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CELLULOSE FIBERS FROM HEMP FOR TEXTILE INDUSTRY

Bachelor Research Project
Chemical Engineering

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Abstract

Fibers containing low levels of non-cellulosic components from biomass are highly desired materials in the textile industry. This work thus aimed to isolate cellulose fibers from hemp, focusing on different chemical treatments. Three alkali treatments were employed: $NaOH/H_2O_2$ (11%), NaOH/NaOCl (11%), and $NaOH/Na_2SO_3$ (11% and 1%), with and without further acid hydrolysis. These treatments were applied on three different types of raw hemp: non-retted, light-retted, and well-retted. After each chemical treatment, fibers with different morphologies and chemical content were obtained and the yield (% w/w) on a dry basis was calculated. The highest yield (75%) resulted from the treatment with $NaOH/H_2O_2$ for the light-retted hemp. A high yield of 72% was obtained with $NaOH/Na_2SO_3$ (1%) without acidification and a yield of 71% with $NaOH/Na_2SO_3$ (1%) with acidification for both light- and well-retted hemp samples. Fibers suitable for textile production are considered to be the longest and strongest ones. Here, such fibers were obtained as a result of $NaOH/H_2O_2$ and NaOH/NaOCl treatments as well as $NaOH/Na_2SO_3$ (1%) without acidification. However, light-retted hemp generally resulted in such fibers, whereas treating the well-retted sample gave very short, fine fibers with a powder aspect. This result is attributed to the degree of retting, which already degraded the fibers and thus further treatment affected the fibers' strength and the length. A very efficient removal of non-cellulosic compounds occurred as a result of treatment with $NaOH/H_2O_2$, whereas a significant decrease in the lignin content occurred. For the light-retted sample, the lignin composition decreased from 46 wt% to 27 wt%, whereas for the well-retted hemp, from 49 wt% to 33 wt%. In addition, effective removal of non-cellulosic components was observed from treating with $NaOH/Na_2SO_3$ (1%), without acidification, for both light- and well-retted hemp. The light-retted sample showed a decrease in the lignin content from 46 wt% to 21 wt% and the well-retted hemp, from 49 wt% to 18 wt% lignin. Therefore, a strong oxidizing agent such as H_2O_2 can rapidly oxidize lignin, leading to its dissolution in the alkaline medium. $NaOH/H_2O_2$ with acid hydrolysis and $NaOH/Na_2SO_3$ (1%) without acid hydrolysis proved to be the most efficient chemical pre-treatments of hemp.

Introduction

The world population is predicted to have a growth of about 2.5 billion in the next two decades, resulting in an increased demand for food and consumer products and commodities [1]. However, in contrast to this, the arable land is more and more limited and the cropland area per capita will decrease considerably. These circumstances will lead not only to a food crisis, but also to the so-called 'cellulose gap', because of stagnation of the cotton production [2]. The concern about climate change and environmental issues might thus come from a surprising place: our closets. Extended manufacturing of cheap textiles, made from synthetic fibers, leads to an increase in pollution and waste. Therefore, a spike in the exploration of sustainable, bio-based resources is induced [3]. One of such resources is represented by the industrial hemp (*Cannabis Sativa L.).*

In recent years, these environmental and political pressures led to an increased attention towards a more bio-based economy. 'Green' materials, such as biomass, are thoroughly researched as possible replacement of the fossil-based resources. Current research intentions focus on the use of crops or other biomass for production of chemicals, plastics and textiles. Moreover, fiber crops rise a great interest as substitute for high-input crops such as cotton and as a way of decreasing the impact the paper industry has on the natural forests [3]. Hemp (*Cannabis Sativa L.*) is one of the various crops with a great potential as a basis for bio-based materials and composites. The main motivation for a future increase in hemp's cultivation and processing is the sustainability and ecological nature of the hemp crop [11].

Concerning the textile industry, industrial hemp plant shows a great potential for the development of natural cellulosic fibers to replace synthetic materials or cotton and decrease negative environmental impacts. As a textile, hemp can provide the warmth and softness of a natural textile fiber but with a greater durability [32]. Seeing this, the research question of this project is: *What is the most effective chemical treatment to remove the non-cellulosic components in hemp fibers, without degrading the cellulose?*

1 Background

R. E. Schultes (1970), the father of modern ethnobotany [12], defines hemp as a green, very abundant and ubiquitous plant, economically valuable, possibly dangerous and certainly in many ways mysterious. His definition is adequate in describing the valuable but contradictory nature of this essential industrial crop [11]. Hemp (*Cannabis sativa L.*), also known as industrial hemp, is one of the world's oldest cultivated and most widely used industrial crops. The cultivation of hemp was very broad until its demand considerably decreased because of regulations and the development of substitute, cheaper materials.

Industrial hemp is considered a low-input crop, its cultivation allowing a diversification of crop rotations in arable farming [7]. In addition, hemp is a fast growing crop, with low requirement for fertilizers and herbicides, producing more fiber yield than most other plant sources, i.e. cotton and flax. Furthermore, in comparison with synthetic fibers, hemp fibers have many benefits such as low cost and

low density, as well as high stiffness and strength [5]. The versatility of hemp plant and its beneficial characteristics give hemp the potential to be a sustainable alternative for present materials [3].

1.1 Importance

In recent years, the demand for natural fibers and the products derived from them has significantly increased. The development of new bio-based products has been highly motivated by the shortage of crude oil and the increase in awareness regarding the environment [11].

Applications

Hemp is a multipurpose crop, with a large diversity of end-use applications (**Figure 1**). The versatility of the hemp plant along with the low-input required for its cultivation and refinery contribute to its great economic worth. Historically, China was the first country to cultivate hemp (2700 BC) and to discover hemp's properties as a medicinal plant. Cultivation spread further across Asia and Europe (about 2000 years ago). The plant's fibers were identified as strong and durable and they were mainly used in sail making and paper industry. Moreover, oils from hemp seeds were used in cooking and cosmetics [3]. As a textile fiber, hemp bast fibers are among the strongest and most durable of all vegetable fibers and particularly in Asia, Central Europe, and North America has been extensively used as a textile fiber for hundreds of years. Cultivation in Europe reached a maximum between the sixteenth and eighteenth century. The fibers were widely processed for sailing equipment, ropes fishing nets, household textiles and clothing [6].

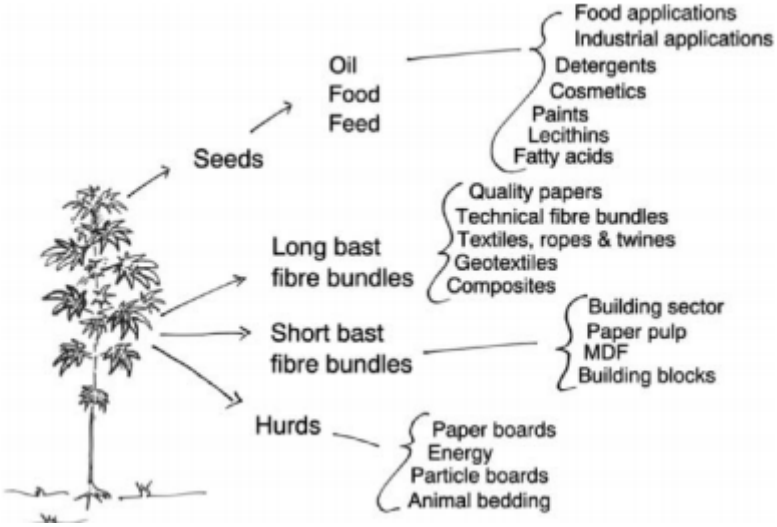


Figure 1 -Different applications of hemp [11]

Hemp – a controversial plant

Despite hemp's great properties and applications, there was a decline in its production due to multiple reasons such as the large-scale development of tropical fibers (e.g. cotton, jute, sisal, etc.), the competition with other cost-effective crops and the absence of laborsaving machinery. Markets diminished drastically and hemp was replaced with cheaper substitutes, even though, in general, they were less durable. Furthermore, the cultivation of hemp was prohibited in many countries because of its association with the production of illegal narcotics [6]. The main impediment that led to the ban on hemp's production in some countries is the THC (delta-9-tetrahydrocannabinol) content of the plant. THC is the principal psychoactive constituent in the female cannabis plant, known for inducing psychotropic or euphoric effect on the user [26]. Cannabis plants with a THC content higher than 0.3 % (dry weight) are called 'Marijuana' plants. Therefore, even though industrial hemp contains less than 0.3% psychoactive ingredients (THC), great confusion between hemp and marijuana plants was generated. Consequently, the diminished importance of hemp has led to research withdrawals and development of new machinery and processing techniques has come to an impasse. Currently, hemp fibers are mainly produced for low and medium-value applications, having as the largest producers China, India and North Korea [6].

Sustainability

According to UNFCCC (United Nations Climate Change) [17], the total greenhouse gas emissions from textile production currently stands at 1.2 billion tons annually (2018). It is estimated that the fashion industry is responsible for 10% of the global carbon emissions and by 2030, the sector's emissions are to increase by more than 60%. The most frequently used fibers in textile industry are polyester and cotton. The production of such fibers has a significant ecological impact, being produced from fossil fuels and requiring large amount of water [18]. Considering this, measures have to be taken to reduce such negative impacts on the environment and to make sustainability the next fashion trend. One option to do so is to replace such fabrics with more environmentally friendly ones, such as hemp.

In contrast to other materials (i.e. cotton), an increase in hemp's cultivation has the potential to positively influence global warming. The reason for this is that during photosynthesis, hemp absorbs carbon dioxide from the atmosphere to form carbohydrates that represent the building structures of the plant [19]. Moreover, hemp does not require any pesticides, fertilizers and herbicides and the amount of water necessary for its cultivation is considerably lower. After cultivation, the roots of hemp's plant aerate the soil and leave it rich and suitable for future crops. What is more, the cultivation of hemp gives about 680 kg of fibers per acre whereas cotton produces only about 226 kg per acre [20].

1.2 Properties of hemp

Physical structure

Hemp stems are 1.5 – 2.5 m tall and 5 – 15 mm in diameter. The hemp stems produce hemp fibers with a 30-40% w/w fiber content [7]. The fibers are organized in layers: primary and secondary. The secondary fibers are distributed in bundles, which produce a distinct layer in the mature stem (**Figure 2**) [5]. For accessing particular product categories, an important aspect is the 3D-structure of the fiber. Length, diameter as well as smoothness of the fibers are fundamental characteristics.

In the textile industry, the length of the fiber is of great importance, as the fiber needs to be spun. A length higher than 15 mm and no longer than 30-60 mm is considered advantageous [27]. Furthermore, for the application in textile industry, the fineness of the fibers needs to be taken into account. Smoothness is influenced by the amount of impurities present such as the remaining non-cellulosic components including hemi-cellulose, lignin, etc.

Figure 2 - Hemp stem, separation of the fibers [9]

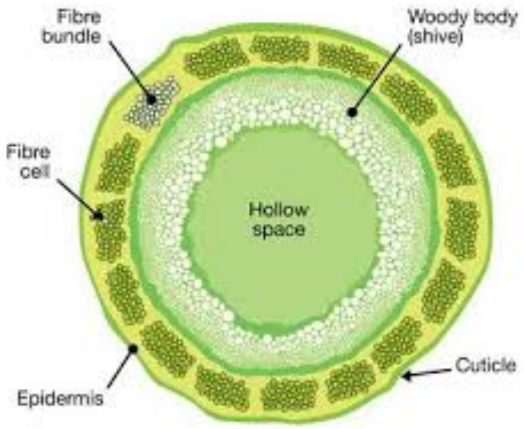


Figure 3 – Cross-sectional area in the hemp stem [10]

Chemical structure

The chemical structure and distribution of the constituents determine the characteristics of the fibers. For this investigation, the bast fiber, which is the outer part of the hemp stem (**Figure 3**), is the component of interest. It consists of primarily cellulose, however, pectins, hemicellulose and phenolic compounds are also present [11]. The chemical composition varies based on different external factors such as harvest time (growing stage), the harvest year, the location of the fibers within hemp stems and fiber processing. In general, hemp fibers have a cellulose content of 53-91%, 4-18% hemicellulose, 1-17% pectin and 1-21% lignin [7]. The cellulose fibers are packed together and bonded via hydrogen bonds and van der Waals interactions, which are coated by hemicellulose and lignin [3].

Cellulose

Cellulose is the most abundant and largest organic polymer in plant cell walls. It is a homogeneous linear polymer of glucan with repeating 1,4-D-glucose units bound by glycosidic bonds (**Figure 4**) [5]. The covalent bonds are formed between the hydroxyl group of C_4 and C_1 atoms by water elimination. The glucose monomers in cellulose are bond within each other via intramolecular hydrogen bonds and form elementary fibrils. Glucose also form bonds with the neighboring molecules: intermolecular interactions, and form 3D-network micro fibrils [5].

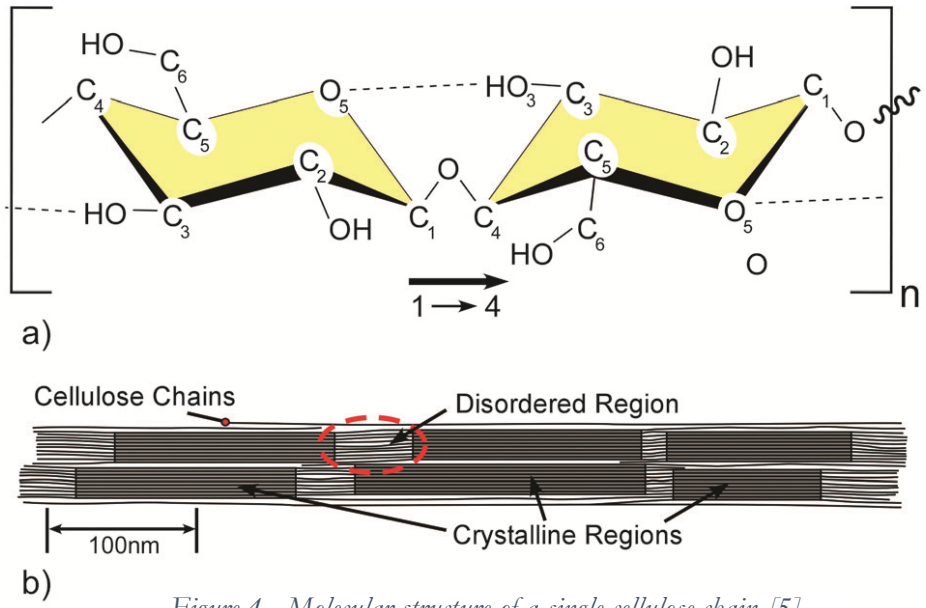


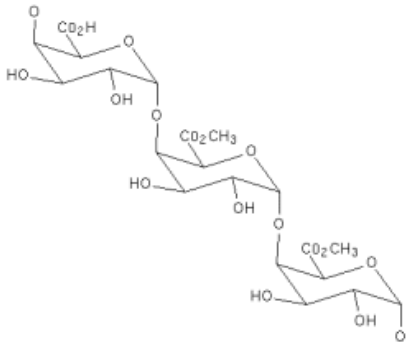
Figure 4 - Molecular structure of a single cellulose chain [5]

Hemicellulose

Hemicellulose is a heterogeneous group of polysaccharides associated with lignin and cellulose in plant cell walls. It is described as having 1,4-linked backbone with an equatorial configuration [5]. Monomers such as xylose, mannose, galactose, arabinose, etc. are sugars found in hemicellulose [8]. Hemicelluloses present in the hemp fibers contribute to the increase in the cell wall's strength by interaction with the other components present in the plant's cell wall [5].

Aromatic substances

Lignin is the main aromatic material present in the plant cell wall. Lignin is a heterogeneous aromatic biopolymer that forms a three-dimensional structure with the ether and carbon-carbon linkages between different units. The linkage between lignin and hemicellulose involves hydroxycinnamic acids.



Pectin (figure 5) is a family of complex linear polysaccharides. Pectin gives the plant's cell walls integrity and cohesion. Pectic polysaccharides are mostly found in the primary cell walls and middle lamella region [5].

Figure 5 - Chemical structure of pectin [38]

Other components

Furthermore, hemp fibers also consist of small quantities of wax, ash, fat and proteins. Most plants are coated with semi-crystalline wax made of long chains of alkane, ester and alcohol waxes. The wax layer serves as a barrier for insects accessing the plant. Minerals such as Ca, K, and Mg are also present and their content depends on agronomic factors and soil contaminations [36].

Mechanical properties

The mechanical properties are determined by the structural characteristics of the fibers i.e. organic components, length, tertiary structure. Density and mechanical properties of hemp fibers along with other natural and synthetic fibers are shown in **Table 1** below. As it can be seen, the density of the hemp fiber is 1.4-1.6 g/cm^3. The tensile strength ranges from 550-1110 MPa, stiffness: 58-70 GPa and elongation at failure of 1.6%. For comparison reasons, the properties of synthetic fibers (glass fibers and carbon fibers) are presented as well. They have higher tensile strengths: 2000-4000 MPa and higher average stiffness: 70-240 GPa. However, glass and carbon fibers have much higher densities than hemp fibers. Thus, the tensile strength and stiffness of the hemp fibers are comparable to those of synthetic fibers and hemp fibers have great potential as alternative for such materials [7].

Table 1 - Mechanical Properties of natural and synthetic fibers [28]

Fiber		**Property**						
		Density (g/cm^3)	Length (mm)	Elongation at failure (%)	Young's modulus(GPa)	Tensile strength (MPa)	Water absorption (%)	Price raw ($US/kg)
Synthetic	E-glass	2.5	Continuous	2.5-3	70-73	2000-3500	-	1.3
	Aramide	1.4	Continuous	3.3-3.7	63-67	3000-3150	-	-
	Carbon	1.4	Continuous	1.4-1.8	230-240	4000	-	-
Natural	Hemp	1.4-1.6	5-55	1.6	58-70	550-1110	8	0.6-1.8
	Flax	1.4-1.5	5-900	1.2-3.2	27-80	345-1830	7	1.5-2.2
	Cotton	1.5-1.6	10-60	3.0-10.0	5.5-13	287-800	8-25	
	Wool	1.3	38-152	13.2-35	2.3-5	50-315	-	-

1.3 Pre-treatments of hemp fibers

A major issue that arises in plant fibers compared to synthetic fibers is the lack of homogeneity of the material. When producing plant fibers, the growing conditions play a crucial role and highly influence the results. There are difference that may occur in cultivar, cultivation area, soil type, climate and fertilization [36]. The quality of the fibers is influenced by the growth conditions. However, refining pre-treatments can be applied to further modify and fractionate the plant stems, depending on the desired product.

In general, the target of the pre-treatments is to increase the content of cellulose in the fibers by degrading the non-cellulosic components (pectin, lignin, etc.) [22]. There are different types of treatments from mechanical treatment (retting), enzymatic treatment, chemical-physical (steam-explosion), chemical treatment, and alike. The focus of this investigation was on the effects of chemical treatments on retted and non-retted hemp fibers, for potential application in textile industry. The desired outcomes are the removal of non-cell components and an increase in cleanliness and fineness of the hemp fibers.

Retting

Hemp, similar to other bast fiber plants, is subject to a process named retting. Retting is usually microbial in nature and the objective is to loosen and separate the bast fiber bundles from the non-fiber fractions of the stem. During this process, microorganisms colonize the stem tissue and partially degrade plant constituents. Retting is influenced by different factors such as plant development and weather conditions, which in turn determine the quality and yield of the fiber [11]. Under-retting, the incomplete degradation of matrix components, reduces the efficiency of the process and the fiber quality. Contrary, over-retting can occur from excessive microbial degradation, where fiber strength is diminished due to extreme thinning of bundles and degradation of the cellulose fibers. Over-retting decreases the potential of hemp fibers for use in textile industry or composites [11].

This work analyzed the effects of the chemical treatments on non-retted hemp as well as light-retted and well-retted hemp (see **Figures 6, 7,** and **8**)

Figure 6 - Light-retted hemp

Figure 7 - Well-retted hemp

Figure 8 - Non-retted hemp

Chemical treatment

Chemical treatments, also known as chemical degumming, implicate the use of different chemicals to remove non-cellulosic compounds, specifically lignin, pectin and hemicellulose from natural fibers. Research shows that alkali, such as sodium hydroxide (NaOH) is very effective for selectively degrading the cementing materials i.e. lignin, pectin, hemicellulose, in natural fibers [21]. Other chemicals, such as oxidizing agents (H_2O_2, NaOCl) and Na_2SO_3 can be used, in addition to the alkali treatment, to improve the process.

Sodium hydroxide effect

Sodium hydroxide plays the principal role in removing lignin by cleavage of the ether bonds present in the lignin's structure [23]. The reaction with sodium hydroxide increases the internal surface area of cellulose, decreasing the degree of polymerization and crystallinity and disrupting the lignin structure [21]. Furthermore, apart from effective removal of hemicellulose and lignin, the alkali procedure can reduce the amorphous hydroxyl group content by the reaction between alkali and hydroxyl groups [7], as shown in the reaction below (1). The alkali substance allows the ionization of pectin carboxylic groups (-COOH) and the formation of the sodium carboxylate (COONa), leading to a decrease in formation of the hydrogen intermolecular bonds [24]. As a result, the hydrophilic nature of natural fibers is decreased and the fibers' surface becomes smooth and clean [7].

$$\text{Fiber} - OH + NaOH \rightarrow \text{Fiber} - O^- Na^+ + H_2O \quad (1)$$

Sodium hydroxide with Sodium sulfite effect

Combined treatment of alkali (NaOH) and sodium sulfite (Na_2SO_3) was reported to improve separation of fibers from fiber bundles, remove lignin and other components [7]. These effects rise from the presence of sulfite groups (SO_3^{2-}), which are introduced into the side chains present in lignin's structure. This mechanism is called sulfonation and it facilitates the lignin's dissolution in the alkaline solution [22]. However, the treatment with sodium sulfite has a great delignification capacity only at minimum concentration. A too high concentration of sodium sulfite can lead to a substantial degradation of the fibers.

Sodium hydroxide and oxidizing agents effect

In addition, the application of oxidizing compounds as bleaching agents further enhances the lignin degradation. A bleaching treatment is applied to remove the phenolic compounds or molecules having chromophore groups, thus whitening the fibers. Moreover, applying a bleaching treatment, lignin is rapidly oxidized, leading to its degradation and dissolution in the alkaline medium. However, it is necessary to take into account the fact that a bleaching treatment can also partially degrade the cellulose [23]. In this project, non-retted and retted hemp was treated with alkaline and oxidizing agents such as hydrogen peroxide and sodium hypochlorite and the efficiency of both treatments was compared.

Alkali treatment followed by acidification effect

Furthermore, the alkali treatment can be further improved if followed by acidification. The treatment of the cellulosic fibers with acidic solution is performed to break down the polysaccharides to simple sugars, allowing the solubilization of both pectin and hemicellulose. In addition, studies show that a sulfuric acid hydrolysis leads to the formation of fine fibers with smooth surfaces [15]. The acid's nature and concentration need to be thoroughly considered because a too harsh treatment can lead to the fiber's complete degradation. In this investigation, alkali procedure followed by acidification with a sulfuric acid solution were applied for light-retted, well-retted and non-retted hemp.

Analysis of biomass chemical composition - TGA

Subsequently to the chemical treatment of the hemp fibers, an analysis must be performed in order to determine changes in the chemical composition and properties of the fibers. A thermogravimetric analysis (TGA) is an easy, inexpensive and fast analytical technique for determination of cellulose and non-cellulosic content [15]. Research shows that the conventional methods used for the determination of cellulose, hemicellulose and lignin content of biomass are inefficient, time-consuming, and inaccurate, and therefore a TGA analysis is a better and a more efficient technique [30]. TGA records the loss of weight of a sample as the temperature is raised at a constant rate (thermal decomposition) [29]. In addition, TGA can be combined with a DTG (differential thermogravimetric) analysis to further identify the composition of lignin in the fibers [16].

Natural fibers are heterogeneous mixtures of organic components and a treatment with heat at high temperatures can lead to different physical and chemical modifications. In general, it was shown that thermal degradation of natural fibers takes place in three steps: one in the temperature range of 220-280 °C, one at 280-300 °C and one at higher temperatures, above 400 °C. The first temperature range is associated with the thermal degradation profile of hemicellulose, while the second and third ones are associated with cellulose and lignin, respectively [25].

2 Methodology

2.1 Materials

The hemp samples were obtained from HempFlax, one of the largest producers of hemp in the Netherlands. HempFlax produces a versatile material with a variety of applications such as composite for construction materials, animal care, horticulture and nutraceuticals [13]. Hemp biomass was delivered in three samples: a non-retted sample and two pre-processed (dew-retted) samples: a light-retted one and a well-retted one (**Figures 6, 7,** and **8**). According to the Product Data Sheet provided by HempFlax [14], the hemp fibers consist of more than 98% fibers with about 2% dust and shives. Moreover, the chemical composition of the hemp fibers is provided as described in **Table 2** below. Nonetheless, the non-retted hemp sample consists of some wooden shives, dirt, and dust.

Table 2 - Chemical composition of raw hemp samples [HempFlax]

Cellulose (%)	Hemicellulose (%)	Pectin (%)	Fat and wax (%)	Minerals (%)	Humidity (%)
66	16	4	1	2	12

For analyzing the results, data for pure components was computed. The compounds were obtained from Sigma-Aldrich. The cellulose used was 'microcrystalline cellulose', for hemicellulose: 'xylan from beechwood' and for lignin: 'alkali lignin'.

2.2 Experimental

Research work on the extraction of cellulose microfibers has been done to a great extent and studies have reported that one of the most efficient methods is alkalization followed by acidification. Different investigations use the same alkalization method with sodium hydroxide as the alkaline agent and sulfuric acid for the final acidification. However, for further improving the system, different oxidizing agents, such as hydrogen peroxide and sodium hypochlorite are used. Therefore, the methodology for this project was divided in three main delignification systems:

1) Alkalization with NaOH (5%) and H_2O_2 (11%)

2) Alkalization with NaOH (5%) and NaOCl (11%)

3) Alkalization with NaOH (5%) and Na_2SO_3 (11% and 1%)

In addition, for comparison purposes, some experiments were conducted without the additional acidification step. Each alkalization treatment with different oxidizing agents was performed on every

sample of hemp: light-retted and well-retted. Moreover, one experiment (alkalization with NaOH (5%) and H_2O_2 (11%)) was performed on non-retted hemp, as a reference.

The changes in the fibers' composition were analyzed by performing a thermogravimetric analysis (TGA) and deconvolution of the peaks using the package 'mixchar' in RStudio (see section above for theory and the Appendix for the R code script). The cellulose extraction along with the acid hydrolysis procedure was adopted from a previously established method in the literature [15].

Typically, the hemp biomass (5 g) was first sonicated using 300 mL deionized water at room temperature. Sonication was performed in order to allow the breakage of the strong bonds in the biomass structure. The supernatant liquid was filtrated using a simple filter paper. Work-up of the filtered biomass was then performed in an oil bath at 55 °C using 100 mL solution of the alkaline agent, sodium hydroxide (5%, w/v) and the specific oxidizing agent: H_2O_2 (11%, v/v) or NaOCl (11%, v/v). The third experiment, using Na_2SO_3, was divided in two parts: one using NaOH (5%) with Na_2SO_3 (11%, w/v) and one with NaOH (5%) and Na_2SO_3 (1%, w/v).

The work-up procedure was carried out for 90 min under vigorous stirring. The alkaline solutions were prepared in bulk and the treatment was applied on every hemp sample successively. Furthermore, the alkaline-treated hemp biomass was washed until neutral pH and filtered using a Buchner funnel. The residue was dried in an oven overnight at 50 °C to reach a constant weight.

Finally, the dried biomass was acid-hydrolyzed using 100 mL solution of 6.0 M sulfuric acid, and stirred vigorously at room temperature for 30 minutes. The reaction was quenched by adding 300 mL of cold deionized water. The obtained slurry was centrifuged at 4000 rpm for 10 min and then washed with copious amounts of deionized water for a neutral pH to be achieved. Prior to the analysis of the products, the hemp biomass was dried in an oven overnight at 60 °C. An overview scheme of the experimental procedure can be found in **Scheme 1**.

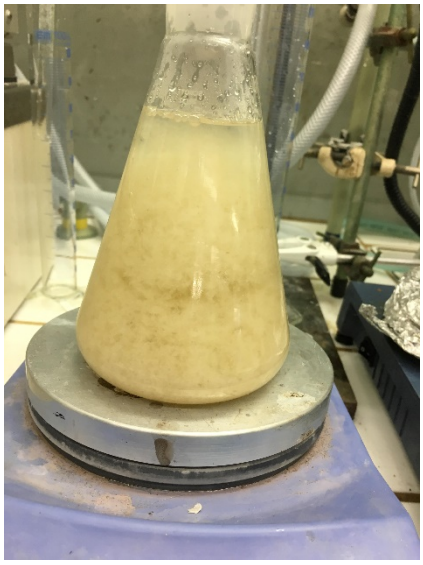
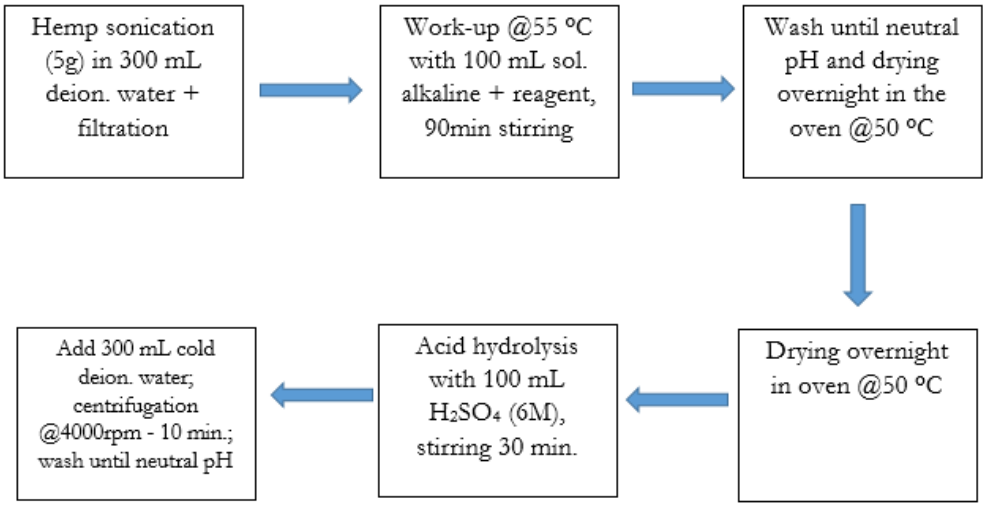


Figure 9 - Treating light-retted hemp with NaOH/H_2O_2, before centrifugation

Figure 10 - Treating well-retted hemp with NaOH/Na_2SO_3, before centrifugation



Scheme 1 - Overview experimental procedure

Thermogravimetric and derivative thermogravimetric (TGA/DTG) analysis

In order to determine the composition of the products and assess which chemical treatment is the most effective for removing the non-cellulosic components in hemp samples, a TGA analysis was performed (see theoretical background in section 1.3). The conditions for this TGA analysis were followed from a previously established procedure in the literature [16].

The TGA/DTG scanning was carried out using a TGA 4000 thermogravimetric analyzer under N_2 atmosphere. Prior to analysis, the obtained fibers were ground into fine powders. The nitrogen flow was 2 L h^{-1}. Pure nitrogen was used as an inert purge gas in order to prevent the presence of air in the pyrolysis zone and to remove gaseous and condensable products evolved during pyrolysis [30]. The temperature rate was set as 5 °C min^{-1}. The powdered samples (2-4 mg) were placed in TGA cups and heated from 30 °C to 700 °C.

Thermogravimetric analysis of the hemp fibers and the changes in composition were analyzed by comparing the kinetic parameters obtained for the treated hemp samples with the ones obtained for the pure components (cellulose, xylan, lignin). The DTG profiles pronounces the TGA peaks and each peak depicts the devolatilization of a particular component [33].

The analysis of the peaks and the determination of the chemical composition of each sample were done using deconvolution computations of the DTG curves in RStudio software (see Appendix for the R code script). The deconvolution was performed using the package 'mixchar' [37]. The fit model for this package includes the standard temperature values (literature-established) for the thermal decomposition of each component (hemicellulose, cellulose and lignin). The 'mixchar' package includes the function 'component_weights(object)', which is the accessor function to extract the mean weights of each component. An example of the output provided by this function can be find in the Appendix.

In addition to this, for comparison reasons, the TGA and DTG of the pure lignin, cellulose and hemicellulose (xylan) were carried out and the data was computed in RStudio to see if the model provided by 'mixchar' package is reasonable. This will be displayed in the section below. The TGA/DTG graphs for the pure compounds can be found in the Appendix section.

3 Results and Discussion

3.1 Visual aspect

Open visual aspect studies revealed that the individualization process of hemp fibers by applying chemical treatments resulted in particular morphologies of the nanofibers. The dominant parameters required in textile applications are the fibers' strength, fineness (to allow the spinning of yarns) and refinability. The smoother the surface of the fiber, the broader the application in textile industry [3]. Ideally, the length of the fibers should be determined by optical microscopy, however, due to time constraints this was not approached in this project. In addition, the smoothness of the fibers is a tactile property and therefore it is subjective. This should be assessed by touching and instinctively evaluating the fibers to obtain basic observations of the material.

Alkaline treatment with NaOH and H_2O_2 + acidification

Non-retted hemp

A treatment on the non-retted hemp sample was performed and it was observed that the non-retted hemp gave fibers that contained many impurities. The fibers were obtained in a very low yield (29%) (**Table 3**), with a short length and they contained pieces of hemp hurd due to the absence of pre-treatment (retting) (**Figure 11**). Therefore, the fibers produced did not have the necessary properties (e.g. smoothness) suitable for textile applications and further treatments on non-retted hemp were not performed.

Figure 11 - Non-retted fibers treated with NaOH/H2O2, pieces of hurd can be seen along with fibers

Light-retted hemp

Figure 12 - Light-retted fibers treated with NaOH/H2O2

After treatment of the light-retted hemp with NaOH and a strong oxidizing agent, H_2O_2, the resulted fibers were relatively long, bleached, clean and soft (**Figure 12**). In addition, the fibers bundles were slightly disconnected and distinct from the crude fibers.

Well-retted hemp

Compared to the light-retted hemp sample, applying the alkali with peroxide treatment on the well-retted hemp resulted in fibers with a very short length and completely disconnected from one another, very prone to becoming powder (**Figure 13**).

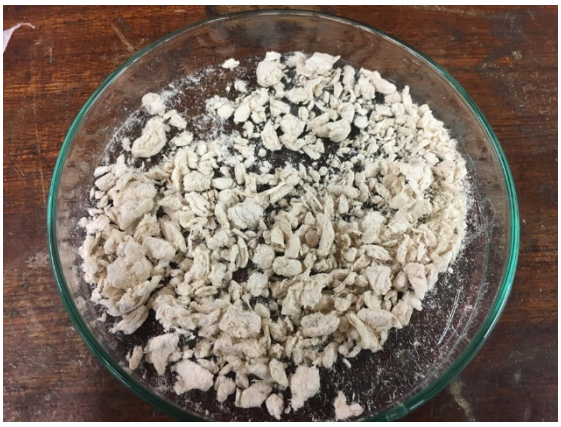


Figure 13 - Well-retted hemp treated with NaOH/H2O2

Alkaline treatment with NaOH and NaOCl + acidification

Light-retted hemp

After treatment with alkali and NaOCl, the light-retted hemp gave fibers similar in aspect with the light-retted with NaOH and H_2O_2 (see figure 11 above). Long fibers with a bleached aspect and soft touch were obtained (**Figure 14**).

Well-retted hemp

Applying similar treatment on the well-retted hemp led to the formation of a very fine powder (see **Figure 15**). In addition, even though a bleaching agent was used, the fibers did not show a high degree of whitening, having a pale-brown color. It is assumed that such fibers are not suitable for textile industry as their strength and durability are considerably reduced compared to the light-retted ones. Moreover, the resulted unbleached fibers are unlikely to endure a dyeing process successfully, this being often required in textile processing.

Figure 14 - Light-retted hemp treated with NaOH/NaOCl

Figure 15 - Well-retted hemp treated with NaOH/NaOCl

Alkaline treatment with NaOH and Na_2SO_3 (11%) + acidification

Light-retted & Well-retted

Unlike the light-retted resulted fibers treated with a bleaching agent (see figures above), using sodium sulphite with a concentration of 11% (w/v) produced very short fibers, in a powder form (**Figure 16**). Similar to the light-retted hemp, the well-retted hemp led to the formation of fibers with the same unbleached, grinded aspect (**Figure 17**).

It was noticed that when the alkali treated fibers were introduced into sulfuric acid for further treatment, the long fibers completely dissolved in the acid, whereas previously (applying the treatments above) the long fibers remained intact. Literature suggests that a too high concentration of sodium sulphite can lead to degradation of the cellulosic fibers and further acid hydrolysis is therefore too harsh. Considering this, another treatment with only 1% Na_2SO_3 was carried out (see section below).

Figure 16 - Light-retted fibers treated with NaOH/Na2SO3 (11%)

Figure 17 - Well-retted hemp treated with NaOH/Na2SO3 (11%)

Alkaline treatment with NaOH and Na_2SO_3 (1%) + acidification

A treatment with solution of NaOH (5%) and Na_2SO_3 (1 %) was applied in order to examine the effect of the sodium sulfite's concentration. For a concentration of Na_2SO_3 of 11%, it was observed that even the light-retted hemp sample completely dissolved during work-up, therefore it was assumed that 11% is a too high concentration and led to complete degradation of the fibers.

Light-retted hemp

Very similar to the fibers produced from treatment with 11% Na_2SO_3, the fibers treated with 1% Na_2SO_3, followed by acid hydrolysis, have a soft aspect and a short length (**Figure 18**). Using a solution with a lower concentration of sodium sulphite was expected not to degrade the fibers while acidification. However, this happened and a treatment with only NaOH/Na_2SO_3 (1%), without acidification was performed (see below).

Figure 18 - Light-retted hemp treated with NaOH/Na2SO3 (1%)

Alkaline treatment with NaOH and Na_2SO_3 (1%) without acidification

Light-retted & Well-retted

The alkaline treatment with 1% Na_2SO_3 without further acid hydrolysis gave a high yield (72%) (see table 3 below) of long, strong fibers (**Figures 19** and **20**).

Figure 19 - Light-retted hemp treated with NaOH/Na2SO3 (1%) no acidification

Figure 20 - Well-retted hemp treated with NaOH/Na2SO3 (1%) no acidification

Discussion: Morphology

Analyzing the morphology of the chemically treated hemp fibers, good insights were gained regarding their suitability for textile industry. A chemical treatment involving a bleaching agent yielded clean and long fibers. Strictly from the aspect point of view, the light-retted hemp proved to give smoother and cleaner fibers, characteristics which deemed appropriate for further textile processing (i.e. dyeing). In addition, for producing textile yarns, long and strong fibers, with a smooth surface are required. Such fibers were obtained by treating the light-retted hemp with

Figure 21 - Grinded well- and light- retted after chemical treatment

solutions of $NaOH/H_2O_2$ (**Figure 12**) and NaOH/NaOCl (**Figure 14**). Applying strong oxidizing agents to break the non-cellulosic components apart, while bleaching the fibers gives relatively good yields of fine and long fibers. Nonetheless, the exact same treatment with alkali and bleaching agents tested on the well-retted hemp resulted in short and fragile fibers (**Figures 13** and **15**). This result might be due to the high level of retting, which likely degraded the cellulose fibers already. The quantity, quality and thus, suitability for textiles, can be further seen by analyzing the chemical composition of the fibers. **Figure 21** shows the grinded well- and light-retted treated hemp samples having an aspect ratio and surface similar to cotton.

3.2 Yield

The yield on a dry basis was calculated after each treatment for every hemp sample. The results are displayed in the table below (**Table 3**).

Table 3: Yield results

Yield (%)			
Treatment	Non-retted hemp	Light-retted hemp	Well-retted hemp
$NaOH/H_2O_2$+ acidification	29 %	74.8 %	65.4 %
NaOH/NaOCl+ acidification	-	70 %	48.48 %
$NaOH/Na_2SO_3$ (11%)+ acidification	-	65.8 %	68.2 %
$NaOH/Na_2SO_3$ (1%)+ acidification	-	71.2 %	60 %
$NaOH/Na_2SO_3$ (1%)no acidification	-	72 %	58.8%

3.3 Thermogravimetric analysis (TGA)

The initiation of thermal degradation can be recognized by a significant decrease in sample weight. Decomposition is due to thermal instability of components such as hemicellulose and pectins. Removal of such components by alkali treatment leads to fibers that are more thermally stable [22].

An example of the TGA and DTG plots (resulted from computing the data provided by the TGA thermobalance) is shown in **Figure 22**. The rest of the plots for each sample can be find in the Appendix.

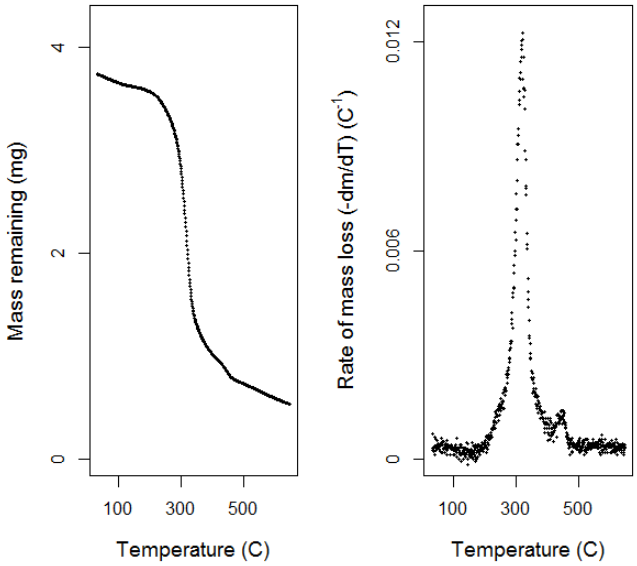


Figure 22 - TGA and DTG plots for Light-retted hemp with NaOH/NaOCl

Looking at the TGA curves obtained in N_2 atmosphere, it can be seen that the devolatilization process begins at around 100 °C. This is due to the presence of water in the samples. The maximum weight loss occurs in the temperature range of 240 – 350 °C. Furthermore, at a temperature of about 350 °C, the slope of the TGA curve changes significantly, resulting in a much slower weight loss at temperatures of 370 – 400 °C.

With regards to the differential thermogravimetric analysis (DTG), for all the samples there appears a peak with a high intensity at about 350 °C. This is related to the decomposition of cellulose. In addition, the presence of a shoulder at lower temperatures, i.e. 270 – 320 °C, is due to the thermal degradation of hemicellulose. The increased activity of hemicellulose in thermal degradation may be associated to its chemical structure. Hemicellulose has a random amorphous structure with little strength, being easily hydrolyzed. Unlike hemicellulose, cellulose is a very long polymer consisted of unbranched glucose units, with a crystalline structure and increase strength and resistance to hydrolysis [35].

Furthermore, the presence of a peak at higher temperatures (above 400 °C) is related to the slow thermal degradation of lignin. Lignin has a different structure from the other biomass constituents. It is composed of three kinds of benzene-propane and is heavily cross-linked, thus having a higher thermal stability and it decomposes at higher temperatures [35]. It is worth mentioning the fact that there is no peak present for the thermal degradation of pectin. This is because, applying an alkali, such as NaOH, completely removes the pectins in the fibers.

The relative intensities of the peaks in the weight loss curves can be associated with the global quantities of the macro-components present in the fibers [30]. The fractions of cellulose, hemicellulose and lignin in the resulted fibers were estimated using deconvolution by Fraser-Suzuki mixture model, using the package 'mixchar' in RStudio [34]. Furthermore, for comparison reasons, the raw, untreated light- and well-retted hemp were analyzed for determining the accurate chemical composition (**Figures 22** and **23**).

Table 4 summarizes the components' fractions results for each sample. Furthermore, each result will be discussed in the next paragraphs and a comparison will be outlined at the end. It is worth mentioning the fact that the weight fractions obtained from TGA are not in accordance to the data provided by HempFlax (see **Table 2**). This might be due to several reasons. For instance, the thermogravimetric analysis might not take into account many other interactions between the components and complex chemical reactions occurring while thermal degradation of biomass. The pyrolysis process is very complex [30] and the given parameters give only a semi-quantitative description of the thermal behavior of the macro-components.

Moreover, the TGA/DTG and deconvolution for the pure cellulose, lignin and hemicellulose turned out to be in relatively good agreement with the model used in the 'mixchar' package in RStudio. However, the output with the weight fractions of each component provide a good insight for comparison but they are not completely reliable. Thus, more research into this analytical method needs to be done.

Table 4 - Overview of results from TGA analysis

Composition (wt%)			
Sample	Cellulose	Hemicellulose	Lignin
Raw LR (light-retted)	27.684	12.536	45.479
Raw WR (well-retted)	38.298	3.331	48.999
LR-NaOH/H_2O_2	52.066	7.055	27.276
WR-NaOH/ H_2O_2	45.265	11.045	33.067
NON-RET.-NaOH/ H_2O_2	75.841	5.572	12.561
LR-NaOH/NaOCl	38.707	6.079	37.999
WR- NaOH/NaOCl	45.770	10.905	33.065
LR-NaOH/Na_2SO_3 (11%)	28.013	19.476	48.201
WR-NaOH/ Na_2SO_3 (11%)	45.770	10.905	33.065
LR-NaOH/ Na_2SO_3 (1%)	28.168	14.277	43.211
LR-NaOH/ Na_2SO_3 (1% no acid)	56.348	12.163	20.706
WR-NaOH/ Na_2SO_3 (1% no acid)	59.631	13.079	18.377

In table 4 above, the mean fractions (wt%) of the components were obtained from deconvolution of the DTG curves in RStudio Software (see script in Appendix). It was assumed that the samples contained about 5-15% humidity and 1-5% fat, wax, proteins, pectins and minerals. In Appendix, the deconvoluted peaks of pure compounds (LG, HC, CL) can be found (**Figures 13, 14, 15**). It can be observed that the fitting model is not very precise and the results do not have a high accuracy. However, they represent a good base for comparison. Underlined in the table, the computed fractions of the raw starting materials can be seen and compared with the fractions of the treated samples. The

most significant increase in cellulose content can be observed for treatment of the light-retted hemp wih $NaOH/H_2O_2$ and treatment with $NaOH/Na_2SO_3$ (1%) without acid hydrolysis.

Untreated hemp fibers

Light-retted hemp

The deconvolution curves as well as the TGA and DTG curves for the raw light-retted hemp are shown in **Figures 23** and **24** below. It can be observed that the non-treated light-retted hemp sample contains a high amount of non-cellulosic compounds: lignin (green curve) and hemicellulose and a lower quantity of cellulose. The cellulose composition was estimated to be 27.684 wt% whereas hemicellulose: 12.536 wt% and lignin: 45.479 wt% (**Table 4**).

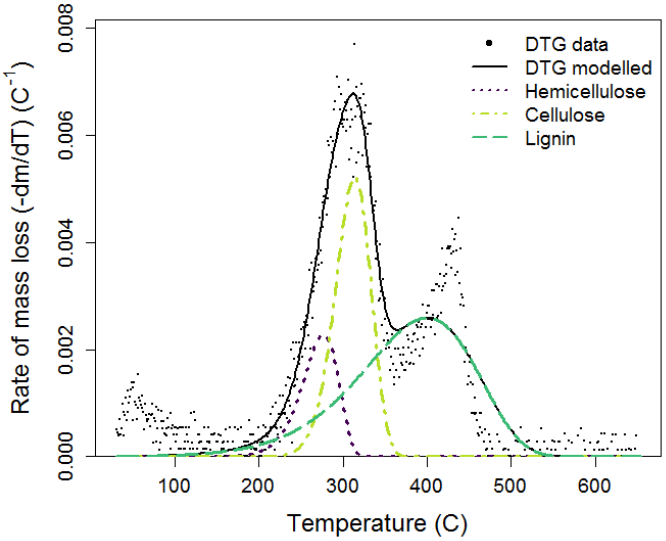


Figure 23 - The deconvolution curves for raw light-retted hemp

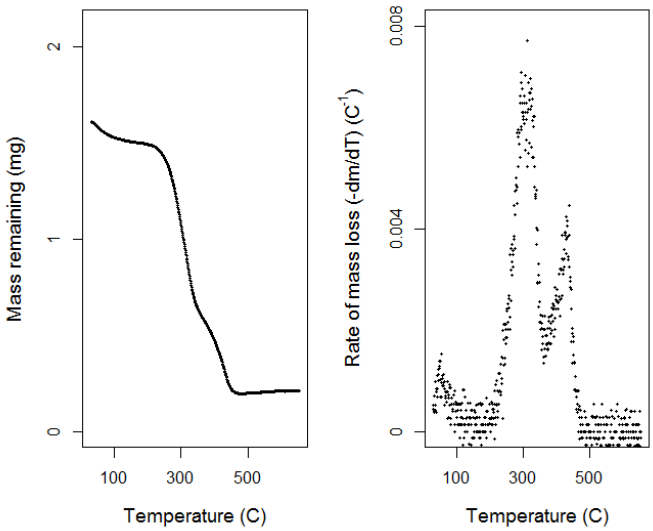


Figure 24 - TGA and DTG curves for raw light-retted hemp

Well-retted hemp

The cellulose composition in the well-retted hemp was estimated to be relatively higher than the one in light-retted hemp (38.298 wt%). In addition, the hemicellulose content is very low: 3.331 wt%. This can be also observed from the deconvoluted curve for hemicellulose in **Figure 25**.

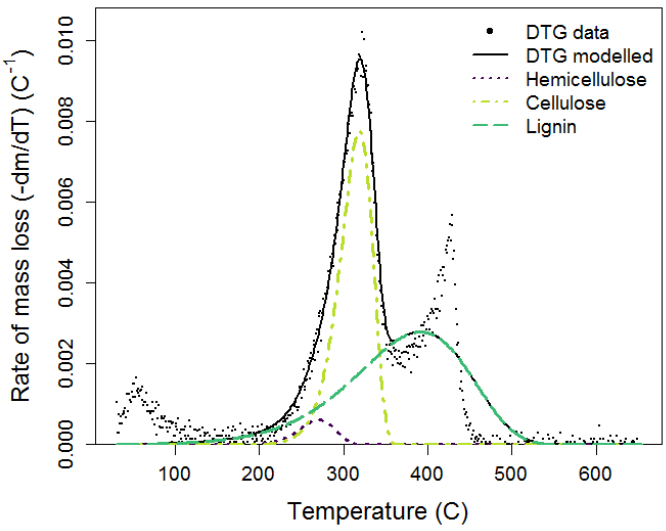


Figure 25 - The deconvolution curves for raw well-retted hemp

Alkaline treatment with NaOH and H_2O_2 + acidification

Non-retted hemp

One sample of raw non-retted hemp was treated with alkali and hydrogen peroxide solution in order to obtain a point of reference and observe the influence of retting (see section 3.1 above). The mean fraction of cellulose obtained from deconvolution was very high: 75.841 wt% (**Table 4**), which is the highest value obtained from all the treated samples. This can also be seen from the intensity of the deconvoluted curves (**Figure 26**). Therefore, regarding the composition of cellulose, the non-retted hemp is the most abundant. The reason for this is that the non-retted hemp also contains hemp hurds, which are high in cellulosic content. However, for textile processing, the hemp fibers need to be clean and separated from the hurds so it was assumed that non-retted hemp is not suitable (see **Figure 11**) and further treatments have not been applied.

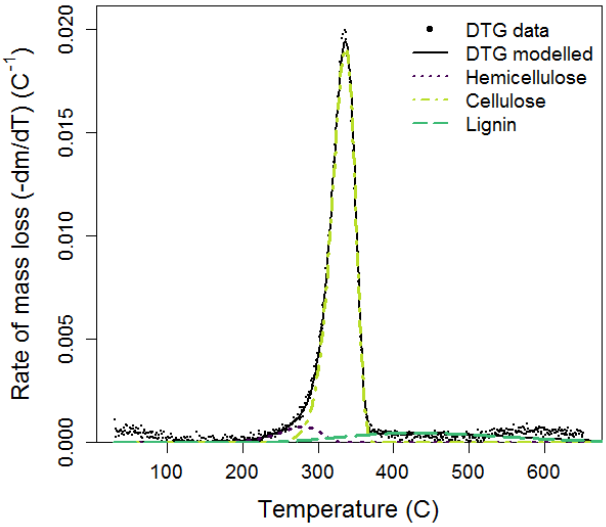


Figure 26 - Deconvoluted curves for non-retted hemp with $NaOH/H_2O_2$

Light-retted hemp

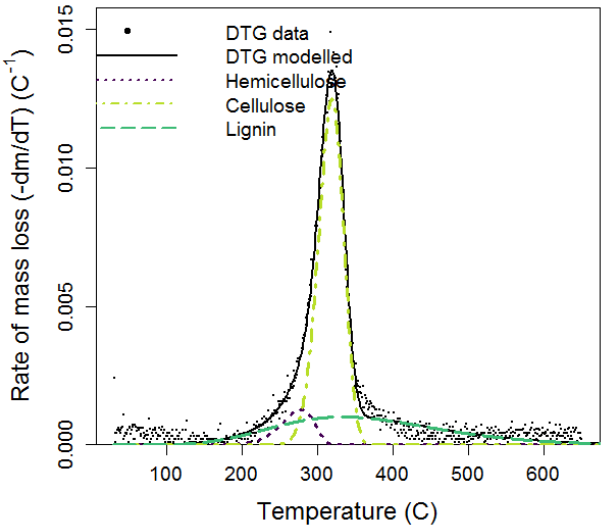


Figure 27 - Deconvoluted curves for light-retted hemp with $NaOH/H_2O_2$

Comparing the treated light-retted hemp with the raw light-retted sample, it was observed a significant increase in the content of cellulose (from 27.6 wt% to 52.06 wt%). Furthermore, it can be seen that the removal of hemicellulose and lignin was efficient, yielding contents of 7.05 wt% and 27.27 wt% respectively. This decrease in the content of non-cellulosic compounds can also be noticed from the intensity of the peaks related to each component in the deconvoluted curves (**Figure 27**).

Well-retted hemp

Well-retted hemp treated with $NaOH/H_2O_2$ gives a small increase in the content of cellulose (obtained 45 wt% compared to 38.29 wt% for the raw well-retted) (**Table 4**). In the same manner, a decrease in lignin and hemicellulose composition was observed, however, not as outstanding as expected.

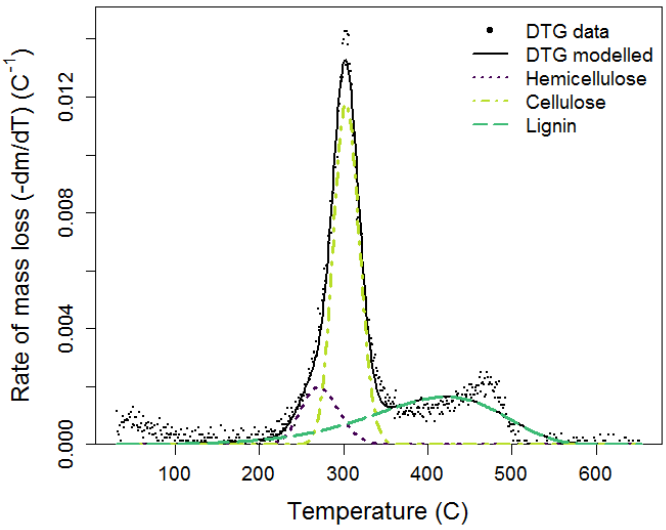


Figure 28 - Deconvoluted curves for well-retted hemp with $NaOH/H_2O_2$

Alkaline treatment with NaOH and NaOCl

Light-retted hemp

Treatment with alkali and the oxidizing agent sodium hypochlorite, followed by acid hydrolysis led to the formation of bleached fibers with an increased amount of cellulose (from 27.6 wt% to 38,7 wt%) and decrease of lignin and hemicellulose (**Table 4**).

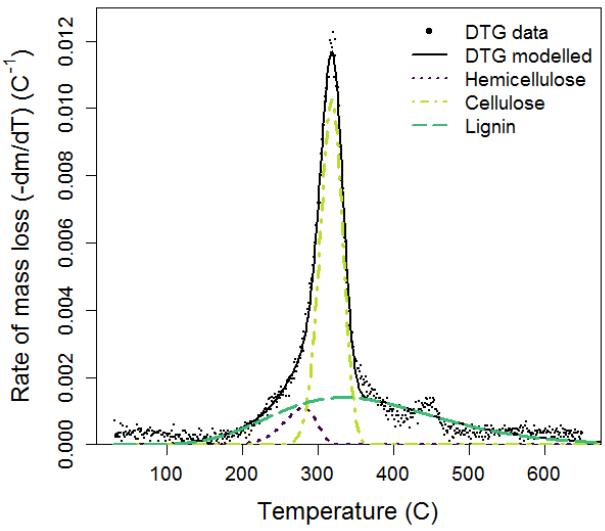


Figure 29 - Deconvoluted curves for light-retted hemp with NaOH/NaOCl

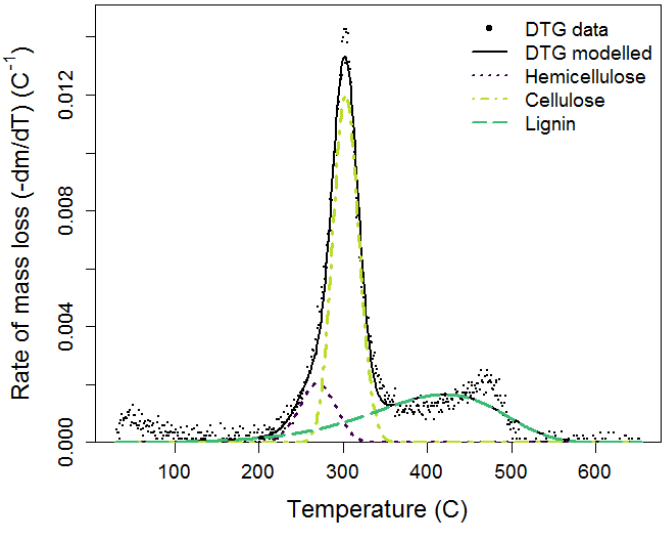


Figure 30 - Deconvoluted curves for well-retted hemp with NaOH/NaOCl

Well-retted hemp

Similar to the light-retted sample, treating the well-retted hemp shows a decrease in the lignin composition (from 48.999 wt% to 33.065 wt%). However, there is an unexpected increase in the hemicellulose composition (from 3.331 wt% to 10.905 wt%). Therefore, the removal of non-cellulosic components did not occur efficiently. This can be attributed to the degree of retting (over-retting might have taken place and the cellulosic fibers might have been already degraded). It was also observed that the fibers obtained from the well-retted hemp had a different morphology compared to the light-retted one (see **Figure 15**).

Alkaline treatment with NaOH and Na_2SO_3 (11%) + acidification

Light-retted hemp

Applying a treatment with alkali solution with Na_2SO_3 (11%) reducing agent led to the formation of fibers in a powder form (see **Figures 16** and **17**). The results for the composition for the treated light-retted sample show that the removal of non-cell components was very inefficient. The deconvolution curves (**Figure 31**) show the same behavior. The peaks representing lignin and hemicellulose have a great intensity whereas the one for cellulose is lower than expected. This outcome might be due to the concentration of 11% for Na_2SO_3, which is viewed also in literature too high, leading to the degradation of the fibers. Similar behavior was present for the well-retted sample, with a slightly more efficient, but not sufficient, removal of lignin and hemicellulose (**Figure 32**).

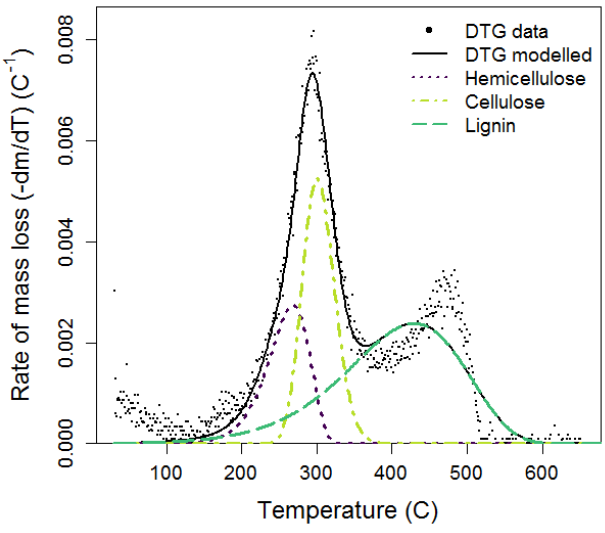


Figure 31 - Deconvoluted curves for light-retted hemp with $NaOH/Na_2SO_3$ (11%)

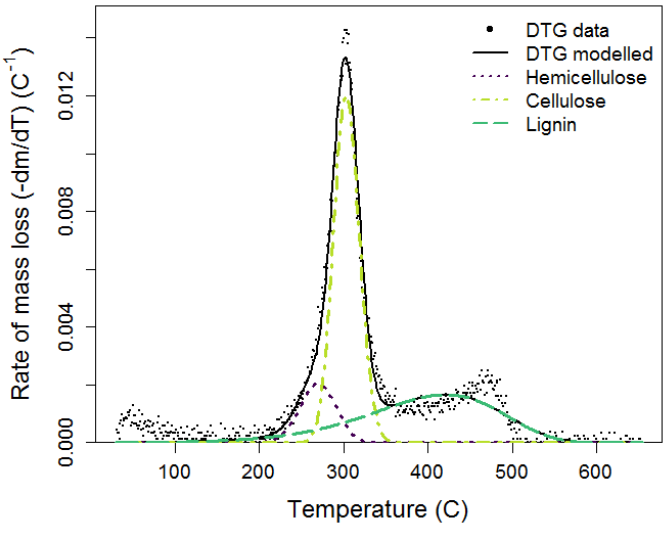


Figure 32 - Deconvoluted curves for well-retted hemp with $NaOH/Na_2SO_3$ (11%)

Alkaline treatments with NaOH and Na_2SO_3 (1%)

Light-retted hemp

Given that a too high concentration of Na_2SO_3 (11%) generated the degradation of the fibers when further treated with acid, an alkali solution with Na_2SO_3 in a lower concentration (1%) was applied. Similar behavior was noticed—with acid hydrolysis, the fibers completely dissolved and fine powder was obtained as shown in **Figure 18**. Looking at the results for the composition, the lignin content was reduced from 45.479 wt% to 43.211 wt%, which is insignificant. The deconovoluted peaks, shown in **Figure 33**, imply the same limited removal of non-cellulosic components. For obvious reasons, the same treatment was not applied for the well-retted hemp.

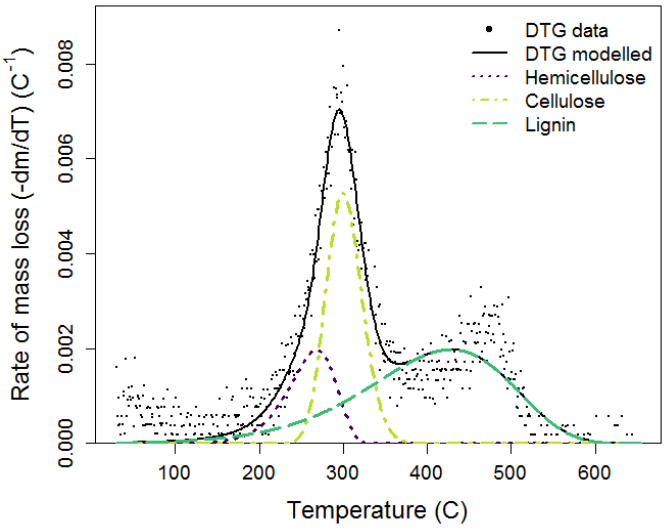


Figure 33 - Deconvoluted curves for light-retted with $NaOH/Na_2SO_3$(1%)

Alkaline treatment with NaOH and Na_2SO_3 (1%) without acidification

Light-retted hemp

Observing the fact that the further acidification step leads to dissolution of the fibers, a similar treatment was carried out, excluding the acid hydrolysis with sulfuric acid. As discussed previously, this led to the formation of long, strong fibers (**Figures 19** and **20**). Analyzing the deconvolution results (**Table 4** and **Figure 34**), it can be noticed that the content of lignin decreased from 45.479 wt% to 20.706 wt%. Furthermore, the cellulose composition significantly increased from 27.684 wt% to 56.348 wt%.

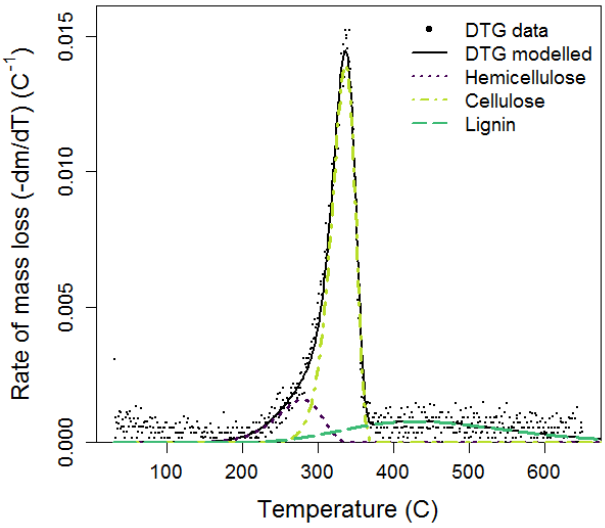


Figure 34 - Deconvolution curves for light-retted hemp with $NaOH/Na_2SO_3$ (1%) - no acid

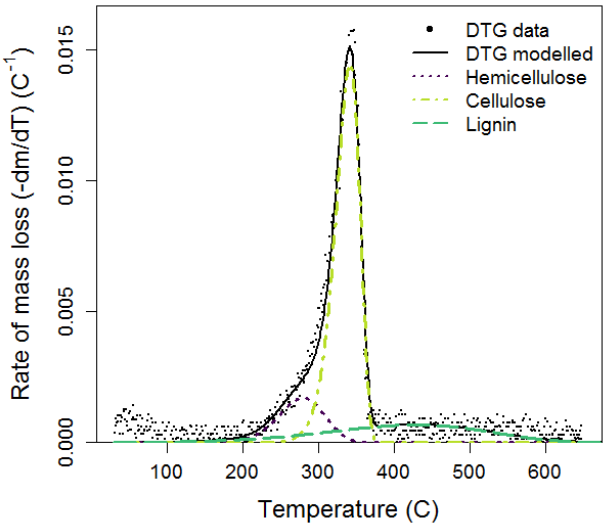


Figure 35 - The deconvoluted curves for well-retted hemp with $NaOH/Na_2SO_3$ (1%) - no acid

Well-retted hemp

Similar to the light-retted sample, treating the well-retted fibers gave good results, proving the effectiveness of this treatment. The weight percentage of lignin diminished from 48.999 wt% to 18.377 wt%. The deconvoluted peaks (**Figure 35**) emphasize this behavior. This decrease is notable as lignin is the most difficult compound to remove from any specific biomass.

4 Conclusions

The focus of this investigation was the isolation of cellulose fibers from hemp through chemical treatments. The objective was to obtain fibers suitable for the textile industry with a low content of non-cellulosic components from hemp biomass, without degrading the cellulose. In order to do so, alkali treatments with oxidizing agents (H_2O_2 and NaOCl) and Na_2SO_3 (11% and 1%) with and without subsequent acidification (H_2SO_4) were applied on light- and well-retted hemp samples and the produced fibers were analyzed with thermogravimetric analysis (TGA) as previously established. The fibers were obtained in several yields, morphologies (aspect ratios), and different compositions. The highest yield (74.8%) was obtained for the treatment with $NaOH/H_2O_2$ for the light-retted hemp. Moreover, high yields (71-72%) were seen for treating light-retted hemp with $NaOH/Na_2SO_3$ (1%) with further acidification and $NaOH/Na_2SO_3$ (1%) without acidification.

Concerning the morphology of the fibers, it is assumed that the fibers suitable for textile production are the longest and strongest ones. Moreover, the smoothness of the surface and the degree of bleaching also play an important role. Fibers with such characteristics were obtained following the chemical treatments with $NaOH/H_2O_2$ and NaOH/NaOCl. Additionally, long fibers in a high yield were resulted from the treatment with NaOH/ Na_2SO_3 (1%) without acidification.

Most importantly, regarding the chemical composition of the fibers, the TGA analysis gave information about the thermal degradation of each component, which were further computed to achieve the chemical content in each sample. The highest content of cellulose and, of course, lowest content of lignin and hemicellulose was present in the non-retted hemp. Notwithstanding this, the fibers contained hemp hurds and dust due the lack of retting, thus not applicable for textile processing. In addition, an efficient removal of non-cellulosic compounds was observed as a result of treatments with $NaOH/H_2O_2$ and $NaOH/Na_2SO_3$(1%) without acidification for both light- and well-retted hemp.

Taking into consideration these aspects, the most convenient morphology and the lowest content of non-cellulosic compounds were obtained from treating hemp with $NaOH/H_2O_2$ and $NaOH/Na_2SO_3$ (1%) without acidification. These treatments proved to be the most efficient for providing cellulose fibers suitable for further textile processing. Depending on the desired end-product, the treatment with H_2O_2 as a bleaching agent is preferred.

5 Future perspectives

Further improvements of chemical delignification of the hemp fibers can be further researched. Having obtained the two most effective treatments for removing non-cell compounds, further focus can be drawn towards the optimization of the process. Different concentrations of the alkali reagent, NaOH, can be experimented, as well as concentration of the oxidizing agents and sulfuric acid. Essentially, an experiment only with NaOH, without the addition of other reagents or acidification, can be carried out and if similar results are obtained, of course the process will be more cost- and time-efficient. Furthermore, the experimental conditions (e.g. reaction temperature, duration of the work-up) might also play an important role. In addition, the mechanical properties of the fibers, such as tensile strength, can be tested, as well as the smoothness and the length of the fibers.

Additional research also need to be done on the analytical techniques for analyzing the composition of the macro-components. For instance, conventional wet methods for determining the composition of cellulose, lignin and hemicellulose can be performed and compared with the thermogravimetric method to further validate the results and/or obtain a better estimation of the chemical composition.

From a different perspective, chemical treatment of the hemp fibers can be combined with steam explosion or/and enzyme treatment for further improving the system and obtaining valuable fibers. The future textile applications for hemp fibers are opportune and almost achieved. However, it will be required for different subjects of agro-industrial production chain (i.e. farmers, fiber producers, product manufacturers) to consolidate their efforts to prevail the limitation regarding the hemp fibers for textile processing. Thus, the progress of the process leans on an interdisciplinary approach [3]. From another angle, blending hemp with cotton could be considered as an option. The soft elasticity of cotton merged with the natural strength of hemp could create a sustainable genre in the fashion industry [32].

6 Acknowledgments

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8 Appendix

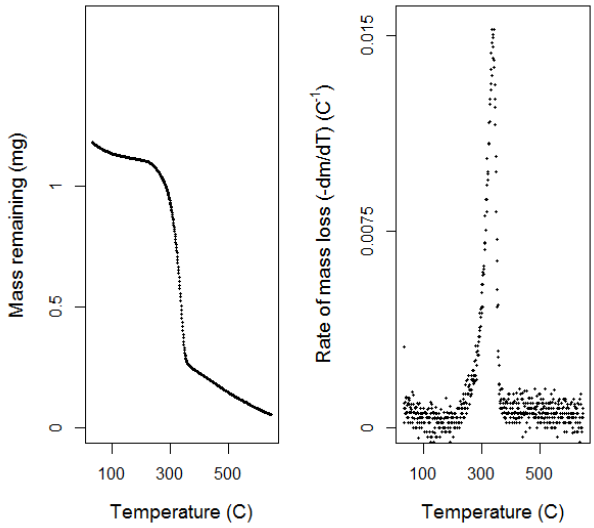

Figure 1 - TGA&DTG graphs for LR-Na2SO3(1%), no acidification

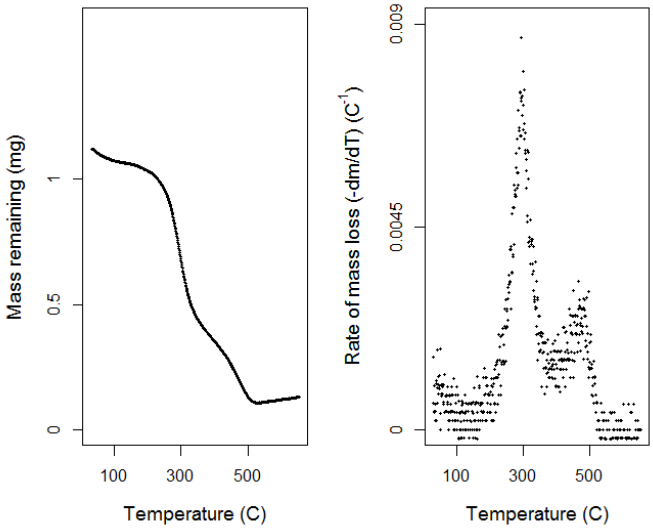

Figure 2 - TGA&DTG graphs for LR-Na2SO3(1%)

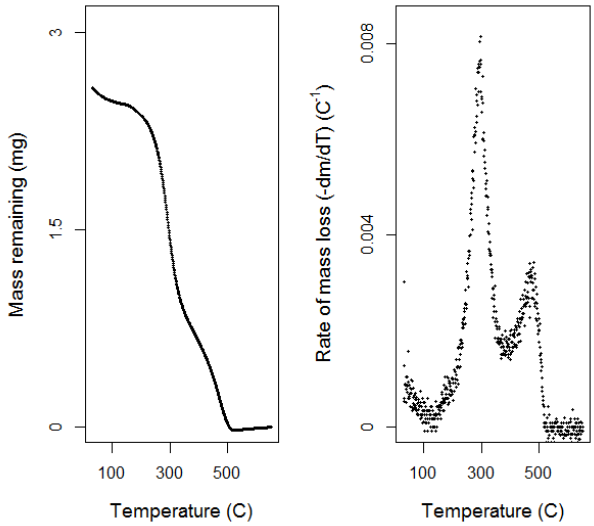

Figure 3 - TGA&DTG graphs for LR-Na2SO3 (11%)

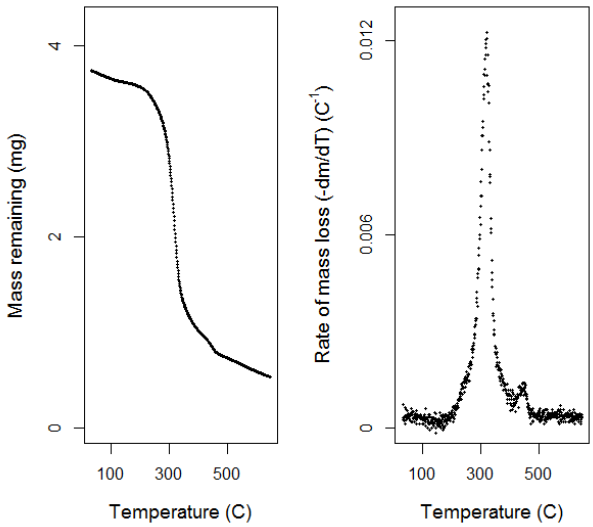

Figure 4 - TGA&DTG graphs for LR-NaOCl

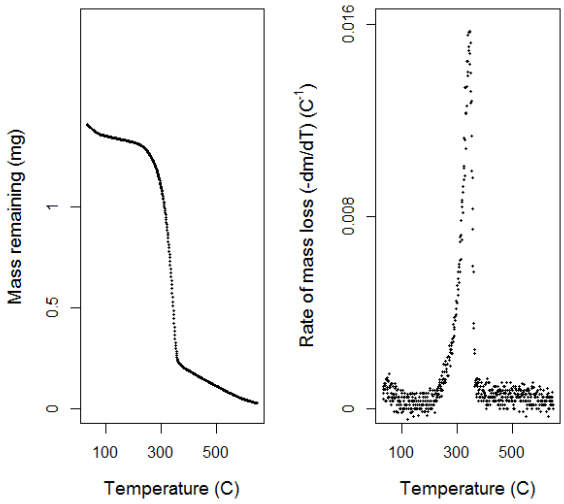

Figure 5 - TGA&DTG graphs for raw LR

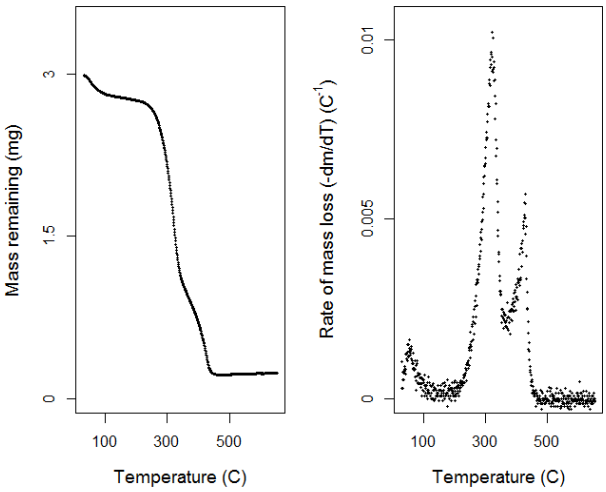

Figure 6 - TGA&DTG graphs for raw WR

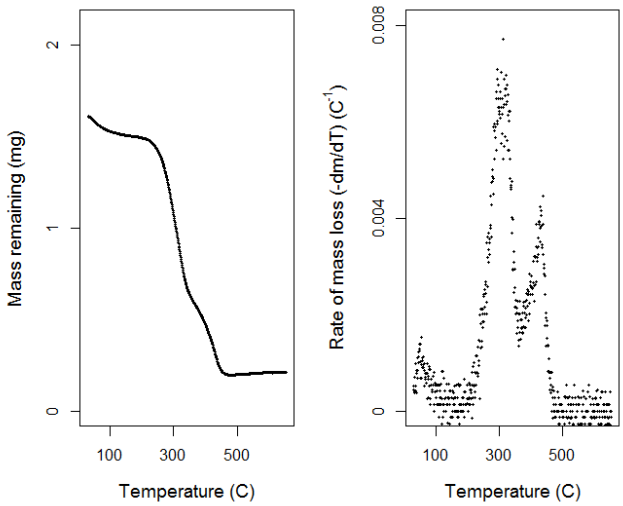

Figure 7 - TGA&DTG graphs for WR-Na2SO3 (1%)

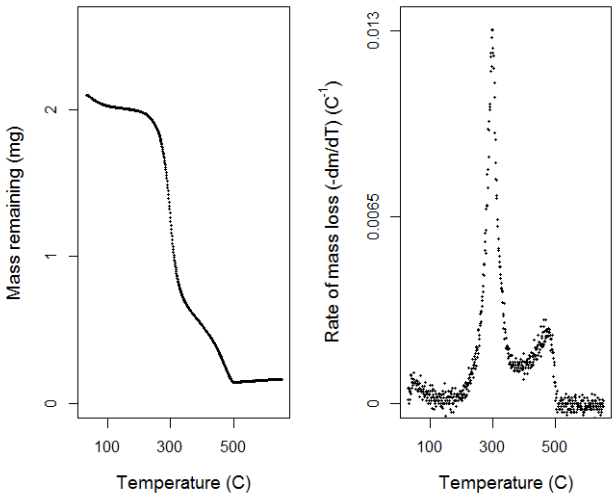

Figure 8 - TGA&DTG graphs for WR-NaOCl

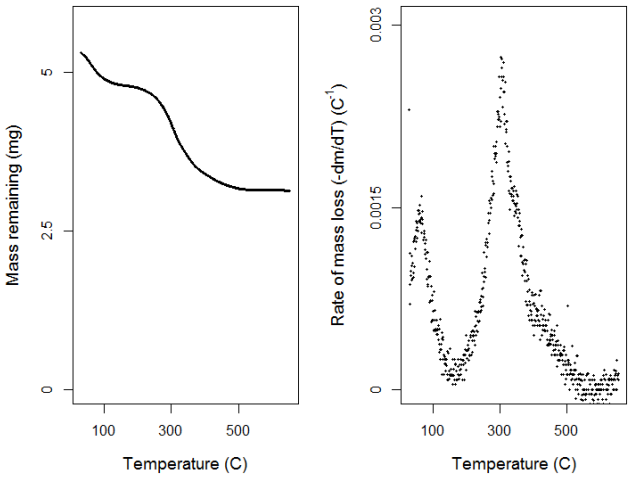

Figure 9 - TGA&DTG graphs for pure lignin

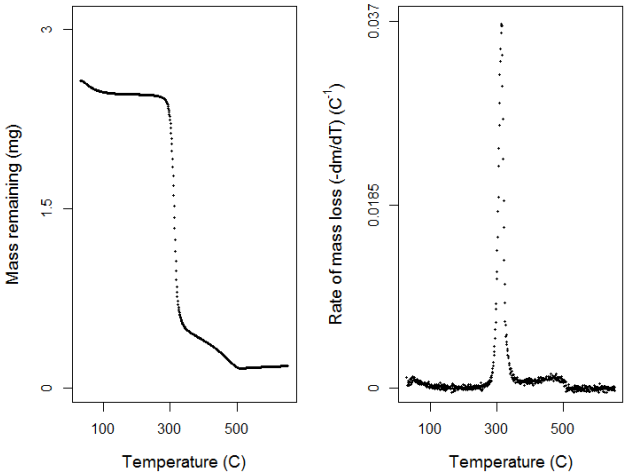

Figure 10 - TGA&DTG graphs for pure cellulose

```r
library(mixchar)
head(WRNa2SO311)
deriv_WRNa2SO311 <- process(WRNa2SO311,
                            init_mass = 1.154391,
                            temp = 'V6',
                            mass = 'V3')
deriv_WRNa2SO311
plot(deriv_WRNa2SO311)
output_WRNa2SO311 <- deconvolve(deriv_WRNa2SO311,lower_temp = 30.54, upper_temp = 653.54)
output_WRNa2SO311
my_starting_vec <- c(height_1 = 0.002, skew_1 = -0.15, Position_1 = 270, width_1 = 50,

                     height_2 = 0.006, skew_2 = -0.15, position_2 = 310, width_2 = 30,
                     height_3 = 0.001, skew_3 = -0.15, position_3 = 450, width_3 = 200)
output_WRNa2so31 <- deconvolve(deriv_WRNa2so31,lower_temp = 30.54, upper_temp = 653.54 ,n_peaks = 3, start_vec = my_starting_vec)
output_WRNa2so31
WRNa2so31_rate <- rate_data(output_WRNa2so31)
head(WRNa2so31_rate)
temp_bounds(output_WRNa2so31)
model_fit(output_WRNa2so31)
component_weights(output_WRNa2so31)
plot(output_WRNa2so31, bw = FALSE)
```

Figure 11 – R-Code Script for the deconvolution computations (example for the well-retted hemp with Na2SO3 - 11%).

```
> component_weights(output_LRH2O2)
          HC        CL        LG value_type
1  7.0555797 52.066617 27.276653       mean
2  0.5757904 28.360370 21.627444       2.5%
3 12.4844459 47.403115 27.075196        50%
4 55.6715381 61.738529 32.637981      97.5%
5 15.0149165  8.815747  2.834186          5
```

Figure 12 - Example output from R representing the mean weight fractions (the first line(mean)): HC=hemicellulose, CL=cellulose, LG=lignin

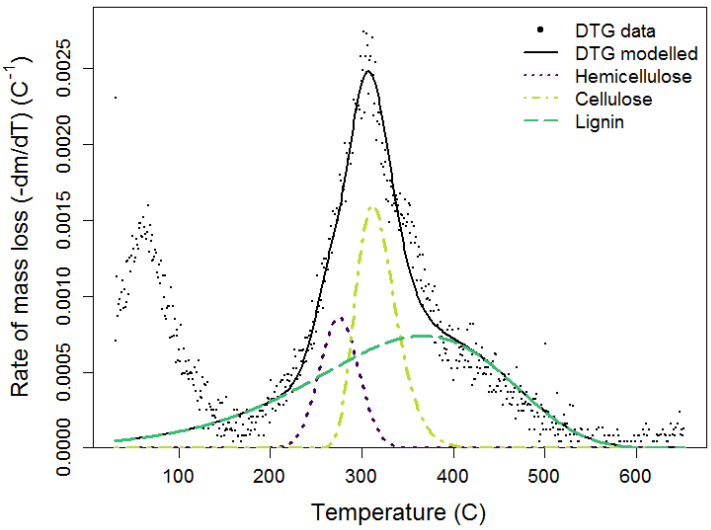

Figure 13 - Deconvoluted peaks for pure lignin

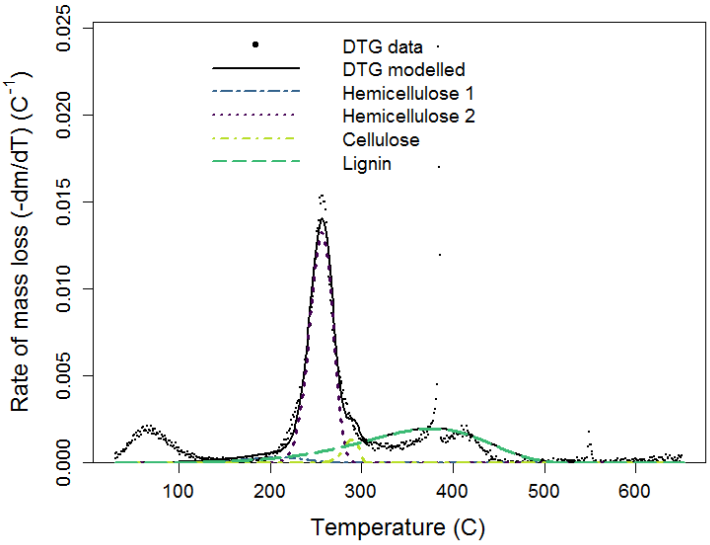

Figure 14 - Deconvoluted peaks for pure hemicellulose (xylan)

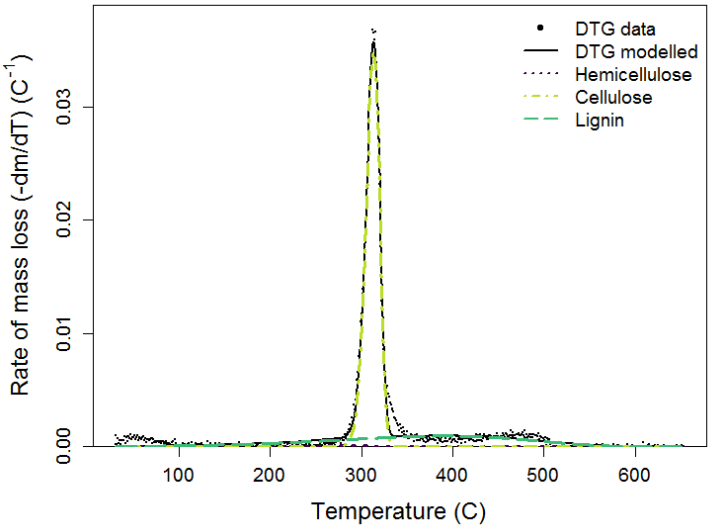

Figure 15 - Deconvoluted peaks for pure cellulose

Table 2 - Chemical composition estimations for pure lignin, pure cellulose, pure xylan. The estimations represent the output from RStdio, package 'mixchar' , after deconvolution

	Composition (wt%)		
Compound	Cellulose	Hemicellulose	Lignin
Pure cellulose (CL)	65.891	0.928	26.167
Pure hemicellulose (HC)	41.762	-	-
Pure lignin (LG)	4.570	19.894	8.680