

# Groene Cellulose

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Ir. K. Molenveld  
Ing. F.E. Giezen  
Dr. Ir. M.J.J. Litjens  
W. Teunissen  
Ing. R.C. Bezemer

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## Abstract

This progress report describes the A&F activities regarding the M&T Green Cellulose project. This industrial feasibility project consists of an extensive literature study, a market study and approach and some initial experiments.

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

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  $T_g$ , glass transition temperature) of several commercial polymers. During this study it is investigated if supercritical carbon dioxide can lower the softening point of cellulose in order to ease cellulose derivatisation.

In this project a literature- and market-study is combined with initial experiments and market approach. The initial experiments revealed that treatments must be performed at elevated temperatures with a severe risk of cellulose degradation. Based on the literature, initial experiments and market study a list of potential applications of supercritical carbon dioxide in cellulose modification is generated (paragraph 5.3).

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# 1 Introduction

This report describes the activities and results of the Green cellulose project. The Green cellulose project consists of a literature study on cellulose modification and cellulose derivatives (paragraph 2.1), supercritical carbon dioxide processing (paragraph 2.2) and polymer processing using supercritical carbon dioxide (paragraph 2.3). A smaller part of this project focuses on a market study (chapter 4) and initial market approach (chapter 5). Some initial experiments on cellulose modification using supercritical carbon dioxide are performed to support this market approach (chapter 3).

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 for fibres or films.

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  $T_g$ , glass transition temperature) of several commercial polymers. During this study it is investigated if the lower softening point of cellulose in  $scCO_2$  can be used to ease cellulose derivatisation.

## 2 Literature study

This literature study consist of three parts:

- cellulose processing and modification
- supercritical carbon dioxide and relevant processing techniques
- supercritical processing of cellulose

### 2.1 Cellulose processing and modification<sup>1,2,3,5</sup>

#### 2.1.1 Introduction

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 a colourless, odourless, and non-toxic polymer solid. It is insoluble in water and common organic solvents, but swellable in polar protic and aprotic liquids. Due to the strong cohesion between the macromolecules via intermolecular force, especially a hydrogen-bond network, cellulose cannot be transformed into the molten state. Due to its molecular structure, supramolecular order and fibrillar morphology, cellulose is a typical fibre polymer and is quite predominantly processed and used in the form of fibres.

Cellulose is generally harvested from highly pure sources of cellulose such as cotton linters or easily harvested sources such as wood. A further source of cellulose, which up to now is just of scientific interest is bacterial cellulose that is produced extracellularly by e.g. *Acetobacter xylinum* strains. Cellulose obtained from cotton linters needs only a treatment with hot sodium hydroxide solution that removes the protein, pectin substances, and wax to produce high quality cellulose. The cellulose from woody plants is isolated by large-scale chemical digestion processes, leaving the cellulose component as a solid in a somewhat degraded state. Delignification of wood is usually performed as a multi-step process, increasing stepwise the specificity of interaction with the components to be dissolved. The whole process comprises of a so-called digestion, removing most of the lignin as lignosulfonic acid (sulfite process) or as alkali or thioglignin (graft and sulfate process respectively) and subsequent bleaching steps for eliminating nearly all of the residual lignin. Purified cellulose generally still contains small amounts of hemicellulose and lignin and should be identified by source and physiochemical treatments is has received.

#### 2.1.2 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<sup>4</sup>. Swelling power generally increases in the order; organic solvent < water < salts < acids < bases. Interaction between cellulose and water plays an important part in the chemistry, physics, and technology of cellulose isolation and processing, and it is the fundamental process in papermaking. Cellulose exhibits a high hygroscopicity due to interaction of its hydroxy groups with water molecules, but is hindered from being dissolved in water by its

ordered supramolecular structure. At least with native cellulose, cellulose-water interaction is limited to the non-crystalline structural regions and the pore and void system.

Other 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 (cadoxen or iron tartaric acid). In most cases, these cellulose solutions are subject to degradation by hydrolysis or air oxidation.

#### *2.1.3 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.<sup>5</sup> It was found that the thermoplasticity of wood is mainly determined by cellulose. Ranges of softening temperatures (glass transition temperatures) that are listed are for example 231-253°C<sup>6</sup>, 180-350°C<sup>7</sup> or 230-245°C<sup>8</sup>. The theoretical crystalline melting temperature of cellulose (estimated at 400°C) is well above its decomposition temperature (200-270°C). 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..

#### *2.1.4 Microcrystalline cellulose*

Commercial forms of microcrystalline cellulose were first mentioned in a patent issued in 1961. Described are stable thixotropic gel systems of aqueous colloidal dispersions of disintegrated cellulose of constant degree of polymerisation (level off DP) at high solids concentration. To prepare these materials a controlled chemical pre-treatment is used to destroy the molecular bonds whereby the cellulose microcrystals are hinged together. Mechanical energy is used to disperse a sufficient amount of the unhinged microcrystals in the aqueous phase. This ensures the characteristic novel rheology and the smooth, fat-like spreadability of the resulting colloidal microcrystalline cellulose gels. Stable gel systems are obtained only when the mechanical energy is introduced into an aqueous suspension of level off DP cellulose in which the total solids

concentration is  $\geq 5\%$  and only if this mechanical energy is sufficient to liberate a minimum number of microcrystals to allow a stable gel. The size and shape of cellulose microcrystals is largely determined by the nature of the starting materials but is usually 15 to 40 microns. The microcrystals consist of cellulose chain of about 250 glucose molecules.

Commercial applications of microcrystalline celluloses are various. Thousands of metric tons of pharmaceutical grade microcrystalline celluloses are used for the preparation of tableting powder mixes. These microcrystalline celluloses are used because of their chemical inactivity, the absence of toxicity and great hygroscopicity (e.g. as tablet dissolvant). Furthermore, microcrystalline celluloses are used to control ice-crystal growth in frozen desserts, as temperature-stable thickeners for salad dressings and sauces and as rheology modifiers in water-based paints and decorative laminates.

Recently the University of Nebraska patented a novel environmentally friendly process for the production of microcrystalline cellulose by reactive extrusion<sup>9</sup>.

#### 2.1.5 *Cellulose derivatives*

The use of cellulose as a chemical raw material started 150 years ago with the discovery of the first cellulose derivatives, and developed to a production volume of more than 5 million tons annually during the 20<sup>th</sup> century.

The main types of cellulose derivatives are:

- Inorganic esters (cellulose nitrates, cellulose sulfates and cellulose phosphates)
- Organic esters (cellulose acetates, cellulose formates, cellulose acetobutyrate)
- Cellulose ethers (carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose)
- Regenerated cellulose (cellophane and rayon)

As a starting material for chemical transformations of cellulose, rather exclusively dissolving-grade wood pulps and to some extent bleached and scoured cotton linters are used. Dissolving pulps are speciality pulps composed of more than 90% pure cellulose. Two basis processes are used to produce dissolving pulp<sup>10</sup>. 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 sulfite 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, in the order of 35% based on wood (see also Figure 1).



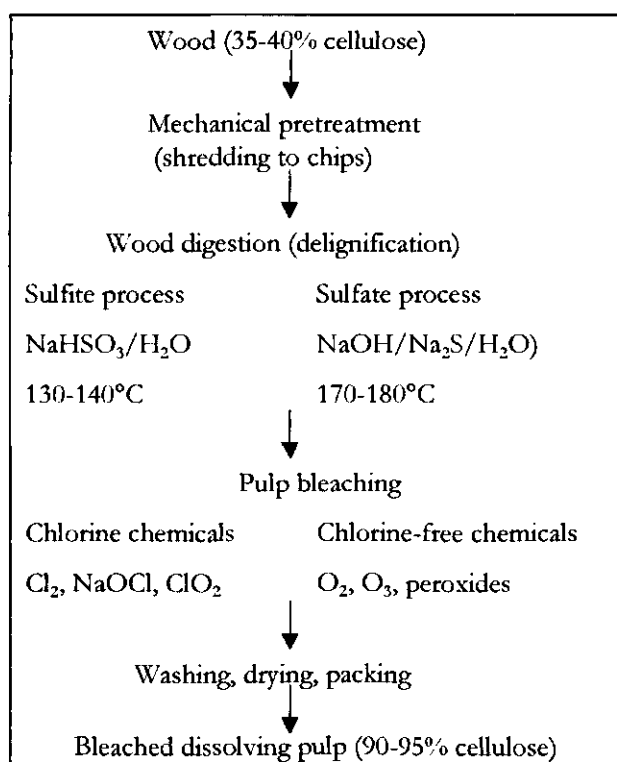


Figure 1 Production of dissolving pulp

#### 2.1.5.1 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. In 1847 Schönbein reports the reaction of cellulose with nitric acid ( $\text{HNO}_3$ ) in a ternary system with a sulphuric acid solution ( $\text{H}_2\text{SO}_4/\text{water}$ )<sup>11</sup>.

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, coatings, films, explosives and propellants with an annual total production world-wide of about 150.000 tons of process pulp.

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  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  in the proper ratio. During the reaction time of 20-30 minutes cellulose maintains its fibrous structure (heterogeneous process). In the late fifties Hercules developed a continuous but still heterogeneous 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.

### 2.1.5.2 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<sup>12</sup>.

Soluble cellulose acetate was first prepared in 1865 by heating cotton and acetic anhydride at 180°C<sup>13</sup>. 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. High-DP, scoured and bleached cotton linters are predominantly employed as the raw material, but also an adequately refined softwood sulfite pulp or even a special grade prehydrolysed sulfate pulp can be used. Cellulose acetate is predominantly 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. These processes are scarcely practised due to the inferior uniformity and general quality of the products obtained.

Recently a novel acetylation process was developed<sup>14,15</sup> including (1) an acetylation stage at high temperature under reduced pressure together with accurate computer control of the temperature (2), a deacetylation stage at high temperature, and (3) successive flash evaporation stage for separation of concentrated acetic acid from the reaction mixture. This process leads to huge reductions in process energy and amounts of reagents, and to great improvement in productivity. Furthermore sulfite pulps with lower  $\alpha$ -cellulose content have come to be applicable for cellulose diacetate production. When conventional acetylation is applied low  $\alpha$ -cellulose pulps, a relatively large quantity of acetone-insoluble fraction is formed which causes serious problems in fiber spinning processes. At high temperatures hemicellulose acetates become soluble in acetone by partial depolymerization.

The total annual production of cellulose acetate is 0.9 million tonnes world-wide.

### 2.1.5.3 Cellulose ethers

Cellulose ethers were first described in literature in 1905 by Suida, who reacted cellulose with dimethyl sulfate to produce methylcellulose. By 1912 the first patents covering the preparation of cellulose ethers appeared. Cellulose ethers on a commercial scale are generally used as end products. The most important properties of cellulose ethers are their solubility combined with chemical stability and non-toxicity. Water solubility<sup>16</sup> and/or organosolubility can be controlled within wide limits via the constitution and the combination of ether groups at the cellulose chain, as well as via the DS, and to some extent via the pattern of substitution. Accordingly, cellulose ethers are generally applied, in the dissolved or highly swollen state, in many areas of industry and domestic life. The spectrum of applications ranges from auxiliaries in large-scale emulsion or suspension polymerisation, through to additives for paints and wall paper adhesives, to viscosity enhancers in cosmetics and foodstuffs. The most important cellulose ethers are carboxymethyl cellulose, methyl cellulose and hydroxyethyl cellulose with annual production capacities of 300.000t, 70.000t and 54.000t respectively.

Industrial etherification of cellulose is exclusively performed in a heterogeneous system, starting from alkali cellulose. Recent developments are centred on the full exploitation of the "mixed ether principle" for tailoring properties to the broad variety of end-use requirements. Besides this, the minimisation of chain degradation during the process in order to obtain a high solution viscosity of the product and the enhancement of reagent yield with the option to decrease the input of chemicals for ecological reasons, plays a major role.

Sodium carboxymethyl cellulose or CMC is an anionic polyelectrolyte prepared by the reaction of sodium chloroacetate with alkali cellulose in an aqueous or aqueous-alcoholic system (slurry process). Crude grades can be prepared dry at high cellulose solids without solvents. A DS between 0.4 and 0.8 is necessary in the technical process of CMC manufacture in order to meet the requirements of application, which usually takes place in an aqueous solution. A considerable amount of the etherifying agent, (up to 30%) is consumed in side reactions with the aqueous NaOH forming predominantly sodium glycolate by hydrolysis of the chloroacetate<sup>17</sup>. The CMC is separated from by-product salts by washing with aqueous alcohol or acetone. A new process that has already been utilised at a practical level results in CMC's with a more homogeneous distribution of substituents and thus a better product quality (stability etc.)<sup>18</sup>. Instead of monochloroacetic acid, *i*-propyl monochloroacetate ester is used as the reagent. Separate additions of NaOH solution to the reaction mixture further improve the process.

The raw material employed in carboxymethyl cellulose manufacture largely depends on the product quality required: for high-viscosity types, cotton linters with a DP up to 4000 are used, and oxygen must be excluded to avoid chain degradation in the strongly alkaline reaction system. Mostly dissolving pulps from hard or soft woods or even from annual plants with a rather low degree of refinement are used. 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 that is soluble in cold water. Commercial products with a DS between 1.5 and 2.0 are obtained by a Williamson reaction of alkali cellulose with gaseous or liquid  $\text{CH}_3\text{Cl}$ . Formation of methyl cellulose consumes caustic and is accompanied by side reactions that lead to the by-products methanol and methyl ether. By-product formation accounts for 20-30% of the  $\text{CH}_3\text{Cl}$  consumption resulting in a reagent yield for etherification of maximally 80%. Purification of methylcellulose takes advantage of its insolubility in hot water. Methylation of alkali cellulose with  $\text{CH}_3\text{Cl}$  represents a typical "heterogeneous derivatization reaction", with the accessibility of the cellulose chains to the reagent determining the course of conversion in this diffusion-controlled process. Methylcellulose is (amongst others) used as thickener, adhesive, binder, film former and suspending aid.

Hydroxyethylcellulose (HEC) is produced by the reaction of cellulose with ethylene oxide. In principle it requires only a catalytic amount of  $\text{OH}^-$  ions for the cleavage of the epoxy ring and the formation of the C-O bond between the reagent and the alcohol. The alkali-catalysed hydroxyethyl ether formation is accompanied by the reaction of water molecules with ethylene oxide to glycol and to polyglycols, with the reagent yield for cellulose etherification amounting to 50-70% of the ethylene oxide input. The hydroxyalkylation of cellulose is generally a thoroughly heterogeneous reaction with the weight ratio of  $\text{NaOH}$ /cellulose varying within the wide limits of 0.3:1 to 1:1 and that of  $\text{H}_2\text{O}$ /cellulose between 1.2:1 to 3.5:1. Frequently a slurry process with an excess of a fairly inert diluent like *i*-propanol, *t*-butanol or acetone is employed in hydroxyethylation. The reaction proceeds at 30-80°C within some hours, and the MS is determined by the ethylene oxide input. HEC is predominantly used in aqueous systems as a thickener or binder, or as a protective colloid and suspension stabiliser. It exhibits an excellent salt compatibility and can be converted to transparent films from aqueous solution.

#### 2.1.5.4 Regenerated cellulose

Cellophane and rayon are forms of cellulose that are regenerated from cellulose xanthate. This so-called viscose process was invented in 1892 by Cross, Bevan and Beadle<sup>19</sup> and is still practised today with an output of about 3 million tons annually worldwide. Cellulose xanthate is prepared via a reaction of alkaline cellulose with carbon disulphide (see Figure 2). Commercially, viscose is spun into an acid bath where the cellulose xanthate decomposes to regenerate cellulose and carbon disulphide, thereby reforming cellulose into fibres or cellophane sheets. Much research and development work has been put into reducing the  $\text{CS}_2$  input<sup>20</sup>. 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.

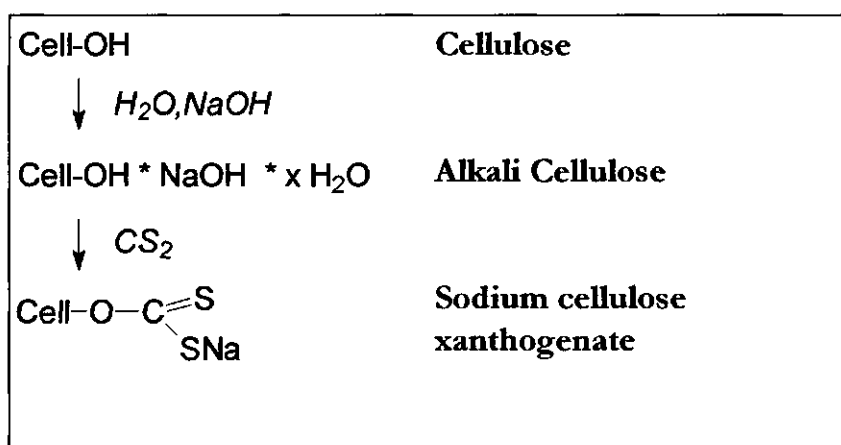


Figure 2 Scheme of cellulose xanthogenate formation

## 2.2 Supercritical carbon dioxide<sup>21,22</sup> and relevant processing techniques

When carbon dioxide is compressed at conditions that exceed 31 °C and 74 bar, it is in its supercritical state (Figure 3). 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 Table 1 and Table 2. . The density, and thereby the solvating power, is adjustable by the pressure and the temperature (Figure 4). Although many supercritical fluids are described (see *e.g.* Table 2) carbon dioxide is the most widely used, because it is non-toxic, non-flammable, inexpensive, and has GRAS (Generally Regarded As Safe) status. Furthermore, in particular its low critical temperature makes it highly suitable for processing heat-sensitive materials, and it is an important advantage that leaves no residue after processing. Supercritical carbon dioxide (scCO<sub>2</sub>) is an apolar solvent with dissolution properties that are comparable with hexane. The carbon dioxide may be collected and reused at limited losses, and is considered to be an ecologically sound solvent.

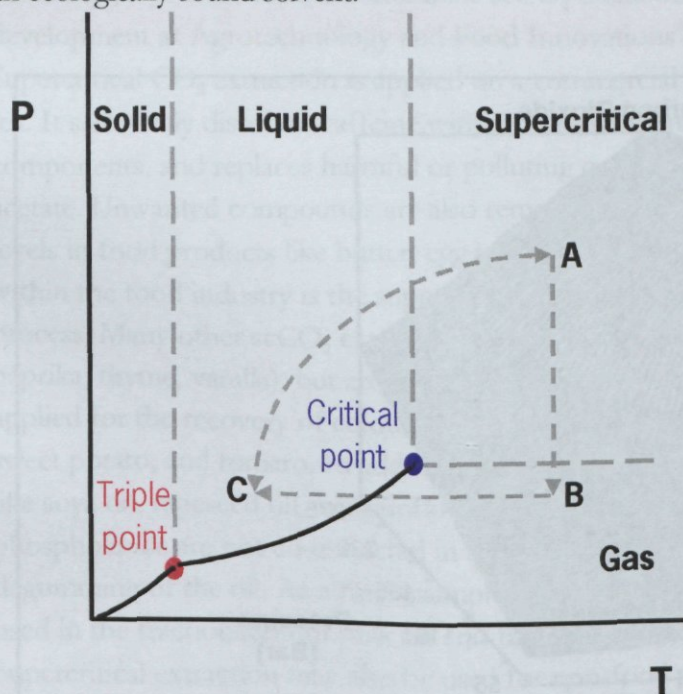


Figure 3 Phase diagram of a pure substance. It includes the triple point (where the solid, liquid, and gas phases are in equilibrium) and the critical point (where the liquid and gas phases are in equilibrium with the supercritical state). For carbon dioxide, the triple point is at -56.6°C and 4.2 bar, and the critical point is at 31.1 °C and 73.8 bar.



Table 1 Some properties of fluids

| Property  | Gas       | Supercritical | Liquid            |
|---|-----------|---------------|-------------------|
| Density ( $\text{g} \cdot \text{cm}^3$ )                          | $10^{-3}$ | 0.3           | 1                 |
| Viscosity ( $\text{g} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ ) | $10^{-4}$ | $10^{-4}$     | $10^{-2}$         |
| Diffusivity ( $\text{cm}^2 \cdot \text{s}^{-1}$ )                 | 0.1       | $10^{-3}$     | $5 \cdot 10^{-6}$ |

Table 2 Critical points of selected fluids<sup>23</sup>

| Fluid          | Critical Temperature ( $^{\circ}\text{C}$ ) | Critical Pressure (bar) |
|----------------|---|-------------------------|
| hydrogen       | -239.9                                      | 13.0                    |
| nitrogen       | -146.9                                      | 34.0                    |
| methane        | -82.6                                       | 46.0                    |
| carbon dioxide | 31.1  | 73.8                    |
| ethane         | 32.2  | 48.8                    |
| nitrous oxide  | 36.5  | 71.7                    |
| propane        | 96.7  | 42.5                    |
| ammonia        | 132.5                                       | 112.5                   |
| methanol       | 239.5                                       | 81.0                    |
| water          | 374.2                                       | 220.5                   |

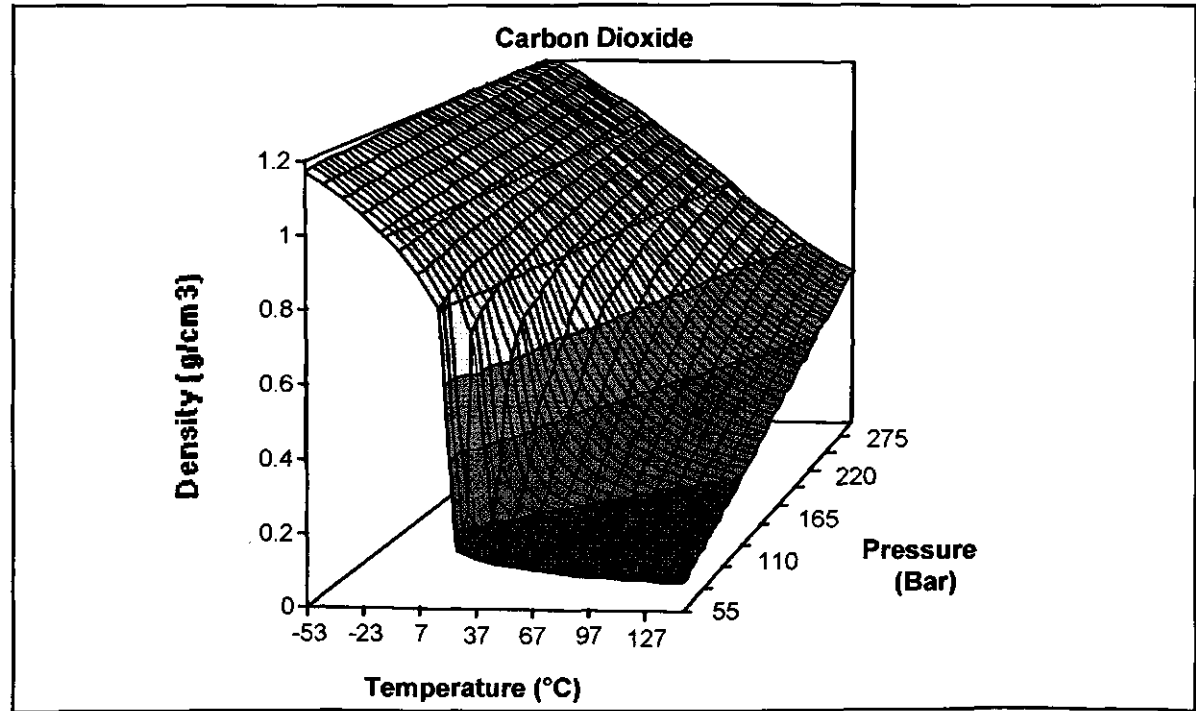


Figure 4 Density of carbon dioxide (vertical axis, expresses as kg/L) as a function of temperature and pressure.

### 2.2.1 *Applications of supercritical carbon dioxide*

scCO<sub>2</sub> is a very suitable solvent for material handling. A wide variety of applications are discussed here shortly.

#### 2.2.1.1 Extraction<sup>23,24,25</sup>

Extractions form by far the largest group of scCO<sub>2</sub> applications. Supercritical extraction technology is widely used in the food and related industries. In scCO<sub>2</sub> extraction, a liquid or solid material is brought into contact with the scCO<sub>2</sub> for extraction. In the subsequent separation step, the dissolving power of the scCO<sub>2</sub> is reduced by reducing the pressure and/or changing the temperature, and the separation or fractionation of the extracted compound occurs. The carbon dioxide that is released is reused in a subsequent extraction cycle. For solid matrices the extraction process is batchwise, but liquid materials may also be extracted in a continuous mode. Because continuous operation offers various advantages over batch operation (e.g. more efficient use of energy and extraction solvent, better control of product quality, increased process flexibility), a process for the continuous scCO<sub>2</sub> extraction of solid materials is presently under development at Agrotechnology and Food Innovations<sup>26</sup>.

Supercritical CO<sub>2</sub> extraction is applied on a commercial scale for the decaffeination of coffee or tea. It selectively dissolves caffeine without removing many of the desirable flavour-precursor components, and replaces harmful or polluting organic solvents like methylene chloride and ethyl acetate. Unwanted compounds are also removed using scCO<sub>2</sub> in the lowering of cholesterol levels in food products like butter, egg yolk, meat, and fish. Another large commercial application within the food industry is the supercritical extraction of hops, for use in the beer brewing process. Many other scCO<sub>2</sub> extracted flavours and fragrances are commercially available (e.g. paprika, thyme, vanilla), but are often not produced in large amounts. Furthermore scCO<sub>2</sub> is applied for the recovery of colourants like  $\beta$ -carotene and lycopene from sources like carrot, sweet potato, and tomato. In addition, it is used for the extraction and fractionation of seed oils like soya oil, rapeseed oil, and sunflower oil. Here, it is a very important feature that phospholipids are not co-extracted in scCO<sub>2</sub> extraction, which eliminates the need for chemical degumming of the oil. As a final example of applications in the food industry, supercritical CO<sub>2</sub> is used in the fractionation of milk fat and fish oils.

Supercritical extraction may also be used for non-food processes, for example in the removal of residual monomer from polymer products. The extraction of methylmethacrylate from the corresponding polymer has been described by Kemmere et al.<sup>27</sup>. Also, it can be used to remove wood extractives from cellulose fibres<sup>28</sup>.

#### 2.2.1.2 Chemical reactions (including enzyme-catalysed reactions)

A wide variety of homogeneous and heterogeneous reactions have been performed in scCO<sub>2</sub><sup>29,30</sup>. Especially polymerisation reactions in scCO<sub>2</sub> have received a lot of attention, as illustrated e.g. in reviews by Cooper (2000)<sup>31</sup> and by Kendall et al.(1999)<sup>32</sup>. They feature many examples of homogeneous polymerisation (e.g. fluoropolymers), precipitation polymerisation, dispersion



polymerisation, emulsion and suspension polymerisation. In addition, they describe the use of CO<sub>2</sub> as a plasticiser in condensation polymerisation, and the formation of polymer blends in scCO<sub>2</sub>. The processing of polymers with scCO<sub>2</sub> is reviewed in section 2.3.

For chemical reactions that are catalysed by enzymes, the reaction conditions must be chosen such that they comply with these efficient yet vulnerable biocatalysts. By doing this, many enzymatic reactions have been performed effectively in scCO<sub>2</sub>. A fine review with emphasis on the many parameters that influence enzyme catalysis in scCO<sub>2</sub> (e.g. pressure, temperature, water content) is given by Mesiano et al.<sup>33</sup>

#### 2.2.1.3 Particle formation

Particle formation with scCO<sub>2</sub> is believed to hold an immense potential for large-scale application in the pharmaceutical industry<sup>34</sup>. A variety of process concepts for particle formation using scCO<sub>2</sub> have been developed, and the influence of process parameters on the nature of the resulting particles has been studied extensively, in order to prepare particles with well-designed characteristics (e.g. crystal form and particle size). Three main classes of particle formation using scCO<sub>2</sub> have been described: (1) Rapid Expansion of Supercritical Solutions (RESS), where an active compound that is dissolved in CO<sub>2</sub> precipitates after an abrupt pressure drop of CO<sub>2</sub> through a small nozzle. (2) Gas Anti-Solvent (GAS) precipitation, where a compound that is dissolved in a liquid solvent precipitates because of the addition of scCO<sub>2</sub>, which acts as an anti-solvent that causes supersaturation of the compound in the liquid solvent. (3) Particles from a Gas-Saturated Solvent (PGSS), where supercritical CO<sub>2</sub> is added and acts as a plasticiser of a polymer compound; when the CO<sub>2</sub> pressure is released abruptly, the polymer compound precipitates. An extensive overview of particle formation processes using scCO<sub>2</sub>, and the type of materials that they comply with, is given in an extensive review by Jung and Perrut<sup>35</sup>.

#### 2.2.1.4 Encapsulation

Encapsulation of ingredients is widely used in the food industry for a number of reasons, including (1) to control the release of e.g. flavours and aromas, (2) to promote easier handling of the ingredient (by converting a liquid into a solid form), (3) to protect the ingredient from light, oxygen, or water, and (4) to mask the taste of bitter compounds<sup>36,37,38</sup>. The ingredients may be encapsulated by various technologies, such as spray drying, spray chilling, extrusion, fluidised bed coating, or coacervation. Alternative techniques using scCO<sub>2</sub> are under development for the food and pharmaceutical industry (for controlled release of drugs). These techniques are in most cases similar to the processes that have been described for particle formation in the former section, but now in the presence of an extra compound that is to be included in the particles that are formed. In a new method for encapsulation, preformed microparticles that are prepared by e.g. extrusion or emulsion stabilization, are loaded with an active ingredient. In this method, the scCO<sub>2</sub> causes the polymers to plasticize and the microparticles to swell, which makes them more accessible for loading with the active ingredient that is dissolved in the scCO<sub>2</sub>. Upon reduction of the pressure to atmospheric conditions the CO<sub>2</sub> is released as a gas, the microparticles shrink to their initial volume, and the active ingredient is trapped in the matrix<sup>39</sup>.

#### 2.2.1.5 Dying of textile

Supercritical CO<sub>2</sub> technology is considered for the dying of textile on a commercial scale<sup>40</sup>. It is expected to be more rapid, more economical, and more environmentally friendly than current processes, which use a lot of water.

#### 2.2.2 *Industrial applications of supercritical carbon dioxide*

The main industrial applications of supercritical CO<sub>2</sub> technology are extractions. The largest applications include the decaffeination of coffee and tea (100000 tonne/year), hop extraction (60000 tonne/year), and the removal of pesticides from rice (30000 tonne/year in one single plant, which started operation in 1999 in Taiwan)<sup>41</sup>. Numerous smaller scale commercial extractions have been described (see also section 2.2.1.1).

Only recently, the first industrial plants for reactions in scCO<sub>2</sub> have started their operation. In 2000, DuPont has opened a 1000 tonnes/year development and manufacturing facility to make Teflon® resins. An increase in capacity has already been planned. In 2002, Thomas Swann & Co has started a multi-purpose synthesis plant for continuous operation at 1000 tonnes/year (e.g. for hydrogenation, alkylation, acylation).

#### 2.2.3 *Ecology and economy of supercritical carbon dioxide processes*

##### 2.2.3.1 Remarks on the ecology of supercritical carbon dioxide processes

Supercritical carbon dioxide is an environmentally friendly alternative for harmful and polluting solvents like methylene chloride, hexane, etc. After its use in the process, a large part of the carbon dioxide is collected in a pure form and recompressed for reuse. When using supercritical technology, no residues of organic solvents are found in the products or waste streams of the process. This means that products are regarded as “green and clean”, which adds to their quality and value. It also means that waste streams like for example extracted seeds, may be considered as agricultural waste or even as a compost to be distributed over farm land; the same seeds, when extracted with organic solvents, should be considered as chemical waste that needs to be incinerated.

##### 2.2.3.2 Remarks on economy of supercritical carbon dioxide processes

Supercritical processes are believed to be expensive, because of their high investment costs as compared with classical low-pressure equipment<sup>31</sup>. However, this is not true when large volumes of materials are to be treated, because the investment costs grow only slowly with an increase in capacity. For this reason, bulk products like coffee, tea, and hops can be processed with scCO<sub>2</sub> treated at low costs per kg. In addition, operating costs are low (manpower, energy, fluids). Over the years, a strong reduction in the capital costs for a plant, and an increased efficiency of scCO<sub>2</sub> processing because of better processing conditions, has improved the economy of supercritical technology considerably: in 1986. The crossover point where classic solvent processing and scCO<sub>2</sub> processing have the same cost structure was about 100 tons/day of coffee, presently this is about 40 tons/day<sup>22</sup>.

## 2.3 Supercritical processing of polymers

### 2.3.1 *Polymer processing with supercritical fluids*<sup>42</sup>

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 (scCO<sub>2</sub>) 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, scCO<sub>2</sub>, which is by far the most widely used supercritical fluid, is relatively cheap, non-toxic and non-flammable. Moreover, the fact that CO<sub>2</sub> 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 CO<sub>2</sub>*

As a result of its low viscosity the sorption of scCO<sub>2</sub> 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 (T<sub>g</sub>) of glassy polymers (semi- or high crystalline) subjected to scCO<sub>2</sub>. The plasticisation is characterised by increased segmental and chain mobility and by an increase in interchain distance. The plasticising effect of CO<sub>2</sub> is the result of the ability of CO<sub>2</sub> molecules to interact with the basic sites in polymer molecules<sup>42</sup>.

It has been shown by various methods that CO<sub>2</sub> is a good plasticizing agent for a host of polymeric materials, including polystyrene, polyethylene, poly(ethylene terephthalate), polyisoprene, polypropylene, poly(vinyl chloride), nylon and poly(2,6-dimethylphenylene oxide)<sup>31</sup>. CO<sub>2</sub> has also been shown to plasticize polymethacrylates, polycarbonates, polyurethanes, polyimides, crosslinked elastomers and networks, and a number of block copolymers and polymer blends<sup>31</sup>. For example the T<sub>g</sub> of PMMA decreases with approximately 40 - 65 °C when processed at CO<sub>2</sub> pressures of 50 till 80 bar<sup>43,44</sup>. The T<sub>g</sub> of Polystyrene (PS) decreases also with ± 50 °C at a pressure of 80 bar<sup>43</sup>. Other research groups have found T<sub>g</sub>-reduction ranging from 75 °C for polycarbonate<sup>43</sup> till 80 °C<sup>45</sup> for Poly(vinylpyrrolidone). In general it may be concluded that the average T<sub>g</sub>-reduction as result of scCO<sub>2</sub> can be estimated at 50 °C for different types of polymers.

### 2.3.3 *Supercritical processing of polysaccharides*

Starch materials have been processed by Rizvi et al.<sup>46</sup> in an extruder with sub-and supercritical carbon dioxide to prepare a range of puffed food products (foams). In this study the sc-CO<sub>2</sub> both acts as a plasticizer and as quenching agent. A controlled pressure drop at the end of the extruder leads to immediate setting of the product structure.

When supercritical processing of cellulose is investigated mostly supercritical water is utilised as reactive solvent<sup>47</sup>. It acts as a strong acid at supercritical conditions and can therefore be applied as hydrolysing agent for cellulose. Also, it can be used to convert cellulose I to cellulose II<sup>48</sup>.

However, the extreme conditions necessary to bring water in its supercritical state, i.e. > 374 °C and > 221 bar, make practical application difficult. To overcome this problem several initiatives have been taken to use sc-CO<sub>2</sub> as an alternative. Zheng et al used the technique of carbon dioxide explosion as a pre-treatment step for cellulose hydrolysis<sup>49</sup>. Main conclusion of this work was that the method increased the accessible surface area of the cellulose significantly. As a result the crystalline fractions of cellulose substrate were better accessible for further chemical modifications. Also, Kim et al. Used supercritical CO<sub>2</sub> pretreatments, in this case to enhance enzymatic cellulose hydrolysis<sup>50</sup>. Kim proved that presence of water was essential during these sc-CO<sub>2</sub> treatments.

At the moment no studies are known that try to use supercritical CO<sub>2</sub> in combination with elevated temperatures and different pH's. The intended (theoretical) effect of the method is presented in Figure 5 where the decrease in T<sub>g</sub> is drawn in a graph derived from literature<sup>5</sup> in which the thermomechanical curves of different types of treated and untreated celluloses are presented.

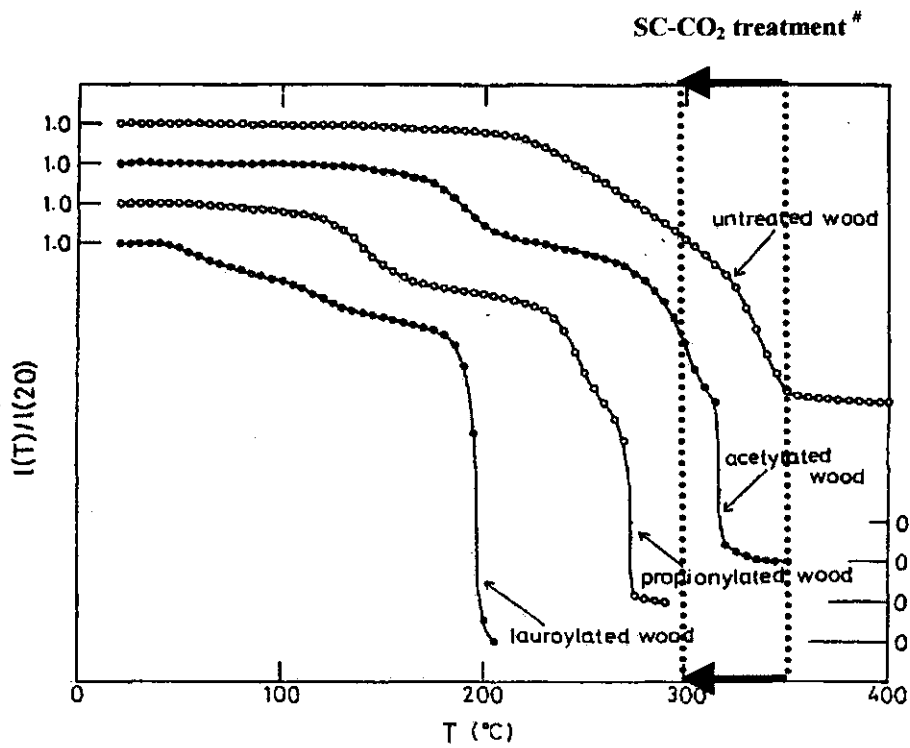


Figure 5 Thermomechanical diagram of different types of acylated wood and untreated wood fibres and (#) intended effect of sc-CO<sub>2</sub>.



### 3 Preliminary Experiments

#### 3.1 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. An advantage of this approach is that it is a general approach and results can be translated to almost all derivatisation reactions or cellulose derivatives.

#### 3.2 Experimental set-up

Four experiments were performed in which cellulose was subjected to supercritical carbon dioxide. The experiments and conditions are listed in Table 3.

Table 3 Experimental set-up

| Experiment | Temperature<br>[°C] | Pressure<br>[bar] | Time<br>[hours] | Remarks                               |
|------------|---------------------|-------------------|-----------------|---------------------------------------|
| No. 1      | 200                 | 200               | 24              | Time including heating and cooling    |
| No. 2      | 250                 | 250               | 24              | Time including heating and cooling    |
| No. 3      | 240                 | 250               | 0.8             | Sample added directly to hot reactor  |
| No. 4      | 240                 | 250               | 2.5             | 5% methanol added to reaction mixture |

A Buckeye V60 dissolving pulp was chosen as a pure source of cellulose. This dissolving pulp consists of 91%  $\alpha$ -cellulose and has a DP of ca. 832.

The supercritical carbon dioxide treatment was performed in a Parr 250 ml or 500 ml stainless steel vessel (Figure 6) which can be heated and stirred, and which can be operated at conditions up to 500 °C and 300 bar. CO<sub>2</sub> is added by a Thar Designs P-200 pump.



Figure 6 Equipment for supercritical CO<sub>2</sub> processing

### 3.2.1 *Initial experiments*

In the first two experiments, 10 grams of the cellulose powder were added to the 500 ml Parr vessel. Subsequently, the vessel was closed and, while stirring, heated to the desired temperature, and CO<sub>2</sub> was added to the desired pressure. In the first experiment the cellulose was subjected to 200 °C and 200 bar, for a period of 18 hours. In the second experiment both the temperature and the pressure were increased, to 250 °C and 250 bar respectively, again for 18 hours. After the indicated time the stirrer was stopped, and the CO<sub>2</sub> was released. The vessel was allowed to cool down, opened, and the cellulose was taken out. The total procedure including the heating and cooling of the vessel lasted circa 24 hours. It appeared that the colour of the celluloses had changed from off-white to brown in the first experiment and even to black in the second experiment.

### 3.2.2 *Experiment with short reaction time*

In an attempt to avoid or to minimise thermal degradation of the cellulose, the treatment time was reduced strongly. In order to do so, the empty 250 ml Parr vessel was closed and heated to 240 °C. After this, ca 1.5 grams of the cellulose powder were added by pouring it into a narrow opening in the lid, after which was subsequently closed. Then, CO<sub>2</sub> was pumped into the vessel to a pressure of 250 bar, and the contents were stirred. After 20 minutes, the stirrer was stopped and the CO<sub>2</sub> was released. The vessel was opened and the cellulose powder was poured out. The total time required from the start of the cellulose addition until the cellulose was taken out, was 50 minutes. The colour of the cellulose had changed from off-white to brown, but appeared to be somewhat lighter brown than in the first experiment.

### 3.2.3 *Experiment the 5% methanol as a co-solvent*

In order to swell or dissolve cellulose, the extensive hydrogen bonding in the crystalline regions must be released. The presence of a small fraction of methanol in the supercritical CO<sub>2</sub> may be helpful in doing this. For this reason an additional experiment was performed with supercritical CO<sub>2</sub> at 240 °C and 250 bar, and including 5 % (w/w) methanol as a co-solvent. The density of CO<sub>2</sub> under the indicated conditions is 283 kg m<sup>-3</sup>, which means that the 250 ml Parr vessel contains 71 grams of CO<sub>2</sub>, and that 3.7 grams of methanol need to be added. So, 3.7 grams of methanol and 5 grams of cellulose powder were added to a 250 ml Parr vessel. The vessel was closed and, while stirring, heated to 240 °C, and CO<sub>2</sub> was pumped to a pressure of 250 bar. The mixture was kept at 240 °C and 250 bar for 20 minutes. After that, the stirrer was stopped, and the CO<sub>2</sub> and methanol (vapour) were released. The vessel was opened and the cellulose was poured out. The total procedure including the heating of the vessel lasted circa 2.5 hours. The colour of the cellulose had changed from off-white to light brown.

### 3.3 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. Since initial experiments indicated that the crystallinity was not always related to the cellulose molar mass additional measurements were performed to determine the alpha-cellulose content. With this method it was attempted to separate the crystalline and amorphous fraction and investigate how the treatments had effected the crystalline and amorphous fractions of cellulose.

#### 3.3.1 *Determination of crystallinity using röntgendiffraction (XRD)*

##### 3.3.1.1 Apparatus

XRD measurements were performed using a Philips röntgendiffractometer PW1830.

In this diffractometer X-rays (Cu K- $\alpha$  radiation) from the anode are reflected by the sample ( $\theta/2\theta$  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  $1^\circ$ , receiving slit 0.2 mm, scatter slit  $1^\circ$ , monochromised using a  $15\mu\text{m}$  Ni-foil). The sample holder is usually held at ambient temperature.

##### 3.3.1.2 Method

For determination of the degree of crystallinity two scans are made from  $7^\circ$  to  $40^\circ 2\theta$ ; one scan of the sample to be analysed, one scan of a amorphous sample (for instance, a ball milled cellulose sample which is milled 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 (see example in Figure 7).



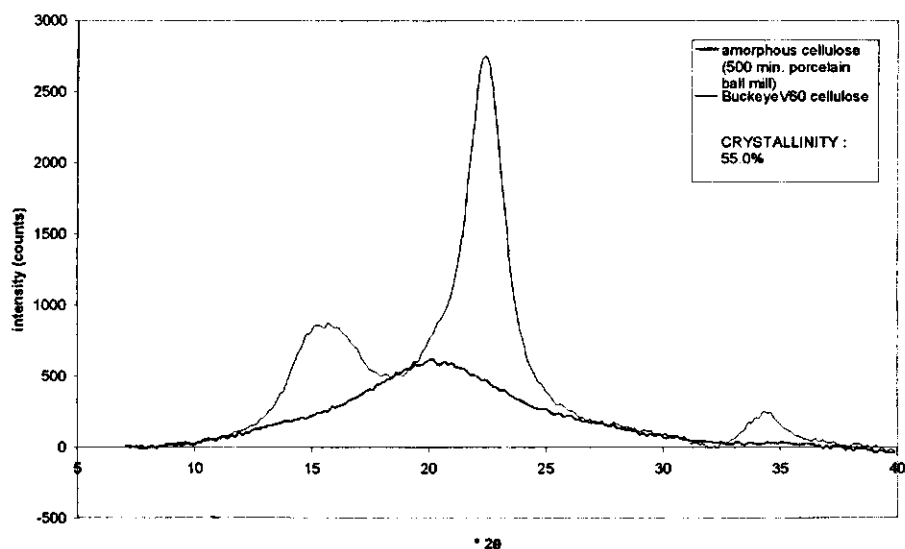


Figure 7 Example of a XRD measurements of dissolving cellulose

### 3.3.1.3 Results

The results of the röntgendiffractiion measurements are listed in 0.

Table 4 Results of determination of crystallinity of different cellulose samples

| Sample                        | Crystallinity (cellulose I type)<br>[%] |
|-------------------------------|---|
| Cellulose V60, not dried      | 55.0                                    |
| Cellulose V60, dried at 105°C | 50.3                                    |
| V60 after treatment No. 1     | 55.3                                    |
| V60 after treatment No. 2     | 1.5                                     |
| V60 after treatment No. 3     | 53.9                                    |
| V60 after treatment No.4      | 53.5                                    |

### 3.3.2 Molecular weight determination of cellulose

#### 3.3.2.1 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 Cu<sup>2+</sup> 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.

### 3.3.2.2 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)

### 3.3.2.3 Results

The results of the molar mass determinations are listed in Table 5.

Table 5 Decrease of molecular weight of dissolving cellulose (Buckeye V60) after treatments

| Sample                        | V rel | Conc.<br>[g/ml] | V intr.<br>[ml/g] | DP  |
|-------------------------------|-------|-----------------|-------------------|-----|
| Cellulose V60, dried at 105°C | 1.749 | 0.00189         | 333.5             | 749 |
| V60 after treatment No. 1     | 1.127 | 0.00196         | 62.5              | 149 |
| V60 after treatment No. 2     | 0.999 | 0.00198         | -0.4              | -1  |
| V60 after treatment No. 3     | 1.184 | 0.00185         | 94.7              | 225 |
| V60 after treatment No. 4     | 1.241 | 0.00198         | 114.5             | 273 |

### 3.3.3 *Alpha cellulose determination*

#### 3.3.3.1 Method

For isolation and determination of the crystalline part of the cellulose a derived method was used based on a TAPPI-method called alpha-, beta- and gamma-cellulose in pulp (T 203 om-93) and TAPPI-method T 235 cm-85 (Alkali solubility of pulp).

In general, the alpha-cellulose is not degraded, higher-molecular-weight cellulose in a pulp; the beta-cellulose is the degraded cellulose, and the gamma-cellulose consists mainly of hemicellulose<sup>51,52</sup>.

A 17.5% sodium hydroxide solution dissolves mainly hemicellulose, a 9.5% sodium hydroxide solution dissolves both hemicellulose and degraded cellulose.

All treated cellulose samples (and a untreated cellulose as reference) were treated with 9.5% or 17.5% solution of sodium hydroxide at 25°C during one hour. The slurry was filtered and washed until neutral pH was reached. After drying the residual material was weighted and crystallinity was determined by röntgendiffraction (XRD).

### 3.3.3.2 Procedure

The cellulose samples were dried under vacuum at 40°C.

In a 100ml conical flasks 1.0g to 1.5g samples were weighted accurately.

50ml of the desired (9.5% or 17.5%) sodium hydroxide solution was added and stirred at 25°C during one hour.

After filtration of the dispersion into a pre-weighted glass filter crucible (G4), 10ml of 50% acetic acid is added to the residues and soaked for 5 to 10 minutes. The residues are then extensively washed with water until pH neutral.

After drying overnight under vacuum at 40°C, the total weight is determined.

The crystallinity of the materials was determined with XRD.

### 3.3.3.3 Results

One sample of treated cellulose (No. 2, treated at 260°C for 24 hours) was excluded from further treatments/analyses because the material was too severely degraded. A summary of the results is listed in Table 6.

Table 6 Results Alpha-, beta and gamma-cellulose determination

| sample                        | Residue, 9.5% NaOH extraction | Residue, 17.5 NaOH extraction |
|-------------------------------|-------------------------------|-------------------------------|
| Cellulose V60, dried at 105°C | 99.4                          | 94.4                          |
| V60 after treatment No. 1     | 61.0                          | 58.4                          |
| V60 after treatment No. 3     | 58.7                          | 58.1                          |
| V60 after treatment No. 4     | 66.5 ?                        | 88.0 ?                        |

All residues were examined using XRD (Table 7).

Table 7 Crystallinity of cellulose samples after NaOH extractions (cellulose III)

| sample                        | Crystallinity residue,<br>9.5% NaOH extraction | Crystallinity residue,<br>17.5 NaOH extraction |
|-------------------------------|--|--|
| Cellulose V60, dried at 105°C | 45.6   | 43.9   |
| V60 after treatment No. 1     | 30.9   | 27.2   |
| V60 after treatment No. 3     | 35.6   | 34.2   |
| V60 after treatment No. 4     | 43.6   | 40.9   |

The treatment with NaOH caused all samples to converse into cellulose II, see Figure 8 for an example and comparison with Figure 7.

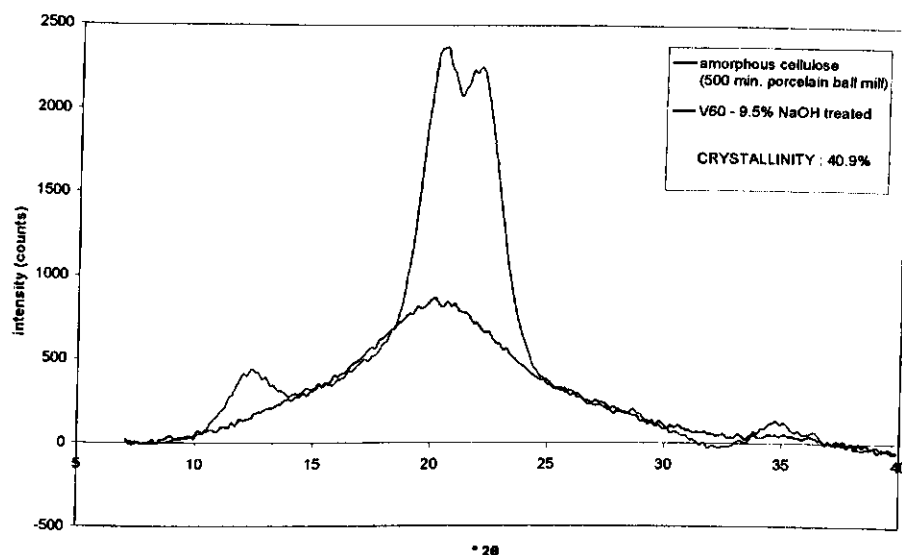


Figure 8 Example of an XRD measurement of a cellulose II sample.

### 3.4 Discussion

The approach of the experiments is to use supercritical carbon dioxide to lower the  $T_g$  below the glass transition temperature cellulose (see Figure 5, paragraph 2.3.3) in order to facilitate the production of cellulose derivatives and to minimise the use of organic solvents. Since the  $T_g$  of cellulose is high (around 300°C) and since the  $T_g$  can be lowered with about 50°C using  $scCO_2$ , treatments are performed at high temperatures (200-260°C). Using the current reactor, heating times and therefore treatment times are relatively long.

With the first two experiments at 200 and 260°C it was studied what would be the maximum treatment temperature avoiding extensive degradation. Combining the results of the röntgendiffractation measurements and viscosity measurements it was found that the treatment at 200°C did not affect the crystalline structure of cellulose (see Table 4), but still a severe drop in the molecular mass occurred (see Table 5). This severe thermal degradation was not expected at 200°C, but could be caused by the acidic character of  $scCO_2$ . After treatment at 260°C the cellulose was completely charred (see Table 5), and the only conclusion that can be drawn from this experiment is that the conditions of the  $scCO_2$  treatment were too harsh. Based on these initial results it was decided to commence experiments at 240°C and at considerably shorter reaction times. Furthermore, it was decided to study the effect of the addition of small amounts of methanol to  $scCO_2$  since methanol is capable of disrupting hydrogen bonding.

Again both treatments at 240°C (No.3 and No.4 in Table 4) did not affect the crystalline structure of cellulose. Reducing treatment times had a positive effect in minimising the cellulose degradation (Table 5), but still extensive degradation occurred.

To study how cellulose degradation occurred in the amorphous and crystalline regions of cellulose a third analyses technique was introduced. Using alkaline extraction alpha-, beta-, and gamma-cellulose content was studied (results are listed in Table 6). Alpha-cellulose is non-degraded, higher-molecular-weight cellulose in a pulp, beta-cellulose is the degraded cellulose and gamma-cellulose consists mainly of hemicellulose. From the measurements it is clear that the starting material is a high alpha-cellulose dissolving pulp with an alpha-cellulose content of 99% and about 5% degraded cellulose. This degradation usually occurs during the extensive purification treatments (see Figure 1). After all treatments the amount of alpha-cellulose has dropped to ca. 58% (samples No.1 and No.3, residue after extraction with 17,5% NaOH). This result can be expected comparing with the results of the viscosity measurements. Strangely the amount of degraded cellulose is low (sample No. 1 and No. 3, difference in residue after extraction with 9.5 and 17,5% NaOH respectively). This could indicate that the cellulose in this case had degraded to more soluble oligomers that in this method are subscribed to hemicelluloses. From the results obtained with sample No. 4 it is obvious that there has been some kind of error. The residue after a 17.5% NaOH extraction can never be lower than the residue after a 9.5% NaOH extraction. Still, they are mentioned in this report since from the results it is expected that in this case the alpha-cellulose content is higher than in sample No. 1 and No. 2. It cannot be indicated which of the two measurements (at 9.5 or at 17.5% NaOH) is incorrect.

The XRD measurements of the extracted samples (Table 7) give an extra check on the accuracy of the method. However, the degree of crystallinity cannot be compared to untreated samples (not NaOH extracted) since the crystalline structure had changed from cellulose I to cellulose II. The degree of crystallinity in cellulose II is always considerably lower than in cellulose I samples. Opposed to the previous crystallinity measurements, after NaOH treatment there is a clear difference in amount of crystallinity due to the  $\text{scCO}_2$  treatments. The starting material has the highest crystallinity, followed by treatment No. 4 and then No. 1 and No. 2. In this case the crystallinity seems to be dependent on the molar mass (viscosity measurements). Cellulose degradation clearly influences the recrystallisation to cellulose II after NaOH treatments.

### 3.5 Conclusions

Until now, no clear positive results have been obtained using supercritical carbon dioxide treatments. Severe degradation occurs after heating to 200°C to 260°C. After the  $\text{scCO}_2$  treatments the crystalline cellulose regions were still intact indicating that degradation has mainly occurred in the amorphous regions. The addition of methanol seems to minimise degradation to some extent. However, it does not affect the crystallinity. The addition of co-solvents should be studied in more detail.

## 4 Market study

### 4.1 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).<sup>53</sup> Sappi is the worlds largest producer of dissolving pulps, their market share is about 15% (600.000 tonnes, see also Figure 9).

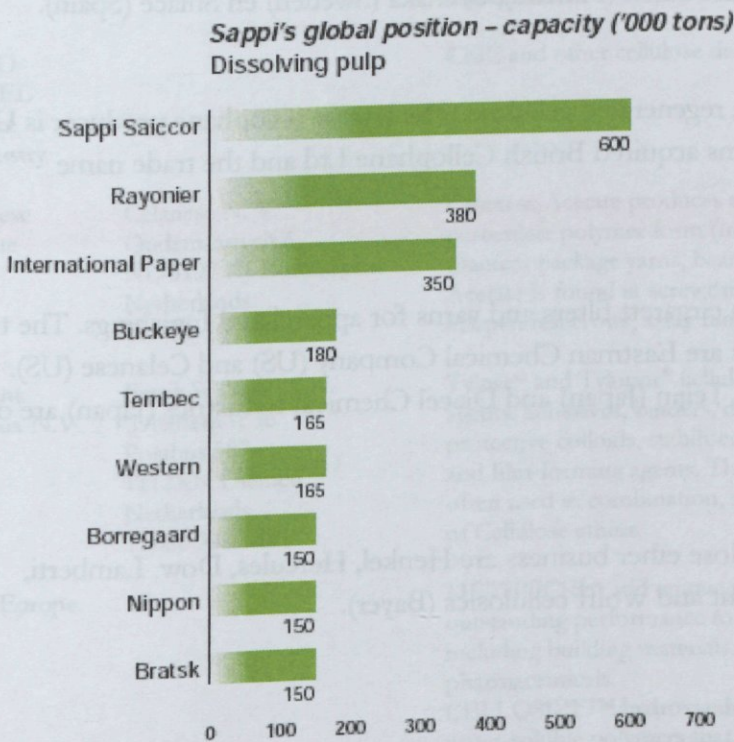


Figure 9 Overview of capacity of several producers of dissolving pulps.

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%)<sup>10</sup>.

## 4.2 Market overview for each product

### 4.2.1 *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 (world wide) of viscose are Accordis and Lenzing AG (an Austrian company). Three other European producers are Säteri (Finland), Svenska (Sweden) and Sniace (Spain).

### 4.2.2 *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.

### 4.2.3 *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.

### 4.2.4 *Cellulose ethers*

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

### 4.2.5 *Cellulose nitrate*

Next to cellulose ethers Wolff cellulosics also produces cellulose nitrates. Other producers are Asahi Kasei (Japan) and Hercules (USA).

### 4.3 Cellulose converting companies

In this paragraph the market study containing companies and their products and/or markets are listed. Furthermore, a short list containing the companies who seem to be the most suitable to contact regarding innovation.

| Company                                | Address etc.   | Their products and markets  |
|--|--|---|
| Acacris                                | Bunschoten Spakenburg<br>NL  | Merger from: Daminco, Orffa Health & Nutrition, Schouten USA, and SoyLife: well established in a variety of fields in the food and health industries.<br>developing, processing, and distributing additives and ingredients for human foods and animal feeds.   |
| AKZO-<br>NOBEL<br>Surface<br>Chemistry |  | CMC and other cellulose derivatives   |
| Celanese<br>Acetate                    | Celanese N. V.<br>Oudemaasweg 6<br>NL-3197 KJ Rotterdam<br>Netherlands<br>T: +31-104909-575      | Celanese Acetate produces acetate in many forms, including a particulate polymer form (most often called flake), continuous filament package yarns, beamed yarns and bands of tow.<br>Acetate is found in screwdriver handles, high-fashion fabrics, ink pen reservoirs, x-ray films and a host of other end uses.  |
| Clariant<br>Benelux N.V.               | Frank Walstra<br>Diemerhof 36<br>Postbus 587<br>1112XN Diemen<br>Netherlands<br>T: 020 3989 881  | Tylose® and Tylopur® cellulose ethers act as water retention agents, adhesives, binders, dispersing agents, thickeners, protective colloids, stabilisers, suspension agents, emulsifiers and film-forming agents. These versatile properties, which are often used in combination, account for the wide range of uses of Cellulose ethers.  |
| Dow Europe                             |  | METHOCEL* add unique physical properties and outstanding performance to a huge array of products, including building materials, food, personal care products, and pharmaceuticals.<br>CELLOSIZETM hydroxyethyl cellulose (HEC) products are water-soluble polymers that are widely used in latex paints, building materials, oilfield chemicals, cleaning and personal care products.<br>ETHOCEL* ethylcellulose resins are versatile, organosoluble, thermoplastic polymers. Ethylcellulose resins are widely used for coating, film forming, binding, and enhancing the performance of many different products ranging from industrial coatings to pharmaceuticals. |
| Eastman                                | see Voridian   |   |
| FMC<br>BioPolymer                      | Corporate Headquarters<br>1735 Market Street<br>Philadelphia, PA 19103<br>USA<br>+1 215-299-6000 | More than 35 years ago FMC BioPolymer introduced Avicel MCC to the food, pharmaceutical and specialty industries.   |
| Henkel                                 |  | cellulose ethers (member of CEFIC Cellulose ethers)   |



|   |  |   |
|---|--|---|
| Hercules                                      | Aqualon divisie –<br>Zwijndrecht (NL)<br>Pulp & Paper – Barneveld<br>(NL)<br>HERC – Barneveld (NL)   | cellulose ethers<br>Aqualon® sodium carboxymethylcellulose (CMC)<br>Blanose™ refined (CMC) cellulose gum (CMC)<br>Culminal® methylcellulose, methylhydroxyethylcellulose,<br>methylhydroxypropylcellulose<br>Galactasol® derivatized and unmodified guar-based<br>galactomannans<br>Natrosol® hydroxyethylcellulose, regular and biostable grades<br>Benecel® hydroxypropyl methylcellulose<br>Klucel® hydroxypropylcellulose<br>PolySurf® cetyl hydroxyethylcellulose<br>PrimaFlo® water-soluble polymer suspension, Hydroxypropyl<br>methylcellulose<br><u>AquaPAC® Regular</u> Premium polyanionic cellulose Fluid-loss<br>control<br><u>AquaPAC® LV</u> Premium polyanionic cellulose Fluid-loss control<br><u>AquaFLO™ HV</u> Polyanionic cellulose Fluid-loss control<br><u>AquaFLO™ LV</u> Polyanionic cellulose Fluid-loss control<br><u>AquaPAC® ULY</u> Polyanionic cellulose |
| Island<br>Pyrochemical<br>Industries<br>(IPI) | 267 East Jericho Turnpike<br>Mineola, New York 11501<br>T: 516-746-2100<br>F: 516-746-2405<br>E: office@islandgroup.com  | Cellulosic Polymer products, delivering high quality film in the<br>following categories.<br>Diacetate Film<br>Triacetate Film<br>Release Film<br>Polarizing Film<br>Animation Cels<br>Photographic Film Base<br>Ethyl Cellulose products are used as inhibiting materials for<br>rocket-propellant grains<br>Ethyl Cellulose Tape<br>End Inhibitor/End Sleeves<br>Ethyl Cellulose Molding Compound   |
| J. Rettenmaier<br>Benelux                     | Voorsterallee 114<br>7203 DR Zutphen (NL)<br>T: 0575 51 03 33<br>F: 0575 51 99 50<br><br>verkoop van Rettenmaier &<br>Söhne GmbH + Co.<br>Rosenberg (D)              | Global market leader in cellulose- and woodfibers.<br>Arbocel (cellulose fiber)<br>Lignocel (woodfiber)<br>Viatop (cellulose granulate)<br>Vivapur (micro crystalline cellulose)  |
| Lamberti (It)                                 | R&D<br>Via Piave, 18<br>21041 Albizzate, VA Italy<br>T: ++39 0331715111<br>F: ++39 0331775577<br>E: <a href="mailto:research@lamberti.com">research@lamberti.com</a> | Specialty chemicals for Textiles, Leather, Oil, Photocuring,<br>Coatings, Paper, Ceramics, Cosmetics, Detergents, Agro, Pvc. :<br>Carboxymethylcellulose<br>Guar derivatives<br>Photocuring Compounds<br>Polyurethanes<br>Acrylic Polymers<br>Dyestuffs<br>Pigments<br>Enzyme derivatives<br>Surfactants<br>Esters and Oleochemical derivatives   |

|                   |  |   |
|-------------------|--|---|
| Lonza             | Lonza Benelux BV<br>Aluminiumstraat 1<br>PO Box 3148<br>4800 DC Breda<br>the Netherlands<br>Tel: +31 76 542 51 00  | Cellulose Triacetate Films (Tacphan TM / FOTOPhan TM)<br>Description TACPHAN and FOTOPHAN are produced in a casting process using cellulose triacetate and plasticizers.  |
| Mare Austria (A)  | Registered Address, Office and Factory<br>Proleberstraße 14<br>A-8712 Niklasdorf<br>T: +43 3842 838740<br>F: +43 3842 8387420  | NIKLACELL<br>Pure and technical CMC with different chainlengths; also available with cationic groups built in.<br>MARECELL<br>Based on different grades of cellulose ethers such as Hydroxyethylcellulose (HEC), Methylcellulose (MC), Carboxymethylcellulose (CMC), these products are designed for special applications.  |
| Mikro-Technik (D) | Fa. Mikro-Technik GmbH & Co. KG<br>Plant and Administration: Industriestr. 4<br>D-63927 Bürgstadt<br>T: +49-9371 / 4005-92<br>F: + 49-9371-4005-70<br>E: info-de@mikro-technik.com | Cellulose powders for application sin Plastics industry, Welding electrode industry, Rubber industry and Filtration<br>Mikro-Technik CMC : Binding Agent, Film Forming Medium, Thickener, Protective Colloid, &Dispersing Agent<br>Pellan: cellulose derivative for feed pellet production (adhesive)   |
| Noviant           | Wisselingseweg 12<br>Postbus 31<br>NL-6500 AA Nijmegen<br>T: 024-371 99 00<br>F: 024-371 99 96   | CMC<br>Cekol Cellulose Gums for food cosmetics, personal care and pharmaceuticals<br>Finnfix CMC for industrial applications<br>Nymcel, special CMC grades for pharmaceuticals<br>CELPOL polyanionic cellulosic polymer for oil and gas drilling<br>CELFLO, Semipure polyanionic cellulosic polymer for oil and gas drilling<br>Cellcosan Special CMC grades for use as thickener in textile printing pastes<br>Cellufix<br>Cellflow Purified cellulose ether products for use in water-based emulsion paints<br>Reomaster Liquid pumpable CMC dispersion |
| PQ Europe         | PQ Nederland B.V.<br>Head Office<br>De Brand 24<br>3823 LJ Amersfoort<br>P.O. Box 664<br>3800 AR Amersfoort<br>The Netherlands<br>tel. +31 33 450 90 30                            | Cellulose ethers (CEFIC lid)<br><br>PQ Europe specialises in the manufacture of inorganic industrial products essentially derived from sand.  |

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|                       |  |  |
|-----------------------|--|--|
| Rhodia acetow         | <a href="http://www.rhodia-acetow.com">www.rhodia-acetow.com</a><br>Rhodia Acetow<br>Engesserstrasse 8<br>D-79108 Freiburg<br>T: (49)761-5113561<br>F: (49)761-5113554 | Rhodia Acetow is the third largest producer of cellulose acetate tow for cigarette filters and one of the top merchant suppliers for cellulose acetate flakes in the world. cellulose acetate flake from wood pulp of exceptional purity, for use in the textile industry as speciality fabrics (veils, linings, silk yarns).<br>The material is marketed under the trade name of Rhodia® Acetol.<br>We manufacture acetate tow and market it under the trade name of Rhodia® Filter Tow, the principal raw material for making cigarette filters.   |
| Sasol Servo BV        | Sasol Servo BV<br>Langestraat 167<br>7491 AE Delden<br>tel.: 074-3775000   | Sasol Servo BV develops, manufactures and sells specialty surfactants and chemicals for a wide range of applications. Oilfield Chemicals, Coating Additives and Pulp & Paper Chemicals   |
| UCB                   | UCB SA<br>Allée de la Recherche, 60<br>1070 Brussels (Belgium)<br>Tel. (322) 559 99 99<br>Fax. (322) 559 99 00   | UCB has integrated its Film Sector with its Chemical Sector to create : SURFACE SPECIALTIES<br><br>Regenerated cellulose films are marketed under the tradenames Cellophane and Rayophane. Areas of speciality include twist-wrapping for confectionery, controlled permeability <u>packaging</u> films for soft cheese and baked goods, adhesive <u>tapes</u> and <u>membranes</u> for industrial uses such as batteries.   |
| Voridian              | Division of Eastman Chemical Company<br>P.O. 2002<br>Kingsport, TN 37662<br>1-423-229-1000<br>1-888-VORIDIAN [1-888-867-4342]  | Voridian is an operating division of Eastman Chemical Company<br>Our Estron acetate yarn and Chromspun solution-dyed acetate yarns come in a variety of colors, lusters, and sizes to match your application.  |
| Wolff Cellulosics (D) |  | Wolff Cellulosics is the competence center for cellulose chemistry within Bayer Chemicals. We have 660 employees and achieve annual sales of EUR 230 million. Our cellulose derivatives are used as raw materials for printing inks and coatings and as additives for building materials.<br><br>High-purity derivatives are also used in food, cosmetics and pharmaceuticals. Wolff Cellulosics is continuously developing new products and new production technologies for derivatives made from the renewable resource cellulose.<br><br>Walocel® M<br>Walsroder® Nitrocellulose and Walsroder® NC-Chips: |

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The parties from this extensive listing that seem to be the most interesting for this research project (based on products and company profile) as potential development partners are AKZO-NOBEL, DOW, Hercules, Noviant, UCB and Wolff Cellulosics.

## **5 Market approach**

### **5.1 Introduction**

In this last chapter a summary of initial company interviews is listed and the results of an internal brainstorm on the use sc-CO<sub>2</sub> of in cellulose modification is summarised. A&F will continue with their market approach in 2005.

### **5.2 Company interviews**

A&F organised a meeting with Dr. Jürgen Engelhardt (Manager Products and Processes) and Dr. Hans-Jürgen Juhl (Manager Products and Applications) from Wolff Cellulosics GmbH. Wolff is part of Wolff Walsrode AG, which is a part of Bayer AG. Bayer's core business is innovation driven and technology intensive. Wolff co-operates with ca. 10 universities and research institutes in Germany. Wolff's R&D department is interested in new products (speciality applications) and raw materials other than wood and cotton. They are looking for polysaccharide derivatives with new functionalities that are not produced by other carbohydrate converting companies and also in more processes having more environmental benign.

Specific interest was shown in the possibilities of the development of new (carbohydrate-based) rheology modifiers or thickeners, food applications and tissue-making. They have already investigated the possibilities of using supercritical CO<sub>2</sub> but liked to gain more information about the possibilities from the current project. They are very interested in processes to produce amorphous cellulose. Near the end of February they will decide if they want to start co-operation on one or more subjects.

Furthermore, A&F spoke to Erik Pras (Product Manager) of Noviant (Nijmegen). Noviant produces CMC for several markets (both food and non-food) and is interested in expanding their product range to other cellulose ethers. The cellulose ethers Noviant produces are prepared via heterogeneous processes in which cellulose remains in the fibrous form. Products are washed using ethanol/water mixtures and washing liquids are effectively recycled within the process. Use of scCO<sub>2</sub> does result in clear advantages over the current heterogeneous process. Two topics might be interesting for Noviant:

- development of novel derivatives
- development of highly pure cellulose pulps with high molecular mass.

This last development in the production of novel cellulose pulps will not be core business of Noviant, but Noviant would support cellulose pulp producing companies in this development.

### **5.3 Possibilities for scCO<sub>2</sub> in cellulose modifications**

The main problem in the modification of cellulose is that it is not soluble in common solvents and that it degrades during modification. Until now, no proof is found that scCO<sub>2</sub> penetrates in the crystalline structure of cellulose, although it is likely that it enters the amorphous parts of cellulose.

Possible research and development topics are:

- $\text{scCO}_2$  as a medium for the modification of amorphous cellulose
- further study on the addition of additional components (alcohols, water) to  $\text{scCO}_2$ , to decrease the hydrophobicity of  $\text{scCO}_2$  and to increase the solubility of cellulose in  $\text{scCO}_2$
- enzymatic modification of cellulose in  $\text{scCO}_2$  for the production of novel derivatives
- surface modifications of cellulose fibres, and specific reaction with cellulose (only primary OH-groups)
- Surface acetylation of cellulose for application in (plastic) compounds
- Create hydrophobic surface of cellulose fibres by reacting with C18 alkanolic acids
- Modification of cellulose, or preparation of amorphous cellulose without lowering of the DP
- Oxidation reactions of cellulose using for example TEMPO in  $\text{scCO}_2$ , specific oxidation of C6-position
- Introduction of charge to cellulose fibres to prepare superabsorbing non-woven-fibres
- Using  $\text{scCO}_2$  in combination with salts as solvent for cellulose in order to reduce the amount of salts

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