Extended Mercerization Prior to Carboxymethyl Cellulose Preparation
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Heléne Almlöf. *Extended Mercerization Prior to Carboxymethyl Cellulose Preparation*

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Abstract

Carboxymethyl cellulose (CMC) is produced commercially in a two-stage process consisting of a mercerization stage, where the pulp is treated with alkali in a water alcohol solution, followed by an etherification stage in which monochloroacetic acid is added to the pulp slurry. In this thesis an extended mercerization stage of a spruce ether pulp was investigated where the parameters studied were the ratio of cellulose I and II, concentration of alkali, temperature and retention time. The influence of the mercerization stage conditions on the etherification stage, were evaluated as the degree of substitution (DS) of the resulting CMC and the filterability of CMC dissolved in water at a concentration of 1%. The DS results suggested that the NaOH concentration in the mercerization stage was the most important of the parameters studied. When the NaOH concentration in the mercerization step was low (9%), a high cellulose II content in the pulp used was found to have no negative impact on the DS of the resulting CMC compared with pulps with only cellulose I. However, when the NaOH concentration was high (27.5%), pulps with high content of cellulose II showed a lower reactivity than those with only cellulose I with respect to the DS of the CMC obtained after a given charge of NaMCA. The results obtained from the filtration ability study of CMC water solutions suggested that both the amount of cellulose II in the original pulp and the temperature had a negative influence on the filtration ability whereas the NaOH concentration in the mercerization stage had a positive influence. The filtration ability was assumed to be influenced highly by the presence of poorly reacted cellulose segments. A retention time between 1-48 h in the mercerization stage had no effect on either the DS or the filtration ability of the CMC.

Using NIR FT Raman spectroscopy molecular structures of CMC and its gel fraction were analyzed with respect to the conditions used in the extended mercerization stage. Here it was found that the alkaline concentration had a very strong influence on the following etherification reaction. FT Raman spectra of CMC samples and their gel fractions prepared with low NaOH concentrations (9%) in the mercerization stage indicated an incomplete transformation of cellulose to Na-cellulose before carboxymethylation to CMC. Low average DS values of the CMC, i.e. between 0.42 and 0.50, were yielded. Such CMC dissolved in water caused very thick and semi solid gum-like gels, probably due to an uneven distribution of substituting groups along the cellulose backbone. FT Raman spectra of CMC mercerized with alkaline concentrations at 18.25 and 27.5% in the mercerization stage indicated, however, that all of the cellulose molecules were totally transferred to CMC of high DS, i.e. between 0.88 and 1.05. When dissolved in water such CMC caused gels when they were prepared from ether pulp with a high fraction of cellulose II.
Papers included in this thesis

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

I. Quantitative analysis of the transformation process of cellulose I → cellulose II using NIR FT Raman spectroscopy and chemometric methods

II. The influence of extended mercerization on some carboxymethyl cellulose properties

III. CMC and its gel fraction - produced by extended mercerization and characterized by NIR FT Raman spectroscopy
   Heléne Almlöf, Karla Schenzel and Ulf Germgård. Manuscript in preparation for submission to Cellulose.

Other publications by the same author

The influence of mercerization on the degree of substitution in carboxymethyl cellulose
   Heléne Almlöf, Bjørn Kreutz, Kristina Jardeby and Ulf Germgård
   Paper presented at The 4th Workshop on Cellulose, Regenerated Cellulose and Cellulose Derivatives at Karlstad University, Karlstad, Sweden on November 17-18, 2009.
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1 Introduction

Cellulose is the most abundant renewable material in the world, being the principal component of plant mass and the most widely encountered natural polymer (Klemm et al. 2001 Vol. 1). Payen was the first to determine the elemental composition of cellulose, reporting in 1838 that it had the empirical formula \( \text{C}_6\text{H}_{10}\text{O}_5 \) (Payen 1842; Krässig 1993). The hydroxyl groups of cellulose can be rather easily reacted, either partially or fully, with various chemicals to provide derivatives with many different and useful properties. Cellulose derivatives, particularly those that are soluble in water, constitute a class of polymers that have attracted considerable interest for a diversity of applications. Carboxymethyl cellulose (CMC) is the most important and widely applied ionic ether: it is used in applications that exploit the specific properties of the solution, e.g. thickeners, binding agents, emulsifiers and stabilizers, in areas such as paper coating, detergents, personal care, pharmaceuticals, food, oil drilling and construction. The production volume is in the region of 300 000 t/a (Klemm et al. 2001 Vol. 2), with the first published CMC report being a patent from 1921.

Cellulose has three reactive hydroxyl groups per anhydroglucose unit that form inter- and intramolecular hydrogen bonds. These bonds influence the chemical reactivity and solubility of cellulose strongly. Cellulose is thus insoluble in most common solvents, so the successful preparation of derivatives requires a special approach. There are two categories of cellulose reactions: homogeneous reactions starting from the dissolved polymer, and heterogeneous reactions in which cellulose remains in either a solid or more or less swollen state during chemical modification. The derivation reaction of cellulose to CMC occurs in a swollen state, where the swelled alkali-cellulose is reactive towards different chemicals and cellulose derivates can therefore be formed.
1.1 The structure of wood

Wood is composed of elongated fibres which are mostly orientated in the longitudinal direction of the stem. The main molecular components of wood are cellulose, hemicellulose and lignin, the amount of which varies depending on the type of fiber in question. The same constituents are distributed differently in the fibre cell wall layers around the central cavity, which is called the lumen. A schematic description of the fibre cell wall is shown in Figure 1.

![Wood structure](image)

Figure 1. Illustration of the fibre structure of wood showing the middle lamella (ML), the primary wall (P), the winding (S₁) and main body (S₂) layers of the secondary wall, the tertiary wall (T) and the lumen (W). Adopted from Krässig 1993.

Norway spruce (Picea abies) consists of approximately 42% cellulose, 29% hemicellulose and 28% lignin with the remaining 1% consisting of extractives and inorganic material. The S₂ layer in spruce is richest in cellulose, with a cellulose concentration of about 50-65%.

1.2 The supramolecular structure of cellulose

The structure of the cell wall, which is a composition of macro-fibrils consisting of aggregates of cellulose chains, is of great importance. Elementary fibrils are the smallest morphological unit, being around 3-20 nm in diameter (Klemm et al. 2001 Vol. 1). These micro-fibrils, the length of which can reach micrometers, aggregate into larger morphological entities with diameters in the range of 10-50 nm. Macro-fibril aggregates of micro-fibrils can reach diameters in the range of 60-360 µm (Fink et al. 1990).
Some parts of a micro-fibril are crystalline (ordered) whilst others are amorphous (disordered), depending on how the cellulose molecules are linked together. Hydrogen bonding is the primary source of cohesion between the cellulose chains, giving rise to these crystalline and amorphous regions. A two-phase model with crystalline and amorphous regions is generally accepted today and is important for understanding the heterogeneous cellulose reactions. The accessibility of cellulose has been reported to be a function of the degree of cellulose crystallinity (Jeffries et al. 1969). The degree of crystallinity of different cellulose samples covers a wide range and depends on the origin and pretreatment of the sample.

1.3 The cellulose molecule

The cellulose molecule is not only linear but also unbranched. It has a strong tendency to form intramolecular (in the same molecule) and intermolecular (between neighbouring molecules) hydrogen bonds depending on their location in the AGU (Klemm et al. 2001 Vol. 1). The intramolecular hydrogen bonds are the main reason for the stiffness and rigidity of the cellulose molecule. Cellulose is not soluble in common solvents as a result of the strong hydrogen bonds between the cellulose chains.

All cellulose substrates are polydisperse, i.e. they always consist of a mixture of molecules of varying length. Native cellulose is composed of two crystalline phases; cellulose Iα and Iβ (Atalla and VanderHart 1984; Atalla 1989). The ratio of Iα/Iβ in the composite varies depending on the source of the cellulose. In wood
pulp, the crystalline form cellulose $\beta$ dominates whereas in bacteria and algae, it is cellulose $\alpha$.

![Cellulose based unit](image)

Figure 3. The structure of cellulose, where $n$ is the number of anhydroglucose units. Adopted from Klemm et al. 2001 Vol. 1.

In the chain-like extended linear macromolecule the glucose units are linked together by $\beta-1,4$-glucosidic bonds formed between the carbon atoms C$_1$ and C$_4$ of adjusted glucose units, as shown in Figure 3. During the chemical reaction forming the acetal linkage of a single oxygen atom linked to two carbons, a molecule of water is given off. Consequently, the glucose unit in the cellulose polymer is referred to as anhydroglucose units (AGU). The cellulose chain has a non-reducing (alcoholic) hydroxyl end group and a reducing (aldehyde) hydrate end group that show different patterns of behaviour.

The degree of polymerization (DP) of wood, i.e. the number of $\beta$-D-glucopyranose units per molecule, is 8000 on average. For cellulose the relationship between molecular weight, $M$, and the DP is shown in Equation 1 (Hong et al. 1978):

$$DP = \frac{M}{162}$$

where 162 is the molecular weight of an AGU. Eq. [1]

Wood cellulose with an average DP of 8000 gives an average molecular mass of $1.3 \cdot 10^6$ g/mol. The degree of polymerization in pulp is normally 2500-5000, which gives a molecular mass of $4-8 \cdot 10^5$ g/mol. This is equivalent to an intrinsic viscosity of 800-1500 dm$^3$/kg of pulp dissolved in copperethylenediamine (COD) (SCAN-CM 15:99).

The chemical character of the cellulose molecule is determined by the sensitivity of the $\beta$-glucosidic linkages between the glucose repeating units to hydrolytic attack and by the presence of three reactive hydroxyl groups, i.e. the primary OH-6 and the two secondary OH-2 and OH-3 in each of the glucose units. These reactive hydroxyl groups are able to undergo etherification and esterification reactions. The reactivity of the hydroxyl groups is to a certain extent dependent on solvent and decreases in the order $OH-2 > OH-6 > OH-3$ in the cellulose molecule when producing CMC in isopropanol, determined by H-NMR (Baar et al. 1994).
1.4 Cellulose swelling

Cellulose can be swelled in some solvents; the degree of swelling is dependant on the solvent used and the nature of the cellulose. It was John Mercer who, as far back as in 1850, observed that when cotton was immersed without tension in a solution of strong caustic soda it shrank in width and length, thereby becoming denser. He also observed that the cotton became stronger and its dye affinity was improved. This was the starting point for the process that came to be known as “mercerization”, which was named after its inventor, and involves cellulose material being treated with a concentrated solution of sodium hydroxide (NaOH). In contrast to the comprehensive work carried out on the swelling of cellulose using alkali hydroxides in water, results using non-aqueous solutions are rather scarce. Experiments using NaOH dissolved in aliphatic alcohols, i.e. isopropanol, show nevertheless that swelling is markedly reduced when compared to aqueous systems, and proceeds much more slowly (Klemm et al. 2001 Vol. 1).

Morphological changes take place in native fibrous cellulose material during swelling with NaOH; swelling can be of either interfibrillar or intrafibrillar in character. Only the disordered amorphous regions of the cellulose micro-fibrils and the regions between the micro-fibrils are swelled in interfibrillar, or intercrystalline, swelling. Such swelling can also disrupt fibril aggregations that either occur naturally or are caused by “hornification”, that occurs when the cellulose is dried, thus enhancing reactivity. The ordered crystalline regions of the cellulose are also penetrated and swelled in the case of intrafibrillar, or intracrystalline, swelling.

An alkali cellulose is formed when cellulose I is treated with strong alkali (mercerization). When this alkali cellulose is washed, a transformation into cellulose II occur. The transformation also occurs when homogeneously dissolved cellulose is precipitated, which is also known as “regeneration”. When transformation to cellulose II once occurs, it is not reversed to cellulose I.

![Figure 4. Possible mechanism of mercerization (Okano and Sarko 1985).](image-url)
The most important swelling complexes are those formed after treatment with sodium hydroxide and are known as alkali-celluloses. They are very important intermediates since they have an enhanced reactivity towards chemical reactions compared to the original cellulose. This means that reagents can penetrate the swelled cellulose structure more easily and react with the hydroxyl groups. The substitution reaction with the hydroxyl groups is easier because the nucleophilic attraction between O-H is decreased in the hydroxyl groups of the swelled alkali-cellulose.

![Schematic diagram of the Na-cellulose I structure according to Fink et al. (1995).](image)

Figure 5. Schematic diagram of the Na-cellulose I structure according to Fink et al. (1995).

It has been observed that the uptake of alkali metal hydroxides by cellulose is not a chemical process in the strict sense but rather an absorption phenomenon. However, this does not exclude the preferential uptake from involving a complex formation between the alkali ions and the hydroxyls of the cellulose. Alkali-cellulose is reported to be found in several different crystalline forms that differ in their unit cell dimensions.

NaOH treatment of cellulose yields the pure cellulose modifications I and II as well as mixtures of cellulose I and II, depending on the alkali concentration. Minimum energy considerations favour a parallel arrangement of cellulose I and an antiparallel of cellulose II. It is difficult, however, to imagine, this total rearrangement of the cellulose structure and no proper explanation and/or mechanism have been proposed. Based on X-ray diffraction measurements made by Okano and Sarko (1985), as well as by Langan et al. (2001), it was concluded that an antiparallel recrystallization had occurred in cellulose II after alkali treatment and washing. Electron microscopic investigations (Maurer and Fengel 1992), molecular dynamics simulations (Kroon-Batenburg et al. 1996), and second harmonic generation measurements (Marubashi et al. 2004), on the other hand, suggest that the orientation of the molecular chain of cellulose II is parallel.
The system of hydrogen bonds in cellulose II appears to be more complicated than that in cellulose I. It results in a higher, intermolecular, cross-linking density, making it therefore less reactive than cellulose I (Kolpack & Blackwell 1976, Kolpack et al. 1978). All of the hydroxyls are positioned favourably for the formation of intermolecular and intramolecular hydrogen bonds in the unit cell structure of cellulose II. Because of the more dense structure and greater involvement of the hydroxyls in the hydrogen bonding of cellulose II the reactivity is lower by reduction of the accessible interfibrillar surface of the cellulose II structure (Krässig 1993).

1.5 Properties of pulp

Pulps produced as raw material for the production of viscose, cellulose ethers and esters are called “dissolving pulps”. The acid sulphite and prehydrolysis kraft processes alone are of major practical importance in the production of such pulps (Kordaschia 1999). A shift is taking place away from traditional, softwood, sulphite pulps in favour of hardwood, prehydrolysis, kraft pulps (Sixta and Borgards 1999). The manufacture of dissolving pulps involves purification and bleaching processes that both ensure that the pulp is chemically pure with respect to cellulose as well as making it brighter. The carbohydrates are depolymerised, whilst the content of ash and resin are both reduced in the production process. One important parameter pertaining to the pulp is the α-cellulose content, which is defined as the pulp fraction that is resistant to sodium hydroxide of 17.5% and 9.45% in strength.
under the conditions prescribed in TAPPI Standard T 203 om-88. It is not, however, the same as the pure cellulose content since only some of the hemicelluloses are dissolved. Sulphite dissolving pulps are produced with \( z \)-cellulose contents of approximately 90-95%, with the rest consisting of hemicelluloses (mainly xylans) and small amounts of residual lignin, resins, etc. Sulphate dissolving pulps have \( z \)-cellulose contents of approximately 94-97 %, with the remainder being mainly hemicellulose of the glucomannan type.

It has been reported that the important properties of pulps intended for the production of cellulose derivates are the brightness, \( z \)-cellulose content, pentosan content (i.e. xylan content), copper number, ether and alcohol extracts, ash content, viscosity, average degree of polymerization (DP), average fibre length and fibre length distribution (Wurz 1961). It has also been reported that the important properties of the technical cellulose used for the dissolving pulp are low contents of lignin, hemicelluloses and extractives as well as a high viscosity (Lönnberg 2001).

1.6 Crystallite length

The levelling-off degree of polymerization (LODP) is the result of the acid hydrolysis that is used as a tool to investigate the supramolecular structure of cellulosic material, and was first investigated by Battista in 1956. When pulp is subjected to acid hydrolysis, glucosidic linkages of the cellulose are broken and the degree of polymerization (DP) decreases. Acidic hydrolysis is a water-splitting reaction that proceeds in three stages: 1) the rapid protonation of the glycosidic oxygen atom, followed by 2) a slow transfer of the positive charge to C1 leading to the acyclic carbonium cation and the simultaneous split of the glycosidic linkage and, finally, 3) the fast addition of water to the carbonium ion.

![Figure 7. Mechanism for the acid hydrolysis of glycosidic linkages.](image)

The DP decreases rapidly until it reaches the “leveling-off”, or “limiting”, degree of polymerization (LODP), as illustrated in Figure 8.
It has been shown that the LODP corresponds to both the average length of the crystallites and the length of the fibre fragments that are obtained after mild ultrasonic treatment of the hydrolysis residue of wood pulp and cotton linters (Battista et al. 1956). The degree of degradation and the amount of material dissolved are related to the degree of accessibility of the cellulose to chemical reactions. The LODP observed in the hydrolysis process is assumed to be a result of the arrangement of cellulose molecules in micro-fibrils with crystalline regions interrupted by amorphous regions. The particles obtained after dissolution of the amorphous fraction of the cellulose are known as “microcrystals” or “crystallites”.

The cleavage of glycosidic bonds by an alkali (alkaline hydrolysis) is usually extremely slow in comparison with acid-catalyzed hydrolysis; the rate of alkaline hydrolysis becomes more pronounced at temperatures above 150°C (Sjöholm 1999). Alkaline hydrolysis creates new reducing ends that are subjected to further peeling reactions. The probable mechanism of alkaline hydrolysis is outlined in Figure 9.
1.7 Carboxymethyl cellulose (CMC)

This water-soluble polymer was invented in 1918, with the first patent being granted in 1921 (DE 332203). CMC is manufactured by reacting sodium monochloroacetate with alkali cellulose. It is almost always in the form of the sodium salt, but instead of using the longer name, sodium carboxymethyl cellulose (NaCMC), it is usually designated simply carboxymethyl cellulose (CMC) (Stigsson 2006). In this thesis, CMC or carboxymethyl cellulose is used as a short name for NaCMC or sodium carboxymethyl cellulose.

![Figure 10. Typical structure of sodium carboxymethylcellulose with a DS of 1.](image)

The preparation of CMC involves two reaction stages: mercerization and etherification. These are carried out in water-alcohol mixtures, i.e. as slurry processes at 10% pulp consistency. The slurry process ensures a good mixing efficiency and thereby a homogeneous reaction, although it also leads to a low degradation of the cellulose chain.

In the first step of the CMC process the dissolving pulp is treated with NaOH in a water-alcohol mixture at 20-30°C, where the alcohol is usually either ethanol or isopropanol. This treatment acts as a swelling and impregnation step and facilitates good penetration of the NaOH into the cellulose structure. The “alkali cellulose” produced is reactive towards, for example, monochloroacetate acid, which is added in the second step either as free acid, MCA, or as its sodium salt, NaMCA. The etherification reaction between the alkali cellulose and the etherification agent is normally carried out at about 60-70°C. NaOH reacts simultaneously with MCA to form the two by-products sodium glycolate and sodium chloride (Krässig 1993).
CMC is produced by Williamson etherification in an aqueous-alcoholic system according to the following reactions (Stigsson et al. 2001):

**Mercerization**

\[
\begin{array}{c}
\text{cellulose} + \text{NaOH} \\
\rightarrow \text{cellulose-Na}^+ \text{OH}^-
\end{array}
\]

**Etherification**

\[
\begin{array}{c}
\text{cellulose-Na}^+ \text{OH}^- + \text{Cl}^- \\
\rightarrow \text{cellulose-Na}^+ \text{Cl}^- + \text{NaOH}
\end{array}
\]

**Side reaction**

\[
\begin{array}{c}
\text{Na}^+ \text{Cl}^- + \text{NaOH} \\
\rightarrow \text{Na}^+ \text{OH}^- + \text{NaCl}
\end{array}
\]

Carboxymethylation is a macro-heterogenous reaction; it occurs only at accessible hydroxyl groups, followed by the slow penetration of the ordered surfaces (Borsa et al. 1992). Cellulose reactivity in a heterogeneous alkali medium depends not only on the cellulose structure at molecular, supermolecular or morphological levels but also on the reaction medium employed. It is known that the reaction rate in ethanol is lower than that in isopropanol since ethanol is better at dissolving sodium hydroxide (Olaru & Olaru 2001). The crystallinity and polymorphism of the cellulose change during the mercerization step; the organic solvent acts as a swelling-restrictive agent and does not permit full hydration of the cellulose chain (Yokota 1985).

Isopropanol is a poorer solvent for sodium hydroxide compared with ethanol, and a two-phase system therefore occurs. Only small amounts of the Na⁺ and the OH⁻ ions enter the alcohol phase, favouring a higher concentration of NaOH in the vicinity of the cellulose, see Figure 11. This results in a substantial
decrystallization and change of polymorphism from cellulose to Na-cellulose during mercerization.

![Diagram of mercerization process](image)

Figure 11. The solvent effect during the mercerization.

It is also reported that different solvent systems affect the characteristics of CMC during its manufacture. When isopropanol is present during the mercerization stage, for example, substitution is more uneven; tri-substituted units occur and substitution on the C₆ carbon is increased (Stigsson et al. 2006).

A pseudo, first-order, kinetic relationship for the carboxymethylation reaction has been proposed for the isopropanol-ethanol system whereby the relationship is given as \( \ln(1.11 - \text{DS}) = -kt + c \) (where \( k \) is the slope, \( t \) the time, \( c \) the intercept and 1.11 the molar ratio MCA/AGU at \( t=0 \)) (Olaru and Olaru 2001). This relationship is governed by the cellulose structure, crystallinity and polymorphism, and probably also by the concentration of the reagent near the hydroxyl groups of the cellulose molecules.

Carboxymethyl cellulose prepared by reacting alkali-cellulose with sodium monochloroacetic acid utilizes the “alkali consumption reaction” mechanism. The methylation proceeds as a nucleophilic substitution by the interaction of the oxonium sodium hydroxide complexes on accessible cellulose hydroxyls with methyl halide. Sodium hydroxide is consumed in this reaction, which means that the initial charge has to be so high that NaOH is present in sufficient supply to maintain an alkaline pH throughout etherification. The reaction requires at least 0.8 mole of NaOH per mole of AGU to remain alkaline if etherification is performed with sodium monochloroacetate. Should monochloroacetic acid be used instead, then an extra mole of NaOH per mole of AGU must be added to neutralize the acid (Klemm et al. 2001. Vol. 2). If the pH during etherification is acidic, an internal esterification occurs and the CMC molecules become cross-linked (Benford D.J.).
1.8 Degree of substitution (DS)

CMC is a cellulose ether where some of the hydrogen atoms on the hydroxyl groups on the C₂, C₃ or C₆ positions in the anhydroglucose unit are replaced by a carboxymethyl group. The DS of a CMC sample is the average number of carboxymethyl groups per anhydroglucose unit. It is one of the most important characteristics of CMC and determines, for example, its solubility in water. The theoretical maximum of the DS value is 3.0 but the DS range for commercially available CMC grades is generally 0.4-1.5 (Heinze and Koschella 2005). Solubility in water is enhanced by increasing DS; CMC has good water solubility above 0.6. Carboxymethyl cellulose of low DS, i.e. less than 0.2, retains the fibrous character of the starting material and is not soluble in water (Borsa and Racz 1995). The DS of CMC can be increased by a multi-step reaction. Applying a one-step reaction gives a maximum DS of around 1.3-1.5 (Heinze and Koschella 2005).

The rheological properties of CMC water solutions have been found to depend on the degree of substitution and the reactivity of the cellulose (Barba et al. 2002). The substitution process that occurs along the hydrocolloid chain results in a CMC that can be either evenly or unevenly substituted, depending upon the conditions used during its preparation. An unevenly distributed CMC or a CMC with a low DS can create the formation of a three-dimensional network structure, especially when CMC is in the form of a gel.

1.9 NIR FT Raman spectroscopy

NIR FT Raman spectroscopy refers to a spectroscopic technique that measures the interaction of radiation with a molecule, as a function of frequency or wavelength. In Raman spectroscopy incident photons disturb the cloud of outer electrons around atom nucleus and oscillating induced dipole of molecule interact with the polarizability ellipsoid of the vibrating molecule. The photons are scattered and in NIR FT Raman spectroscopy pure excitation vibrational scattering is observed in the wavelength range close to infrared light, i.e. at 780-2500 nm. The most common molecular vibrations that occur are stretching and bending. Stretching occurs when the distance between the atoms in the bonding direction of the molecule is altered, whereas bending applies when the angle between the atoms in the molecule changes. There are four different types of bending: scissoring, rocking, wagging and twisting.

Vibrational spectroscopy in general and Raman spectroscopy in particular, has played an important role in the investigation of cellulose structures. The fundamental studies carried out by Atalla and co-workers confirmed the advantage of this analytical method over IR and NMR spectroscopy in determining the
molecular conformations and hydrogen bonding patterns of cellulose and cellulosic biomaterials (Wiley and Atalla 1987). The methods used that would allow the transformation order of the lattice conversion of cellulose I to cellulose II be followed with respect to the reaction conditions used are based on $^{13}$C CP/MAS NMR spectroscopy (Kunze et al. 1981) and WAXS (Borusiak and Garbarcyk 2003). These techniques are time-consuming and expensive so it is necessary, in accordance with new spectroscopic approaches, to establish reliable and rapid methods of analysis for the quantification or prediction of the physical and chemical properties of complex molecules such as cellulose. The information concerning crystallinity of cellulose II can also be obtained by FT Raman and this method normally uses a calibration with WAXS (wide angle X-ray scattering) data (Röder et al. 2006).

1.10 Objectives of the study

One of the most important properties of the cellulose raw material used in the manufacture of CMC is its reactivity and, in this case, its ability to be etherified. The literature shows that approximately 35-50% of the hydroxyl groups can be etherified in cotton or dissolving pulps (Krässig 1993). The accessibility of hydroxyl depends on the packing efficiency of the cellulose polymer chains. Well-packed cellulose chains experience strong hydrogen bonding whereas an amorphous structure is more open. The ease with which a hydroxyl centre can be derivatized in a cellulosic material is found to be directly dependent upon its crystallinity (Tasker and Badyal 1994). In practice, the main problems encountered are often poor accessibility in the fibre or the presence of fibre parts that have poor reactivity which, in dissolving pulps, may be fibres with a high content of cellulose II. One important criterion for the transformation of cellulose into Na-cellulose for further processing to cellulose ethers is the transformation of cellulose I to cellulose II as a function of the NaOH concentration. The ratio of cellulose I and II in the cellulose raw material is supposed to influence the level of reactivity in the etherification stage; earlier studies using solid state $^{13}$C-CP/MAS-NMR and NIR (Near Infrared Spectroscopy) show that the cellulose II content can vary between 2 and 4% in bleached spruce sulphite pulps (Fälldin 2002). The final degree of substitution, the filterability and the gel-fraction in the resulting CMC, along with the ratio of cellulose I and II in the original pulp, were studied in order to investigate whether or not the lower level of reactivity of cellulose II affects the resulting CMC. The objective of this study also included the investigation of a possible correlation between the conditions in the mercerization process, the DS, the filterability and the gel-fraction in CMC. This was carried out by varying the NaOH concentration, time and temperature in the mercerization stage. The charge of NaMCA in the etherification stage was kept constant (1.21 mol NaMCA/mol AGU) since the focus was on the mercerization stage.
2 Materials and Methods

2.1 Materials

The following chemicals were used in the preparation of the CMC: Isopropanol (purity 99.7 %, VWR International), methanol (purity 99.8 %, VWR International), NaOH (purity 97 %, MERCK) and sodium monochloroacetate (C₃H₅ClNaO₂) (purity 97 %, Fluka).

Original ether pulp

One fully-bleached and dried sulphite dissolving pulp produced from Picea abies (Norwegian spruce), denoted here as “ether pulp”, was provided by Borregaard Chemcell, Sarpsborg, Norway. It was a high molecular weight ether pulp with an intrinsic viscosity of 1500 cm³/g, S₁₈ value of 7.5 %, ISO brightness of 85 % and cellulose II content of less than 3 %.

NaOH-pretreated ether pulp prior to CMC preparation

A large sample of ether pulp (0.5 kg) was ground into a fine powder in a knife mill (Fritsch Pulverisette 19). Samples of the powdered pulp (30 g/sample) were mixed with 1 litre of alkaline water of 18% NaOH, corresponding to 29.2 mol NaOH/mol AGU. They were then shaken for 30 minutes in plastic glove boxes at room temperature in an anaerobic atmosphere before being washed with ion-free water to a neutral pH, air dried and stored at room temperature. The samples obtained were assumed to consist of pure cellulose II, with a possible content of amorphous cellulose but no cellulose I. These pulps are denoted here as “NaOH-pretreated ether pulps”. A number of samples of the powdered pulp were only mixed with ion-free water, air dried and stored at room temperature as a reference to the NaOH-pretreated pulps. They were assumed to consist of pure cellulose I, and possibly amorphous cellulose, but no cellulose II.

Alkali-treated ether pulp prior to analysis

Samples of 30 g powdered ether pulp were subjected to alkali treatment, using different concentrations of NaOH, in a similar way as described for the NaOH-pretreated ether pulp above. The ether pulps were mercerized at the following NaOH concentrations: 0%, 2%, 4%, 5%, 6%, 8%, 9%, 10%, 12%, 14%, 15%, 16%, 18%, 20%, 22%, 24%, 26% and 28%. This corresponds to 0, 2.8, 5.6, 7.1, 8.7, 11.8, 13.4, 15.0, 18.4, 21.9, 23.7, 25.5, 29.2, 33.1, 37.0, 41.1, 45.3 and 49.6 mol NaOH/mol AGU.
2.2 CMC-synthesis

The carboxymethylation procedure
A 17.5 g sample of the ether pulp was introduced into a glass reactor together with 224 ml isopropanol and 20.3 ml deionised water. The impeller was held at 350 rpm throughout the reaction and a water cooler was mounted at the top of the glass reactor to condense the vaporized solvent. Nitrogen gas (N\textsubscript{2}) was added continuously to the solution to remove the oxygen from the glass reactor. Either 3.0 g, 6.7 g or 11 g of NaOH were mixed with 10 ml of deionised water and 39 ml of isopropanol and were added to the solution 15 minutes later. The NaOH-charges corresponded to 0.65, 1.55 and 2.55 mol NaOH/mol AGU. The mixture was left at 20°C, 30°C and 40°C for 1 hour, 24.5 hours or 48 hours. In the next step, 49 ml of 87% 2-propanol were mixed with 15.2 g of sodium monochloroacetate (NaMCA), corresponding to 1.21 mol NaMCA/mol AGU, before being added to the reaction mixture. The temperature was raised during a period of 30 min to 60°C and then left for 60 min at 60°C. The reaction was terminated by adding acetic acid to the solution. After filtration, the product was washed with 350 ml of 87% isopropanol and then three times with 350 ml of 70% methanol. The product thus obtained was CMC.

2.3 Analysis methods

Determining the DS of the CMC
A 0.5 g sample of CMC, calculated as oven-dry product, was heated to 700°C for 15-20 min; the resulting ash was cooled in a glass desiccator containing silica gel as the drying agent. The ash was then dissolved in 6 ml boiling deionised water before being titrated with 0.1 N H\textsubscript{2}SO\textsubscript{4} (using 702 SM Titrino from Metrohm\textsuperscript{®}) until the solution reached a pH of 4.4. Equation 2 (Hong et al. 1978) was then used to calculate the DS value from the amount of titrated acid (b ml) and CMC (G g) used.

\[
DS = \frac{0.162}{1 - 0.080} \left( \frac{0.1b}{G} \right) \quad \text{Eq. [2]}
\]
**Filtration test**

The filtration test is a method whereby a dilute, water solution of CMC (1%) is filtered under standard conditions at a fixed temperature and under a specific pressure. The amount of liquid that passes through the filter during a given time is then measured. The CMC powder is dissolved in water to a 1% solution at 20°C during a period of 60 min. The solution is then diluted to 0.5%, stirred for 5 min and cooled to 14°C prior to filtration. The amount of filtrate that passes through the filter in intervals of one minute is collected during a period of 5 minutes. Each liquor sample is then weighed. The individual weight of each liquor sample is plotted versus time; the $dm/dt$ gradient, where $m$ is the weight of the filtrate and $t$ is time, is used to estimate the degree of unreacted material and gel particles. Finally, the filtrate weight accumulated during five minutes is calculated and used as the “filtration value”.

**Experimental equipment**

The experimental design was set up using Umetrics software MODDE 7 so that observation data could be collected systematically. The use of a statistical method enabled the main and interaction effects to be identified within a small number of experiments (Eriksson et al. 2000). The parameters were fully factorized at two levels for each variable and a response surface MLR (multiple linear regressions) was fitted. This design is coupled strongly to the MLR obtained relating the responses DS and filtration value to four factors: cellulose II (= fraction of cellulose II in the ether pulp), NaOH (= NaOH concentration), $T_e$ (= temperature) and $T_i$ (= time) in the mercerization stage. A total of 23 experiments were carried out, including some complementary triple trials corresponding to the reference levels used in the project not included in the original plan. The reference values used during the mercerization stage were: 17.5 g pulp, 1 hour, 20°C, and 27.5% NaOH, which corresponds to 2.55 mol NaOH/mol AGU.

**FT Raman spectroscopy**

NIR FT Raman spectra of the samples were acquired using a Bruker RFS 100 spectrometer equipped with a liquid nitrogen-cooled Ge diode as the detector. A Nd:YAG-laser, operating with the exciting line $\lambda_0 = 1064$ nm and a maximum power of 1500 mW, served as the light source for the excitation of Raman scattering. All of the FT Raman spectra were recorded over the frequency range 3400–100 cm$^{-1}$ using an operating spectral resolution of 4 cm$^{-1}$. The cellulosic samples were analyzed in small aluminium wells of the sampling accessory placed across the normal sample holders; 180° backscattering geometry was applied. The spectra were averaged over 400 scans using 350 mW laser power output. These
measurements were repeated twice for each sample under the same conditions and an average spectrum was calculated.

**Acid hydrolysis of alkali treated ether pulp**

A sample of 2.00 g of the alkali-treated ether pulp was put in a flask together with 200 ml 3 M HCl (aq). The flask was then put in a water bath of 80 °C, where hydrolysis took place, for a period of one hour whilst being gently shaken. The hydrolysis process was arrested by cooling the flask in an ice-bath and the residue was filtered off on a glass filter (porosity 4) with a diameter of 3 cm. The filtrate was then washed with deionised water until it was neutral before being dried at room temperature. The intrinsic viscosity was determined according to SCAN-CM 15:99.

**Using filtration to remove the gel fraction in CMC**

The amount of gel and undissolved residuals found in the CMC solution was used as a measure of the reactivity of the cellulose in the ether pulp; filtration was used to isolate the gel and undissolved residuals. 9 g of the CMC was dissolved in 2 l of deionised water by stirring the solution for approximately 2 h at 1200 rpm. The solution was then filtered on a RBU glass filter of VitraPOR® Borosilicate 3.3, with a volume of 4000 ml, to separate the gel and undissolved residuals. The glass filter used was a Por. 3 with a pore size of 15-40 µm.

**The gel fraction**

The gel fraction of the CMC water solution was determined after filtration, being calculated as follows:

\[
\text{Gel fraction} = \left( \frac{G_i}{G_f} \right) \times 100 \quad \text{Eq. [3]}
\]

where \(G_i\) is the initial weight of the dry CMC and \(G_f\) is the weight of the dry insoluble part after extraction with water and a following filtration stage.
3 NIR FT Raman spectroscopy and chemometric methods for quantitative analysis of the transformation process of cellulose I → cellulose II (Paper I)

3.1 FT Raman spectra of cellulose I and cellulose II

Vibrational signals between 1500 cm\(^{-1}\) and 150 cm\(^{-1}\) generally provide the most important structural information of the cellulose molecule. The fine resolution of the convoluted vibrational spectra of cellulose pulps allows significant differences to be observed clearly between cellulose I and cellulose II, as shown by the FT Raman spectra in Figure 12.

![Figure 12. FT Raman spectra and second derivations of model compounds for cellulose I and cellulose II.](image)

The spectra and, for clarity, their second derivatives in the peaks are represented in the range 1500-200 cm\(^{-1}\) in Figure 12. Here, the stretching modes of the anhydroglucopyranose units of the cellulose skeletons, i.e. \(\nu(C-C)\), \(\nu(C-O)\) and \(\nu(C-O-C)\), can be seen along with the bending vibrations of the HCC, HCO, COH and CH\(_2\) groups at 1265 cm\(^{-1}\) and 1295 cm\(^{-1}\). The ring deformation vibrations of the glucopyranose skeletons \(\delta(CCC)\), \(\delta(CO)\) and \(\delta(CCO)\) are detected mainly in the frequency range lower than 600 cm\(^{-1}\). The differences in spectra are particularly obvious for the peaks at 360 cm\(^{-1}\) for cellulose II and 380 cm\(^{-1}\) for cellulose I. The vibrational modes assigned are derived from the paper of Wiley and Atalla (1987)
as well as from later work by the authors and the literature cited therein (Schenzel and Fischer 2001). The values assigned are not always unambiguous, however, due to the fact that most of the Raman lines are not pure group vibrations. In the frequency range 1500-200 cm$^{-1}$, only the internal vibrations of the methylene groups, i.e. the bending vibrations $\delta$(CH$_2$), may be described as being group modes, which is why these signals tend to be utilized in several quantitative analyses (Schenzel and Fischer 2005).

The lattice structures of the cellulose allomorphs are stabilized considerably by hydrogen bonding, so it has to be assumed that changes such as frequency shifts or decreases in the signal intensity of Raman lines are caused by lattice conversion processes. The signal assigned to the twisting mode of the methylene groups indicates indeed such behaviour, shifting from 1295 cm$^{-1}$ in cellulose I to 1265 cm$^{-1}$ in cellulose II, as seen in Figures 12 and 13.

![Figure 13. FT Raman spectra of generated mixtures of cellulose I and II representing adjusted degrees of the polymorphic transformation cellulose I $\rightarrow$ cellulose II.](image)

Typical changes in the conformation of the cellulose skeletons as a result of the breakdown and change in crystal lattice structure were observed in the range of the methylene bending vibrations, $\delta$(CH$_2$), in the FT Raman spectra. They indicate the simultaneous presence of two stereo chemically nonequivalent CH$_2$OH groups issued from the rotation of the side chains about the C(5)-C(6) atoms in cellulose I. In cellulose II, on the other hand, only one type of the CH$_2$OH groups is present. Consequently, the two scissoring vibrations of the methylene groups at 1477 cm$^{-1}$ and 1455 cm$^{-1}$ merge into one single signal at 1461 cm$^{-1}$ during the polymorphic
transformation process (Wiley and Atalla 1987; Schenzel and Fischer 2001). Changes were also detected for the glucopyranose ring deformations in the low frequency range, Figure 13. The intensity of the signal at 379 cm\(^{-1}\) decreased, whilst that of the peak at 352 cm\(^{-1}\) increased, because of the transition from the glucopyranose ring conformation of cellulose I to the ring conformation of cellulose II. Furthermore, a clear broadening of Raman signals is observed due to the cellulose lattice conversion, thus illustrating the breakdown of cellulose I crystal lattice structures resulting from the different chemical environments of the glucopyranose units. Earlier studies indicate that a decrease in the crystallinity of cellulose I is to be expected, owing to the transformation of the cellulose lattice (Schenzel and Fischer 2005). Atalla et al. (1984) had suggested previously that a third component is formed when pulps are treated with caustic solutions. WAXS investigations on alkali-treated cellulose fibres confirmed indeed that the cellulose I crystallinity of cotton decreased during the mercerization reaction (Borysiak and Garbarczyk 2003).

3.2 Quantitative analysis of the transformation process of cellulose I → cellulose II

Chemometric methods, i.e. multivariate calibration, classification and clustering of analytical data, tend to be used for analysis the quantification or prediction of the physical and chemical properties of complex molecules such as cellulose. Here, the method of multivariate calibration assists in developing a model that is capable of determining the order of the lattice conversion of cellulose I → cellulose II quantitatively. A partial least square regression algorithm (PLS) was applied to the FT Raman spectral data of cellulose I/cellulose II calibration mixtures generated to represent various adjusted degrees of the polymorphic transformation.

The obtained, multivariate, calibration model was tested on ether pulps treated with varying NaOH concentrations according to: 0, 2, 4, 6, 8... 28%, as described in Chapter 2.1. The FT Raman spectra of the alkali-treated pulps were examined thereafter using the multivariate lattice conversion model, see Figure 14.
Figure 14. Cellulose I → cellulose II transformation process of ether pulps treated with different NaOH solutions, \( C_{NaOH} \): 0, 2, 4, 6... 28%.

The prediction curve in Figure 14 illustrates the course of the conversion of cellulose I → cellulose II in the alkali-treated pulps as a function of the NaOH concentration used for each single treatment; these results are also given numerically in Table 1.

Table 1. Percentual proportions of cellulose I \( (C_{cell\ I\ Raman} \%)) \) and cellulose II \( (C_{cell\ II\ Raman} \%) \) determined by the chemometric model of the cellulose lattice conversion and percentual proportions of amorphous cellulose I \( (C_{cell\ amorph\ I\ Raman} \%)) \) derived from the cellulose I crystallinity model of Schenzel and Fischer (2005), representing modeled and corrected lattice conversion orders of the ether pulps treated with different NaOH concentrations.

<table>
<thead>
<tr>
<th>Concentration of alkali treatment ( C_{NaOH} ) (%)</th>
<th>Percentual content of cellulose I ( C_{cell\ I\ Raman} %)</th>
<th>Percentual content of cellulose II ( C_{cell\ II\ Raman} %)) and corrected lattice conversion order</th>
<th>Percentual content of amorphous cellulose I ( C_{cell\ amorph\ I\ Raman} %))</th>
</tr>
</thead>
<tbody>
<tr>
<td>modeled</td>
<td>corrected</td>
<td>modeled</td>
<td>corrected</td>
</tr>
<tr>
<td>0</td>
<td>83</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
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<tr>
<td>4</td>
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<td>2</td>
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<td>6</td>
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<td>24</td>
<td>9</td>
<td>91</td>
<td>52</td>
</tr>
<tr>
<td>26</td>
<td>12</td>
<td>88</td>
<td>49</td>
</tr>
<tr>
<td>28</td>
<td>7</td>
<td>95</td>
<td>54</td>
</tr>
</tbody>
</table>
It becomes clear that the conversion of cellulose I → cellulose II does not occur at NaOH concentrations lower than 6%. However, if the NaOH concentration is between 6-12%, the percentual content of cellulose I in the samples decreases significantly and that of cellulose II increases greatly. Around 94% of cellulose II is yielded if the NaOH concentration is at least 14%, see Figure 14 and Table 1. Increasing the NaOH concentration from 14 to 20% did not cause any further transformation of cellulose I → cellulose II. The contrary was, in fact, found to apply: alkali treatment at even higher concentrations, i.e. 24 and 26%, induced a small decrease in the lattice conversion order. Thus, at these NaOH concentrations, only 88-91% of the cellulose II component was obtained. Finally, the conversion order of cellulose I → cellulose II was slightly higher at 94% if the pulps were treated with alkali solutions of 28% in strength. These results are in excellent agreement with those found in the WAXS investigations of Borysiak and Garbarczyk (2003).

The point of inflection of the curve in Figure 14 was calculated to determine a 50% lattice transformation, and was reached when the NaOH concentration was 9%. This result agrees very well with those yielded by IR spectroscopy on the mercerized beech sulphite pulp investigated by Sixta and Borgards (1999).

### 3.3 Quantifying amorphous cellulose with respect to the lattice conversion of cellulose

The crystallinity of cellulose I in the alkali-treated ether pulps that showed signs of an increase in the amorphous component and were perceived to be result of lattice transformation were also examined (Atalla et al. 1984; Borysiak and Garbarczyk 2003). The percentual proportions of the amorphous part of the cellulose were determined for each alkali-treated pulp sample using the multivariate calibration model of Schenzel and Fischer (2005). The model allows the crystallinity of cellulose I (Xc Raman (%)) of each pulp sample to be determined, which then makes the percentual proportion of the amorphous phase (Camorph, Raman (%)) accessible.

These percentual proportions of amorphous cellulose in the alkali-treated ether pulps (Camorph, Raman (%)) are represented in Table 1 and correspond to the percentual proportions of crystalline cellulose I (Ccell I Raman (%)) and cellulose II (Ccell II Raman (%)). They are determined using the multivariate cellulose lattice conversion model and are based on the NaOH concentrations used in the treatment of the pulp.

Using the model developed by Schenzel and Fischer (2005) the percentual proportions of amorphous cellulose for the ether pulps treated with concentrations of 0-5% NaOH were found to be 15-18%. The corresponding amount of cellulose II, determined by the chemometric lattice conversion model was found to be 17-
20%. Assuming that 17-20% of cellulose II, or a lattice conversion order of 17-20%, cannot be correct under these conditions, these percentual proportions of cellulose II must in actual fact be an amorphous form of cellulose I, cf. Table 1.

A strong increase in the amorphous fraction of the cellulose was detected with the progression of the transformation of cellulose I → cellulose II, in agreement with Borysiak and Garbarczyk (2003); see Table 1 and compare the band shape of the FT Raman spectra in Figure 13. The amorphous part of this cellulose increased rapidly from 20 to 38% when the NaOH concentrations used to treat the pulps was increased from 6 to 14%. The lattice conversion order of cellulose I → cellulose II, determined by the multivariate calibration model, increased simultaneously from 20 to 94%. These differences in amorphous fraction probably depend on a decrease in the crystalline fraction due to the swelling and formation of Na-cellulose when the original ether pulp is subjected to the NaOH-treatment process.

NaOH concentrations between 15 and 28% gave an amorphous cellulose fraction of 37-39% and lattice conversion orders of cellulose I → cellulose II of 88-94%. Although NaOH concentrations of 24 and 26% induced a small reduction in the lattice conversion orders, there was no change in the percentual proportion of the amorphous part of the cellulose. Thus, the crystallinity of the cellulose does not provide an interpretation of this effect, which was also described by Borysiak and Garbarczyk (2003).

Taking the results of both multivariate quantification methods into consideration, it was deduced that around 20% of cellulose I must be amorphous in order to initiate the transformation process of cellulose I → cellulose II. This proportion was approximately doubled when the samples were treated with NaOH concentrations in the range of 6-14%. These NaOH concentrations caused orders of transformation of about 20-94% for cellulose I → cellulose II, which correspond to the corrected lattice conversion orders of 0-57%. Here, the percentual amount of amorphous cellulose in each sample served as an amendment for the actual lattice conversion order. About 40% of cellulose I exist in the amorphous phase when the polymorphic transformation process is completed: no increase can be detected in this phase when higher NaOH concentrations are used to treat the pulps. Only a small amount of about 6% of the crystalline cellulose I remain when the polymorphic conversion process has been completed.
3.4 Differences in the LODP of alkali-treated pulp

The intrinsic viscosity was measured after acidic hydrolysis at 3 M HCl for ether pulps treated with varying NaOH concentrations according to: 0, 2, 4, 6, 8… 28%, as described in Chapter 2.1. Values of intrinsic viscosity (SCAN-CM 15:99) were recalculated to LODP using Equation 4 (Gruber and Gruber 1981). The constants \( k \) and \( \alpha \) have a value of 2.28 and 0.76, respectively.

\[
[n] = k \cdot DP^\alpha 
\]

Eq. [4]

Figure 15. The LODP of alkali-treated ether pulp after acid hydrolysis (3M HCl) versus the NaOH concentration in the alkali-treatment of the ether pulp.

Figure 15 shows that the LODP of the alkali-treated pulps, analyzed after acid hydrolysis, decreased from 144 for the original pulp to approximately 60 for pulp treated with alkali at the highest NaOH concentration. These LODP values are far beneath the degree of polymerization of the original ether pulp (~5000). As can be seen in the figure, the LODP decreases rapidly with increasing NaOH concentrations up to about 10%, corresponding to 15.0 mol NaOH/mol AGU.
The reduction in the LODP was probably a result of the swelling action taking place in both the amorphous and the crystalline regions in the cellulose. Cellulose swelling probably only took place in the amorphous parts of the cellulose and on the surfaces of the cellulose particles at NaOH concentrations below 10%. At higher concentrations it is probable that only the most crystalline regions are intact; the structure of the cellulose is also likely to differ. This change in skeletal structure is in agreement with the prediction curve shown in Figure 14, which illustrates the course of the conversion of cellulose I → cellulose II in the alkali-treated pulps as a function of the NaOH concentration used for each single treatment.

The LODP obtained at NaOH concentrations exceeding 10%, as seen in Figure 15, probably only depended on the quantity of pure crystalline cellulose that remained in the cellulose.
4 The influence of extended mercerization on some carboxymethyl cellulose properties (Paper II)

The numerical values of the parameters studied are given in Table 2, along with the DS values and the filtration values of the CMC obtained. A total of 20 mercerization experiments were carried out in this study, including some complementary triple trials that corresponded to the reference levels used in the project. The reference values used during the mercerization stage were: 17.5 g pulp, 1 hour, 20°C and 27.5% NaOH, which corresponds to 2.55 mol NaOH/mol AGU. The long mercerization times used should be noted, i.e. 1 and 48 hours. The DS values obtained were either 0.4-0.5 or 0.9-1.0 and the filtration values varied between 0-27.5 g/min.

Table 2. The experimental parameters used and the DS and the filtration values obtained.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Main cellulose type in pulp before mercerization</th>
<th>Temperature of mercerization (°C)</th>
<th>Time of mercerization (h)</th>
<th>NaOH concentration (%)</th>
<th>mol NaOH/mol AGU</th>
<th>DS</th>
<th>Filtration value dm/dt after 5 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cellulose I</td>
<td>20</td>
<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.42</td>
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<td>0.65</td>
<td>0.49</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
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<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.48</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
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<td>40</td>
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<td>9.0</td>
<td>0.65</td>
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<tr>
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<tr>
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<td>0.46</td>
<td>1.2</td>
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<td>27.5</td>
<td>2.55</td>
<td>0.93</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*The NaOH concentration in the water fraction of the water-isopropanol system in the mercerization stage prior to CMC preparation.
4.1 The DS of CMC

The main and interactive effects on the DS of the CMC showed that the NaOH concentration influenced the mercerization stage significantly, and that it correlated positively to the DS of the CMC, Figure 16. It can also be observed that a high cellulose II fraction had a negative influence on the DS. Note that the NaMCA charge in these experiments was constant, corresponding to 1.21 mol NaMCA/mol AGU.

An interaction effect was found for a high fraction of cellulose II and the NaOH concentration; this interaction had a negative influence on the DS. The retention time and temperature in the mercerization stage is not shown in Figure 16, as neither prolonged time nor prolonged temperature had any influence on the DS of the CMC in the intervals studied, i.e. 1-48 hour and 20-40°C. The independence of time in the mercerization stage was probably due to the fact that the major molecular transition is fast; it has been reported to be reached in less than 15 minutes (Borysiak & Garbarczyk 2003) and, since the shortest mercerization time in this study was 1 hour, the retention time had therefore no influence. Thus, the results showed that the NaOH concentration should be high in order to obtain a high DS; the reason for this is probably the formation of alkali cellulose, which has

![Bar chart showing the effects of NaOH and cellulose II fraction on DS, with 95% confidence limits. Terms on the x-axis: NaOH = NaOH concentration in the mercerization stage and Cellulose II = cellulose II fraction in the ether pulp when the NaMCA charge in the etherification stage was fixed.](image-url)
a greater affinity for chemical reactions than the original cellulose. This is in agreement with Sixta, who claims that increasing the NaOH concentration beyond approximately 7% (70-80 g/dm³) at room temperature leads to a gradual change from the native cellulose I structure to the Na-cellulose I structure. The lattice transformation to Na-cellulose I is completed when the NaOH concentration is approximately 14%-16% (160-190 g/dm³) (Sixta 2006). He also claims that over the range of NaOH concentrations from about 14% to 22% (160-270 g/dm³), the structure of Na-cellulose I prevail, whilst a further lattice transformation to Na-cellulose II arises beyond this concentration level. The structure of Na-cellulose gives rise to improved reactivity with chemical reactants due to the hydroxyl groups on C₆ and C₂ being more accessible than in the native cellulose I structure. Dependence on a high NaOH concentration is probably also due to the decrease in the content of crystalline cellulose with increasing additions of NaOH (Schenzel et al. 2009). A high concentration of NaOH in the mercerization step probably alters the size of the crystallites and introduces crystal defects so that the internal surface area increases, thus facilitating the penetration of NaOH. This means that the reactants in the etherification stage can penetrate the swelled cellulose structure and react with the hydroxyl groups more easily when compared to the unswelled material (Krässig 1993).

In the present study cellulose swelling probably only took place in the amorphous parts of the cellulose and on the surfaces of the cellulose segments at the NaOH concentration of 9%. At concentrations of 27.5%, on the other hand, it is probable that only the most crystalline regions were intact. This agrees with the results of the LODP, given in Figure 15, and earlier studies showing that maximum swelling of cellulose fibres occurs when the NaOH is approximately 10% in strength (Bartunek and Heuser 1925) and that the cellulose crystallites become shorter at 18% NaOH (Gruber 2006). Substitution was most probably uneven along the cellulose backbone when the NaOH concentration was only 9%; the AGU-units were probably more homogenous substituted along the cellulose backbone, on the other hand, when the NaOH concentration was 27.5%.
Figure 17 shows that the DS of the CMC at concentrations of 9% NaOH was not influenced significantly by the cellulose II fraction in the pulp whereas at 27.5% NaOH it was influence negatively by the cellulose II. The figure shows that the DS was reduced from approximately 1.03 to 0.94 when the cellulose II fraction was increased from 0% to 100% at the NaOH concentration of 27.5%. A high NaOH concentration (i.e. 27.5%) is thus beneficial in the mercerization stage if the DS needs to be high; the DS is lower at this concentration if the cellulose II content is high in the original ether pulp. The difference in reactivity between cellulose I and II at high concentration levels of NaOH may be due to the fact that the cellulose structure then becomes the “bottleneck” of the reaction. It seems that it is necessary for the pulp to have a certain degree of swelling prior to etherification if a negative influence caused by cellulose II is to be observed.

The carboxymethylation of cellulose is a heterogeneous reaction, the rate of which depends upon the cellulose structure and diffusion of the reagents, NaOH and NaMCA, within the cellulose structure (Salmi et al. 1994). Thus, one important parameter in determining the accessibility of cellulose to chemical modifications is the degree of swelling. A slight increase in the swelling of cellulose after alkalization occurs, as demonstrated by thermogravimetry of samples saturated with water before and after alkalization (Barba et al. 2002). There was also an increase in the amorphous cellulose fraction after mercerization, see Table 1. Based on this it is proposed here that the small difference in DS at high NaOH concentrations found between the CMC grades produced from pulp samples with different contents of cellulose I and II were probably due to a difference in the swelling of the cellulose. The diffusion of the reagents within the structure of cellulose II is probably enhanced by the increase in swelling and the increase in the fraction of amorphous cellulose that follows mercerization.
4.2 The filtration ability of CMC water solutions

Filtration test with CMC of 1% in water were carried out and the filtration value was determined for different CMC-samples. The numbers were recalculated to “filtration value” as described in chapter 2.3. The results of the filtration study showed that the NaOH concentration, the temperature in the mercerization stage and the content of cellulose II in the original pulp were important individual factors for the filtration efficiency of CMC water solutions, see Figure 18.

![Figure 18. The main and interactive effects for the filtration test, including 95% confidence limits. Terms on x-axis: Cellulose II = cellulose II fraction in the ether pulp, Te = temperature and NaOH = NaOH concentration in the mercerization stage.]

It can be seen that a high fraction of cellulose II in the original pulp and a high temperature in the mercerization stage affected the filtration ability negatively, whilst the NaOH concentration in the mercerization stage was positive, it was not statistically significant. The figure also shows that the interaction between a high fraction of cellulose II in the original pulp and the temperature in the mercerization stage correlated positively with the filtration value of CMC water solutions. Both the interaction terms of a high fraction of cellulose II in the original pulp and the NaOH concentration in the mercerization stage, as well as the temperature and the NaOH concentration in the mercerization stage, correlated negatively with the filtration value. The retention time in the mercerization stage is not shown in Figure 18 as it had no influence on the filtration value.
Figure 19. The filtration value for 1% CMC water solutions versus the temperature in the mercerization stage.

Figure 19 shows how the filtration value was affected by the temperature in the mercerization stage and by the amount of cellulose II in the original pulp. The filtration value for 1% CMC water solutions is influenced by the temperature in the proceeding mercerization stage and then by the content of cellulose II in the pulp prior to etherification. The amount of cellulose II in the original pulp had a strong influence on the filtration value of the resulting CMC water solution at a low temperature (20°C). At a high temperature (40°C), however, the filtration value was influenced less by the amount of cellulose II in the original pulp. This can be explained by the fact that the pulp swells, i.e., mercerizes, more efficiently at low temperatures (Sisson and Sander 1941), which results in a more uniform carboxymethylation of the pulp in the etherification stage. A more even distribution of the ether groups can be assumed to result in an ether solution that filters more easily when the CMC has been dissolved in water.
Figure 20 shows how the filtration value was affected by the NaOH concentration in the mercerization stage and the amount of cellulose II in the original pulp. At a high NaOH concentration (27.5%) the amount of cellulose II influenced the filtration value of the resulting CMC water solution significantly. Conversely, the filtration value was only slightly dependent on the amount of cellulose II in the original pulp when the NaOH concentration was low (9%). This influence of the NaOH concentration can be explained by the fact that cellulose II is more compact than cellulose I and therefore less reactive. Higher NaOH concentrations swell the cellulose structure and, at low concentrations, this swelling effect becomes the bottleneck for the reaction. At higher concentrations, on the other hand, the type of cellulose used becomes the bottleneck.

The low filtration ability of the CMC water solutions indicated that they contained gel particles generated by cellulose II. This probably depended on the denser chemical structure of cellulose II which, in the etherification reaction, resulted in substitution reactions mainly on the surfaces of the fibrils; it was therefore most likely that an uneven substitution was obtained. It has been reported earlier that cellulose derivatives containing non-substituted segments can form associations by intermolecular interactions and thereby form gels in solutions, which verifies the results obtained in this study (Clasen & Kulicke 2001; Enebro et al. 2007; Gelman 1982). The best conditions in the mercerization stage for producing good filterability were found at a high NaOH concentration, a low temperature in the mercerization stage and a low fraction of cellulose II in the original pulp. The retention time in the mercerization stage seemed to have no influence on the filtration value of CMC water solutions. It should, however, be observed that only long retention times (≥1 h) were included here.
5 CMC and its gel fraction (Paper III)

This section deals with the gel fraction in CMC that is produced by extended mercerization and characterized by NIR FT Raman spectroscopy. A total of 23 mercerization experiments were carried out in this study, including some complementary triple trials that corresponded to the reference levels used in the project. The reference values used during the mercerization stage were: 17.5 g pulp, 1 hour, 20°C and 27.5% NaOH, which corresponds to 2.55 mol NaOH/mol AGU. The numerical values of the parameters studied in the mercerization stage, the subsequent CMC results pertaining to the DS values and the amounts of gels of the CMC obtained are all given in Table 3.

Table 3. The experimental parameters used and the resulting CMC values obtained with respect to the DS and the amount of gel fraction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Main cellulose type in pulp before mercerization</th>
<th>Temperature of mercerization (°C)</th>
<th>Time of mercerization (h)</th>
<th>*NaOH concentration (%)</th>
<th>mol NaOH/mol AGU</th>
<th>DS</th>
<th>Gel fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>cellulose I</td>
<td>20</td>
<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.42</td>
<td>65.9</td>
</tr>
<tr>
<td>2</td>
<td>cellulose II</td>
<td>20</td>
<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.49</td>
<td>66.8</td>
</tr>
<tr>
<td>3</td>
<td>cellulose I</td>
<td>40</td>
<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.48</td>
<td>65.5</td>
</tr>
<tr>
<td>4</td>
<td>cellulose II</td>
<td>40</td>
<td>1</td>
<td>9.0</td>
<td>0.65</td>
<td>0.47</td>
<td>70.4</td>
</tr>
<tr>
<td>5</td>
<td>cellulose I</td>
<td>20</td>
<td>48</td>
<td>9.0</td>
<td>0.65</td>
<td>0.50</td>
<td>67.0</td>
</tr>
<tr>
<td>6</td>
<td>cellulose II</td>
<td>20</td>
<td>48</td>
<td>9.0</td>
<td>0.65</td>
<td>0.46</td>
<td>75.3</td>
</tr>
<tr>
<td>7</td>
<td>cellulose I</td>
<td>40</td>
<td>48</td>
<td>9.0</td>
<td>0.65</td>
<td>0.47</td>
<td>68.6</td>
</tr>
<tr>
<td>8</td>
<td>cellulose II</td>
<td>40</td>
<td>48</td>
<td>9.0</td>
<td>0.65</td>
<td>0.46</td>
<td>78.1</td>
</tr>
<tr>
<td>9</td>
<td>cellulose I</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>1.03</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>cellulose I</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>1.05</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>cellulose I</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>1.02</td>
<td>0.6</td>
</tr>
<tr>
<td>12</td>
<td>cellulose II</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>0.92</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>cellulose II</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>0.96</td>
<td>2.46</td>
</tr>
<tr>
<td>14</td>
<td>cellulose II</td>
<td>20</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>0.95</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>cellulose I</td>
<td>40</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>1.05</td>
<td>17.5</td>
</tr>
<tr>
<td>16</td>
<td>cellulose II</td>
<td>40</td>
<td>1</td>
<td>27.5</td>
<td>2.55</td>
<td>0.93</td>
<td>65.9</td>
</tr>
<tr>
<td>17</td>
<td>cellulose I</td>
<td>20</td>
<td>48</td>
<td>27.5</td>
<td>2.55</td>
<td>1.04</td>
<td>0.3</td>
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<tr>
<td>18</td>
<td>cellulose II</td>
<td>20</td>
<td>48</td>
<td>27.5</td>
<td>2.55</td>
<td>0.93</td>
<td>75.3</td>
</tr>
<tr>
<td>19</td>
<td>cellulose I</td>
<td>40</td>
<td>48</td>
<td>27.5</td>
<td>2.55</td>
<td>1.00</td>
<td>0.1</td>
</tr>
<tr>
<td>20</td>
<td>cellulose II</td>
<td>40</td>
<td>48</td>
<td>27.5</td>
<td>2.55</td>
<td>0.93</td>
<td>22.8</td>
</tr>
<tr>
<td>21</td>
<td>50/50 mix I &amp; II**</td>
<td>30</td>
<td>24.5</td>
<td>18.25</td>
<td>1.35</td>
<td>0.88</td>
<td>-</td>
</tr>
<tr>
<td>22</td>
<td>50/50 mix I &amp; II**</td>
<td>30</td>
<td>24.5</td>
<td>18.25</td>
<td>1.35</td>
<td>0.92</td>
<td>10.6</td>
</tr>
<tr>
<td>23</td>
<td>50/50 mix I &amp; II**</td>
<td>30</td>
<td>24.5</td>
<td>18.25</td>
<td>1.35</td>
<td>0.92</td>
<td>-</td>
</tr>
</tbody>
</table>

*The NaOH concentration in the water fraction of the water-isopropanol system in the mercerization stage prior to CMC preparation.

**A mixture of 50% cellulose I and 50% cellulose II.
5.1 The gel fraction in CMC water solutions

It was claimed earlier in chapter 4 that the filtration of CMC water solutions increased when the content of cellulose II was decreased in the original pulp prior to mercerization. Higher NaOH concentrations and lower temperatures in the mercerization stage also increased the filtration ability of the solution. Similar conclusions could also be drawn for the amount of gel fraction obtained in CMC water solutions. Thus, the amount of gel in CMC water solutions was highly dependent on the NaOH concentration in the mercerization stage and the fraction of cellulose II in the original pulp. CMC prepared using a low NaOH concentration (9 %) in the mercerization stage resulted in CMC water solutions rich in very thick and semi solid gum-like gels; solutions prepared from pulp rich in cellulose II tended to have a higher content of gels. Independent on the NaOH concentration in the mercerization stage, the amount of gel fraction in CMC water solutions was higher for CMC prepared from pulp with high fraction of cellulose II compared with pulps with only cellulose I, see Table 3.

This gel formation was probably due to a low DS but also to an uneven distribution of substituting groups on the cellulose backbone. Generally speaking, most of the chemical modification reaction at low DS occurs in amorphous regions or on the surfaces of residual crystalline domains, where aggregates of non-substituted or poorly substituted regions may appear as highly swollen opaque or transparent macrogel particles. The results are different rheological properties and a solution with a different behaviour pattern (Rinaudo et al. 2000). It has been reported earlier that carboxymethylation of spruce sulphite cellulose by the heterogeneous reaction method yields a substantial fraction of insoluble residuals of CMC that mainly consists of low substituted cellulose segments (Jardeby et al. 2004).
5.2 FT Raman spectra of CMC

Obvious differences between the three methods of preparation described in Table 3 were detected by the FT Raman spectra shown in Figure 21. The samples, which were prepared under similar reaction conditions, showed great structural similarities.

![FT Raman spectra of CMC](image)

Figure 21. FT Raman spectra of CMC samples 1-23 ordered with respect to the preparation methods used. CMC samples 1, 3, 5, 7 were prepared from ether pulp with a high fraction of cellulose I. CMC samples 2, 4, 6, 8 were prepared from ether pulp with a high fraction of cellulose II. CMC samples 9-23 were prepared from cellulose I or II, or mixtures of those cellulose polymorphs.

CMC samples 1, 3, 5 and 7, which were prepared from ether pulp with a high fraction of cellulose I and a low NaOH concentration (9%) in the mercerization stage, indicated skeletal structures of cellulose I type in their FT Raman spectra. In contrast to this, CMC samples 2, 4, 6 and 8, prepared from ether pulp consisting of a high fraction of cellulose II and low NaOH concentration (9%) in the mercerization stage, represent skeletal structure of the cellulose II type. These results suggest that the low NaOH concentration (9%) in the mercerization stage was not sufficient to complete the transformation reaction from cellulose to Na-cellulose prior to carboxymethylation to CMC. Low degrees of substitution (DS) between 0.42 and 0.50 were therefore obtained for these samples of CMC.

It can be concluded from the FT Raman spectra of the CMC of these two preparation groups (1, 3, 5 and 7; 2, 4, 6 and 8) that neither a variation in the retention time of between 1 and 48 h nor a variation in the mercerization
temperature of between 20°C and 40°C were found to influence the change in the skeletal structure of the cellulose.

The third group of CMC samples, i.e. 9-23, was prepared from cellulose I or II as well as from mixtures of these; the NaOH concentration was 18.25% or 27.5% in the mercerization stage. The Raman spectra of these samples indicated that the structure of the cellulose skeleton seemed to be influenced strongly by carboxymethylation. The Raman spectra of CMC samples 9-23 represent skeletal structures that are apparently different to those of the CMC samples of the first two preparation groups. This is most probably due to a successful transformation from cellulose to Na-cellulose when the NaOH concentration was either 18.25 or 27.5% during the mercerization stage. A positive impact could be assumed on the carboxymethylation of the cellulose during the etherification step, causing the DS to increase to 0.88-1.05.

![Figure 22. FT Raman spectra of a model compound of amorphous cellulose, CMC sample 9 and NaOH-pretreated ether pulp.](image)

In Figure 22 the FT Raman spectra of a model compound of amorphous cellulose and the NaOH-pretreated ether pulp are shown in comparison to the spectrum of CMC sample 9, which represents the third CMC preparation group. It is obvious that some of the Raman signals appear in each of these spectra at approximately the same wave number; this is particularly true for the signals that characterize the cellulose of type II, i.e. the NaOH-pretreated ether pulp, and the amorphous form. Here, the signals at 1460 cm⁻¹ assigned to methylene bendings δ(CH₂), the signal at
1265 cm\(^{-1}\) assigned to methylene twisting \(\tau(CH_2)\) and the glycopyranose ring deformations at 355 cm\(^{-1}\) belong to the characteristic signals. The successful etherification of CMC sample 9 is proved by the characteristic signals at 1611 cm\(^{-1}\), 1416 cm\(^{-1}\) and 1329 cm\(^{-1}\), which are assigned to the asymmetric stretching \(\nu_{as}(\text{COO}^-)\) mode of an acetate salt and its corresponding symmetric stretching \(\nu_s(\text{COO}^-)\) mode as well as the methylene wagging mode \(\omega(CH_2)\) of an ether group. Typical skeletal stretching of \((-CH_2-O-CH_2-)\) ether groups is indicated by a broad signal with its maximum at 1116 cm\(^{-1}\). Such vibrational behaviour clearly reflects the pattern of substitution of the cellulose backbone due to the etherification reaction; it characterizes the skeletal structure of cellulose modification II in the presence of distinct parts of amorphous cellulose. The amorphous structures are indicated by the broadening of single Raman signals at 1116 cm\(^{-1}\) of the CMC sample 9 in comparison to those of the mercerized ether pulp; it can be observed directly in the Raman spectrum of amorphous cellulose, as shown in Figure 22.

5.3 FT Raman spectra of CMC and the gel fraction

The FT Raman spectra of CMC samples 1, 2, 3 and 4 and their gel fractions are shown in Figures 23 and 24.

![Figure 23. FT Raman spectra of CMC samples 1 and 3, and their gel fractions.](image-url)
Figure 24. FT Raman spectra of CMC samples 2 and 4, and their gel fractions.

The spectra in Figures 23 and 24 illustrate that the typical double peak of cellulose at 1120 cm⁻¹ and 1095 cm⁻¹ shows a different intensity relation in the spectra of the gel fraction than in the original CMC samples. The signal at 1095 cm⁻¹ in the spectra of the gel fraction always appears at great intensity, whereas it doesn’t change at 1120 cm⁻¹ for the gel fraction compared to the original CMC sample. Similar intensity relations were observed in the spectra of CMC samples 5, 6, 7 and 8 with respect to their gel fraction. Here, differences in the hydrogen bonding patterns between the original CMC samples 1-8 and their gel fractions can be observed. The differences in hydrogen bonding depend most likely on a more uneven substitution and lower DS within the gel fraction than in the original CMC. This assumption seems to be confirmed by the different behaviour of CMC samples 9-23, and their gel fractions, according to the Raman spectra in Figure 25.

From the spectra in Figures 23 and 24 it can also be observed that the gel fraction and the original CMC samples had the same skeletal structure of cellulose. CMC samples 1 and 3, and their gel fractions, indicated skeletal structures of cellulose I, while CMC samples 2 and 4, and their gel fractions, indicated structures of cellulose II in their FT Raman spectra. Hence, the cellulose II structure was not more occurrence in the gel fractions compared to the original CMC samples.
No major differences in intensity in the typical Raman signals for the original CMC and its gel fraction were observed, as Figure 25 illustrates for CMC samples 18 and 20. This is also true for CMC samples 15, 16, 17 and 22, indicating that there are no differences in the hydrogen bonding patterns between the original CMC and its gel fraction. The higher DS values of theses CMC, i.e. between 0.88 and 1.05, form the basis for such an interpretation.
5.4 The amount of cellulose I and cellulose II in ether pulp and in CMC

Using the experimental results of the present study, and based on the multivariate calibration model of Schenzel, Almlöf and Germgård (2009), the amounts of cellulose I and cellulose II were determined for the original ether pulp before and after pre-treatment with 18% NaOH, and for the resulting CMC.

The cellulose I fraction in the pulp decreased, and the fraction of cellulose II increased, after the original ether pulp was subjected to NaOH-pretreatment where the NaOH concentration was 18%. The amounts of cellulose I and cellulose II present in the original and the NaOH-pretreated ether pulps, and CMC samples 1-8 are summarized in Table 4.

Table 4. The amount of cellulose I and cellulose II in the original ether pulp before and after pre-treatment with 18% NaOH, and the resulting CMC samples 1-8.

<table>
<thead>
<tr>
<th></th>
<th>Cellulose I (%)</th>
<th>Cellulose II (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original ether pulp</td>
<td>78</td>
<td>3*</td>
</tr>
<tr>
<td>NaOH-pretreated ether pulp</td>
<td>9</td>
<td>91</td>
</tr>
<tr>
<td>CMC 1 (cellulose I and 9% NaOH)</td>
<td>68</td>
<td>32</td>
</tr>
<tr>
<td>CMC 2 (cellulose II and 9% NaOH)</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>CMC 3 (cellulose I and 9% NaOH)</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>CMC 4 (cellulose I and 9% NaOH)</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>CMC 5 (cellulose I and 9% NaOH)</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td>CMC 6 (cellulose II and 9% NaOH)</td>
<td>24</td>
<td>76</td>
</tr>
<tr>
<td>CMC 7 (cellulose I and 9% NaOH)</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>CMC 8 (cellulose II and 9% NaOH)</td>
<td>24</td>
<td>76</td>
</tr>
</tbody>
</table>

*Value from NMR (Fälldin 2002)

The results showed that the average content of cellulose I in CMC samples 1, 3, 5 and 7 was 69% and the average content of cellulose II in CMC samples 2, 4, 6 and 8 was 76%. This indicates clearly that the structure of the cellulose was unchanged when a low NaOH concentration (9%) was used in the mercerization stage when preparing CMC. The reason for this is most probably due to the fact that the NaOH concentration was not high enough to complete the transformation from cellulose to Na-cellulose prior to carboxymethylation into CMC.
The amounts of cellulose I and cellulose II contained in CMC samples 1-8 are presented in Figures 26 and 27 which show a possible scheme for the changes in the structure of the cellulose backbone during the CMC process.

**Original ether pulp**
- Amorphous cellulose: 11%
- Hemicellulose: 8%
- Cellulose II: 3%
- Cellulose I: 78%

**CMC samples 1, 3, 5 and 7**
- CMC or amorphous cellulose: 31%
- Mercerization with 9% NaOH
- Etherification
- Cellulose I: ~69%

Figure 26. Principal scheme for the change in structure of the cellulose backbone in the original ether pulp during the CMC process with a low NaOH concentration (9%) in the mercerization stage.

**NaOH-pretreated ether pulp**
- Cellulose I: 9%
- Cellulose II: 91%

**CMC samples 2, 4, 6, and 8**
- CMC or amorphous cellulose: 24%
- Mercerization with 9% NaOH
- Etherification
- Cellulose II: ~76%

Figure 27. Principal scheme for the change in structure of the cellulose backbone in the NaOH-pretreated ether pulp during the CMC process with a low NaOH concentration (9%) in the mercerization stage.
6 Conclusions

This thesis discusses the extended mercerization of cellulose prior to it being etherified with sodium monochloroacetate to form carboxymethyl cellulose (CMC). It has then been clearly demonstrated that FT Raman spectroscopy is an effective method for characterizing of native cellulose in pulps and also for carboxymethyl cellulose. Based on FT Raman spectroscopy a new, multivariate, calibration model was developed to quantify the polymorphic transformation process of cellulose I to cellulose II during mercerization. The calibration model appears attractive due to its simple applicability: the analysis time can be very short ($\leq 10$ minutes) and only minor sample preparation is required.

The lattice conversion process of cellulose I $\rightarrow$ cellulose II can be described, in general, as being a system of three participating forms of cellulose: crystalline cellulose I, amorphous cellulose and cellulose II.

In the thesis it has been shown that the NaOH concentration in the mercerization stage prior to CMC preparation had an influence on the following etherification reaction when the addition of NaMCA was 1.21 mol/mol AGU. A low NaOH concentration (9%) in the mercerization stage resulted in an incomplete transformation of the cellulose to Na-cellulose and low average DS values of the CMC of between 0.42 and 0.50 were obtained. When dissolved in water such CMC caused very thick and semi solid gum-like gels, probably due to an uneven distribution of substituting groups along the cellulose backbone. High NaOH concentrations (18.25 or 27.5%) in the mercerization stage, on the other hand, gave cellulose molecules that were totally converted into CMC after the addition of NaMCA; DS values of between 0.88 and 1.05 were then obtained. When dissolved in water such CMC caused gels when they were prepared from ether pulp with a high fraction of cellulose II.

Neither a mercerization time of between 1 and 48 h nor a mercerization temperature of between 20°C and 40°C influenced the average DS of CMC. It was also found that a retention time of between 1 and 48 hours in the mercerization stage had no effect on the filtration ability of CMC water solutions.

The filtration ability of CMC water solutions increased when the content of cellulose II in the original pulp was low, the NaOH concentration in the mercerization stage was high and the temperature in the mercerization stage was low. CMC prepared using a low NaOH concentration (9 %) in the mercerization stage resulted in CMC water solutions rich in very thick and semi solid gum-like gels. Independent on the NaOH concentration in the mercerization stage, the amount of gel fraction in CMC water solutions was higher for CMC prepared from pulp with high fraction of cellulose II compared with pulps with only cellulose I. The formation of gel in each specific case affected the filtration ability inversely,
and was probably greater when the evenness of the distribution of substituting groups on the cellulose backbone was reduced.

Compared with cellulose I, the fraction of cellulose II in the pulp had no negative influence on the resulting DS value of the CMC when the NaOH concentration was 9%, which corresponds to 0.65 mol NaOH/mol AGU. However, when the NaOH concentration was 27.5%, corresponding to 2.55 mol NaOH/mol AGU in the mercerization stage, the fraction of cellulose II had a negative influence on the DS value of the resulting CMC. These results indicate that when CMC is being produced the pulp must undergo a certain degree of swelling and the transformation from cellulose to Na-cellulose must be complete prior to the etherification stage if any negative influence caused by cellulose II is to be observed on its reactivity.
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8 References


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Extended Mercerization Prior to Carboxymethyl Cellulose Preparation

Carboxymethyl cellulose (CMC) is produced commercially in a two-stage process consisting of a mercerization stage, where the pulp is treated with alkali in a water alcohol solution, followed by an etherification stage in which monochloroacetic acid is added to the pulp slurry. In this thesis an extended mercerization stage of a spruce ether pulp was investigated where the parameters studied were the ratio of cellulose I and II, concentration of alkali, temperature and retention time. The influence of the mercerization stage conditions on the etherification stage, were evaluated as the degree of substitution (DS) of the resulting CMC and the filterability of CMC dissolved in water at a concentration of 1%. The DS results suggested that the NaOH concentration in the mercerization stage was the most important of the parameters studied. When the NaOH concentration in the mercerization step was low (9%), a high cellulose II content in the pulp used was found to have no negative impact on the DS of the resulting CMC compared with pulps with only cellulose I. However, when the NaOH concentration was high (27.5%), pulps with high content of cellulose II showed a lower reactivity than those with only cellulose I with respect to the DS of the CMC obtained after a given charge of NaMCA.

The results obtained from the filtration ability study of CMC water solutions suggested that both the amount of cellulose II in the original pulp and the temperature had a negative influence on the filtration ability whereas the NaOH concentration in the mercerization stage had a positive influence. The filtration ability was assumed to be influenced highly by the presence of poorly reacted cellulose segments. A retention time between 1-48 h in the mercerization stage had no effect on either the DS or the filtration ability of the CMC.

Using NIR FT Raman spectroscopy molecular structures of CMC and its gel fraction were analyzed with respect to the conditions used in the extended mercerization stage. Here it was found that the alkaline concentration had a very strong influence on the following etherification reaction. FT Raman spectra of CMC samples and their gel fractions prepared with low NaOH concentrations (9%) in the mercerization stage indicated an incomplete transformation of cellulose to Na-cellulose before carboxymethylation to CMC. Low average DS values of the CMC, i.e. between 0.42 and 0.50, were yielded. Such CMC dissolved in water caused very thick and semi solid gum-like gels, probably due to an uneven distribution of substituting groups along the cellulose backbone. FT Raman spectra of CMC mercerized with alkaline concentrations at 18.25 and 27.5% in the mercerization stage indicated, however, that all of the cellulose molecules were totally transferred to CMC of high DS, i.e. between 0.88 and 1.05. When dissolved in water such CMC caused gels when they were prepared from ether pulp with a high fraction of cellulose II.