
Shredding (min)	1 hr	1 hr	1 hr
Shredding Temp (^{o}C)	25	25	25
Type of shredder			

ALKALISED CELLULOSE & PRESS SODA ANALYSIS						
% SiA	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0027	4.0013	4.0042	4.0068	4.0010	4.0024
Vol of NaOH (ml)	4.33	4.35	4.54	4.63	4.47	4.51
% Soda in alkalised cellulose	15.66	15.64	15.44	15.34	15.53	15.48
Average % SiA	15.65		15.39		15.50	
% CiA	A	B	A	B	A	B
Mass of filter paper before drying (g)	75.0280	75.8361	77.1055	73.2125	75.0246	75.8254
Mass of alkalised cellulose + F/P after drying (g)	76.3631	77.1877	78.3912	74.4980	76.3177	77.1475
Mass of cellulose (g)	1.3351	1.3516	1.2857	1.2855	1.2931	1.3221
% CiA	33.35	33.78	32.11	32.08	32.32	33.03
Average % CiA	33.57		32.10		32.68	
Total HemiCell in steep soda						
Bulk Density						
Time (min)	6.00		6.00		6.00	
Weight of Cylinder (g)	550.50		550.50		550.20	
Weight of Cylinder + Alkalised cellulose (g)	648.70		671.80		663.00	
Weight of Alkalised cellulose (g)	98.20		121.30		112.80	
Cylinder Volume (ml)	700.00		700.00		700.00	

Bulk Density (g/l)	140.29	173.29	161.14
STEP 3: AGEING			
STEP 4: XANTHATION			
Xanthation time (min)	75	75	75
Xanthation temp. (^oC)	30	30	30
Dissolving temp. (^oC)	18	18	18
Dissolving time (hr)	5.5	5.5	5.5
Ripening at 18 ^oC (hr)	12	12	12
Viscose Composition			
Target CiV (%)	9.40	9.40	9.40
Target SiV (%)	5.60	5.60	5.60
Target AR	0.60	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50	18.50
S.G of NaOH used	1.2006	1.2006	1.2006
Alkalised cellulose Analysis			
% CiA	33.57	32.10	32.68
% SiA	15.65	15.39	15.50
% weight CS_2	33.00	33.00	33.00

Mass of Alkalised cellulose mercerised (g)	250.00		250.00		250.00	
Mass of cell in Alkalised cellulose (g)	83.92		80.24		81.69	
Mass of CS_2 required (g)	27.69		26.48		26.96	
Volume of CS_2 required (ml)	21.96		21.00		21.38	
Total mass of viscose to be made (g)	892.74		853.61		869.04	
Mass of Soda solution to be added (g)	615.05		577.13		592.09	
Mass of Soda for given mass of viscose (g)	49.99		47.80		48.67	
Mass of Soda in Alkalised cellulose (g)	39.13		38.48		38.76	
Mass of Soda to be added (g)	10.86		9.32		9.91	
Mass of % w/w NaOH required (g)	58.72		50.37		53.56	
Volume of % w/w NaOH required (ml)	48.91		41.95		44.61	
Total volume of water required (ml)	556.33		526.77		538.53	
CHARGES REQUIRED FOR VISCOSE MAKING						
Alkali Cellulose (g)	250.00		250.00		250.00	
18.5% NaOH (ml)	48.9		42.0		44.6	
CS2 (ml)	22.0		21.0		21.4	
Water (ml)	556.3		526.8		538.5	
STEP 5: RIPENING						
Viscose Analysis:						
% CiV	A	B	A	B	A	B
Wet mass of viscose (g)	1.2036		1.2063		1.2015	

Dry mass of viscose (g)	0.1123		0.1136		0.1127	
% CiV	9.33		9.42		9.38	
% SiV	A	B	A	B	A	B
Mass of sample (g)	4.0021		4.0017		4.0037	
Vol of NaOH (ml)	9.57		9.60		9.60	
% SiV	5.43		5.40		5.40	
Ball Fall	A	B	A	B	A	B
12 Hours	69.00	69.00	39.00	40.00	82.00	81.00
Average time (seconds)	69.00		39.50		81.50	
Hottenroth Number	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	12.50	12.70	16.50	16.60	17.60	17.50
Average Hottenroth No After Ripening (cc)	12.60		16.55		17.55	
Viscose Blockage Constant (Kw)						
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	16.00	1.88	18.00	1.67	14.00	2.14
40	21.00	1.90	23.00	1.74	18.00	2.22
50	25.00	2.00	27.00	1.85	21.00	2.38
60	29.00	2.07	32.00	1.88	25.00	2.40
70	32.00	2.19	36.00	1.94	28.00	2.50
80	36.00	2.22	40.00	2.00	30.00	2.67

90	38.00	2.37	43.00	2.09	33.00	2.73
K	3.0357		7.3913		8.0952	
	9.7143		11.4976		16.1905	
	7.0345		2.3611		1.9429	
	12.0905		7.0833		10.2000	
	3.5417		5.6667		17.0000	
	14.9123		9.4884		6.1818	
Average Kw	8.39		7.25		9.94	
Coulter Count Before Filtration	1	2	1	2	1	2
Zero - Shear Viscosity (Carreau-model)						
Zero - Shear Viscosity (cP)	12768		6585		16507	
Zero - Shear Viscosity (cP)	12806		6645		16077	
Zero - Shear Viscosity (cP)	12879		6618		16055	
Average Zero - Shear Viscosity (cP)	12818		6616		16213	
Alkalised cellulose & Press Soda Analysis:						
Hemi in Press Soda g/l	0.00		0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00		0.00	
Gamma Cellulose g/l*5	0.00		0.00		0.00	
Beta Cellulose g/l*5	0.00		0.00		0.00	
Bulk Density g/l	140.29		173.29		161.14	

Viscosity of AC before ageing (cps)	14.10	15.24	12.63
Viscosity of AC going into xanthation (cps)	5.19	5.12	5.17
DP of AC going into xanthation	333	327	331
Hemi in Aged AC			
Hemi in Aged AC*2.5			
CiA %	33.57	32.10	32.68
SiA %	15.65	15.39	15.50
Ageing time	4hrs	4hrs	4hrs
Viscose Analysis:			
CiV (%)	9.33	9.42	9.38
SiV (%)	5.43	5.40	5.40
Actual AR	0.58	0.57	0.58
Kw after ripening	8.39	7.25	9.94
Ball Fall after ripening (s)	69.00	39.50	81.50
Zero - Shear Viscosity (Carreau-model) (cps)	12818	6616	16213
Kw corrected for Ball Fall	6.69	10.09	6.70
Hottenroth after ripening (cc)	12.60	16.55	17.55

Table 26: Viscose data for kneaded followed by enzyme batch 2

Pulp Type	**Kneaded and Enzyme-Treated Batch 2**		
Run	**1**	**2**	**3**
STEP 1: STEEPING PULP BLEND			

PULP 1						
Soda source	18.50		18.50		18.50	
Moisture of pulp 1 (%)	7.92		7.92		7.92	
Blend Percentage 1	100.00		100.00		100.00	
Total Vol Soda Required (ml)	2960.00		2960.00		2960.00	
Vol required (ml)	2960.00		2960.00		2960.00	
Density of Soda Source	1.2006		1.2006		1.2006	
Mass (g)	3553.78		3553.78		3553.78	
Required consistency (%)	5.00		5.00		5.00	
Mass of bone-dry pulp (g)	187.04		187.04		187.04	
Mass of air-dry pulp required (g)	203.1		203.1		203.1	
PEG DOSAGE						
Target Press Range (g)	5510 - 5515		5510 - 5515		5510 - 5515	
Press Range (g)	5511.40		5514.30		5510.50	
STEP 2: SHREDDING						
Shredding (min)	1 hr		1 hr		1 hr	
Shredding Temp (^{o}C)	25		25		25	
Type of shredder						
ALKALISED CELLULOSE & PRESS SODA ANALYSIS						
% SiA	A	B	A	B	A	B
Mass of alkali cellulose (g)	4.0021	4.0019	4.0061	4.0050	4.0021	4.0044
Vol of NaOH (ml)	4.48	4.20	4.58	4.45	4.72	4.69

% Soda in alkalised cellulose	15.51	15.79	15.40	15.53	15.27	15.29
Average % SiA	15.65		15.46		15.28	
% CiA	A	B	A	B	A	B
Mass of filter paper before drying (g)	75.0154	75.8285	76.6189	76.1205	74.7987	76.4507
Mass of alkalised cellulose + F/P after drying (g)	76.3368	77.1338	77.9515	77.4575	76.0914	77.7571
Mass of cellulose (g)	1.3214	1.3053	1.3326	1.3370	1.2927	1.3064
% CiA	33.02	32.62	33.26	33.38	32.30	32.62
Average % CiA	32.82		33.32		32.46	
Total HemiCell in steep soda						
Bulk Density						
Time (min)	6.00		6.00		6.00	
Weight of Cylinder (g)	550.40		550.50		550.60	
Weight of Cylinder + Alkalised cellulose (g)	656.80		667.30		657.10	
Weight of Alkalised cellulose (g)	106.40		116.80		106.50	
Cylinder Volume (ml)	700.00		700.00		700.00	
Bulk Density (g/l)	152.00		166.86		152.14	
STEP 3: AGEING						
STEP 4: XANTHATION						

Xanthation time (min)	75	75	75
Xanthation temp. (°C)	30	30	30
Dissolving temp. (°C)	18	18	18
Dissolving time (hr)	5.5	5.5	5.5
Ripening at 18 °C (hr)	12	12	12
Viscose Composition			
Target CiV (%)	9.40	9.40	9.40
Target SiV (%)	5.60	5.60	5.60
Target AR	0.60	0.60	0.60
Concentration of NaOH in lab (% W/W)	18.50	18.50	18.50
S.G of NaOH used	1.2006	1.2006	1.2006
Alkalised cellulose Analysis			
% CiA	32.82	33.32	32.46
% SiA	15.65	15.46	15.28
% weight CS_2	33.00	33.00	33.00
Mass of Alkalised cellulose mercerised (g)	250.00	250.00	250.00
Mass of cell in Alkalised cellulose (g)	82.04	83.31	81.16
Mass of CS_2 required (g)	27.07	27.49	26.78
Volume of CS_2 required (ml)	21.47	21.80	21.24

Total mass of viscose to be made (g)	872.80		886.27		863.36	
Mass of Soda solution to be added (g)	595.73		608.78		586.58	
Mass of Soda for given mass of viscose (g)	48.88		49.63		48.35	
Mass of Soda in Alkalised cellulose (g)	39.13		38.66		38.21	
Mass of Soda to be added (g)	9.75		10.97		10.14	
Mass of % w/w NaOH required (g)	52.68		59.31		54.82	
Volume of % w/w NaOH required (ml)	43.88		49.40		45.66	
Total volume of water required (ml)	543.04		549.47		531.76	
CHARGES REQUIRED FOR VISCOSE MAKING						
Alkali Cellulose (g)	250.00		250.00		250.00	
18.5% NaOH (ml)	43.9		49.4		45.7	
CS2 (ml)	21.5		21.8		21.2	
Water (ml)	543.0		549.5		531.8	
STEP 5: RIPENING						
Viscose Analysis:						
% CiV	A	B	A	B	A	B
Wet mass of viscose (g)	1.2060		1.2034		1.2037	
Dry mass of viscose (g)	0.1122		0.1128		0.1109	
% CiV	9.30		9.37		9.21	

% SiV	A	B	A	B	A	B
Mass of sample (g)	4.0063		4.0025		4.0005	
Vol of NaOH (ml)	9.75		9.62		9.47	
% SiV	5.24		5.38		5.53	
Ball Fall	A	B	A	B	A	B
12 Hours	95.00	95.00	68.00	68.00	100.00	100.00
Average time (seconds)	95.00		68.00		100.00	
Hottenroth Number	A	B	A	B	A	B
Volume of Ammonium Chloride (ml)	10.50	10.60	11.02	11.02	15.60	15.60
Average Hottenroth No After Ripening (cc)	10.55		11.02		15.60	
Viscose Blockage Constant (Kw)						
Time (min)	Vol (ml)	t/v	Vol (ml)	t/v	Vol (ml)	t/v
30	16.00	1.88	17.00	1.76	12.00	2.50
40	19.00	2.11	20.00	2.00	14.00	2.86
50	22.00	2.27	22.00	2.27	16.00	3.13
60	25.00	2.40	24.00	2.50	18.00	3.33
70	29.00	2.41	27.00	2.59	20.00	3.50
80	32.00	2.50	29.00	2.76	22.00	3.64
90	34.00	2.65	31.00	2.90	23.00	3.91

K	23.4868		24.0000		36.4286	
	17.0813		27.8182		27.3214	
	12.9818		23.1818		21.2500	
	1.4069		9.4444		17.0000	
	8.7931		16.9349		13.9091	
	15.0000		14.7497		28.2213	
Average Kw	13.13		19.35		24.02	
Coulter Count Before Filtration	1	2	1	2	1	2
Zero - Shear Viscosity (Carreau-model)						
Zero - Shear Viscosity (cP)	16243		11933		16994	
Zero - Shear Viscosity (cP)	16283		11826		16999	
Zero - Shear Viscosity (cP)	16221		11726		16972	
Average Zero - Shear Viscosity (cP)	16249		11828		16988	
Alkalised cellulose & Press Soda Analysis:						
Hemi in Press Soda g/l	0.00		0.00		0.00	
Hemi in Press Soda g/l*5	0.00		0.00		0.00	
Gamma Cellulose g/l*5	0.00		0.00		0.00	
Beta Cellulose g/l*5	0.00		0.00		0.00	
Bulk Density g/l	152.00		166.86		152.14	
Viscosity of AC before ageing (cps)	15.59		13.97		13.53	
Viscosity of AC going into xanthation (cps)	5.46		5.44		5.44	

DP of AC going into xanthation	353	352	352
Hemi in Aged AC			
Hemi in Aged AC*2.5			
CiA %	32.82	33.32	32.46
SiA %	15.65	15.46	15.28
Ageing time	3h30mins	3h30mins	3h50mins
Viscose Analysis:			
CiV (%)	9.30	9.37	9.21
SiV (%)	5.24	5.38	5.53
Actual AR	0.56	0.57	0.60
Kw after ripening	13.13	19.35	24.02
Ball Fall after ripening (s)	95.00	68.00	100.00
Zero - Shear Viscosity (Carreau-model) (cps)	16249	11828	16988
Kw corrected for Ball Fall	7.60	15.65	13.21
Hottenroth after ripening (cc)	10.55	11.02	15.60