Toward the cottonisation of hemp fibers by steam explosion

Flame-retardant fibers

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Abstract

The goal of this work is to produce cottonized hemp fibers with improved thermal stability for textile and/or composite applications. It was first found that the fine hemp fibers produced from technical non-retted hemp fibers by steam explosion exhibited an enhanced thermal stability. An efficient and inexpensive process was developed using a mixture of urea/etidronic acid (HEDP) in aqueous solution in order to achieve a high phosphorus content and produce flame retardant fibers by chemical grafting. ICP, ^{31}P and ^{13}C NMR, SEM, thermogravimetric, Pyrolysis-Combustion Flow Calorimetry analyses and a flame test using a lighter were used to characterize the grafted fibers. Fibers modified with relatively high P and N contents have been produced (≈ 6 wt% and ≈ 4 wt% respectively) but lower grafting rates (P ≈ 0.5 % and N ≈ 0.35%) are sufficient to produce non-flammable fibers. A synergistic effect between N and P has been proposed to induce the formation of a stable char.

Keywords: Hemp fibers, HEDP/urea, steam explosion, thermal grafting

Introduction

In recent years, there has been a renewed interest in natural fibers such as hemp, flax and ramie because of their inherent qualities including biodegradability, local availability, low density and ease of recycling. Such advantages of natural fibers over synthetic fibers have motivated the researchers to develop new material applications like composites and textiles with a lower environmental impact. New academic and industrial developments have been described in the fields of furniture, automotive industry, building (Bismarck et al., 2005, Pickering et al., 2016). Hemp is a bast fiber plant grown in temperate climate which provides low cost technical fibers and many industrial products (Shahza, 2012). Hemp technical fibers are in fact composed of unitary fine fibers (10-15 mm long and 15-20 µm diameter) cemented by lignin and non-cellulosic polysaccharides (Garcia-Jaldon et al., 1998). New promising applications for hemp fibers include fiber-reinforced composites, insulating products, textile and non-woven soft materials.

However, some important disadvantages are associated with natural fibers, limiting their broad utilization. Bast fibers and especially hemp fibers are coarse and stiff and display wide variations in dimension and in quality. In addition, the procedures involved for fibers extraction (retting and mechanical processes) impact the properties of the resulting fibers. The non-cellulosic content (lignin, hemicelluloses, pectins) is particularly important for hemp (Thomsen et al., 2006). These hydrophilic components negatively affect the spinability (for textile applications), the adhesion of the fiber to a hydrophobic matrix and the moisture absorption resulting in poor strength properties of resulting composite for materials applications. Another important drawback with natural fibers is their low thermal stability and high flammability which negatively impact the development of natural fibers-based materials especially for building and transport applications.

The thermal decomposition of lignocellulosic natural fibers has been the subject of many publications and it is well known that lignin decomposes at higher temperature compared to polysaccharides and generates higher char yield (Yan et al, 2007). However, studies have shown that the pyrolysis of cellulosic fibers does not correspond to the superposition of the three main components (lignin, cellulose and hemicellulose) (Dorez et al, 2014, Pasangulapati et al., 2012). In fact, the pyrolysis of natural fibers is a complex process and

interactions between these components have been already highlighted such as catalytic effects of char and ash generated from decompositions of sugars (Pasangulapati et al., 2012). Dorez et al. (2014) have observed that for low lignin and high cellulose content fibers a particular interaction may occur between the biopolymers which would impact the degradation pathways leading to an increase of the char yield higher than expected.

The chemical modification of natural fibers can be done in order to decrease their flammability (Costes et al., 2017). It has been reported that the flame retardancy of lignocellulosic fibers can be improved by modification with phosphorous components. Phosphorylation of cellulose in presence of urea in aqueous media has been described for decades. Phosphorylating agents such as phosphoric acid, diammonium hydrogen phosphate, phosphonic acid have been successfully grafted on cellulosic fibers (Blanchard and Graves, 2003, Coleman et al., 2011). In these reactions, urea acts as a swelling agent for cellulose and a catalyst for phosphorylation. More recently, the grafting of vinyl phosphonic acid on cotton or flax fabrics using chemical or physical processes has been studied (Sonnier et al. 2015, Teixeira et al., 2018, Hajj et al, 2018, Hajj et al. 2019). The modified fibers have been evaluated in terms of thermal stability and flame retardancy. It has been clearly shown that the presence of a critical phosphorous content in the fibers leads to a decrease in thermal stability but promotes the formation of char and the production of a self-extinguishing material.

In a recent paper, we described the production of fine hemp fibers using a steam explosion (SE) process (Sauvageon et al., 2018). The optimization of the process parameters was done using a systematical approach and an image processing allowing the production of superior quality cottonized hemp fibers with low variability. In the present work, their thermal stability has been first examined. We also reported the chemical modification of the cottonized hemp fibers by a phosphorous agent in order to improve their flame retardancy. The phosphorylation step was performed using a simple and industrially acceptable method, by impregnation of the fibers in an aqueous solution of phosphonic acid and urea followed by a cooking step.

1. Experimental part

a. Materials

The fibers of industrial hemp (Cannabis sativa L.) investigated in this study were cultivated close to Bar-sur-Aube (France). Stems were cut a few centimeters above ground and harvested without retting in autumn 2016. Fibers were isolated, dried and kept in a dry and well ventilated place. 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP), urea, sodium hydroxide, sodium chlorite, glacial acetic acid purchased from Sigma-Aldrich were used as received.

b. Steam explosion (SE) treatment

The fibers were impregnated with a solution of sodium hydroxide (8 wt %) during 15 hours at room temperature using a weight ratio water/biomass of 15/1 and then filter-pressed (6.8 atm = 100 psi) to remove the excess water. The 100 g of impregnated hemp fibers were loaded into the reactor and exposed to 190°C for 4 min. The sample was then exploded by sudden-dropped in pressure and released in the discharge tank. The framework of the steam explosion facility has been described in a previous publication (Simangunsong et al., 2018). The exploded hemp fibers (EF) were separated from the liquid fraction by vacuum filtration and dried at 40°C for 24 hours.

c. Bleaching process

The bleached fibers were obtained using the acid-chlorite delignification treatment. Raw and exploded fibers were placed in a double jacketed glass reactor with deionized water (83.3 mL/g fibers), glacial acetic acid (1.998 mL/g fibers) and sodium chlorite (1.998 mg/ g fibers). The mixture was heated at 70 °C for 6 h where a whitish solid residue consisting essentially of holocelluloses was obtained. After cooling, the bleached fibers were recovered through vacuum filtration. Hence, the raw and bleached exploded fibers (named respectively BRF and BEF) were recovered after excessive washing with deionized water / vacuum filtration until neutralization of the filtrate pH and fibers drying overnight in a fume hood.

d. Phosphorylation

Fibers (10 g) were impregnated during (1 h) with a solution mixture composed of 100 ml of distilled water, 30 g of urea and 13 g of HEDP which corresponds to a mass percentage of 30% of urea and 13% of HEDP. The impregnated fibers were subjected to a drying step in an

oven under vacuum at 60 °C overnight. The grafting is achieved by applying a cooking step at 150 °C for 2 h for the different fibers and as a function of time (0h, 0.5h, 1h, 1.5h, 2h, 3h, 4h) only for the bleached exploded fibers. At the end of the treatment, the phosphorylated fibers were washed 5 times with distilled water and then vacuum filtrated before being dried under a fume hood for 48h.

The phosphorylated fibers are labelled as X Y, with X corresponding to the nature of treatment (i.e. RF, EF, BRF or BEF) and Y the time of cooking after impregnation (0-4 h).

e. Characterizations

Elemental analysis. Inductively coupled plasma atoms emission spectroscopy (ICP-MS) was used for the determination of the phosphorus elemental content in the samples. 0.15 g of the phosphorylated fibers were mixed with 5 mL of a nitric acid solution in glass tube. The tubes were placed in a mineralizing unit (Ultrawave system) and left to react for 30 min along a ramp of 20 min to reach 230 °C and 110 bars. The samples were then left for 10 min at this temperature and pressure until total mineralization. After mineralization, the samples were diluted with 50 ml of demineralized water and filtered before being analyzed.

A Thermo Finnigan Flash EA 112 Series was used for the elemental analysis of nitrogen, carbon, oxygen and hydrogen. The combustion of the samples (1.5 mg) to be analyzed takes place at high temperature (1000 °C) in the presence of tungstic anhydride, under an oxidative atmosphere for 15 s. This decomposition gives CO_2, H_2O, SO_2, NOx which is reduced in N_2 in presence of copper. These gaseous products are subsequently analyzed by gas chromatography. The results are recorded and analyzed by "Eager 300" software which directly calculates the percentage of each element present in the compound.

Analytical procedure. Carbohydrate and Klason lignin contents were measured on extractive free fibers according to the laboratory analytical procedure (LAP) provided by the National Renewable Energy Laboratory (NREL). Samples were hydrolyzed with 72% sulfuric acid for 1 h and then autoclaved after being diluted to 3% sulfuric acid through the addition of water. The autoclaved samples were filtered, and the dried residue was weighed to give the Klason lignin content. Monosaccharide contents in the filtrate were quantified using high-

performance anion-exchange chromatography with pulsed amperometric detection (HPAEC PAD).

Solid state NMR analysis. Previously milled hemp fibers were compressed in a 4-mm diameter zirconium oxide rotor equipped with a specific Kel-F caps for solid phase material analysis. Cross-polarization and magic angle rotation (CP / MAS) of the ^{13}C and ^{31}P NMR experiments were performed on a Bruker Avance-300 spectrometer operating at a frequency of 100.59 MHz. All spectra are acquired at room temperature using a 4 mm Bruker -MAS probe. The spectra were obtained after x scans and were processed offline using NUTS NMR processing software. The spectra were phased and the setting of the baseline was done manually.

Scanning electron microscopy (SEM). Images of polished sections of fibers were acquired with an environmental scanning electron microscope (FEI Quanta 200). Samples were metallized in high vacuum sputtering metallizer Bal-Tec CED 030 Balzers to stabilize them during the analysis. The micrographs were then obtained under high vacuum at a voltage of 15 kV and a working distance of 10 mm. SEM is equipped with an energy dispersive X-ray spectroscopy (Oxford INCA Energy system) which was used to determine the phosphorus location in the hemp fibers.

Thermogravimetric analysis (TGA). A thermogravimetric apparatus (Setaram Setsys) was used to analyze the thermal degradation of hemp fibers. Samples (10 mg ± 1mg) were heated under nitrogen atmosphere (100 ml/min) in alumina ceramic crucibles from 30 to 900 °C at a heating rate of 10 °C/min. Residual weight at 750 °C, temperature at 5% of mass loss (T5%) and maximum degradation temperature Tmax (i.e. temperature of the mass loss rate peak) were determined.

Pyrolysis combustion flow calorimetry (PCFC). A pyrolysis combustion flow calorimeter (Fire Testing Technology) was used to investigate the fire behavior of samples at microscale (2-4 mg). Samples were pyrolyzed at 1 ˚C/s under nitrogen flow from 90 to 750 ˚C (anaerobic

pyrolysis – method A according to the standard ASTM D7309). Pyrolysis gases were carried to a combustor in the presence of N_2/O_2 (80/20) flow. In such conditions, all gases are fully oxidized. Heat Rate Release (HRR) is calculated according to Huggett's relation [35]. According to this relation, 1 kg of consumed oxygen corresponds to 13.1 MJ of heat release. Each test was performed twice to ensure the reproducibility of our measurements. The peak of heat rate release (pHRR), the temperature at pHRR (TpHRR), the total heat release (THR), and the heat of combustion (Δh) were determined.

Preliminary fire test on fibers. An unstandardized fire test was carried out to assess the flammability of some Hemp fiber. Long hemp fibers were glued to a rectangular aluminum box (around 2 cm length and 0.3-0.5 cm diameter) and maintained vertically. A lighter was used to ignite the top of fabrics. This method allows the fibers self-extinguishment to be evaluated, i.e. absence of flame spreading. The residue is also weighted after complete burning. The initial weight of each fiber is subtracted to the residue weight to calculate the mass loss percentage. For self-extinguishing fibers, complete burning is reached by multiple flame applications. This test is reproducible and allows assessing the self-extinguishment and the charring of the fabrics. This information is sufficient to guide our research and development efforts.

2. Results

The steam explosion of raw hemp technical fibers (RF) was performed according to a previously described method after a basic impregnation (NaOH, 8% w/w). The optimal parameters of our previous study (190°C, 4 min) were used to produced exploded fibers (EF) composed of ~ 90% of elementary fibers (Sauvageon et al., 2018). Bleaching treatments were performed starting from raw and exploded fibers (producing respectively BRF and BEF). The chemical composition of hemps fibers determined at each stage of treatment is given in Table 1.

The composition of the raw hemp fibers used in this study (RF) is in accordance with previous works with a high cellulose content (Glc = 79.6%) and a relatively high amount of pectins (GalU = 2.8% and Rha = 0.9% data not shown). After SE treatment, an almost total disappearance of pectins and hemicellulosic components is observed, rationalized by an extensive hydrolysis of non-cellulosic polysaccharides during the steaming process. This observation is justified by the alkali hydrolysis of the middle lamella during the SE involving

the separation of elementary hemp fibers. As expected, after the bleaching step cellulose rich fibers were recovered.

The thermal decomposition of the RF, EF, BRF and BEF at microscale was carried out by thermogravimetric analysis and PCFC (Table 1 and Figure 1A). For RF, the thermal behavior is in accordance with that of previously described lignocellulosic fibers. A multi stage process is obtained including an initial weight loss between 50°C and 120°C due to the removal of moisture, and between 200°C and 400°C due to the degradation of non-cellulosic components, the decomposition of cellulose and the broad thermal degradation of lignin.
The bleaching does not modify significantly the thermal decomposition of hemp fibers, except a small reduction in char content (about 3 wt%), despite the strong enhancement of cellulose amount, the disappearance of pectins and the reduction of lignin content. On the contrary steam explosion leads to drastic changes in fibers decomposition. Thermal stability of steam exploded fibers is enhanced (Tmax and TpHRR increase by 25-30 °C) while pHRR is strongly increased (Figure 2). A significant decrease in char content (about 7-10 wt% in TGA and PCFC) is also observed leading to an increase of THR (and also heat of combustion).

The phosphorylation of BEF was carried out using HEDP in presence of urea according to a previously described method (Blanchard and Graves, 2003). The fiber is first impregnated in an aqueous solution of HEDP/urea, dried at 60°C and then oven-cooked at 150°C. The impact of the duration of the cooking step on the phosphorylation was examined for exploded and bleached fibers (from 0 to 4 hours, BEF0-4). As can be seen in Table 2, an increasing amount of phosphorus and nitrogen is incorporated on the fibers when increasing the cooking time. N and P contents continuously increased up to 2 h of cooking (BEF2) and then reached a plateau with a N/P ratio close to 0.6 (see Supplementary Material, SM1). Phosphorus and nitrogen contents were also measured for unbleached and/or raw fibers after 2h of cooking (RF2, EF2, BRF2). It can be observed that the contents are not significantly different from those measured for exploded and bleached fibers. It is then concluded that the steam explosion and bleaching treatments did not improve or prevent the grafting.

Polished sections of EF2, BRF2 and BEF2 were also observed using SEM and phosphorus mapping was carried out (Figure 3). In all cases, phosphorus is observed in the whole fibers

section, evidencing that the flame retardant was able to diffuse to the bulk, even for raw and unbleached fibers, confirming that the steam explosion and the bleaching step did not impact this diffusion. The bulk grafting observed by SEM is in accordance with the relatively high P contents (up to 6%) given in Table 2.

BEF2 has been analyzed by solid ^{31}P and ^{13}C NMR. The spectra are given in Supplementary Material section (SM2 and SM3). Spectrum ^{13}C showed the characteristic signals of a cellulosic fiber. The signals between 58-68 ppm, 80-91 ppm, at 101 ppm and 109 ppm attested the presence of C6, C4 and C1 carbon respectively (Focher et al., 2001). The absence of signal in the aromatic region and at 56 ppm was in accordance with a low concentration of residual lignin. Small signals in the ^{13}C spectrum have been observed and can be assigned to etidronic acid moieties (20 ppm and 65 ppm) and to urea (160 ppm), in accordance with the P and N contents (5.33% and 3.12% respectively, see Table 2). The ^{31}P NMR spectrum (SM3) showed the presence of two signals at 0.4 ppm and at 10.0 ppm indicating the grafting of one of the two phosphonic groups on the fiber.

Thermal decomposition of the phosphorylated fibers at microscale has been analyzed using PCFC and TGA (Table 2, Figures 1B, 4A and 4B). Figure 1A shows that the thermal decomposition of RF2, EF2, RBF2 and BEV2 is similar, the influence of steam explosion process previously observed on non-phosphorylated fibers (Figure 1A) being no longer detectable.

Figure 4 shows the thermal decomposition of exploded and bleached fibers with various phosphorus contents. It can be observed a first small weight loss around 100 °C due to water release. This step is significantly important for phosphorylated fibers probably because the presence of phosphorus moiety increased the hydrophilicity of the fibers. The main decomposition step occurs after 200 °C. The temperature of this step is considerably reduced in presence of phosphorus. Higher is the phosphorus content, lower is the decomposition temperature. Moreover, the intensity of this step is also reduced in presence of phosphorus. After 300°C, the weight loss continued at a low rate up to 900 °C. The residue content at 750°C is also directly dependent on the phosphorus content. It is well known that phosphorus-based flame retardants decompose in phosphoric acid which can phosphorylate

cellulose leading to the formation of phosphorus ester. These esters accelerate the dehydration of cellulose and promote charring (Chapple and Anandjiwala 2010).

Figure 4B gives the HRR curves of the same exploded and bleached fibers in PCFC. The intensity of the main pHRR decreases strongly when phosphorus content increases from 200 W/g to 20 W/g with 6.19 wt % of phosphorus. The temperature of pHRR also decreases from 365 to 226 °C. The area under the peak (i.e. the THR) decreases from 10.3 to less than 1 kJ/g. Heat of complete combustion Δh can be calculated from THR and residue fraction f according to equation 1:

$$\Delta h = \frac{THR}{1 - f}$$

Heat of combustion decreases when phosphorus content increases, evidencing that phosphorylation not only improves the charring but also modifies the composition of gases release. Indeed, the char being carbon-rich, an increase in char content leads to gases containing less carbon atoms, i.e. with a lower heat of combustion.

A preliminary non-standardized fire test was carried out on phosphorylated hemp fibers. Results are summarized in Table 2. It can be found that fibers with a low phosphorus content (<0.5 wt%) ignited and burnt completely. When phosphorus content reached ≈0.5 wt%, the fibers ignited but become self-extinguishing. For higher P content, the fibers did not ignite, whichever the preliminary treatment used (i.e. steam explosion or bleaching).

3- Discussion

As described in a previous publication (Sauvageon et al., 2018) steam explosion appeared to be an efficient process for the cottonization of hemp. It can be seen from Figure 3 that the fibers are well separated, this process allowing the individualization of unitary fibers from technical hemp fibers.

Unexpectedly, in this work we demonstrated that in contrast to bleaching (removal of lignin) which did not significantly modify the thermal decomposition of the fibers, the cottonization process greatly increased the thermal stability of the resulting material (+25-30 °C). Such a significant change is not fully understood but cannot be explained by the changes in the overall composition as listed in Table 1. We assume that the steam explosion caused

structural changes impacting the ability to its components to interact. These results seem to be consistent with those of Dorez et al. (2014) performed on flax, hemp and cotton linter fibers. These authors have shown that low lignin and high cellulose contents could lead to the promotion of char formation during pyrolysis by affecting the degradation pathway of cellulose. Similarly, it has been recently reported that nanofibrilated cellulose exhibited an increased flame retardant effect probably because a higher char forming action of the cellulose nanofibers (Costes et al., 2016, Fox et al., 2013). Nevertheless, in the present study, at microscale, the higher thermal stability is accompanied by a decline in residue content and an increase of pHRR.

The phosphorylation of hemp fibers using urea/etidronic acid resulted in a reduction of thermal stability, pHRR, THR and Δh and in an increase of char content. These observations are in accordance with other natural fibers modified with phosphorus flame retardants (Coleman et al., 2011, Pandya and Bhagwat, 1981). Figure 5 shows the comparison between phosphorylated flax (Sonnier et al. 2015, Hajj et al. 2018, Hajj et al.2019) and hemp (this study) fibers using various phosphorylating agents and treatments. Both fibers have similar composition, especially low lignin content. It can be found that THR decreased similarly for both fibers when phosphorus content increased regardless of the nature of the phosphorylating agent, the flame retardancy appearing to be only dependent on phosphorus content. This fact was already highlighted in previous work about flax (Sonnier et al. 2015, Hajj et al. 2018, Hajj et al. 2019). Nevertheless, in the present study, nitrogen FR was also incorporated into hemp fibers (Table 2). Nitrogen is believed to act as synergist for phosphorus FR, especially because nitrogen-containing gases can promote expansion of the residues and dilute fuels as blowing gases. However, such effects cannot be highlighted in PCFC, the insulating effect of the char layer being not effective at the microscale.

The fire test showed that self-extinguishing is reached at lower phosphorus content (0.5 wt%) compared to a previous study, performed from phosphorylated flax fibers (0.8-1 wt%) (Hajj et al, 2018). Although the comparison is only qualitative, it could be proposed that the present modification combining a phosphorus FR (i.e. a char promoter) and urea (i.e. a source of blowing gases) is very effective in improving the flame-retardant effect.

Figure 6 shows the variation of the residue rate from the lighter test (oxidative atmosphere when flame vanishes) as a function of the residue level obtained by PCFC at 750 °C. For low phosphorus contents (< ≈ 0.5 wt%), the residue levels in an inert atmosphere (PCFC) were higher compared to the fire test. This observation is in accordance with our previous works and is rationalized by a degradation of the char formed in presence of oxidative atmosphere. Starting from flax fabric grafted with a relatively high P content (2.31%), Hajj et al. (2018) found significantly lower residue values by the fire test compared to TGA at 750 °C. However, in our study for P > ≈ 0.5 wt% the results clearly showed that the amount of residue obtained by the lighter is close to that obtained by PCFC. This difference in behavior could be related to the presence of the nitrogen element as previously mentioned. The presence of nitrogen in combination with phosphorus has been described to induce through a synergistic effect a more stable char even in an oxidative atmosphere. The formation of active intermediates possessing P=N groups has been previously reported (Pandya and Bhagwat, 1981). These highly reactive P=N containing group intermediates would be expected to react with cellulose at high temperature promoting dehydration and char-formation reactions. It seems that there is a threshold (phosphorus level of 0.52% and nitrogen 0.35%) from which this behavior is observed.

3. Conclusion

In this study, we described an efficient method for the production of flame retarded fine hemp fibers. A steam explosion process was used for the hemp fibers refining. Unexpectedly, steam exploded cottonized fibers exhibited an enhanced thermal stability but also lower residue content and higher pHRR at microscale compared to raw fibers. Etidronic acid and urea were used for fibers chemical modification based on a simple and inexpensive grafting method without solvent. The fibers were successfully functionalized in bulk with relatively high P and N contents. A significant improvement in the thermal and fire properties was observed by the lighter test, PCFC and TGA. Fire properties at microscale are continuously improved with the increase in phosphorus and nitrogen contents. A synergistic effect of nitrogen in combination with phosphorus has been proposed to explain the self-extinguishing behavior at relatively low phosphorus content and the relatively high stability of the char formed even in oxidative atmosphere.

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Figures

Figure 1. Thermogravimetric curves for various hemp fibers

Figure 2 – HRR curves for RF, EF, BRF and BEF in PCFC

Figure 3 – Phosphorus mapping of unbleached exploded hemp fibers (EF2), bleached raw hemp fibers (BRF2) and bleached exploded hemp fibers (BEF2)

Figure 4. – Thermogravimetric curves (A) and HRR curves at PCFC (B) for bleached exploded hemp fibers with various levels of phosphorylation

Figure 5 – THR versus phosphorus content for modified flax and hemp fibers (data for flax can be found in Sonnier et al. 2015, Hajj et al. 2018, Hajj et al. 2019)

Figure 6 Char yield obtained from fire test versus residue content at 750 °C obtained from PCFC (labels correspond to phosphorus content of flax fabrics).

Figure 1.

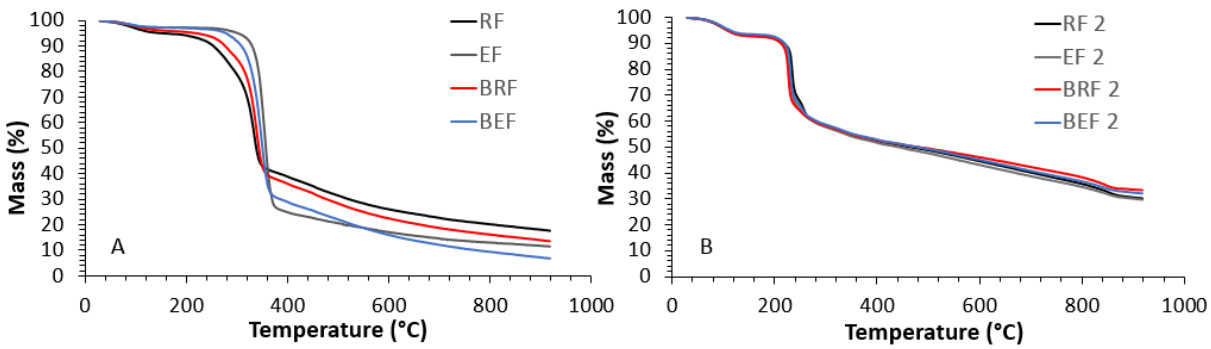


Figure 2

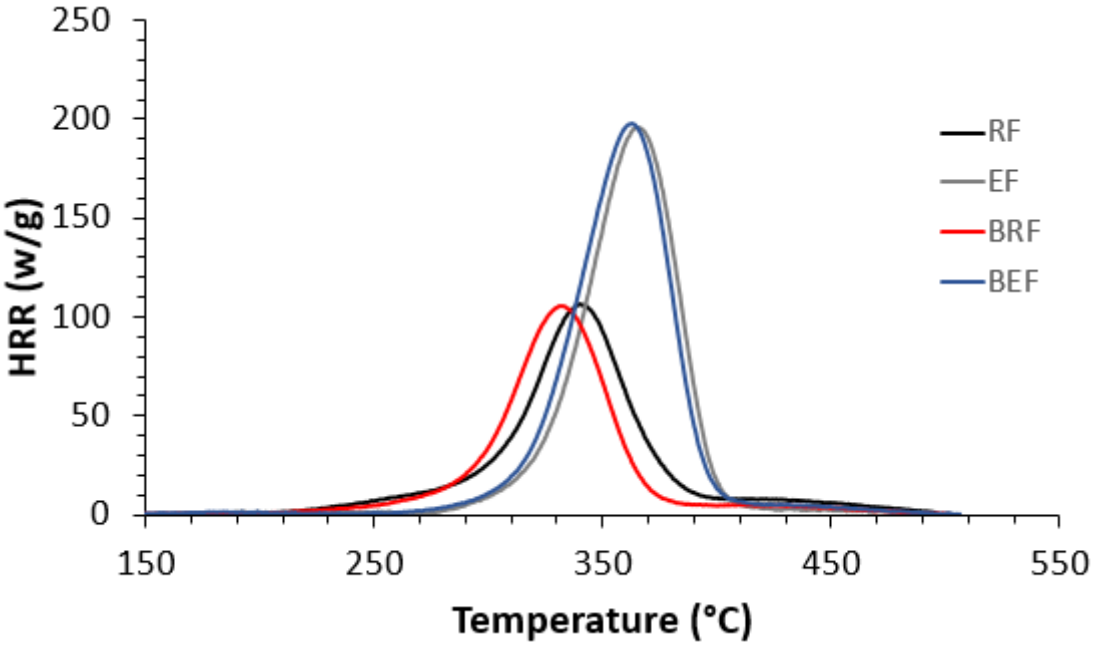

250
200
150
100
50
0
HRR (w/g)
150
250
350
450
550
Temperature (°C)
RF
EF
BRF
BEF

Figure 3

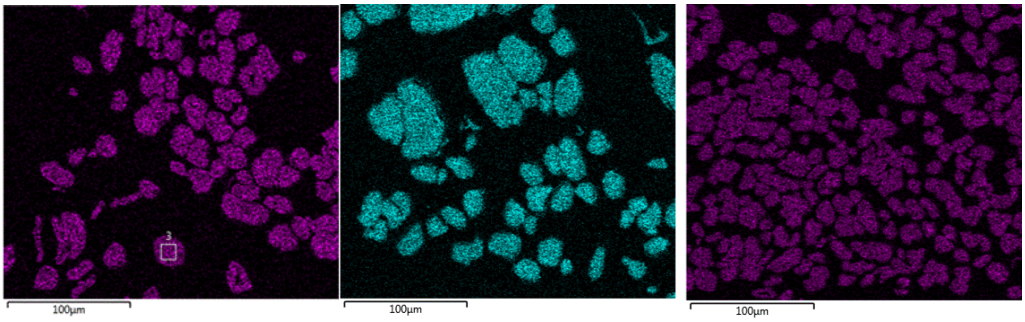


Figure 4

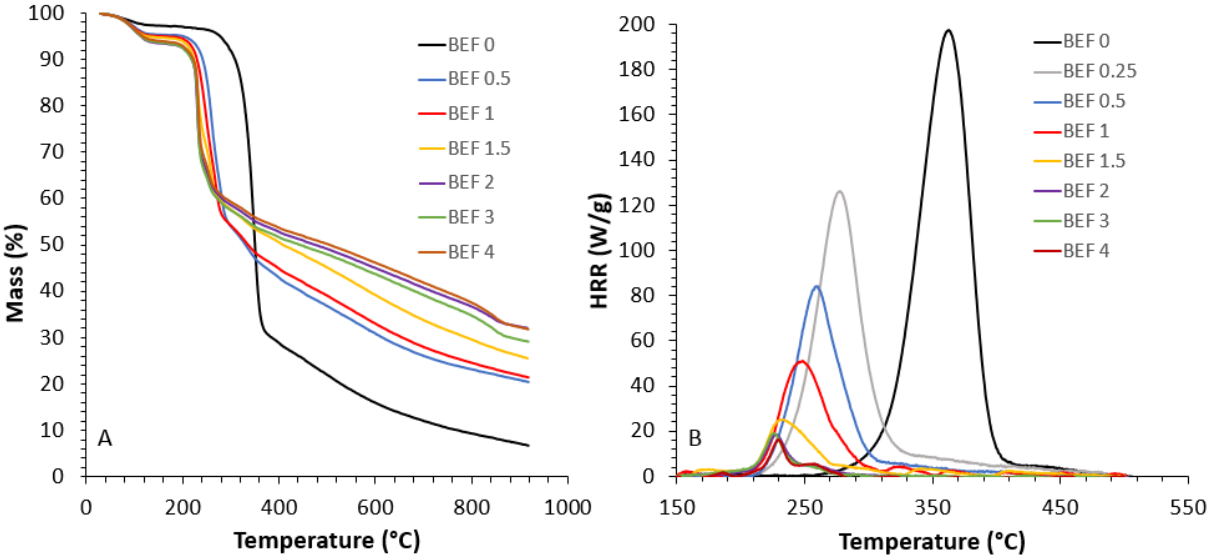

Mass (%)
Temperature (°C)
A
BEF 0
BEF 0.5
BEF 1
BEF 1.5
BEF 2
BEF 3
BEF 4
HRR (W/g)
Temperature (°C)
B
BEF 0
BEF 0.25
BEF 0.5
BEF 1
BEF 1.5
BEF 2
BEF 3
BEF 4

Figure 5

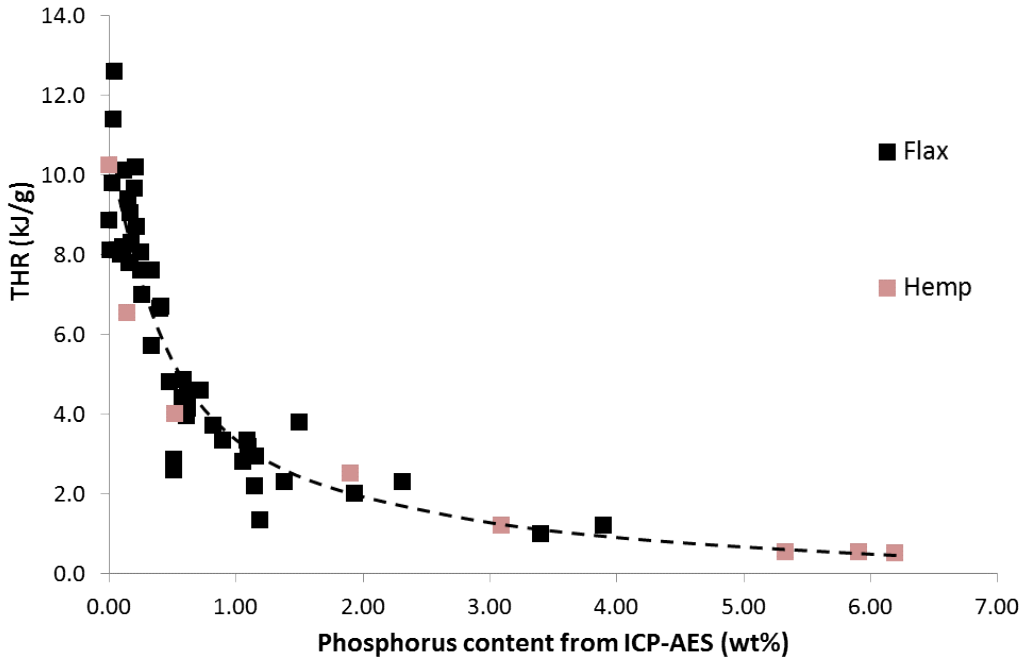

14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
THR (kJ/g)
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
Phosphorus content from ICP-AES (wt%)
Flax
Hemp

Figure 6

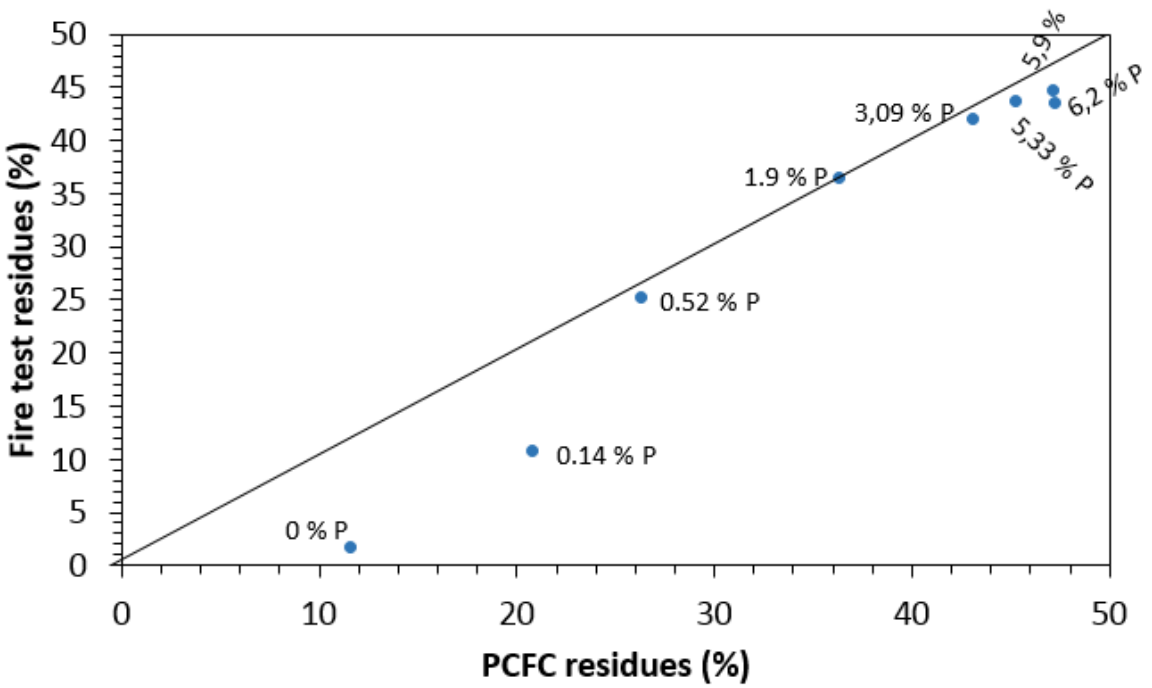

Fire test residues (%)
PCFC residues (%)
0
5
10
15
20
25
30
35
40
45
50
0
10
20
30
40
50
5,9 %
6,2 % P
3,09 % P
5,33 % P
1.9 % P
0.52 % P
0.14 % P
0 % P

Table 1. Composition of non-treated and treated hemp fibers and main data from thermogravimetric analysis and PCFC.

Fibers	Chemical analysis						TGA					PCFC				
	lignin	Glc	Xyl	Man	GalU	Other sugars	T5% (°C)	Tmax (°C)	Residue at 750 °C (%)	Residue at 800 °C (%)	Residue at 900 °C (%)	pHRR (W/g)	TpHRR (°C)	THR (kJ/g)	Δh (kJ/g)	Residue at 750 °C (%)
RF[a]	6.5	79.6	1.3	5.0	2.8	4.6	151	332	21.2	20.1	18	103	337	6.8	8.7	21.9
EF[b]	6.8	91.6	0.5	0.7	0.1	0.3	300	358	13.6	13	12	179	362	9.8	11.1	11.5
BRF[c]	3.0	95.1	0.7	0.9	0.0	0.2	219	336	17.3	16.1	14	110	332	6.4	8.1	20.5
BEF[d]	4.6	93.2	0.6	0.7	0.0	0.2	278	350	10.5	9.3	7.1	198	365	10.3	11.7	11.7

[a]Raw fibers ; [b]Exploded fibers ; [c]Bleached raw fibers ; [d]Bleached exploded fibers

[a]Raw fibers ; [b]Exploded fibers ; [c]Bleached raw fibers ; [d]Bleached exploded fibers

Table 2. Main data for phosphorylated hemp fibers: thermogravimetric analysis, PCFC and fire test.

Phosph. Fibers	P content (wt%)	N content (wt%)	N/P	TGA			PCFC					Fire test		
				T5% (°C)	Tmax (°C)	Residue at 750 °C (%)	pHRR (W/g)	TpHRR (°C)	THR (kJ/g)	Δh (kJ/g)	Residue at 750 °C	Ignition	Propagation	Self-extinguishment
BEF 0	0	<0,05	-	278	350	10.5	198	365	10.3	11.7	12	Yes	Yes	No
BEF 0.5	0.52	0.4	0.67	201	260	24.4	84	262	4	5.4	26	Yes	Yes	Yes
BEF 1	1.9	0.8	0.72	158	249	26.1	52	250	2.5	3.9	36	No	/	/
BEF 1.5	3.09	1.7	0.55	127	232	31.6	25	235	1.2	2.1	43	No	/	/
BEF 2	5.33	3.1	0.58	114	230	39	17	230	0.6	1.0	45	No	/	/
BEF 3	5.91	3.7	0.62	115	232	40	19	226	0.6	1.0	47	No	/	/
BEF 4	6.19	3.8	0.61	117	233	40	14	227	0.5	0.9	47	No	/	/
RF 2	5.38	3.3	0.67	107	230	40	24	234	1.1	2.0	46	No	/	/
EF 2	5.98	3.7	0.61	108	234	37	15	226	0.7	1.3	45	No	/	/
BRF 2	5.38	3.3	0.54	108	227	40	19	226	0.8	1.5	45	No	/	/