Groene Cellulose
Tussenrapportage project 0351-04-03-08-004

Ir. K. Molenveld
Ing. F.E. Giezen
Dr. Ir. M.J.J. Litjens
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Colofon

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Agrotechnology & Food Innovations B.V.
P.O. Box 17
NL-6700 AA Wageningen
Tel: +31 (0)317 475 024
E-mail: info.agrotechnologyandfood@wur.nl
Internet: www.agrotechnologyandfood.wur.nl

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Abstract

This intermediate report describes the progress in the Green cellulose project. At present the literature studies are in progress and also a start has been made with the market study. Furthermore, two experimental trails have been performed until now. The literature report contains general information on cellulose derivatives, supercritical carbon dioxide processing and polymer processing using supercritical carbon dioxide. In the end report more details on the various subjects will be included. The market overview gives insight in market volume, the most important products and producers of cellulose derivatives. So far, the experiments have not been successful since no change in crystallinity was observed and severe cellulose degradation occurred. However, this could indicate that using supercritical carbon dioxide might be used to modify solely the amorphous regions. In future experiments reaction times will be lowered and co-solvents will be added.
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Literature
1 Introduction

This progress report describes the A&F activities regarding the M&T Green Cellulose project. The industrial feasibility project consists of an extensive literature study, a market study and approach and some experiments. At present the literature studies are in progress and also a start has been made with the market study. Furthermore, two experiments have been performed until now.

The aim of this feasibility study is to investigate whether current (organic) solvents that are used during the production of cellulose derivatives can be (partly) replaced by using supercritical carbon dioxide as solvent or plasticiser. Possible end products are cellulose esters, cellulose ethers and regenerated cellulose.

Native cellulose cannot be melt processed since its degradation temperature is lower than its softening temperature. Supercritical carbon dioxide is capable of lowering the softening temperature (or rather the Tg, glass transition temperature) of polymers. During this study it will be investigated if supercritical carbon dioxide can lower the softening point of cellulose in order to ease cellulose derivatisation.
2 Literature study

This literature study consists of three parts:
- cellulose processing and modification
- supercritical carbon dioxide and relevant processing techniques
- supercritical processing of cellulose

2.1 Cellulose processing and modification

Cellulose is the most abundant organic polymer; approximately $10^{15}$ kg/yr is synthesised and degraded. Native cellulose is highly crystalline (on average 70%) and has a high molecular weight (DP up to 10,000). Cellulose is generally harvested from highly pure sources of cellulose such as cotton or easily harvested sources such as wood. Purified cellulose generally still contains small amounts of hemicellulose and lignin and should be identified by source and physiochemical treatments is has received.

2.1.1 Cellulose swelling and solubility

Because of its high degree of crystallinity and extensive hydrogen bonding in the crystalline regions, cellulose is difficult to dissolve or modify. Swelling of cellulose is essential for subsequent modification. Swelling power generally increases in the order: organic solvent < water < salts < acids < bases. Important swelling agents for cellulose include alkali hydroxides (especially NaOH), inorganic acids (sulphuric-, hydrochloric- and phosphoric acid), and solutions of metal salts. Alkali swelling is used in the mercerisation process, whereby the crystalline cellulose I structure is converted to a second crystalline modification, cellulose II. Swelling and conversion to alkali cellulose is employed in the production of cellulose derivatives such as carboxymethyl cellulose (CMC).

Since cellulose is both a polar and crystalline polymer, it is difficult to find a good solvent. Also, the thermodynamics are problematical. Alkali hydroxides are useful cellulose solvents; pure cellulose is soluble in 17.5% sodium hydroxide. Furthermore, cellulose can be dissolved by indirect dispersion, which involves conversion to a cellulose derivative such as nitrate, acetate, or xanthate, and subsequent dissolution in a compatible solvent. Also, cellulose solutions can be produced in cuprammonium hydroxide, cupriethylenediamine, mineral acids, tetraalkylammonium hydroxides, or solution of heavy metal complexes (cadexen or iron tartaric acid). In most cases, these cellulose solutions are subject to degradation by hydrolysis or air oxidation.

2.1.2 Cellulose thermal behaviour and degradation

TGA studies of cellulose reveal a small endotherm around 100°C due to evaporation of water and a strong endotherm at 310-350°C due to degradation reactions. At higher temperatures further exothermic degradation reactions occur. Impurities like hemicelluloses enhance thermal degradation, and thermal degradation is also dependent on pretreatments. The thermoplasticity of wood has been extensively studied. It was found that the thermoplasticity of wood is mainly...
determined by cellulose. Ranges of softening temperatures that are listed are for example 231-253°C or 180-350°C. The crystalline melting temperature of cellulose is well above its decomposition temperature. Thus, no melting of cellulose can occur at temperatures that do not cause pyrolysis. The above properties of cellulose can be altered by converting cellulose into derivatives, for example cellulose nitrate, cellulose acetate, benzyl cellulose etc..

2.1.3 Cellulose derivatives
The main types of cellulose derivatives are:
- Inorganic esters (cellulose nitrates)
- Organic esters (cellulose acetates)
- Cellulose ethers (carboxymethyl cellulose, methyl cellulose)
- Regenerated cellulose (cellophane and rayon)

All these cellulose derivatives are prepared from dissolving pulps. Dissolving pulps are speciality pulps composed of more than 90% pure cellulose. Two basis processes are used to produce dissolving pulp. The sulfite process produces pulp with a cellulose content up to 92 percent. The pre-hydrolysis sulfate (kraft) process produces pulps with a cellulose content up to 96%. Special alkaline purification treatments can yield even higher cellulose levels up to 96% for the sulfite process and up to 98% for the sulfate process. The 90- to 92 percent cellulose content sulfate pulps are used mostly to make viscose rayon for textiles and cellophane. The 96-98 percent cellulose content sulfate pulps are used to make rayon yarn for industrial products such as tire cord, rayon staple for high-quality fabrics and various acetate and other speciality products. Since essentially all lignin and hemicelluloses are removed, dissolving pulps have the lowest yields, on the order of 35% bases on wood.

2.1.3.1 Cellulose nitrates
Cellulose nitrate is the oldest cellulose derivative. It was first prepared in 1833, when crude cellulose such as linen, paper, or sawdust was treated with concentrated nitric acid to produce a highly degraded, unstable product. Initially cellulose nitrate was used as a military explosive. The first successful synthetic plastic, celluloid, was produced in 1870 from a mixture of cellulose nitrate and camphor. Nowadays, cellulose nitrate is used in industrial lacquer finishes, explosives and propellants.

Before World War II cellulose nitrate was manufactured primarily from cotton linters. Nowadays, higher quality wood pulps are mainly used. Initially cellulose nitrates were prepared via a batch process, in which a relatively small quantity of cellulose (15 kg) is agitated in a vessel containing 500 kg HNO₃/H₂SO₄/H₂O in the proper ratio. During the reaction time of 20-30 minutes cellulose maintains its fibrous structure. In the late fifties Hercules developed a continuous process for the manufacture of cellulose nitrate and currently all cellulose nitrate is produced by a continuous automated process. Latest developments are aimed at reactant recovery and gas phase processes.
2.1.3.2 Cellulose acetates

Cellulose forms esters with organic acids, anhydrides and acid chlorides. Cellulose esters of almost any organic acid can be prepared, but because of practical limitations, esters of acids containing more than four carbon atoms have not achieved commercial significance. Cellulose acetate is the most important organic ester because of its broad application range.

Soluble cellulose acetate was first prepared in 1865 by heating cotton and acetic anhydride at 180°C. Using sulphuric acid as a catalyst permitted preparation at lower temperatures, and later, partial hydrolysis of the triacetate gave an acetone-soluble cellulose acetate. During World War I, cellulose acetate replaced the highly flammable cellulose nitrate coating on aeroplane wings and in fuselage fabrics. After World War I, it found extensive use in photographic and x-ray films, spun fibres and moulding plastics. Nowadays, cellulose acetate is used mainly in textile fibres and filter material for cigarettes. Furthermore, Cellulose acetate film is used in display packaging, decorative signs and pressure sensitive tapes. Injection-moulded cellulose acetates are used in toothbrush handles, combs, brushes etc. Low viscosity cellulose acetate is used in lacquers and protective coatings.

Cellulose acetates can be prepared either by a fibrous acetylation or a true solution process. Almost all cellulose acetate, with the exception of fibrous triacetate, is prepared by the solution process employing sulphuric acid as the catalyst with acetic anhydride in an acetic acid solvent. The acetylation reaction is heterogeneous and topochemical wherein successive layers of the cellulose fibres react and are solubilised in the medium, thus exposing new surfaces for reaction. The reaction course is controlled by the rates of diffusion of the reagents into the cellulose fibres, and, therefore, the cellulose must be swollen or activated before acetylation to achieve uniform reaction and avoid unreacted fibres in the solution. A considerable amount of cellulose acetate is still manufactured by a batch process. In order to reduce production costs, efforts have been made to develop continuous processes which includes continuous activation, acetylation, hydrolyses and precipitation. Most cellulose acetate is produced from wood pulp, traditionally sulphite pulp, Cellulose I, which is less thermodynamically stable, is more reactive towards acetylation than cellulose II. Sulphuric acid is the most common catalyst.

2.1.3.3 Cellulose ethers

Cellulose ethers were first described in literature in 1905. By 1912 the first patents covering the preparation of cellulose ethers appeared. The most important cellulose ethers are carboxymethyl cellulose and methyl cellulose.

Sodium carboxymethyl cellulose or CMC is an anionic polyelectrolyte prepared by the reaction of sodium chloroacetate with alkali cellulose. The reaction is carried out in a slurry of sodium hydroxide, water, cellulose and monochloroacetic acid in organic diluents such as t-butyl alcohol, isopropyl alcohol or ethyl alcohol. Curd grades can be prepared dry at high cellulose solids without solvents. The CMC is separated form by-product salts by washing with aqueous alcohol or acetone. CMC is soluble in hot or cold water, insoluble in organic solvents, but soluble in aqueous lower alcohols or acetone. CMC is used both in food and non-food applications, where thickening, suspending, stabilising, binding, and film-forming properties are important.
Methyl cellulose is a non-ionic polymer soluble in cold water that is prepared by the reaction of alkali cellulose with methyl chloride. Formation of methyl cellulose consumes caustic and is accompanied by side reactions that lead to the by-products methanol and methyl ether. Purification of methyl cellulose takes advantage of its insolubility in hot water. Methyl cellulose is (amongst others) used as thickener, adhesive, binder, film former and suspending aid.

2.1.3.4 Regenerated cellulose
Cellophane and rayon are forms of cellulose that are regenerated from cellulose xanthate. Cellulose xanthate is prepared via a reaction of alkaline cellulose with carbon disulfide. Commercially, viscose is spun into an acid bath where the cellulose xanthate decomposes to regenerate cellulose and cabon disulfide, thereby reforming cellulose into fibres or cellophane sheets. Cellophane is among the oldest packaging materials and is still the best film for clarity, crisp hand, and the dimensional stability vital for good high speed machine printability. Coatings are always applied to cellophane to give almost any desired property. For example, nitro-cellulose or Saran coatings are used to reduce moisture or oxygen permeability respectively; polyethylene or ionomers are used for heat sealing.
2.2 Supercritical carbon-dioxide\(^\text{67}\) and relevant processing techniques

When carbon dioxide is compressed at conditions that exceed 31 °C and 74 bar, it is in its supercritical state (Figuur 1). This is a stable state that favourably combines the dissolving characteristics of a liquid (density, solvating power) with the transport properties of a gas (viscosity, diffusivity); see Tabel 1. The density, and thereby the solvating power, is adjustable by the pressure and the temperature (Figuur 2). Furthermore supercritical carbon dioxide (scCO\(_2\)) is non-toxic, non-flammable, chemically inert, and cheap. It leaves no residue, is environmentally sound, and has regulatory approval from all major food and drug agencies. This makes scCO\(_2\) a very interesting solvent for various applications.

![Phase diagram](image)

**Figuur 1** Phase diagram of a pure substance. It includes the triple point (where the solid, liquid, and gas phases are in equilibrium) and the critical point (where the liquid and gas phases are in equilibrium with the supercritical state). For carbon dioxide, the triple point is at -56.6°C and 4.2 bar, and the critical point is at 31.1 °C and 73.8 bar.

**Tabel 1** Some properties of fluids

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>Supercritical</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g · cm(^{-3}))</td>
<td>10(^{-3})</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity (g · cm(^{-3}) · s(^{-1}))</td>
<td>10(^{-4})</td>
<td>10(^{-4})</td>
<td>10(^{-2})</td>
</tr>
<tr>
<td>Diffusivity (cm(^{2}) · s(^{-1}))</td>
<td>0.1</td>
<td>10(^{-3})</td>
<td>5 · 10(^{-6})</td>
</tr>
</tbody>
</table>

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Figuur 2  Density of carbon dioxide (vertical axis, expresses as kg/L) as a function of temperature and pressure.

2.2.1  *Applications of supercritical carbon dioxide*

$\text{scCO}_2$ is a very suitable solvent for material handling. A wide variety of applications is discussed here shortly.

2.2.1.1  Extraction

Extractions with sc$\text{CO}_2$ make good use of its tuneable solvating properties: both the yield and the selectivity of an extraction are influenced by small changes in temperature and pressure. This makes that supercritical extraction technology is widely used in the food and related industries, where it serves either to recover a range of natural products from liquid or solid matrices, or to remove unwanted components (e.g. decaffeination of coffee)$^{8,9}$.

2.2.1.2  Chemical reactions

A wide variety of homogeneous and heterogeneous reactions have been performed in sc$\text{CO}_2$, including many polymerisations$^{10,11,12}$. 

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2.2.3 Enzyme-catalysed reactions
Many enzymatic reactions have been performed in scCO₂. The adjustable solvating power of scCO₂ (and a tuneable selectivity in the dissolution of related compounds) forms a strong combination with the natural selectivity of enzyme catalysis. A fine review with emphasis on the many parameters that influence enzyme catalysis in scCO₂ (e.g. pressure, temperature, water content) is given by Mesiano et al.¹³

2.2.4 Particle design
A variety of process concepts have been developed for particle formation using scCO₂. An overview of these processes, and the type of materials that they comply with, is given in an extensive review by Jung and Perrut¹⁴.
2.3 Super critical processing of cellulose

2.3.1 Polymer processing with supercritical fluids

Due to its solid-liquid properties supercritical carbon dioxide shows unique and valuable potential for the enhanced processing of many materials, including polymers. The ability of supercritical carbon dioxide (scCO₂) to swell and plasticise polymers is important for impregnation, extraction and modification of polymeric materials. The plasticisation also reduces viscosity and facilitates the processing of polymers due to low shear stresses. Opportunities exist for improving the processing of many polymeric materials ranging from textile to food and biomaterials.

Major advantage of supercritical fluids is that they may replace many environmentally harmful solvents currently used in industry. For example, scCO₂, which is by far the most widely used supercritical fluid, is relatively cheap, non-toxic and non-flammable. Moreover, the fact that CO₂ is a gas under ambient conditions makes its removal from the polymeric product very easy, avoiding the costly processes of drying or solvent removal, which is very important in the processing of polymer base materials.

2.3.2 Plasticisation of polymers with supercritical CO₂

As a result of its low viscosity the sorption of scCO₂ in polymers is relatively high. The strong sorption results in swelling of the polymer, which changes the mechanical and physical properties of the polymers. The most important effect is the reduction of glass transition temperature (Tg) of glassy polymers (semi- or high crystalline) subjected to scCO₂. The plasticisation is characterised by increased segmental and chain mobility and by an increase in interchain distance. The plasticising effect of CO₂ is the result of the ability of CO₂ molecules to interact with the basic sites in polymer molecules.

The reduction of Tg of polymers subjected to scCO₂ has been studied for a number of materials. For example the Tg of PMMA decreases with approximately 40 - 65 °C when processed at CO₂ pressures of 50 till 80 bar. The Tg of Polystyrene (PS) decreases also with ± 50 °C at a pressure of 80 bar. Other research groups have found Tg-reduction ranging form 75 °C for polycarbonate till 80 °C for Poly(vinylpyrrolidone). In general it may be concluded that the average Tg-reduction as result of scCO₂ can be estimated at 50 °C for all different types of polymers.
3 Market Study

3.1 Introduction
The production of cellulose derivatives can be estimated from the annual production of dissolving pulps. Dissolving pulps are speciality pulps composed of more than 90% pure cellulose, used for chemical conversion into products such as rayon, cellophane and cellulose acetate. The world annual production of dissolving pulp is 4 million tonnes (0.7 million tonnes in Europe). Sappi is the worlds largest producer of dissolving pulps, their market share is about 15% (600.000 tonnes, see also Figuur 3).

![Sappi's global position - capacity ('000 tons)](image)

Dissolving pulp

Figuur 3 Overview of capacity of several producers of dissolving pulps.

The most important cellulose derivatives (based on market share) are viscose fibres (62%). Other important uses are cellulose acetate fibres (15%), cellophane (8%) and cellulose nitrates (8%)\(^5\).
3.2 Market overview for each product

3.2.1 Viscose
Viscose is the most important cellulose derivative based on market share. It is a regenerated cellulose. In the Netherlands the former Enka company (later AKZO NOBEL and then Accordis) was an important producer of viscose. Nowadays, viscose production has mainly moved away from Europe to Asia. An example is the joint venture of AKZO NOBEL (Accordis) with the Indian Birla Group (joint venture name is Centak Chemicals Ltd). The two largest producers (worldwide) of viscose are Accordis and Lenzing AG (an Austrian company). Three other European producers are Säteri (Finland), Svenska (Sweden) and Sniace (Spain).

3.2.2 Cellophane
Like Viscose, Cellophane is also a regenerated cellulose. The largest cellophane producer is UCB (Innovia films). In 1996 UCB Films acquired British Cellophane Ltd and the trade name Cellophane.

3.2.3 Cellulose acetate
Cellulose acetate is mainly used in cigarette filters and yarns for apparel and furnishings. The two largest cellulose acetate producers are Eastman Chemical Company (US) and Celanese (US). Rhodia (France), Novaceta (Italy) Teijin (Japan) and Diacel Chemical Industries (Japan) are other cellulose acetate producers.

3.2.4 Cellulose ethers
Important companies in the cellulose ether business are Henkel, Hercules, Dow, Lamberti, Clariant, AKZO NOBEL, Noviant and Wolff cellulosics (Bayer).

3.2.5 Cellulose nitrate
Next to cellulose ethers Wolff cellulosics also produces cellulose nitrates. Other producers are Asahi Kasei (Japan) and Hercules (USA).
4 Preliminary experiments

4.1 Introduction
Within this desk study, limited time is reserved for experimental trials. Preparation of actual cellulose derivatives is not possible within the scope of this study. Therefore, preliminary experiments are performed in order to find proof of actual swelling or dissolving of pure cellulose in supercritical carbon dioxide. Swelling of dissolving facilitates derivatisation of cellulose and alters the crystalline structure of cellulose, which can be measured using röntgendiffraction.

4.2 Experimental set-up
Two experiments were performed in which cellulose was subjected to supercritical carbon dioxide. A Buckeye V60 dissolving pulp was chosen as a pure source of cellulose. This dissolving pulp consists of 91% α–cellulose and has a DP of ca. 832. The supercritical carbon dioxide treatment was performed at 250 bar during 24 hours at both 200 and 260°C. After the treatments the colour of the celluloses had changed from of-white to brown or even black. The effect of the treatment was examined using XRD and viscosity measurements.

4.3 Analysis
Only native cellulose has a cellulose I crystalline structure. To examine the effect of the supercritical process it was studied using röntgendiffraction (XRD) whether the crystalline structure of the cellulose had changed to cellulose II or the amount of crystallinity had dropped. Since treatments were performed at high temperatures viscosity measurements were performed to examine the effect of the treatments on the cellulose molar mass.

4.3.1 Determination of crystallinity using röntgendiffraction (XRD)

4.3.1.1 Apparatus
Philips röntgendiffractometer PW1830.
In this diffractometer X-rays (Cu K-α radiation) from the anode are reflected by the sample (θ/2θ symmetric reflection) are detected by a moving detector. Two slits on the anode control the beam dimensions (primary optics), yielding a beam that covers the complete sample surface, whereas the reflected beam is controlled by the secondary optics. (Usual parameters: divergence slit 1°, receiving slit 0.2 mm, scatter slit 1°, monochromised using a 15μm Ni-foil).
The sample holder is usually held at ambient temperature.

4.3.1.2 Method
For determination of the degree of crystallinity two scans are made from 7° to 40° 2θ; one scan of the sample to be analysed, one scan of a amorphous sample (for instance, a ball milled cellulose sample which is grinded until no crystallinity can be observed with röntgendiffraction).
After baseline corrections, the scan of the amorphous sample will be fitted into the scan of the sample to be analysed.

The area of the scan of the sample to be analysed minus the area of the scan of the amorphous sample represents the crystalline fraction. This crystalline fraction divided by the total area calculates the content of crystallinity.

Figuur 4 Example of a sample of dissolving cellulose:

![Graph showing intensity counts across a range of 2θ values]

4.3.1.3 Results
The results of the röntgendiffraction measurements are listed in Tabel 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (cellulose I type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose V60, not dried</td>
<td>55.0%</td>
</tr>
<tr>
<td>Cellulose V60, dried at 105°C</td>
<td>50.3%</td>
</tr>
<tr>
<td>V60 CO₂ treated at 200°C</td>
<td>55.3%</td>
</tr>
<tr>
<td>V60 CO₂ treated at 260°C</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

From this table it is clear that the treatment at 200°C did not effect the crystallinity. However, after the treatment at 260°C crystallinity had dropped to almost zero.

4.3.2 Molecular weight determination of cellulose

4.3.2.1 Method
The method used is a derivative of a standard method TAPPI T230 om-82.
This procedure determines the viscosity of a solution of 0.5% cellulose in copper(II)ethylene-diamine (cuen: 1mol/l Cu2+ and 2mol/l ethylene-diamine).
The average molecular weight of dissolved cellulose (and the weight) determines the viscosity. So if the samples degrade, the molecular weight decreases and so will the viscosity.
By also determining the viscosity of a blank solution (50% demineralised water + 50% cuen), the intrinsic viscosity can be calculated and with the Mark-Houwink equation (with known constants), the degree of polymerisation of the cellulose can be determined.

4.3.2.2 Procedure
In a 100ml conical flasks 25ml demineralised water is added to 100mg of sample.
After addition of glass pearls (20 pieces, 6mm diameter), the mixture is slowly stirred overnight (150rpm). During stirring, 25ml of cuen solution is slowly added and flushed with nitrogen to remove oxygen. The time (3 hours) of dissolving should be constant for all samples due to degradation of the sample in this corrosive environment.
The viscosity is determined by capillary viscometry at 25°C.
(Cannon-Fenske capillary type 100, AVS-K ~0.015)

4.3.2.3 Results
The results of the molar mass determinations are listed in Tabel 3.

Tabel 3 Decrease of molecular weight of dissolving cellulose (Buckeye V60) after treatment in supercritical CO₂ at 200°C and 260°C for 24 hours:

<table>
<thead>
<tr>
<th>Code nr.</th>
<th>Sample</th>
<th>V rel</th>
<th>Conc. [g/ml]</th>
<th>V intr. [ml/g]</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Buckeye V60</td>
<td>1.749</td>
<td>0.00189</td>
<td>333.5</td>
<td>749</td>
</tr>
<tr>
<td>2</td>
<td>V60, treatment at 200°C</td>
<td>1.127</td>
<td>0.00196</td>
<td>62.5</td>
<td>149</td>
</tr>
<tr>
<td>3</td>
<td>V60, treatment at 260°C</td>
<td>0.999</td>
<td>0.00198</td>
<td>-0.4</td>
<td>-1</td>
</tr>
</tbody>
</table>

The molar mass determinations indicate severe degradation of cellulose both at 200°C and 260°C.

4.4 Discussion
Combining the results of the röntgendiffraction measurements and viscosity measurements it was found that after treatment at 200°C no effect on the crystalline structure of cellulose was found, but still a severe drop in the molecular mass occurred. This indicates that degradation (chain scission) mainly occurs in the amorphous regions and no evidence of penetration of supercritical carbon dioxide into the crystalline regions was found. This severe thermal degradation was not expected at 200°C, but could be initiated by the supercritical carbon dioxide that has an acidic character. This result would suggest that the supercritical carbon dioxide did penetrate into the amorphous regions of cellulose.
After treatment at 260°C the cellulose was completely charred, and the only conclusion that can be drawn is that the conditions of the supercritical treatment were too harsh.
4.5 Conclusions

Until now, no obvious positive results have been obtained using supercritical carbon dioxide treatments. Severe degradation occurs after heating to 200°C or 260°C for 24 hours. After the treatment at 200°C the crystalline cellulose regions were still intact indicating that degradation has occurred in the amorphous regions. Next experiments will be performed at short reaction times and also the effect of a co-solvent like for example methanol will be studied.
Literature

7. Mermelstein, N.H., Supercritical fluid extraction gets renewed attention. Food Technology, January 1999