



Some Aspects on Pulp Pre-treatment Prior to Viscose Preparation

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Faculty of Technology and Science

Chemical Engineering

Karlstad University Studies | 2012:23

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LICENTIATE THESIS

Karlstad University Studies | 2012:23

ISSN 1403-8099

ISBN 978-91-7063-427-7

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Distribution:
Karlstad University
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Chemical Engineering
SE-651 88 Karlstad, Sweden
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Print: Universitetstryckeriet, Karlstad 2012

WWW.KAU.SE

Abstract

Large amounts of carbon disulphide are consumed in the conventional production of viscose. Until a novel, eco-friendly, wood-based process for the production of cellulose textile fibres has been developed and implemented, it is important to try to find ways to improve the conventional viscose process, e.g. in terms of reducing the carbon disulphide requirement of the process. The aim of this thesis was to reduce the amount of carbon disulphide consumed in the preparation of high-viscosity viscose by pre-treating pulps with enzymes. It also aimed at investigating and linking the different measurements of reactivity, i.e. gamma number, Fock reactivity and K_w , and determining the sensitivity of the gamma number to the hemicellulose content of pulp.

Reactivity was measured as Fock reactivity and gamma number. The gamma number of viscose solutions remained unchanged when an enzyme stage was used prior to the viscose process. The gamma number analysis was found to be selective not only to cellulose but also to the hemicellulosic material. It was verified that both cellulose and hemicellulose molecules in the pulp material were substituted in the viscose preparation stages, showing that the gamma number of the pulp is due to both substituted cellulose and substituted hemicelluloses. The mechanisms responsible for the Fock reactivity, or the filter-clogging value (K_w) on the one hand and the gamma number on the other, are probably not the same.

It was speculated that the analysis method employed in Fock's test and the filter-clogging value measure the results on a fibre level, whereas the gamma number measures changes mainly on a molecular level. This could explain the difference in the levels of reactivity found in this study.

Papers included in this thesis

This thesis is a summary of the following publications, referred to as Papers I to III.

I. Some Aspects of the Reactivity of Pulp Intended for High-Viscosity Viscose

Linda Östberg, Helena Håkansson and Ulf Germgård (2012).

Published in BioResources 7(1), 743-755.

II. Some Aspects of the Activation of Dissolving Pulps and the Influence on the Reactivity in a Following Viscose Preparation Stage

Linda Östberg and Ulf Germgård.

Submitted to O Papel.

III. The Influence of the Hemicellulose Content in Dissolving Pulps on the Gamma Number of Viscose Dopes

Linda Östberg, Niklas Kvarnlöf and Ulf Germgård.

Submitted to Nordic Pulp & Paper Research Journal

Linda Östberg's contribution to the papers

Linda Östberg performed all the experimental work and is the main author of all three papers.

Other publications by the same author

Dissolution of Dissolving Pulps in Alkaline Solvents after Enzyme Pretreatments

Helene Almlöf Ambjörnsson, Linda Östberg and Ulf Germgård.
The manuscript is being prepared for submission.

Activation of Dissolving Pulp with Enzymes Prior to Preparation of High Viscosity Viscose

Linda Östberg, Helena Håkansson and Ulf Germgård.

Paper was presented at the 4th Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives at Karlstad University, Karlstad, Sweden on Nov. 17-18, 2009.

Enzyme Activation of Pulp and its Influence on the Gamma Number of Viscose

Linda Östberg, Helena Håkansson and Ulf Germgård.

Poster presented at the IAWS 2011, Stockholm, Sweden on Aug. 31 to Sept. 2, 2011.

Lab-scale Preparation of High Viscosity Viscose at Karlstad University

Linda Östberg, Helena Håkansson and Ulf Germgård.

Poster presented at the annual meeting of IAWS, Stockholm, Sweden on Aug. 31 to Sept. 2, 2011.

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Poster presented at the 1st Avancell Conference, Gothenburg, Sweden on Oct. 18-19, 2011.

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1 Introduction

1.1 Background

Cellulose is a natural, organic, polymer found in trees, plants etc., from which different types of cellulose-based fibres could be obtained. It has been estimated that nature produces approximately 180 billion tons of cellulose every year (Engelhardt 1995). Accordingly, cellulose is the most common polymer on earth.

Man makes use of the cellulose in many ways – in the form of planks as a construction material, in the form of fibres as a raw material for paper and board, in the form of wood as well as waste-paper as a bioenergy source. In addition, chemical pulp could be purified into regenerated cellulose, referred to as viscose.

In order to manufacture viscose wood need to be chipped and subjected to a chemical pulping process. Either an acidic sulphite process or a prehydrolysis kraft pulping process could be used for the manufacture of dissolving pulp, the raw material for the viscose process. Both softwood and hardwood could be used as raw material for dissolving pulp.

1.2 Manufacture of regenerated cellulose

Regeneration of cellulose has two major objectives. One is to purify the dissolving pulp starting material from any remaining lignin and/or hemicellulose and the other to transform a biological fibre built up of cellulose molecules into a sample of cellulose molecules only, without the biological ultra-structure.

In order to prepare the regenerated cellulose two different options prevail. One is to use a direct solvent system in which the cellulose of the dissolving pulp is dissolved directly in the solvent to form a spinning solution which is then spun through pressing the solution through narrow spinning nozzles. The second alternative is to use an indirect solvent process in which a cellulose derivative is first formed from the cellulose. The cellulose derivative is then dissolved in a solvent to prepare a spinning solution before being used in a spinning process.

Many processes have been developed with the aim of preparing regenerated cellulose fibres from natural cellulose. Some of them, for example Lyocell, have been studied further in an industrial context. Despite that these alternative

processes exist, the conventional viscose method is the dominating process today. It is dominating even with the obvious environmental and health problems associated with carbon disulphide. Until a final solution with an implemented eco-friendly viscose process becomes reality, it is important to try to find ways to improve the conventional viscose process towards less carbon disulphide requirements.

1.3 Why viscose?

Viscose textiles became very popular and the global consumption increased steadily and was at its peak immediately after the Second World War (Danielsson 2008; Bauer 1960). However, with the advantage of cheap oil on the market after the war, oil took over as preferred raw material for textile production and textile fibre production based on dissolving pulp lost in popularity. Oil was simply too cheap for any other material to compete. However, unlike pulp mills for paper pulp, dissolving pulp mills were usually quite small which indicated a less developed competitiveness. In addition the environmental aspects – not least the occupational health and safety issues for the workers in viscose mills – were problematic. Altogether this meant that viscose production has nearly disappeared from Europe while the corresponding capacity has moved to Asia and especially China (Aizenstein 2011), where environmental legislation is less strict and labour is less expensive.

Another alternative to cellulose-based textile fibres is cotton. It consists almost of pure cellulose. Cotton, however, is grown mostly in areas with scarcity of water and where the land is required for producing food for growing populations. Its cultivation has a major impact on the environment, and particularly so in India and Uzbekistan. In the period 1997-2001 the volume of water that was required to meet the world consumption of cotton was $2.56 \cdot 10^{11} \text{m}^3$ p.a. (Chapagain *et al.* 2006). As awareness of the importance of the water footprint of cotton production increases in a globally heated world, as oil prices sky rockets and as the viscose production processes are being developed the interest in viscose has seen a new dawn since around 2005. However, in order to completely sweep out cotton a novel eco-friendly wood-based process for the production of cellulose textile fibres will be required. Until this becomes reality there are good reasons to develop the conventional viscose process e.g. in terms of reducing the carbon disulphide requirement of the process.

1.4 History: Producing synthetic fibre from cellulose

1.4.1 Cuproammonium rayon

In 1857 M.E. Schwitzer dissolved cellulose, copper oxide and ammonium in a solution. His intention was to form a filament for a light bulb, but nowadays he is credited for discovering cuproammonium rayon. Cuproammonium rayon is formed basically by mixing cellulose, cupric oxide and ammonium before forcing the resulting substance through a spinneret so that it is extruded into filaments. The fine yarn produced is generally known under the brand name Bemberg. This fibre is the rayon fibre that resembles silk most closely (Woodings 2001).

In 1890 Louis Henri Despeissis successfully produced artificial fibre from cellulose dissolved in a solution cuproammonium, albeit on a laboratory scale. He applied for a patent but, due to the lack of payment, the patent was not granted. Figure 1 gives a schematic diagram of the production of artificial silk by the cuproammonium process.

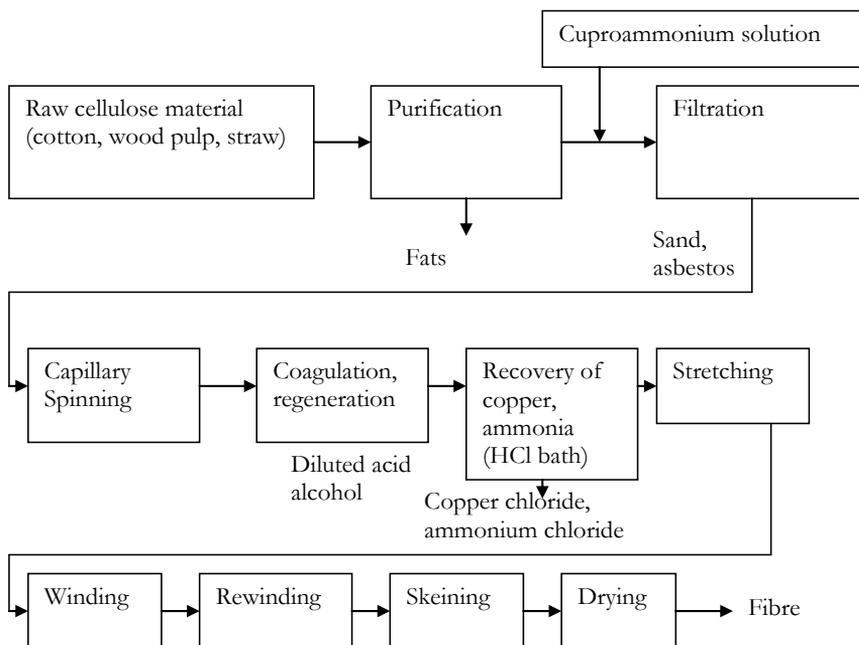


Figure 1. The production of artificial silk using the cuproammonium process.

The German scientists Fremery and Urban developed the process for generating rayon from cellulose between 1890 and 1895. They based their

process on the observation that cellulose is soluble in ammonium copper oxide and that it can be regenerated from the solution by the addition of an acid. Cellulose is an insoluble material. However, it has been found to dissolve in i.a. the cuproammonium complex $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$. Named after M.E. Schweitzer, this is commonly known as Schweitzer's reagent. The cellulose is regenerated from the solution by adding sulphuric acid. This was the first commercial application of the cellulose-cuproammonium solution system. Max Fremery and John Urban applied for a patent in 1897 under the name of a third person, Hermann Pauly: German patent 98 642 (1897) (Woodings 2001). Figure 2 gives a schematic diagram of the cuproammonium process by Fremery, Urban and Pauly.

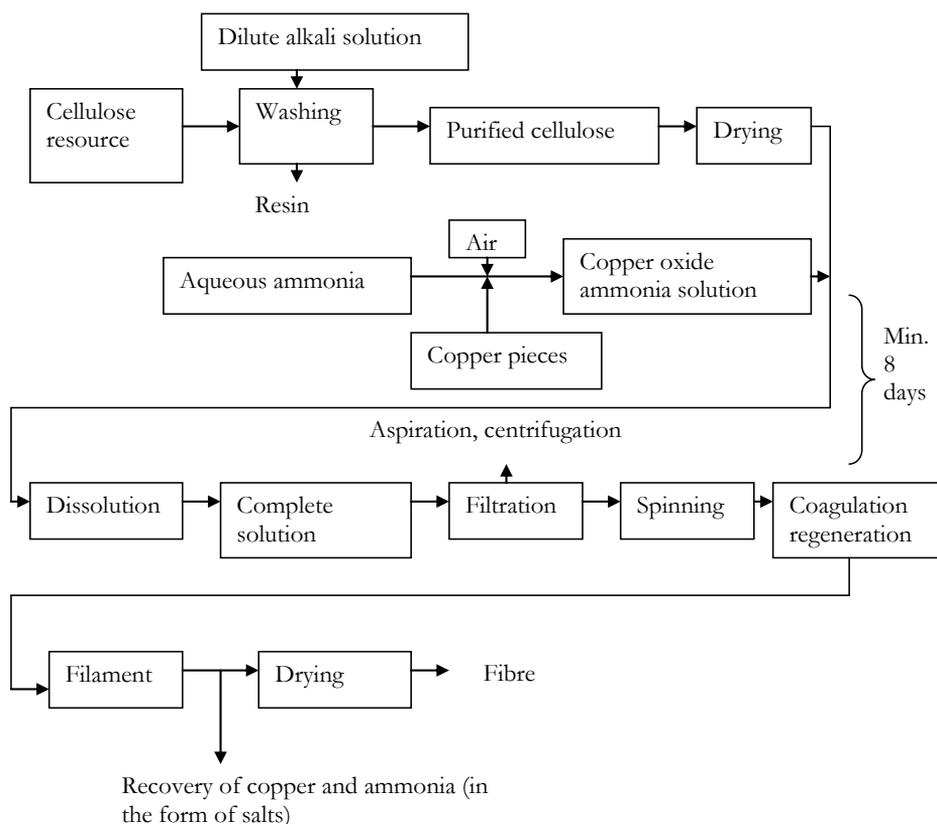


Figure 2. The cuproammonium process by Fremery, Urban and Pauly 1897 (German patent 98 642 (1897)).

1.4.2 Viscose

Viscose is an old cellulose product that was produced commercially in 1891 by two Englishmen, Charles F. Cross and Edward J. Bevan, and patented by Cross, Bevan and Clayton Beadle in 1882. The British patents were later taken over by Courtaulds in 1904 (Cross *et al.* 1882; Seymour 1989; Borbély 2008). Cross was educated at the Universities of London, Zurich and Manchester. In the later city, he met Bevan with whom he started working on the nature of cellulose. Later on they came across Clayton and, in 1891, the three of them applied for a patent on the dissolution and regeneration of cellulose. Their invention consisted of a two-step process, in which wood pulp was first dissolved in a blend of carbon disulphide and alkali solution to produce xanthate. The solution was then pressed through spinnerets in an acidic solution, which regenerated the cellulose and gave fibres of “viscose”. Figure 3 gives a schematic diagram of the production of conventional viscose.

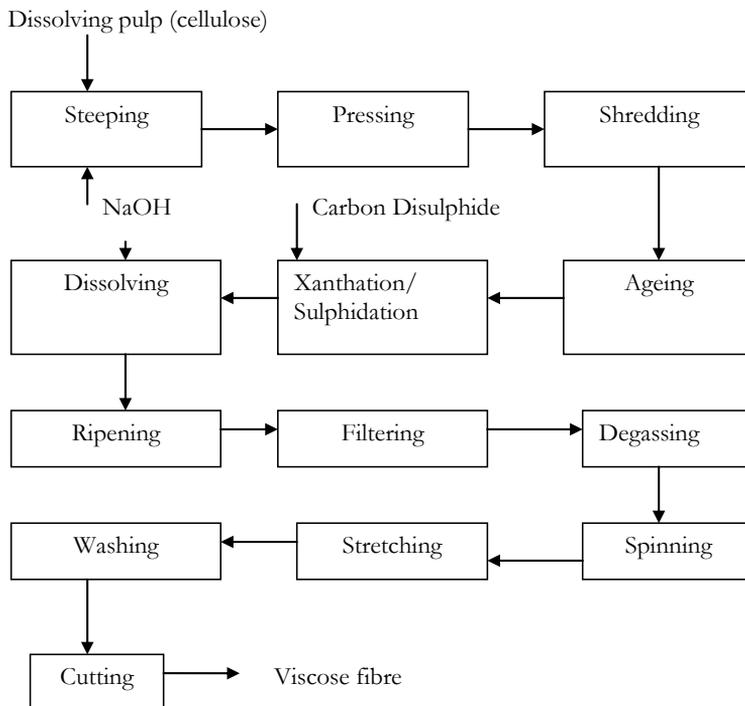


Figure 3. The conventional viscose production process.

Figure 3 shows that the dissolving pulp is immersed into aqueous sodium hydroxide in the steeping- or mercerization step to swell the cellulose fibres and produce alkali cellulose (AC). Then the AC is squeezed in the press step in

order to obtain the correct amount of cellulose in the AC. The AC is then shredded into small pieces to increase the surface area and thereby allowing the carbon disulphide to react more easily with the AC in the subsequent process steps. The AC is pre-aged to reduce the length of the cellulose molecules to the correct degree of polymerization. Shortening the cellulose chains is necessary to decrease the viscosity: the viscose solution would otherwise be too difficult to process. The aged AC is then mixed with carbon disulphide to form cellulose xanthate, as can be seen in Figure 4.

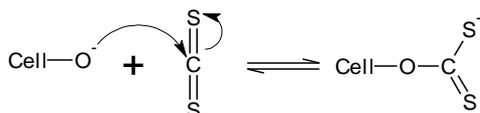


Figure 4. Alkali cellulose in reaction with carbon disulphide, forming cellulose xanthate (Sjöström 1981).

The risk of explosion involved means that this step of the process must take place in a low pressure environment. The xanthate that is formed in the xanthation step is dissolved in a weak sodium hydroxide solution and stirred thoroughly to obtain the desired composition of the viscose. The viscose is then stirred gently in the ripening process for approximately 15–16 h. A redistribution of the xanthate groups occurs in this step, causing a more homogenous derivative of the cellulose chain. The viscose is then filtered to remove unsolved materials that could cause clogging in the spinning process.

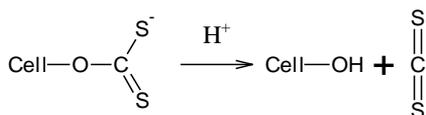


Figure 5. The regeneration of cellulose in an acidic environment (Sjöström 1981).

Regeneration takes place in an acidic bath; the reaction is shown in Figure 5. The carbon disulphide that is released during regeneration is recovered and reused in the process. Although the recovery of carbon disulphide is usually performed using a condensation method, there is also a catalytic method whereby carbon disulphide and hydrogen sulphide are converted into sulphuric acid which can then be used in the acidic regeneration bath (Woodings 2001).

1.4.3 High viscosity viscose

The preparation of high viscosity viscose lacks the ageing step that is a part of the conventional method of preparing viscose in order to maintain a sufficiently high level of cellulose viscosity. A schematic diagram of the production process of high viscosity viscose is shown in Figure 6.

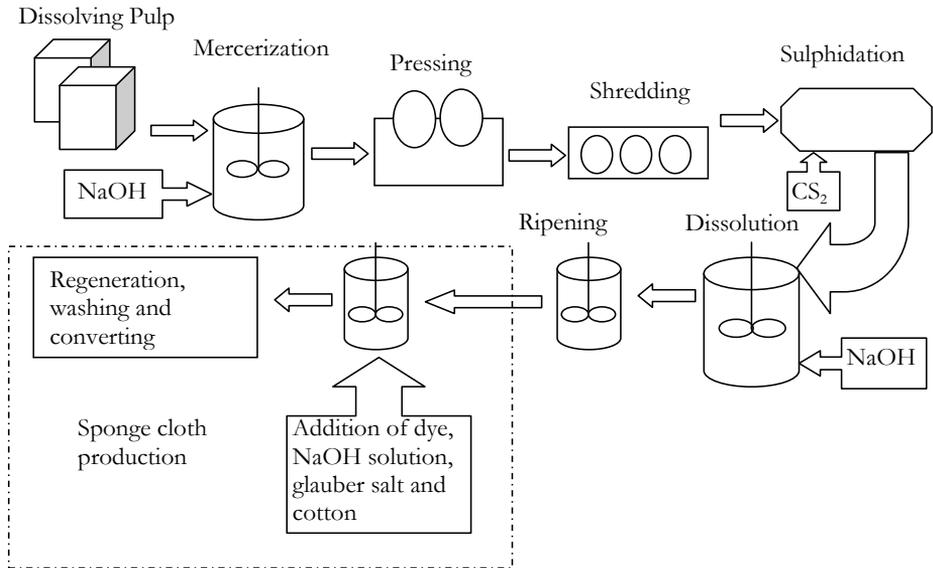


Figure 6. Schematic diagram of the various steps in the production of high viscosity viscose and the following spongecloth production.

Other differences between the two viscose processes include the higher charge of carbon disulphide and the higher content of cellulose in the viscose produced. Even the regeneration of cellulose is different, taking place on a conveyor belt that travels through an alkaline bath instead of through spinnerets in an acidic bath. Also, the demands based on the quality of the final viscose are quite different. In the case of high viscosity viscose and in this case the following sponge cloth production, the gamma number has been the important parameter of quality rather than other measurements: it has traditionally been linked to the regeneration of the cellulose. A too high gamma number decrease the regeneration rate and can cause non-regenerated fields in the sponge material. A too low gamma number can cause a too rapid regeneration. This can cause problems with the adding of glaubersalt in the sponge material. Glaubersalt is linked with the formation of pores in the sponge cloth and good formation of pores leads to high absorbency in the final fabric, and that is a desirable characteristics when producing, for example, sponge cloth or other cleaning products. Table 1 gives an example of the limit values of a specific producer of high viscosity viscose. Production plants can have typical values other than those shown in the table, which can be due to different production volumes or end products.

Table 1. An example of typical values for a specific producer of high viscosity viscose.

Quality parameter	Typical value
NaOH content (%)	~8-9
Cellulose content (%)	~9-10
Ball Fall Time (s)	~300-400
Gamma Number (%)	~65-70

1.4.4 Lyocell technology

Lyocell, the generic name for cellulose fibres produced by direct solution, was first made in the laboratory during the 1940's. It was later made in a pilot plant in Coventry, England, in the early 1980's (Woodings 2001). Several attempts have been made to create a new solvent for the direct solution of cellulose. The most successful so far has been N-methyl morpholine-N-oxide (NMMO), see Figure 7.

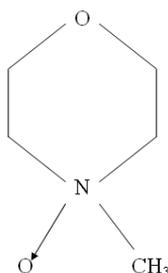


Figure 7. The structure of N-methyl morpholine-N-oxide (NMMO).

A semi-commercial plant was commissioned at Grimsby, England, by Courtaulds in 1988. The operation of the plant enabled the production process to be tested and developed further. The plant's good results provided the company with sufficient confidence to commence full-scale market development and, just a few years later, the first full-scale commercial plant was constructed in the U.S.A. in Mobile, Alabama, in 1992 (Woodings 2001). The trade name of Courtaulds Lyocell fibre was *Tencel*; Lenzing, their major competitor, sold their Lyocell fibre under the trade name *Lyocell by Lenzing* (Borbély 2008).

The principles of making Lyocell are quite simple. The pulp is dissolved in the dilute aqueous amine oxide known as NMMO; the subsequent extraction of excess water is an effective way of producing a homogenous solution. The fibres are formed when the highly viscous solution is spun into an air gap; they are then coagulated in a water/amine oxide solution. The fibres produced are washed and dried, whilst the washing liquors are recovered and recycled (Woodings 2001). Figure 8 gives a schematic diagram of the production of Lyocell.

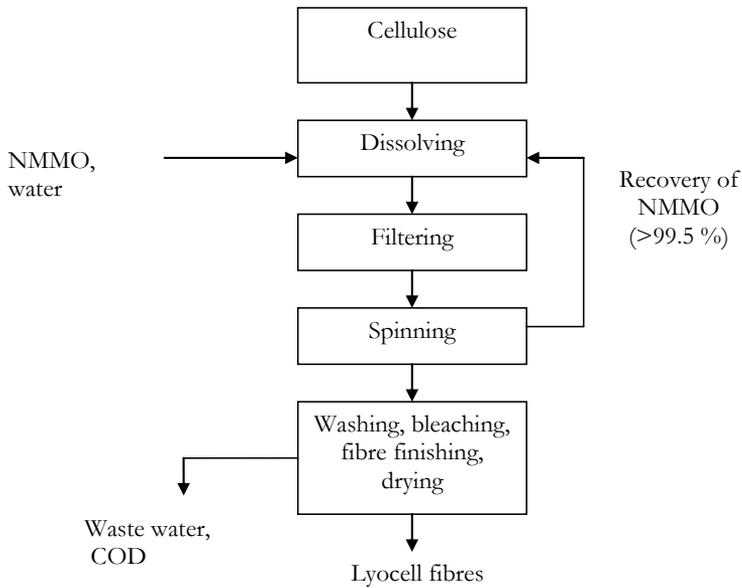


Figure 8. The Lyocell process.

Lyocell is similar in strength to polyester and stronger than all other man-made staple cellulosic material. All man-made cellulosic products lose strength and modulus when wetted, but Lyocell loses the least (Woodings 2001). Lyocell can be processed into a strong paper. In general Lyocell papers are strong, with high opacity and low air resistance. The end-uses being explored are consequently mostly filtration applications, as well as use as an additive in standard paper to increase the strength.

1.4.5 Cellulose carbamate technology

In the carbamate process, a cellulose carbamate derivative is prepared by swelling the cellulose (approx. 400 DP) in an aqueous ammonia solution. The solution is then reacted with 10 % urea solution at 155 °C. The cellulose carbamate derivative can easily be hydro degraded, but cellulose with various degrees of polymerization cannot be dissolved. The cellulose carbamate process was developed as an environmentally friendly alternative to the traditional viscose process (Laszkiewics and Domasik 1989).

As can be seen in Figure 9 the process can have two different spinning procedures.

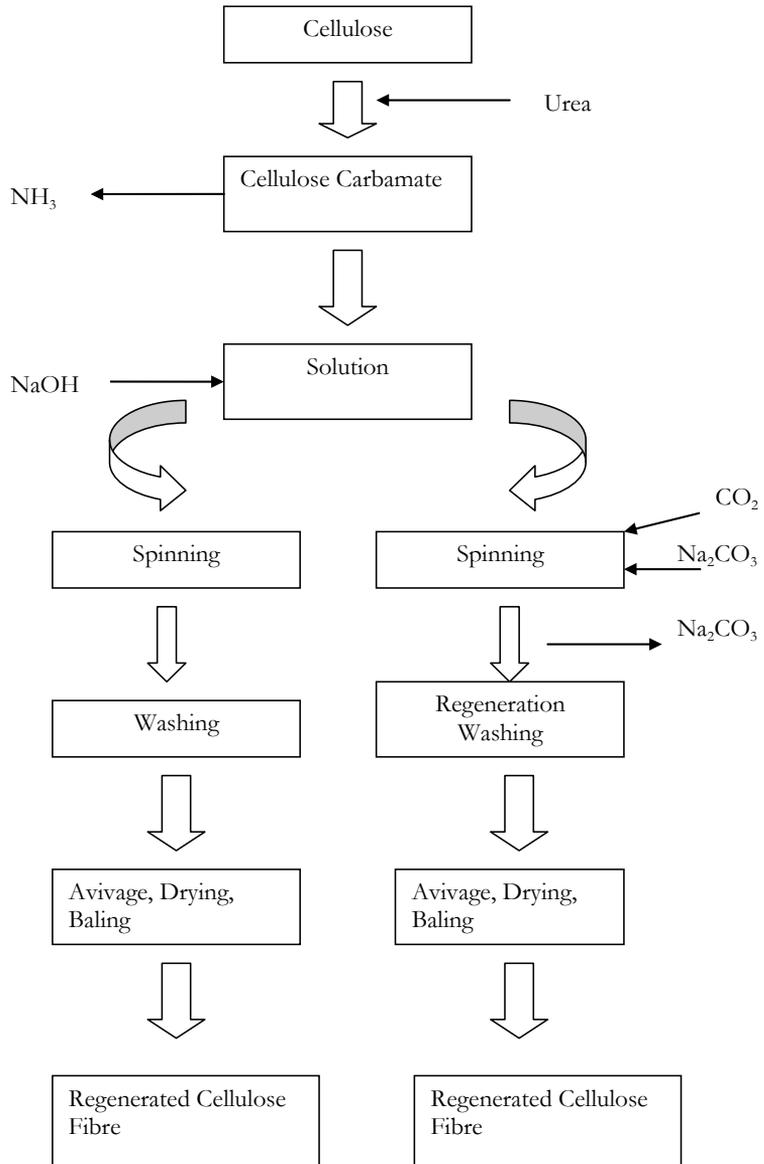


Figure 9. The Carbamate process (adapted from Söderlund 2007).

1.4.6 Biocelsol

The Biocelsol process uses cellulase enzymes instead of carbon disulphide to dissolve cellulose and to produce regenerated cellulosic products. The enzyme pre-treated pulp can be dissolved in an alkali solvent and then formed into cellulosic products in an acidic coagulation bath (Marcincin *et al.* 2007). Figure 10 gives a schematic diagram of the production of Biocelsol fibres and films.

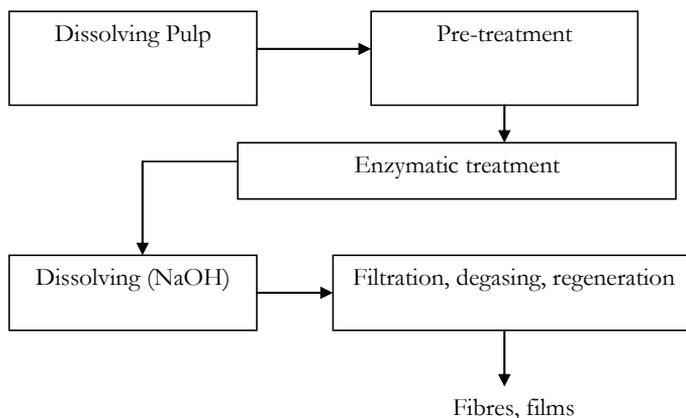


Figure 10. The Biocelsol process.

1.2 Cellulose

Cellulose was first discovered, isolated and named by the French professor Anselme Payen in 1838. He observed that the composition of non-lignified plant material (~ 44 % carbon, 6 % hydrogen and 50 % oxygen) was different from that of lignified plant material (54 % carbon, 6% hydrogen and 40 % oxygen) (Payen 1833). In 1921 the Swiss organic chemist Paul Karrer proposed that cellulose was composed of at the least 50 % cellobiose, which was another important discovery of the structure of cellulose (Karrer and Widmer 1921; Karrer 1925). Based on X-ray crystallography data of ramie cellulose, Sponsler and Dore postulated in 1926 the chain-like molecular structure consisting of covalently bound anhydroglucose units (AGU), as shown in Figure 11 (Sponsler and Dore 1926). Although the chain-like molecular structure was proven to be right, the type of linkage proposed (1→1, 4→4) was incorrect. A few years later, however, the British chemist Norman Haworth proposed the correct type of linkage (1→4). It is now known that an unbranched homopolysaccharide,



Figure 13. Fragments of cellulose chains on top of each other. Cellulose I_α at the top and cellulose I_β at the bottom (adapted from Lennholm & Henriksson 2007).

Cellulose is composed of cellulose molecules in fibrils and fibril aggregates, which leads to more or less-ordered regions being formed by the hydrogen bonds within the cellulose chains (Klemm *et al.* 2002; Fengel and Wegener 1984).

1.3 Reactivity of cellulose

Reactivity is not a simple parameter that could be measured in an objective manner. It is essential that the methods of analysis, and their capabilities, are understood when researching the reactivity of cellulose. Clearly, reactivity will depend on the reagent chosen and a lot of other more or less important conditions. A method that requires industrial conditions, using chemicals employed in industrial processes, and thereafter the calculation of the percentage of a clearly defined factor, is presumed to be reasonably acceptable. If, on the other hand, there is some kind of indirect correlation where one parameter is measured and then either reinterpreted or another is calculated, conclusions could only be drawn with great caution. Moreover a change in the “reactivity” measured using some pre-treatment instead of conventional methods may be influenced when using the pre-treatment, when the actual reactivity is not affected in the same way. It is well known that common measuring methods, such as kappa number, limiting viscosity number and accelerated yellowing, could be extremely problematic in many cases and can often lead to the wrong conclusions if this is not taken into account. Common methods of measuring reactivity have been described by Roffael (1998).

When measuring reactivity as filterability (K_w), the measured reactivity can, for example, be a product of fibre shortening instead of increased actual reactivity on molecular level. Using Fock reactivity as measured reactivity is not uncomplicated either. Fock reactivity, an old wet chemistry method, comprises oxidation with dichromate. Dichromate, like permanganate oxidizes a lot of structures but not everything and for sure there could still be some special structures left in the pulp, not reactive towards the chemical used – or on the contrary – it reacts with structures that carbon disulphide does not react with. The gamma number is determined by making spectrophotometric measurements of viscose dissolved in sodium hydroxide. Even this method is problematic as not only cellulose but also hemi cellulose can be substituted and this result in a too high gamma number. Also, if the measurements are performed after different storage times, the comparison is erratic since the gamma number analysis could produce different results as the gamma number is reduced with increasing storage time.

It has been reported that the structure and morphology of the cellulose fibre determine how reactive and accessible the cellulose is to chemicals (Krässig 1993; Elg Christoffersson *et al.* 2002). It has also been reported that cellulose reactivity is related to the dissociation of fibril aggregates into elementary fibrils (Fahmy and Mobarak 1971). Hornification, the irreversible collapse of the polymer structure, also affects the reactivity of pulp (Fernandes *et al.* 2004). In recent years several studies have been made on increasing the reactivity of pulp (Kvarnlöf *et al.* 2005; Köpcke *et al.* 2008; Ibarra *et al.* 2010; Engström *et al.* 2006). The focus of these publications has been on reactivity as measured either by the Fock Test or as filterability, K_w , in accordance with Treiber (Treiber 1962).

1.4 Enzymes

An enzyme is a protein that functions as a catalyst in chemical reactions. They act with great specificity and often catalyse only one specific reaction. An enzyme consists of a sequence of amino acids; they are folded in a special three dimensional structure that determines the function of the enzyme. The word, which was first used by the German physiologist Friedrich Wilhelm Kühne, is derived from the Greek: *en* means in and *zyme* means leaven (Berg *et al.* 2002; Kühne 1877). An enzyme can catalyse a reaction by binding its active site to the substrate, forming an enzyme-substrate complex; the activation energy for the reaction is lowered by a stabilization of the transition state.

Cellulases are enzymes that hydrolyze 1,4- β -D-glucosidic bonds of the cellulose chain. The cellulose must bind to the surface of the cellulose molecule for hydrolysis to take place (Zhang and Lynd 2004). Cellulases could be divided into three different groups, depending on the enzymatic degradation it catalyse in the cellulosic chain:

- Endoglucanases, randomly cleaves internal bonds at amorphous sites that create new chain ends and chains with varying length.
- Exoglucanases, cleaves two to four units from the ends of the exposed chains, resulting mainly in cellobiose (C₁₂H₂₂O₁₁). Exoglucanase can degrade both amorphous and crystalline parts in the cellulosic chain.
- Cellobiases, hydrolyze cellobiose to glucose (C₆H₁₂O₆) (Lynd et al. 2002).

Xylanases are a group of enzymes that catalyse the endohydrolysis of 1,4- β -D-xylosidic linkages in xylan (Collins *et al.* 2005). Xylan is a major part of hemicellulose in hardwood. Glucomannan is a major part of hemicellulose (Timell 1967). In order to decrease the hemicellulose content various pre-treatments of pulps have been developed and investigated, e.g. the use of enzymes (Guan *et al.*, 1998, Zhou *et al.*, 2001; Köpcke *et al.*, 2008), ni-TREN (Nickel tris(2-aminoethyl)amine complex) and cuen (Copper ethylenediamine complex) extraction (Janzon *et al.*, 2006; Puls *et al.*, 2006.) and alkali extraction (Wallis *et al.*, 1990).

Enzymes has been used in the pulp and paper industry to improve drainability and beatability (Kamaya 1996; Gil *et al.* 2009; Bhardwaj *et al.* 1996; Buchert *et al.* 1998; Cadena *et al.* 2010), deinking (Welt and Dinus 1994; Gübitz *et al.* 1998; Leduc *et al.* 2011; Heitmann *et al.* 1992; Prasad *et al.* 1993) and delignification (Ibarra *et al.* 2006), as well as producing dissolving pulp from kraft pulp (Bajpai and Bajpai 2001; Gehmayr *et al.* 2010)), producing nano-scale cellulose (Pääkkö *et al.* 2007) and enhancing the reactivity of cellulose (Henriksson *et al.* 2005; Engström *et al.* 2006; Kvarnlöf *et al.* 2005; Ibarra *et al.* 2010; Ioelovich and Leykin 2009; Rahkamo *et al.* 1996; Rahkamo *et al.* 1998; Cao and Tan 2006).

A detailed study of enzymes will not be included in this work.

1.5 Objective of this study

The objective of Paper I was to reduce the consumption of carbon disulphide when preparing high-viscosity viscose by pre-treating pulps with enzymes prior to viscose preparation. In Paper II the aim was to investigate and link the different measurements of reactivity that is gamma number, Fock reactivity and K_w . It was also an objective to quantify the effect an enzymatic pre-treatment stage had on the requirement of carbon disulphide in the manufacture of high DP viscose. Determining the sensitivity of the gamma number to the hemicellulose content of pulp was the aim of Paper III.

2 Materials and Methods

2.1 Materials

2.1.1 Pulps

Paper I and II: Domsjö Cellulose 2200, a commercial spruce/pine dissolving pulp, manufactured in a two-stage (pH 5/pH 1.5) sodium sulphite cooking process had a limiting viscosity number of 540 dm³/kg after TCF-bleaching. The brightness was 92 % ISO and the α -cellulose content 91%. The dissolving pulp, provided by Domsjö Fabriker AB, Sweden, had been dried and cut into sheets at their mill. One sample of this pulp was pre-treated in the laboratory using the steam explosion method STEX (3 min, 226°C) and resulted in a pulp (Domsjö, STEX) with properties that differed to those of the untreated reference pulp (Domsjö, reference), see Table 2.

Table 2 Properties of Domsjö Cellulose 2200, with or without STEX treatment (Paper II).

Pulp	Viscosity (ml/g)	DP_w	Mean length (mm)	Mean width (μ m)	Mean shape (%)
Domsjö 2200, reference	530	745	1.72	25.5	77.8
Domsjö 2200, STEX	280	368	1.53	25.4	76.6

Paper I and III: Södra Cell AB, Sweden, provided the commercial northern (TCF) bleached softwood kraft pulp, produced for tissue production with a limiting viscosity number of 627 dm³/kg. This was composed of 70% spruce and 30% pine and with an ISO brightness of 86%. This pulp had been dried and cut into sheets at Södra Cell AB.

Table 3 The carbohydrate content of the untreated Kraft pulp and the untreated sulphite dissolving pulp (Paper I).

Type of pulp	Cellulose (%)	Glucomannan (%)	Galactan + Arabinan (%)	Xylan (%)	Total hemi-cellulose (%)
Kraft pulp	82.9	8.1	0.7	8.3	17.1
Dissolving Pulp	96.0	2.4	0.1	1.5	4.0

Table 4 The carbohydrate content of the enzyme-treated pulp samples prepared from the sulphite dissolving pulp. The enzyme treatment was done with xylanase (10 AXU/g pulp and 100 AXU/g pulp) with or without a following alkaline extraction. In one case was endoglucanase also added (4.5 ECU/g pulp) (Paper I).

Xylanase (AXU/g pulp)	Alkali extraction	Endo-glucanase (ECU/g pulp)	Cellulose (%)	Glucomanann (%)	Galactan + Arabinan (%)	Xylan (%)	Total hemi-cellulose (%)
0	No	0	96.2	2.3	0.1	1.4	3.8
0	Yes	0	98.0	1.6	0	0.4	2.0
10	No	0	96.4	2.3	0	1.3	3.6
10	Yes	0	98.0	1.6	0	0.4	2.0
100	No	0	96.4	2.3	0	1.3	3.6
100	Yes	0	98.2	1.4	0	0.4	1.9
100	Yes	4.5	98.0	1.6	0	0.4	2.0

Paper III: One softwood, acidic, magnesium sulphite pulp prepared for producing greaseproof paper (85 % ISO brightness, limiting viscosity number of 1256 dm³/kg) obtained from Nordic Paper AB, Sweden, was also used. This pulp was never dried before use in this study.

2.1.2 Enzymes

The enzymes used in the pre-treatment of the pulps prior to the preparation of viscose were a commercial monocomponent endoglucanase preparation (Fibre Care R[®]) and a commercial xylanase preparation (Pulpzyme HC[®]). Both were provided by Novozymes A/S, Denmark. The enzyme activity was determined by the manufacturer and expressed in Endo Cellulase Units (ECU) per unit mass of material as being 4500 ECU/g (for the endoglucanase enzyme), and in

Active Xylanase Units (AXU) per unit mass of material as 1000 AXU/g (for the xylanase enzyme).

2.1.3 Chemicals

The chemicals used were sodium hydroxide (NaOH) (purity 99 % from VWR International) and carbon disulphide (CS₂) (purity ≥99% from SIGMA-ALDRICH).

2.2 Methods

2.2.1 Pulp treatments

Endoglucanase pre-treatment

The endoglucanase enzymatic step was performed in a glass beaker. The sheets of pulp were cut into pieces 1x1 cm in size and a sample corresponding to 25 g of oven dry pulp was added to the beaker along with 475 g of deionised water. The beaker was placed in a water bath and tempered to 45 °C under continuous stirring. An exact amount of enzyme was added to the pulp slurry, which was stirred continuously and kept at constant temperature for various lengths of time. The enzyme-treated pulp was then dewatered to a dryness of approximately 30%. In the subsequent mercerizing step the extra water in the enzyme treated pulp was accounted for, and compensated by, an extra addition of sodium hydroxide to the mercerization vessel.

Xylanase pre-treatment

The xylanase enzymatic step was performed in plastic bags in a water bath at 60 °C for 2 h, testing three different charges of enzyme (0, 10 and 100 AXU/g pulp). A calculated amount of xylanase was added to a phosphate buffer solution (11 mM NaH₂PO₄ and 9 mM Na₂HPO₄) and dry pulp was added to give a pulp consistency of 3%. The pH was set to 7 (the optimal level as described by the enzyme manufacturer). After completion of the treatment, the enzyme was denaturalized with hot deionised water (90 °C) and filtered through a Büchner funnel. The xylan was removed from the enzymatically treated pulps by means of an alkali extraction performed with 9% NaOH solution at room temperature for 1 h and at 4% pulp consistency. The pulps were then washed with deionised water and filtered through a Büchner funnel until the filtrate reached pH 5 and a pulp dryness of approx. 30%.

Alkali extraction

The cold caustic extractions (CCE) on the pulp were performed with 5% (w/w) NaOH and 10% (w/w) NaOH in 5% pulp consistency at 25°C for 2 h. Washing and filtration processes were then performed until the filtrate reached pH 7.

PFI mill treatment

PFI mill treatment of the pulps was performed according to ISO 5264-2.

Steam explosion

The steam explosion was performed according to Kihlman (Kihlman *et al.*, 2011) using STEX equipment (Bösch *et al.*, 2010) seen in the schematic picture in Figure 14.

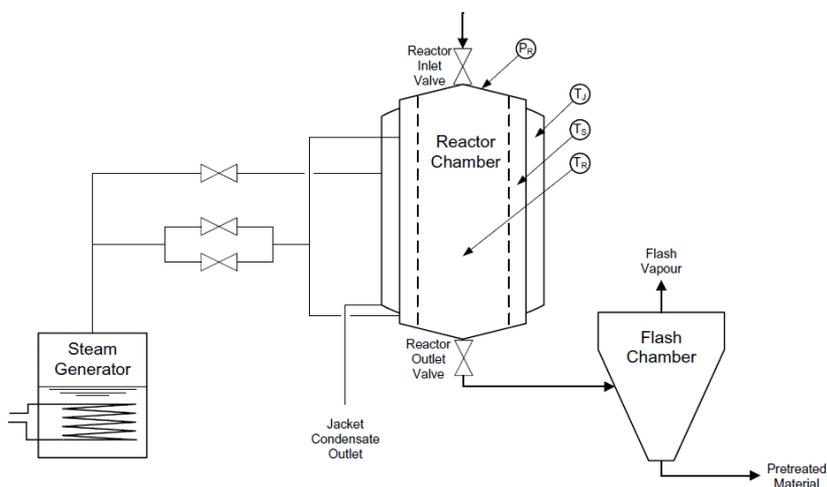


Figure 14. The steam explosion equipment (Bösch *et al.* 2010).

The reactor was supplied with high pressure steam from an electrical boiler and the pressure was controlled by use of a valve to the desired pressure that corresponded to a certain temperature (190–226 °C). The reactor was loaded with pulp (50% dryness) and the valve was closed. The reactor was then rapidly heated with the high pressure steam to reach the desired temperature. After the reaction time the outlet valve was opened and the material emptied into a flash chamber where excess steam was flashed from the pulp slurry. The control system comprised of a PM851K01 controller and an industrial IT 800×A 5.0 (ABB, Sweden). After attaining the temperature desired in the chamber, the

steam inlet valve was closed and steam was introduced through a PID-regulated control valve to maintain a constant temperature.

2.2.2 Fock's Test

The Fock reactivity test was carried out according to Fock (1959). A sample of pulp weighing 0.50 g, calculated as oven dry pulp, was transferred to a 100 ml Erlenmeyer flask with a glass stopcock and a magnet. Then 50 ml NaOH (9% w/w) and 1 ml CS₂ were added and the bottle was sealed with the stopcock. The mixture was stirred continuously with the magnetic stirrer for 3 h before being transferred into a round flask and deionised water added to obtain a total weight of 100 g. The round flask was sealed with a stopper and shaken vigorously to obtain a homogenous solution. 40 ml of the solution was centrifuged at 6000 rpm for 5 min, after which 10 ml of the liquid phase was transferred to a 100 ml beaker and neutralized with 3 ml sulphuric acid (20% w/w). The mixture was left to de-gas for 15-20 h at 25°C. A magnet was added to the beaker along with 20 ml of sulphuric acid (68% w/w) and the mixture was mixed, with a magnetic stirrer for 1 h. The mixture was transferred into a round flask and 10 ml of potassium dichromate (K₂Cr₂O₇) (1/6 mol/dm³) was added. It was boiled with reflux for 1 h in order to oxidize. The mixture was left to cool until it reached room temperature before being transferred into a 100 ml measuring cylinder and diluted to the 100 ml mark with deionised water. Then 40 ml was transferred to a beaker and 5 ml of potassium iodide (KI) (10% w/w) was added; the iodine produced in the beaker was titrated with sodium thiosulphate (Na₂S₂O₃) (0.1 mol/dm³) using starch (thyodene) as an indicator. The reactivity was calculated based on the amount of non-reduced Cr⁶⁺ that remained after the oxidative reaction that occurred between the potassium dichromate and the cellulose.

2.2.3 Limiting viscosity number

The limiting viscosity number was measured according to ISO 5351-1:2004. In Paper I (Figure 3) and paper II (Figure 1) the limiting viscosity number was showed as TAPPI CCA viscosity using a conversion diagram (Götze 1967).

2.2.4 Carbohydrate analysis

The analysis of the carbohydrates was performed according to SCAN-CM 71.

2.2.5 Alkali solubility

The alkali solubility was carried out according to ISO 692-1982(E).

2.2.6 Gamma number

The gamma number was determined by making spectrophotometric measurements of viscose dissolved in sodium hydroxide (Rahman 1971).

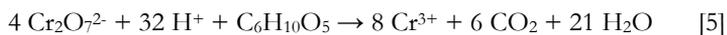
The gamma number of the viscose solution was measured after 16 h of ageing. Approximately 1 g of viscose was taken for analysis and the weight was noted. The viscose was dissolved in 50 ml sodium hydroxide solution (1% w/w de-aired with nitrogen gas for 30 min) during a period of 30-40 min in a 250 ml beaker equipped with a magnetic stirrer. The dissolved viscose was then transferred to a 100 ml measuring cylinder and diluted to the 100 ml mark with NaOH solution (1% w/w de-aired with nitrogen gas for 30 min). The measuring cylinder was shaken vigorously and 5 ml of the solution was immediately transferred to a 100 ml Erlenmeyer flask containing 1.8 g anionic exchanger (Amberlite, IRA-402). The anionic exchanger was allowed to affect the solution for 10 min. The solution was then separated from the anionic exchanger by washing it with deionised water, through a glass funnel containing a filter paper, into a measuring cylinder. The cylinder was filled to the 250 ml mark with deionised water and shaken vigorously. The absorbance was then measured at 303 nm (UV-160 1PC, visible spectrophotometer, Shimadzu) using deionised water as the reference.

The cellulose content of the viscose was determined by spreading 2 g of viscose into a thin film between two glass plates. The plates were then pulled apart and placed in hydrochloric acid (42 ml/l, 25°C) until the cellulose films loosened from the plates. The films were then washed with water to remove the acid; after pressing they were washed with acetone and pressed once again. Finally, the films were dried at 105 °C to a constant weight and the cellulose content was determined as the total weight of the dry sample.

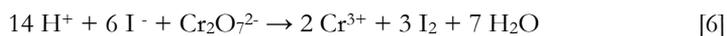
3 Calculations

The reactivity of pulp according to Fock

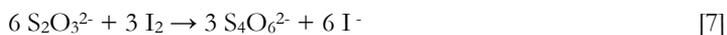
The calculation of the Fock reactivity is based on the amount of unreduced Cr(VI) that remains after the oxidative reaction between potassium dichromate and cellulose has taken place:



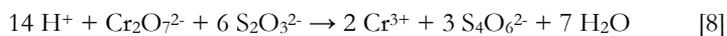
The unreduced Cr(VI) in reaction [5] is reduced by iodide to Cr(III):



The iodine is then titrated with sodium thiosulphate:



The addition of reactions [6] and [7] give:



The amount of oxidized cellulose is calculated indirectly in the following way:

The amount of reacted dichromate, A :

$$A = (V_1 * C_1) - (V_2 * C_2 * a) * 1/6 \quad (1)$$

V_1 = dichromate added (ℓ)

C_1 = concentration of dichromate (mol/ℓ)

V_2 = sodium thiosulphate used (ℓ)

C_2 = concentration of sodium thiosulphate (mol/ℓ)

$a = 100/40$ (dilution of the sample in the volumetric flask (100ml) and the amount used for titration (40 ml))

$1/6 \Rightarrow$ each dichromate ion consumes 6 thiosulphate ions

The transformation from dichromate to cellulose, B :

$$B = A*(M*1/4) \quad (2)$$

where M =molecular weight of a glucose unit (g/mol) and $1/4 \Rightarrow$ cellulose consumes 4 dichromate ions (Reaction [5]).

The amount of cellulose that reacted with carbon disulphide (%), C , is given by:

$$C = ((100*b)/y)*B \quad (3)$$

where $b=100/10.4$ (the first dilution to 100 g and the amount used is 10.4 g (10 ml)) and y =weight (g) of the sample (dry weight).

Gamma Number

The gamma number is given in per cent, where 100% corresponds to a degree of substitution of 1.0 (Barthelemy and Williams 1945). The theoretical maximum esterification corresponds to a gamma number of 300%, *i.e.* a degree of substitution of 3.0. The gamma number is reduced as the result of the xanthate groups splitting whilst the viscose is ripening. This reduction is rapid initially and levels off after a period of time. During the ripening phase the xanthate groups are also being rearranged between the positions of the glucose units (Schwaighofer *et al.* 2010) as well as between cellulose chains (Fischer *et al.* 2005). The gamma number was calculated using the formula below:

$$\gamma = \frac{A_{303} \times 546.48}{\text{sample weight} \times \% \text{ cellulose}} \quad (4)$$

The constant 546.48 is derived from the dilution factors, the molecular weight of glucose and the molar extinction coefficient (Dux and Phifer 1957). A molar extinction coefficient of 14822 was used in the current investigation.

4 Summary of Results

4.1 Paper I

The objective was to reduce the consumption of carbon disulphide when preparing high-viscosity viscose by pre-treating the dissolving pulps with enzymes prior to viscose preparation.

A commercial spruce/pine dissolving pulp, manufactured in a two-stage (pH 5/pH 1.5) sodium sulphite cooking process was used. The pulp was bleached to an ISO brightness of 92 % using hydrogen peroxide.

Enzyme treatment reduced the viscosity of the pulp samples, which meant that the cellulose chain length became shorter due to the enzyme reactions. This is shown for two enzyme charges in Figure 20.

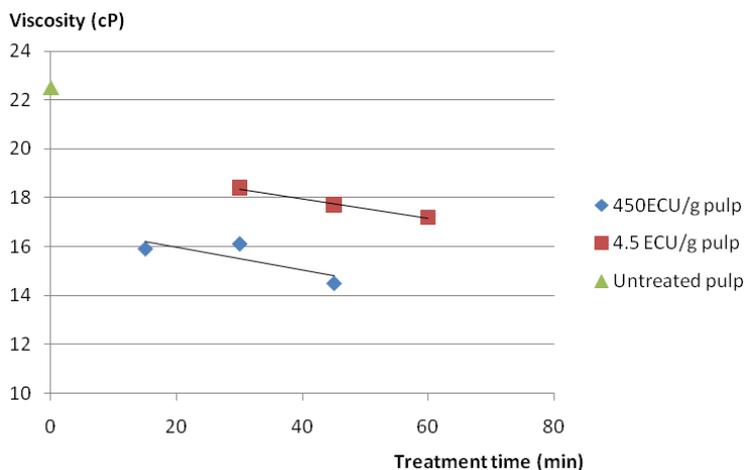


Figure 20.The viscosity of the sulphite dissolving pulp versus the treatment time for two concentrations of endoglucanase (4.5 and 450 ECU/g pulp) of the same type of pulp.

It can be seen that a higher enzyme charge and a longer reaction time both led to lower viscosity. A reduction of the viscosity could have a negative impact when producing viscose grades intended for high-strength products as strong viscose products need relatively long cellulose chains.

The correlation between the gamma number and the carbon disulphide charge for some laboratory viscose samples and one mill-produced viscose sample is shown in Figure 21.

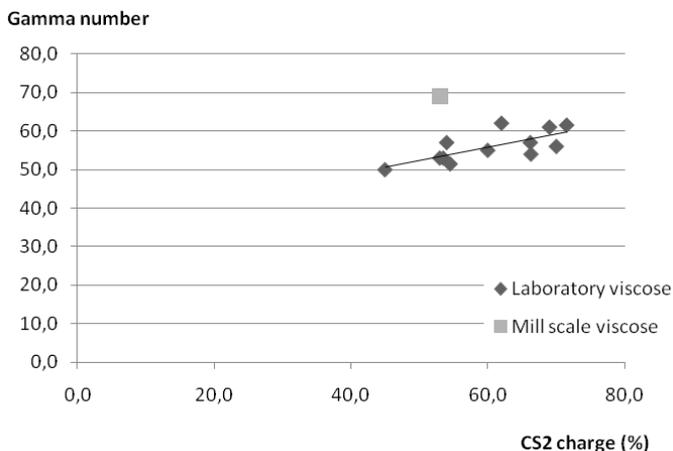


Figure 21. The gamma number versus the carbon disulphide charge for viscose prepared from sulphite dissolving pulp on laboratory and industrial scales. The dissolving pulp used was identical in both cases.

As can be seen the gamma number increased slightly with increasing carbon disulphide charge but the correlation was relatively weak. It could also be seen that none of the laboratory samples reached the corresponding level obtained in the industrial production. Thus, there seemed to be a difference between small, laboratory-scale experiments and large, industrial-scale production. The difference could be due to several factors, such as a difference in mixing efficiency as industrial mixing is better than laboratory mixing due to the high viscosity, a difference due to the varied volume/surface ratio, a difference in storage times before the gamma number was analysed, etc. Thus, the result indicates that it is easier to obtain a high gamma number on industrial scale than on laboratory scale.

A new set of experiments were carried out to find out if a correlation between the reactivity according to Fock of the starting pulp and the gamma number of the resulting viscose solution prevails. The results are shown in Figure 22. Thus, it is clear that there was no direct correlation between these two parameters. It is also seen that whether or not enzymes were used, the same gamma number was obtained.

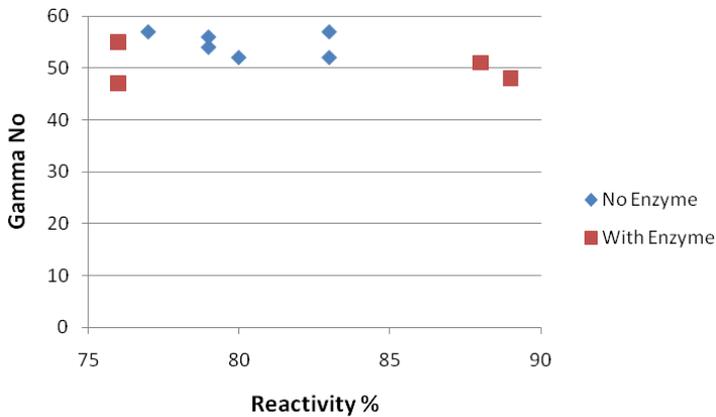


Figure 22. The gamma number versus the pulp reactivity according to Fock for viscose samples prepared from the sulphite dissolving pulp at different conditions. Enzyme charge: 4.5 ECU/g pulp.

Thus, although reactivity according to Fock's test (Fock 1959) is an established indicator of the suitability of dissolving pulps for viscose preparation it cannot according to the results of this study, be used as the sole method of measuring pulp reactivity. Fock's test is a small-scale test using a large excess of carbon disulphide and sodium hydroxide and it measures the dissolution ability of cellulose after the reaction.. Contrary to this, the gamma number is a direct measurement of the degree of substitution actually obtained on the cellulose backbone prior to the regeneration stage. From a chemical point of view it is a measure of the sulphur content of the viscose (Barthelemy *et al.*, 1945). The Fock reactivity of the pulp and the gamma number of the viscose solution could be expected to be totally correlated, but that did not seem to be the case.

4.2 Paper II

The aim was to investigate and link the different measurements of reactivity measured as gamma number, Fock reactivity and K_w . Another objective was to quantify the effect an enzymatic pre-treatment stage has on the requirement of carbon disulphide in the manufacture of high DP viscose.

A commercial spruce/pine dissolving pulp used, manufactured by two stage (pH 5/ pH 1.5) sodium sulphite cooking was used.

As can be seen in Figure 23, the amount of carbon disulphide required is not affected in this case, when the comparison is made at a specific gamma number. Thus, it seemed that the substitution of the cellulose backbone was not

facilitated by the endoglucanase pre-treatment independently of the endoglucanase charge.

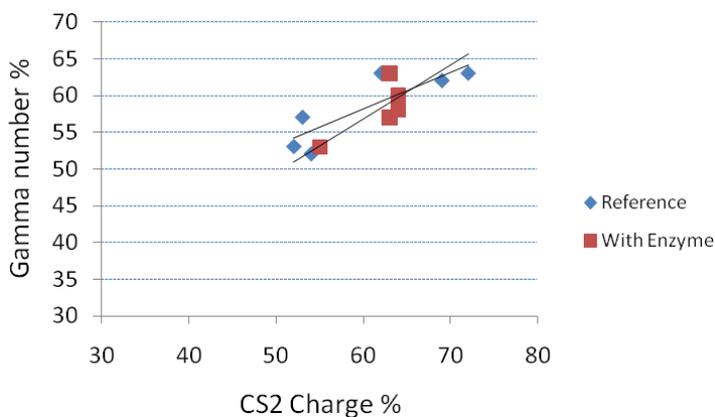


Figure 23. The gamma number of the viscose solution versus the charge of carbon disulphide for laboratory samples with or without enzyme pre-treatment. Enzymatic conditions used: 450 or 900 ECU/g, 2h, 40°C, pH 7.5.

Based on the results obtained it could be speculated that the gamma number, *i.e.* the degree of substitution, is a molecular property that is influenced by properties on a molecular level, *e.g.* cellulose crystallinity, chemical charge and temperature. Similarly, it is proposed that the reactivity according either to Fock's test or the filter clogging value are, in both cases, particularly dependent on the formation of gel in the analysis liquors or viscose solutions.

It may then be assumed that the improvement in reactivity obtained when using Fock's test or the filter clogging value is partly due to the reduction in the length of the cellulose chain that occurs during the enzymatic treatment. The corresponding improvement in reactivity could then be obtained for other methods that cut chains, *e.g.* strong acidic treatment. In fact Henriksson *et al.* (2005) reported such results earlier; the fact that the Fock reactivity is improved by lower DP measured as lower intrinsic viscosity has been shown by Javed and Germgård (Javed and Germgård, 2011).

4.3 Paper III

The aim was to determine the sensitivity of the gamma number to the hemicellulose content of pulp.

Two pulps, one commercial bleached acid sulphite softwood pulp (magnesium base) and one bleached commercial softwood kraft pulp, were used as raw materials. The pulps were washed and then extracted with 5% or 10% alkali in room temperature, with the intention of reducing the hemicellulose content of the pulp samples.

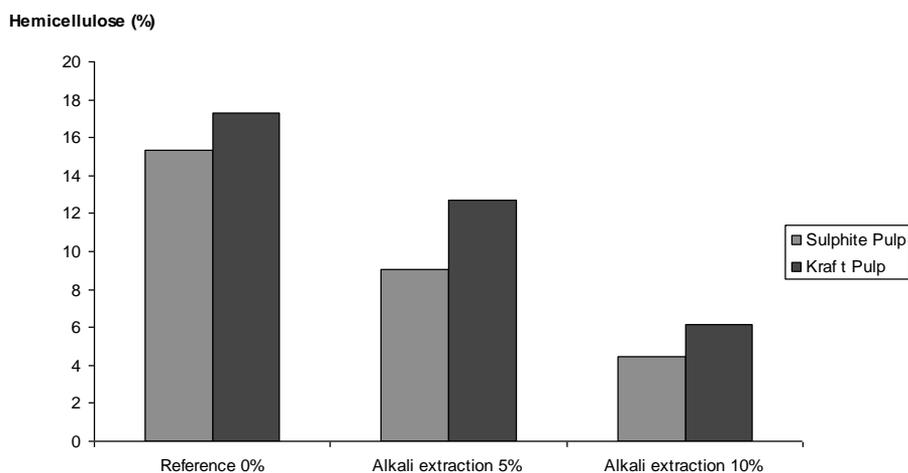


Figure 24. The hemicellulose content of the two pulps before and after an alkali extraction at room temperature with 5 or 10% NaOH solutions. The consistency of the pulp during the extraction was 5%.

As can be seen in Figure 24, it is obvious that the hemicellulose content of both pulps was reduced significantly by the cold caustic extraction. Thus, a CCE treatment is an efficient way of reducing the content of hemicellulose in both types of pulp.

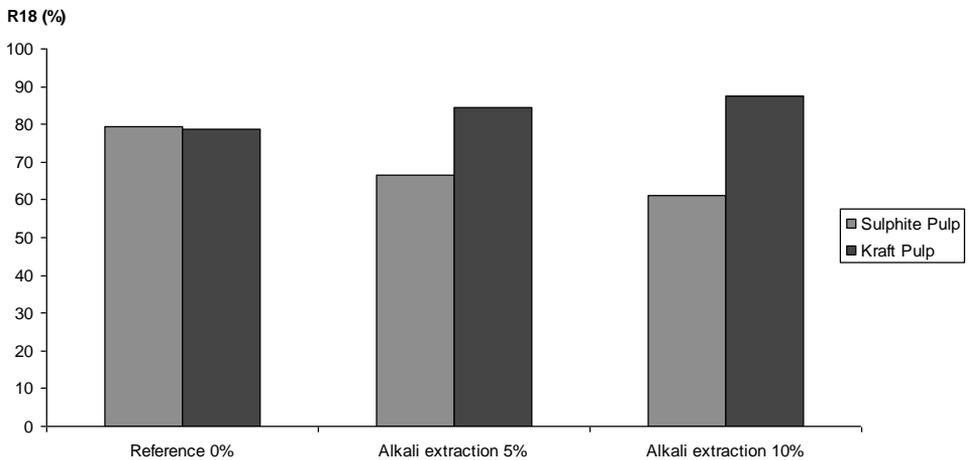


Figure 25. The R₁₈ values of the pulp samples after cold alkali extraction.

As the cold alkali stages used in this study resulted in lower R₁₈ for the sulphite pulp, see Figure 25, it seemed that the extraction stage increased the solubility of both the hemicellulose and the less crystalline cellulose in a following R₁₈ stage. A cold caustic extraction stage is therefore not a good method for increasing the R₁₈ value of a sulphite pulp.

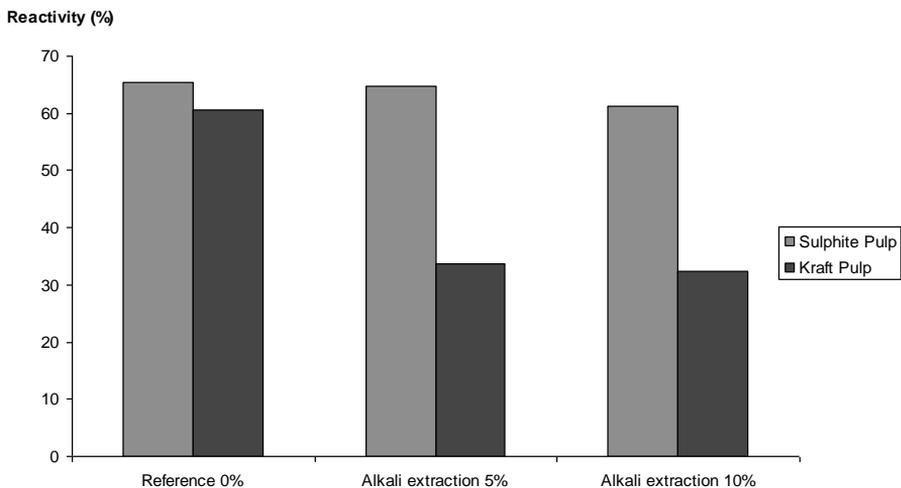


Figure 26. Reactivity according to Fock for the pulps.

As can be seen in Figure 26 it is interesting to note that the reactivity of the kraft pulp, measured as Fock's test, decreased considerably when the pulp was alkali extracted. The corresponding reactivity of the NaOH extracted sulphite pulp samples also decreased but to a much lesser degree than the kraft pulp. Thus, a cold caustic extraction of the starting pulps resulted in a lower reactivity

for both types of pulp. The results suggest that a high reactivity (according to Fock) requires the presence of a certain amount of hemicellulose and perhaps a certain content of amorphous cellulose. It could be assumed that the structure of the fibre wall becomes more compact when the hemicellulose content decreases and the reactivity therefore also decrease. This is surprising as dissolving pulps with high levels of reactivity are usually expected to be those with particularly low hemicellulose content.

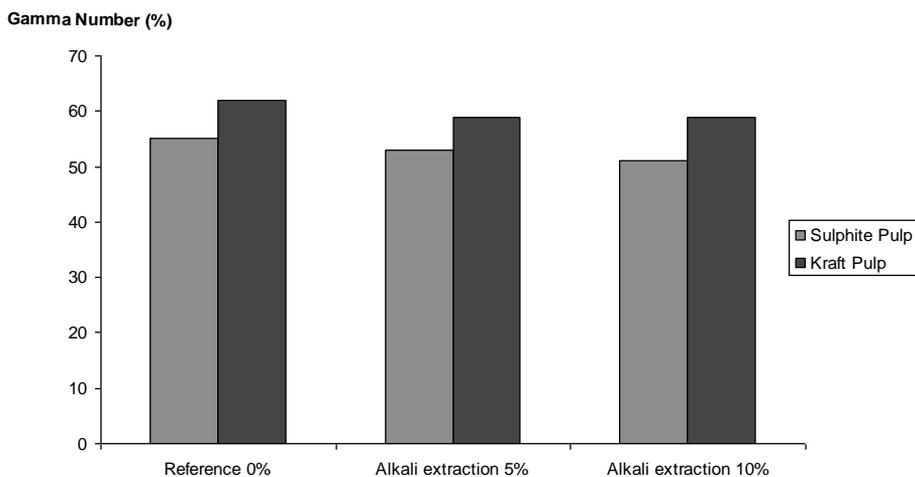


Figure 27. The gamma number of the viscose made from sulphite and kraft pulps.

Figure 27 shows that the viscose made from sulphite pulp had a slightly lower gamma number when it had been treated with alkali. It appears to be a correlation between the gamma number and hemicellulose content of the sulphite pulp. The hemicellulose content of the kraft pulp, on the other hand, seemed to have only a minor effect on the gamma number as the gamma number was mainly intact while the hemicellulose content according to Figure 24 was significantly lower after the alkali extraction.

5 Conclusions

The enzyme charge or the retention time had to be kept down to avoid a severe loss of the limiting viscosity number of the cellulose. The Fock reactivity of dissolving pulps increased if an endoglucanase stage was used as pre-treatment and was unchanged when a xylanase stage replaced the endoglucanase treatment as pre-treatment. The Fock reactivity of dissolving pulps increased after a mild enzyme treatment with an endoglucanase enzyme, but the reactivity of the pulps according to Fock's test was found to be a poor indicator of the gamma number of the prepared viscose solutions.

The gamma number of viscose solutions was unchanged when an enzyme stage was used prior to the viscose process. The gamma number analysis was found not to be selective only to cellulose but also to the hemicellulosic material. It was verified that both cellulose and hemicellulose molecules in the pulp material were substituted in the viscose preparation stages which means that the gamma number of the pulp is due, not only to substituted cellulose but also to substituted hemicelluloses. However, the presence of hemicellulose in the viscose dope leads to a higher risk for gel formation and a higher consumption of carbon disulphide, resulting in a higher gamma number.

The mechanisms responsible for the Fock reactivity or the filter clogging value (K_w) on one hand, and the gamma number on the other, are probably not the same. It was speculated that the analysis method for Fock's test and the fibre clogging value measure the results on a fibre level while the gamma number analysis is mainly measuring changes on a molecular level. This could be the reason to the difference in reactivity found in the study.

It has also been shown that a cold alkali extraction of two chemical pulps intended for paper production significantly reduced the hemicellulose content of the pulps. Such an extraction influenced the R_{18} value, the Fock reactivity and the gamma number of the viscose dope made from these pulps.

7 Acknowledgements

From experience I can tell you that this last page of a thesis is the most widely read page of the entire publication. It is here you think that you will find out whether you have meant something in the life of the PhD student (or not). While this may be true to some level, you have to weigh my verdict with the disturbingly low level of sanity left in this PhD student after several years of studying high viscosity viscose and handling of elderly and troublesome laboratory equipment.

Firstly, I thank my daughter, Alexandra, and my dear Anders for their unconditional love and support in spite of my absent-mindedness while working on this thesis. Not forgetting my mother, Elisabeth, and my father, Olle, who have always stood by me and encouraged me. I love you!

My thanks also go to my supervisors, Professor Ulf Germgård, Dr. Niklas Kvarnlöf and Dr. Helena Håkansson for valuable, essential and supporting discussions.

I am deeply indebted to Dr. Martin Ragnar, without you this thesis would probably not have been written. Your comments and joyous acclamations have been of great value to me. Thank you!

Special thanks are given to my colleagues and friends, past and present, but especially Heléne Almlöf Ambjörnsson, my best (and only) office roommate.

M.Sc. Woril Turner and Mrs. Maureen Sondell are thanked for their language revision.

The Swedish Governmental Agency for Innovation Systems (VINNOVA) and the industry participants in this project are gratefully acknowledged for their financial support.

Freudenberg HP is thanked for valuable discussions concerning the experimental results that were obtained.

Domsjö Fabriker AB is thanked for supplying dissolving pulp, Nordic Paper for supplying sulphite pulp, Södra for supplying kraft pulp and Novozyme A/S for supplying enzymes. My appreciation is extended to the staff of Metso Fiber Laboratory for valuable discussions pertaining to laboratory analysis.

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