Steam Explosion as the Pretreatment Method of Lignocellulosic Biomass

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***Abstract* – The aim of this article is to estimate the influence of steam explosion auto-hydrolysis (SEA) on hemp fibres, shives, and flax shive microstructure, and the influence of steam explosion process temperature, time and pressure on the disintegration level of lignocellulosic biomass. The acquired results are discussed and interpreted by the Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). These treatments have been performed to make fibres that are useful for further nanotechnological processes.**

***Keywords* – steam explosion, lignocellulosic, biomass, hemp, flax, lignin.**

I. INTRODUCTION

Lately, the research has been conducted on the novel nanomaterials manufactured from renewable resources. An important class of nanomaterials has been nanofibers and fibrils from different cellulose sources, which result in unique properties when incorporated in different polymers. The sources of these nanomaterials have been wheat straw, bacterial cellulose, kraft pulp, sugar beet pulp, potato, swede root [1], and also local renewable resources grown in Latvia – hemp and flax.

II. MATERIALS AND METHODS

The present article considers the disintegration of fibres and shives from different hemp varieties (Purini, Bialobrzeskie) and flax (Vesa) grown in the Latvian Agricultural Science Centre of Latgale by steam explosion.

Steam explosion auto-hydrolysis (SEA) being one of the most prospective pre-treatment technologies facilitates separation of the lignocellulosic biomass components in a single course of action providing the source for biofuels, chemicals, and nano-materials [2].

Since the lignocellulosic material, under conditions of steam explosion, can provide “self-sufficient” chemical and physical transformation [2], hydrolysis and defibration can be achieved without any additional reagents (except steam). Further fractionation [3] of the biomass products after SEA is rather simple (Fig. 1).

All SEA products have a variety of applications [3]. Hemicelluloses, during the SEA can be hydrolysed to sugars – xylose, mannose, arabinose, etc. and used as molasses, the substrate for fodder yeast or bio-ethanol. The xylose sugar can be hydrogenated to xylitol (sweetener) and can also be dehydrogenated to furfural – an excellent feedstock for chemical processing [2].

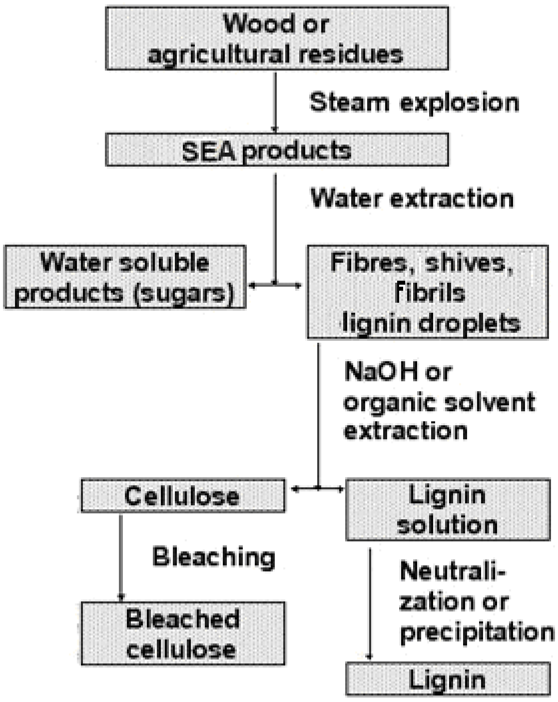


Fig. 1. Fractionation of steam exploded biomass [4]

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_0 can be expressed as [4]:

$$R_0 = t * \exp[[T - 100]/14{,}75] \qquad (1)$$

Where: duration of the value of treatment time (t, minutes) and temperature (T, ^{0}C) express the SEA severity against the base temperature T_{base} or reference = 100 ^{0}C. R_0 dimension is minutes but in practice $\log R_0$ is used. In the current paper, $\log R_0$ falls under the range from 3.52 to 4.45 (Table 1).

A. *Fourier Infrared Spectroscopy*

Fourier transform infrared (FTIR) spectra of the samples under investigation have been recorded in KBr pellets by Spectrum One (Perkin Elmer, UK) FTIR spectrometer in the range of 4000–400cm^{-1} (resolution: 4cm^{-1}). About 2 mg of precipitation has been crushed into powder. The fibre particles have been mixed with KBr and pressed into a disc about 1mm thick.

B. *Scanning Electron Microscopy (SEM)*

SEM micrographs of fibre and shive surface and cross-sections have been taken using a scanning electron microscope VEGA Tescan 5136M (Czech Republic – UK). Prior to SEM evaluation, the samples have been coated with gold by means of a plasma sputtering apparatus.

III. RESULTS AND DISCUSSION

Table 1 shows changes after SEA treatment and hydrothermal and alkali treatment of biomass, also precipitation (lignin), evaporable fractions, residue after SEA, water and alkaline treatment.

Evaporation intensity in fibres corresponds to pressure of 23 bar (7.5%) (Table I) and increases at pressure of 32 bar (13.8%). After SEA treatment, at pressure of 32 bar water treatment follows, where all water soluble components are removed leaving dry residue of 75.3% in fibres, hemp shives of variety *Purini* 72.1%, hemp shives of variety *Bialobrzeskie* 67.8% (no significant difference compared with the milled shives 1mm 67.4%) and flax shives 65.9%. Drying has been carried out at room temperature, while there is no change in mass. During the last treatment with 0.4 wt.% NaOH and subsequent washing content of extracted components decrease at the increase in pressure.

TABLE I

MODES OF HEMP AND FLAX SAMPLES AFTER SEA TREATMENT

Samples	Pressure, bar	$\log R_0$	Evaporable fractions, %	Residue, %	Water solub., %	Resid. after wat., %	Alk. solub.,%	Precipitation (lignin),%	Resid. after alk. extr., %
hemp variety *Purini*, fibres	-	0	0	100	7.3	92.7	4.5	0.2	88.2
	23	3.53	7.5	92.5	10.7	81.9	4.5	0.6	77.3
	32	3.97	13.8	86.2	10.8	75.3	7.1	2.3	68.3
Shives									
hemp variety *Purini*	-	0	0	100	12.6	87.4	12.5	2.4	74.9
	32	3.97	20.2	79.8	12.5	67.3	23.8	17	43.4
		4.45	20.1	79.9	7.7	72.1	30.1	22.3	42
hemp variety *Bialobrzeskie*	-	0	0	100	6.4	93.6	13.4	2.6	80.1
	32	3.97	16.9	83.1	13.2	69.8	21.4	16.6	48.4
		4.45	25.9	74.1	6.3	67.8	24.4	19.6	43.4
hemp variety *Bialobrzeskie* (milled 1 mm)	-	0	0	100	7.4	92.6	14.6	2.6	78
	32	3.97	19	81.0	16.2	64.8	19.5	12.7	45.3
		445	22.5	77.5	10.2	67.4	25.5	15.6	41.8
Flax (Vesa)	-	0	0	100	5.6	94.4	11.5	1.5	82.8
	32	3.97	14.7	85.3	14.5	70.8	16.7	11.1	54.1
		4.45	25.9	74.1	8.2	65.9	19.3	6.3	46.6

A. *Spectroscopic Characterisation of Lignins*

Fourier transform infrared spectroscopy (FTIR) has been used for lignin identification. The results of FTIR spectroscopy are presented in Fig. 2. Table 2 shows the infrared spectra absorption bands of some typical non-wood (hemp and flax) lignins.

TABLE II

HEMP AND FLAX SHIVE LIGNIN ABSORPTION BANDS IN FTIR SPECTRA

Band wavenumber, cm^{-1}	Band origin	Lignin
1700	carbonylgroups, C=O stretching (conjugated C=O)	flax, hemp
1600, 1512	aromatic skeletal stretching vibration	flax, hemp
1463-1427	C-H deformation and aromatic ring vibration, a considerable contribution from the C-H bonds oft he -OCH3groups	flax, hemp
1365, 1329	symmetric C-H bending from methoxyl group and C1-O vibrations in syringyl derivatives	flax, hemp
1270	guaiacyl ring breathing with C-O stretching	flax, hemp
1218	C-O(H) stretching of phenolic OH and ether	flax, hemp
1150	C-O-C stretching	flax, hemp
1117	ether stretching	flax, hemp
1090	C—O stretching	flax
1030	Calkyl– O ether vibrations methoxyl and β– O – 4 in guaiacol	flax, hemp
916	epoxy groups	hemp
855	C-H deformation and ring vibration, aromatic CH out of plane bending	flax
816	C-H deformation and ring vibration, aromatic CH out of plane bending	hemp

FTIR is a versatile and rapid technique for the identification and determination of lignin content. Typical bands are found at about 1500 and 1600cm-1 and between 1470 and 1460cm-1 [5].

FTIR can give information on the lignin type, methoxyl groups, carbonyl groups, and hydroxyl groups [6]. FTIR spectra of hemp fibres and shive variety of Purini and variety Bialobrzeskie and flax shive processes are assigned in accordance with [7, 8, 9, 11]. FTIR spectra reflect the chemical structure and the purity of lignins. Common features and particular vibrations, specific to each lignin, are found in the spectra.

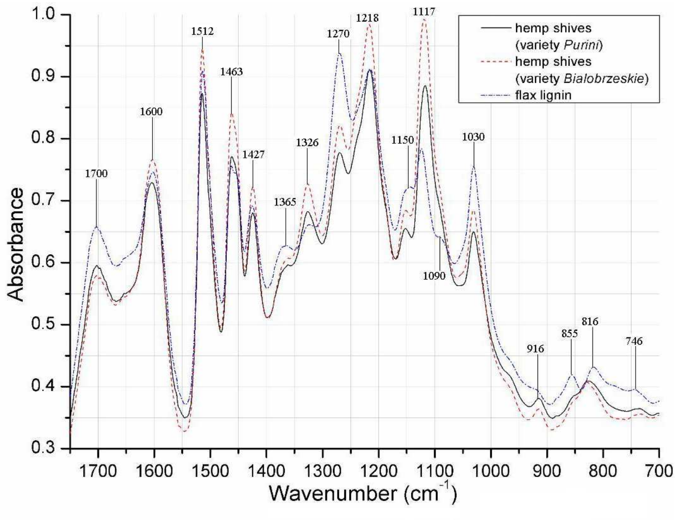


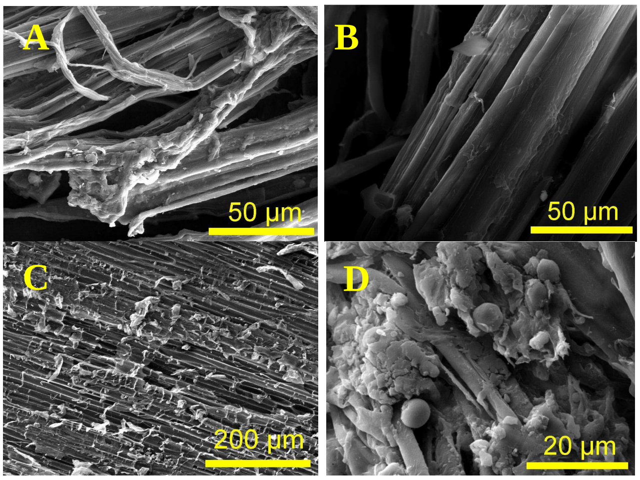
Fig. 2. FTIR spectrograms of hemp and flax lignin corresponding to frequency range of 1700-700 cm-1

As hemp belongs to Angiosperm phylum community hemp, lignins are hardwood type lignins [10], 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.

Different lignins can be primarily discriminated according to the position and intensity of the characteristic peaks in their spectra, so FTIR spectra can be regarded as the first step of their identification.

B. Morphological Characterization

Scanning electron microscopy has been used to study the morphology of hemp fibres, shives and flax shives and to follow the removal of the pectins, hemicelluloses, lignin and ash after steam explosion. SEM is a well adopted technique to visualize the formation of lignin droplets at the surface of the shives (Fig. 3, D), as well as the separation of bundle fibres to individualize elementary fibre (Fig. 3, A).



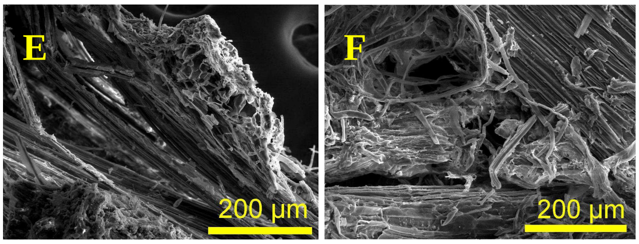


Fig. 3. A – hemp fibres SEA (logR$_0$ 3,97); B – hemp fibres SEA (logR$_0$ 3,97) + water treatment + 4 wt.% NaOH treatment; C – untreated hemp shives; D – hemp shives (*Purini*) SEA (logR$_0$ 4,45); E – untreated flax shives; F – flax shives SEA (logR$_0$ 4,45)

As seen from micrographs in Fig. 3, SEA treated (A) hemp fibres of variety *Purini* are separated in elementary fibres. Some surface and structure defects seen on the micrograph can appear during hemp stalk primary processing or combing. 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. However, after water treatment and 4 wt.% NaOH treatment surface of fibres is clean (B), also insoluble substances are removed by 0,4 wt.% NaOH after-treatment.

After SEA (logR$_0$ 4,45) hemp shives of variety Purini (Fig. 3, D) have also separated, and it is possible to observe domains which can be lignin cluster moulding (by estimating the studies of wood after SEA). On lax shive surface can see observable domains of lignin, what also shows the precipitated lignin in Table 2, which is only 11% compared to hemp shives 22% and FTIR spectral analysis (Fig. 2).

IV. CONCLUSIONS

Morphological and spectroscopic analyses of fibres and shives have been carried out, and it has been found that water and alkali treated by SEA could be usable for further nanotechnologic processing. Results of this study have shown that SEA treatment combined with hydrothermal and alkali treatment allows partial removing of constituents from hemp fibres and shives including hemicelluloses, pectins/waxes and oils covering the external surface of the shive cell wall. FTIR analysis has shown differences between the spectra for the hemp and flax lignins of absorption bands at 916 cm^{-1} (epoxy groups), 816 cm^{-1} (C–H deformation and ring vibration, aromatic CH out of plane bending) and 1091cm-^{1} (C–O stretching).

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Anna Putniņa, Silvija Kukle, Jānis Grāvītis. Tvaika sprādziena autohidrolīze kā lignocelulozes biomasas pirmapstrādes metode
Viena no svarīgākajām nanomateriālu klasēm ir nanošķiedras un fibrillas no dažādiem celulozes avotiem, kas spēj radīt unikālas īpašības savienojumā ar dažādiem polimēriem. Šo nanomateriālu avoti ir kviešu salmi, baktēriju celuloze, cukurbietes, kartupeļi, kā arī Latvijā audzētie vietējie atjaunojamie resursi - kaņepes un lini. Šajā rakstā tiek analizēta tvaika sprādziena autohidrolīzes (TAS) un ūdens un 0,4% sārma pēcapstrādes ietekme uz kaņepju šķirnes „Pūriņi" šķiedrām un spaļiem, „Bialobrzeskie" spaļiem un linu spaļiem. Eksperimentālajā daļā tiek pielietota tvaika sprādziena tehnoloģija, lai sašķeltu šķiedras un spaļus un atdalītu no tiem lignīnu, hemicelulozi, pektīnu, vaskus un sašķeltu tos elementārajās šķiedrās. Eksperimenta rezultātā jāsecina, ka, palielinoties TAS, apstrāde barguma parametram ($logR_0$), kas šeit ir robežās no 3,53 – 4,45, attiecīgi samazinās sausais atlikums pēc sekojošu ūdenī šķīstošu un sārmā šķīstošu komponentu ekstrakcijas. Izvēlētās apstrādes ļauj sadalīt kaņepju šķiedru un spaļu kompleksus. Izmantojot infrasarkano (IS) Furjē spektroskopiju, tika identificētas ekstrakcijas rezultātā radušās nogulsnes t.s. lignīnu. Paraugu mikrogrāfijas pie atšķirīgiem palielinājumiem, ļauj analizēt šķiedru un spaļu virsmas struktūru. Pēc kaņepju šķirnes "Pūriņi" spaļu mikrogrāfijas jāsecina, ka pēc TSA ($logR_0$ 4,45) uz spaļu virsmas redzami sfēriski veidojumi, kas ir lignīns (pēc iepriekšējiem koksnes pētījumiem). FTIR analīzē ir pamanāmas nelielas atšķirības starp kaņepju spaļu un linu spaļu lignīniem pie absorbcijas virsotnēm 916 cm^{-1} (epoksīda grupas), 816 cm^{-1}(C-H saites deformācijas un gredzena vibrācijas, aromātiskās C-H saites leņķiskās vibrācijas) un 1091 cm^{-1} (C-O saites izstiepšanās).

Анна Путниня, Силвия Кукле, Янис Гравитис. Паровой взрыв как метод предварительной обработки лигноцеллюлозной биомассы
Важный класс наноматериалов - нановолокна и волокна из различных источников целлюлозы, которые были показаны в результате уникальных свойств при включении в различные полимеры. Источники этих наноматериалов - пшеничная солома, бактериальная целлюлоза, крафт-целлюлоза, целлюлозно-сахарная свекла, картофель, корень брюквы, а также местные возобновляемые ресурсы, выращенные в Латвии - конопля и лен. В статье анализируется воздействие автогидролиза парового взрыва (ПВ) и последующей обработки водой и 0.4% щелочным раствором на костру и волокно двух пород конопли («Pūriņi» и «Bialobrzeskie») и льна. Технология ПВ позволяет расщепить волокна и костру и отелить лигнин, хемицеллюлозу, пектины и воски. Результаты экспериментов показывают, что, увеличивая параметр строгости ПВ ($logR_0$ (3,53...4,45)), достигается снижение сухого остатка субстрата после обработки водой и щелочным раствором. Выбранные виды обработки позволяют разделить комплекс волокон и костры. Анализ FTIR идентифицировал осадки после экстракций, в том числе лигнин. Образцы экспериментов наблюдались сканирующим электрическим микрографом, с помощью которого были обнаружены сферические образования лигнина на поверхности частиц костры после обработки ПВ при $logR_0$ (4,45). FTIR анализ показал некоторые различия между спектрами для конопли и льна лигнинов полосы поглощения при 916 $см^{-1}$ (эпоксидные группы), 816 $см$-^{1} (C-H деформации и вибрации кольца, ароматические C-H из плоскости изгиба) и 1091cm^{-1} (C-O растяжение).