

# STEX Treated and Untreated Hemp Fiber Comparative Structural Analysis

Anna Putnina<sup>1</sup>, Silvija Kukle<sup>2, 1-2</sup> Riga Technical University, Janis Gravitis, Latvian State Institute of Wood Chemistry

**Abstract** – In this article, the architecture of hemp fibres as a source of high strength cellulose is analyzed. In the experimental part, steam explosion technology is applied to disintegrate technical hemp fibres to elementary fibres with the aim to find out the best procedure, without resort to environmentally harmful chemical pre-treatments, to solving the problems on further nano-level environmentally friendly hemp cellulose disintegration. Influence of pre-treatment intensity, steam explosion process temperature and pressure are investigated on disintegration level of fibres of hemp variety *Bialobrzieskie*, and the acquired results are discussed.

**Keywords** – auto-hydrolysis, cellulose, disintegration, elementary fibres, hemp, steam explosion.

## I. INTRODUCTION

Some new industrial uses of plant cellulose have been developed and are found to be promising. One of them is the usage of cellulose nano-particles as fillers to improve mechanical and barrier properties of biocomposites [1], which form a rapidly developing branch of biotechnology. Therefore, it is of interest to determine the potential of hemp fibres, to find appropriate solutions and sustainable systems. In this context, disintegration of technical hemp fibres to elementary fibres is an important milestone with the aim to find out the best technologies, without the usage of environmentally harmful chemical pre-treatments, to solving the problems on further nano-level environmentally friendly hemp cellulose disintegration.

Each lignocellulosic fibre is a natural composite in which rigid cellulose micro-fibrils are embedded in a soft matrix composed of lignin and hemicellulose [2]. Hemicelluloses and, to some extent, pectins are primary components of the binding substance of the elementary bast fibres, while lignin plays the part of stabilizer and screen for other fibrogenous substances (Fig. 1.) [3]. The degree of polymerization in hemicelluloses is much lower than in cellulose ranging from 20 to 300. By attached ferulic acid and p-coumaric residues, hemicellulose can form covalent bonds to lignins [4]. Hydrogen bonds are formed between xylan and cellulose. Due to this linking effect of hemicelluloses, hemicelluloses degradation leads to disintegration of the fibres into cellulose micro-fibrils resulting in lower fibre bundle strength [5]. Mainly the acid residues attached to hemicellulose make it highly hydrophilic and increase the fibre water uptake, which increases the risk of microbiological fibre degradation. It has been found that hemicellulose is thermally degraded at a lower temperature (150-180°C) than cellulose (200-230°C) by wet oxidation [6] and composite manufacturing [7]. The

amorphous regions of fibres are susceptible to acid attack and, under controlled conditions, could be removed leaving crystalline regions intact.

To prepare harvested hemp for further processing different technologies could be used. During water retting or dew-retting the hemp bast is separated into large fibre bundles, after additional treatment is required to defibrillate these bundles into single fibres and/or small fibre bundles. For this purpose degradation or disruption of the middle lamellae between the single fibres are necessary. Enzyme treatment [8] – [10], wet oxidation [11], [22] and NaOH treatment [12], [13] can degrade pectin and lignin in the middle lamellae between the single fibres. Physical defibrillation methods include steam explosion [14], [15] and ultrasound treatment [16].

As reported in [17], the content of cellulose in hemp fibres increased by steam explosion in retted hemp fibres from 73% to 85-90%, but in raw hemp fibres from 60-64% to 73-75%. It is obvious that retting has to be included before steam explosion. The results of other studies showed that most lignins from lignocellulosic fibres were removed, when oxidative conditions were applied since they were decomposed to low molecular phenolic compounds and oxidized to carboxylic acids [18].

## II. MATERIALS AND METHODS

Disintegration of dew-retted hemp fibres of the variety *Bialobrzieskie* grown in the Agricultural Science Centre of Latgale by alkali treatment and steam explosion has been investigated. As first, alkali treatment method of fibres under investigation with 3 wt. % and 4 wt. % NaOH during 1 h at a temperature 800°C has been used.

The second applied method of steam explosion (STEX) auto-hydrolysis (also referred as steam explosion, steam explosion pulping, flash auto-hydrolysis or steam cracking) principally is a simple technique [18]. The biomass (wood or non-wood forest material, agricultural waste and fibre materials, waste from forestry, municipal and plantation management) for sustainable use has been treated with saturated steam, usually at pressures up to 40 atmospheres. The treatment time varies from some seconds to some minutes.

SEM (VEGA Tescan 5136M) micrographs and FTIR diagrams of both sample groups are analyzed. Regardless of simplicity of process physics and its automatization, experiments are time- and labour-consuming before and after STEX treatment.

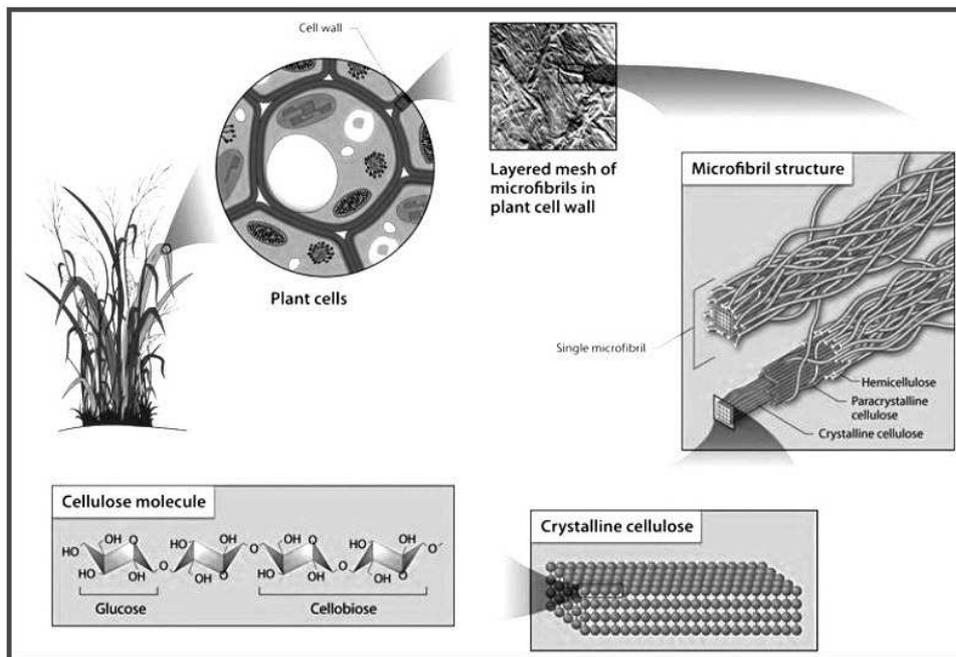


Fig. 1. Scheme of the cellulose cell wall and micro-fibril organization [44].

Fourier-transform infrared spectroscopy (FTIR) has been used to characterize influence of treatment parameters on such hemp fibre constituents as lignins, hemicelluloses and extractives. FTIR spectroscopy is a powerful analytical method, but the interpretation of the spectral data is usually complicated due to peak overlapping and broadening.

### III. ALKALI TREATMENT

Sodium hydroxide (NaOH) is the most commonly used chemical for bleaching and/or cleaning the surface of plant fibres. It is reported that alkali treatment removes lignins, pectins, hemicelluloses, ash, and results in some extraction during the process [19]. Investigations of hemp fibre alkali treatment effects show when the NaOH concentration was increased, the density of the alkali-treated hemp fibres decreased from 1.249 g/cm<sup>3</sup> to 1.127 g/cm<sup>3</sup> after alkali treatment (6 wt.% NaOH), corresponding weight loss – 13.6 % [20]. At the same time, a range of investigations indicate that rather severe pre-treatment regimes could change the fine structure of the crystalline cellulose I to amorphous cellulose II [21]. Some resources report that alkalinized plant fibres used as reinforcements in composites improve mechanical properties, but other investigations show that effects are different for different plant origins, different varieties of fibre types and with different impact on such mechanical properties as tensile strength, modulus of elasticity and impact strength [22].

As seen from micrographs of Fig. 2, untreated elementary hemp fibres of the hemp variety *Białobrzeskie* are joint in bundles by amorphous matrix, at a higher magnification the void regions present in the bundle become visible; some surface and structure defects seen on the micrograph could appear during hemp stalk primary processing or combing (Fig.

1). After alkali treatment (4 wt.% NaOH, 1 h, T 800°C) some fibre bundles are separated to smaller bundles or elementary fibres (Fig. 3); surface of one to two µm diameter elementary fibres is quite clean, only a few non-soluble plasters, probably lignins are seen on fibre bundle surface (Fig. 3).

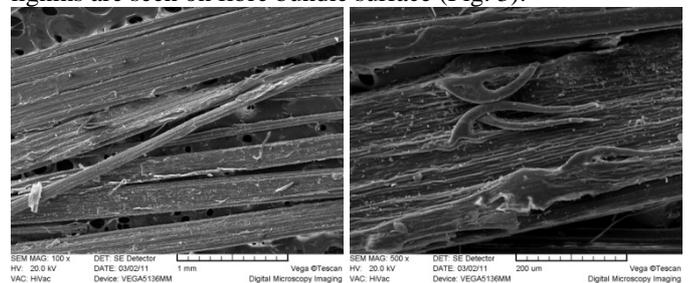


Fig.2. Untreated hemp fibre micrographs at magnification of 100x and 500x.

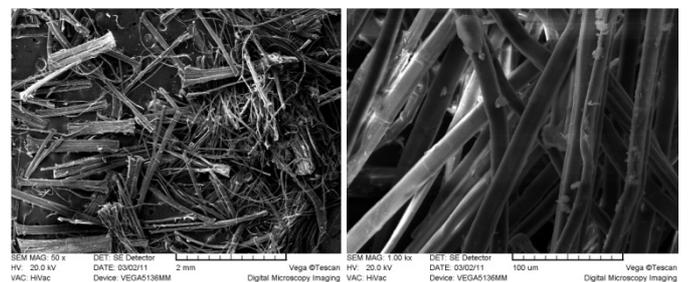


Fig.3. Alkali (4 wt.% NaOH) treated hemp fibre micrographs at magnification of 50x and 1000x.

As micrographs are qualitative sources to follow transformations which happen during treatments, fourier-transform infrared spectroscopy (FTIR) has been used to characterize in detail the influence of alkali treatment parameters on such hemp fibres constituents as lignins, hemicelluloses and extractives.

Together with hemicellulose, lignins form a matrix for cellulose fibres. Lignins in fibres are complex hydrocarbon polymers with aliphatic and aromatic constituents, forming a three dimensional network. Apart from forming the matrix in the secondary cell walls of plant fibres, lignins also decrease the permeation of water through the cell walls. As mechanical properties of lignin ( $E = 4$  GPa) compared to cellulose ( $E = 70-135$  GPa) are low [23] and water through the cell walls of technical fibres has to be removed for further applications, the removal of lignin from technical fibres is more than desirable.

As hemp belongs to Angiosperm phylum community hemp, lignins are hardwood type lignins [24], which have higher methoxyl content, are less condensed and are more amenable to chemical conversion than lignins derived from conifers.

Hemp fibre hardwood lignins contain residues derived from both coniferyl and sinapyl alcohols (lignin type GS, S/G ratio 0.8).

#### FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. As each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present [25].

FTIR allows the measurement of variations of hemp fibre composition after chemical treatment. Table 1 summarizes the major bands observed in the FTIR spectrum of hemp fibres and their assignments to chemical group vibrations and molecules.

Although infrared spectroscopy is useful for several types of analysis, but at the same time a range of interpretation problems appear becoming apparent sometimes in diametrically opposite explanations of FTIR graph absorption bands.

The intensities of peaks around  $1327$  and  $1271$   $\text{cm}^{-1}$  (ring breathing of S and G units, respectively) after resolution enhancement could be used to estimate the S and G contents.

Absorbance peak at the frequency  $1618$   $\text{cm}^{-1}$  with the highest absorbance value was found as more intensive and broad ( $1605$  to  $1639$   $\text{cm}^{-1}$ ) for hemp lignins [26]. Unfortunately lignin content of hemp fibres depends upon hemp variety and could be in a range from 3 % (*Uso*) till 13 % (*Futura 77*) [27], and supposedly the family of lignins differs, too.

As seen from graphs of Fig. 4, absorbance intensity as a result of alkali treatment (4 wt.% NaOH) decreases substantially in frequency range  $1600 - 1800$   $\text{cm}^{-1}$  and  $3300 - 3550$   $\text{cm}^{-1}$ . Investigations [28] of hemp fibre structural

morphology changes subjected to bleaching show that lignin contents of untreated fibres under investigation are 6.61 % (4.89 % non-soluble, 1.72 % soluble) and after bleaching they decrease to 3.18 % (3.18 % non-soluble, 0.35 % soluble); hemicellulose content at the same time decreases from 10.66 % (untreated fibres) to 1.85 % after treatment.

TABLE 1  
INFRARED PRINCIPAL BANDS [45]

Wavenumber ( $\text{cm}^{-1}$ )	Vibration	Source
3300	O-H linked shearing	Polysaccharides
2885	C-H symmetrical stretching	Polysaccharides
2850	CH <sub>2</sub> symmetrical stretching	Wax
1732	C=O unconjugated	Xylans (Hemicelluloses)
1650-1630	OH (water)	Water
1505	C=C aromatic symmetrical stretching	Lignin
1425	CH <sub>2</sub> symmetrical bending C=C stretching in aromatic groups	Pectins, lignins, hemicelluloses, calcium pectates
1370	in-the-plane CH bending	Polysaccharides
1335	C-O aromatic ring	Cellulose
1240	C-O aryl group	Lignin
1162	C-O-C asymmetrical stretching	Cellulose, hemicellulose
895	glycosidic bonds	Polysaccharides
670	C-OH out-of-plane bending	Cellulose

FTIR graphs (Fig. 4, 5) for B hemp variety fibres obtained in our experiment show disappearance of the absorption band corresponding to the frequency range  $1700-1750$   $\text{cm}^{-1}$  with the peak at  $1732$   $\text{cm}^{-1}$ . Such absorption band is addressed to functional groups of C=O or COOH- [29] by most of authors, where 1738 correspond to hemicellulose, 1736 to pectins and waxes. At frequency ranges  $1732-1720$  absorbance decreases, if hydrolyzed hemicellulose is removed from fibre surface as seen from graphs of Fig. 4. As a result of 4 wt. % NaOH treatment, pectins and waxes are removed as well (Fig. 4) [22].

The (methyl-esterified) carboxyl groups are absorbed in the range of  $1749$   $\text{cm}^{-1}$  and the absorbance at  $1605-1630$   $\text{cm}^{-1}$  is caused by the ionized COO<sup>-</sup> groups [30] – [36]. The following ratio has, therefore, been used as a measure for the degree of esterification [32], [37]:

$$DM = a_{1749}/(a_{1630}+a_{1749}). \quad (1)$$

DM values calculated by using the equation (1) decrease from 0.21 (non-treated) to 0.16 for 4 wt.% NaOH treated fibres. Actually values of this factor are impossible to calculate precisely after treatment because absorbance peak has been removed at all.

Absorption intensity of bands at frequency range  $1300-1450$   $\text{cm}^{-1}$  are higher for alkali treated hemp fibres. Crystallinity index

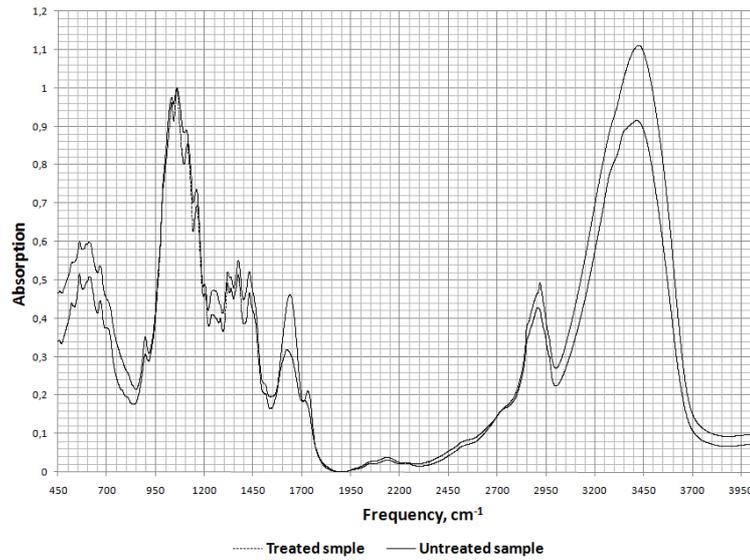


Fig. 4. FTIR spectrograms of untreated and alkali treated (4 wt.% NaOH) hemp fibres.

(CrI) supposed to be some kind of the measure of cellulose crystallinity level [38], [29]:

$$\text{CrI} = a_{1372}/a_{2900} \quad (2)$$

Calculations of CrI after baseline corrections (equation 2) shows the increase in crystallinity after 4 wt.% NaOH alkali treatment from 0.17 to 0.21 (29%). According to the calculated CrI values, alkaline-treated fibre exhibits a substantial increase in crystallinity. It corresponds to the thesis that alkalization depolymerizes the native cellulose I molecular structure producing short length crystallites [22].

The baseline-corrected absorption peaks at 1430 and 897  $\text{cm}^{-1}$  correspond to the sensitive absorption frequencies of crystalline and amorphous cellulose structures, respectively [39], [40], [29].

$$\text{LOI} = a_{1429}/a_{893} \quad (3)$$

LOI values decrease for alkali treated fibres from 2.43 to 2.25 (7%). LOI describes the order of crystallinity rather than the amount of crystalline cellulose. This observation is in accordance with the results reported in the literature, where no significant change or the increase in LOI is published for similar treatment conditions [41], [42], [22].

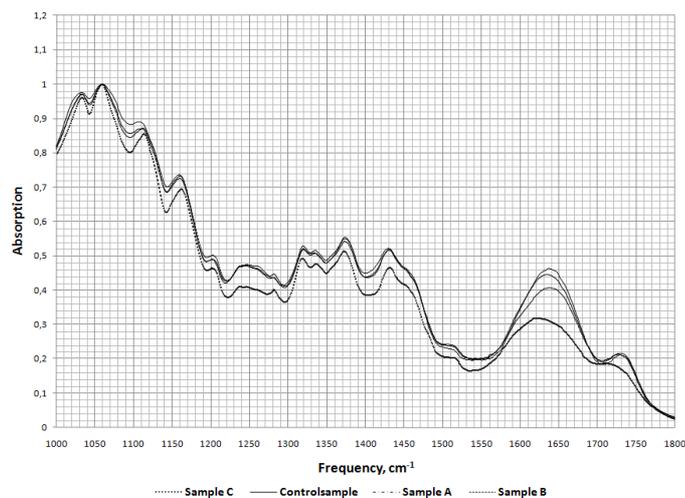


Fig. 5. FTIR spectrograms of hemp fibres subjected to steam explosion treatment corresponding to frequency range 1000-1800  $\text{cm}^{-1}$ .

The disappearance of the peak among 1245–1259 cm<sup>-1</sup> after alkalization seen in Fig. 4 indicates the removal of hemicellulose materials rather than lignins [22].

One of the most noticeable modifications of FTIR graphs (Fig. 5) before and after STEX treatment is the disappearance of the absorbance peak centred at 1732 cm<sup>-1</sup> at a pressure of 23 bar, characteristic of hemicelluloses.

Substantial decrease in absorbance intensity at the frequency range 1580-1680 cm<sup>-1</sup> allows to suppose that lignin content in the dry residue decrease after STEX treatment (log R<sub>0</sub> = 3,42). Investigations of [28] reported that lignins of hemp have most powerful absorption band at the frequency range 1605-1639 cm<sup>-1</sup>. Crystallinity index calculated by using the equation (1) has increased by 47 % (from 0.29 to 0.43) after STEX treatment at a pressure of 23 bar and at temperature 220°C. Values of lateral order index LOI increase from 2.4 till 3 after treatment.

#### IV. STEX

Among the number of chemical and physical processes occurring during the STEX treatment, two of them are the most important:

- the functional groups are cut off during the process and thereby acid molecules are formed in the system (for example, acetic groups in hemicelluloses provide formation of the acetic acid). These newly formed acids act as catalysts of hydrolysis of the treated material (auto-hydrolysis);

- after abrupt release of the pressure at the end of the SEA process, the difference of pressure in the tissues of the material

and surroundings blasts the material providing an effective deliberation of wood or other plant biomass.

After treatment, within a split second, the biomass is decompressed (exploded) to one atmosphere. Empirically, the so-called severity parameter or the reaction ordinate R<sub>0</sub> can be expressed as [18]:

$$R_0 = t * \exp [(T- 100)/ 14.75](4)$$

where: duration of treatment (t, minutes) and temperature (T, °C) express the STEX severity against the base temperature T<sub>base</sub> or reference = 100 °C. R<sub>0</sub> dimension is minutes, but in practice log R<sub>0</sub> is used. In the current article, logR<sub>0</sub> falls under the range from 2.36 to 3.42 (Table 2).

Since the lignocellulosic material, under conditions of steam explosion, can provide “self-sufficient” chemical and physical transformation, both hydrolysis and defibrillation can be achieved just by the “tools” inherent in the system itself, without any additional reagents except steam. Further fractionation of the biomass products after SEA is rather simple [2].

Hemicellulose recovery in acid hydrolysates can only be maximized at lower treatment severities, whereas the development of substrate accessibility requires more drastic conditions in which sugar losses are inevitable [43]. To account for this heterogeneity, such STEX treatment parameters as temperature, residence time into the steam reactor, steam pressure are considered as experiment variables (Table 2).

V. TABLE 2  
STEAM EXPLOSION TREATMENT PARAMETERS

Variants	Moisture, %		Evaporable fractions, %	STEX parameters			
	Before STEX	After STEX		Time, s	Temperature, °C	Pressure, bar	logR <sub>0</sub>
A	6,51	~ 75	7,0	60	180	10	2,36
B	6,51	~ 75	7,0	60	200	16	2,94
C	6,51	~ 75	8,4	60	220	23	3,42

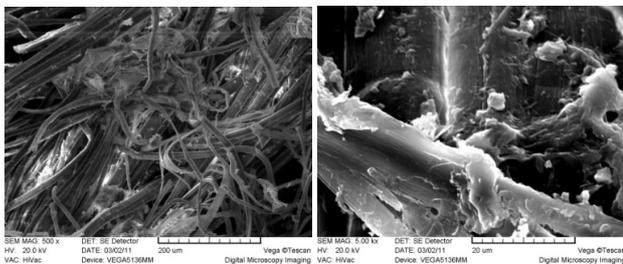


Fig.6. Hemp fibre SEM micrographs after STEX, pressure 23 bar, temperature 220 °C.

fibre bundles are separated to 10-20 µm diameter components and extracted amorphous clusters of matrix seen as separate units or loose appliques on fibre surfaces. Some of non-cellulosic substances are evaporated (loss 8,4 % of weight) during STEX treatment (Table 2). Disintegration and/or weakening of the binding of fibres in the bundles are decisively important for further separation of the hemp fibres in subsequent operations.

To more severe STEX treatment (logR<sub>0</sub> = 3,42) hemp fibres, seen in micrographs of Fig.6, are subjected, where

TABLE 3  
HEMP FIBER ABSORPTION PEAKS BEFORE AND AFTER STEX

I, cm <sup>-1</sup>	3425	2920	2850	1730	1620	1430	1372	1335	1318	1280	1238	1205	1160	1103	1058	1030	893
II, cm <sup>-1</sup>	3410	2910	2850	-	1635	1430	1372	1335	1320	1280	1245	1205	1160	1112	1058	1030	893

I Frequencies, corresponding to absorption peaks of hemp fibres, cm<sup>-1</sup>

II Frequencies, corresponded to absorption peaks after STEX, cm<sup>-1</sup>

## VI. CONCLUSIONS

With growing STEX intensity from log R<sub>0</sub> = 0 to log R<sub>0</sub> = 3.42 to a considerable extent (2.4 times) the extraction level of water soluble components increases.

Examination of FTIR spectrograms of untreated and treated hemp fibres allow evaluation of alkali and steam explosion treatment removal effectiveness of hemicelluloses and pectins.

4 wt.% NaOH treatment and medium severe STEX treatment results in the growth of cellulose crystallinity index 28 % and 47 % respectively showed that both treatments led to depolymerization of the native cellulose I molecular structure producing short length crystallites. A high crystallinity index results in stiff, strong fibres.

Medium severe STEX treatment combined with following hydrothermal and alkali treatments allow removing of approximately 26 % constituents from hemp fibres including hemicelluloses, pectins/waxes, water.

Medium severe STEX treatment (log R<sub>0</sub> = 3.42) leads to partial disintegration of hemp fibre bundles. More severe STEX intensity (higher log R<sub>0</sub> value) could increase the level of disintegration. –The use of mechanical/physical treatment just after STEX treatment could separate fibre bundles to the micro-level diameter fibres.

More extensive research is needed, aimed directly at the mechanical homogenization of cellulose fibres.

## ACKNOWLEDGEMENTS

This research has been supported by the European Social Fund within the project «Support for the Implementation of Doctoral Studies at Riga Technical University».

## REFERENCES

- [1] Fan M. Elementary hemp fibres and strength. *BioResources* 5(4), 2010, 2307-2322
- [2] Gravitis J. Nano level structures in wood cell wall composites. *Cellulose Chemistry and Technology*, 2006, 40(5), 291-298
- [3] Szalkowski Z.: *Podstawy chemicznej technologii surowcow I wlokeien lykowych*, Warszawa, 1967
- [4] Bjerre AB, Schmidt AS. Development of chemical and biological processes for production of bioethanol: Optimization of the wet oxidation process and characterization of products. 1997, Riso-R-967(EN), Riso National Laboratory: pp 5-9
- [5] Morvan C, Jauneau A, Flaman A, Millet J, Demarty M. Degradation of flax polysaccharides with purified endo-polygalacturonase. *Carbohydrate Polymers*, 1990,13, 149-163
- [6] Bjerre AB, Olesen AB, Fernqvist T, Plöger A, Schmidt AS. Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose. *Biotechnol Bioeng*, 1996, 49, 568-577
- [7] Madsen, B., 2004. Properties of plant fibre yarn polymer composites – An experimental study. Ph.D. thesis, BYG-DTU, Technical University of Denmark, ISBN 87-7877-145-5
- [8] Thygesen A., Thomsen A.B., Skammelsen Schmidt A., Jorgensen H., Ahring B.K., Olsson L. Production of cellulose and hemicellulose-degrading enzymes by filamentous fungi cultivated on wet-oxidised wheat straw. *Enzyme Microbial Technology*, 2003, 32 (5), 606-615
- [9] Madsen F.T., Burgert I., Jungnikl K., Felby C., Thomsen A.B. Effect of enzyme treatment and steam explosion on tensile properties of single hemp fiber. 12th International Symposium on Wood and Pulping Chemistry (ISWPC), 2003, Madison, P80
- [10] Brühlmann F., Leupin M., Erisman K.H., Fiechter A. Enzymatic degumming of ramie bast fibers. *Journal of Biotechnology*, 2000,76, 43-50
- [11] Thomsen A.B., Rasmussen S., Bohn V., Nielsen K.V., Thygesen A., Hemp raw materials: The effect of cultivar, growth conditions and pretreatment on the chemical composition of the fibres. Riso National Laboratory. Report No.: R-1507
- [12] Wang H.M., Postle R., Kessler R.W., Kessler W. Removing pectin and lignin during chemical processing of hemp for textile applications. *Textile Research Journal*, 2003, 73, 664-669
- [13] Garcia-Jaldon C., Dupeyre D., Vignon M.R. Fibres from semi-retted hemp bundles by steam explosion treatment. *Biomass & Bioenergy*, 1998, 14, 251-260
- [14] Madsen et al., 2003; Vignon M.R., Garcia-Jaldon C., Dupeyre D. Steam explosion of the woody hemp chénevoite. *International Journal of Biological Macromolecules*, 1995, 17, 395-404
- [15] Zimmer H, Kloss D. *Ultraschallaufschluss von Hanf. Ziele-Technologie-Anwendung-Resultate-Qualitätsmanagement*. Proceedings of the Bioresource Hemp '95 Symposium; Frankfurt, Germany. Nova-Institute
- [16] Klinke H.B., Ahring B.K., Schmidt A.S., Thomsen A.B. Characterization of degradation products from alkaline wet oxidation of wheat straw. *Bioresour Technol*, 2002, 82, 15-26
- [17] Thygesen A. Properties of hemp fibre polymer composites -An optimisation of fibre properties using novel defibration methods and fibres characterisation, PhD thesis, The Royal Agricultural and Veterinary University of Denmark, ISBN 87-550-3440-3
- [18] Gravitis J., Dobele G., Abolins J., Tupciauskas R. & Veveris A. Non-sulphur lignin studies under biorefinery concept and evaluation of energy consumption by steam explosion. Paris, January, 2011
- [19] N. Sgriccia, M.C. Hawley, M. Misra // *Compos. Part A: Appl.Sci.Manuf.* 39 (2008) 1632
- [20] N.P.G. Surdana, Yingjun Piao, Jae Kyoong Lim. Mechanical properties of hems and hemp/PP composites: effects of chemical surface treatment. *Materials Physics and Mechanics* 11 (2011) 1-8
- [21] Zeronian, S. H. In *Cellulose Chemistry and Its Applications*; Nevell, T. P.; Zeronian, S. H. Eds.; Ellis Horwood: Chichester, 1985, p. 159
- [22] Mwaikambo, L.J. and M.P. Ansell, *Chemical Modification of Hemp, Sisal, Jute, and Kapok Fibers by Alkalization*. *Journal of Applied Polymer Science*, 2002, 84: p. 2222-2234.
- [23] Bledzki, A.K. and J. Gassan, *Composites reinforced with cellulose based fibres*. *Progress in Polymer Science*, 1999, 24(2): p. 221-274
- [24] Thysingen A. Hemp fiber microstructure and use of fungal defibration to obtain fibers for composite materials., *Journal of Natural Fibres*, 2006, 19-37
- [25] Introduction to Fourier Transform Infrared Spectrometry, Thermo Nicolet Corporation, P/N 169-707500, 2001, [www.thermoficolet.com](http://www.thermoficolet.com)
- [26] Colom, X. and F. Carrillo, Crystallinity changes in lyocell and viscose-type fibres by caustic treatment. *European Polymer Journal*, 2002, 38(11): p. 2225-2230

- [27] Rio, J., Gutierrez, A. and Composition of non-woody plant lignins and cinnamic acids by Py-GC/MS, Py/TMAH and FT-IR. Rio, J., Gutierrez, A. and Rodriguez, I.M. Journal of Analytical and Applied Pyrolysis, 1-2, 2007, Vol. 79, lpp. 39-46
- [28] Wang, B, Sain, M & Okzman, K 2007, 'Study of structural morphology of hemp fiber from the micro to the nanoscale', Applied Composite Materials, vol 14, no. 2, pp. 89-103.
- [29] Korte, S. Processing-Property Relationships of Hemp Fibre. Canterbury: University of Canterbury, 2006
- [30] Synytsya, A., J. Copikova, P. Matejka, and V. Machovic, Fourier transform Raman and infrared spectroscopy of pectins. Carbohydrate Polymers, 2003. 54(1): p. 97-106
- [31] Sene, C., M.C. McCann, R.H. Wilson, and R. Grinter, Fourier-Transform Raman and Fourier-Transform Infrared Spectroscopy (An Investigation of Five Higher Plant Cell Walls and Their Components). Plant Physiology, 1994. 106: p. 1623-1631
- [32] Chatjigakis, A.K., C. Pappas, N.Proxenia, O.Kalantzi, P.Rodis, and M. Polissiou, FT-IR spectroscopic determination of the degree of esterification of cell wall pectins from stored peaches and correlation to textural changes. Carbohydrate Polymers, 1998. 37(4): p. 395-408
- [33] Manrique, G.D. and F.M. Lajolo, FT-IR spectroscopy as a tool for measuring degree of methyl esterification in pectins isolated from ripening papaya fruit. Postharvest Biology and Technology, 2002. 25(1): p. 99-107
- [34] Kacurakova, M. and R.H. Wilson, Developments in mid-infrared FT-IR spectroscopy of selected carbohydrates. Carbohydrate Polymers, 2001. 44(4): p. 291-303
- [35] Kamnev, A.A., M. Colina, J. Rodriguez, N.M. Pritchkina, and V.V. Ignatov, Comparative spectroscopic characterization of different pectins and their sources. Food Hydrocolloids, 1998. 12(3): p. 263-271
- [36] Filippov, M.P., Practical infrared spectroscopy of pectic substances. Food Hydrocolloids, 1992. 6(1): p. 115-142
- [37] Barros, A.S., I. Mafra, D. Ferreira, S. Cardoso, A. Reis, J.A. Lopes da Silva, I. Delgadillo, D.N. Rutledge, and M.A. Coimbra, Determination of the degree of methylesterification of pectic polysaccharides by FT-IR using an outer product PLS1 regression. Carbohydrate Polymers, 2002. 50(1): p. 85-94
- [38] Nelson, M.L. and R.T. O'Connor, Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part II. A New Infrared Ratio for Estimation of Crystallinity in Celluloses I and II. Journal of Applied Polymer Science, 1964. 8: p. 1325-1341
- [39] Oh, S.Y., D.I. Yoo, Y. Shin, and G. Seo, FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide. Carbohydrate Research, 2005. 340 (3): p. 417-428
- [40] Shanks, R.A. and S. Ouajai, Morphology and Structure of Hemp Fibre after Bioscouring. Macromolecular Bioscience, 2005. 5: p. 124-134
- [41] Gassan, J. and A.K. Bledzki, Alkali Treatment of Jute Fibers: Relationship Between Structure and Mechanical Properties. Journal of Applied Polymer Science, 1999. 71: p. 623-629
- [42] Ouajai, S. and R.A. Shanks, Composition, structure and thermal degradation of hemp cellulose after chemical treatments. Polymer Degradation and Stability, 2005. 89(2): p. 327-335
- [43] Luiz Pereira Ramos. The Chemistry involved in the steam treatment of lignocellulosic materials. Quim. Nova, Vol. 26, No. 6, 863-871, 2003
- [44] Cellulosic Bionanocomposites: A Review of Preparation, Properties and Applications. Siqueira, G., Bras, J. un Dufresne, A. 2010. gada, Polymers, Sēj. 2, lpp. 728-765. ISSN 2073-4360
- [45] Li, Y. Processing of Hemp Fibre Using Enzyme/Fungal Treatment for Composites, University of Waikato, 2009

**Anna Putnina**, Mg. sc. ing., Assistant  
Riga Technical University, Institute of Textile Materials Technologies and Design. Azenes Str. 14, LV – 1048, Riga, Latvia,  
+ 371 28899974, E – MAIL: ANNA.PUTNINA@RTU.LV

**Janis Gravitis**, Dr. habil. Chem prof.,  
Laboratory of Biomass Eco-Efficient Conversation,  
Dzerbenes Str. 27, Riga LV-1006, Latvia,  
+ 37122544448, e-mail: jgravit@edi.lv

**Silvija Kukle**, Dr. hab. sc. ing., Professor  
Riga Technical University, Institute of Textile Materials Technologies and Design  
Azenes Str. 14, LV – 1048, Riga, Latvia,  
+ 371 67089816, e – mail: skukle@latnet.lv

#### **Anna Putniņa, Silvija Kukle, Jānis Grāvītis. Ar STEX apstrādāto un neapstrādāto kaņepju šķiedru salīdzinošā strukturālā analīze**

Kaņepes ir atjaunojams dabas resurss ar lielu biomasas ražu, tās var uzskatīt par potenciālu un bagātīgu vietējo biomasas materiālu plašam lietojumam. Šajā rakstā tiek analizēta kaņepju šķiedru struktūra kā augstas stiprības celulozes avots. Eksperimentālajā daļā tiek pielietota tvaika sprādziena tehnoloģija, lai sašķeltu tehniskās kaņepju šķiedras elementārajās šķiedrās, lai rastu labāko veidu, kā iegūt šķiedras bez videi kaitīgām ķīmiskām pirmsapstrādēm un risinātu problēmas turpmākai videi draudzīgai nanomēroga kaņepju celulozes dezintegrācijai. Pirmapstrādes intensitātes ietekme, tvaika sprādziena procesa temperatūra un spiediens ietekmē kaņepju šķirnes Bialobreskie šķiedru dezintegrācijas līmeni. Palielinot STEX apstrādes tvaika spiedienu līdz 23 bariem SEM mikrografijās redzams, ka ievērojami palielinājies elementāršķiedru īpatsvars, kā arī notikusi autohidrolīze elementāršķiedru līmenī saplēšot šūnu sienīgas; parādījušās nanoizmēra šķiedras. Tomēr vēl joprojām daļa šķiedru kūlīšu nav sadalījušies. Eksperimenta rezultātā jāsecina, ka STEX apstrāde ar piemēroto intensīvāko apstrādes režīmu  $R_0$  3.42 un sekojošu ūdenī šķīstošu un sārma šķīstošu komponentu ekstrakciju ļauj sadalīt kaņepju šķiedru kompleksus, daļēji līdz izmēriem, kas atbilst vērpšanas suspensiju veidošanai.

#### **Анна Путнина, Силвия Кукле, Янис Гравитис. Сравнительный структурный анализ конопляного волокна, обработанного и не обработанного STEX**

Конопля является возобновляемым ресурсом с высоким выходом биомассы и может рассматриваться, как потенциальный местный биомассный материал, годный для широкого ряда применений. В этой статье анализируется строение волокон конопли как основы для высокопрочной целлюлозы. В экспериментальной части для дезинтегрирования волокон конопли на элементарные волокна была применена технология парового взрыва с целью найти лучший метод без использования предварительных химических обработок, вредных для окружающей среды, и в перспективе решить проблему с дальнейшим экологически дружелюбным способом дезинтегрирования наноуровневой конопляной целлюлозы. Увеличение пара STEX при обработке давлением до 23 бар, микрография SEM показывает, что значительное увеличение доли накалывания произошло на уровне перфорированного автогидролиза при разрыве стенки клетки, а также выявлении признаков появления наноразмерных волокон. Тем не менее, еще остаётся часть расслоения, которая не разлагается. Исследовано влияние интенсивности предварительных обработок, температуры и давления в процессе парового взрыва на уровень дезинтегрирования волокон конопли сорта Биалобреские, а также рассмотрены полученные результаты.