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Toward the cottonisation of hemp fibers by steam explosion – Part 1: Defibration and morphological characterization

4

5 Abstract

6

7 Fine hemp fibers (cottonized hemp) were processed using steam explosion. The quantification of the defibration rate was performed by image processing. Based on this method, the hemp 8 9 defibration was optimized using a response-surface methodology based on three-variable 10 central composite design for the production of elementary fibers with low variability. Optimal parameters for the steam processes were as follow: time = 4.1 min, temperature = 191°C . 11 Biomass was impregnated with a solution of NaOH (8 %) before treatment, leading to a 12 defibration rate of 91.2 %, which is producing \approx 50% fibers with length < 3 mm in good 13 agreement with the experimental data. Damaged fibers originating from the conjugated effect 14 of steam explosion and alkali hydrolysis were also observed. 15

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17 Key words : Hemp fibers; steam explosion; elementary fibers

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1 Introduction

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Natural fibers have accompanied human societies since prehistoric times. During the last 3 century, the success of the petrochemical industry dramatically slowed the growth of bio-4 based materials. Cheap petroleum-based materials have replaced natural fibers like hemp and 5 6 flax in almost all their traditional utilizations (1). Recently, environmental awareness and the 7 growing global waste problem have spurred much interest in renewable resources. The current development of natural fibers and bio-based materials are motivated by legislation as well as 8 customers' demands for more sustainable and environment-friendly products (2). As a result, 9 10 the environmental impact of a material is now to be considered at all stages of its life cycle, including during production, recycling and final disposal. The major advantages of natural 11 fibers over synthetic ones are their low specific weight, their local availability and their 12 13 biodegradability and/or possible thermal recycling (3). This has motivated researchers to utilize natural plant fibers for material applications such as textile, non woven and as 14 15 reinforcement in composites. New developments in packaging, furniture, building and automotive industries have been described. (4,2,5-7)16

Hemp is one of the bast fibers grown in temperate climates which have provided many 17 18 important products such as fibers for textile, seeds (oil), as well as pulp and paper. Hemp elementary fibers are on average 13 to 15 mm long with a diameter between 15 to 20 µm 19 (5,8). They potentially display very interesting properties for industrial applications such as 20 high tenacity, good tensile strength and excellent moisture resistance (9-11). On the other 21 hand, one of the major characteristic of hemp fibers and of natural fibers in general, limiting 22 large-scale high-quality industrial developments, is their non-uniformity, their wide variation 23 in dimension and in quality such as strength and fineness. In addition to the natural variability 24 of the feedstock, the procedures used for the extraction of the technical fibers from the stem of 25

bast plant (retting process) greatly impact the morphology and the properties of the fibers 1 2 (12-16). Hemp technical fibers are coarser and stiffer than other bast fibers such as flax and they have relatively high lignin content (4 to 8 %) (14). They are composed of elementary 3 fibers, cemented by intercellular components (mainly lignin and pectin). Refined processing, 4 chemical and enzymatic approaches have already been proposed in the literature to produce 5 fine / elementary fibers from technical hemp. Chemical processing (also called degumming) 6 traditionally performed using sodium hydroxide solution is effective for removing non 7 cellulosic components attached to hemp fibers and to release unitary fibers. Nevertheless, the 8 limitations of this chemical approach include the production of relatively short fibers with low 9 tensile strength and environmental issues regarding the liquid effluent disposal. Thus the 10 availability of (elementary) fibers with the required quality for textile and composite 11 industries (cottonised hemp) is still a challenging issue to fulfill the industrial demand (4,17– 12 13 20).

Steam explosion (SE) is currently one of the most valuable pretreatment technologies for 14 15 cellulosic bioethanol production (21-24). After impregnation, biomass is treated with hot 16 steam (around 200°C) under pressure (around 1.5-3 MPa) during a few minutes followed by an explosive decompression. The effect of SE on biomass combines a chemical hydrolysis 17 18 during the stream treatment and defibration during the explosive decompression (25). Steam explosion process has been previously experimented for the extraction of fibers and primarily 19 micro, nano/fibers from biomass. Reported on Kessler et al. (25), the production of linen from 20 flax by SE is made after a soda impregnation. Cellulose nano-fibrils were successfully 21 produced from pineapple leaf, banana stem, jute and hemp by successive steam explosion 22 techniques combined with chemical treatments (26-28). Vignon et al. (29) studied the 23 production of fibers from chenevotte by steam explosion after acid impregnation. It was 24 shown that temperatures around 220° C – 230C were required. At T < 210°C delignification 25

rates were low while at $T > 240^{\circ}$ C, degradation and fiber damage were observed. The 1 production of hemp fibers and microfibers using steam treatments has already been studied 2 (30-32). In these previous studies, the chemical composition of the produced fibers was 3 generally examined (lignin, sugar content, cellulose DP). However, SE has never been 4 successfully employed and optimized for the production of elementary fibers starting from 5 technical hemp and in the perspective of minimizing variability as well as fibers damage. 6 7 Although this technique has been described in several works for the production of fibers, interaction effect of process parameters and complexity of fiber characterization have caused 8 difficulties for the evaluation and optimization of the SE process. Three major parameters 9 were found to have significant effects in a SE process: the temperature and the duration of the 10 steam treatment and the conditions of the impregnation of the fibers prior to the SE. Statistical 11 methods were often employed to investigate the optimum conditions for a biomass treatment. 12 Response Surface Methodology (RSM) was used to design a systematic experimental method 13 and has been extensively described for the optimization of biomass pretreatment in cellulosic 14 15 biomass-to-fermentable sugars conversion (30, 33). To the best of our knowledge, RSM has never been described for the optimization of a defibration process. 16

17

In this paper, the optimization of elementary NaOH-impregnated hemp fibers extraction using SE is described. An original quantification method was developed in order to follow the defibration rate by image processing. Defibration was evaluated and optimized using RSM to design systematical experimental method for the production of superior quality fibers with a low variability.

23

24 Materials and methods

1. Raw material 1

2 In this study, fibers of industrial hemp (Cannabis sativa L.) were investigated. The hemp was cultivated close to Shefford, Quebec, Canada (N45.21, O72.34). It was sown in April 2013 3 and harvested in September 2013. Plants were cultivated according to common farming 4 practices in Quebec. Stems were cut a few centimeters above ground and were subjected to 5 6 winter retting. Fibers were isolated, dried and kept in a dry and well ventilated place. Prior to 7 impregnation and steam explosion treatment, samples were cut into 2-3 cm pieces.

8

9

2. Impregnation

10 Biomass was impregnated with a solution of sodium hydroxide (0; 4; 8 wt %). The fibers were macerated during 15 hours at room temperature using a weight ratio water/biomass of 11 15/1 after what the biomass was filter-pressed (6.8 atm = 100 psi) to remove the excess water. 12 13

14

3. Steam explosion treatment

After pressing, the fibers were transferred into a 4.8 L steam gun where about 100 g (dry 15 basis) of biomass was cooked at temperatures ranging from 190°C to 210°C for 1, 3 or 5 16 minutes by addition of steam in a pressure-resistant reactor. After the cooking period, a 17 18 pneumatic valve is open and the vapor phase exits the reactor through a nozzle entraining as well the fibers. The investigated biomass was treated at the Industrial Research Chair on 19 Cellulosic Ethanol and Biocommodities (CRIEC-B) of the University of Sherbrooke, Canada. 20

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4. Washing, drying and carding

23 A washing step was necessary after the steam treatment to remove the residual NaOH in the fibers. Therefore biomass was washed with 1.5 L of water at 12°C, without stirring during 15 24 minutes and then filter-pressed (6.8 atm = 100 psi). This washing step was repeated three 25

times after what the fibers were dried in an oven at 104°C during 24h. After drying the fibers
were conditioned at 20°C ± 2°C and 65% H.R. ± 4% H.R.

A typical carding machine with a main cylinder and three pairs of worker and stripper rollers
was used, whereby a cylindrical surface of the cylinder is provided with a specifically
clothing for natural fibers.

6

7

5. Statistical approach

A systematic experimental method was designed to optimize the steam explosion treatment of hemp fibers using Central Composite Design (CCD) and Response Surface Methodology (RSM). Sodium hydroxide (NaOH) concentration in the impregnation liquid, reaction temperature and residence time were studied as three independent variables. The experiment matrix is representated in Table 1 and JMP software (version 11.0.0) was used for regression analysis.

14

15 **6.** SEM analysis

Scanning electron microscopy (SEM) analysis was carried out with Hitachi 3000 microscope.
All images were taken at an accelerating voltage of 15 kV. The fibers were put parallel to
obtain a lock and cut. The cross section was observed with the SEM and pictures were taken
Image Pro Premier 9.2 was used for the pictures analysis.

20

21 **7. Defibration rate**

A wick of fibers was made for each sample and cut to obtain a cross sections of a lot of fibers.
Four pictures of each wick were taken with a X250 magnification SEM. The perimeter of
each fiber was manually drawn with Image-Pro Plus software version 6.0.0.260. From these
data, the area of each section of unit fiber was measured. Then, the area of each section of

1 fibers bundle was measured. A formula was determined to calculate a rate of defibration (D
2 %):

$$D(\%) = \frac{\Sigma(areas of unit fibers)}{\Sigma(areas of all the fibers)} * 100$$

3

4

8. Diameter of hemp fibers

A wick of fibers was made for each sample and cut to obtain a cross sections of a lot of fibers.
Four pictures of each wick were taken with a X250 magnification SEM. The perimeter of
each fiber was drawn with Image-Pro Plus software version 6.0.0.260. From these data, the
mean diameter was measured. Between 600 and 1500 fibers were measured for each sample
and the mean diameter was measured for each fiber.

10

11 9. Length of hemp fibers

Fibers were spread on a glass plate using oil allowing their optimal separation. Six pictures of each sample were taken with an optical microscope and they were analyzed with the software Image Pro Premier 9.2. The lengths of the fibers were measured (between 150 and 300 fibers) for each sample.

16 **Results and discussion**

17

Technical hemp fibers were processed using SE after 15 h impregnation at room temperature in a sodium hydroxide solution for which concentrations varied from 0-8%. Prior to impregnation, hemp fibers had to be cut into 2-3 cm pieces in order to facilitate their transfer from the reactor into the blow down chamber during the explosive decompression. Table 1 shows the results obtained from 17 SE experiments performed at temperature varying from 190°C to 210°C, for 1 min to 5 min. Log R° which describes the SE treatment severity as a

function of the treatment time and temperature (30, 33) are also given in the Table 1. It was 1 previously shown that the thermal degradation of cellulose was limited for a SE with $LogR^{\circ} <$ 2 4.0 (34). As a result, the experimental conditions for the SE procedures covered a large range 3 of severity but below 4.0 (Log $R^{\circ} = 2.6 - 3.9$) in order to limit the cellulosic fibers 4 degradation. The morphological characteristics of the untreated and treated fibers were 5 examined. The evaluation of the results for each experiment was based on the SEM analysis 6 of the cross section aiming of the changes in the structure of the fibers bundles after carding. 7 Examples of SEM pictures cross sections for untreated and treated hemp samples (samples 1 8 and 3) are given in Fig. 1. The defibration rate (in %) for each sample was established by 9 image processing based on the sections of undamaged elementary fiber and on the sections of 10 bundles (see experimental section). The defibration rates for untreated (control) and treated 11 fibers (sample 1 to 17) are given in Table 1. 12

13

14 Table 1. SE conditions and defibration rates D (%) for untreated and treated fibers.

	Steam explosion conditions					
sample	T(°C)	t(min)	LogR°	NaOH (%) ^a	D (%) ^b	
control	-	-		-	2.1	
1	190	1	2.6	0	34.3	
2	190	3	3.1	4	75.3	
3	210	5	3.9	8	82.7	
4	200	5	3.6	4	77.7	
5	210	3	3.7	4	63.7	
6	210	1	3.2	0	49.7	
7	200	3	3.4	4	85.1	

8	190	5	3.3	0	33.3
9	210	5	3.9	0	37.1
10	200	3	3.4	8	91.6
11	200	1	2.9	4	46.8
12	200	3	3.4	0	34.1
13	200	3	3.4	4	79.4
14	210	1	3.2	8	75.6
15	190	1	2.6	8	71.1
16	190	5	3.3	8	83.5
17	200	3	3.4	4	76.5

1

^aNaOH concentration in water of the solution used for the fibers impregnation at room temperature
 during 15h. ^b Defibration rate

4

5 From Fig. 1A it appears that the untreated hemp sample is composed of bundles having an 6 average diameter of 100 μ m to 500 μ m and containing 5 to 30 single fibers. The percentage of 7 isolated single fibers in the sample is very low (2.1%). This observation is in accordance with 8 previously described works (34). In contrast, after treatment, it can be seen from Fig. 1B and 9 C that the fibers are well separated. In Fig1B (sample 1), the sample is composed of thinner 10 bundles with significantly more individual fibers (D = 34.3%) while in Fig 1C, the sample is 11 mostly composed of single fibers (D = 82.7%).



Fig. 1. SEM photos of cross sections of untreated and SE treated hemp samples : A. Hemp fibers without
treatment, sample 0. B. Hemp fibers after SE, sample 1; C. Hemp fibers after SE, sample 3.

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18

The response-surface plots concerning the defibration rates as a function of the three variables 5 studied (t, T, NaOH %) are provided in Fig. 2. Figure 2A and 2B depict the interaction 6 7 between temperature and catalyst, as well as time and catalyst respectively. These figures demonstrate the important impact of sodium hydroxide concentration on the defibration rates 8 9 even at low cooking time and temperature. This effect was already observed by Sutka et al. (31,32) and is justified by the mild alkali hydrolysis, which degraded the middle lamella thus 10 separating the elementary fibers. The alkali presoaking allowed the production of thinner 11 fibers, with a smooth surface and removed a large part of the non-cellulosic components (32). 12 13



Fig. 2. Response surface plot on defibration rate. A – Effect of temperature and NaOH concentration at residence
time of 3 min. B – Effect of residence time and NaOH concentration at reaction temperature of 200°C. C –
Effect of temperature and residence time at NaOH concentration of 4%.

Fig. 2C shows the interaction between time and temperature. Results show that the defibration rate was low for short residence time and increased with temperature. D% increased with cooking time, although it reached a maximum and decreased again for longer cooking periods. This can be explained by a degradation of individual cellulose fibers due to a combination of the SE severity (33) with the phenomenon of peeling commonly observed in alkaline conditions (34). An example of the damaged fiber observed in sample 3 is given in the Fig.3.

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- 10

11 Fig. 3. Example of a damaged fiber. (x 500) (T = 210° C. t = 5 min, NaOH % = 8 %)

12

13 The cooking parameters were optimized using the CCD based on the model obtained and the input criteria. The optimization of the defibration rate was carried out based on the three 14 variables which were in the range of experimental runs. JMP software predicted that 15 optimized conditions for defibration rate could be obtained when the residence time, reaction 16 temperature and NaOH concentration were at 4.1 min, 191°C and 8 %, respectively, giving a 17 18 defibration rate of 91.2 %. These optimized conditions are very close to those of sample 10 (200°C, 3 min, NaOH 8%) which gave an actual defibration rate of 91.6%, in good agreement 19 with the value calculated using the model. 20

The average diameters of all the fiber bundles were determined from the cross section 1 obtained from their SEM pictures (Fig. 1). The average diameter of the raw fibers (41.1 µm) 2 is slightly higher than the value reported by Ilczyszyn F et al. (11) (30 µm). Fig 4.A shows 3 that the raw hemp displayed a broad range of diameters with very thick fiber bundles (> 150 4 µm). After SE, significantly finer fibers were collected with average diameters ranging from 5 15.5 μ m to 25.5 μ m. It appears that thicker fibers (> 19 μ m) were obtained for the treatments 6 without sodium hydroxide (samples 1, 6, 8, 9 and 12). This observation confirms the major 7 role of this reagent in removing the non-cellulosic material attached to fibers (essentially 8 lignin and pectic components) thus releasing individual fibers. Fig.4B, C, D shows the 9 10 diameter distributions for steam-exploded samples 1, 5, 10 respectively. A narrower range of diameters was observed with average diameters usually below 50 µm. Sample 10 (Fig 4.D) 11 corresponds to the highest defibration yields (D = 91.6 %), the diameter range obtained was in 12 13 accordance with the values described for hemp individual fibers (17-23 μ m).



15 Fig. 4. Diameters distribution of hemp fibers. A – Untreated fibers ; B – 190°C, 1min, NaOH 0% ; C – 210°C,

16 3min, NaOH 4%; D – 200°C, 3min, NaOH 8%.

Longitudinal SEM views of hemp fibers before and after SE treatment are shown in Fig. 5. For untreated samples, fiber bundles showing some splitting due to the mechanical separation during carding can be seen clearly (Fig. 5, A1 & A2). As previously observed, the effect of SE are clear in Fig 5, B & C. Using less severe conditions (sample 1, Fig. 5, B1 & B2), less thick fibers bundles composed of 2 to 5 elementary fibers were observed. For sample 3, the uniformity of the fibers was clearly improved. Nevertheless, fibers damages due to the harsh conditions used (NaOH impregnation and explosive decompression) and/or the subsequent mechanical carding were also observed.



x50 2 mm

x300 300 um

HL



Fig. 5. SEM images of untreated and treated hemp samples (longitudinal view). A. Hemp fibers without
treatment, sample 0, A1 x50, A2 x300. B. Hemp fibers after SE, sample 1, B1 x50, B2 X300. C. Hemp fibers
after SE, sample 3, C1 x50, C2 X300.

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The fibers length distributions for samples 1, 10, 13 and for the raw fibers are reported in Fig. 7 8 6. The raw hemp fiber gauge length was found in a 1 to 30 mm range which is in accordance with previous works. After SE, shorter fibers were recovered (< 20 mm). Results show that a 9 significant decrease of the fibers length with a high content in short fibers (< 3 mm) was 10 observed for the more severe conditions (Fig. 6). Samples 13 and 10 were produced using the 11 same conditions but with 2 different concentrations of NaOH during the impregnation step 12 (4% and 8 % respectively). The larger proportion ($\approx 50\%$) of short fibers (< 3 mm) obtained 13 with higher soda concentration can be justified by (1) the reduction in the number of 14 elementary fibers in the bundles as previously proposed and in accordance with the 15 defibration rate values (79.4 % and 91.6% respectively), (2) elementary fibers damage 16 because of the conjugated effect of steam explosion and alkali hydrolysis, (3) the technical 17 options in the present study : as previously explained the hemp fibers had to be cut into small 18 pieces prior to the treatment because of the geometry of the steam explosion facility. As a 19

result, future developments for textile applications would necessitate a technological
 adaptation of the reactor for the production of longue fibers.

3



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Fig. 6. Frequency distribution of lengths for untreated and treated hemp samples: Control: Hemp without
treatment; n°1: Hemp fibers after SE sample 1. n°13: Hemp fibers after SE with T = 200°C, t = 3 min and
[NaOH] = 4%; n°10: Hemp fibers after SE with T = 200°C, t = 3min and [NaOH] = 8%.

9

10 Conclusions

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12 In this paper we described the optimization of hemp fine fiber extraction using SE processes. A method by image processing was developed to quantify the defibration rate and to 13 characterize the fibers. Based on this method, a systematical experimental approach was 14 developed for the first time for the production of superior quality short fibers (< 3 mm length) 15 with low variability, composed of \approx 92% of elementary fibers. However, damaged fibers due 16 to the conjugated effect of steam explosion and alkali hydrolysis were also observed. A full 17 chemical and morphological characterization of exploded fibers will be presented in a 18 19 following publication. Utilizations of these fibers in the fields composite should be considered because of the physical characteristics of the fibers. 20

21

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