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Extraction of highly purified microfibrils from the renewable resources by using green technology

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The main task in preparing hemp shives for further processing is to remove noncellulosic substances without usage of strong chemical treatments applying the steam explosion (SE) auto-hydrolysis process. The results indicate that the SE has significant effects on lignin removal and distribution of hemp shives. Effects of pre-treatment temperature and duration on characteristics of the steam exploded shives are studied by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Key words: hemp shives, steam explosion, lignin, biomass

INTRODUCTION

The synthetic man-made fibres can be replaced by the micro- and nano-scale cellulosic fibres obtained by green technologies. Eco-efficient green chemistry and industrial ecology are the guidelines for the development of next-generation materials, processes and products.

Hemp (*Cannabis sativa*) (Fig. 1 (A)) suitable for the Latvian climate is one of the fastest growing plants with a potential in a number of industrial areas. Hemp fibres obtained from straw can be used effectively in many applications, whereas shives are considered as an invalid part and are often combusted to get cheap fuel. At the same time, it is shown that shives (Fig. 1(B)), woody core particles of hemp stems, can be used in different fields, such as livestock bedding [1], horticultural mulch [2], chemical absorbents [3] and industrial insulating building materials [4] demonstrating excellent properties. By now, it is important to investigate a new processing technology that will broaden application areas, as well as improve efficiency of the usage of the shives comprising 80% of the plant biomass.

Several methods generally based on successive chemical [7, 8] and mechanical [9] treatments are used to extract highly purified micro-fibrils from the plant cell wall. The steam explosion (SE) auto-hydrolysis is currently comprehensively studied as a promising green pre-treatment tech-

Fig. 1. Hemp plants: A – hemp field [5]; B – shives [6]

nology [10] to obtain micro-fibrils of cellulose and also to remove lignin from the cellulose. Removal of lignin after SE makes the cellulose accessible for further processing, for example, by electro-spinning – a novel process of forcing a suspension by electric field through a spinneret to obtain superfine fibres.

Effective usage of SE for treatment of the shives could provide lignin-free cellulose micro-fibrils. This could provide new application areas for shives where they could not be possible to use by now.

METHODOLOGY

Hemp shives of the local variety 'Purini' grown on the experimental fields of the Latgalian Agriculture Research Center LLZC (Latvia, Vilani District) were used as lignocellulosic biomass. Laboratory-type steam explosion equipment was used to make steam explosion treatment experiments [16].

After steam explosion treatment, within a split second, the biomass is decompressed (exploded) to one atmosphere. Empirically, the so-called severity parameter or the reaction ordinate R_0 can be expressed as [11]:

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

where t, min is duration of treatment, T, °C is temperature.

The SE severity is expressed against the base temperature $T_{\text{base or reference}} = 100$ °C. R_0 dimension is minutes but in practice $\log R_0$ is used. In the current article, the severity parameter ($\log R_0$) falls in a range from 3.98 to 4.45 (Table).

Similar SE results may be achieved at different combinations of t and T. However, there is certainly a contribution from other factors such as moisture content of the sample, size of particles, volume of a reactor etc. During the SE treatment, the biomass is subject to high pressure of saturated steam and rapid decompression resulting in substantial breakdown of the lignocellulosic structure, hydrolysis of hemicelluloses, depolymerisation of lignin components and defibrillation.

In current research two sample groups of hemp variety 'Purini' shives are subjected to the SE treatment changing processing severity by treatment time t (SE1WA and SE3WA). Post-treatment was also provided with the aim to fractionate the main components of hemp-hemicellulose, cellulose and lignin. SE hemp pulp is extracted with water removing all the soluble saccharides and oligosaccharides resulting from the hemicelluloses during the SE process, as well as a small part of the lignin degradation products. Two products were obtained after the extraction: the pulp extracted by water and the water extract. In addition to all the above mentioned treatments, the shives biomass was treated with 0.4 wt.% NaOH to remove the degradation products of lignin. There remains the alkali extracted mass, which is cellulose, and alkaline extract which has SE lignin degradation products. To separate lignin from the alkaline solution 34 wt.% hydrochloric acid (HCl) treatment is used. After lignin precipitation and discharging the neutralized solution is filtered.

Table. **Modes of hemp shive samples SE treatment and after-treatment**

Sample label	P, bar	T, °C	t, min	$\log R_0$	Evap. frct, %	Residue, %	Water solub., %	Resid. after wat., %	Alk. solub.,%	Precipitation (lignin), %	Resid. after alk. extr., %
Untreated	0	0	0	0	0	100	12.6	87.4	12.5	2.4	74.9
SE1WA	32	235	1	3.98	20.2	79.8	12.5	67.3	23.8	17	43.4
SE3WA	32	235	3	4.45	20.1	79.9	7.7	72.1	30.1	22.3	42

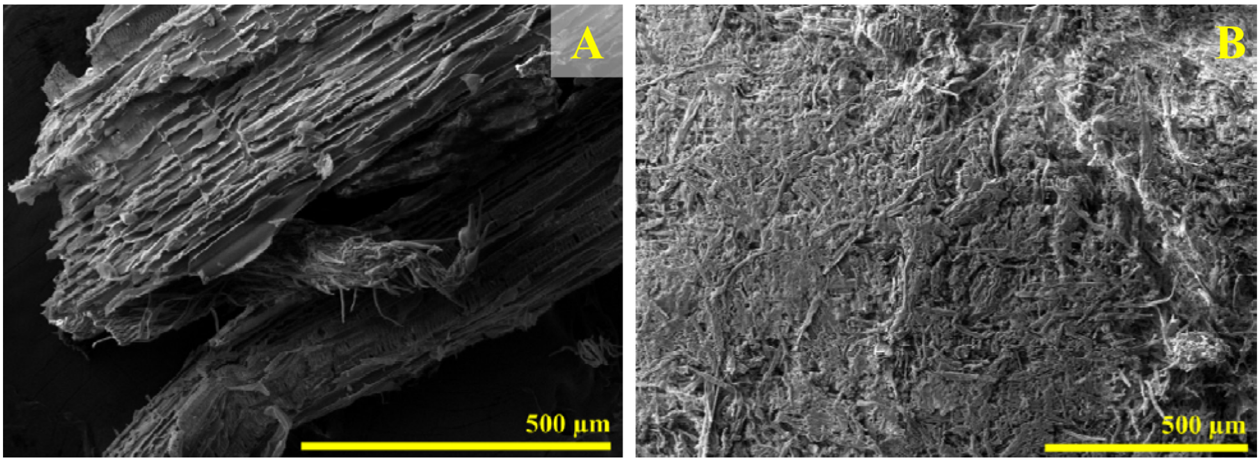

Fig. 2. SEM micrographs of hemp shives before SE (A) and after SE (235 °C, 32 bar, 3 min (B))

RESULTS AND DISCUSSION

SEM methods were used for identification of morphological changes and differences of treated hemp shives in comparison to untreated shives (Fig. 2). The micrograph of steam exploded hemp shives shows defibrillation, which has taken place during the steam explosion process. SE severity logR_0 = 4.45 allows to uncover the internal structure (Fig. 2 (B)) of the shive variety 'Purini'.

It was found that after SE the precipitated substance of spherical domains (Fig. 3 (A)) appeared. As EDX analysis shows (Fig. 3 (B)), spherical domains contain mainly carbon. From this it is possible to conclude that the spherical domains are lignin clusters moulding. Sometimes, different kinds of microorganisms and funguses can be found in cellulose materials, but in that case spherical domains should contain nitrogen (N).

Formation of lignin spherical clusters has been also found earlier in wood pulp [12] obtained by SE. During SE lignin has a tendency to redistribute and deposit in the form of spherical particles on the outer and inner surfaces of cells as well as inside the cell wall, between partially separated concentric cell wall lamellae [12]. It has been observed that the increase of the severity parameter from log$R_0$3.98 to log$R_0$4.45 also increases concentration of the lignin domains on the fibre surfaces (Fig. 4 (A) and (B)). In the same way, change of the severity parameter influences the amount of the lignin precipitates (Table).

In common with other materials, the chemical composition at the microscopic level determines the ability to perform various functions for the usefulness of natural fibres. FTIR has been mostly successful in accurate analysis of both major (cellulose, hemicellulose and lignin) and minor (mineral, pectin, waxes) constituents of natural fibres. Interface, properties and change in chemical compositions of natural fibres and composites could also be effectively identified by using FTIR [13].

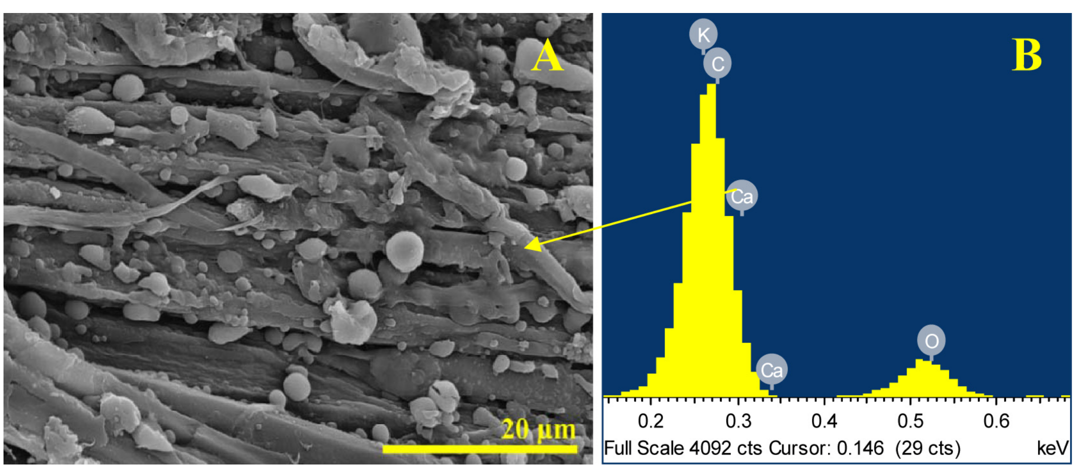

Fig. 3. A – SEM micrograph of hemp shives after SE (235 °C, 32 bar, 3 min); B – EDX analysis after SE (235 °C, 32 bar, 3 min)

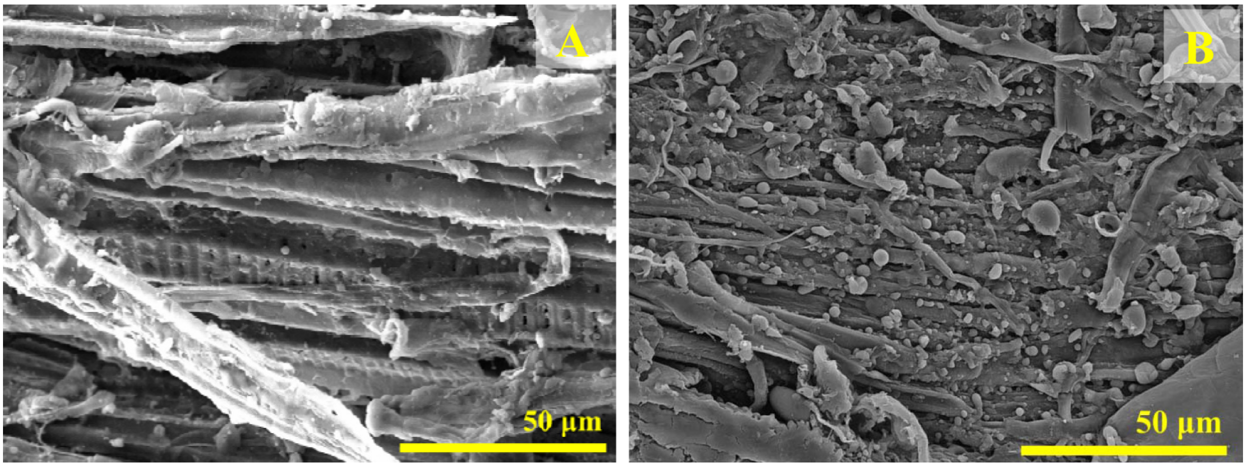

Fig. 4. A – SEM micrograph of hemp shives after SE (235 °C, 32 bar, 1 min); B – after SE (235 °C, 32 bar, 3 min)

The results of hemp shives by FTIR spectroscopy confirmed the changes of SE treated and after-treated hemp shives. SE treated fibres showed the characteristic peaks of cellulose I although without a carbonyl peak at 1 739 cm^{-1}, non-cellulosic components including pectin, hemicelluloses and lignin were removed by SE and after-treatments (Fig. 5). Observable removal of lignin can be seen at the peak 1 739 cm^{-1} (C=O stretch in unconjugated cations, carbonyls and in ester groups (frequently of carbohydrate origin)) and at the peak 1 606 cm^{-1} (aromatic skeletal vibrations plus C=O stretch) [14]. The increase in the intensity of the band at 879 cm^{-1} in regenerated cellulose indicated structural transformation from cellulose I into cellulose II. Cellulose I has a parallel closed-packed structure. The vibration of b-1,4-glycosidic linkage was limited and less intensity obtained. Transformation to cellulose II caused a structure with reduced packing thus the intensity of the vibration band at 879 cm^{-1} increased [15].

FTIR is widely used for qualitative characterization of lignin. Spectrum indicates the practically identical lignin sample (SE1 and SE3) structure and functional groups quantity (Fig. 6). The spectra of precipitated lignin from

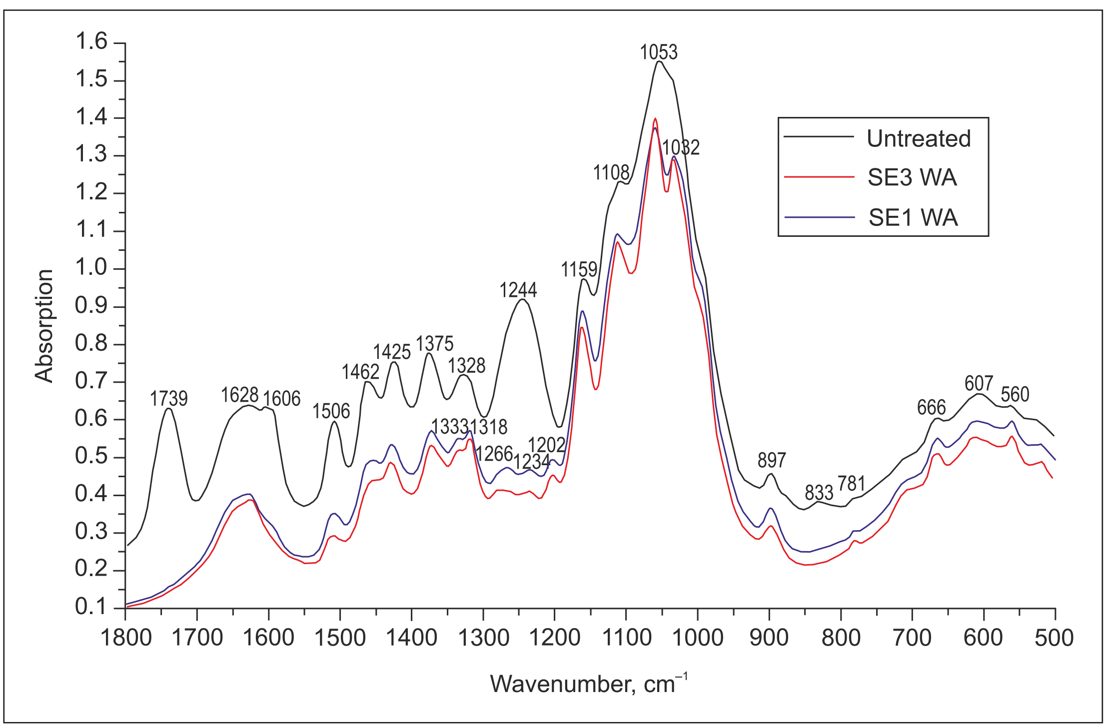

Fig. 5. FTIR spectrograms of untreated and SE treated hemp shives combined with the following hydrothermal and alkali treatment ones

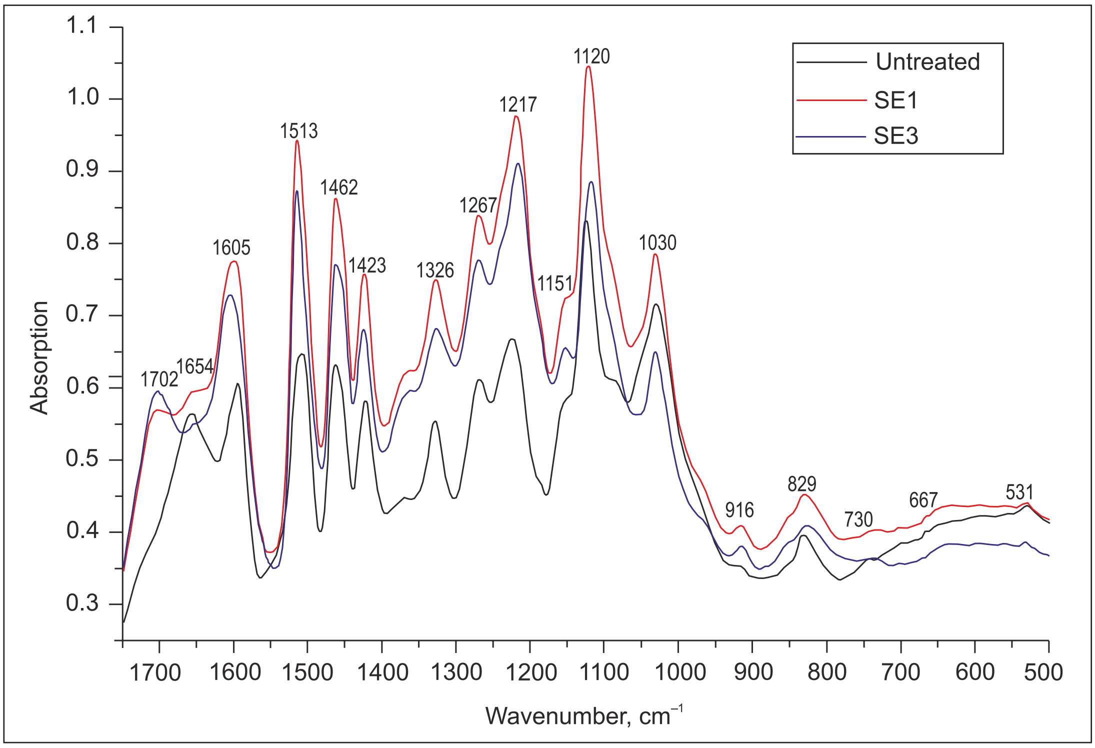

Fig. 6. FTIR spectrograms of hemp shives lignin

hemp shives show that the extraction result is obtained lignin. It is demonstrated by the characteristic of lignin absorption bands and typical lignin functional groups [14].

CONCLUSIONS

The increase of the severity parameter from log$R_0$3.98 to log$R_0$4.45 also increases the lignin domains on fibre surfaces and influences fibre defibrillation. It is also shown by the FTIR spectres.

The study has shown that the SE treatment combined with the following hydrothermal and alkali treatments allow removing of ~30.1% constituents from hemp shives, including hemicelluloses, pectins / waxes and oils covering the external surface of the shive cell wall, and depolymerise the native cellulose structure. FTIR analysis showed differences between the spectra of untreated and SE treated hemp shives combined with the following hydrothermal and alkali treatments. The precipitate spectra analysis shows that the hemp shives SE treatment and following after-treatments result in lignin sediments which are approved by the presence of characteristic lignin absorption bands and typical lignin functional groups.

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IŠGRYNINTŲ MIKROSKAIDULŲ IŠTRAUKIMAS IŠ ATSINAUJINANČIŲJŲ IŠTEKLIŲ NAUDOJANT ŽALIĄSIAS TECHNOLOGIJAS

Santrauka

Pagrindinė užduotis ruošiant kanapių spalius tolesniam apdorojimui yra pašalinti neceliuliozines medžiagas nenaudojant agresyvaus cheminio apdorojimo, o taikant sprogdinimo garu (SE) auto-hidrolizės procesus. Rezultatai rodo, kad SE veikia lignino pašalinimą ir kanapių spalių pasiskirstymą. Išankstinio apdorojimo temperatūros ir trukmės poveikis garu išsprogdintų spalių charakteristikoms yra nagrinėjamos skenuojant elektroniniu mikroskopu (SEM) ir infraraudonąja Furje transformacijos spektroskopija (FTIR).

Raktažodžiai: kanapių spaliai, sprogdinimas garu, ligninas, biomasė

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УДАЛЕНИЕ СИЛЬНО ОБОГАЩЕННЫХ МИКРОЭЛЕМЕНТОВ ИЗ ВОЗОБНОВЛЯЕМЫХ ИСТОЧНИКОВ ЭНЕРГИИ ПРИ ИСПОЛЬЗОВАНИИ ЗЕЛЕНЫХ ТЕХНОЛОГИЙ

Резюме

При подготовке костры конопля для дальнейшей обработки необходимо удалить нецеллюлозные материалы без применения сильного воздействия применив паровой взрыв (SE) в авто-гидролизных процессах. Результаты исследования показывают, что SE сильно влияет на удаление лигнина из костры капля. Влияние температуры предварительной обработки и ее продолжение на характеристики костры исследовались электронным микроскопом (SEM) и инфракрасной Фурье спектроскопией (FTIR).

Ключевые слова: костра конопля, взрывание паром, лигнин, биомасса