

I.

Het verminderen of veranderen van lignine in bomen door genetische manipulatie, waaraan wordt gewerkt door Boerjan et al., is niet zonder risico's voor de bomen.

(Wout Boerjan et al. (1998). Genetic engineering of lignin biosynthesis in poplar and its impact on paper pulping. 8th Int. Cell Walls Meeting, session 6.04 Walls as raw materials)

II.

Het gemakkelijk te extraheren xytaan uit hennep houtpijp is een potentiële grondstof voor biologisch afbreekbaar plastic.

(Charles L. Smart and Roy L. Whistler (1949). Films from hemicellulose acetates, Science (110): 713)

III.

De wetenschap komt sneller vooruit als ook over "mislukte experimenten" gerapporteerd wordt en de verslagen hiervan openbaar worden gemaakt.

Het ontbreken van de door Dolk et al. aangekondigde publicaties over de mogelijkheden om met behulp van UV-absorptie van het effluent de hoeveelheid afgebroken lignine te schatten valt in dit verband te betreuren.

(Dolk, M. et al. (1983). Preliminary results of a study of the delignification of Western Hemlock using a "flow-through" reactor. ISWPC Proceedings, vol.2: 146)

IV.

Tal van wetenschappelijke artikelen, proefschriften en handboeken zijn gewijd aan molecuulstructuren van lignine, met mogelijke afbraakroutes en afbraakproducten. Het is opmerkelijk dat het verwijderen van lignine met natronloog met slechts twee overall reactievergelijkingen beschreven kan worden.

V.

Het verschil in de invloed van natronloog op het verwijderen van cellulose uit naaldhout of uit hennep houtpijp geeft aan dat het afbraakmechanisme van cellulose en het transport van de afbraakproducten nadere opheldering behoeven.

VI.

Het op papier uiteenzetten in een proefschrift van de mogelijkheden om van hennep houtpijp papier te maken is een stap, maar geen garantie, voor het opzetten van een fabriek voor het verwerken van hennep houtpijp tot papierpulp.

VII.

De technologische ontwikkelingen hebben alkalische hoge-opbrengstprocessen aantrekkelijk gemaakt voor de verwerking hennephoutpijp tot papierpulp.

VIII.

Het opdragen van een proefschrift aan één of meerdere personen ligt alleen voor de hand als het tot standkomen van het proefschrift de wens van deze personen was of zou zijn geweest.

IX.

Dit proefschrift is totstandgekomen binnen het Wageningen Universiteit en Research Centrum avant la lettre.

X.

Over twintig jaar is het kopen van incontinentie-materiaal met net zo weinig taboes omgeven als de aanschaf van tampons of maandverband in 1998.

XI.

Op technisch gebied is veel veranderd. Minder dan 60 jaar geleden werd kelderruimte van de Technische Hogeschool Delft ingericht om experimenten te kunnen doen bij constante temperatuur, te regelen met lampen (de experimenten bij 7,5 °C moesten worden beperkt tot de wintermaanden); tegenwoordig wordt voor dergelijke experimenten volstaan met de aanschaf van een waterbad.

(Darcy van der Want (1939). Cellulose - Natriumhydroxyde - Water. De opname van natriumhydroxyde en water door watten, bij loogconcentraties van 0-50%)

XII.

Het sociale gedrag van mensen in hun dagelijkse werk lijkt in 40 jaar tijd weinig te zijn veranderd.

(J.J. Voskuil (1996). Het Bureau Deel 1 - Meneer Beerta)

Stellingen bij het proefschrift:
ALKALINE HEMP WOODY CORE PULPING
impregnation characteristics, kinetic modelling and papermaking qualities

Birgitte de Groot,
Wageningen, 9 oktober 1998.

ALKALINE HEMP WOODY CORE PULPING
impregnation characteristics, kinetic modelling
and papermaking qualities

Promotor: dr ir K. van 't Riet
hoogleraar in de levensmiddelenproceskunde

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2005 201 09113

Birgitte de Groot

ALKALINE HEMP WOODY CORE PULPING
impregnation characteristics, kinetic modelling
and papermaking qualities

Proefschrift

ter verkrijging van de graad van doctor
op gezag van de rector magnificus
van de Landbouwwuniversiteit Wageningen,
dr C.M. Karssen,
in het openbaar te verdedigen
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VOORWOORD

Vele personen hebben ertoe bijgedragen dat dit proefschrift er gekomen is. Om te beginnen de boeren in de Veenkoloniën, verenigd in de Werkgroep Veenkoloniën, zonder hun inzet was papier uit vezelhennep niet veel meer dan een idee gebleven. Verder de medewerkers van Wetenschapswinkel van de Landbouwwuniversiteit Wageningen, de Werkgroep Hennepverwerking en het Transferpunt Landbouwwuniversiteit. De enthousiaste collega's binnen de sectie Proceskunde, met name Dick van Zuilichem en medewerkers Willem Stolp en Jacqueline Gaakeer zijn van onschatbare waarde. De volgende studenten hebben hun steen(tje) aan het onderzoek bijgedragen: Lia Blinde, Mari de Meijer, Richard Sikkema, Ingrid Kuppen en Ariëtte Matser. De vele collega's in het buitenland, met name Matti Dolk, Astrid Labidi, Rick Gustafson, Alberto Venica, Joseph McCarty, Kyösti Sarkanen, Josef Gratzl, Marvin Bagby en Jan Jansson wil ik bedanken voor de gesprekken en de rondleidingen door hun laboratoria. Dit heeft veel bijgedragen aan de opbouw en inrichting van de labs en het ontwerp en bouwen van de doorstroomreactor, waarna zeker de mensen van de werkplaats en tekenkamer van het Biotechnion niet vergeten mogen worden. Verder wil ik de collega's binnen de hennepgroep bedanken voor het enthousiasme en inzet, en de heren Klaas van 't Riet, Rick van der Zwan, Jan van Dam en Per Ahlgren voor de begeleiding. Ook de assistenten Hans van der Kolk, Richard Gosselink en Wouter Theunissen wil ik hier met name noemen. Van de mensen die met hun enthousiasme, ideeën en inzet de sfeer verhoogden wil ik met name Jan Egbert Harsveld van der Veen en Monique van den Berg bedanken voor de peptalks; Monique ook nog voor de verzorging tijdens vele weekenden. Verder heb ik steun gehad aan familie, vrienden en burens. Ale Smidts bedank ik daarbij nog voor het verzorgen van de tuin, tijdens de weekenden in het afgelopen jaar, toen dit proefschrift afgerond werd.

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1. GENERAL INTRODUCTION

1.1 INTRODUCTION

The aim of this thesis is to elucidate alkaline processing of hemp woody core. The acquired knowledge of the fibrous material, its behaviour in alkaline processes and its papermaking properties contribute to the judgement of the feasibility of alkaline pulping processes for fibre hemp.

In 1980 a group of farmers in the northeastern region in the Netherlands initiated the search for a profitable 'fourth crop', that would broaden the agricultural rotation scheme, to reduce pesticide and herbicide requirements. This led to renewed interest in cultivation of fibre hemp in the Netherlands. The non-food, easy growing crop, may provide the pulp and paper industry with domestic fibres. A range of preliminary trials on growing, harvesting, ensilage, fibre cleaning and separation, and pulp and paper processing were set up (De Groot *et al.* 1989). The promising results persuaded regional and national governments to support a larger research project. The Dutch hemp programme was started in 1990 at a number of agricultural research institutes (DLO) and at Wageningen Agricultural University (WAU). The studies accomplished in this thesis were part of this programme. The experiments described in this thesis were performed at the Food and Bioprocess Engineering Group (WAU) and at the Agrotechnological Research Institute (ATO-DLO) in Wageningen.

1.2 HEMP WOODY CORE FOR PAPER APPLICATIONS

Like other bast fibre crops, hemp has traditionally been regarded as a raw material for textile products. The outer parts of the hemp stem consist of long bast fibres: 5-50 mm, with an average fibre length of 16 mm. The bast fibres were used either for sailing and fishing equipment like canvas, yarns, ropes and twines, or for strong, thin, durable paper.

The inner parts, known as woody core or shives, consist of fibres with a length of 0.5-0.6 mm, and an average fibre length of 0.55 mm. Hemp woody core represents about 65% of the dry weight of the stem. This material is commonly discarded, or used as fuel. Nonetheless,

botanically as well as chemically, hemp woody core is comparable with hardwood, as is shown in tables 2.1 and 2.2 in Chapter 2. It should be noted that hemp, like flax and kenaf, is a dicotyledon. This implies that the silica content is low, contrary to monocotyledonous fibre crops like straw or other grasses. Therefore, hemp pulping processes will not require special effluent treatment due to high silica contents, to recycle process chemicals.

While hemp bast fibres have been used for paper since the invention of pulping processes for papermaking around 105 AD in China, hemp woody core fibres are still little used for this purpose. However, some work has been done, indicating that hemp woody core could be processed and used similarly as hardwood fibres. Literature on experiments in the USA (Dewey and Merrill 1916), in Germany (Wedekind *et al.* 1937; Wedekind 1938) and more recently in Italy (Bosia 1975; Bosia and Nisi 1978), and the results of our own prefeasibility studies (De Groot and Harsveld van der Veen 1988; De Groot *et al.* 1988) show that hemp woody core as raw material for papermaking is worth considering and that alkaline pulping is a potential pulping process for hemp woody core. It was preferred to study pulping of hemp woody core fibres separately from hemp bast fibres, to explore the potential of hemp woody fibres core in alkaline pulping maximally, as the fibre types differ significantly in properties and composition.

These were the starting points for the more fundamental research on kinetics of alkaline delignification of hemp woody core described in this thesis. In the following paragraphs of this chapter relevant trends in pulp and paper production for hemp woody core application and market opportunities for fibre hemp are discussed. Finally, the outline of this thesis is presented.

1.3 TRENDS IN PULP AND PAPER PRODUCTION

1.3.1 Alkaline delignification processes for annual fibre crops

Alkaline processes based on sodium hydroxide (NaOH) are commonly used wood and non-wood pulping.

The kraft process is the major wood and non-wood pulping process. It is used for about 90% of the world production of lignin-free pulp (Matussek *et al.* 1996). In this process fibres are separated and purified with a solution of sodium sulphide and sodium hydroxide, at a temperature of about 170 °C. The conventional kraft cooking process, combined with a chlorine-based bleaching system is malodorous and polluting. Environmental concerns of paper consumers and

governmental restriction have urged pulping mills to develop improved pulping technologies and less polluting bleaching systems (Ahlgren 1991; Anonymous 1997).

For monocotyledons the silica in the effluent complicates recausticizing, by which reaction chemicals are recovered. Silica is not a problem for hemp pulping, but could be a problem if also other annual fibre crops were to be processed in the same pulp mill.

Large scale pulp production using annual, non-wood fibre sources will introduce high costs for storage and transport. Adapted alkaline pulping processes have been described, mainly for straw or other monocotyledons, to enable smaller scale of production.

Sodium may be replaced by potassium, using the process effluent as fertilizer (avoiding high chemical recovery costs) for less polluting small-scale pulping (Wong 1994; Sameshima and Ohtani 1995). However, fertilizer producing processes are not of interest for most countries in western Europe, as there is no shortage of fertilizer.

Otherwise, processes using alkaline chemicals like borate and phosphate, that enable the use of autocausticizing recovery systems, have been developed to reduce costs of recovery equipment (Janson 1980; 1992; Janson *et al.* 1994). Such a process may prove worthwhile for hemp woody core pulping.

Another strategy to facilitate production on smaller scale is to omit the sulphide in the kraft process. In general, non-sulphur sodium hydroxide pulping can be operated with cheaper recovery, as furnace temperatures can be lower than needed to reduce sodium sulphate to sodium sulphide. Furthermore, smaller recovery units have been developed recently to provide modular recovery expansion for kraft mills (Lecsek 1994; Meadows 1996).

1.3.2 Fibre sources

Paper products, varying from massive board and sanitary paper to currency paper, are composed of a mixture of pulps and additives. The pulp recipe depends for instance on availability of raw material and end use of the product. About 11% of the world's virgin pulp is made out of non-wood fibres, with straw (46%), bagasse (14%) and bamboo (6%) as the most important sources. Most of this non-wood pulp (74%) is produced in China (Atchison 1996). The world hemp paper pulp production is estimated at 120.000 tons/year (FAO 1991), about 0.05% of the total paper production. Hemp pulps are generally blended with other pulps for paper production. There is at this moment no significant production of 100% true hemp paper.

The Chinese pulp mix consists of about 60% non-wood pulp, 25% recycled fibres and less than

15% wood pulp. In contrast to China, most European countries, the USA and Canada use little non-wood pulp. The total fibre mix for paper in Europe consists of about 56% wood pulp and 44% recycled fibres (Matussek *et al.* 1996). Most market pulps in Europe are produced in Sweden, Finland and Portugal. The net imported pulp to Europe, about 23% of the used market pulp, is mainly produced in Canada and the USA (Stefan 1995). The amount of market pulp in western Europe is expected to decline due to higher levels of integration of paper and pulp production. Traditionally, spruce and pine are used for chemical softwood pulp, to produce strong, thick paper. Chemical hardwood pulp is increasingly used since the last 25 years (Baker 1995). To reduce the costs for fibre stock, larger use is being made of relatively fast growing trees, like poplar and eucalyptus, and of different grades of recycled paper. The technology to process softwood fibres was adapted to pulp hardwood fibres adequately, screening and cleaning was introduced to purify recycled fibre stock. This 'upgrading', the use of cheaper and cheaper fibre stocks for production of higher and higher paper grades is enabled by technology development, which started in the past decades and is a continuing process.

1.3.3 Hardwood pulp

Traditionally used only as filler pulps, hardwood pulps have become important paper furnishes in recent years; fine papers may contain 70-90% hardwood (Baker 1995). In order to exploit hardwoods to their maximum potential, refining processes must be gentle and cutting should be avoided by using adapted refiner plate profiles and medium consistency refining. Mechanical processes used for fibre separation and fibrillation also shorten the fibres. This is a minor problem for softwood fibres of about 3 mm length, but may be damaging for hardwood fibres of 1 mm and less. This is the reason why thermo-mechanical processes are not used for hardwood fibres.

Hardwood pulps can produce a well formed strong sheet, to a point where softwood and hardwood pulps give nearly identical properties (Baker 1995).

Bleached softwood kraft pulp is still the dominant market grade worldwide (17 million tons were produced in 1994), but the importance of bleached hardwood kraft is increasing. In 1994, 12.9 million tons were produced, a rise with 13% compared to 1993 (Stefan 1995). Printing and writing grade papers in the Netherlands consist of about equal amounts of hardwood and softwood fibres. Prices of bleached softwood grades are just about 10% higher than prices of bleached hardwood grades.

1.3.4 High yield hardwood pulping

Currently, alkaline chemi-thermomechanical pulping (CTMP) processes developed for high yield hardwood (HYH) pulping are successfully in operation in Canada (Ford and Sharman 1996; Meadows 1996). The hardwood pulps produced with the alkaline peroxide mechanical pulping (APMP) process are used as ingredient in European paper grades.

High yield processes maximize the use of fibre resources, use only oxygen-based chemistry for bleaching and can be designed for low water use, or with a zero liquid effluent installation. The simple process technology allows the economical construction of relatively small plants of 50-200,000 tons/year. It has been suggested that HYH mills in Europe could be installed in areas where appropriate fibre supply is available, such as in Spain and Portugal (using eucalypt) and in Scandinavia, Russia and the Baltic States (using birch). Hemp woody core might be processed similarly.

1.4 MARKET OPPORTUNITIES FOR FIBRE HEMP

Table 1.1
Paper market potential for hemp pulp (data: Van Kemenade *et al.* 1993)

fibre	% (w/w) of fibrous matter	potential Dutch market in air dry tons/year	comparable pulp/cellulose	purpose
bast fibres	35	3,000	cotton linters cellulose abaca cellulose	thin, strong and durable specialty papers
		60,000	softwood CTMP ¹ softwood cellulose	strength in testliner, LWC ² , sanitary
woody core	65	130,000	hardwood CTMP (aspen)	smoothness, printability in board and coated grades
		560,000	hardwood cellulose (birch, eucalypt, mixed hardwoods)	smoothness, printability in printing and writing grades

1 CTMP: chemi-thermomechanical pulping

2 LWC: light weight coated paper grades

Table 1.1 summarizes the potential markets for hemp bast and hemp woody core fibres. The bast

fibres are very valuable, but the specialty paper market for e.g. banknotes, tea-bags, cigarette paper is relatively small. Large scale fibre hemp cultivation can therefore only be viable if the produced pulp can compete on the wood pulp market for bulk applications like linerboard, tissue, hygienic, printing and writing paper grades.

Also, other market outlets are being explored for hemp bast fibres, such as geotextiles and other nonwovens, and fibre reinforced composite and building materials. These fibres can be used as an environmentally friendly alternative for glass fibres for reinforcement of plastic components in cars. It is claimed that hemp bast fibres are more economic than flax fibres, and matching or surpassing flax fibres in terms of performance potential (Anonymous 1996).

The market outlet for paper purposes for hardwood type fibres is large and growing, hemp woody core pulp might be developed to fit in this market.

1.5 OUTLINE OF THIS THESIS

Considering that hemp woody core is botanically and chemically comparable to hardwood, it may be possible to process this material for similar pulp qualities as hardwood. As the hardwood pulp market is important and growing, it is worthwhile to investigate the characteristics of hemp woody core pulping. Sodium hydroxide (NaOH) is used, as this is the most important ingredient in modern pulping systems, and strategies are being worked out to enable alkaline pulping on relatively small scale. In this thesis impregnation characteristics, kinetic modelling and paper-making qualities of hemp woody core, using NaOH are discussed and related to literature data and data of commercially available pulps.

In chapter 2 the impregnation characteristics of hemp woody core are examined. The effects of temperature elevation to 70 °C and peroxide addition are analyzed. These conditions are used in alkaline peroxide mechanical pulping (APMP). Pulp yield and chemical composition are studied in relation to NaOH concentration. Also, apparent pore size distribution, as monitored with ¹H NMR spin-spin relaxation, is introduced and discussed.

Chapter 3 is a study of the delignification of hemp woody core with 1M NaOH. A model is derived, which is validated with literature data for softwood and hardwood delignification. In chapter 4 the developed model is extended for various NaOH concentrations. Similarly, the kinetics of xylan degradation and extraction, and the kinetics of cellulose degradation are modelled, concluding with the kinetics of pulp yield.

In chapter 5 paper strength and surface properties of test sheets, produced from alkaline woody core pulps, and the effects of beating, pulp yield and pulp composition are discussed. Furthermore, the polymerization degree is related to strength properties of paper and modelled as function of pulping conditions and time. Also literature data on cellulose degradation and depolymerisation are modelled and discussed.

In chapter 6 the consequences of this research for future research projects are discussed, followed by recommendations for realisation of alkaline processing of fibre hemp and other domestically produced fibre sources.

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2. ALKALINE SWELLING OF HEMP WOODY CORE CHIPS

SUMMARY

Swelling of hemp woody core chips after alkaline (peroxide) impregnation at 70 °C, as is practised in alkaline peroxide mechanical pulping (APMP) processes, is examined in relation to pulp yield and chemical composition of the chips. In contrast to wood chips, maximum swelling is attained at elevated temperature (70 °C) without chemical treatment, possibly as the result of relatively high porosity of hemp woody core cell walls. Alkaline swelling at 70 °C correlates with the xylan:lignin ratio. Swelling at ambient temperature shows some correlation with acidic group content. Apparent pore size distributions were examined, using ¹H NMR spin-spin relaxation. Several apparent pore size distributions can be distinguished within each sample. Elevated temperature, NaOH and peroxide addition influence the apparent pore size distribution and the total pore volume in different ways. Addition of peroxide results in a remarkable increase of the apparent pore sizes. This emphasizes its importance, apart from bleaching, in APMP pulping, enhancing fiber flexibility and fibrillation.

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2.1 INTRODUCTION

Hemp woody core may be a suitable raw material for the production of pulp of opacity and printability comparable with hardwood pulps (De Groot *et al.* 1994). The stem of fiber hemp (*Cannabis sativa vulgaris*, an annual dicotyledon with a height of 2-4 meters) consists of long bast fibers and a woody core. Both the papermaking potentials for bast fibers (industrially processed in France as raw material for specialty papers), as well as for woody core have been investigated on request of Dutch farmers searching for alternative crops. Alkaline peroxide mechanical pulping (APMP) can be used for production of pulp from hemp woody core, analogous to hardwood pulping (Cort and Bohn 1991).

APMP is a sulfite-free alternative for conventional chemi-thermomechanical pulping (CTMP). Basically, wood chips are impregnated at 70 °C with alkaline peroxide. The advantages over CTMP processes are: improved impregnation, allowing a less critical chip size, and resulting in a lower shive content (bundles of unseparated fibers), a higher amount of longer and flexible fibers, fewer fines (fiber fragments) and a lower energy consumption. Moreover, sulfur free effluent treatment is less complicated (Bohn and Sferrazza 1989; Black 1990; Cort and Bohn 1991).

Chemical methods for upgrading strength of mechanical pulp raise the acidic group content and result in increased swelling. Impregnation of wood with aqueous sodium hydroxide solutions enhances hydration and simultaneously extracts cell wall components. Fiber walls swell when more water is absorbed than material is extracted. Both accessibility of fiber walls to aqueous reagents and ability of fibers to conform and bond during papermaking are increased Sjöström *et al.* 1965; Stone and Scallan 1967; Katz *et al.* 1981; Scallan 1983).

Wood pulp has properties of a gel, containing ionizable carboxylic acid groups (such as glucuronic acid groups, linked to the xylan backbone, Timell 1967). In water, wood contains a higher ionic concentration (counter-ions of bound ionic groups) than the surrounding bulk water. The wood gel swells as a result of the entry of water until the osmotic pressure differential is balanced by the cohesive forces of the macromolecular network. Swelling is observed when the pH is raised, because of conversion of weak acidic groups (dissociated to a small degree) to the dissociated sodium salt form (Grignon and Scallan 1980; Scallan 1983). A plateau is found from pH 5 to 11, when carboxylate groups are fully converted to Na⁺ salts. Beyond pH 11 swelling is reduced, as the ionic strength of the bulk solution diminishes the osmotic pressure differential. Similarly, swelling is reduced by the presence of salt (Grignon and Scallan 1980; Scallan 1983).

Carboxylate formation is promoted by pH and temperature elevation (saponification of carboxylic esters and alkaline degradation, Sjöström *et al.* 1965; Katz *et al.* 1981; Beatson *et al.* 1985). Alkaline peroxide initiates oxidation of lignin and formation of more carboxyl groups (Backman and Gellerstedt 1993). Oxidation of reducing-end groups and diols in carbohydrates may also result in carboxyl group formation (Gratzl 1987; Isbell and Frush 1987). Furthermore, peroxide bleached pulps display a high ionic charge in relation to acidic group content, indicating that phenolic groups in lignin become ionized (Lloyd and Horne 1993).

Swelling of wood chips is enhanced by extraction. Cohesive forces in the wood gel originate from the strength of the lignocellulose matrix (Scallan 1974). During growth, the cell wall is expanded by the introduction of more rigid lignin, displacing the flexible carbohydrate matrix and causing the formation of built-in stresses. Removal of material releases the stress and results in more porous cell walls and leads to both higher swelling rate and higher maximum swelling (Stone and Scallan 1967; Stone and Scallan 1968; Mantanis *et al.* 1994) Increased swelling with lignin and carbohydrate removal was found for high yield sulfite pulps (Willis *et al.* 1986).

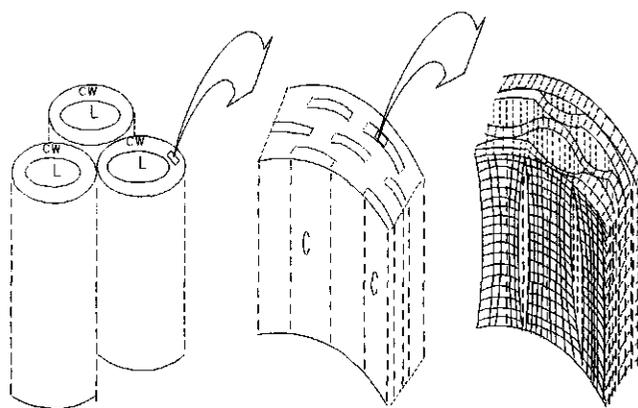


Figure 2.1.A (left) Model of wood fibers (CW: cell wall, L: lumen), with **Figure 2.1.B** (middle) fiber wall material (C: cellulose fibrils surrounded by a lignin-hemicellulose matrix, after Kerr and Goring 1975) and **Figure 2.1.C** (right) insight within cellulose fibrils (the honeycomb model for cell wall swelling by Scallan (1974) is used to visualize swelling in more detail).

Figure 2.1 illustrates that wood cell walls (figure 2.1.A) are built up of clusters of cellulose fibrils, surrounded by lignin-hemicellulose matrix (figure 2.1.B, after Kerr and Goring 1975). Scallan's honeycomb model for cell wall swelling (Scallan 1974) can also be used to visualize in more detail swelling of cellulose (figure 2.1.C). Voids between the cellulose fibrils and within the hemicellulose-lignin matrix are accessible to water-soluble (spherical) molecules (Stone and Scallan 1968), with a smallest diameter varying from 0.8 nm (glucose) to 14 nm (dextran 100), confining the minimum distances of accessible pores (at the fiber surface).

Heating lignin-containing pulps at 70 °C and higher also enhances swelling. At this temperature wet lignin is softened, allowing hemicellulose expansion (Salmén 1984; 1990; Eriksson *et al.* 1991). Hemicellulose contributes most to fiber swelling, but heating has no large impact on swelling of hemicellulose as wet hemicellulose is already softened at room temperature (Cousins 1978; Back and Salmén 1982).

In this article the effects of APMP impregnation conditions on pulp yield, chemical composition and swelling of hemp woody core chips are examined. Special attention is given to NaOH concentration, which has a large effect on hemicellulose content (De Groot *et al.* 1995) and its influence on swelling. The effects of NaOH concentration at room temperature and 70 °C, and at 70 °C with peroxide addition are evaluated.

2.2 MATERIAL AND METHODS

Presteamed hemp woody core chips, as used for APMP trials at our institute (2 g, length: 12.1 mm, width: 3.8 mm, thickness: 1.3 mm, all averages), were impregnated (after removal of air from the chips through evacuation) for 90 min with an excess of reaction liquor, using 200 ml demineralized water or NaOH (analytical grade) solution (of 0.05, 0.1, 0.25, 0.5, 1 or 2M). The experiments were carried out at ambient temperature or at 70 °C. Also a series with peroxide addition was carried out at 70 °C. The used peroxide recipe, time and temperature are based on preliminary trials and literature data (Bohn and Sferrazza 1989; Andrews and Singh 1979). Hemp chips were impregnated with 100 ml demineralized water. Sodium silicate (technical grade, 3 ml 36%), diethylenetriaminepenta-acetate (DTPA, 1 ml 40 g/l Dissolvine D40 technical grade), and magnesium sulfate (analytical grade, 1 ml 10 g/l) were added to a NaOH solution, with hydrogen peroxide (technical grade, 3 ml 30.4%) as the last ingredient. The amount of NaOH was adjusted, as silicate increased the alkalinity with 0.02 M. The total volume in which the chemicals were

dissolved was 100 ml, which was added immediately to the 100 ml demineralized water in which the chips were impregnated and put in temperature bath at 70 °C for 90 min. The hydroxide concentrations were 0.02, 0.05, 0.1, 0.25, 0.5, 1 and 2M. DTPA is added as chelating agent, to remove trace metals that may react with peroxide ions, minimizing catalytic decomposition of hydrogen peroxide. Sodium silicate is added to buffer and stabilize the hydrogen peroxide to minimize decomposition. Magnesium sulfate is added to form a colloidal suspension of magnesium silicate, adsorbing trace metal catalysts (Andrews and Singh 1979).

All data were compared with the results on a reference sample obtained by impregnation with 200 ml demineralized water for 90 min at ambient temperature (yield = 100).

The resulting chips were washed 3 times with 500 ml hot demineralized water and 3 times with cold 500 ml demineralized water, after which the chips were stored overnight in 500 ml demineralized water at 6 °C. Duplicate samples were used to determine: 1. dry matter content (Tappi Standard Method T264), 2. Klason lignin (Tappi Standard Method T222), soluble lignin (Tappi Useful Method UM 250) and carbohydrate composition (De Groot *et al.* 1995), 3. acidic group content (Katz *et al.* 1984; Scallan *et al.* 1989), 4. uronic acid content (for samples treated at 70 °C, El Rayah Ahmed and Labavitch 1977), 5. fiber saturation point (fsp, Aggebrandt and Samuelson 1964; Stone and Scallan 1968; Scallan 1978), and 6. water retention value (wrv, Hopner *et al.* 1955; Tappi Useful Method UM 256).

The acidic group content of the chips was measured using conductometric titration (Katz *et al.* 1984; Scallan *et al.* 1989). The chips were extensively washed in demineralized water, disintegrated in 100 ml demi water for 25 seconds (in a blender, total volume 200 ml) and were further examined in a never-dried condition. The fiberized material was converted to hydrogen form (soaked twice in 0.1 M hydrochloric acid for 45 min and washed with demineralized water), drained and dispersed in 450 ml 0.001M NaCl (in demineralized water). 2 ml 0.1M hydrochloric acid was added, after which the fiberized material was titrated under nitrogen atmosphere with 0.1M NaOH, dispensed from a micro-burette. Every 5 min 0.5 ml was added, which allowed sufficient time to reach equilibrium.

Fsp of the chips was determined with the solute exclusion technique, using dextran 2000 (blue dextran, as used in calibration of gel filtration columns) with an average diameter of 56 nm, concentrations of dextran 2000 solutions were determined with UV-VIS measurements at 616 nm (the wavelength at which maximum absorption was found at our laboratory, close to the value of 620 nm used by others (Zviedrans and Graham 1981; Ohta *et al.* 1985).

Wrv of the chips was determined after centrifuging with a centrifugal force of 900g, for 30 min

(Hopner *et al.* 1955; Tappi Useful Method UM 256).

For swelling calculations, fsp values were used. Fsp is based on one gram of dry material, which will contain an increasing number of fibers as the yield is lowered. To judge whether swelling (increase in cell wall) occurs, the amount of solid material plus water in a fixed number of fibers must be compared (Stone and Scallan 1967). For simplicity, this was measured gravimetrically instead of volumetrically (as the material density is not measured, and probably changing with material extraction). Swelling is calculated as $(fsp+1)*yield$, the total amount of water added to the amount of fibers after extraction, calculated on 1g starting material.

Pore size distribution in the chips was measured qualitatively, using 1H NMR spin-spin (T_2) relaxation measurements. The basic idea is that the molecules of water in the vicinity of a solid surface are perturbed because of the interaction with the solid surface (Li *et al.* 1993). The measurements were performed on a Bruker AMX 400 wb spectrometer, at a frequency of 400 MHz. A Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used with a 90° pulse of $64 \mu s$ and 180° pulses of $128 \mu s$ at intervals of $200 \mu s$. Only the maximal points of 8192 echoes per sequence were acquired resulting in a multi-exponential decay curve. To improve signal to noise ratio 8 accumulations were recorded. All experiments were performed at room temperature ($21^\circ C$). A continuous analysis method was used to calculate values of T_2 , with a computer program performing a non-linear least-square fit (Provencher, S.W. 1982).

2.3 RESULTS AND DISCUSSION

2.3.1 Pulp yield, xylan and lignin fractions

The effects of impregnation on pulp yield, xylan and lignin removal are shown respectively in figures 2.2-2.4. At ambient temperature, more cell wall material is removed with higher NaOH concentrations (figure 2.2), however beyond 1M the rate of extraction was diminished. At $70^\circ C$, increased amounts of material are extracted. At $70^\circ C$ and using the peroxide recipe, even more material from hemp woody core is removed. Apparently, both temperature elevation and peroxide addition promotes extractability.

The residual xylan fraction (amount on pulp multiplied with yield and divided by original xylan content) curves in figure 2.3 resemble the yield curves. Xylan extraction is almost complete at $70^\circ C$, with 2M NaOH and peroxide addition. Nelson and Schuerch (1956; 1957) found similarly for

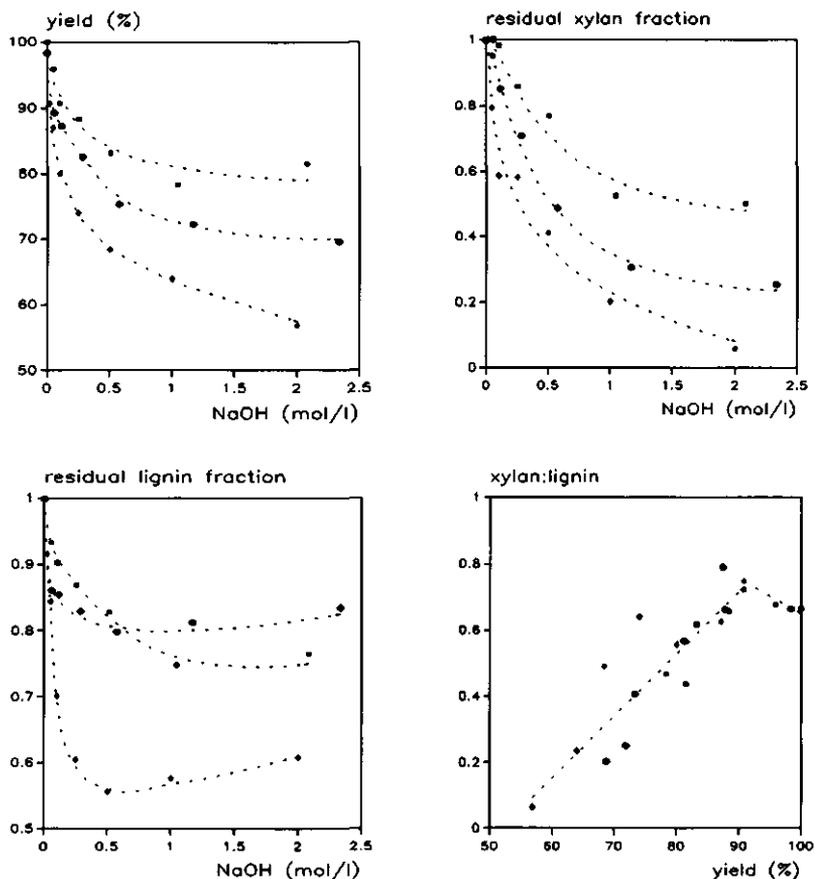


Figure 2.2 (upper left) Yield for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, at 20 °C (■), 70 °C (•), 70 °C with peroxide addition (◊). **Figure 2.3** (upper right) Xylan fraction for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2.2. **Figure 2.4** (lower left) Lignin fraction for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2.2. **Figure 2.5** (lower right) Xylan:lignin ratio for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2.2.

Table 2.1
Pulp Yield, Xylan and Uronic acid content, and their ratio for chips treated at 70 °C with and without peroxide

	alkalinity as [NaOH] (mol/l)	yield (%)	xyl. ¹ on pulp (%)	uronic acid ² on pulp (%)	uronic acid: xyl. ratio
treatment at 70 °C	0	98.3	17.6	8.41	0.48
	0.059	89.3	19.9	7.07	0.36
	0.12	87.3	16.9	5.78	0.34
	0.29	82.6	14.9	5.73	0.39
	0.57	75.4	11.2	4.51	0.40
	1.2	72.3	7.35	2.69	0.37
	2.3	69.6	6.33	2.49	0.39
treatment at 70 °C with H ₂ O ₂ addition ³	0.020	90.8	19.7	4.77	0.24
	0.052	87.1	15.8	4.46	0.28
	0.10	80.0	12.7	4.31	0.34
	0.26	74.0	13.7	3.66	0.27
	0.51	68.4	10.4	3.18	0.31
	1.0	64.0	5.51	2.09	0.38
	2.1	56.9	1.79	1.50	0.84

1. xylose units on pulp calculated as polymer constituents (xylan)
2. uronic acid residues on pulp calculated as glucuronyl polymer constituents (e.g. glucuronic acid side groups of xylan)
3. including silicate (added for H₂O₂ stabilization, increasing alkalinity with 0.02 M)

milled hardwood that higher amounts of hemicellulose could be extracted at higher temperatures. For samples extracted at 70 °C, uronic acid content was measured. Initially, hemp woody core contains a high amount of uronic acid (8.4% uronic acid on 17.6% xylan, table 2.1), compared with 2.2 to 6.3% for extractive-free hardwood species (Fengel and Wegener 1984). This may be due to residual pectic acids (extractives), that are removed with NaOH (De Groot *et al.* 1995). The uronic acid content in the samples treated with NaOH is lower and proportional to the xylan content, with a ratio of 0.37 ± 0.02 . Peroxide treatment, up to an alkalinity of 1M, gave a ratio of 0.30 ± 0.04 . It is probable that this somewhat lower ratio is the result of preferred solution of fractions with higher uronic acid contents, this explanation was also proposed for similar results with alkaline pulping (Sjöström 1993). The ratio at 2M NaOH is much higher, but both xylan and uronic acid contents are low, respectively 1.5% and 1.8%.

The lignin fraction curves in figure 2.4 show a pattern deviating from yield and xylan fraction curves. For samples treated without peroxide a relatively high residual lignin fraction, more than

75%, remains in the chips. The effect of temperature elevation alone on lignin removal is small. Lower lignin contents were obtained after similar treatment with peroxide addition, resulting in a high xylan:lignin ratio for some samples (figure 2.5).

Less lignin is extracted at alkalinities of 1 and 2M, than with 0.5M NaOH at 70 °C, both with and without peroxide addition. Also, at these higher alkalinities, less lignin is extracted at 70 °C than at 20 °C. Possibly, physical factors inhibit lignin extraction at higher NaOH concentrations. The softened, rearranged lignin droplets may be enclosed in the swollen cell wall, while the more linear xylan fragments successfully find their way through the narrowed pores.

2.3.2 Acidic group content

Acidic group content was measured, as these groups are involved in hydration and swelling (Scallan 1983), the results are shown in figure 2.6.

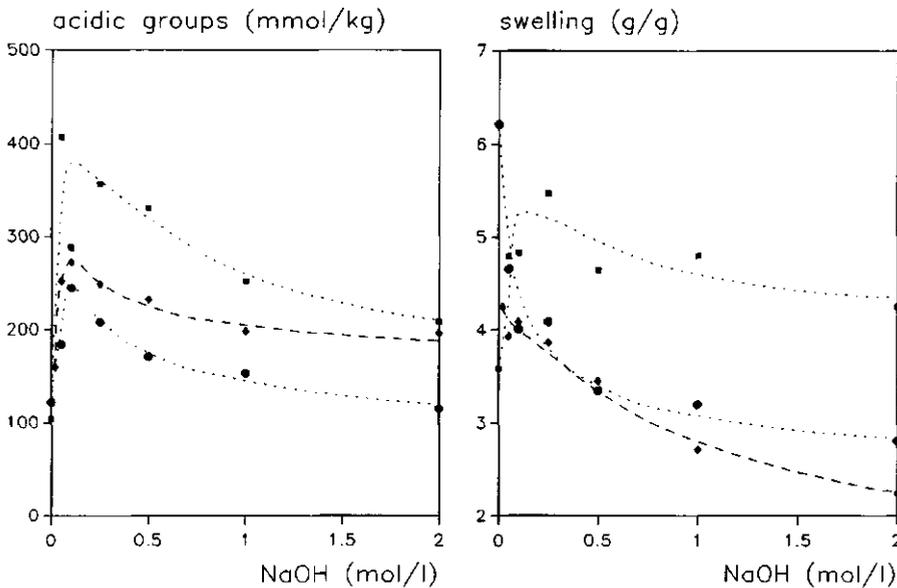


Figure 2.6 (left) Acidic group content measured in hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations at 20 °C (■), 70 °C (●), and 70 °C with peroxide addition (◆). **Figure 2.7** (right) Swelling measured in hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2.6.

For chips treated at ambient temperature with demineralized water only, an acidic group content of 100 mmol/kg dry pulp is found. Treating chips at ambient temperature with 0.05M NaOH raised the measured acidic group content towards 400 mmol/kg. The increase is expected, since carboxylic esters are saponified and carboxylic groups are ionized and converted to Na⁺ salts (Sjöström *et al.* 1965; Grignon and Scallan 1980; Katz *et al.* 1981; Scallan 1983). The measured acidic group content is relatively high, compared to 170 mmol/kg reported for mechanical aspen and black spruce pulp (after treatment with 0.05M NaOH at ambient temperature, Katz *et al.* 1981).

Chips treated at 70 °C with 0.05M and 0.1M NaOH (with or without peroxide addition) also show a rise of acidic group content. Lower amounts of acidic groups are found using 0.25M NaOH and higher and the samples contain less acidic groups than the chips treated at ambient temperature. This is probably the result of the extraction of (glucurono)xylan (containing most of the carboxylic groups). The values for hemp woody core at lower yields are in the range of 201 mmol/kg, reported for high yield (66%) kraft pulp (Katz *et al.* 1984). Compared to the use of NaOH only, more acidic groups are found when hydrogen peroxide is used, which was expected as the result of oxidation reactions in lignin and reducing end groups and diols in carbohydrates, with formation of more carboxyl groups (Gratzl 1987; Isbell and Frush 1987, Backman and Gellerstedt 1993) and ionization of free phenolic groups in lignin (Lloyd and Horne 1993).

2.3.3 Fiber swelling

After impregnation, material is removed from the hemp woody core chips and is replaced by water. Swelling occurs when the amount of water that is taken up by the fibers exceeds the amount of extracted material. The amount of water present within the fibers (w/w) has been measured with the fiber saturation point (fsp) method, which is based on the solute exclusion technique (measuring the amount of water within the fibers that is inaccessible to large dextran macromolecules, Aggebrandt and Samuelson 1964; Stone and Scallan 1968; Scallan 1978).

The results are shown in figure 2.7. Using demineralized water, raising the temperature to 70 °C almost doubles fiber swelling, presumably as the result of lignin softening (Salmén 1984, 1990; Eriksson *et al.* 1991). Using NaOH at ambient temperature, swelling increases with concentrations up to 0.25M. Higher NaOH concentrations promote shrinkage, accompanied by material removal. At 70 °C increasing NaOH concentrations results in decreased swelling, with lower values than at ambient temperature for equal NaOH concentrations. Thus, temperature rise com-

bined with alkaline extraction does not improve swelling of hemp woody core, in contrast with swelling of softwood or hardwood after material removal (Willis *et al.* 1986; Mantanis *et al.* 1994).

Light aspenwood absorbed twice as much sulfite cooking liquor (at about 70 °C) as birchwood, which was attributed to its lower density (300 kg/m³), compared to birch (500 kg/m³, Rydholm 1985). The density of hemp woody core, 200 kg/m³, is even lower. Thus, the described phenomena can be attributed to the originally spacious structure of hemp woody core fibers, allowing maximum absorption with demineralized water at 70 °C. Consequently, higher NaOH concentrations mainly promote extraction, accompanied by pore fusion, resulting in shrinkage.

Swelling was compared with yield, lignin or xylan contents, xylan:lignin ratio and acidic group contents. For samples treated at 70 °C under alkaline conditions, best correlation was found with xylan:lignin ratio ($r^2=93\%$), as is illustrated in figure 2.8, omitting the value found for swelling in demineralized water. This higher water absorbency of hemp woody core chips at 70 °C may be explained by the presence of hydrated pectic substances, that are dissolved with NaOH (De Groot *et al.* 1995). The samples treated at ambient temperature show little correlation with xylan:lignin ratio. Here, the best correlation was found with acidic group content ($r^2=69\%$), as is illustrated in figure 2.9. Apparently, the effects of acidic group content are strongest at ambient temperature. While at 70 °C, when lignin is softened, xylan:lignin ratio becomes the most important factor of the features measured.

The water retention value (wrv), the water held by wet fibers after centrifuging under standard conditions (Hopner *et al.* 1955; Tappi Useful Method UM 256), can be used as less time consuming alternative for fsp measurements (Scallan and Carles 1972). A comparison of fsp and wrv for the hemp woody core samples (figure 2.10) shows that when no chemicals are used at ambient temperature, wrv is high and fsp is low. Possibly, at ambient temperature extractives and relatively voluminous xylan clusters cause a high wrv, but also shield cavities in the fibers, thus preventing entrance of dextran molecules (causing a low fsp). Temperature rise causes lignin softening, apparently changing the fiber structure and accessibility of pores for dextran molecules. Excluding this value resulted in a linear relationship between wrv and fsp as shown in figure 2.10, with $r^2=70\%$. It thus follows that for measuring alkaline swelling of hemp woody core, for values up to 5 g/g, wrv may be used as indication of fsp, with considerable care. Compared to literature values (Stone and Scallan 1967; Katz *et al.* 1981), the measured fsp and wrv are very

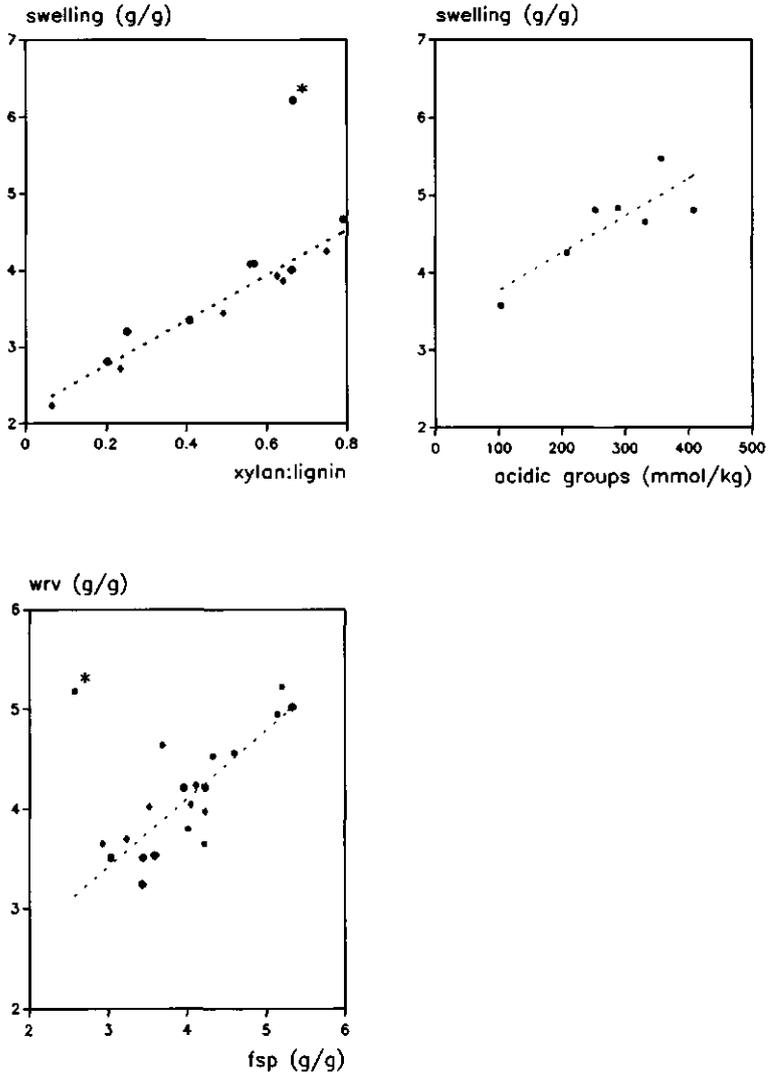


Figure 2.8 (upper left) Swelling of hemp woody core chips (calculated with fsp) versus xylan:lignin ratio at 70 °C (●) and at 70 °C with peroxide addition (◆); the sample treated with demi water (●*) is excluded for regression line (....) calculation. **Figure 2.9** (upper right) Swelling of hemp woody core chips (calculated with fsp) versus acidic group content at 20 °C (■) and regression line (....). **Figure 2.10** (lower left) Wrv versus fsp; the sample treated with demi water at 20 °C (■*) is excluded for regression line (....) calculation.

high. Apparently, the spacious structure enables maximal utilization of water absorbing capacity (related to the high acidic groups content and the xylan:lignin ratio) within the hemp woody corefibers.

2.3.4 Pore size distribution

How alkaline peroxide treatment is affecting the distribution of water within the fibers, is reflected in pore size distribution.

Pore size distribution can be investigated with size exclusion chromatography, as developed by Stone and Scallan (1968). However, the method is very time consuming, while only the minimum accessible pore size distribution is evaluated. Pores within the fibers that contribute to swelling, may not necessarily be accessible from the outer surface for larger particles.

Alternatively, pore size distribution can be investigated qualitatively with ^1H NMR spin-spin relaxation (Li *et al.* 1993), a faster method that also investigates the inner fiber wall. Spin-spin relaxation time of water molecules, T_2 , increases with pore size, as molecules close to a surface have a shorter NMR relaxation time than those of an unperturbed bulk liquid. Charged molecules of a surface also affect T_2 positively.

Pore size distribution of five selected hemp woody core samples was studied with spin-spin relaxation, tables 2.2 and 2.3 showing the characteristics of the samples, with the corresponding T_2 values and relative pore volumes (calculated by integration). The most remarkable feature is that two or three separate apparent pore size distribution groups were found in each sample. As T_2 is not necessarily linearly proportional to pore size increase (chemical composition of pore wall also influences relaxation time), the observed separate apparent pore size distributions may in fact be the result of similar apparent pore size distributions, with differently charged pore walls. It is thus conceivable that different apparent pore size distributions are observed within cellulose fibrils, the surrounding lignin-hemicellulose matrix and in the middle lamella near the fiber surfaces respectively.

Supposing that apparently small pores result from lower ionic charge, the lowest T_2 is found for pores in the middle lamella, with relatively high lignin concentrations (A); higher T_2 is found for pores within cellulose (B) and the largest T_2 is found for pores in the lignin-hemicellulose matrix (C) (electrostatic repulsion of carboxylic acid groups in hemicellulose). The following explanations are based on these assumptions.

Raising the temperature (in demineralized water for samples 1 and 2, and at an alkalinity of 0.1M

for samples 3 and 4) results in softened lignin and shrinkage of the apparently small pores (A, in table 2.3).

Table 2.2
Yield, Lignin, Xylan and Acidic group content.

	treatment	yield (%)	lignin on start (%)	xylan on start (%)	acidic group content (mmol/kg)
1.	demi water, 20 °C	100	26.1	17.4	104
2.	demi water, 70 °C	98.3	26.0	17.3	122
3.	0.1M NaOH, 20 °C	90.8	23.6	17.1	288
4.	0.1M NaOH, 70 °C	87.3	22.3	14.8	245
5.	0.1M NaOH + H ₂ O ₂ , 70 °C	80.0	18.3	10.2	273

Table 2.3
FSP, Swelling, Relative Swelling, Relaxation time (T₂) and Pore Volume Distribution.

	treatment	fsp (g/g)	swelling (fsp+1)*yield (g/g)	rel. swelling (3.58=100%) (%)	T ₂ (10 ⁻³ s)	pore volume within sample (%)
1.	demi water, 20 °C	2.58	3.58	100	A. 0.068	39.1
					B. 0.142	44.8
					C. 0.357	16.1
2.	demi water, 70 °C	5.32	6.22	173.7	A. 0.047	13.6
					B. 0.087	44.3
					C. 0.197	42.1
3.	0.1M NaOH, 20 °C	4.32	4.83	134.9	A/B. 0.070	78.8
					C. 0.245	21.2
4.	0.1M NaOH, 70 °C	3.59	4.00	111.7	A. 0.048	28.7
					B. 0.102	50.3
					C. 0.276	21.0
5.	0.1M NaOH + H ₂ O ₂ , 70 °C	4.10	4.08	114.0	A. 0.080	46.1
					B. 0.204	35.2
					C. 0.586	18.8

Increasing alkalinity to 0.1M (comparing samples 1 and 3 at 20 °C, and samples 2 and 4 at 70 °C) decreases yield and enlarges acidic group content (table 2.2), in addition effects on apparent pore size differ at 20 and 70 °C (table 2.3). At 20 °C more and smaller pores are formed within the lignin-hemicellulose and cellulose matrices (B,C). Pores of apparently medium size within cellulose fibrils (B) are shrunk to about the same size as those within lignin (A). At 70 °C fewer, but larger pores are formed within the lignin-hemicellulose and cellulose layers (B,C), and more of the pore volume is found within the lignin area (A).

Addition of peroxide (comparing samples 4 and 5) causes further yield loss and a decreased xylan:lignin ratio, but also results in remarkably higher T_2 and enlarged apparent pore sizes, especially in the lignin-hemicellulose and cellulose matrices. Possibly this is what makes peroxide attractive for high yield pulp production (apart from the bleaching effect), enhancing fiber flexibility and fibrillation by creating microstructure.

2.4 CONCLUSIONS

For hemp woody core, maximum swelling was found after treatment with demineralized water at 70 °C (lignin softening, without material removal). NaOH addition not only increases acidic group content, but also promotes material removal (extraction of hemicellulose). In contrast to wood species, swelling within the hemp woody core fiber is not enhanced by decreasing yield. Probably, the low density of the hemp woody core chips (in comparison with softwood and hardwood) allows relatively high water absorption, with the result that material removal does not enhance further expansion of remaining material.

Alkaline swelling of hemp woody core at 70 °C, was found to correlate with xylan:lignin ratio. At ambient temperature some correlation between swelling and acidic group content was found. Examining pore sizes by ^1H NMR spin-spin relaxation measurements, separate pore size distribution groups were found within each sample. This previously unreported phenomenon could be a result of varying chemical and physical conditions within the hemp woody core cell wall. Smaller T_2 and apparent pores sizes are expected to be situated in the less polar lignin mass, higher T_2 and apparently bigger pores in the cellulose fibrils, and the highest T_2 and apparently biggest pores in the lignin-hemicellulose matrix (electrostatic repulsion of carboxylic groups). Addition of peroxide results in remarkably enlarged apparent pore sizes. Possibly this combination of material removal and increased pore size is necessary for fiber separation and fibrillation.

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3. SIMPLIFIED KINETIC MODELLING OF ALKALINE DELIGNIFICATION OF HEMP WOODY CORE

SUMMARY

Alkaline delignification of hemp woody core was studied to support the development and optimization of an efficient and non-polluting alkaline pulping process. Shavings of hemp woody core were delignified isothermally at several temperatures with 1 M sodium hydroxide in a flow-through reactor. From literature data and from experimental data reported in this article, it appears that the initial delignification stage is completed before customary reaction temperatures are reached. Consequently, modelling of alkaline delignification kinetics can be restricted to the bulk and residual delignification stages. This can be described with two simultaneous first order reactions:

$$L/L_0 = a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t), \text{ with } k_i = A_i \exp(-E_{ai}/(RT)).$$

This equation has been solved integrally, calculating a_2 , a_3 , E_{a2} , E_{a3} , A_2 and A_3 for the best fit for the experimental data, resulting in an accurate description of the delignification reactions. This kinetic model has also been applied on literature data, supporting its validity for alkaline delignification kinetics in general.

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3.1 INTRODUCTION

The Dutch government is supporting an integral investigation on the potentials of fibre hemp, *Cannabis sativa vulgaris*, as a raw material for pulp and paper markets (De Groot *et al.* 1988). The aim of the programme is development of environmentally safe and economically feasible pulping processes for annual fibre crops. The stem of fibre hemp, an annual dicotyledon, consists of long bast fibres and a woody core. Both the potentials for the bast fibres (known as raw material for specialty papers), as well as for woody core are being investigated. Alkaline delignification with sodium hydroxide is a potential pulping process for hemp woody core and a basis for alkaline-oxygen or alkaline-peroxide processes. Kinetics and mechanisms of alkaline delignification of this material are being studied to support the development and optimization of such a process.

The woody core of fibre hemp, representing 70 % (w/w) of the hemp stem, consists of short fibres (0.6 mm), with a chemical composition similar to that of hardwood (table 3.1). The milder circumstances used for alkaline delignification of hardwoods in comparison with softwoods (Rydholm 1965) may also apply for this material. Furthermore, as the biological structures in hemp are needed for only one growing season, less condensed polymer structures may be present, compared to perennial wood.

Table 3.1
The chemical composition of some fibre crops and wood species (on unextracted dry wood basis)

	glucan	xylan	mannan	arabinan	galactan	lignin
Gymnospermae						
Coniferae						
Picea abies ¹	44.3	7.6	10.3	0.5	1.9	28.6
Pinus sylvestris ¹	44.8	7.2	7.6	0.6	1.3	27.8
Angiospermae						
Dicotyledonae						
Betula verrucosa ¹	37.5	24.6	0.5	0.5	1.0	19.5
Cannabis sativa						
woody core	37.7	16.7	1.2	0.3	0.6	22.1
bast fibres	66.7	1.5	1.9	0.7	1.7	4.0
Monocotyledonae						
Triticum vulgare ²	30.4	12.2	0.4	2.2	0.7	9.9 ³

¹Rydholm 1965. ²Nordkvist 1989. ³AcBr-lignin

The following knowledge about alkaline delignification of perennial wood may be used in the description of kinetics and mechanisms of alkaline delignification of hemp woody core.

1. Alkaline impregnation affects swelling and the formation of a certain tunnel-network in the cell walls, facilitating the removal of reaction products from the lignocellulosic matrix (Stone and Scallan 1965 and 1968; Ahlgren *et al.* 1971; Scallan 1974; Kerr and Goring 1975a).

2. In the pulping process an initial, bulk and residual delignification stage can be distinguished (Aurell 1964; Aurell and Hartler 1965; Lémon and Teder 1973). In the initial stage (during the heating up period) hemicelluloses are deacetylated and a considerable amount of hemicellulose is dissolved, while also a small amount of lignin is removed. During the bulk stage most of the lignin polymer is degraded and dissolved in the cooking liquor, a smaller amount of the remaining hemicelluloses is dissolved or degraded, while the degree of polymerisation of the cellulose decreases. During the residual stage the lignin removal proceeds very slowly, while cellulose and remaining hemicellulose are decomposed further.

3. During the initial delignification stage in alkaline pulping with sodium hydroxide, phenolic α -O-4-linkages in lignin are cleaved and some phenolic β -O-4-linkages are cleaved (Gierer 1970), followed by the diffusion of extractable lignin components. The dominating reaction during the bulk stage is the cleavage of non-phenolic β -O-4-linkages (Gierer and Norén 1980; Ljunggren 1980). The residual delignification stage has been assigned to cleavage of carbon-carbon linkages in lignin (Gierer 1985) and to carbohydrate degradation, releasing lignin-carbohydrate fragments (Gellerstedt and Lindfors 1984).

4. Two models are regarded, the consecutive model and the simultaneous reaction model. The consecutive model describes delignification, following the described concept (Kerr 1970; Gustafson *et al.* 1983). The transition point from initial to bulk stage is set at a certain lignin content. As the lignin content at the transition from bulk to the residual period is varying with reaction circumstances, this point is set variably (depending on the circumstances used).

Alternatively the initial, bulk and rest delignification stages can be modelled as the result of three simultaneous first order reactions (Dolk *et al.* 1989). In this model the weight fraction of lignin remaining in the lignocellulose matrix, calculated on starting material (L/L_0), is described with:

$$L/L_0 = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) \quad (3.1)$$

with $k_i = A_i \exp -E_{a_i}/(RT)$, a_1 representing the fraction of lignin fragments released through the cleavage of α -O-4-linkages, a_2 representing the fraction of lignin fragments released through the cleavage of β -O-4-linkages and a_3 representing the fraction of lignin fragments released through

the cleavage of carbon-carbon linkages in lignin or through carbohydrate cleavage. As the molecular weight of a lignin polymer subjected to the cleavage reactions is unknown, the total weight is used instead of the amount of lignin moles. The graphical presentation of this model shows three stages (see e.g. figure 3.5), with varying transition points. The simultaneous model has been used to describe soda pulping of Western hemlock wood (Dolk *et al.* 1989) and poplar wood (Labidi and Pla 1992b) and kraft pulping of Douglas-fir (Chiang *et al.* 1990). A stepwise calculation method is used, first the values for the fractions a_i are estimated, then the reaction rate k_i for each temperature curve is calculated, followed by the calculation of activation energy E_{a_i} from the calculated k_i 's at each temperature.

In our study the simultaneous reaction model is preferred, as all cleavage reactions will take place simultaneously during the pulping process. In this view, the consecutive model can be regarded as a simplification of the simultaneous reaction model.

5. Delignification can be regarded as the degelation of a solid polymer, followed by depolymerisation and solubilization of the polymer fragments, involving a number of consecutive reactions (Szabo and Goring 1968; Bolker and Brenner 1970; Yan and Johnson 1981). The described models implicate the assumption that the depolymerisation into removable fragments is the rate-determining step. The calculated first order kinetic rate constants are regarded as lumped parameters of overall reaction patterns.

6. It is possible that the first reaction in the simultaneous model is not controlled by chemical reactions and the extraction of low molecular weight polymers is dominating in this stage of the process (Dolk *et al.* 1989; Labidi and Pla 1992b). Furthermore, these articles show that $a_i \exp(-k_i t)$ in equation (3.1), describing this reaction, is mainly used to fit the curve to time = 0, $L/L_0 = 1$. This has led to the hypothesis, to be proven in this article, that this reaction may be regarded as occurring separately in time, as in the consecutive model. Fast chemical reactions take place (e.g. the cleavage of phenolic α -O-4 linkages) at the lower temperatures occurring during the warming up period, while removable fragments are extracted. Consequently, delignification at reaction temperature can be described with two simultaneous reactions representing 'bulk' and 'rest delignification' only.

3.2 MATERIAL AND METHODS

Hemp woody core shavings were used (7.1 g, length: 7.6 mm, width: 4.0, thickness: 0.2 mm, all

averages). Diffusion effects can be neglected: preliminary batch delignification studies with hemp woody core chips with thicknesses of 0.5, 1.0 and 2 mm (1 M NaOH, 6 to 30 min, liquor to wood ratio 30:1) showed no significant effect of chip thickness on delignification rates; using shavings should therefore be more than efficacious to avoid diffusion effects. The shavings have been impregnated with 500 ml of 1 M NaOH during 30 min at room temperature, to obtain a homogeneous distribution of the cooking liquor at the reaction sites at the start of the delignification process. To study isothermal kinetics and degradation mechanisms either a batch reactor with a high liquor to wood ratio (Chiang *et al.* 1990) or a flow-through reactor is used (Dolk *et al.* 1986; Venica *et al.* 1989; Pekkala 1989; Labidi and Pla 1992a). The used flow-through reactors are derived from the ones that were used in early kinetic and mechanism studies (Macklin and Maass 1932; Yllner and Ostberg 1957). In a flow-through reactor secondary reactions are prevented, as the degradation products are continuously removed. After preheating in an oven, such a reactor is filled with the raw material and connected to the system, after which the cooking liquor is flown through the reactor.

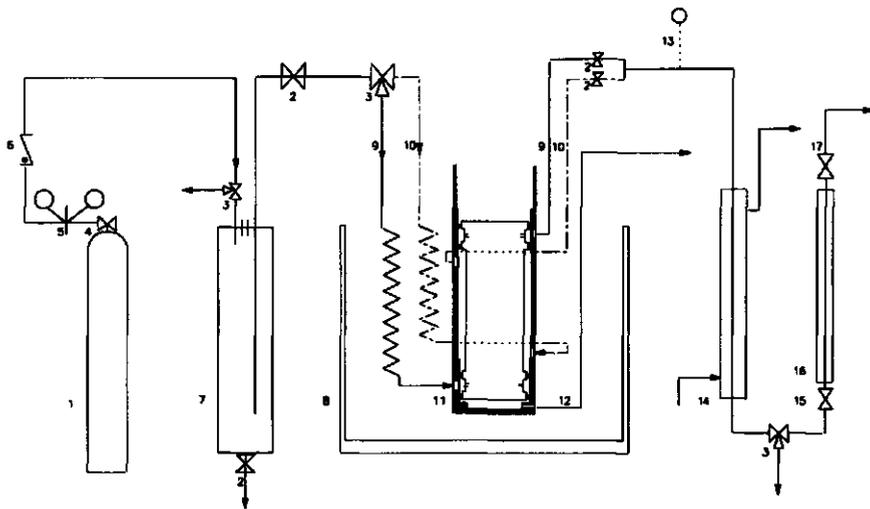


Figure 3.1 Flow-through setting (not to scale) with (1) nitrogen pressure vessel; (2) ball valves; (3) 3-way ball valves; (4) valve; (5) pressure regulator (circa 10 bar); (6) back pressure valve; (7) tank with pulping liquor; (8) constant temperature bath, with silicon oil; (9) reaction liquor flow (through the reactor); (10) preheating liquor flow (between reactor and reactor jacketing); (11) reactor jacketing; (12) air outlet; (13) pressure check; (14) heat exchanger; (15) flow control; (16) flow meter; (17) valve. Reactor, jacketing and piping in stainless steel.

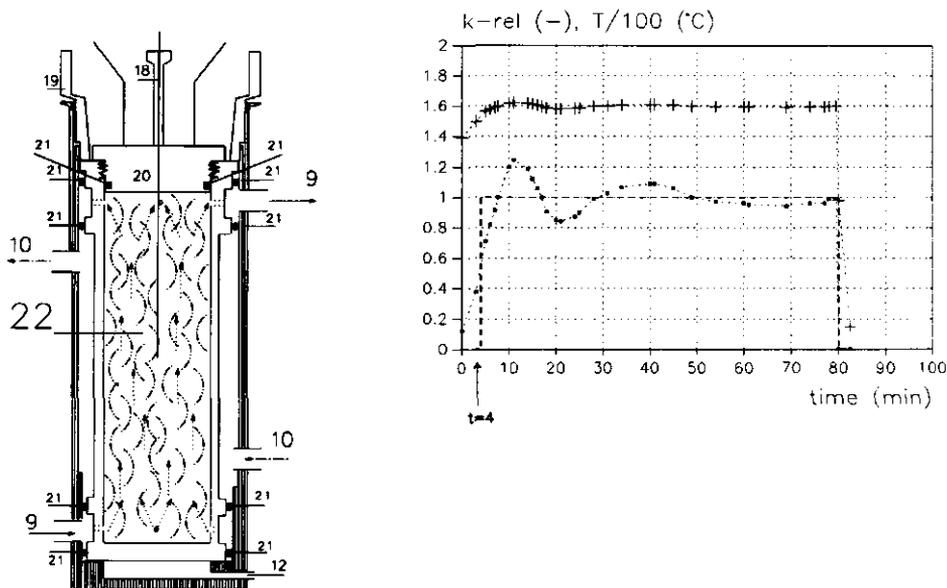


Figure 3.2 (Left) Flow-through reactor in jacketing with: (9) reaction liquor flow (through the reactor); (10) preheating liquor flow (between reactor and reactor jacketing); (12) air outlet; (18) thermo-couple; (19) locking lid; (20) reactor lid; (21) polyethylene O-rings; (22) hemp shavings
Figure 3.3 (Right) Relative reaction rate (-) at used temperature (-+, $T/100$ in $^{\circ}\text{C}$), resulting in a total reaction period diminished with 4 min for k_2 ($k\text{-relative}=1$) at 160°C .

Filling the hot reactor is a hazardous job and meanwhile the reactor will cool again, resulting in a heating up time of about 10 minutes or more (Tirtowidjojo 1988; Labidi and Pla 1992a). To reduce the heating up time and to facilitate the filling of the reactor, a new flow-through reactor has been designed, with separate preheating and reaction chambers, that can be filled in situ.

This flow-through reactor (figure 3.2) can be put in the setting (figure 3.1) and be preheated, e.g. with hot water through the preheating liquor flow (between reactor and reactor jacketing (10)).

The reactor jacketing and the tubings through which the liquor flows are

(pre-)heated in a silicon oil bath (8). Just before the experiments are started, the delignification liquor can be put in the tank (7) at atmospheric pressure and the reactor can be further preheated with cooking liquor. Then the impregnated shavings are put in the reactor, the reactor is closed and the three-way valves are switched so that the liquor is flowing through the reactor (9). It takes 6 min before the reaction temperature is reached. To estimate the net effect of the heating up period on the reaction rate, the reaction temperature and the resulting relative reaction rate for

k_2 is shown in figure 3.3, for a reaction temperature set on 160 °C. It is assumed that $E_{a2}/R = 18000$, then $k_2 = A_2 \exp(-E_{a2}/RT) = A_2 \exp(-18000/433)$. The resulting k at different temperatures during the heating up period can be calculated, as $k\text{-relative} = k/k_2 = (\exp(-18000/T))/(\exp(-18000/433))$. The area under the curve of $k\text{-relative}$ is equal to an area which is put under the line $k\text{-relative}=1$ ($T=160$ °C), resulting in a correction for the net total reaction time at $T=160$ °C. In the example of figure 3.3, the net total reaction time is the total reaction time diminished with roughly 4 min. The correction of 4 min was used in all calculations.

The average residence time of the reaction liquor for the described experiments has been 1.6 min (free volume of 47 ml, flow rate of 30 ml/min), the reaction time was varied between 5 and 240 minutes, using 1 M NaOH solution. At the end of the delignification process it takes 0.5 min to cool the reactor content below 100 °C, after which the reactor is placed in an ice-bath. A procedure similar to that for the warming up period, shown in figure 3.3, reveals that this cooling down period can be neglected.

The resulting pulp has been washed with 500 ml 0.01 M NaOH, 3 times with 500 ml hot tap water and 3 times with 500 ml deionized water (Dolk *et al.* 1989), after which the fibre mass has been dried (over night at room temperature, followed by 50 hours at 70 °C). The dry matter content (TAPPI Standard Method T264), Klason lignin (TAPPI Standard Method T222) and acid soluble lignin (TAPPI Useful Method 250) have been measured. The carbohydrate composition was analyzed using HPLC, with fucose as internal standard. The effects of impregnation and heating up were analyzed separately (table 3.2), also examining the extractable fraction (TAPPI Standard Method T264), the amount of uronic acids (according to El Rayah Ahmed and Labavitch 1977) and acetyl groups (according to Voragen *et al.* 1986).

For kinetic modelling the non linear routines of Genstat 5, a general statistical program (Digby *et al.* 1989) have been used. All variables are calculated in one routine with $\ln(L/L_0) = \ln((a_2 \exp(-k_2t) + a_3 \exp(-k_3t)))$.

3.3 RESULTS AND DISCUSSION

3.3.1 Impregnation and heating up period

To examine the hypothesis that the initial stage in the alkaline delignification process is completed before significant further delignification starts (at temperatures of 150 °C and higher),

the removal of material has been examined during the impregnation and the warming up period. The amounts of lignin, cellulose and hemicellulose present in respectively starting material, material after impregnation and material after heating up period (all calculated as percentages of starting material) have been analyzed. As is shown in table 3.2, circa 30 % of the starting material can be removed with 1 M NaOH at room temperature. More than 60% of the xylan is solubilized before the heating up period starts. Since glucan is not significantly removed, the impregnated material consists of circa 57 % glucan, probably mainly cellulose. A small fraction of the lignin (11 %) is removed, the remaining lignin is forming circa 28 % of the impregnated material. During impregnation of Western hemlock wood only 7 % of the lignin can be dissolved (Chiang *et al.* 1990), while in various hardwood species 13 to 30 % of the lignin has been dissolved, accompanied with some hemicellulose (resulting in yields between 85 and 90 %, Wallis and Wearne 1985).

Table 3.2

Removal of compounds from hemp woody core during impregnation and heating up period. Detected dry matter (mean values) as a percentage (w/w) of starting material, standard deviation in parentheses (n.d.= not determined)

	starting material	after impregnation during 30 min with 1 M NaOH at 20 °C	after heating up during 5 min from 100 to 140 °C
lignin	22.10 (0.18)	19.59 (2.06)	14.98 (0.69)
cellulose			
glucan ¹	37.74 (0.10)	39.55 (4.19)	39.31 (1.03)
hemicellulose			
xylan	16.65 (0.06)	6.25 (1.63)	3.69 (0.20)
mannan	1.16 (0.06)	0.90 (0.07)	0.00
arabinan	0.34 (0.01)	0.33 (0.16)	0.00
rhamnan	0.45 (0.03)	0.22 (0.09)	0.00
galactan	0.61 (0.08)	0.57 (0.13)	0.33 (0.01)
uronic acids	3.34 (0.12)	3.01 (0.79)	n.d.
acetyl groups	4.29 (0.13)	0.00	n.d.
extractives	8.87 (0.05)	2.68 (0.13)	2.02 (0.15)
total	95.55 (0.82)	73.10 (9.25)	60.33 (2.08)
total yield	100	69.42 (0.38)	57.58 (1.03)

¹For simplicity all glucan has been assigned to cellulose.

Table 3.2 shows that during the heating up period (of 5 min) another 12 % of the starting material is removed. A considerable amount of lignin is removed (21 %), leaving 68 % of the original lignin in the material. Using a longer warming up period (20 and 35 min) results in the removal of the same amount of lignin as with a warming up period of 5 min. After the warming up period the fibrous material consists for 67 % of cellulose, 26 % of lignin and 7 % of hemicellulose. The pulp yield (dry matter) on starting material (58 %) is considerably lower, compared to perennial wood (e.g. 80 % for Western hemlock (Dolk *et al.* 1989), 76 % for birch (Aurell 1964)), resulting in a higher cellulose content and a lower xylan and lignin content. The higher amount of extractives and the presence of less condensed, and therefore more easily degradable and removable xylan and lignin fragments may explain these results for a large deal. The results show that during impregnation at 20 °C about 11 % of the lignin is removed and that during the warming up period, about 21 % of the lignin is removed. As longer warming up periods have no effect on the amount of lignin that is removed, it can be assumed that the initial delignification stage is completed during the warming up period.

3.3.2 Modelling of bulk and rest delignification period

In case that the initial stage is completed during the warming up period, the first term on the right hand side of equation (3.1) can be left out. Alkaline delignification of hemp woody core can then be described with two simultaneous reactions : $L/L_0 = a_2 \exp(-k_2t) + a_3 \exp(-k_3t)$ (3.2)

The fitting procedure results in:

$$L/L_0 = 0.617 \exp(-k_2t) + 0.037 \exp(-k_3t),$$

with $\ln k_2 = 36.53 - 143600/(8.314 T)$,

$$\ln k_3 = 41.39 - 172800/(8.314 T),$$

and r^2 (adjusted for the number of parameters) = 98.4 %.

Figure 3.4 is showing the calculated model curves and the measured data. On the y-axis the natural logarithm of L/L_0 is displayed, so that different reaction stages can be distinguished. The two stages seem to correspond with the bulk and the rest delignification stages. The calculated activation energies are respectively 143.6 ± 5.2 kJ/mol and 172.8 ± 37.2 kJ/mol, which is within the range of the values found for bulk and rest delignification in literature for perennial wood. With $a_2 = 0.617 \pm 0.036$ and $a_3 = 0.037 \pm 0.006$ this results in $a_1 = 1 - 0.617 - 0.037 = 0.346 \pm 0.042$ that has been removed during the initial delignification stage. The value of 32.2 % (from $(22.10 - 14.98)/22.10$) in table 3.2), found as the lignin loss after impregnation and heating up

periods is within the margins of the value of a_1 found here.

The equation may be simplified further, using $a_2 = (1-a_1)-a_3 = 0.678-a_3$. Then the fitting procedure results in: $L/L_0 = 0.640 \exp(-k_2 t) + 0.038 \exp(-k_3 t)$, with $a_3 = 0.038$, ($a_2 = 0.678 - 0.038 = 0.640$), $\ln A_2 = 36.51$, $\ln A_3 = 40.97$, $E_{a2} = 143.5$, $E_{a3} = 171.2$ and r^2 (adjusted for the number of parameters) = 98.4 %. These results are within the range of the values found without this simplification.

The calculated reaction rate constant k_2 at a certain reaction temperature is much higher than for softwood (ca. 4 times as high as for Western hemlock (Dolk *et al.* 1989)) and slightly higher than for hardwood (ca. 1.5 times as high as for poplar (Labidi and Pla 1992b)). This is in accordance with the expectations that the milder circumstances for alkaline delignification of hardwood in comparison with softwoods (Rydholm 1965) can be applied to hemp woody core and that the delignification of hemp woody core may be faster in comparison with hardwood (e.g. due to the presence of less condensed polymer structures). The reaction rate constant k_3 for hemp woody core is ten times smaller than k_2 , and not significantly different from softwood (Dolk *et al.* 1989). The involved lignin fraction in this reaction is small (4 %).

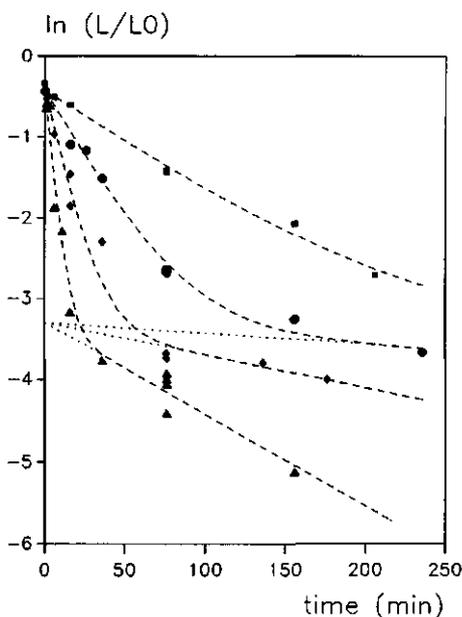


Figure 3.4 Alkaline delignification kinetics for hemp woody core (shavings) in a flow-through reactor with 1 M NaOH (30 ml/min), at 150 (■), 160 (●), 170 (◆) and 180 (▲) °C, modelled with 2 simultaneous reactions, using integral calculation (--- model).

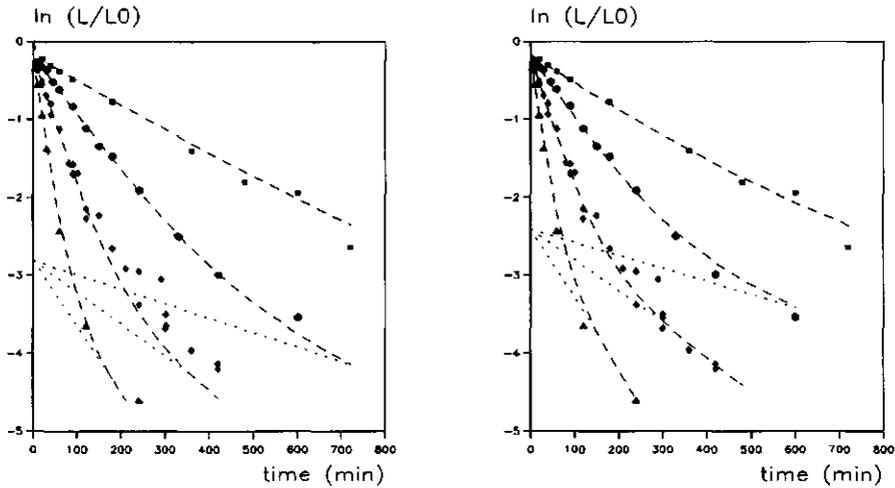


Figure 3.5 (Left) Alkaline delignification kinetics for Western hemlock, at 150 (■), 160 (●), 170 (◆) and 180 (▲) °C, modelled with 3 simultaneous reactions, using stepwise calculation (--- model), data and model: Dolk *et al.* 1989.

Figure 3.6 (Right) Alkaline delignification kinetics for Western hemlock, at 150 (■), 160 (●), 170 (◆) and 180 (▲) °C, modelled with 2 simultaneous reactions, using integral calculation (--- model), data: Dolk *et al.* 1989.

3.3.3 Application of the model on literature data

3.3.3.1 Western hemlock

Dolk *et al.* (1989) used a three term model, using stepwise calculation. First a_1 , a_2 , a_3 and k_1 were determined, using the best estimates available from preliminary trials. Then k_2 and k_3 were calculated, after which E_{a1} , E_{a2} and E_{a3} were calculated. This resulted in:

$$L/L_0 = 0.16 \exp(-k_1 t) + 0.78 \exp(-k_2 t) + 0.06 \exp(-k_3 t),$$

with $\ln k_1 = 22.09 - 80100/(8.314 T)$,

$$\ln k_2 = 31.61 - 131100/(8.314 T),$$

$$\ln k_3 = 26.31 - 117000/(8.314 T).$$

Figure 3.5 shows this stepwise calculated model and the experimental data. Obviously, there are no data to verify the correctness of the fit for the first reaction stage, the first term of the equation is only used to fit the curve to $L/L_0=1$ at $\text{time}=0$.

It is clear from figure 3.5 that values at 170 °C, for reaction periods longer than 240 minutes are not fitted perfectly. There are 9 data points for T=150 °C, 14 data points for T=160 °C, 30 data points for T=170 °C and 7 data points for T=180 °C. This means that data points at T=150 or 180 °C have twice as much influence on the model as data points at T=160 °C, and four times as much influence as the data points at T=170 °C. This is probably the main reason why there has not been found a better fit.

Figure 3.6 shows the integrally calculated two term model, with the data points taken from Dolk *et al.* (1989), omitting the first term and using $a_3 = (1-a_1)-a_2 = 0.840 - a_2$:

$$L/L_0 = 0.751 \exp(-k_2 t) + 0.089 \exp(-k_3 t),$$

with $\ln k_2 = 30.27 - 125900/(8.314 T),$

$$\ln k_3 = 29.90 - 130300/(8.314 T),$$

and r^2 (adjusted for the number of parameters) = 99.1 %. The calculated activation energies are respectively 125.9 ± 4.0 kJ/mol and 130.3 ± 10.9 kJ/mol, $a_2 = 0.751 \pm 0.021$ (resulting in $a_3 = 0.840 - 0.751 = 0.089$), which are not very far from the values calculated by Dolk *et al.* (1989). The fit for data at 170 °C seems better, without a negative effect on the other curves.

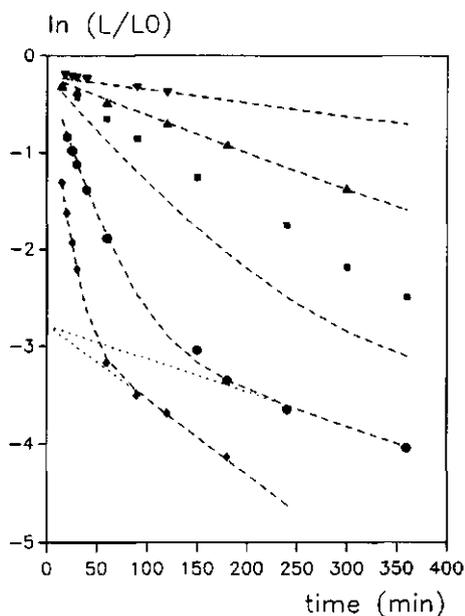


Figure 3.7 Alkaline delignification kinetics for poplar wood, at 130 (▼), 140 (▲), 150 (■), 160 (●) and 170 (◆) °C, modelled with 2 simultaneous reactions, using integral calculation, omitting data for T=150 °C for modelling (--- model), data: Labidi 1989.

3.3.3.2 Poplar wood

Labidi and Pla (1992b) also used a three term model, with stepwise calculation. First the reaction curve for each reaction temperature was calculated, then the average values for a_1 , a_2 and a_3 were calculated, resulting in: $L/L_0 = 0.19 \exp(-k_1t) + 0.75 \exp(-k_2t) + 0.06 \exp(-k_3t)$. The values for k_2 at each temperature curve were used to calculate the activation energy E_{a2} with $\ln k_2 = \ln A_2 - E_{a2}/RT$, resulting in $E_{a2} = 143.1$ kJ/mol. An integral calculation method may result in a more detailed picture, as $\ln A_3$ and E_{A3} may be calculated too. Attempts on an integral fitting of kindly provided data (Labidi 1989), proved it difficult to get a good fit, especially as the data at 150 °C didn't seem to match with the other data. Figure 3.7 illustrates this: omitting the data of 150 °C gives an excellent fit for all, except for the data at 150 °C. With the data of 150 °C omitted and using $a_3 = (1-a_1)-a_2 = 0.810 - a_3$, the result is:

$$L/L_0 = 0.748 \exp(-k_2t) + 0.062 \exp(-k_3t),$$

with $\ln k_2 = 38.15 - 149600/(8.314T)$,

$$\ln k_3 = 29.44 - 126400/(8.314T),$$

and r^2 (adjusted for the number of parameters) = 99.9 %. The calculated activation energies are respectively 149.6 ± 1.6 kJ/mol and 126.4 ± 5.0 kJ/mol, $a_2 = 0.748 \pm 0.003$ (resulting in $a_3 = 0.810 - 0.748 = 0.062$). The value for E_{a2} found by Labidi and Pla (1992b) is not far from the value found with the integral modelling method and the values for a_2 and a_3 are identical.

3.4 CONCLUSIONS

The results support the hypothesis that the initial delignification takes place during the impregnation step and the heating up period. Consequently, alkaline delignification with sodium hydroxide at customary reaction temperatures may be modelled with a two term model, both for annual fibre crops like hemp, as well as for perennial woods like Western hemlock and poplar. The two term model describes the kinetics of the delignification process at reaction temperature, which can be applied in process optimization. An integral calculation of the variables in the model may lead to a more accurate fit than stepwise calculation. The fraction involved in the initial delignification follows from the calculations with the two term model: $a_1 = 1 - a_2 - a_3$. Moreover, if the lignin losses in the impregnation and heating up periods have been measured, it is possible now to use this as the value for a_1 . This has the additional advantage that the number of fitting parameters (using $a_3 = (1 - a_1) - a_2$) is decreased with one.

The delignification mechanisms as have been unravelled by Gierer and co-workers seem to apply, cleavage of phenolic α -O-4 and, in a smaller extent, β -O-4 linkages taking place during the heating up period and cleavage of β -O-4 linkages in non-phenolic units taking place during the bulk period. As has been mentioned earlier, it is clear that the calculated values must be seen primarily as lumped parameters of overall reaction patterns.

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NOMENCLATURE

L	= lignin in pulp, as percentage of starting material (w/w)	[-]
L ₀	= lignin in pulp at t=0, as percentage of starting material (w/w)	[-]
a _i	= lignin fraction, participating in each reaction	[-]
t	= time	[min]
k _i	= reaction rate constant = A _i exp (-E _{ai} /RT)	[1/min]
A _i	= constant (= k _∞)	[-]
E _{ai}	= activation energy	[J/mol]
R	= gas constant = 8.314	[J/(mol.K)]
T	= absolute temperature	[K]

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4. ALKALINE PULPING OF HEMP WOODY CORE: KINETIC MODELLING OF LIGNIN, XYLAN AND CELLULOSE EXTRACTION AND DEGRADATION

SUMMARY

The kinetics of alkaline degradation of lignin, xylan and cellulose in relation to pulp yield were studied for hemp woody core to support development and optimization of a non-polluting alkaline pulping process. Shavings of hemp woody core were impregnated at room temperature with various sodium hydroxide concentrations (0.25-2.0M NaOH) and delignified isothermally at various reaction temperatures (150-180 °C) in a flow-through reactor. Extraction and degradation of xylan from hemp woody core strongly depended on the NaOH concentration used. Consequently, to attain a certain lignin content, lower NaOH concentrations result in higher pulp yields. Extended pulping diminished the differences in pulp yields, due to further xylan degradation. The kinetics of lignin, xylan and cellulose degradation were modelled as a function of reaction time, temperature and NaOH concentration. The combined models resulted in a pulp yield model for hemp woody core, suitable for process optimization purposes.

Degradation kinetics of perennial wood can be modelled similarly, which was illustrated using literature data on spruce and poplar.

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4.1 INTRODUCTION

To support development of alkaline pulping as one of the potential pulping processes for hemp woody core, the kinetics of alkaline degradation reactions for the major components (using sodium hydroxide) have been studied and modelled.

The chemical degradation processes of the major components (lignin, xylan and cellulose) under alkaline conditions, as has been described for perennial woods, are discussed briefly as background information, together with the data of a previous study on delignification of hemp woody core with 1M NaOH (De Groot *et al.* 1994).

Lignin is an amorphous polymer, consisting of 5-500 substituted phenylpropanoid units. Delignification facilitates disintegration of wood into fibrous components and eliminates colouring substances (Sarkanen and Ludwig 1971; Rydholm 1965). Important delignification reactions are: 1. cleavage of phenolic α -O-4-linkages, 2. cleavage of non-phenolic β -O-4-linkages, 3. removal of residual lignin fractions, either by cleavage of carbon-carbon linkages or by carbohydrate degradation, releasing lignin-carbohydrate fragments (Gierer 1970; Gierer and Norén 1980; Ljunggren 1980; Gellerstedt and Lindfors 1984; Gierer 1985).

Xylan is the major hemicellulose component in hardwoods and in woody parts of dicotyledonous annual fibre crops like hemp. Hardwood xylan consists of linear chains of about 200 D-xylopyranose units, connected by β -(1 \rightarrow 4)-glycosidic bonds (Timell 1967). About one of every 10 xylose residues contains a β -(1 \rightarrow 2)-linked 4-O-methyl-D-glucuronic acid residue, at least 7 out of 10 xylose residues are esterified with an O-acetyl group at C-2 or at C-3. Swelling and expansion of the hemicellulose layer suppresses cross-fibre fragmentation and promotes fibrillation and formation of interfibre bonds during papermaking (Nolan 1953; Tappi Forest Biology Subcommittee 1960; Amidon 1981). This results in increased beating rates, and better mechanical properties and opacity of the paper (Horio *et al.* 1955; Fiserova *et al.* 1987; Genco *et al.* 1990).

Wood cellulose, the basis for papermaking fibres, consists of linear chains of 7000-15000 D-glucopyranose units, connected by β -(1 \rightarrow 4) glycosidic linkages (Fengel and Wegener 1984).

Important degradation reactions for both xylan and cellulose are peeling (chemical degradation initiated at reducing end groups), which consumes a large amount of alkaline cooking liquor, and alkaline hydrolysis of glycosidic linkages, which results in depolymerization and secondary peeling reactions. Furthermore, the acetyl groups in xylan are removed during impregnation and heating up periods and most of the glucuronic acid groups in xylan are split off by alkaline

hydrolysis at reaction temperature, influencing the solubility (Timell *et al.* 1959; Kiss 1974; Fengel and Wegener 1984; Sjöström 1993). Yield losses of cellulose are assumed to be determined by peeling reactions. Due to the high polymerization degree of cellulose, hydrolytic reactions will primarily lead to a lower polymerization degree, without noticeable yield losses. Furthermore, cellulose has a higher crystallinity than hemicellulose and is consequently more resistant to alkaline hydrolysis (Rydholm 1965). Yield losses of xylan are assumed to be determined by dissolution, followed both by hydrolysis and peeling reactions.

Whereas many studies on reaction kinetics of delignification have been published, there is no literature available in which reaction kinetics are described separately for hemicellulose and cellulose degradation. For softwoods, the overall kinetics of carbohydrate degradation have been investigated (Rekunen *et al.* 1980). In the kraft pulping process an initial, bulk and residual stage can be distinguished (Aurell 1964; Lémon and Teder 1973). In the initial stage (during the heating up period) hemicellulosic polysaccharides are deacetylated and a considerable amount dissolves or partly degrades by peeling reactions (Jacopian 1958; Johansson and Samuelson 1977). This results in dissolution of xylan, with a relatively high degree of polymerization (Axelsson *et al.* 1962), while also a small amount of lignin is removed. The maximum concentration of hemicelluloses occurs roughly at the end of the heating up period (Simonson 1971). During the bulk stage, at reaction temperatures (above 150 °C), most of the lignin polymers and remaining hemicelluloses degrade and dissolve in the cooking liquor, and the degree of polymerisation of cellulose decreases. Lignin removal proceeds very slowly during the residual stage, while cellulose and remaining hemicellulose are decomposed further.

Sodium hydroxide stimulates both extraction and degradation reactions. Impregnation with NaOH results in swelling of wood fibres and a higher cell wall permeability, facilitating extraction of soluble polymers and removal of degradation products from the lignocellulosic matrix (Stone and Scallan 1965, 1968; Ahlgren *et al.* 1971; Scallan 1974; Kerr and Goring 1975). A part of the xylan is extractable with NaOH at room temperature (up to 40% with 1M NaOH, McDonald 1952), xylan from less lignified plant materials (e.g. grasses) can be obtained in high yields by alkaline extraction at room temperature (Puls *et al.* 1988). NaOH also promotes cleavage of non-phenolic β -O-4-linkages in lignin and peeling and alkaline hydrolysis in xylan and cellulose. For softwood, Olm and Tistad (1979) found that initial delignification is a reaction of zero order with respect to NaOH concentration in the range of technical interest, while the carbohydrate degradation rate in the initial pulping stage is slightly depending (with an order of about 0.1) on NaOH concentration (Rekunen *et al.* 1980). For hardwoods, it is known that xylan degradation increases

with higher NaOH concentrations (Yllner *et al.* 1957; Aurell 1964), especially during the initial stage (Yllner *et al.* 1957; Olm and Tistad 1979). Bulk delignification rate is almost proportional to NaOH concentration (Lusby and Maass 1937; Wilder and Daleski 1965; Gierer 1980; Ljunggren 1980), with almost first order reaction rate for both softwood and hardwood species (Nordén and Teder 1979; Nelson and Gniel 1986; Labidi and Pla 1992). The carbohydrate degradation rate for softwoods during this reaction stage has the same dependence on NaOH concentration, but is twice as slow as the delignification rate (Rekunen *et al.* 1980). However, the residual delignification rate is also of almost first order with respect to NaOH concentration (Nordén and Teder 1979), while the carbohydrate degradation rate has the same dependence, and is twice as fast (Rekunen *et al.* 1980).

The bulk and residual delignification stages for hemp woody core, using 1M NaOH in a flow-through reactor, can be described as the result of two simultaneous overall reactions at reaction temperature, initial delignification taking place during impregnation and heating up periods (De Groot *et al.* 1994). Consequently, the weight fraction of lignin remaining in the lignocellulose matrix, calculated on starting material, can be described as:

$$L/L_0 = a_2 \exp(-k_2t) + a_3 \exp(-k_3t) \quad (4.1)$$

with $k_i = A_i \exp(-E_a_i/RT)$ (De Groot *et al.* 1994). This is the starting point for modelling delignification with various NaOH concentrations. Similarly, in this study carbohydrate degradation reactions at reaction temperature are assumed to take place simultaneously, regarding the described consecutive stages in a pulping process as the result of simultaneous overall reactions.

The purpose of this study is to describe the overall degradation processes for lignin, xylan and cellulose as a function of NaOH concentration, reaction time and temperature, taking into account effects of impregnation and heating up. The models are combined to calculate pulp yield for optimization purposes and can be applied to alkaline-oxygen or alkaline-peroxide processes.

4.2 MATERIAL AND METHODS

Hemp woody core shavings were used (7.1 g, length: 7.6 mm, width: 4.0, thickness: 0.2 mm, all averages). Diffusion effects can be neglected: batch delignification studies with hemp woody core chips with thicknesses of 0.5, 1.0 and 2 mm (1 M NaOH, 6 to 30 min, liquor to wood ratio 30:1) showed no significant effect of chip thickness on delignification rates, using shavings should

therefore be more than efficacious to avoid diffusion effects. Shavings were impregnated with 500 ml NaOH solution (with the same concentration as used in the flow-through reactor) during 30 min at room temperature, to obtain a homogeneous distribution of cooking liquor at reaction sites at the start of the delignification process. To reduce the heating up period and to facilitate filling of the reactor, a flow-through reactor was used with separate preheating and reaction chambers, that can be filled in situ (De Groot *et al.* 1994). The average residence time of the reaction liquor was 1.6 min (free volume of 47 ml, flow rate of 30 ml/min). The effect of impregnation and extraction at room temperature was examined separately (following the procedure as described for the delignification experiments), by extraction in the flow-through reactor at room temperature, during 80 min.

The resulting pulp (or extracted material) was washed with 500 ml 0.01 M NaOH, 3 times with 500 ml hot tap water and 3 times with 500 ml deionized water (Dolk *et al.* 1989), after which the fibre mass was air dried (over night at room temperature, followed by 50 hours at 70 °C). Dry matter content (TAPPI Standard Method T264 1991), Klason lignin (TAPPI Standard Method T222 1991) and acid soluble lignin (TAPPI Useful Method 250 1991) were measured. Carbohydrate composition was analyzed using HPLC, with pulsed amperometric detection, using a gold electrode. The monosaccharides were separated on a Dionex anion exchange column (Carbo PAC PA1), with a NaOH gradient as eluent. Fucose was used as internal standard.

The total reaction time was diminished with 4 min for all calculations, to compensate for effects of lower temperatures during the heating up period (De Groot *et al.* 1994). For kinetic modelling the non linear routines of Genstat 5, a general statistical program (Digby *et al.* 1989) have been used. The accuracy with which a calculated model fits experimental data is given by r^2_{adj} , the percentage of variance accounted for, adjusted for the number of parameters.

4.3 RESULTS AND DISCUSSION

4.3.1 Effects of impregnation at room temperature

The influence of sodium hydroxide on removal of the major components in hemp woody core was studied, extracting hemp shavings at room temperature. The results are shown in Table 4.1. No cellulose, up to 11 % of the lignin and almost 80% of the xylan was removed (with 2M NaOH). Especially xylan extraction depended on NaOH concentration. This might be explained

by the influence of NaOH on degree of swelling and permeability of lignocellulosic material.

The percentage of xylan in woody core shavings extracted at room temperature is high, as compared with hardwoods and less lignified materials (up to 60% was removed with 2M NaOH, Booker and Schuerch 1958). The lower density (circa 200 kg/m³ for hemp woody core and e.g. circa 460 kg/m³ for poplar wood) may contribute to extractability of xylan.

Quantitative analysis of cellulose is difficult, and the absolute amounts of cellulose may be underestimated (Garleb *et al.* 1989). Swelling and increased permeability of lignocellulosic material, due to impregnation with NaOH, may facilitate cellulose analysis, which may explain the higher value found with 1.06M NaOH (Table 4.1).

Table 4.1

Removal of major components from hemp woody core after impregnation (30 min) and extraction during 80 min in a flow-through reactor at room temperature. Detected dry matter (mean values) as a percentage (w/w) of starting material.

		lignin	cellulose ¹	xylan	yield
Starting material		22.10	37.74	16.65	100 ²
After impregnation and extraction with	0.255M NaOH	21.27	35.54	10.94	79.22
	0.524M NaOH	21.78	36.14	9.28	73.71
	1.06M NaOH	20.71	40.25	6.14	69.59
	2.06M NaOH	19.65	37.07	3.49	65.90

¹ For simplicity all glucan has been assigned to cellulose

² Starting material also contains extractives and acetyl groups, which are removed during impregnation (De Groot *et al.* 1994), and are not studied here.

4.3.2 Degradation of hemp woody core at reaction temperature

The composition of pulps obtained at various reaction conditions was analyzed. These data, together with data from our previous study on delignification of hemp woody core with 1M NaOH (De Groot *et al.* 1994) are shown in Table 4.2 and these were used for modelling of the degradation kinetics of lignin, cellulose and xylan.

4.3.2.1 Delignification

Some lignin was removed during the impregnation process (Table 4.1), while a considerable amount of lignin was removed during the heating up period, with 1M NaOH (De Groot *et al.* 1994).

The fraction of lignin fragments removed during impregnation and heating up period is predominantly released through cleavage of α -O-4 linkages in phenolic units (Gierer 1980), which is independent of NaOH concentration (provided the pH exceeds about 12, to ensure complete enolization). Therefore, the amount of lignin, present after impregnation and heating up period, $a_{2L}+a_{3L}$, is assumed to be equal for all NaOH concentrations used. Both reaction rates k_{2L} and k_{3L} , with which respectively lignin fraction a_{2L} and a_{3L} are removed, are depending on NaOH concentration. Therefore, the following equation was used for the fitting procedure:

$$L/L_0 = a_{2L} \exp(-k_{2L} [\text{OH}]^d t) + a_{3L} \exp(-k_{3L} [\text{OH}]^f t) \quad (4.2)$$

with $k_{iL} = A_{iL} \exp(-E_{a_{iL}}/(RT))$.

Using the data from Table 4.2, this resulted in:

$$L/L_0 = 0.586 \exp(-k_{2L} [\text{OH}]^{0.7} t) + 0.092 \exp(-k_{3L} [\text{OH}]^{0.9} t)$$

with $\ln k_{2L} = 31.99 - 127300/(8.314T)$, $\ln k_{3L} = 25.08 - 108800/(8.314T)$

and $r^2_{\text{adj}} = 94.4\%$. The calculated values are within the ranges of values found for perennial wood. The calculated activation energies for bulk and rest delignification stages are respectively 127.3 ± 11.1 kJ/mol and 108.9 ± 79.2 kJ/mol. The amount of lignin that is involved in the rest delignification is relatively small, and has less influence on the modelling, which explains the high calculated standard error. The fraction removed during impregnation and heating up periods $a_{iL} = 1 - (a_{2L} + a_{3L}) = 1 - (0.586 + 0.092) = 0.322$. All calculated values are within the ranges of values found for delignification with 1M NaOH (De Groot *et al.* 1994). The results are illustrated in Figure 4.1.

Simplifying the equation, assuming both reactions are of first order with respect to NaOH concentration, resulted in an acceptable value for r^2_{adj} : 93.3 %, with $a_{2L}=0.578$, $a_{3L}=0.098$, $\ln k_{2L} = 31.37 - 124800/(8.314T)$ and $\ln k_{3L} = 33.47 - 139800/(8.314T)$. The value for $E_{a_{3L}}$ (139.8 ± 84.1) again has a high calculated standard error, this implies that the chosen value for the best fit can vary much more than the chosen value for $E_{a_{2L}}$ (124.8 ± 10.1). Both fitting procedures result in a value for k_{3L} that is 5 to 8 times smaller than the value for k_{2L} . All calculated values are within the range found in the first fitting procedure.

4.3.2.2 Xylan degradation

During impregnation a substantial amount of xylan can be removed (Table 4.1). The amount of xylan that is left after impregnation is variable, depending on NaOH concentration used (which influences swelling and permeability of the material). This fraction may be removed by extraction and/or degradation and can be described with: $a_{2X} + a_{3X} = b \exp(-c [\text{OH}])$ (4.3)

with c = an overall rate constant (depending on impregnation period and temperature), a_{2X} and a_{3X} representing the two xylan fractions removed at reaction temperature. During the heating up period more xylan can be removed (15% with 1M NaOH, De Groot *et al.* 1994). This may be the result of peeling reactions that are starting during the heating up period and continue at reaction temperature. Possibly, swelling and permeability of the material were increased at higher temperatures, these effects were not studied.

The kinetics of xylan degradation at reaction temperature were modelled with the same approach as was used for the delignification kinetics. The weight fraction of xylan remaining in the lignocellulose matrix, calculated on starting material (X/X_0) can be described with:

$$X/X_0 = a_{2X} \exp(-k_{2X} [\text{OH}]^d t) + a_{3X} \exp(-k_{3X} [\text{OH}]^f t) \quad (4.4)$$

with a_{2X} and a_{3X} representing respectively the fraction of xylan fragments released through peeling (and subsequent extraction) and through alkaline hydrolysis. Removal of xylan was fitted (using the data from Tables 4.1 and 4.2), solving equation (3) and (4) in one routine, which resulted in:

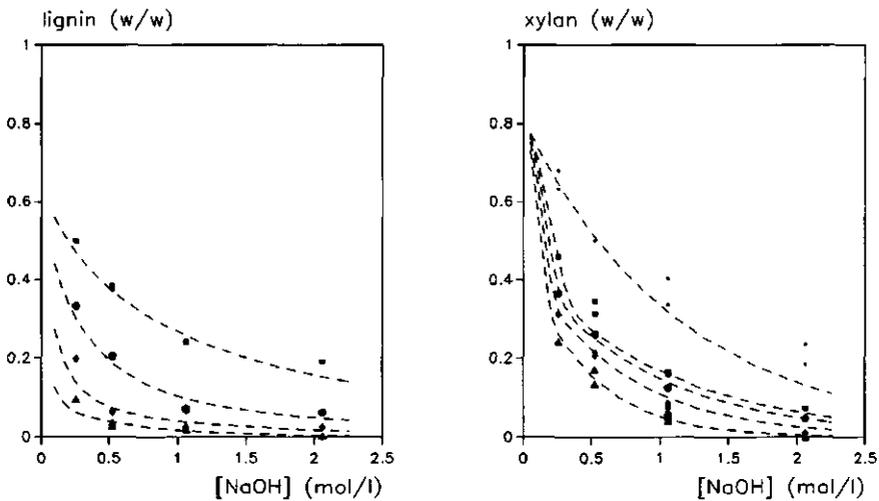


Figure 4.1 (Left) Alkaline delignification kinetics for hemp woody core (shavings) in a flow-through reactor with varying NaOH concentrations, during 80 min, at 150 (■), 160 (○), 170 (◆) and 180 (▲) °C, modelled with 2 simultaneous reactions, using integral calculation (--- model). **Figure 4.2** (Right) Kinetics for alkaline xylan degradation for hemp woody core (shavings) in a flow-through reactor with varying NaOH concentrations, during 80 min, at 20 (□), 150 (■), 160 (○), 170 (◆) and 180 (▲) °C, modelled with 2 simultaneous reactions, using integral calculation (--- model).

$$X/X_0 = a_{2X} \exp(-k_{2X} [\text{OH}]^{2.7} t) + a_{3X} \exp(-k_{3X} [\text{OH}]^{1.1} t)$$

$$\text{with } a_{2X} = 0.375 \exp(-0.884 [\text{OH}]), \ln k_{2X} = 24.65 - 89130/(8.314 T),$$

$$a_{3X} = 0.433 \exp(-0.884 [\text{OH}]), \ln k_{3X} = 36.49 - 152900/(8.314 T)$$

and $r_{\text{adj}}^2 = 94.5\%$. The results are illustrated in Figure 4.2. The first reaction equation has a relatively high reaction rate and the calculated activation energy is low (89.13 ± 31.1 kJ/mol), within the range of the activation energies found for peeling reactions (102.8 kJ/mol, Haas *et al.* 1967; 88.6 kJ/mol, Lai and Sarkanen 1969; varying between 84.4 and 102.4 kJ/mol, Young and Liss 1978). For the second reaction equation a lower reaction rate was found, accompanied with a higher calculated activation energy (152.9 ± 31.1 kJ/mol), which is close to the activation energy for alkaline hydrolysis of glycosidic bonds (150.1 kJ/mol, Lai and Sarkanen 1967).

The fraction of xylan that is assumed to be extracted during impregnation and heating up period is calculated as $a_{1X} = 1 - b \exp(-c[\text{OH}])$, which varies from 0.355 to 0.869 for respectively 0.255M and 2.06M NaOH. The estimated value for k_{2X} is relatively high (0.502 ± 0.331 at 150 °C), implicating that this reaction is completed in an early stage of the process. Consequently, not all values from Table 4.2 are influencing the estimated value for k_{2X} , affecting the accuracy of the estimation. As the calculated dependency on NaOH is very strong, also other mechanisms such as extraction (after peeling) may be involved.

Simplifying the equation, assuming both reactions are of first order with respect to NaOH concentration, resulted also in an acceptable value of 93.7 % for r_{adj}^2 , with $a_{2X} = 0.374 \exp(-1.005[\text{OH}])$, $a_{3X} = 0.475 \exp(-1.005[\text{OH}])$, $\ln k_{2X} = 54.68 - 202300/(8.314 T)$ and $\ln k_{3X} = 37.67 - 157400/(8.314 T)$. The value of $E_{a_{2X}}$ (202.3 kJ/mol) differs considerably from the value found in the first fitting procedure (89.13 kJ/mol). This reflects the mentioned inaccuracy of the estimation of k_{2X} and $E_{a_{2X}}$, due to a limited number of data points influencing the estimation.

4.3.2.3 Cellulose degradation

The kinetics of cellulose degradation were also modelled with the same approach as was used for the description of the delignification kinetics. As little or no cellulose was removed during impregnation (Table 4.1) and heating up periods (De Groot *et al.* 1994), the amount of cellulose present after impregnation and heating up periods was assumed to be the same for all NaOH concentrations used. As most of the cellulose removal will be due to peeling only, the weight fraction of cellulose calculated on starting material (C/C_0) can be described with:

$$C/C_0 = a_{2C} \exp(-k_{2C} [\text{OH}]^d t) \quad (4.5)$$

This resulted for the data from Table 4.2 in: $C/C_0 = 0.922 \exp(-k_{2C} [\text{OH}]^{2.1} t)$, with $\ln k_{2C} = 27.22-124300/(8.314T)$ and $r^2_{\text{adj}} = 90.3\%$. The results are illustrated in Figure 4.3. The calculated activation energy is 124.7 ± 14.9 kJ/mol, which is relatively high for peeling reactions, but relatively low for hydrolysis of glycosidic bonds. Possibly the accessibility of the material (which is low compared with xylan, and may be improved by swelling) has influenced the overall reaction equation.

The results imply that a fraction of $a_{1C}=1-0.922=0.078$ was removed during impregnation and heating up periods. Possibly, this fraction of glucan is part of minor hemicelluloses in hemp woody core (e.g. combined with 1.16% mannan to glucomannan (Glc:Man=2:3, removed when heated up from 100 to 140°C in NaOH, De Groot *et al.* 1994). Simplifying the equation, assuming the reaction is of first order with respect to NaOH concentration, resulted in a considerably lower value of 81.2% for r^2_{adj} , with $a_{2C}=0.945$, $\ln k_{2C}=27.09-122830/(8.314T)$. This implies that this simplified model should not be used.

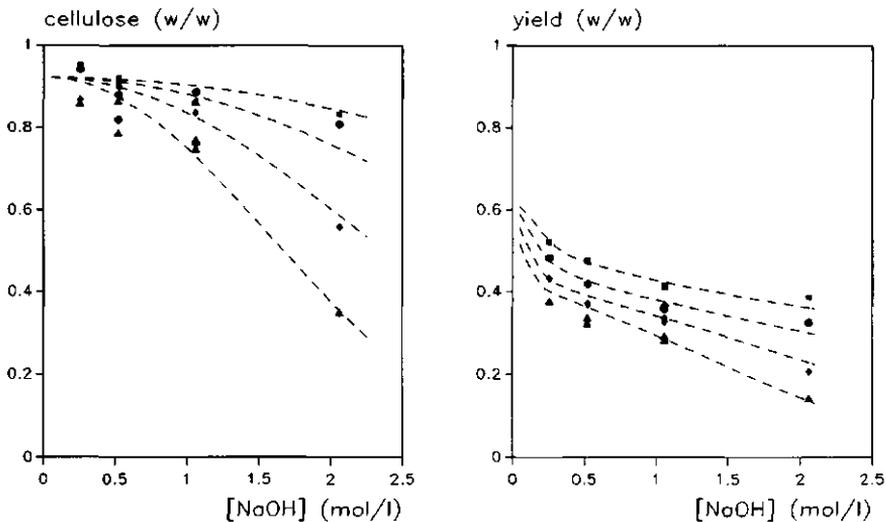


Figure 4.3 (Left) Kinetics for alkaline cellulose degradation for hemp woody core (shavings) in a flow-through reactor with varying NaOH concentrations, at 150 (■), 160 (●), 170 (◆) and 180 (▲) °C, modelled with 1 reaction, using integral calculation (--- model).

Figure 4.4 (Right) Kinetics for alkaline degradation for hemp woody core (shavings): pulp yield in a flow-through reactor with varying NaOH concentrations, during 80 min, at 150 (■), 160 (●), 170 (◆) and 180 (▲) °C, adding reaction equations for degradation of lignin, xylan and cellulose (--- model).

4.3.2.4 Pulp yield

Equations for pulp yield and lignin content of pulps are necessary tools for process control and optimization (Juvekar and Genco 1991) and can be useful for examination of alternative processes, such as extended delignification (Mera and Chamberlin 1988). Pulp yield as fraction of starting material is given by $Y/Y_0 = L/Y_0 + X/Y_0 + C/Y_0$ (4.6)

This can be written as $Y/Y_0 = (L_0/Y_0)*(L/L_0) + (X_0/Y_0)*(X/X_0) + (C_0/Y_0)*(C/C_0)$. With the data in Table 4.1 and the computed models for lignin, xylan and cellulose degradation this leads to:

$$Y/Y_0 = 0.221 * (a_{2L} \exp(-k_{2L} [\text{OH}]^{0.7} t) + a_{3L} \exp(-k_{3L} [\text{OH}]^{0.9} t)) + \\ 0.167 * (a_{2X} \exp(-k_{2X} [\text{OH}]^{2.7} t) + a_{3X} \exp(-k_{3X} [\text{OH}]^{1.1} t)) + \\ 0.377 * (a_{2C} \exp(-k_{2C} [\text{OH}]^{2.1} t))$$

This is illustrated in Figure 4.4. During impregnation and heating up periods 40 - 50% of the material is removed with the used NaOH concentrations.

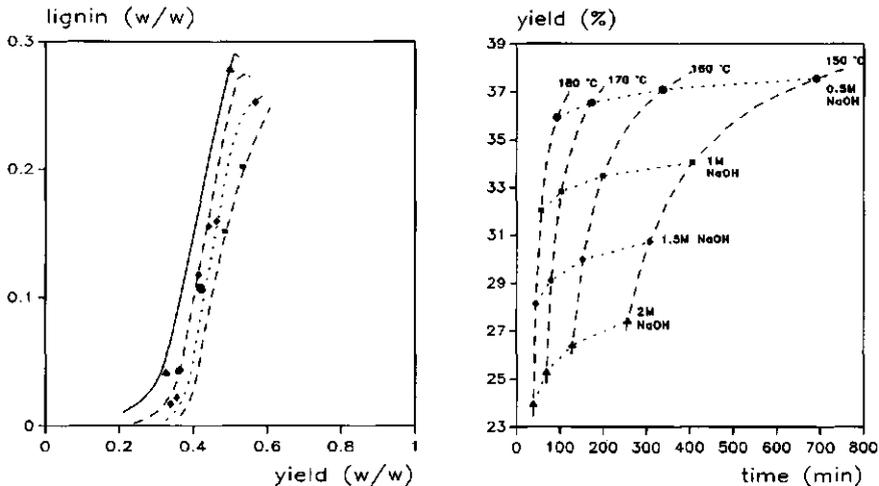


Figure 4.5 (Left) Lignin content versus pulp yield, for hemp woody core (shavings) in a flow-through reactor with 0.255 (■), 0.524 (○), 1.06 (◆) and 2.06 M NaOH (▲) (model: --- 0.255M, 0.524M, --- 1.06M and ___ 2.06M NaOH).

Figure 4.6 (Right) Alkaline delignification of hemp woody core (shavings) in a flow through reactor. Different conditions are needed to obtain a pulp with 2% lignin, using delignification and yield models. Pulp yield versus reaction time, --- isotherms (150, 160, 170 and 180 °C), constant NaOH concentrations (0.5 (●...), 1 (■...), 1.5 (◆...) and 2M NaOH (▲...)).

The influence of NaOH concentration on pulp yield and lignin content is depicted in Figure 4.5. It demonstrates that higher NaOH concentrations result in lower pulp yields at equal lignin contents and that at low lignin contents further delignification is accompanied by relatively high yield losses. Figure 4.6 shows that if a lignin content of 2% on pulp is desired, pulp yields vary with NaOH concentration, reaction time and temperature. Relatively high pulp yields can be obtained with 0.5M NaOH at 180 °C, as compared to higher NaOH concentrations. Lowering the reaction temperature to 160 °C, may raise the pulp yield (with 1%), but has a negative effect on reaction time (which increases from 100 to 340 min). Depending on process costs and pulp prices, different pulping conditions may be optimal for pulp production. Further elaboration of the possibilities to use this yield model for example optimized pulp production is beyond the scope of this chapter.

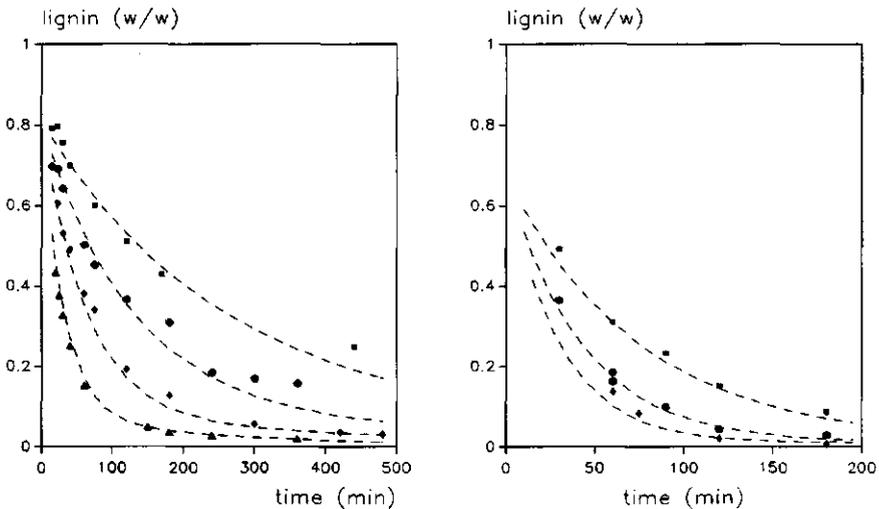


Figure 4.7 (Left) Alkaline delignification kinetics for poplar, with 0.125 (■), 0.25 (●), 0.5 (◆) and 1M NaOH (▲), at 160°C, modelled with 2 simultaneous reactions, using integral calculation. (--- model), data: Labidi 1989.

Figure 4.8 (Right) Alkaline delignification kinetics for spruce, with 1.4 (■), 2.9 (●) and 4.5M NaOH (◆), modelled with 1 reaction equation, (--- model), data: Lusby and Maass 1937.

4.3.3 Application of the modelling approach on literature data

4.3.3.1 Poplar wood

For poplar wood, data were used on delignification in a flow-through reactor with 0.125, 0.25, 0.5 and 1.0M NaOH at 160 °C and with 1.0M NaOH at 130, 140 and 170 °C (Labidi 1989). Unfortunately these data are not accompanied with yield data, hence the modelling approach could only be tested for delignification kinetics. The data were fitted with the integral calculation method, in the same way as the data for delignification of hemp woody core, resulting in:

$$L/L_0 = 0.686 \exp(-k_{2L} [\text{OH}^-]^{1.2} t) + 0.066 \exp(-k_{3L} [\text{OH}^-]^{1.2} t)$$

$$\text{with } \ln k_{2L} = 42.29 - 164400/(8.314T), \ln k_{3L} = 29.67 - 132690/(8.314T)$$

and $r^2_{\text{adj}} = 99.5\%$. Labidi used stepwise modelling, and restricted modelling to the experimental data at 160 °C. The results obtained with the integral calculation method are close to the results found by Labidi and the model is applicable on the range of reaction temperatures used. The fitting results are illustrated in Figure 4.7, for the data at 160 °C.

4.3.3.2 Spruce

There are no recent data published on alkaline delignification of softwood with varying NaOH concentrations. Some older data for delignification of spruce with 1.4, 2.9 and 4.5 M NaOH (Lusby and Maass 1937) could be fitted with:

$$L/L_0 = 0.695 \exp(-k_{2L} [\text{OH}^-]^{0.67} t) + 0.004$$

$$\text{with } \ln k_{2L} = 27.23 - 114200/(8.314T),$$

($r^2_{\text{adj}} = 98.2\%$), which is illustrated in Figure 4.8.

The data were accompanied by pulp yield figures, which could be fitted with the same method, resulting in:

$$Y/Y_0 = (0.589 \exp(-k_{2Y} [\text{OH}^-]^{0.61} t) + 0.122$$

$$\text{with } \ln k_{2Y} = 38.47 - 159500/(8.314T)$$

and $r^2_{\text{adj}} = 96.8\%$, which is illustrated in Figure 4.9. The major components of spruce wood are cellulose, lignin, glucomannan and xylan (Aurell and Hartler 1965). Degradation of the different components could be fitted with a simple overall equation. Remarkably, the lignin:carbohydrates ration is not affected by the NaOH concentration used. Furthermore, NaOH concentration seems to have less influence on carbohydrate degradation in spruce than in hemp woody core, as the exponent in the equation for spruce yield is relatively low. In Figure 4.10 lignin content on pulp versus pulp yield is depicted, for 1.4, 2.9 and 4.5M NaOH, at 160 °C.

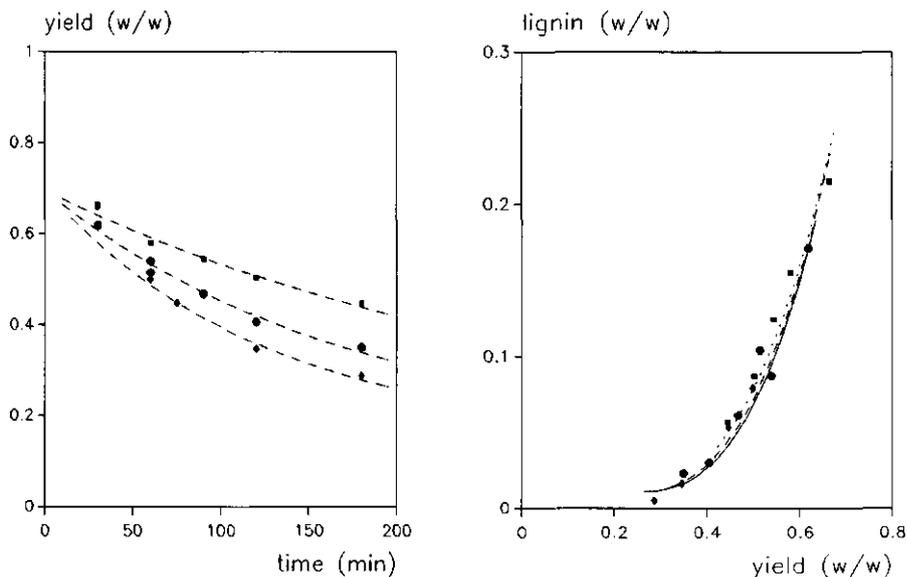


Figure 4.9 (Left) Kinetics for alkaline degradation for spruce: pulp yield in a flow-through reactor with 1.4 (■), 2.9 (●) and 4.5M NaOH (◆), modelled with 1 reaction equation, (--- model), data: Lusby and Maass 1937. **Figure 4.10** (Right) Lignin content versus pulp yield, for spruce in a flow-through reactor with 1.4 (■), 2.9 (●) and 4.5M NaOH (◆), (model: 1.4M, --- 2.9M, ___ 4.5M), data: Lusby and Maass 1937.

It can be noticed that here, higher NaOH concentrations result in equal pulp yields at equal lignin contents. This is different from the results found for hemp. It would be interesting to repeat this study for lower NaOH concentrations, to find out whether this behaviour is a result of the material used. Possibly, maximal swelling is attained with 1.4 M NaOH with this material. If, at lower NaOH concentrations lower amounts of hemicellulose are removed (as a result of less swelling and extraction), higher pulp yields may be obtained using lower NaOH concentrations.

4.4 CONCLUSIONS

Xylan extraction and/or degradation plays an important role in alkaline pulping of hemp woody core, especially when high-yield pulps are to be produced. The reaction equations as found for hemp woody core have not been described in literature for continuous pulping of wood with

sodium hydroxide, possibly this is characteristic for (dicotyledonous) annual fibre crops, like hemp. In contrast with older data on softwoods (Lusby and Maass 1937), to attain a certain lignin content, lower NaOH concentrations (using longer reaction periods) result in higher pulp yields.

The modelling approach here described can be used for development and control of new alkaline pulping processes, or testing new pulping materials, such as annual crops. This will be elaborated further (for example: optimization is possible on yield, energy use, developed strength, pollution load) and published separately.

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NOMENCLATURE

A_{iJ}	= constant (= k_{∞})	[-]
C	= cellulose in pulp, as fraction of starting material (w/w)	[-]
C_0	= fraction of cellulose in starting material (w/w)	[-]
Ea_{iJ}	= activation energy	[J/mol]
L	= lignin in pulp, as fraction of starting material (w/w)	[-]
L_0	= fraction of lignin in starting material (w/w)	[-]
R	= gas constant = 8.314	[J/(mol.K)]
T	= absolute temperature	[K]
X	= xylan in pulp, as fraction of starting material (w/w)	[-]
X_0	= fraction of xylan in starting material (w/w)	[-]
Y	= pulp yield, as fraction of starting material (w/w)	[-]
Y_0	= 100 % (total fraction of starting material (w/w))	[-]
a_{iJ}	= fraction participating in each reaction	[-]
b	= fraction of xylan, remaining in pulp after impregnation (w/w)	[-]
c	= overall rate constant	[-]
d	= exponential value	[-]
f	= exponential value	[-]
k_{iJ}	= reaction rate constant = $A_{iJ} \exp(-Ea_{iJ}/RT)$	[1/min.(l/mol) ^d]
[OH ⁻]	= OH ⁻ concentration	[mol/l]
t	= time	[min]
suffixes:		
i	= 1, 2 or 3	
J	= C (cellulose), L (lignin), X (xylan) or Y (yield)	

Table 4.2

Removal of major components from hemp woody core during bulk and residual delignification stages, in a flow-through reactor. Detected dry matter as a percentage (w/w) of starting material, in relation to sodium hydroxide concentration ([NaOH]), temperature (T) and reaction time (t), n.d.= not determined.

nr.	[NaOH] (mol/l)	T (°C)	t (min)	Yield (% w/w)	Lignin (% w/w)	Cellulose ¹ (% w/w)	Xylan (% w/w)
1	0.255	150	40	56.60	12.80	35.30	8.39
2	0.255	150	80	52.26	11.02	35.92	7.66
3	0.255	160	40	53.33	10.80	35.48	8.13
4	0.255	160	80	48.40	7.33	35.51	6.08
5	0.255	170	40	46.86	6.63	n.d.	n.d.
6	0.255	170	80	43.29	4.34	32.75	5.20
7	0.255	180	40	42.77	3.64	35.10	5.71
8	0.255	180	80	37.70	2.09	32.40	4.01
9	0.524	150	80	47.86	8.28	34.15	5.21
10	0.524	150	80	47.51	8.47	34.76	5.72
11	0.524	160	80	41.85	4.52	33.21	4.34
12	0.524	160	80	42.02	4.46	n.d.	n.d.
13	0.524	170	80	37.14	1.37	33.89	3.42
14	0.524	170	80	36.94	1.44	34.49	3.54
15	0.524	180	80	33.71	0.77	32.60	2.85
16	0.524	180	80	32.36	0.58	29.65	2.22
17	1.06	150	4.5	58.59	15.67	39.24	3.89
18	1.06	150	10	53.89	13.28	36.71	3.47
19	1.06	150	20	51.10	12.03	35.57	2.73
20	1.06	150	40	43.30	6.87	36.01	2.33
21	1.06	150	80	44.57	5.36	n.d.	n.d.
22	1.06	150	80	41.58	5.29	37.94	2.66
23	1.06	150	80	40.96	5.32	38.59	2.75
24	1.06	150	160	39.87	2.80	28.95	2.03
25	1.06	150	210	35.91	1.48	30.61	1.69
26	1.06	160	4.5	56.54	14.29	38.28	3.49
27	1.06	160	20	46.11	7.37	33.78	2.54
28	1.06	160	30	44.02	6.86	35.14	2.79
29	1.06	160	40	41.35	4.87	n.d.	2.32
30	1.06	160	80	35.81	1.52	33.47	2.08
31	1.06	160	80	36.37	1.58	34.78	2.07
32	1.06	160	160	35.44	0.77	31.53	2.02
33	1.06	160	240	33.73	0.57	29.27	1.69

¹For simplicity all glucan has been assigned to cellulose

Table 4.2 (continued)

nr.	[NaOH] (mol/l)	T (°C)	t (min)	Yield (% w/w)	Lignin (% w/w)	Cellulose ¹ (% w/w)	Xylan (% w/w)
34	1.06	170	5	55.10	13.86	n.d.	n.d.
35	1.06	170	5	54.92	13.08	38.92	3.39
36	1.06	170	5	54.14	13.34	38.36	2.92
37	1.06	170	10	45.14	8.36	32.62	2.30
38	1.06	170	10	49.53	n.d.	30.74	2.45
39	1.06	170	20	43.69	3.46	32.55	2.21
40	1.06	170	20	40.34	5.13	30.13	2.31
41	1.06	170	40	35.68	2.22	29.59	2.26
42	1.06	170	80	32.82	0.53	32.63	1.23
43	1.06	170	80	33.56	0.56	31.53	1.40
44	1.06	170	140	32.96	0.50	28.15	1.46
45	1.06	170	160	30.55	0.67	n.d.	1.25
46	1.06	170	180	31.30	0.57	27.92	1.26
47	1.06	180	5	51.76	11.57	n.d.	n.d.
48	1.06	180	5	51.78	12.18	38.54	2.44
49	1.06	180	7	51.95	11.98	34.70	3.03
50	1.06	180	10	41.12	3.40	34.24	1.90
51	1.06	180	15	36.96	2.53	31.29	1.79
52	1.06	180	20	33.76	0.93	32.70	1.86
53	1.06	180	40	34.61	0.51	29.28	1.37
54	1.06	180	80	28.58	0.27	28.15	0.94
55	1.06	180	80	30.63	0.38	32.52	1.03
56	1.06	180	80	29.23	0.44	28.80	0.82
57	1.06	180	80	28.24	0.41	29.01	0.66
58	1.06	180	160	21.36	0.13	20.60	0.44
59	2.06	150	10	52.00	15.83	33.54	1.33
60	2.06	150	80	38.60	4.20	33.55	1.19
61	2.06	160	10	49.71	13.85	35.02	1.45
62	2.06	160	80	32.56	1.36	30.49	0.78
63	2.06	170	10	45.93	9.93	36.91	0.99
64	2.06	170	80	20.59	0.52	21.06	0.14
65	2.06	180	10	41.78	7.74	33.01	0.93
66	2.06	180	80	14.18	0.05	13.21	0.0

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5. ALKALINE HEMP WOODY CORE PULPING: PULP AND PAPER CHARACTERISTICS

SUMMARY

Strength and surface properties of test sheets, produced from alkaline hemp woody core pulp were examined. The development of bulk and tear with beating are similar as found for straw pulp; maximum tear strength is attained without beating. Burst and tensile strength, scattering and opacity develop similarly as for hardwood pulps, with less mechanical energy needed. Tear strength is not affected by pulp yield or composition, whereas lower tensile and burst strength are found with decreased yield and lower xylan content. As the paper strength and surface properties of hemp woody core pulp are comparable with those for hardwood and straw pulps, it is conceivable that similar amounts of alkaline hemp woody core pulp can be used in pulp mixes for printing paper grades.

The polymerization degree (DP) of hemp woody core pulps is related to the paper strength properties, and modelled as function of pulping conditions and time. The influence of NaOH concentration on depolymerization and cellulose degradation is much stronger than reported for wood pulps. This may be related to the low density of hemp woody core, preventing diffusion effects.

Finally, crystallinity was examined and related to cellulose degradation of alkaline hemp woody core pulp.

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This chapter is submitted for publication

5.1 INTRODUCTION

Recently, the kinetics of alkaline delignification of hemp woody core were described and modelled, and phenomena related to alkaline swelling were studied (De Groot *et al.* 1994; 1995; 1997). Hemp woody core fibres are chemically and botanically related to hardwood fibres (De Groot *et al.* 1994). Typically, hardwood pulps have good opacity and formation properties, but display lower strength than softwood pulps. Bleached hardwood and softwood pulps are used in equal amounts in fine paper and printing paper grades (Rydholm 1985a,n; Kocurek 1989; Baker 1995).

In general, fibre bonding and fibre length are influencing paper strength. Fibre bonding determines tensile and burst strength, while fibre length is important for tear strength (Rydholm 1985m; Strand *et al.* 1994; Saltin and Strand 1992; Seth and Page 1988; Page 1994). Physical treatments like beating generate fibres with fibrillated surfaces and produce more flexible fibres, conforming more easily to the shape of neighbouring fibres. This results in enhanced interfibre bonding, improved wet-web, tensile and burst strength and diminished paper bulk (Atack 1978; Iyengar 1982; Rydholm 1985i; Jimenez *et al.* 1993; Dasgupta 1994; Broderick *et al.* 1996).

Paper surface properties like scattering (ability of a paper surface to scatter incoming light) and opacity (degree in which the fibre surfaces prevent light transmission through the sheet) are determined by unbound surface (Clark 1985h; Rydholm 1985j; Strand *et al.* 1994). Increased interfibre bonds result in less unbound surface and less scattering (Stratton 1991), and decreased opacity as fibres merge into one another (Rydholm 1985j). Opacity and scattering have been related to paper density, tensile and burst strength (Rydholm 1985i; Dasgupta 1994).

For wood pulps, strength properties increase with decreased pulp yield until maximum tensile strength is reached, at about 60% yield, while tear strength rises further (Rydholm 1985b,c). The three main chemical effects of pulping are delignification, hemicellulose dissolution and depolymerization of remaining carbohydrates (Rydholm 1985c). The cellulose fraction of the cell wall carries the stress load, while the hemicellulose-lignin matrix distributes the stress among the fibres (Gumagul *et al.* 1992). Lignin is essentially hydrophobic and predominantly present at fibre surfaces. Lignin removal contributes to the development of interfibre bonds on beating (Rydholm 1985c,i,o; Clark 1985b,g). Hemicelluloses increase the area of interfibre contact, participating in interfibre bonds and filling out minor void spaces at the contact areas. This improves interfibre bonding and strength properties which mainly depend on it, such as tensile

and burst strength (Rydholm 1985k). During pulping, some cell wall carbohydrates dissolve and partly degrade, resulting in fibre weakening. Important degradation reactions for polysaccharides are peeling (chemical degradation initiated at reducing-end groups) and alkaline hydrolysis of glycosidic linkages, resulting in secondary peeling reactions (Fengel and Wegener 1984; Sjöström 1993). On prolonged cooking, carbohydrate degradation and lower tensile and burst strength of paper are found.

Yield losses of polysaccharides are assumed to be determined by peeling reactions, while hydrolytic reactions will primarily lead to a lower polymerization degree (DP). In general, all strength properties decrease with decreasing DP, especially tear strength. DP is an indication of the degradation of high-molecular carbohydrates, mainly cellulose. However, at high DP levels relatively high lignin contents may lower the paper strength (Rydholm 1985d,g,p). Usually, paper with satisfactory strength can be produced with pulps with a DP of 500 or higher (Clark 1985a). During pulping, crystallinity of cellulose may be raised as amorphous parts are degraded relatively easily. Prolonged pulping may damage cellulose fibres, resulting in lowered crystallinity. (Newman *et al.* 1993). The degree of crystallinity can be estimated from X-ray diagrams. Cotton, and bast fibres of flax and ramie are 70% crystalline, wood pulps about 65% (Stamm 1964; Fengel and Wegener 1984). Native cellulose I can be changed into hydrated or mercerized cellulose II with concentrated sodium hydroxide solutions (Stamm 1964; Sjöström 1993). This is accompanied with reduced bonding between the structural chains and increased penetrability and reactivity of the structure. The chain conformation of cellulose I enables the formation of two intramolecular hydrogen bonds, parallel to the glycosidic linkage. The chain formation of cellulose II allows only one similar bond, resulting in strength loss (Kroon-Batenburg *et al.* 1990).

Whether the described knowledge on wood pulps in relation to paper qualities applies to alkaline hemp woody core pulp and paper, is examined in this article. Furthermore, the papermaking potentials of this pulp are established in relation to commercial straw and hardwood pulps.

5.2 MATERIAL AND METHODS

1000 g of dry (pulps A, B, C and E) or presteamed hemp woody core chips (pulps D, D bleached, F, F bleached, G, and G bleached, chip length: 12.1 mm, width: 3.8 mm, thickness: 1.3 mm, all averages), were impregnated during 16 hours with 15 l NaOH solution (technical grade,

concentrations specified in tables 1 and 2) at 20 °C, to remove the air prior to cooking and to attain equal NaOH concentration throughout the chips. The pulping experiments A-G were carried out at 168 °C, in a rotating cooker of 85 l, with 25 l cooking liquor (10 l were added to the impregnation liquor and hemp woody core chips in the cooker).

About 400 g (dry weight) of pulps D, F and G was bleached, with a starting consistency of about 15% (pulp on liquor, w/w), using an H-E/H-P bleaching sequence. Hypochlorite stage (H): 12% sodium hypochlorite (on pulp, w/w) was applied, with addition of 3% NaOH, to maintain alkaline conditions, the consistency was lowered to 10% with hot tap water. The pulp was bleached at 70 °C, during 1 hour, with frequent mixing (every 15 min). Extraction stage (E/H): After washing, the pulp was dewatered by thorough pressing, 3% NaOH (on pulp, w/w) was used, with addition of 0.3 % sodium hypochlorite, the consistency was lowered to 10% with hot tap water. The pulp was extracted at 70 °C, during 1 hour, with frequent mixing (every 15 min). Peroxide stage (P): After washing, the pulp was dewatered by thorough pressing and impregnated with 6% H₂O₂ (added as last ingredient), 3% sodium silicate (technical grade), 3% NaOH (technical grade) and 0.5% DTPA (Dissolvine D40, technical grade), consistency was 10%. The pulp was bleached at 70 °C, during 90 minutes, with frequent mixing (every 15 min). The bleached pulp was washed with hot tap water until neutral. The used recipe was based on preliminary trials and literature data (Singh 1979a,c-f).

Separate samples (in twofold) were used to determine: Dry matter content (TAPPI Standard Method T264), carbohydrate composition, Klason (TAPPI Standard Method T222) and acid soluble lignin (TAPPI Useful Method 250). Carbohydrate composition was analyzed with HPLC, using pulsed amperometric detection and a gold electrode. The monosaccharides were separated on a Dionex anion exchange column (Carbo PAC PA1), with a NaOH gradient as eluent. Fucose was used as internal standard.

For DP measurements, also pulps delignified in a flow-through reactor (De Groot *et al.* 1994; 1995) were used. DP was measured according to TAPPI Standard Method T230. DP is calculated as function of intrinsic viscosity $[\eta]$, equalling $[\eta]/0.42$ for $[\eta] \leq 450$ ml/g, while $DP^{0.76} = [\eta]/2.29$ for $[\eta] > 450$ ml/g (Marx-Figini 1978; 1982). As reference pulp standard bleached kraft was used, with a DP of 2016. Some pulps (see table 2) were pretreated during 3 hours with sodium chlorite, as described by Wise *et al.* (1946), to remove lignin, as for pulps with higher lignin content measurement of viscosity is difficult (Rydholm 1985h).

Crystallinity was measured using wide angle X-ray spectroscopy (WAXS) diffractograms with the method of Hermans and Weidinger (1949), as described by Hulleman *et al.* (1994).

Fibre length was measured with a Kajaani FS-200 optical analyzer, in accordance with TAPPI Standard Method T271.

Further physical pulp and paper characteristics were determined using ISO 5267 (Determination of drainability - part 1: Schopper-Riegler method), TAPPI Standard Methods T248 (Laboratory beating of pulp (PFI mill method)), T205 (Forming handsheets for physical tests of pulp), T220 (Physical testing of pulp handsheets), T411 (Thickness (caliper) of paper, paperboard and combined board), T414 (Internal tearing resistance of paper (Elmendorf-type method)), T494 (Tensile breaking properties of paper and paperboard (using constant rate of elongation apparatus)), T403 (Bursting strength of paper), T452 (Brightness of pulp, paper and paperboard (directional reflectance at 457 nm)), T425 (Opacity of paper, scattering coefficient).

For kinetic modelling the non linear routines of Genstat 5, a general statistical program (Digby *et al.* 1989), have been used. The accuracy with which a calculated model fits experimental data is given by r^2_{adj} , the percentage of variance accounted for, adjusted for the number of parameters.

5.3 RESULTS AND DISCUSSION

Table 5.1

Pulps tested. All pulps were delignified at 168 °C, with NaOH and during reaction time as specified. Yield is calculated as percentage (w/w) of starting material, xylan and lignin contents are calculated as percentage (w/w) of pulp.

	time (min)	[NaOH] (mol/l)	yield (%)	xylan (%)	lignin (%)	DP (units)
pulp A	54	0.55	54.89	13.57	10.94	2755
pulp B	67	0.80	41.53	10.83	7.08	2459
pulp C	100	0.89	38.12	10.63	4.80	1749
pulp D	85	1.13	34.00	4.47	3.98	666
pulp D, bleached ¹	85	1.13	32.73	4.01	1.41	504
pulp E	56	2.48	24.45	2.91	2.43	378
pulp F, bleached ^{1,2}	96	1.13	29.51	4.30	1.29	444
pulp G, bleached ^{1,2}	91	1.13	30.28	4.05	1.38	480

¹ Bleached with H-E-H-P sequence as described in Material and Methods

² For pulps F bleached and G bleached no PFI-beating curves were made, the characteristics of the unbeaten pulp will be used in paragraph 5.3.5.

5.3.1 Pulp characteristics

The applied pulping conditions and the resulting characteristics of hemp woody core pulps used for paper tests are presented in table 5.1. The fibre length of unscreened, bleached pulp D bleached was measured with a Kajaani FS-200 optical analyzer. The pulp has a rather short weight averaged fibre length of 0.61 mm, 86.2% (weight averaged) of the fibres are longer than 0.25 mm, which is a little less than found for kraft hardwood cellulose (87-97%) and more than found for straw cellulose (82%). Short fibres length may contribute to lower tear (Page 1994) and wet-web strength (tensile and stretch), reducing the runnability on a paper machine (Seth 1995). However, in pulp mixes short fibres also improve mass uniformity and paper formation, contributing to wet-web properties (Kerekes and Schell 1995) and improving printability in fine paper and printing paper grades (Baker 1995). This suggests that adding a certain amount of hemp woody core fibres to a pulp mix may be beneficial.

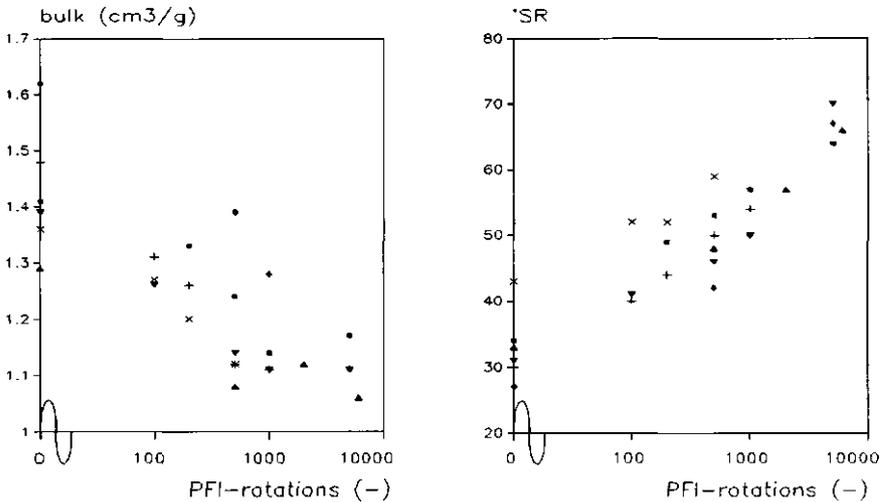


Figure 5.1 (Left) Bulk of hemp woody core test sheets diminishing with number of PFI-rotations, for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

Figure 5.2 (Right) Schopper-Riegler freeness increasing with number of PFI-rotations for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

5.3.2 Beating response: bulk and freeness

Figure 5.1 shows how bulk (specific volume) of hemp woody core pulp changes with number of rotations in a PFI mill. Bulk values are known to vary from $1 \text{ cm}^3/\text{g}$ for extremely well beaten pulp to $1.8 \text{ cm}^3/\text{g}$ for unbeaten chemical pulp (Clark 1985d), and give an indication of the dewatering characteristics of a pulp on a paper machine. The strength of hemp pulp develops very easily, as bulk is reduced from about 1.5 to $1.2 \text{ cm}^3/\text{g}$ within only 500 PFI rotations, while normally for hardwood pulps 2000 PFI rotations are required. In this respect the pulp is comparable with straw pulp, known to develop with a similar ease. Low bulk indicates that wet pulp is very compactable and that very smooth paper can be formed. Figure 5.1 also shows that mild delignification (pulp A) results in higher initial bulk, diminishing rapidly with further beating.

Figure 5.2 illustrates how freeness of hemp woody core pulp changes with number of rotations in a PFI mill. Freeness is a characteristic measuring the water drainage of diluted pulp. Correlations of freeness with bulk may be found (when applied to similar pulps, beaten with the same kind of beating, Clark 1985f). Bulk and freeness of the tested hemp woody core pulps develop similarly, until bulk is diminished to around $1.1 \text{ cm}^3/\text{g}$ after about 1000 PFI-rotations. However, with more beating, bulk values remain around $1.1 \text{ cm}^3/\text{g}$ while freeness values still increase. This may be the result of increased amounts of fines. In general, freeness can be raised significantly by the presence of debris and filler, while no noticeable differences in drainage time and runnability on the paper machine are found (Clark 1985c).

5.3.3 Strength and surface properties in relation to PFI beating

The tear factor is around $3.5 \text{ mN}\cdot\text{m}^2/\text{g}$, which is about 50% lower than found for hardwood). This low tear strength, expected for short fibred material, diminishes slightly with longer beating (figure 5.3). The tear values found for pulp E are very low (around $2 \text{ mN}\cdot\text{m}^2/\text{g}$), indicating that this pulp may be cooked too severely, affecting its fibre strength.

Highest tear strengths are found for unbeaten pulp, suggesting that delignified unbeaten hemp woody core fibres cohere adequately, which is similarly found for straw pulp (Clark 1985e), with tear values in the same range. The cohesion of unbeaten hardwood and softwood fibres is often too low to distribute the tear load effectively. Beating improves cohesion; tear strength of these pulps first increases, before it diminishes with further beating (and with some fibre shortening).

Figures 5.4 and 5.5 show that tensile and burst strength of the hemp woody core pulps develop very rapidly, after 500 PFI rotations maximum tensile strength is attained for most pulps. The burst

factor slightly increases further with more beating, probably the result of both improved stress distribution and better fibre interaction (Dasgupta 1994, Seth 1995). The measured tensile and burst values are in the ranges of straw pulp (respectively 6-8 km and 3-5 kPa.m²/g) and bleached hardwood kraft pulp (respectively 7-10 km and 4-7 kPa.m²/g).

Figure 5.6 shows that the scattering coefficient for all hemp woody core pulps diminishes with beating (less unbound surface). The scattering coefficients for both bleached and unbleached pulp D decrease from 38 to 33 %, confirming that the effect of bleaching agents hardly affect light scattering (Singh 1979b). Diminished scattering and opacity with increased beating (figures 5.6 and 5.7) correspond with increased density (decreased bulk) and burst strengths (figures 5.1 and 5.5), which has also been found for wood pulps (Stratton 1991; Rydholm 1985; Dasgupta 1994). Tensile strength (figure 5.4) diminishes after attaining maximum tensile strength, which may be related to damaged fibre structure and reduction in fibre strength on prolonged beating, Dasgupta 1994).

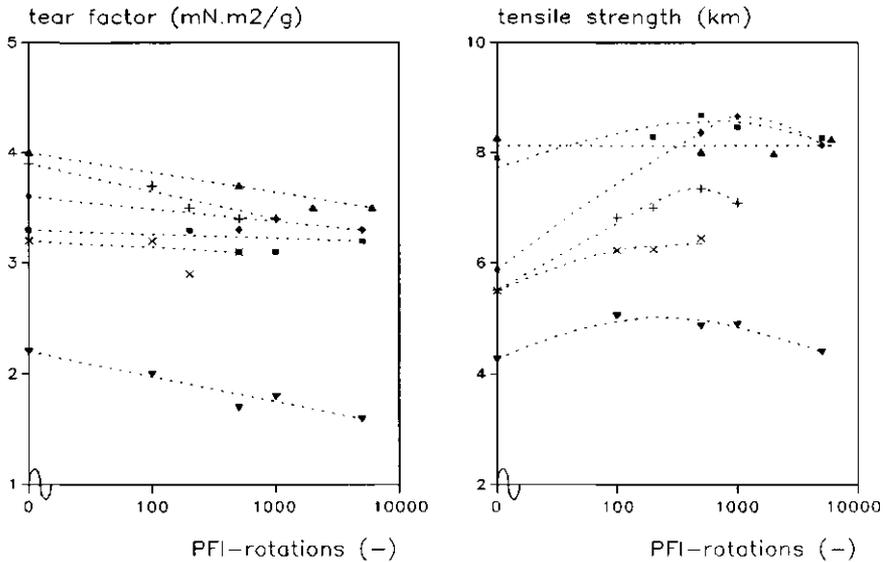


Figure 5.3 (Left) Tear factor slightly diminishing with number of PFI-rotations for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

Figure 5.4 (Right) Tensile strength developing with number of PFI-rotations for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

5.3.4 Strength and surface properties in relation to pulp yield and pulp composition

The tear strength of hemp woody core pulp is not strongly affected by pulp composition (figure 5.3 and table 5.1). In this respect hemp woody core pulp is unlike hardwood and softwood pulps, where decreasing pulp yields correspond with increasing tear strengths (Rydholm 1985b,c). The lower tear strength of pulp E may be related to cellulose degradation and change in crystal lattice (see 5.3.6).

Approximately equal tensile strengths (about 8 km) are found for pulps A, B and C (with yields decreasing from 55 to 38%). The lower yields of pulps D, D bleached and E (respectively 34, 33 and 24%) correspond with lower tensile strengths (about 7, 6 and 5 km respectively, figure 5.4). A similar pattern is found for softwood and hardwood pulps (Rydholm 1985b,c). The lower tensile strength of pulps D, D bleached and E may be related to lower xylan contents (respectively 4.3, 4.0 and 2.9%, table 5.1) and decreased interfibre bonding.

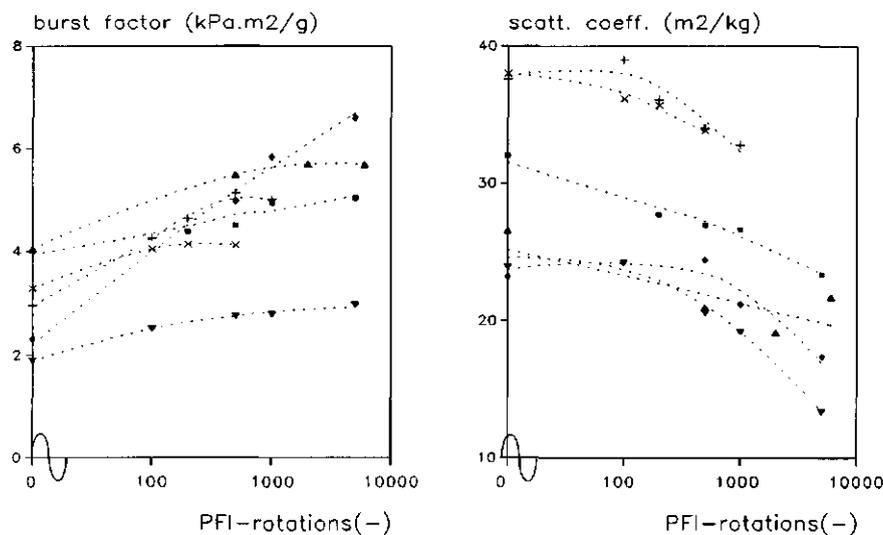


Figure 5.5 (Left) Burst factor developing with number of PFI-rotations for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

Figure 5.6 (Right) Scattering factor decreasing with number of PFI-rotations for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼).

A similar relation for burst strength and pulp yield is expected and found: lower pulp yields correspond with lower burst strengths (table 5.1 and figure 5.5). Beating has a strong impact, especially on pulp A (with a relative high lignin content of 14%), needing more beating to obtain maximum burst strength, than to develop maximum tensile strength.

In general, the specific scattering coefficient is hardly altered by changes in bleaching or pulping conditions, unless the content of hemicelluloses (and the pulp yield) is affected (Rydholm 1985f). Increased scattering has been found with lower yields (34 and 33%) for unbleached and bleached pulps D (figure 5.6), with relatively low xylan contents. Also, these higher scattering coefficients correlate with lower tensile strengths of pulps D and D bleached (figure 5.4), which is expected (higher scattering coefficients are indicative for lower bonding). However, as pulp E with lower yield and xylan content, displays low tensile strength and low scattering (figures 5.4 and 5.6), also other factors (like cellulose degradation) may be important for light scattering.

The levels of brightness of hemp woody core pulp (figure 5.7) are in the range as reported for unbleached kraft and semi-bleached kraft hardwood pulps (respectively 40 and 75%, Rydholm 1985e). The arrows in figure 5.7 indicate the direction of change in opacity and brightness with increased beating. Typically, brightness and opacity are influenced by the removal of coloured materials (condensed and degraded lignin), and by beating, influencing the area of unbound fibre surfaces remaining available for light scattering (Singh 1979g, Rydholm 1985f). Both brightness and opacity of the hemp woody core pulps diminish with beating. However, these changes are small compared to the different levels of brightness found for pulp D bleached (with a lignin content of 1.4%), pulps C, D and E (with lignin contents between 2 and 5%), and pulps A and B (with lignin contents of 11 and 7%). Thus, relatively high lignin contents (pulps A and B) seem to influence brightness more than PFI-beating does. Bleaching drastically increases brightness and decreases opacity (some lignin is removed and coloured components are bleached). Opacity of pulps A, B, C, D and E are in the same range, all opacity values are lowered with PFI-beating.

5.3.5 DP

In figure 5.8 maximum tear factor, tensile and burst strength, as measured for the pulps described in table 5.1, are plotted against the polymerization degree (DP). In general, all strength properties of a pulp decrease with decreasing DP (Rydholm 1985g,p). For hemp woody core pulp, the impact on paper strength (and especially on tear factor) appears to be negligible when DP is higher than 1000.

In figure 5.9, DP of unbleached pulps A-G and 1-15 (table 5.2) are plotted against pulp yield. DP

values first rise with decreasing yield, which may be the effect of hemicellulose dissolution and increased average DP of the remaining carbohydrates. Thereafter, DP diminishes with decreasing yield and more severe pulping conditions. Consequently, DP was first modelled as function consisting of two degradation terms, both depending on pulping variables (absolute temperature T , NaOH concentration $[OH]$ and time t). However, modelling the data with a two-term function was not successful. It was concluded that hemicellulose dissolution can not be modelled with the present data set (only two datum points are in the area where DP rises with diminishing yield). The datum points are fitted with a function consisting of only one degradation term. The omission of the values of pulps 1 and 2, and adding a constant improving the fitting, DP of pulps A-G and 3-15 is modelled with:

$$DP = a_{DP} \exp(-k_{DP} [OH]^f t) + d \quad (5.1)$$

with $\ln k_{DP} = \ln A_{DP} - E_{a_{DP}}/(8.314 T)$

This resulted in:

$$DP = 2403 \exp(-k_{DP} [OH]^{2.2} t) + 512$$

with $\ln k_{DP} = 48.23 - 193000/(8.314 T)$

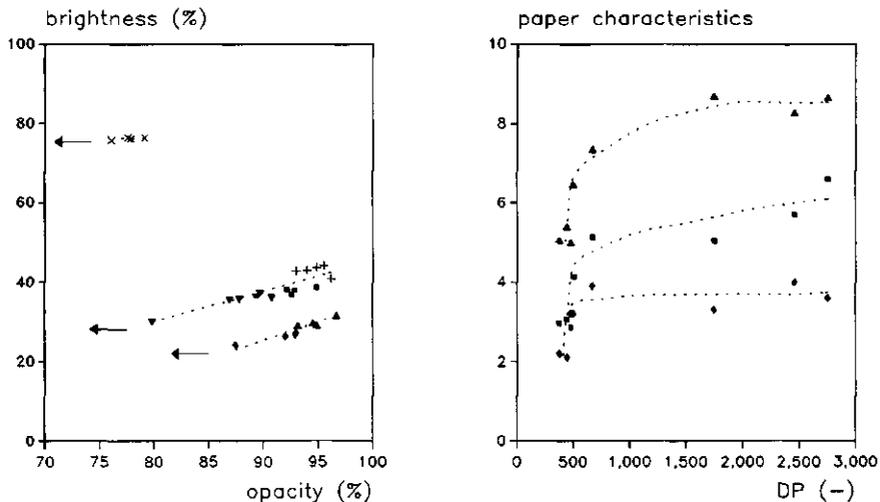


Figure 5.7 (Left) Brightness and opacity development for pulps A (♦), B (▲), C (■), D (+), D bleached (x) and E (▼). **Figure 5.8 (Right)** Paper characteristics in relation to DP for pulps A-E, D bleached, F bleached and G bleached (described in table 5.1): tensile strength (▲) in km, burst factor (■) in kPa.m²/g and tear factor (♦) in mN.m²/g.

with $r^2_{adj} = 87.9\%$ and estimated standard error of observed DP values (s/\sqrt{n}) = 329. The added constant $d = 512 \pm 201$ suggests that a certain fraction of the cellulose, with 512 glucose units per polymer is more resistant than the bulk of the material. This is also reported for wood pulps treated with dilute acid, resulting in a leveling-off degree of polymerization between 150 and 300 (Fengel and Wegener 1984).

The calculated activation energy 193.0 ± 40 kJ/mole is within the range of 179 kJ/mol (Kubes *et al.* 1983) calculated for diminishing pulp viscosity of unbleached alkaline black spruce pulp.

The NaOH concentration is very important for cellulose depolymerization, as it is for cellulose degradation of hemp woody core, where a similar dependence was found (De Groot *et al.* 1995), while Kubes *et al.* (1983) found a linear relationship between velocity constant and alkali concentration. This impact of NaOH found for hemp woody core may be related its relative low density (De Groot *et al.* 1997), facilitating cellulose accessibility and avoiding uneven NaOH concentrations (that may occur in more compact wood chips, and may explain lower impact of NaOH concentration on cellulose degradation and depolymerization in comparison to hemp woody core chips).

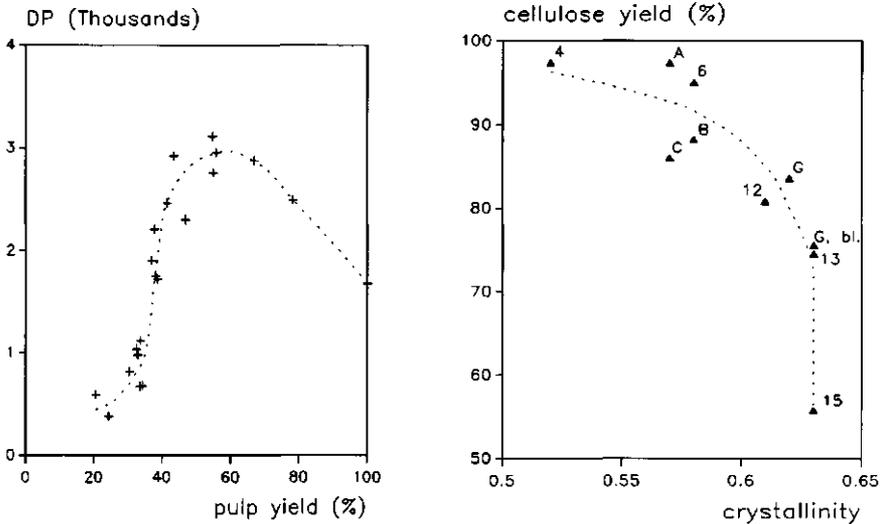


Figure 5.9 (Left) DP versus pulp yield for pulps A-G and 1-15 (described in table 5.2).

Figure 5.10 (Right) Cellulose yield versus crystallinity for pulps A, B, C, G, G bleached, 4, 6, 12, 13 and 15 (described in tables 5.1 and 5.2).

Table 5.2

Pulps used for DP modelling. All pulps were delignified at process temperatures, with NaOH concentrations and during reaction times as specified.

	temp. (°C)	[NaOH] (mol/l)	time (min)	yield (%)	cell./ cell _{start} × 100 (%)	lign./ pulp × 100 (%)	DP	dissolved in cuene (%)
pulp A	168	0.55	54	54.89	97.33	10.9	2755 ± 201	80.0
pulp B	168	0.80	67	41.53	88.21	7.08	2459 ± 145	98.0
pulp C	168	0.89	100	38.12	86.03	4.80	1749 ± 13	100
pulp F	168	1.13	96	34.42	85.32	3.76	676 ± 1	97.8
pulp G	168	1.13	91	33.62	83.56	3.64	670 ± 13	95.4
pulp D	168	1.13	85	33.59	80.37	3.98	666 ± 30	98.6
pulp E	168	2.48	56	24.45	56.75	2.43	378 ± 21	100
1	starting material			100	100	19.9 ¹	1676 ± 55	94.5
2	20	0.255	76	78.95	97.25	5.60 ¹	2489 ± 109	95.4
3	130	1.06	34	55.64	97.58	1.39 ¹	2954 ± 185	98.5
4	20	2.06	76	66.77	97.39	3.62 ¹	2874 ± 19	98.4
5	130	1.06	18	54.56	97.20	1.56 ¹	3111 ± 22	98.6
6	150	2.06	76	38.60	95.02	10.9	1720 ± 41	79.4
7	170	0.255	36	46.86	87.75	14.2	2298 ± 99	63.5
8	170	0.255	76	43.29	86.78	10.0	2919 ± 3	76.0
9	180	0.524	76	33.71	86.37	2.30	1118 ± 19	100
10	180	0.255	76	37.70	85.84	5.54	2207 ± 114	98.0
11	180	1.06	11	36.96	82.92	6.84	1900 ± 171	78.8
12	160	2.06	76	32.56	80.80	4.18	1033 ± 21	98.5
13	170	1.06	136	32.95	74.59	1.50	974 ± 64	95.6
14	170	1.06	156	30.55	n.d. ²	2.19	812 ± 4	99.5
15	170	2.06	76	20.59	55.79	2.54	587 ± 0	99.9

¹ DP was measured after chlorite treatment to reduce the lignin content (originally samples 1-5 contained of 22.1, 26.9, 27.2, 27.8 and 30.1% lignin on pulp respectively).

² n.d. = not determined

The DP is diminishing faster than the cellulose content. At 170 °C, the calculated velocity constant for depolymerization k_{DP} is about 10 times the velocity constant found for cellulose degradation, with $E_{AC} = 124.7 \pm 14.9$ kJ/mole (De Groot *et al.* 1995). This is conceivable, as depolymerization proceeds mainly by alkaline hydrolysis, each fragmentation removing multiple glycosidic units from a cellulose molecule, while cellulose yield loss is mainly the result of peeling, degrading reducing-end units one by one and thus with a lower velocity rate.

A similar difference between depolymerization and cellulose degradation was found after fitting

data of Lai and Sarkanen (1967) for degradation of cotton cellulose. As they used 1.13 mol/l NaOH in all experiments involved, NaOH is not a variable. For simple comparison, exponent f as calculated for hemp woody core (respectively 2.2 and 2.1) is used. For depolymerization this resulted in:

$$\text{DP} = 654 \exp(-k_{\text{DP}} 1.13^{2.2} t) + 85$$

$$\text{with } \ln k_{\text{DP}} = 31.94 - 138700/(8.314 T)$$

with $r^2_{\text{adj}} = 96.5\%$ and estimated standard error of observed DP values = 22.

For cellulose degradation this resulted in:

$$\text{cellulose fraction} = 0.987 \exp(-k_{\text{C}} 1.13^{2.1} t)$$

$$\text{with } \ln k_{\text{C}} = 32.18 - 147000/(8.314 T)$$

with $r^2_{\text{adj}} = 98.6\%$ and estimated standard error of observed remaining cellulose fraction = 0.11.

This results in a k_{DP} of about 8 times the velocity constant k_{C} , while calculated activation energies for yield loss and depolymerization are within the same magnitude, respectively $E_{\text{A,DP}} = 138.7 \pm 3.2$ kJ/mole and $E_{\text{A,C}} = 147.0 \pm 2.4$ kJ/mole. The calculated leveling-off degree of polymerization (85 ± 42) is in the range of the value of 60, reported for NaOH treatment (mercerization) of cotton linters (Fengel and Wegener 1984). Although the bleached cotton and the hemp woody core chips are quite different materials (in uniformity, DP, cellulose content), it is obvious that the difference in velocity constants k_{DP} and k_{C} originates similarly from respectively fragmentation and peeling effects.

5.3.6 Crystallinity

During pulping, cellulose is degraded and crystallinity of cellulose may be raised, while hemicellulose and less crystalline cellulose is removed. In figure 5.10 cellulose degradation versus crystallinity is plotted (pulp described in tables 5.1 and 5.2), the maximum crystallinity for alkaline hemp woody core pulp appears to be 0.63. Increased cellulose degradation (pulp 15) has no effect on crystallinity. Apparently, remaining amorphous and crystalline cellulose are degraded simultaneously.

Pulp E was found to consist of about 50% cellulose I and 50% cellulose II. The change in crystal lattice explains the substantially lower strength characteristics (figures 5.3-5.5) found for this pulp.

5.4 CONCLUSIONS

The effects of pulping and beating on hemp woody core pulp and on wood pulps are largely similar. An exception is the development of tear strength, not much affected by pulp composition or yield, while beating has a negative effect, which is similarly found for straw pulp. This indicates that little effort is needed (chemically or physically) to develop maximum attainable tear strength.

Another difference is the stronger influence of NaOH concentration on depolymerization and cellulose degradation. This may be related to the relative low density of hemp woody core, facilitating cellulose accessibility and reactions with NaOH.

Hemp woody core pulp is comparable with wood pulp (e.g. similar brightness, crystallinity) and chemically and botanically related to hardwood fibres (and not to straw fibres). However, in beating response hemp woody core pulp resembles the easily developing straw pulps, while tear factor and tensile strength are also in the same range. Burst factors measured for hemp woody core are in the range of the values found for bleached hardwood kraft pulp.

Therefore, it is conceivable to further develop alkaline woody core pulping for similar purposes as hardwood and straw pulp, as component in pulp mixes for printing grade paper.

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6. GENERAL DISCUSSION

6.1 HEMP WOODY CORE AS RAW MATERIAL

Woody core, representing 65 % of the mass of the hemp stem, consists of fibres with a chemical composition similar to that of hardwood. In Chapters 3 and 4 it is shown that the milder circumstances, in comparison to softwood pulping, used for alkaline delignification of hardwoods can be applied.

The density of hemp woody core, 200 kg/m³, is lower than the density of hardwoods. Less condensed polymer structures (compared to perennial wood) may be present, as in the hemp stem these structures are formed during only one growing season.

6.2 IMPREGNATION

6.2.1 The importance of swelling

Maximum swelling of hemp woody core chips at elevated temperature (70 °C) is attained without chemical treatment, in contrast to wood chips. Possibly, this is the result of the relatively high porosity of hemp woody core cell walls, enabling maximum swelling without chemical pretreatment. The spacious structure of hemp woody core fibres may allow maximum absorption with demineralized water at 70 °C.

Temperature rise combined with alkaline extraction does not improve swelling of hemp woody core, neither does swelling of hemp woody core chips increase with decreasing yield, both in contrast to what is described on softwood or hardwood swelling (Willis *et al.* 1986; Mantanis *et al.* 1994).

Probably, the low density of the hemp woody core chips allows such a high water absorption that swelling is maximal before any substantial material is removed through chemical impregnation and temperature elevation.

Although swelling of hemp woody core chips differs from what has been described for wood, paper strength increases substantially after impregnation of hemp chips with NaOH. The preliminary conclusion is that not swelling, but alkaline lignin softening and extraction, also

resulting from impregnation, is necessary for improved paper strength. Lignin softening and extraction result in relatively flexible fibres, promote separation of individual fibres at the middle lamella and enable fibrillation without substantial yield loss. Thus, fibre strength is preserved and bonding potential of individual fibres is increased. These are both important features for paper strength.

As pulp yield diminishes with increasing NaOH concentration, the needed amount for lignin softening and extraction should be optimized for paper strength and yield.

6.2.2 NMR relaxation measurements

Examining pore sizes by ^1H NMR spin-spin relaxation measurements, separate pore size distribution groups were found within each sample. This previously unreported phenomenon could be a result of varying chemical and physical conditions within the hemp woody core cell wall.

As the chemical composition of the pore wall also influences the relaxation time, the observed separate apparent pore size distributions may be the result of differently charged pore walls with similar pore size distributions.

It is conceivable that different apparent pore size distributions are observed within cellulose fibrils, the surrounding lignin-hemicellulose matrix and in the middle lamella near the fibre surfaces, respectively.

6.2.3 The role of peroxide

Addition of peroxide causes yield loss and a decreased xylan : lignin ratio and increases the amount of acidic groups. It also results in remarkably higher relaxation time and enlarged apparent pore sizes (chapter 2), especially in the lignin-hemicellulose and cellulose matrices. Possibly, peroxide in high yield pulp production is not only used for bleaching, but also for improving fibre flexibility and fibrillation by creating e.g. increased amounts of acidic groups.

6.3 MODELLING REACTION KINETICS

So far, kinetic delignification has been modelled (for wood pulping), with stepwise calculation methods (e.g. Dolk *et al.* 1989; Labidi and Pla 1992) to describe three simultaneous overall

reactions.

In this study an integral calculation of variables is applied, which leads to a more accurate fit.

6.3.1 Delignification

Fast chemical reactions take place at the relatively low temperatures occurring during the warming up period, while soluble fragments are extracted. The fraction of lignin fragments removed during impregnation and heating up period is predominantly released through cleavage of α -O-4 linkages in phenolic units (Gierer 1980), which is independent of NaOH concentration, provided the pH exceeds about 12, to ensure complete enolization. The hypothesis that initial delignification reaction is already completed after impregnation and heating up, is supported by the results of this study, described in chapter 2. The only function of the equation for initial delignification is to fit the delignification curve to its starting point.

Consequently, delignification at reaction temperature can be described with just two simultaneous reactions representing 'bulk' and 'rest delignification'. The calculated activation energies are 143.6 ± 5.2 kJ/mol and 172.8 ± 37.2 kJ/mol respectively, both within the ranges of values found for perennial wood.

The calculated reaction rate constant k_2 at a certain reaction temperature is much higher than reported for softwood: circa 4 times as high as for Western hemlock (Dolk *et al.* 1989), and slightly higher than for hardwood: circa 1.5 times as high as for poplar (Labidi and Pla 1992). This is in accordance with the expectations that the milder circumstances for alkaline delignification of hardwood in comparison with softwoods (Rydholm 1985) can be applied to hemp woody core and that the delignification of hemp woody core may be faster in comparison with hardwood (e.g. due to the presence of less condensed polymer structures).

The reaction rate constant k_3 for hemp woody core is ten times smaller than k_2 , and not significantly different from softwood (Dolk *et al.* 1989). However, the involved lignin fraction in this reaction is small (4 %).

6.3.2 Xylan degradation

Little has been reported about xylan and cellulose degradation kinetics (separately or as carbohydrate-fraction) in hardwood pulping. It is known that part of the xylan is extractable with NaOH at room temperature (up to 40% with 1M NaOH, McDonald 1952), and that increased

extraction temperatures raise the amounts of extractable hemicellulose (Nelson and Schuerch 1956; 1957). Xylan from less lignified plant materials (e.g. grasses) can be obtained in high yields by alkaline extraction at room temperature (Puls *et al.* 1988).

Furthermore, it is known that xylan degradation in hardwoods increases with higher NaOH concentrations (Yllner *et al.* 1957; Aurell 1964), especially during the initial stage (Yllner *et al.* 1957; Olm and Tistad 1979).

The reaction equations calculated in this study for alkaline degradation of xylan in hemp woody core have not been described elsewhere in literature for wood pulping. Possibly they are characteristic for (dicotyledonous) annual fibre crops in general. It was found that xylan extraction depends highly on NaOH concentration. This results - for pulps with identical lignin contents - in lower pulp yields when higher NaOH concentrations are applied. For hardwood no similar calculations have been reported. Possibly, similar degradation reactions as found for hemp woody core are to be found here as the chemical compositions are comparable. For softwoods, higher NaOH concentrations result in similar pulp yields at identical lignin contents (Lusby and Maass 1937).

6.3.3 Cellulose degradation and reduction of DP

The influence of NaOH concentration on depolymerization and on cellulose degradation is much stronger than reported for softwood pulps. This impact of NaOH found for hemp woody core may be related to its relative low density, facilitating cellulose accessibility and avoiding uneven distribution of NaOH concentrations that may occur in more compact wood chips. This may explain lower impact of NaOH concentration on cellulose degradation and depolymerization in softwood, compared to hemp woody core chips. This may similarly be the reason that xylan extraction highly depends on NaOH concentration (paragraphs 4.3.2.2 and 6.3.2).

The relatively low density of hemp woody core is an important feature, as was also mentioned in chapter 2 and paragraph 6.2.1 for impregnation characteristics.

The calculated activation energy 193.0 ± 40 kJ/mol for carbohydrate depolymerization of hemp woody core is within the range of 179 kJ/mol calculated for diminishing pulp viscosity of unbleached alkaline black spruce pulp (Kubes *et al.* 1983).

6.4 PAPER CHARACTERISTICS

The alkaline hemp woody core pulp has a rather short weight averaged fibre length of 0.61 mm, 86.2% (weight averaged) of the fibres are longer than 0.25 mm, which is a little less than found for kraft hardwood cellulose (87-97%) and more than found for straw cellulose (82%). Also in many paper characteristics hemp woody core pulp resembles hardwood and/or straw pulp:

The pulp strength develops very easily, as bulk is reduced from about 1.5 to 1.2 cm³/g within only 500 PFI rotations. In this respect the pulp is comparable with straw pulp, known to develop with a similar ease, while normally for hardwood pulps 2000 PFI rotations are required.

Burst and tensile strength, scattering and opacity develop similarly as for hardwood pulps, with less mechanical energy needed.

The development of tear with beating is similar as found for straw pulp: maximum tear strength is attained without beating. This indicates that delignified unbeaten hemp woody core fibres cohere adequately, which is similarly found for straw pulp (Clark 1985), with tear values in the same range.

Tear strength is not affected by pulp yield or composition, in this respect hemp woody core pulp is unlike hardwood and softwood pulps, where decreasing pulp yields correspond with increasing tear strengths (Rydholm 1985).

The levels of brightness of hemp woody core pulp are in the range as reported for unbleached kraft and semi-bleached kraft hardwood pulps (respectively 40 and 75%, Rydholm 1985).

6.5 CONCLUSIONS

The similarities and differences of hemp woody core fibres and wood species and straw have been evaluated.

The impregnation characteristics of hemp woody core, as investigated in chapter 2, show that this material is dissolved more easily in NaOH. Maximal swelling is reached without chemical addition.

Therefore, alkaline impregnation of hemp woody core should be performed with a minimal amount of NaOH, to ensure an optimum pulp yield. It was demonstrated that peroxide not only bleaches the pulp, but also affects lignin solubility and apparent pore size distribution.

It has been established in chapter 3 that the delignification kinetics of woody and of hemp woody core can be described satisfactorily with a simplified simultaneous model, the sum of only two overall reactions. Modelling delignification kinetics with 1M NaOH, shows that hemp woody core follows the general kinetic patterns that have been found for wood. The hypothesis that hemp woody core can be delignified similarly as hardwood has been asserted. The bulk delignification of hemp woody core can even be completed in less time, or can be performed under milder conditions than needed for hardwood.

The simultaneous model has been further elaborated and implemented successfully on xylan and cellulose extraction and degradation (chapter 4). Closer examination of degradation kinetics reveals that the pulp yield of hemp woody core varies with the concentration of NaOH used. For hemp woody core this implies that low NaOH concentrations should be used to preserve xylan, to maximize pulp yield at any lignin content.

The same model can also be used to calculate polymerisation degree of the produced pulp, as a function of time, temperature and NaOH concentration (chapter 5). Also literature data on depolymerisation and cellulose degradation of cotton linters have been modelled successfully.

NaOH concentration strongly influences depolymerisation and cellulose degradation in hemp woody core. This can be related to the relatively low density of hemp woody core, facilitating cellulose accessibility and reaction with NaOH.

The integral calculation method used in this thesis can be used for modelling pulping kinetics of any wood or non-wood material.

Finally, it was demonstrated that hemp woody core pulp is comparable to straw and hardwood pulps as papermaking raw material (chapter 5).

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SUMMARY

The aim of this thesis is to elucidate alkaline processing of hemp woody core, supporting the development and optimization of an efficient and non-polluting pulping process. This study has been a constituent of an integral programme to study fibre hemp.

It is known that the outer part of the fibre hemp stem can be used for textile and specialty paper purposes. The inner part consists of hemp woody core, which resembles hardwood and might be processed similarly for paper pulp. Literature data and prefeasibility studies show that alkaline processes can be used to produce hemp woody core pulp for papermaking.

Alkaline processes, based on sodium hydroxide (NaOH) are used for many wood and non-wood species. The most important process is the kraft process, but alternative NaOH based processes for pulp production have been investigated too. The currently developed alkaline process for high yield hardwood pulping may also be implemented for hemp woody core.

Pulp mixes for papermaking can vary, depending on the available fibre sources. The technological developments and the growing market outlet for hardwood fibres increase the possibilities to use hemp woody core for papermaking.

In chapter 2 swelling of hemp woody core chips after alkaline (peroxide) impregnation at 70 °C has been studied, as is practised in alkaline peroxide mechanical pulping (APMP) processes. Swelling of hemp woody core chips has been examined in relation to pulp yield and chemical composition of the chips after impregnation.

In contrast to wood chips, maximum swelling is attained at 70 °C without chemical treatment, possibly as the result of relatively high porosity of hemp woody core cell walls.

Alkaline swelling at 70 °C correlates with the xylan:lignin ratio. Swelling at ambient temperature shows some correlation with acidic group content.

Apparent pore size distributions have been examined, using ^1H NMR spin-spin relaxation. Several apparent pore size distributions can be distinguished within each sample. Elevated temperature, NaOH and peroxide addition influence the apparent pore size distribution and the total pore volume in different ways.

Addition of peroxide results in remarkable increase of the apparent pore sizes. This emphasizes its importance, not only as bleaching chemical in the APMP process, but also promoting fibre flexibility.

Alkaline delignification of hemp woody core is studied in chapter 3. Shavings of hemp woody core were delignified isothermally at several temperatures with 1M NaOH in a flow-through

reactor. From literature data and from experimental data reported in this chapter, it appears that the initial delignification stage is completed before customary reaction temperatures are reached. Consequently, modelling of alkaline delignification kinetics can be restricted to the bulk and residual delignification stages. This can be described with two simultaneous first order reactions: $L/L_0 = a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t)$, with $k_i = A_i \exp(-E_{a_i}/RT)$.

This equation has been solved integrally, calculating a_2 , a_3 , E_{a_2} , E_{a_3} , A_2 and A_3 for the best fit for the experimental data, resulting in an accurate description of the delignification reactions. This kinetic model has also been applied on literature data, supporting its validity for alkaline delignification kinetics in general.

This model is also used in chapter 4, to describe the kinetics of alkaline delignification in more detail, and to describe the degradation of xylan and cellulose.

Shavings of hemp woody core were impregnated at room temperature with various NaOH concentrations (0.25-2.0M) and delignified isothermally at various reaction temperatures (150-180 °C) in a flow-through reactor.

Extraction and degradation of xylan from hemp woody core strongly depends on NaOH concentration. Consequently, to attain a certain lignin content, lower NaOH concentrations result in higher pulp yields. Extended pulping diminishes the differences in pulp yields, due to further xylan degradation.

The kinetics of lignin, xylan and cellulose degradation are modelled as a function of reaction time, temperature and NaOH concentration. The combined models resulted in a pulp yield model for hemp woody core, suitable for process optimization purposes.

Degradation kinetics of perennial wood can be modelled similarly, which was illustrated using literature data on spruce and poplar.

In chapter 5 strength and surface properties of test sheets, produced from alkaline hemp woody core pulp were examined.

The development of bulk and tear with beating are similar as found for straw pulp; maximum tear strength is attained without beating. Burst and tensile strength, scattering and opacity develop similarly as for hardwood pulps, with less mechanical energy needed. Tear strength is not affected by pulp yield or composition, whereas lower tensile and burst strength are found with decreased yield and lower xylan content.

As the paper strength and surface properties of hemp woody core pulp are comparable with those for hardwood and straw pulps, it is conceivable that similar amounts of alkaline hemp woody core pulp can be used in pulp mixes for printing paper grades.

The polymerization degree (DP) of hemp woody core pulps has been related to the paper strength

properties, and modelled as function of pulping conditions and time.

The influence of NaOH concentration on depolymerization and cellulose degradation is much stronger than reported in literature for other pulps. This may be related to the low density of hemp woody core, preventing diffusion effects.

Finally, crystallinity has been examined and related to cellulose degradation of alkaline hemp woody core pulp.

In chapter 6 the results and conclusions are discussed.

It is emphasised that hemp woody core has a lower density than hardwood or softwood. It is suggested that this is the cause for maximal swelling without NaOH addition, the found xylan and yield losses with NaOH impregnation, and the strong dependency of cellulose degradation and depolymerisation on NaOH concentration.

In general, it was confirmed that hemp woody core can be delignified similarly as hardwood. The modelling techniques used have been proved to be generally applicable on degradation and depolymerisation kinetics, not only for hemp woody core, but also for hardwood and softwood species.

The paper characteristics are comparable both to hardwood and to straw pulp characteristics.

SAMENVATTING

Het doel van dit proefschrift is de alkalische verwerking van hennep houtpijp te verhelderen, ter ondersteuning van de ontwikkeling en optimalisatie van een efficiënt en milieuvriendelijk pulpproces. Deze studie is onderdeel geweest van een integraal onderzoeksprogramma naar vezelhennepe.

Het is bekend dat het buitenste deel van de vezelhennepe stengel gebruikt kan worden voor touw, textiel en speciale papersoorten. De kern van de stengel bestaat uit hennep houtpijp, dat veel overeenkomsten met loofhout heeft en op een zelfde wijze verwerkt zou kunnen worden tot papierpulp. Literatuurgegevens en prefeasibility studies laten zien dat alkalische processen gebruikt kunnen worden voor het vervaardigen van hennep houtpijppulp voor papierproductie.

Pulpprocessen op basis van natronloog (NaOH) hebben een groot toepassingsgebied, van eenjarige gewassen tot loof- en naaldhout. Het belangrijkste proces is het kraftproces, maar er zijn ook alternatieve pulpmethoden op basis van NaOH bekend. De recentelijk ontwikkelde 'hogere opbrengst'-processen voor loofhout zouden ook toegepast kunnen worden voor hennep houtpijp. De samenstelling van pulpmengsels voor papier kan variëren, afhankelijk van de beschikbare vezels. De technologische ontwikkelingen en het groeiende marktpotentieel voor loofhoutvezels verbeteren de mogelijkheden voor de inzet van hennep houtpijp voor papierproductie.

In hoofdstuk 2 wordt de zwelling van hennep houtpijpchips bestudeerd, onder invloed van impregnatie met NaOH bij 70 °C, met en zonder peroxide-toevoeging, zoals dit ook gebeurt bij het zogenoemde alkalisch-peroxide-mechanische pulp proces (APMP-proces). De zwelling is bestudeerd in relatie tot pulp opbrengst en chemische samenstelling van de hennep houtpijpchips na impregnatie.

In tegenstelling tot houtchips, wordt maximale zwelling van hennep houtpijpchips bij 70 °C bereikt zonder toevoeging van chemicaliën. Mogelijk is dit het gevolg van de relatief hoge porositeit van de celwanden van hennep houtpijp.

Bij 70 °C correleert de alkalische zwelling van hennep houtpijp met de verhouding xylaan:lignine. Zwelling bij kamertemperatuur vertoont enige correlatie met de hoeveelheid zure groepen die in de vezelmasse gemeten wordt.

De schijnbare poriegrootteverdeling in hennep houtpijpchips is bestudeerd met ¹H NMR spin-spin relaxatie. Verscheidene schijnbare poriegrootteverdelingen kunnen worden waargenomen in elk onderzocht monster. Temperatuursverhoging, gebruik van NaOH en peroxide-toevoeging beïnvloeden de schijnbare poriegrootteverdeling en het totale porie-volume op verschillen

manieren.

Toevoeging van peroxide resulteert in opmerkelijke verhoging van de schijnbare poriegrootten. Dit benadrukt het belang van peroxide in het APMP-proces, niet alleen voor het bleken van de pulp, maar ook om de vezels flexibeler te maken.

In hoofdstuk 3 wordt de alkalische delignificatie van hennephoutpijp bestudeerd. Schaafsels van hennephoutpijp zijn isotherm gedelignificeerd in een met 1M NaOH doorstroomde reactor, bij verschillende temperaturen. Uit literatuurgegevens en de gegevens in dit hoofdstuk blijkt dat de initiële delignificatie-fase afgerond is voordat de gebruikelijke reactietemperaturen bereikt zijn. Hieruit volgt dat het modelleren van alkalische delignificatie beperkt kan worden tot de bulk- en restdelignificatie-fasen. Dit kan beschreven worden met twee tegelijkertijd verlopende eerste orde reacties: $L/L_0 = a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t)$, met $k_i = A_i \exp(-E_{a_i}/RT)$.

Deze vergelijking is integraal opgelost, waarbij de best passende waarden voor a_2 , a_3 , E_{a_2} , E_{a_3} , A_2 en A_3 berekend zijn voor de experimentele gegevens, resulterend in een accurate beschrijving van de delignificatiereacties. Dit kinetische model is ook toegepast op literatuurgegevens, waardoor de geldigheid voor alkalische delignificatie-kinetiek in het algemeen wordt ondersteund.

Dit model wordt verder uitgewerkt in hoofdstuk 4 voor een meer gedetailleerde beschrijving van de kinetiek van alkalische delignificatie en de beschrijving van xylaan- en cellulose-afbraak.

Hennephoutpijpschaafsels zijn geïmpregneerd met verschillende NaOH-oplossingen (0.25-2.0 M) en isotherm gedelignificeerd bij verschillende temperaturen (150-180 °C) in een met deze NaOH-oplossingen doorstroomde reactor.

De extractie en degradatie van xylaan uit hennephoutpijp hangt sterk af van de gebruikte NaOH-concentratie. Als gevolg hiervan resulteren lagere NaOH-concentraties in hogere pulpopbrengsten, uitgaande van een zelfde te bereiken ligninegehalte. Een verlenging van de reactietijd leidt tot kleinere verschillen in pulpopbrengst, als gevolg van xylaanafbraak.

De kinetiek van lignine-, xylaan- en cellulosedegradatie zijn gemodelleerd als functie van reactietijd en -temperatuur en van NaOH-concentratie. De gecombineerde modellen resulteren in een pulpopbrengstmodel voor hennephoutpijp, te gebruiken voor optimalisatie.

Degradatiekinetiek voor meerjarig hout kan op een zelfde wijze gemodelleerd worden, hetgeen geïllustreerd wordt met literatuurgegevens voor populier en spar.

In hoofdstuk 5 worden sterkte- en oppervlakte-eigenschappen van testpapier, gemaakt uit alkalische hennephoutpijppulp, bestudeerd.

De ontwikkeling van bulk en scheursterkte met vermaling komen overeen met die voor stropulp; maximale scheursterkte wordt bereikt zonder vermaling. Berst- en treksterkte, lichtverstrooiing en opaciteit ontwikkelen zich overeenkomstig loofhout, waarbij minder mechanische energie nodig

is. Pulpopbrengst of -samenstelling heeft geen effect op scheursterkte, terwijl lagere trek- en berststerkten gevonden worden bij afgenomen pulpopbrengst en bij een afgenomen xytaan-gehalte.

Daar de papiersterkten en oppervlakte-eigenschappen voor hennephoutpijppulp vergeleken kunnen worden met die van loofhout- en stropulp, is het aannemelijk dat vergelijkbare hoeveelheden alkalisch ontsloten hennephoutpijppulp ingezet kunnen worden in pulpmengsels voor schrijf- en drukpapier.

De polymerisatiegraad van hennephoutpijppulp wordt gerelateerd aan papiersterktekarakteristieken en is gemodelleerd als functie van pulpomstandigheden en reactietijd.

De invloed van NaOH-concentratie op depolymerisatie en cellulose-afbraak is veel groter dan wordt gerapporteerd in de literatuur voor andere pulpsoorten. Mogelijk is dit gerelateerd aan de lage dichtheid van hennephoutpijp, waardoor diffusie-effecten vermeden worden.

Tenslotte wordt de kristalliniteit bestudeerd en gerelateerd aan cellulose-afbraak in alkalisch ontsloten hennephoutpijppulp.

In hoofdstuk 6 worden de resultaten en conclusies bediscussieerd.

Het wordt benadrukt dat hennephoutpijp een lagere dichtheid heeft dan loof- of naaldhout. Dit kan de oorzaak zijn voor een maximale zwelling zonder NaOH-toevoeging, de gevonden xytaan en opbrengstverliezen na NaOH-impregnatie, en de sterke afhankelijkheid van cellulose-degradatie en depolymerisatie van de NaOH-concentratie.

In het algemeen wordt bevestigd dat hennephoutpijp op een zelfde wijze als loofhout gedelignificeerd kan worden. Aangetoond is dat de gebruikte modelleringstechnieken algemeen toepasbaar zijn op degradatie- en depolymerisatie-kinetiek, niet alleen voor hennephoutpijp, maar ook voor loofhout- en naaldhoutsoorten.

De papierkarakteristieken zijn vergelijkbaar met die van loofhout- en stropulp.

CURRICULUM VITAE

Birgitte de Groot werd op 28 juni 1960 te Leiden geboren. Na het behalen van het diploma Gymnasium- β in Middelburg studeerde zij Levensmiddelentechnologie aan de Landbouwuniversiteit Wageningen. De afstudeerrichting was Proceskunde, met bijvakken Industriële Bedrijfskunde en Informatica. Tijdens haar studie was zij stagiaire bij papierfabrieken in Frankrijk, Finland en Duitsland.

Vanaf 1987 was zij coördinator van de werkgroep Hennepverwerking aan de Landbouwuniversiteit, bij de sectie Proceskunde. Vanaf 1990 was zij onderzoeksmedewerker bij ATO-DLO te Wageningen, bij de sectie Papier- en Pulptechnologie, voor het onderzoek naar alkalische pulpprocessen voor hennephoutpijp. Tevens werkte zij bij de afdeling Industriële Microbiologie en Structuuranalyse aan het ontwikkelen en testen van bio-afbreekbare polymeren als coatings voor verpakkingen van verse levensmiddelen. Sinds 1997 is zij procesingenieur voor grondstofkwaliteit en testcoördinatie bij de afdeling Productie van SCA Hygiene Products Genep B.V.