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Hemp raw materials: The effect of cultivar, growth conditions and pretreatment on the chemical composition of the fibres

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Abstract:

Hemp raw materials were analyzed chemically to determine their content of cellulose, hemicellulose, lignin and ashes. Correction for ashes was only necessary in the first step of the chemical analysis: the Neutral Detergent Fibre step. The hemp fibers contained 73-77% w/w cellulose, 7-9% w/w hemicellulose and 4-6% w/w lignin, while the hemp shives contained 48% w/w cellulose, 21-25% w/w hemicellulose and 17-19% w/w lignin. Among the four investigated cultivars, Felina contained least lignin, while Futura and Fasamo contained least cellulose. Hemp yarn had the same color as retted hemp fibers but was more cellulose rich. Steam explosion, wet oxidation and hydrothermal treatment were used for defibration of retted hemp fibers. These pretreatments removed lignin and hemicellulose resulting in loss of dry matter of 15-73% w/w and in loss of cellulose of 0-69% w/w. Steam explosion treatment generally gave the biggest losses. Alkali gave greater losses due to the effect of alkali in opening the structure of the molecules making them more accessible for degradation.

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Preface

The present study is part of investigations in natural raw materials carried out at Risø National Laboratory. Vibeke Bohn and Kristina Vad Nielsen were studying environmental engineering at the Technical University of Denmark and Risø National Laboratory in year 1999-2000. This project is a preparation for a master thesis in hemp fibers. This work took place in the beginning of the HeFiNaC-project "High performance hemp fibers and improved fibre networks for composites" supported by the Danish Research Agency of the Ministry of Science

Vibeke Bohn and Kristina Vad Nielsen would like to thank supervisors Anne Belinda Thomsen, Risø and Michael Søgaard Jørgensen, Department of Technology and Social Sciences, DTU. The help and assistance from Stephen Mallon, Tomas Fernqvist and Anders Woidemann are gratefully acknowledged. Kenneth Svensson provided hemp stems (Køge-Ringsted Landboforening) and Bodil Engberg Pallesen provided retted hemp (Landbrugets Rådgivningscenter in Skejby). Vidhi Brorsen provided hemp yarn (HempValley) that was evaluated by textile craftsman Lisbeth Hungeberg.

1 Introduction

Plant fibers from wood and agricultural crops like flax, hemp and willow are renewable materials those have a potential for creating "green" products and replacing fossil hydrocarbon materials harmful for the environment (Schmidt et al, 1998; Bjerre, 1997). Since the 1970s, research has been carried out to find alternative sources of energy to fossil fuels (Bjerre et al, 1996), and based on environmental concerns work has been done to apply natural fibers in preference to synthetic or chemically produced cellulose (Pallesen, 1996; Goth et al). Natural fibers have advantages compared to synthetic materials in being ecologically and toxicologically harmless, biological degradable and CO_2-neutral (Goth et al). This project concerns industrial hemp *(Cannabis Sativa)*. Hemp contains cellulose fibers and a woody material called shives. Fibers and shives are used in a range of products like textiles, paper and building materials.

1.1 Anatomy of the stem

The hemp stem can reach a height of more than four meters when the plant has good growth conditions (Vogl, 1996). A cross section of the hemp stem shows different layers (Figure 1). The outside of the stem is covered with bark, also called epidermis (Pallesen, 1996). Inside the hemp stems are bast fibers and the woody core, called shives. The bast fibers are bound by the middle lamella and arranged in bundles those run from top to bottom of the stem (Vignon et al, 1995).

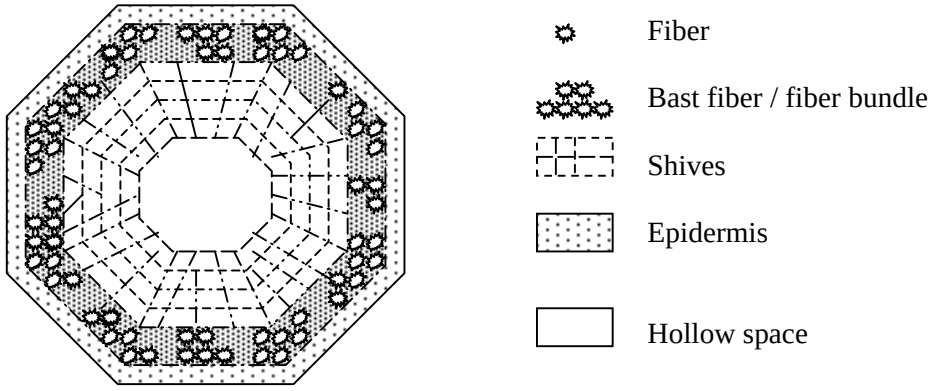

Figure 1. Cross section of a hemp stem showed as a model with the layers of epidermis, cortex with fiber bundles, shives and cavity in the middle (Adapted from Pallesen, 1996).

Each fiber bundle consists of single fibers (Pallesen, 1996). There are two types of fibers, the useful primary fibers (5-55 mm long) and the short secondary fibers (app. 2 mm long) (Vogl, 1996). The bast fibers are 10 to 100 times longer than the woody fibers in the shives. Their diameters are approximately the same; however the cell walls of the bast fibers are 5 to 10 times thicker than those of woody fibers (Table 1) (Vignon et al, 1995). The fiber content is given in relation to the weight of the whole stem. In hemp 20-35% w/w of the stem is fibers (Vogl, 1996). The cultivar Felina 34 contains 30-40 w/w fibers and Fedora 19 contains 25-30% w/w fibers (Zimmermann, 1997).

Table 1. Dimensions of hemp fibers showed as the range in µm (Vignon et al, 1995).

	Bast fibers	Woody fibers in Shives
Length (µm)	5000-55000	200-600
Diameter (µm)	20-40	10-30
Wall thickness (µm)	5-10	1-2

1.2 Plant fibers

Plant fibers consist mainly of cellulose, hemicellulose and lignin and minor contents of wax, and minerals (Figure 2). In hemp, the distribution between the components is different in fibers and shives. The fibers contain more than 50% w/w cellulose, while the shives contain less cellulose and more lignin.

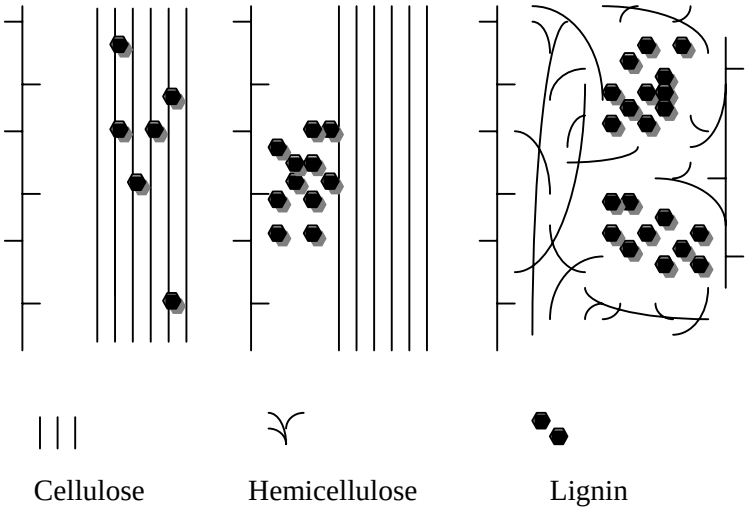

Figure 2. A structural model of the plant cell wall showed with cellulose fibrils, lignin and hemicellulose. Lignin binds to hemicellulose, since hemicellulose hydroxyl groups are much more accessible to lignin than those of cellulose.

1.2.1 Cellulose

Cellulose is a homogeneous linear polymer constructed of repeating glucose units (Figure 3). It is a highly crystalline polysaccharide resistant to enzymatic hydrolysis. Cellulose is up to 6 µm long and the largest naturally occurring polymer. The main function of cellulose is to provide strength to the plant. Due to the high number of hydrogen bonds between the chains, cellulose fibers have a high tensile strength in axial direction (Sørensen, 1997). Cellulose is only found in microfibrils and never as individual molecules. The microfibrils contain about 40 cellulose chains in cross sections and are 30-40 Å in diameter. The microfibrils have both amorphous and crystalline regions (Bjerre & Schmidt, 1997).

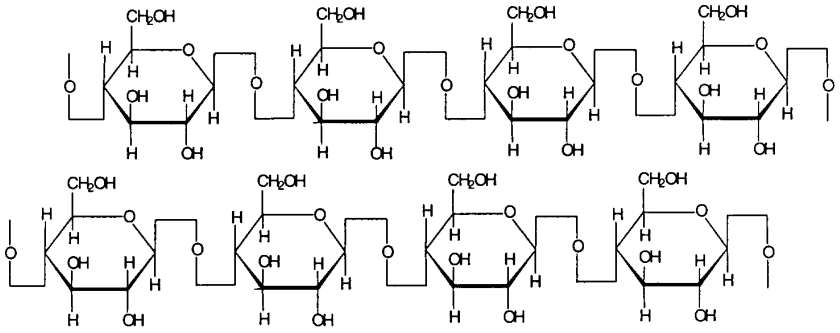

Figure 3. Cellulose molecule constructed of glucose monomers. Parallel cellulose chains form hydrogen bonds resulting in crystalline microfibrils. (Bjerre & Schmidt, 1997).

1.2.2 Hemicellulose

Hemicellulose can be extracted in alkaline solutions (Sørensen, 1997). The role of hemicellulose is to provide linkage between cellulose and lignin. Unlike cellulose it has a heterogeneous and branched structure consisting of various pentose sugars (Figure 4, Bjerre & Schmidt, 1997). The functions of hemicellulose are not all known, but it is part of the encrusting material filling the cavities between the microfibrils. Because of the amorphous structure, its hydroxyl groups are much more accessible to water than those of cellulose. This means that hemicellulose is a major contributor to the hygroscopicity of plant fibers (Sørensen, 1997).

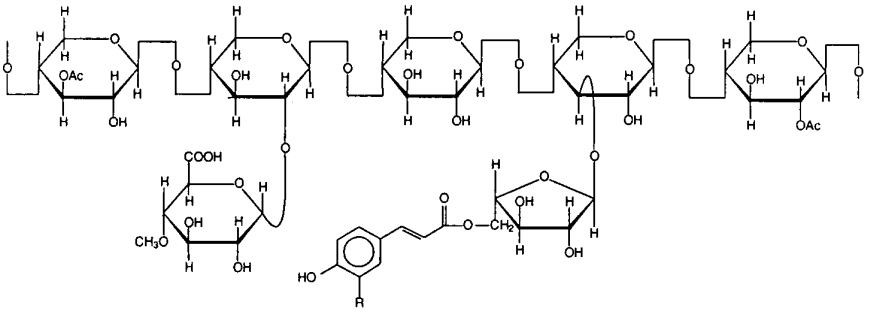

Figure 4. The structure of hemicellulose in non-woody fibers (grasses) showed as the acetylated xylan chain with α-1,2 bond to 4-O-methyl glucuronic acid (left side group) and with α-1,3 bond to L-arabinofuranose, which also is linked to phenolic acid (right side group) (Puls & Schuseil, 1993).

1.2.3 Lignin

Lignin is a strengthening material usually located between the cellulose microfibrils, were it gives strength and provides protection against attack by pathogens and consumption by herbivores, both insect and mammalian, due to its phenolic components (Bjerre & Schmidt, 1997). Lignin is insoluble in most solvents, due to its high molecular weight, complex structure and chemical attachment to hemicellulose. Lignin attaches to the hydroxyl groups of the polysaccharides cellulose and hemicellulose mainly by ether linkage. Lignin may be considered as three dimensional phenyl propane networks held together by ether and carbon-carbon bonds (Figure 5). The double bonds in lignin give the plant fibers a dark color. If lignin is oxidized and the double bonds are broken, the

fiber that it is part of will become brighter. Lignin has varying amounts of related acids esterified to the core (Bjerre & Schmidt, 1997). Lignin is a much less hydrophilic material than hemicellulose and cellulose. Lignin is partly fluent during hot pressing, and therefore might be able to bind fibers together (Sørensen, 1997).

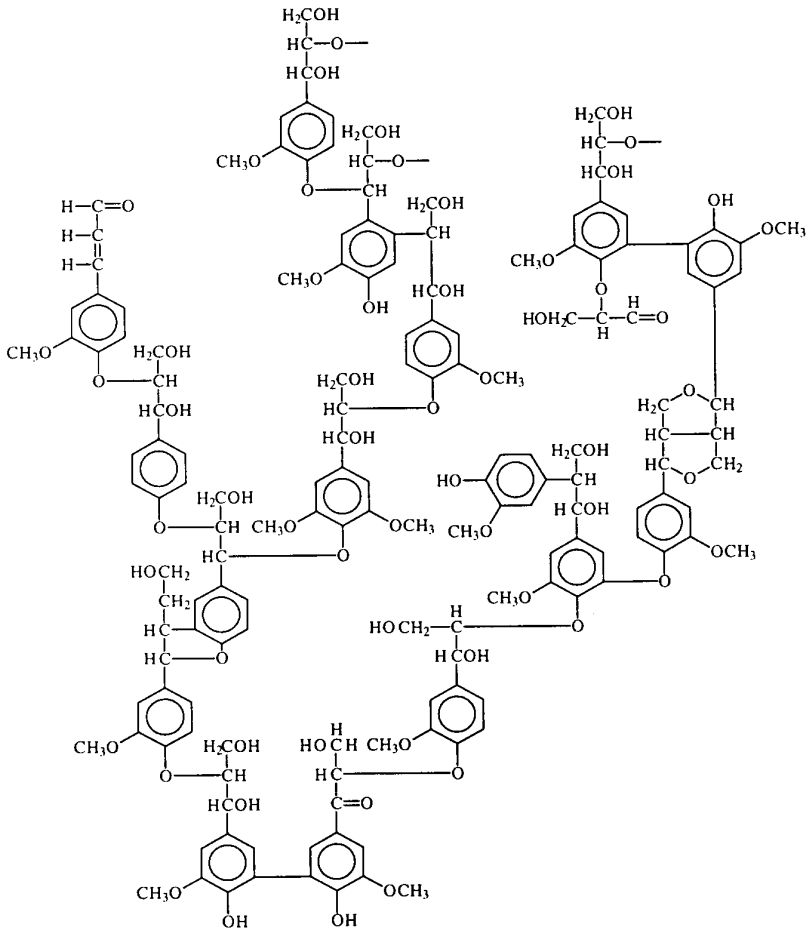

Figure 5. The lignin molecule has a complex structure that probably always is variable (Bjerre & Schmidt, 1997).

1.2.4 Wax

Most plants are covered with semi-crystalline wax consisting of mainly long-chain alkane, ester and alcohol waxes. Esters and fatty acids are common but minor components, while alcohols often comprise a major portion of the wax. The effect of the wax layer is to prevent water loss from a young plant and incidentally to glance off liquids from the surface of the leaves. On the outer part of the plant, wax is formed. The wax layer is the first barrier for insects accessing the plant. Cutin is embedded in wax and a lipophilic amorphous polymer largely held together by ester linkages (Sun, 1996).

1.2.5 Ash

The main plant fiber minerals include calcium (Ca), potassium (K), phosphors (P) and magnesium (Mg). The mineral content in softwood is 0.02-1% w/w and in Hardwoods 0-5% w/w (Tsoumis, 1991). The mineral content in plant fibers depend on agronomic factors and the amount of soil contaminations (Sun, 1996).

1.3 Chemical composition of hemp

Investigations have been carried out in order to characterize hemp for chemical composition. Available values from literature can be found in Table 2.

Table 2. Values found in literature about chemical composition of hemp stems, hemp fibers and hemp shives.

	Hemp stem	Hemp fibers	Hemp shives
Ash (% w/w)	-	4 (f)	1-2 (b,f)
Cellulose (% w/w)	70 (e)	55-72 (a, c-d, f)	34-44 (c-d, f)
Hemicellulose (% w/w)	22 (e)	7-19 (a, c-d, f)	31-37 (c), 18 (d, f)
Lignin (% w/w)	6 (e)	2-5 (a, c-d, f)	19-28 (b-d, f)
Pectin (% w/w)	-	4-8 (a)	4 (f)
Water sol. mat. (% w/w)	-	2 (a)	-
Fat and wax (% w/w)	-	0.7-1.3 (a, f)	1 (f)

(a): (Textileforum, 1996), (b) (Krotov, 1995), (c) (Triolo, 1980).
(d): Cultivars: Fibrimon 56, Fedora 19 and Kompolti (Van der Werf, 1994)
(e): (Hon, 1996), (f) (Vignon et al, 1995).

1.4 Variability among natural fibers

A major problem in plant fibers compared to synthetic fibers is missing homogeneity of the material. Synthetic fibers can be produced in a specific way and the produced fibers will be of a consistent quality. When plant fibers are produced, growth conditions have a huge influence on the results. Differences occur because of difference in cultivar, cultivation area, soil type, climate, and fertilization (Kessler et al, 1997).

The retting process affects the fiber color, the separation of the fiber bundles, the fiber composition and the fiber strength (Pallesen, 1996). The quality of the fibers depends on the cultivar and the growth conditions and the location of the fiber in the plant stem. The fiber content and the fiber strength are highest in the middle of the stem (Vogl, 1996). Due to the macroscopic structure there are major differences in the morphological structure and chemical composition between top and bottom of the plant (Kessler et al, 1997).

1.5 Quality of flax fibers and yarn

The fibers of flax and hemp are of a similar nature so parameters determining flax can classify hemp too. In order to establish standards for the linen industry, the current methods for characterization of flax fibers have been investigated (RB Rusell Agricultural Research Centre, USA, (Morrison et al, 1999)). Expert-graders and buyers normally determine the quality of flax fibers after retting. They use their experience to subjectively evaluate the fibers with use of eyes and hands. Physical and chemical tests are also used for characterization, but no clear understanding exists of how chemical factors relate to the quality. At RB Rusell Agricultural Research Centre, light microscopy, chemical analysis, Raman spectroscopy and nuclear magnetic resonance spectroscopy (NMR) were used for analyzing flax fibers and yarn. Light microscopy revealed that low quality fibers contained large fragments of epidermis. High quality fibers were divided into smaller bundles and elementary fibers. Chemical analysis

showed that the amounts of fatty acids and alcohols were lowest in high quality fibers and yarn. Especially a fatty acid called 8,16-dihydroxyhexadecanoic acid could be used as a marker for qualities in yarns. High qualities of fibers and yarn had lower percentages of wax and cutin (21 g/kg and 4 g/kg respectively) compared to low quality of fibers and yarn (27 g/kg and 14 g/kg respectively). Raman spectroscopy supported this conclusion. NMR and Raman spectroscopy indicated higher amounts of crystalline cellulose in high quality material (Morrison et al, 1999).

1.6 Pretreatment of fibers

Pretreatment processes for hemp are used to modify and fractionate the plant stems to isolate the fibers. Often lignin is broken down making cellulose and/or hemicellulose accessible for further processing (Bjerre et al, 1995; Schmidt et al, 1998; Bjerre & Schmidt, 1997). Processing can influence cleanliness of fibers, fiber length, fineness and chemical composition (Kessler et al, 1997). Roughly the pretreatment processes can be divided into mechanical, biological and chemical-physical processes. The mechanical pretreatment separates the materials into smaller particles. An example of this is milling, where pieces of raw material are crushed in a hammer mill. The purpose could be to make the hemicellulose accessible for enzymes (Schmidt et al, 1998) or process short cellulose fibers for textile or non-textile purposes (Kessler et al, 1997).

Biological pretreatment includes retting where microorganisms separate the fibers and shives in a hemp stem. The fibers could then be used in textiles and the shives for animal bedding. Chemical pretreatment is e.g. used in the paper industry to cleanse cellulose of lignin and hemicellulose (Schmidt et al, 1998). Wet oxidation, hydrothermal treatment and steam explosion are all chemical-physical pretreatments, where a chemical treatment is combined with a physical treatment. The goal of plant fiber pre-treatment is to fulfill different requirements for the production of fiber materials (Figure 6).

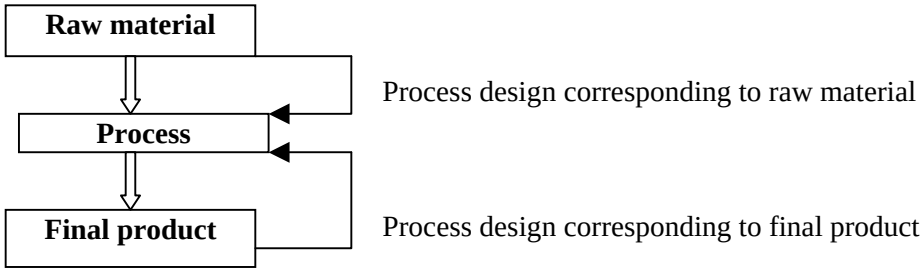

Figure 6. Product-property flow sheet made for pre-treatments (Kessler et al, 1997).

1.6.1 Milling

In milling, pieces of hemp stems are crushed in a hammer mill to break the lignocellulose into pieces of a certain size. This can make it easier to mix a hemp sample evenly or separate fibers and shives mechanically. When the pieces are small, the lignocellulose material is easier penetrated by chemicals and can be submitted to modification or chemical analysis.

1.6.2 Retting

Retting of hemp stems is a process where microorganisms break down the lignin and pectin that bind the shives and fibers together. These can then be separated in a processing plant. In cold water retting, hemp stems are left in cold water for about 2 weeks. The process produces much wastewater. In hot water retting stems are retted in a

tank with water at 36°C for 6-8 days. The retted fibers are of a high quality, but the process consumes energy and produces wastewater. The most simple and commonly used method for retting hemp is field retting. When the stem is harvested it is left in the field for 2-6 weeks. The quality of the produced fibers depends strongly on the weather conditions (Vogl, 1996). Field retting is economically advantageous because leaves and roots remain in the field after retting and provide nutrients to the following crop (Bocsa & Karus, 1998).

1.6.3 Wet Oxidation

Wet oxidation is a process where a sample is treated with water and oxygen at elevated temperature (125-320 °C, 0.5-20 MPa). Wet oxidation combined with alkaline hydrolysis efficiently dissolves hemicellulose, while cellulose remains insoluble (Schmidt et al 1998). The process is suitable for obtaining a solid cellulose-rich fraction and an aqueous hemicellulose-rich fraction. The oxygen present at wet oxidation bleaches the fibers (Bjerre & Schmidt, 1997).

Lignin dissolves easily in alkaline solution. The carbon-carbon linkages and ether linkages become very accessible for oxidation. This explains why lignin is very reactive and why it is degraded to CO_2, H_2O and organic compounds. Hemicellulose is soluble in alkali due to hydrolysis and is unstable during wet oxidation because of the branched structure of the molecule. Cellulose is more stable due to its crystalline structure.

The requirement of oxygen and base makes the wet oxidation process more expensive. However, calculations have shown that the cost of the raw material dominates other costs. To make it economical both dissolved hemicellulose, the solid cellulose and possibly the lignin should be utilized (Bjerre & Schmidt, 1997).

1.6.4 Hydrothermal treatment

Hydrothermal treatment works with water at elevated temperatures. In these investigations, the treatment is carried out similar to wet oxidation, but without added oxygen.

1.6.5 Steam Explosion

Steam explosion is a process where a sample is treated with steam at high temperature (190-230°C, Bjerre & Schmidt (1997)). Often the sample is impregnated with chemicals and then steam exploded. When the reaction is to be stopped, the pressure is instantly released and the sample is blown into a container (Vignon et al, 1995). In the steam explosion process hemp is chemically modified and mechanically defibrated. The hot steam softens the material and the fibers separate by the mechanical action at the discharge (Vignon et al, 1995). During the steam explosion process variables are reaction temperature, time and extrusion speed (Goth et al). During the process undesired inhibitors of microorganisms are formed (Schmidt et al, 1998). For economic reasons, a high fiber yield is important. The main fiber loss in steam explosion is observed during opening. Fiber bundles that are incompletely elementarized (under retted) are eliminated. On the other hand trash particles and degraded short fiber fragments (over retted) are separated (Goth et al).

1.6.6 Wet oxidation and steam explosion compared

By wet oxidation more hemicellulose and lignin are solubilised than by steam explosion. More cellulose is solubilised and degraded by stem explosion than by wet oxidation. For wet oxidation, much of the hemicellulose is found in solution, which makes it available

for fermentation. In steam explosion, both hemicellulose and cellulose are converted or degraded. Losses of hemicellulose and cellulose in total are 20% w/w for steaming and 16% w/w for wet oxidation (Bjerre & Schmidt, 1997).

1.7 Aims

The purpose of this study is to classify hemp raw materials chemically and to investigate the importance of growth conditions and the effect of chemical-physical pretreatments on the composition of hemp raw materials. The results are related to a sample of hemp yarn. The investigations are presented in the following.

1.7.1 Evaluation of analysis method

The chemical classification of hemp samples included determination of dry matter, ash, cellulose, hemicellulose, lignin and non cell wall material (NCWM). The method was developed by Goering and van Soest and modified at Risø. The chemical analysis method and a method for determination of wax were evaluated.

1.7.2 Fibers and shives

Separated fibers and shives from retted Fedora 19 at Skejby in Jutland and unretted Fedora 19 from Køge-Ringsted on Zealand were analyzed. It was evaluated if chemical analysis would be suitable for determination of the distribution between fibers and shives in a sample.

1.7.3 Effects of growth conditions

In order to establish knowledge about the influence on chemical composition of different cultivars and varying growth conditions, analyses were carried out on hemp stems from field trials in Køge-Ringsted.

1.7.4 Effects of chemical-physical pretreatments

In order to establish knowledge about modification of hemp raw materials, wet oxidation, hydrothermal treatment and steam explosion were carried out on retted Fedora 19 from Skejby trials.

1.7.5 Hemp yarn

Characterized hemp fibers were compared to a sample of hemp yarn to investigate the qualities obtained in the industry.

2 Materials and methods

In the following sections the hemp materials are described, including the methods for the analyses. The samples came from different suppliers and different degrees of information about the samples were available.

2.1 Hemp samples

Samples of crushed hemp stem separated into fibers and shives and a sample of hemp yarn were analyzed. The samples and how they were treated are described here:

2.1.1 Samples from Køge-Ringsted trials

Køge-Ringsted Landboforening had field trials with hemp in 1998. The sowing was done the 19th of May (Køge-Ringsted, 1998). The late sowing time resulted in a low hemp stem yield in the harvest. Køge-Ringsted Landboforening grew the five cultivars: Fedora 19, Felina 34, Fedrina 74, Futura 77 and Fasamo. Some of the cultivars were

grown at different plant density, others fertilized with different levels of nitrogen. See Table 3 for details about the cultivars.

Table 3. Height and thickness of hemp stems grown at standard conditions for Fedora, Fedrina, Felina, Fasamo and Futura after harvest (Køge-Ringsted, 1998).

	Height (m)	Stem thickness (m)	Comment
Fedrina	2.33	1.1	
Fedora	2.27	0.7	Early cultivar
Felina	2.15	0.8	
Fasamo	2.05	0.6	Earlier than the other cultivars
Futura	2.50	1.1	Very tall and late cultivar

The area for the trial was ready for sowing in the beginning of May. This means that when the trials started some weeds were established at the boundary line of the parcel. However, pesticides were not added to the field. At the end of July the hemp grew a lot, and weeds were overgrown. A few stems were at a late time (August-September) sporadically attacked by mould and fungus. The climatic conditions for fungal attack were optimal in 1998.

Fasamo was a cultivar that regarding seeds looked promising. This was harvested for seeds at the 21st of September but only 10% w/w of the seeds was ripened, since the weather had been too cold and too wet during the summer.

Before chemical analysis the hemp stems had been stripped of leaves, the upper 1/3 containing seed had been removed and the stems were crushed in a hammer-mill to a maximum size of 2 mm. Fedora 19, was separated by hand with a set of sieves into shives and fibers.

2.1.2 Samples from Skejby trials

Fedora 19 was the chosen cultivar for trials at the Danish Agricultural Advisory Centre in 1998, because it ripens early. Due to weather conditions and variation of soil type there are no specific time for when the hemp have field retted long enough. But generally the retting times elapsed for a few weeks (Pers. Comm. Pallesen, 1999).

Fedora 19 was grown, the hemp stems were field retted and mechanically separated with a short fiber process line developed at the Danish Agricultural Advisory Centre into fibers and shives. Fibers and shives were stored in plastic bags. By mechanical separation an amount of shives remain with the fibers. Some pure fibers were separated by hand to see what influence the remaining shives had in the mechanically treated Fedora 19.

2.1.3 Hemp yarn sample

A hemp yarn sample was given from the company Hemp Valley (Brorsen, 1999). That sample was of a very good quality suitable for knitted fabrics (Hungeberg, 1999).

2.1.4 Overview of samples and analyses

The cultivars Felina, Fedora, Fedrina and Fasamo were studies with varied addition of fertilizer and plant density. Pre-treatment was done on Fedora 19. The total experimental setup is shown in Table 4.

Table 4. Overview of the analyzed samples and analyses carried out. Where just the name of the cultivar is mentioned, the sample consists of non-retted crushed hemp stem from Køge-Ringsted trials. Retted Fedora 19 came from Skejby-trials and the company HempValley supplied hemp yarn.

Sample	Analysis	Sample	Analysis
Felina	Full	Fedrina	Ash
Felina 50N	Full	Fedrina 50N	Ash
Felina 100N	Full	Fedrina 100N	Ash
Felina 150N	Ash	Fedrina 150N	Ash
Felina 100 plants/m^2	Ash	Fedrina 100 plants/m^2	Ash
Felina 200 plants/m^2	Ash	Fedrina 200 plants/m^2	Ash
Felina 300 plants/m^2	Ash	Fedrina 300 plants/m^2	Ash
Fedora	Full	Fasamo	Full
Fedora, pure fibers	Full	Futura	Full
Fedora, pure shives	Full	Retted Fedora 19 (fibers incl. remainder of shives)	Full + treatment
Fedora 100 plants/m^2	Ash	Retted Fedora 19, pure fibers	Full
Fedora 200 plants/m^2	Ash	Retted Fedora 19, pure shives	Full
Fedora 300 plants/m^2	Ash	Hemp yarn	Full

Full = Full chemical characterization, Ash = Ash determination. Retted Fedora 19 was used as raw material for chemical-physical pretreatment experiments.

2.2 Fiber analysis

The analysis used for determining non cell wall material (NCWM), lignin, hemicellulose and cellulose was described by Goering & van Soest (1970) and modified at Risø. Dry matter and ash contents were determined in parallel. In the sequential analysis the same raw material is used throughout the analysis. A hemp sample is weighed out, a chemical treatment is carried out in order to remove a certain component in the sample, and the sample is dried and weighed out again. The loss of dry matter equals the removed content in the sample. After two of the steps, a small amount of the dry sample is taken out for ash determination to correct the analysis for the ash content. It was evaluated if drying the samples at lower temperature would affect the results obtained from the fiber analysis. The analysis is presented in the following sections.

2.2.1 Dry matter and ash contents

Dry matter was determined by weight loss after drying an amount of hemp-material at 105°C overnight. The ash content was determined by weight of residuals in weight-% of initial dry mass from incineration at 500 °C for 3 hours.

2.2.2 Non Cell Wall Material, NCWM

Non cell wall material is defined as the material in the sample that is not minerals (= ash), hemicellulose, permanganate lignin or cellulose. This includes wax, fatty acids and pectin. Sample (2.5 g) was weighed out in a beaker and boiled in 250 ml of neutral detergent for one hour. The sample and detergent was washed into a filter of pore size 3 with a small amount of hot water. Sample was washed with hot water and with acetone. The filter was dried overnight at 105°C and weighed out again to determine the weight loss. 0.4 g of sample was weighed out and was incinerated for 3 hours at 500°C.

2.2.3 Hemicellulose

The sample was weighed out in a beaker and boiled for an hour in acid detergent. Sample was washed into a filter and washed with hot water and with acetone. Weight loss was determined after drying. 0.4 g of the sample was incinerated.

2.2.4 Lignin

In this analysis permanganate lignin is found. Other methods for determining lignin can give results different from the permanganate lignin. Filter and sample was weighed out. Sample was treated with potassium permanganate and lignin buffer solution 2:1 by volume for 90 minutes. The filter was sucked dry and filled with demineralising solution. After 5 minutes the filter was sucked dry and demineralising was repeated. Sample was washed with 80% v/v ethanol and acetone. Weight loss was determined after drying overnight.

2.2.5 Cellulose

Both crystalline and amorphous cellulose is found in the analysis. Filter and sample was weighed out. Sample was treated with 72% sulfuric acid for 3 hours and then rinsed with hot water. Weight loss was determined after drying.

2.2.6 Residue

The fibers and shives contain cutin and other non-soluble breakdown products not dissolved in the detergents or in the sulfuric acid. However, not much is known about the residues and they will not be further commented.

2.2.7 Method for determination of wax content

The hemp sample was weighed out and corrected for dry matter. Then the sample was extracted in a soxhlet apparatus with ethanol for 5 hours. After extraction the sample was dried overnight at 105°C and was weighed out again. Wax was determined by weight loss.

2.3 Chemical-physical pretreatments

Retted Fedora 19 hemp fibers from Skejby trials were used in all the chemical-physical pretreatment experiments. The fibers were impregnated with chemicals prior to pretreatment or chemicals were added to the treatment (Table 5). The wet oxidation and hydrothermal experiments were carried out in a specially designed loop-reactor with a working capacity of 1 L, constructed at Risø National Laboratory (Figure 7). Immersing the reactor in heating- or cooling bath controlled the temperature (Bjerre & Schmidt, 1997; Bjerre et al, 1996). 1 L of water was added with the hemp sample. Chemicals and oxygen were added before the suspension was heated. In the tests without oxygen, N_2 atmosphere was used. In tests with base, the chosen one was Na_2CO_3. All tests were run for 10 minutes at 170°C.

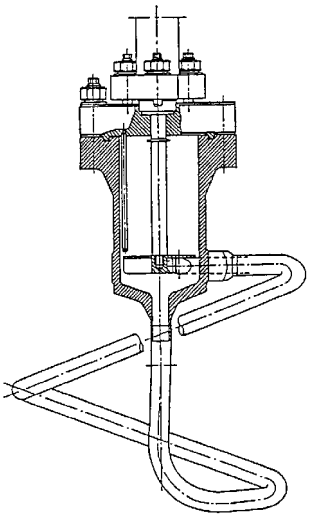

Figure 7. Loop autoclave for wet oxidation and hydrothermal treatment experiment.

Steam explosion was carried out in a steam explosion facility at Risø (Figure 8). The hemp samples were impregnated with chemicals for one hour before steaming. The samples were all steamed at 200°C for 10 minutes. The oxidant for bleaching was H_2O_2.

After the chemical-physical pretreatments, the samples were filtered to separate the cellulose-rich fraction (filter cake) from the filtrate. The filter cake was washed and then dried for a week at 20°C and 65% relative humidity. They were stored in paper bags (Bjerre & Schmidt, 1997). The filter cake was weighed and the composition was analyzed.

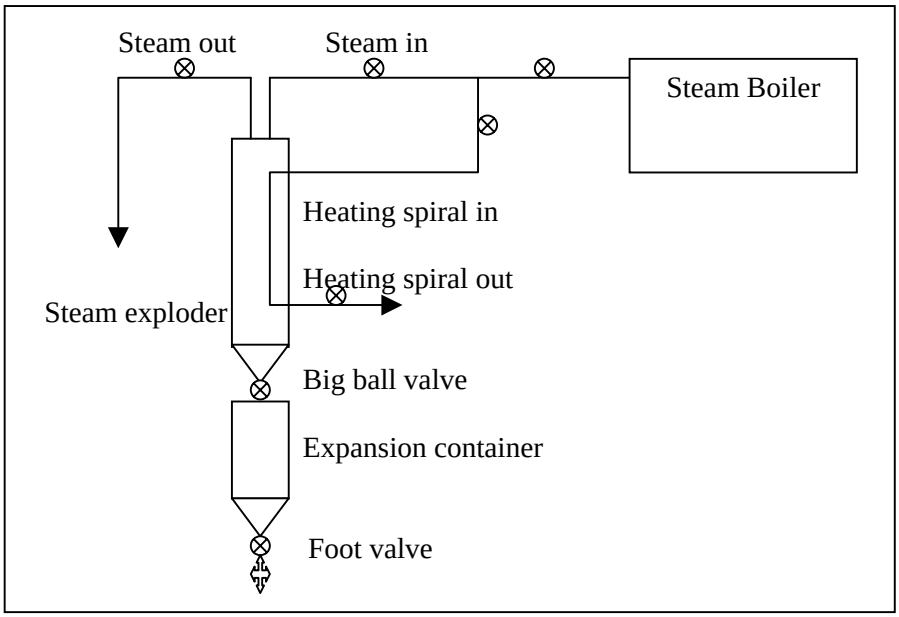

Figure 8. Model of the steam explosion facility used in the experiments at 200°C for 10 minutes (From internal log-book).

Table 5. Experimental conditions used in the physical-chemical pretreatment experiments. The reaction time was 10 minutes in all the experiments.

Chemical-physical Pretreatment	Mass of hemp, g	*Process temperature, ℃*	Impregnation prior to process	Addition to process
Wet oxidation	10	170	-	5 g Na_2CO_3, 10 bars O_2
Hydrothermal treat.	10	170	-	5 g Na_2CO_3
Hydrothermal treat.	10	170	-	-
Wet oxidation	10	170	-	10 bars O_2
Steam explosion	50	200	-	-
Steam explosion	50	200	5% Na_2CO_3	-
Steam explosion	50	200	5% Na_2CO_3+2% H_2O_2	-
Steam explosion	50	200	2% H_2O_2	-

2.4 Calculations

The chemical composition of each sample was calculated in a spreadsheet. In cases where analysis was carried out for pure fibers, pure shives and a mixture of the two components, the distribution between them were calculated.

2.4.1 Determination of dry matter and ashes

The dry matter and ash contents in the raw material in weight-% were calculated as follows;

$$\text{Dry matter (\%)} = \frac{\text{Residue after drying (g)}}{\text{Raw Material (g)}} \times 100\% \quad [1]$$

$$\text{Total ashes (\%)} = \frac{\text{Residue after ashing (g)}}{\text{Residue after drying (g)}} \times 100\% \quad [2]$$

2.4.2 Sequential fiber analysis

NDF (Neutral Detergent Fiber) was the amount of fibers that continued in the analysis after the NCWM had been removed.

$$\text{NDF (\%)} = 100\% - \frac{\text{Raw Material (dry) (g)} - \text{NDF (g)}}{\text{Raw material (dry) (g)}} \times 100\% \quad [3]$$

Minerals were accounted for in the ashes, so the NCWM had to be corrected for content of ashes. Minerals were removed in the neutral detergent, but an amount remains with the fibers. This smaller amount was included in the NDF [3], so the NCWM was corrected.

$$\text{NDF ash (\%)} = \frac{\text{residue after ashing (g)}}{\text{NDF sample (g)}} \times 100\% \quad [4]$$

$$\text{NCWM (\%)} = 100\% - \text{NDF (\%)} - (\text{Total ash (\%)} - \text{NDF ash (\%)}) \quad [5]$$

ADF (Acid Detergent Fiber) was the amount of fibers continuing in the analysis after the hemicellulose had been removed from the NDF. A small sample from the NDF was taken out for ashes. The amount of NDF that continued in the flow in the sequential analysis was called NDFflow.

$$\textbf{Removed from NDFflow (\%)} = \frac{\textbf{NDFflow (g) - residue after acid detergent (g)}}{\textbf{NDFflow (g)}} \times 100\%$$

To get the scale right the fraction of material removed by the acid detergent had to be corrected:

$$\text{Removed from NDF (\%)} = \text{Removed from NDFflow (\%)} \times \text{NDF (\%)}/100\%$$

The percentage of sample removed by acid detergent was calculated as follows:

$$\text{ADF}(\%) = \text{NDF}(\%) - \frac{\text{NDF}(\%) \times (\text{NDFflow}(\text{g}) - \text{res. after acid deterg.}(\text{g}))}{\text{NDFflow}(\text{g})} \quad [6]$$

A part of the minerals were still in the NDF and an even smaller amount was still found in the ADF.

$$\text{ADF ash}(\%) = \frac{\text{residue after ashing}(\text{g})}{\text{ADF sample}(\text{g})} \times 100\% \quad [7]$$

The amount of hemicellulose in the raw material was the difference between NDF and ADF. The difference was corrected for the content of ash (minerals) in the neutral detergent and for the small amount still present in the ADF, but already corrected for.

$$\text{Hemicellulose}(\%) = \text{NDF}(\%) - \text{ADF}(\%) - \text{NDFash}(\%) + \text{ADFash}(\%) \quad [8]$$

PF (Permanganate Fiber), the continued amount of fibers in the analyses after the lignin, was removed from the ADF. A small sample from the ADF was taken out for incineration and the fibers that continued in the analyses were called ADFflow.

$$\text{Removed from ADFflow}(\%) = \frac{\text{ADFflow}(\text{g}) - \text{residue after Pem.lignin}(\text{g})}{\text{ADFflow}(\text{g})}$$

To get the scale right the fraction of material removed by the permanganate lignin was corrected:

$$\text{Lignin}(\%) = \text{ADF}(\%) \times \frac{\text{ADFflow}(\text{g}) - \text{residue after Pem.lignin}(\text{g})}{\text{ADFflow}(\text{g})} \quad [9]$$

The remainder of minerals that might be left in the PF was negligible, so no sample was taken out for determination of ashes. PFflow was the amount of fibers that continued in the analysis. The content of cellulose was what was removed by the sulfuric acid. Compared to the PF this was:

$$\frac{\text{Cellulose}(\%)}{\text{PF}(\%)} = \frac{\text{PFflow}(\text{g}) - \text{residue after sulf. acid}(\text{g})}{\text{PFflow}(\text{g})}$$

and

$$\text{PF}(\%) = \text{ADF}(\%) - \text{Lignin}(\%)$$

so

$$\text{Cellulose}(\%) = (\text{ADF}(\%) - \text{Lignin}(\%)) \times \frac{\text{PFflow}(\text{g}) - \text{residue after sulf. acid}(\text{g})}{\text{PFflow}(\text{g})} \quad [11]$$

2.4.3 Content of fibers in mixed samples

The distribution between fibers and shives in mixed samples was calculated. Cellulose was the main fiber component and therefore assumed as the most accurately determined component.

$$\text{Cellulose}_{\text{sample}}\left(\tfrac{\text{g}}{100\text{g}}\right) = \text{Fibre in sample}(\%) \times \text{Cellulose}_{\text{fib}}\left(\tfrac{\text{g}}{\text{g}}\right) + (100\% - \text{Fibre in sample}(\%)) \times \text{Cellulose}_{\text{shiv}}\left(\tfrac{\text{g}}{\text{g}}\right)$$

$$\text{Fibre in sample}(\%) = \frac{\text{Cellulose}_{\text{sample}}\left(\tfrac{\text{g}}{100\text{g}}\right) - \text{Cellulose}_{\text{shiv}}\left(\tfrac{\text{g}}{100\text{g}}\right)}{\text{Cellulose}_{\text{fib}}\left(\tfrac{\text{g}}{\text{g}}\right) - \text{Cellulose}_{\text{shiv}}\left(\tfrac{\text{g}}{\text{g}}\right)}$$

2.4.4 Calculations of loss of dry matter and cellulose in pretreated samples

The content of dry matter in the raw material and the pretreated fibers were calculated as:

$$\text{Dry matter}(\text{g}) = \text{Sample weight}(\text{g}) * \text{Dry matter fraction}\left(\tfrac{\text{g}}{\text{g}}\right)$$

The loss of dry matter during a chemical-physical pretreatment was calculated as:

$$\text{Loss of dry matter (\%)} = \frac{\text{Dry matter before treatment (g)} - \text{Dry matter after treatment (g)}}{\text{Dry matter before treatment (g)}} \times 100\%$$

Contents of cellulose were calculated as follows:

$$\text{Cellulose (g)} = \text{Dry matter (g)} * \text{Cellulose}\left(\frac{\text{g}}{\text{g}}\right)$$

The loss of cellulose in the dry matter during chemical-physical pretreatments was:

$$\text{Loss of Cellulose (\%)} = \frac{\text{Cellulose before treatment (g)} - \text{Cellulose after treatment (g)}}{\text{Cellulose before treatment (g)}} \times 100\%$$

3 Results and discussion

3.1 Evaluation of the chemical analysis method

The results on chemical composition of hemp fibers and hemp shives obtained in this study are found in Table 6. The cellulose contents were higher than the literature values both for fibers and shives (Table 2). The hemicellulose contents for both fibers and shives were in the low end of the range given by the literature values. The lignin content of the fibers was similar to values found in literature (Table 2). The only value that was outside the ranges was for cellulose and could be due to the cultivars investigated.

Table 6. Chemical composition measured in fibers and shives from the hemp cultivar Fedora 19 (% w/w).

	Fibers	Shives
Ash (% w/w)	2 – 3	1 – 2
Cellulose (% w/w)	73 – 77	47 – 48
Hemicellulose (% w/w)	7 – 9	21 – 25
Lignin (% w/w)	4 – 6	16 – 19
NCWM[1] (% w/w)	6 – 7	8 – 9

1: NCWM was calculated as the sum of wax, water-soluble material and pectin.

In order to evaluate the correction for contents of ash in the sequential fiber analysis, samples were taken out after each step in the procedure. Three samples were evaluated; crushed hemp stems from Køge-Ringsted trials of Felina and Futura and pure fibers from Skejby-trials of retted Fedora 19 (Table 7). A small content of ash was found in Neutral Detergent Fiber in the range of 0.4-0.6% w/w. Ash contents in Acid Detergent Fiber and Permanganate Fiber were in the range 0-0.1% w/w, which is so low that it is not necessary to correct for the ash content. Neutral Detergent should be corrected for the ash content.

Table 7. Ash content in Neutral Detergent Fiber, Acid Detergent Fiber and Permanganate Fiber in crushed hemp stems of Felina and Futura from Køge-Ringsted trials and pure fibers from retted Fedora 19 from Skejby-trials.

	Ash in NDF (% w/w)	Ash in ADF (% w/w)	Ash in PF (% w/w)
Felina	0.58	0	0
Futura	0.42	0	0
Pure fibers	0.47	0.063	0.048

3.1.1 Evaluation of temperature for drying samples

The analysis carried out drying at 60°C did not show significantly different values than the analysis where samples were dried at 105°C (Figure 9). The only difference was the amount of NCWM, which was slightly higher for the sample dried at 60°C. However, this could not be due to difference in temperatures, as the analysis for NCWM was the first step in the analysis procedure.

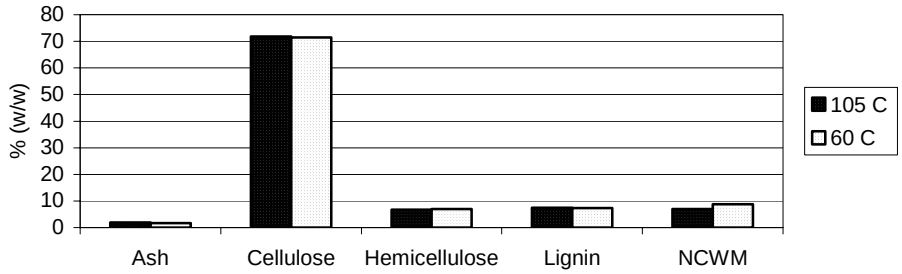

Figure 9. Chemical composition of retted Fedora 19 measured with drying at 105° C overnight or 60° C overnight between each analysis step.

3.1.2 Evaluation of method for determination of wax content

The results obtained from the wax-analysis method were unsteady. The weighing procedure was changed in order to obtain better results, which did not help. The thimble that the fibers were held in took up moisture from the air too quickly. Instead, solvent including extracted waxes could be concentrated and analyzed by gas chromatography or mass spectrometry, so the exact amount of wax could be determined.

3.2 Fibers and shives in hemp samples

3.2.1 Unretted Fedora 19 from Køge-Ringsted trials

The samples from Køge-Ringsted consisted of crushed hemp stems. Analyses were carried out in order to identify differences between cultivars. The stem is normally separated into fibers and shives before industrial utilization. In order to characterize these two fractions, fibers and shives from unretted Fedora 19 were separated by hand with a set of sieves and analyzed chemically for their contents of ash, cellulose, hemicellulose, lignin and non cell wall material (NCWM). These results were used for estimating the relative content of shives and fibers.

Shives are rich in lignin and hemicellulose whereas fibers are rich in cellulose (Table 8). Based on the fraction of cellulose in unretted Fedora 19, the amount of fibers in the stem was calculated. Calculated from the cellulose fraction, the distribution of fibers and shives in the stem were app. 43% w/w fibers and about 57% w/w shives. These values are very high compared to values from literature that states fiber contents in the range of 20-35% w/w (Vogl, 1996). The content of hemicellulose in the stem (10% w/w) is closer to fibers (9% w/w) than to shives (21% w/w). This indicates that the shives have not been penetrated completely by chemicals when analyzing the whole hemp stem.

Table 8. Chemical composition measured in stems, fibers and shives (weight-%) in unretted Fedora 19 hemp grown in 1998 in Køge-Ringsted on Zealand.

	Ash	Cellulose	Hemicellulose	Lignin	NCWM
Stem (% w/w)	4	60	10	12	12
Fibers (% w/w)	3	77	9	4	6
Shives (% w/w)	2	47	21	19	9

3.2.2 Retted Fedora 19 from Skejby-trials

The retted Fedora 19 from the Skejby-trials contained a small amount of shives after being mechanically separated. To determine the composition, pure fibers and shives were analyzed. Contents of cellulose indicated that there was 8% w/w of shives in the mechanically separated fibers. As seen from Table 9, lignin and cellulose differs with only a few weight-percent for mechanically separated fibers and pure fibers so the small amount of shives in the mechanically separated fibers is not of chemical importance.

Table 9. Chemical composition in weight-% of mechanical separated fibers, pure fibers and shives from retted Fedora 19.

	Ash % w/w	Cellulose % w/w	Hemicellulose % w/w	Lignin % w/w	NCWM % w/w
Mech. sep. Fiber	2	71	7	8	7
Pure fiber	2	73	7	6	7
Shives	1	48	25	16	8

- *The separated fibers contained a remainder of shives. A sample was therefore separated completely by hand with forceps to characterize pure fibers and shives. The hemp was grown in 1998 in Skejby, Jutland.*

3.2.3 Retted and unretted Fedora 19 compared

Lignin and non cell wall material are degraded during the retting process. The epidermis layer is degraded and fibers and shives are separated. Retted fibers from Fedora 19 contained higher amounts of lignin and non cell wall material but lower amounts of cellulose, hemicellulose and ash than unretted fibers (Table 8 and 9). This indicates that pure fibers are not affected chemically by retting. The retted fibers were medium grey and the raw fibers were yellowish. The darker color showed that the lignin in the retted fibers was oxidized and thereby formed more double bonds than the lignin in unretted fibers.

Retted shives contain higher amounts of cellulose and hemicellulose but lower amounts of lignin, ash and non cell wall material. This was in accordance with the theory of the retting process where lignin and NCWM are degraded. The color of retted shives was yellowish with grey spots on the surface, so the lignin on the spots was probably oxidized. Unretted shives were yellow like the fibers.

3.3 Effects of growth conditions

3.3.1 Cultivar

Among the cultivars Felina, Fasamo, Futura and Fedora (Figure 10), Felina had less lignin and Fedora less hemicellulose. Felina and Fedora had the same amounts of cellulose and non cell wall material (NCWM). Fasamo is a cultivar that is relatively small and early and sets many seeds. Futura is tall and late and sets few seeds. (Ringsted, 1998). This information was not reflected in the chemical composition of the plants, as Fasamo and Futura had the most similar compositions of the four cultivars analyzed. Ash content is an indication of the mineral-uptake of the plant. The cultivars investigated contained about the same amount of ashes. Content of cellulose in the stem might be an indication of a high content of fibers because the fibers contain more cellulose than shives. Therefore, Fedora and Felina might contain more fibers than the other cultivars analyzed.

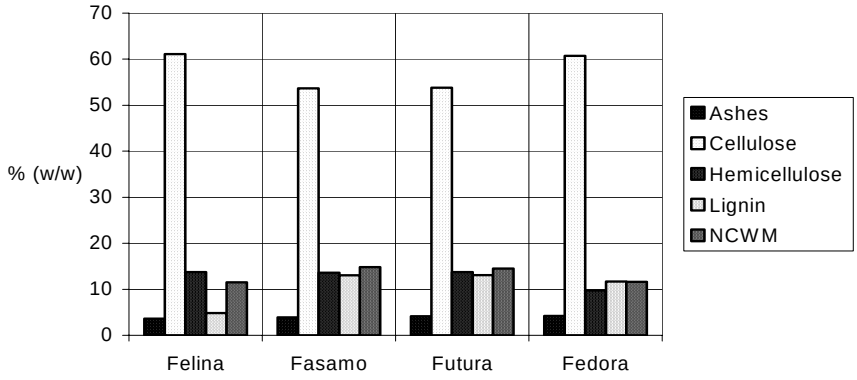

Figure 10. Chemical composition in weight-% of Felina, Fasamo, Futura and Fedora stems.

3.3.2 Plant density

Felina, Fedrina and Fedora were grown at standard conditions at plant densities of 100-300 plants/m^2. As seen on Figure 11, Felina had the same ash content and thereby mineral uptake for plant densities in the range 100-200 plants/m^2. For Felina and Fedrina with the density 300 plants/m^2, the mineral uptake was higher compared to the lower densities. The uptake of minerals for Fedrina increased versus the plant density. The plant density did not affect Fedora.

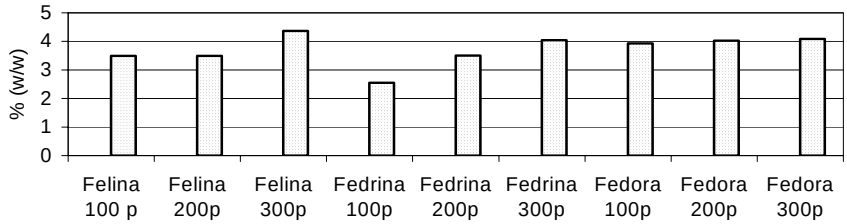

Figure 11. Ash content measured in weight-% in Felina, Fedrina and Fedora at plant densities of 100-300 plants/m^2.

3.3.3 Nitrogen fertilizer

Contents of ash are illustrated in Figure 12 for Felina and Fedrina grown at nitrogen levels of 50-150 kg N/ha. The ash content was a little higher at 100 kg N/ha than at both 50 and 150 kg N/ha. However the values were similar (3-4% w/w), so the mineral uptake did not appear very affected by the amounts of nitrogen. The chemical compositions of Felina at 50 and 100 kg N/ha were almost identical (Figure 13), so the composition did not seem to be affected by the nitrogen levels.

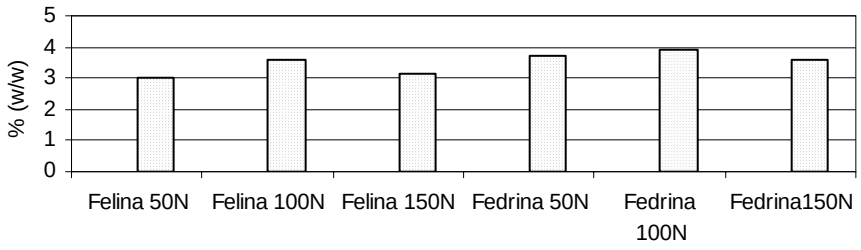

Figure 12. Ash content in weight-% in Felina and Fedrina at different levels of nitrogen fertilization

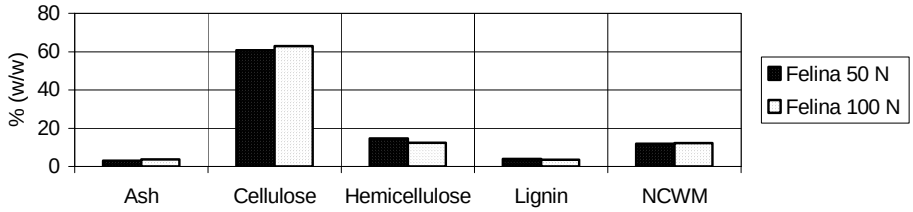

Figure 13. Chemical composition (% w/w) of Felina hemp fertilized with 50/100 kg N/ha.

3.4 Effects of chemical-physical pretreatments

Fedora 19 from Skejby trials was used as raw material in the chemical-physical pretreatment processes. This was done in order to compare the raw material with the material modified by a pretreatment process. All chemical-physical pretreatments increased the amount of cellulose, decreased the amount of lignin and almost completely removed the non cell wall material in the sample (Figure 14 and 15).

3.4.1 Effects on loss of dry matter

It was important how the incoming material was modified and to avoid cellulose degradation during the pretreatment process. The chemical-physical pretreatment conditions given in Table 5, resulted in loss of dry matter ranging between 15-73% w/w and in loss of cellulose ranging between 0-69% w/w (Table 10). In wet oxidation and hydrothermal treatment the losses of dry matter were smaller (15-29% w/w) than in the steam explosion (17-73% w/w). Correspondingly losses of cellulose in wet oxidation and hydrothermal treatment were smaller (0-12% w/w) than in steam explosion experiments (0-69% w/w).

All three pretreatment experiments with alkali addition removed the biggest part of the dry matter compared to when alkali was not added. The alkali probably had a too strong effect on opening the structure of the plant constituents. Not only hemicellulose and

lignin, but also some cellulose was degraded. The three processes in this project that removed least dry matter were wet oxidation with oxygen and no alkali, hydrothermal treatment without additives and steam explosion without impregnation (15-17% w/w).

Chemical-physical treatment should either be chosen where losses are small or the dissolved material in the liquid fraction can be utilized. However, literature states that losses of the polysaccharides cellulose and hemicellulose in total are 16% w/w for wet oxidation and 20% w/w for steam explosion (Bjerre & Schmidt, 1997). This indicates that these processes could be optimized so losses are minimized when used on hemp. Optimization parameters are additives, temperature and reaction time.

Table 10. Fiber loss and fiber color after pre-treatment of retted Fedora 19 hemp fibers with remaining shives.

Physical-chemical Pretreatment	Loss of dry matter, % w/w	Loss of cellulose, % w/w	Color of fibers after treatment	Color and nature of shives after treatment
Wet oxidation (+base & oxygen)	29	12	White	Yellowish
Hydrothermal treatment (+base)	24	8	Light grey	Yellowish grey
Hydrothermal treatment	17	0	Medium grey	Yellowish grey
Wet oxidation (+ oxygen)	15	0	Light grey	Yellowish grey
Steam explosion	17	0	Dark brown	Dark brown, entangled with fibers
Steam explosion (+base)	73	69	Medium grey	Light grey
Steam explosion (+base & oxidant)	49	40	Very light yellow-green	Light yellow-green, a bit entangled with fibers
Steam explosion (+oxidant)	33	16	Medium brown	Medium brown, entangled with fibers

3.4.2 Effects on visual appearance of the samples

Originally being medium grey, the pretreatments gave fiber colors ranging from white to dark brown (Table 10). Wet oxidation gave the palest fibers, light grey without alkali and white with alkali. Hydrothermal treatment gave medium grey fibers without alkali and light grey with alkali. Generally, steam exploded fibers that were not impregnated with alkali turned brown during the treatment. They became medium brown with the oxidant H_2O_2 and dark brown without oxidant. Steam exploded fibers impregnated with alkali kept their original grey color and steam exploded fibers impregnated with both alkali and H_2O_2 gave very bright fibers. Of all the chemical-physical pretreatment experiments, the brightest fibers were obtained when alkali, that opens the structure of the molecules, was combined with an oxidant that could open the double bonds.

The remainder of shives in the samples changed color too (Table 10). In most pretreatments the shives were still separate from the fibers, so it is assumable that it would be easy to clean a fiber sample of shives. However, in three steam-explosion experiments the shives had a color almost identical to the fibers. They were to some degree dissolved and were entangled with the fibers. It might therefore be more difficult to separate the remainder of shives.

3.4.3 Effects on chemical composition of samples

All chemical-physical pretreatments changed the chemical composition of the hemp raw material (Figure 14 & 15). Contents of cellulose increased from 72% w/w in the raw material to 83-90% w/w after treatment. NCWM was in all experiments almost completely removed. Lignin was to some extent removed in all chemical-physical pretreatments. Wet oxidation and hydrothermal treatments modified the sample in a uniform manner (Figure 14). The ash fraction differed a bit, as hydrothermal treatment gave an ash content of 0.5-0.8% w/w and wet oxidation gave an ash content of 2.7-3.7% w/w.

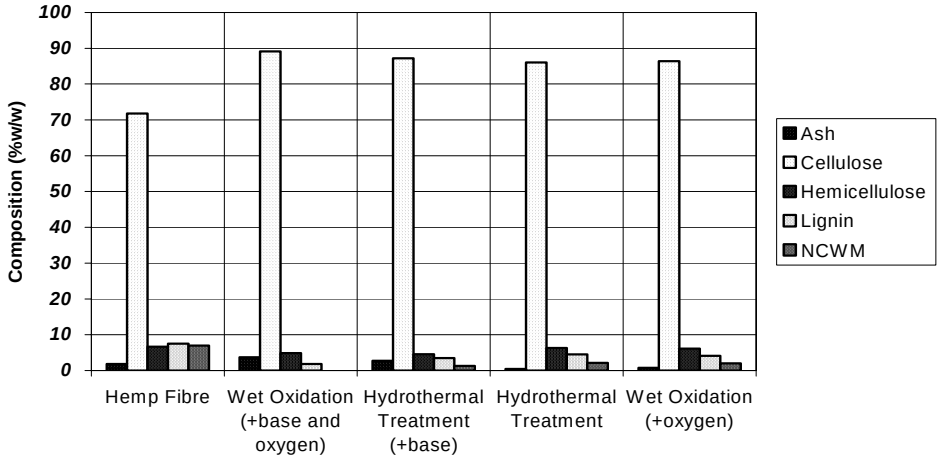

Figure 14. Chemical composition showed in weight-% of hemp fibers to show the effect of wet oxidation and hydrothermal treatment.

The chemical composition of the fibers after steam explosion was mainly dependent on if impregnation in alkali was applied (Figure 15). With alkali, the cellulose content was a bit lower, 83-85% w/w, compared to steam explosion without alkali (86-90% w/w). This difference was mainly reflected in contents of hemicellulose. Fibers impregnated with alkali contained 8-9% w/w hemicellulose, without alkali it was 3-4% w/w. Thus alkali had a negative effect on the extraction of hemicellulose.

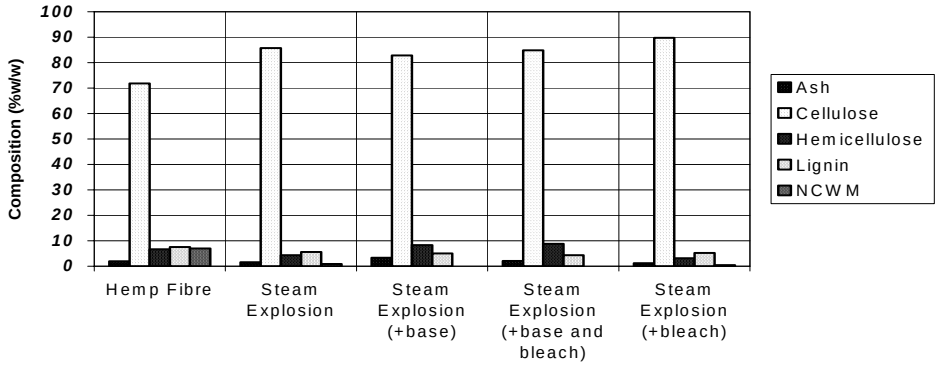

Figure 15. Chemical composition of hemp fibers in weight-% measured before and after impregnation with chemicals and steam explosion.

3.5 Hemp yarn

Hemp yarn of a good quality for textiles was characterized chemically in order to compare the yarn with hemp fibers and fibers modified through chemical-physical pretreatment. The hemp yarn had almost the same color, medium grey, as retted Fedora 19. The yarn was therefore probably made from retted hemp fibers. The sample of yarn showed significantly higher amounts of cellulose than the sample of pure fibers from Fedora 19 (Figure 16). Contents of ash, hemicellulose, lignin and non cell wall material were all lower in yarn than in retted fibers. The fibers for the yarn were probably treated to decrease contents other than cellulose, because the cellulose is the compound with strengthening properties. The distribution of components in the hemp yarn was similar to the distribution of components in the hydrothermal treated fibers (Figure 16).

If hemp fibers are used for textile purposes it is likely, that a white color of the fibers is desirable. White fibers were obtained, when fibers were wet oxidized with alkali in the process. However, almost 1/3 of the hemp raw material and 12% w/w of the cellulose were lost during this process. Further investigations in minimizing the loss would be required. A remainder of shives with the retted fibers was not important chemically, but the shives would probably interfere mechanically in a spinning process.

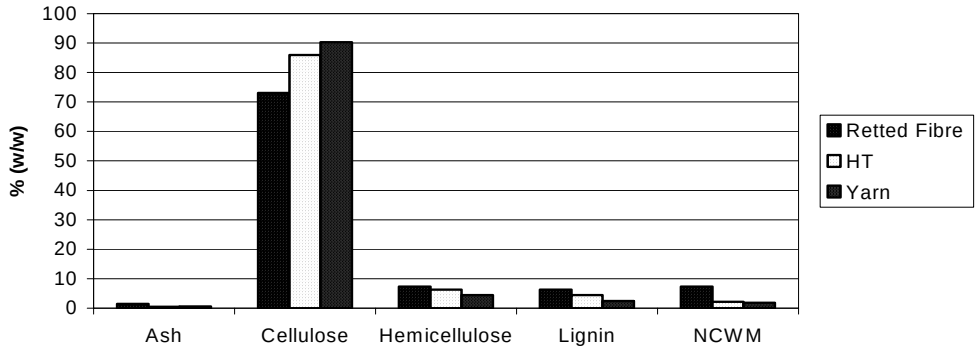

Figure 16. Chemical composition in weight-% of fibers from retted Fedora 19 from Skejby-trials the same fiber submitted to hydrothermal treatment and compared to hemp yarn. All samples were medium grey.

4 Conclusion

- The hemp fibers were rich in cellulose (73-77% w/w) and contained less hemicellulose (7-9% w/w) and lignin (4-6% w/w). The shives contained less cellulose than fibers (47-48% w/w) and much hemicellulose (21-25% w/w) and lignin (16-19% w/w).
- Different cultivars of hemp had slightly different compositions. In the cultivars analyzed, Felina had lower lignin content than Fasamo, Futura and Fedora. Fedora had a low content of hemicellulose while Fasamo and Futura had a low content of cellulose.
- Different levels of nitrogen did not affect the content of minerals and the chemical composition in the Felina and Fedrina hemp cultivars.

- The pretreatments tested degraded and dissolved especially hemicellulose, lignin and NCWM. Generally losses of dry matter and cellulose were bigger for steam explosion than for wet oxidation and hydrothermal treatment. When alkali was added to the pretreatment processes, more dry matter was degraded. The processes with the lowest dry matter loss were wet oxidation (15% w/w), hydrothermal treatment without alkali (17% w/w) and pure steam explosion (17% w/w). In these three processes no cellulose was degraded.
- Originally being medium grey, the colors of the pretreated fibers ranged from white to dark brown. The brightest colors where obtained when alkali was combined with an oxidant. Wet oxidation and hydrothermal treatment in general gave brighter color of fibers than steam explosion.
- The chemical composition of the yarn was similar to pretreated fibers and contained more cellulose than retted fibers.

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Mission

To promote an innovative and environmentally sustainable technological development within the areas of energy, industrial technology and bioproduction through research, innovation and advisory services.

Vision

Risø's research **shall extend the boundaries** for the understanding of nature's processes and interactions right down to the molecular nanoscale.

The results obtained shall **set new trends** for the development of sustainable technologies within the fields of energy, industrial technology and biotechnology.

The efforts made **shall benefit** Danish society and lead to the development of new multi-billion industries.