

# 1 Vapothermal curing of hemp shives: influence on some chemical and physical properties

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8

## 9 Abstract

10 In a perspective of a sustainable development, a new generation of construction materials based on  
11 renewable plant resources has emerged to face environmental issues. However, the formulation of  
12 structural vegetal concretes (based on plant aggregates, a mineral binder and water) requires to  
13 enhance the compatibility of plant aggregates and binder.

14 This paper presents an experimental study that evaluates the influence of vapothermal treatment, a  
15 promising method of cure under saturated water vapour pressure, on chemical composition and  
16 physical properties (loss of mass, absorption, and specific gravity) of hemp shives, entering in the  
17 composition of vegetal concrete. Indeed, developing bio-based concrete by vapothermal curing  
18 requires identifying the appropriate curing conditions both from the point of view of the hemp  
19 aggregates and the binder. In particular, these curing conditions must respect a compromise between  
20 the preservation of the physical and chemical properties of hemp shives and an efficient curing of the  
21 binder.

22 Several levels of curing temperatures were defined between 150 and 230°C (carbonization) and results  
23 of Treated Hemp Shives (THS) were compared with those of Raw Hemp Shives (RHS). The  
24 experimental results showed physical modifications explained by chemical transformations that affects  
25 the hemicellulose, cellulose and lignin composition of TSH and modifies the structure of hemp shives.  
26 The effect of vapothermal curing on hemp shives was determined through X-Ray Diffraction XRD  
27 and thermogravimetry TG. The loss of mass of THS increases as the curing temperature increases and  
28 specific gravity decreases. As for water absorption, which relates to the hydrophilic character of the  
29 treated hemp shives, it decreases slightly. This experimental study made it possible to assess the  
30 interest of a vapothermal curing in a prospect of using hemp shives in binder interaction in order to  
31 perform structural vegetal concrete.

32

33 Keywords: *Vapothermal treatment; Hemp shives; Chemical transformations; Binder interaction*

34

## 35 1. Introduction

36 The building sector is known to be responsible for one of the world's main sources of CO<sub>2</sub> emissions,  
37 through the production of building materials and the energy consumption of buildings in the operating

38 phase: heating, ventilation and air conditioning (United Nations Environment Programme, 2009). In  
39 France, this sector represents 44% of the energy consumed, i.e. more than 120 million tons of CO<sub>2</sub>  
40 each year (Commissariat Général au Développement Durable, 2020). Particularly, the cement industry  
41 is responsible of large volumes of CO<sub>2</sub> emitted during the manufacture of Portland cement clinker  
42 (Gartner, 2004). Today, most research efforts are focused on the production of building materials that  
43 help reduce environmental impact and can promote sustainable development and circular economy.

44

45 Among the materials developed that can meet these challenges, vegetal concretes are promising. They  
46 are composed by the association of vegetal aggregates with a mineral binder. Binders based on cement  
47 or lime are mainly used (Amziane and Arnaud, 2013). The positive environmental impact of these  
48 materials in terms of their contribution to the fight against global warming is due to the biogenic  
49 carbon stored by plant aggregates. It corresponds to the atmospheric CO<sub>2</sub> absorbed during the  
50 photosynthesis of plants and trapped inside the material during its entire life cycle, thus reducing its  
51 carbon footprint (Amziane, 2016). Vegetal concretes are rather oriented towards non-structural  
52 applications as insulation, coatings, noise barriers, etc. Research works are multiplied to try to develop  
53 structural vegetal concrete. However, in this case, cement remains the binder that guarantees good  
54 mechanical performance.

55

56 Nevertheless, the deployment of vegetal concretes in construction applications is limited by various  
57 problems encountered after introducing plant aggregates in the binder. The hydrophilic nature of plant  
58 aggregates can lead to a decrease in the amount of water available for hydration of the binder (Jami et  
59 al., 2019; Nozahic, 2012). Water absorption by these lignocellulosic aggregates leads to water  
60 additions to the mix to preserve the workability of the concrete, resulting in low mechanical strengths.  
61 These quantities of water can solubilize some extractible molecules from plant aggregates, such as  
62 polysaccharides (sugars), pectins, tannins, or waxes. Some of these molecules are capable of reacting  
63 with the binder, modifying the hardening of the materials (Amziane and Arnaud, 2013). The fraction  
64 of water not consumed by binder hydration must then be removed. It follows that one of the major  
65 problems reported for lignocellulosic concretes is drying, especially as the material is more heavily  
66 loaded with lignocellulosic materials. In addition, experience shows dimensional instability of vegetal  
67 concretes (Hillis, 1984). This phenomenon is to be correlated with the important water recovery of the  
68 vegetable aggregates and thus of the vegetal concretes. So, a lot of researches were carried out to  
69 improve the compatibility between the plant aggregates and the binder (Aderinsola Sadiku and Sanusi,  
70 2014; Khazma et al., 2014, 2012, 2011; Miranda de Lima et al., 2015; Pasca et al., 2010).

71

72 Among the different approaches used generally for energy recovery from biomass, can be found the  
73 hydrothermal treatment (Funke et al., 2013; Huang and Yuan, 2016; Rulkens, 2008; Shafie et al.,  
74 2018). It is a process in which, biomass is heated and converted into useful resources in water or other

75 suitable solvents at certain temperatures and pressures (Krylova and Zaitchenko, 2018; Toor et al.,  
76 2011; Vogel, 2019). Many studies have investigated hydrothermal treatment and its influence on  
77 biomass (Krylova and Zaitchenko, 2018; Olszewski et al., 2020; Peterson et al., 2008; Sevilla and  
78 Fuertes, 2009; Sharma et al., 2020; Titirici et al., 2015; Volpe et al., 2020). When the treatment occurs  
79 in saturated vapor instead of being submerged in water, it is called vapo-thermal treatment. This curing  
80 on biomass has been patented in 2009 (German Patent Nr. DE 10 2009 010 233 A1, 2009), **but there is**  
81 **a lack of published studies on vapo-thermal treatment (Funke et al., 2013; Shafie et al., 2018; Yeoh et**  
82 **al., 2018).** Researchers have reported that the treatment in or outside water can have an effect on the  
83 carbon composition of treated vegetals (Funke et al., 2013). As the vapo-thermal treatment can be  
84 considered as a hydrothermal treatment where the water is in its gaseous form, there is often confusion  
85 between the two terms. In 1913, it was suggested by Bergius that hydrothermal reactions were  
86 responsible for the formation of fossil fuels, particularly coal. At low temperatures between 180 and  
87 250°C, this treatment is known as carbonization. The main product is a hydrochar which has a similar  
88 property to that of a low-rank coal. At intermediate temperature ranges between 250 and 375°C, the  
89 process is known as liquefaction, resulting in the production of a liquid fuel (biocrude) that can be  
90 upgraded to petroleum-derived products. At higher temperatures above 375°C, the process is known as  
91 gasification, resulting in the production of a syngas (Biller and Ross, 2016; Huang and Yuan, 2016). It  
92 is interesting to note that most of the papers focus on rather severe reaction conditions, mainly above  
93 250°C (Guillot, 2019).

94

95 At the same time, vapo-thermal treatments have been used in construction materials domain and have  
96 led to a significant influence on the mechanical properties of the Ultra High Performance Concrete  
97 (Galvánková et al., 2016). Through autoclaving, the degree of hydration of these **sand-lime**  
98 **(autoclaved aerated concrete (AAC) and dense bricks)** have been considerably increased. The main  
99 reasons for the improved mechanical properties are the formation of a homogeneous cement paste  
100 matrix, consisting of closely connected Calcium Silicate Hydrates C-S-H crystalline fibers, which  
101 develop a more stable structure than amorphous C-S-H phases formed in Ordinary Portland Cement  
102 OPC (Fontana et al., 2009). Vapo-thermal treatment has also shown positive effects on the hardening  
103 of cellular concrete (Fakhratov et al., 2017; Stumm, 2010). These results can serve as a starting point  
104 for further studies on the effect of vapo-thermal curing on the hardening of other types of concrete.  
105 Hence the idea of combining the production of vegetal concrete with vapo-thermal treatment is **totally**  
106 **innovative, and it** can potentially have a significant influence on the improvement of mechanical  
107 performances in a perspective of development of green and structural building materials.

108

109 The objective of this study is then to carry out a vapo-thermal treatment on hemp shives in order to  
110 understand the influence of this curing on the modification of the hemp structure, from the point of  
111 view of their physical, chemical, mineralogical and thermal behaviour. This study is part of an

112 approach of production of a structural vegetal concrete based on hemp shives and lime (lower carbon  
 113 footprint than cement). The vapo-thermal treatment is a “green” solution (cure at temperatures below  
 114 230°C) that will be used for the hardening of the binder. This experimental investigation is the first  
 115 step that provides important informations on the degree of transformation of the hemp under  
 116 vapo-thermal curing. Beyond the modified physical properties of the hemp shives following the  
 117 different curing conditions, this project is mainly focused on the evolution of the chemical composition  
 118 of the plant particles before and after treatment.

119

## 120 2. Materials and Methods

121 The Raw Hemp Shives (RHS) “Technichanvre” consist of the inner part of the plant dried, defibered  
 122 and sifted. These aggregates coming from hemp culture are processed and packaged in France. They  
 123 are subject to the "Label Granulat Chanvre", which defines specifications on hemp, and which  
 124 ultimately allows the insurability of hemp concrete constructions. The dimensions of the particles are  
 125 of the order of 2 to 25 mm. Their color goes from light green to off-white (Fig. 1). Table. 1 presents  
 126 the main physical properties of the RHS used.

127



128

129 **Fig. 1** Raw hemp shives

130

131 **Table. 1** Main physical properties of RHS

Physical properties	132
Bulk density (kg/m <sup>3</sup> )	110 133
Water retention capacity (ml/l) EN-13041	370 134
pH in suspension at 10%	6.7 – 7.2 135
Thermal conductivity (W/mK)	0.048 136
Specific gravity (Helium pycnometer)	1.5 137
	138

139

140 In our study, hemp shives were dried at 40°C. Four hemp samples of 10g each were placed into tea  
 141 balls in a specific autoclave (Fig. 2). The samples underwent a vapo-thermal cure in a closed autoclave  
 142 system, under water vapour pressure (5-38 bar) varying according to the temperature based on the  
 143 Clausius-Clapeyron equation. Several temperatures were investigated: 150°C, 170°C, 190°C, 210°C

144 and 230°C. The complete cycle **included** 2 hours of temperature rise and four different plateau times  
145 (2, 4, 6 and 8 hours). After the vapothermal treatment, the samples **were** dried at 40 °C for 7 days  
146 before undergoing the different analyses.

147



148

149 **Fig. 2** Hems shives in the tea ball, tea ball on the gridded support, tea balls in the autoclave, the  
150 autoclave system (From left to right)

151

152 Several parameters **were** monitored before and after vapothermal curing, on dried hemp samples. First  
153 of all, visual aspect of hemp samples **was** observed. The color of the shives is an important clue to  
154 understand and explain the changes observed on the treated hemp.

155 **Depending on the type of analysis performed, the dried aggregates were finely grinded by a "Retsch**  
156 **RS 200" machine.**

157 **Neutral monosaccharide composition (method used by INRA Versailles) was determined on of dried**  
158 **alcohol-insoluble material (grinded samples) after hydrolysis in 2.5 M trifluoroacetic acid for 1.5h at**  
159 **100°C. To determine the cellulose content, the residual part obtained after the monosaccharide analysis**  
160 **was rinsed with water and then hydrolyzed with sulfuric acid H<sub>2</sub>SO<sub>4</sub>. The released monosaccharides**  
161 **were diluted and samples were analysed by HPAEC on an ICS-5000 instrument (Thermo Fisher**  
162 **Scientific) with a CarboPac PA20 analytical anion exchange column (3 mm × 150 mm; Thermo Fisher**  
163 **Scientific), PA20 guard column (3 mm × 30 mm), borate trap, and a pulsed amperometric detector.**  
164 **The samples were eluted using an isocratic gradient of 8 mM NaOH from 0 to 6 min, followed by a**  
165 **linear gradient of 8 mM NaOH to 1 mM NaOH from 6 to 23 min. At 23.1 min, the gradient was**  
166 **increased to 500 mM NaOH to elute the acidic sugars. Hemicellulose and cellulose contents are**  
167 **calculated as weight percentages of the samples.**

168 **For lignin quantification, Klason method based on the insolubility of lignin in a concentrated acid**  
169 **medium that hydrolyzes and dissolves the other parietal constituents (cellulose and hemicelluloses) is**  
170 **used (Hochegger et al., 2019). 72% of H<sub>2</sub>SO<sub>4</sub> is added gradually to samples of alcohol-insoluble**  
171 **material in small increments while stirring. The mixture stayed for 2 h in a water bath maintained at 20**  
172 **± 1°C while being stirred frequently. Water is added in order to dilute the solution (3% of H<sub>2</sub>SO<sub>4</sub>). The**  
173 **latter is boiled for 4 h maintaining constant volume. The insoluble residue (lignin) is allowed to settle**  
174 **until the supernatant solution is clear. The lignin is then transferred quantitatively to the filter using**  
175 **hot water. The lignin is washed free of acid with hot water and dried to constant weight in an oven at**

176 105 ± 3°C. The lignin content is calculated from the oven-dry weight of the residue and reported as  
177 weight percentage of the sample.

178 The percentage of other proteins and minerals was calculated by subtracting the sum of the  
179 percentages of the constituents (hemicellulose, cellulose and lignin) from the total percentage 100%.

180 The thermogravimetric analysis was applied by the thermal analyzer NETZSCH STA 449 F3 Jupiter.  
181 The temperature program used ranged from 105 °C to 1000 °C with a ramp of 10 °C/ min.

182 XRD analyses were performed by a BRUKER D8 advance diffractometer, with an angular range of  
183  $2\theta=10^\circ-50^\circ$  and a Cobalt anode X-ray tube source (Co-K $\alpha$ :  $\lambda = 1,74\text{\AA}$ ).

184 Loss of mass was determined by mass weighing of the samples (non-grinded) before and after the  
185 treatment. Each weighing at a given temperature and time was carried out on four hemp samples of  
186 10g each. Water absorption was carried out after drying the aggregates and then calculating their  
187 absorption coefficient at 48 hours according to the technical recommendations of RILEM TC 236-  
188 BBM (Amziane et al., 2017). Specific gravity (grinded samples) was measured using the Helium  
189 pycnometer "micromeritics AccuPyc 1330".

190









### 191 3. Results and discussion

#### 192 3.1. Visual aspect of hems shives after vapo-thermal treatment

193 The visual aspect of the hemp shives after vapo-thermal treatments are presented in **Table. 2**. The  
194 treated hemp started to go to a light brown color at the lowest vapo-thermal temperature (150°C), and  
195 ended up with a dark brown color at the temperature of 230°C. At the intermediate temperatures, the  
196 treated hemp passes through different shades of brown: slightly dark, dark and very dark. However, no  
197 visual difference was noted when curing times are increased from 2 to 8 hours for a fixed temperature.  
198 It is also noted that at temperatures above 190°C, the hemp becomes crumbly and loses progressively  
199 its integrity.

200

201 **Table. 2** Visual aspect of THS at different temperatures as a function of time

T (°C)	Time (h)			
	2	4	6	8
150				
170				



202

203 The change in color of THS as a function of temperature can therefore be explained by a series of  
 204 chemical transformations that the material has undergone between 180 and 250°C, the range  
 205 commonly used for the heat treatment of biomass (Esteves and Pereira, 2008). The increase in  
 206 temperature and pressure in the autoclave has an effect on the structure of the hemp and modifies its  
 207 chemical composition by degrading the cell wall compounds and extractives (Esteves and Pereira,  
 208 2008; Sauvageon, 2017). The chemical modifications due to high temperatures depend on the duration  
 209 and temperature of the cure, temperature being the main factor.

210 More specifically, the darkening of hemp shives after curing is often explained as the result of the  
 211 formation of oxidation and degradation products or low molecular weight sugars that can absorb  
 212 visible light. Darkening can also be the result of lignin condensation reactions and the formation of by-  
 213 products that contribute to the increase in the intensity of the red tone (Výbohová et al., 2018).

214 The crumbly state observed above 190°C is explained by the fact that the hemp passes gradually by a  
 215 progressive carbonization that alters the hemp shives structure.

216

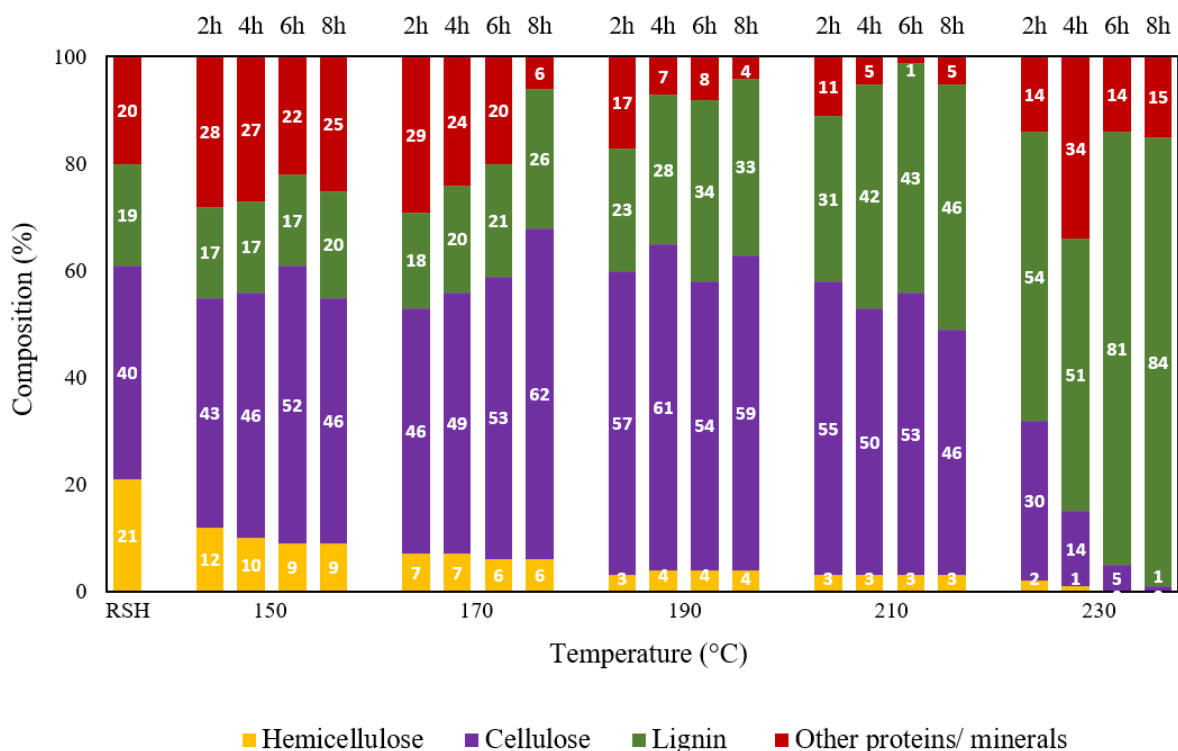
### 217 **3.2. Chemical, thermal and mineralogical modifications of hems shives by vapo** 218 **thermal** 219 **treatment**

#### 219 3.2.1. Chemical composition

220 **Fig. 3** shows the chemical composition of RHS and vapo

221 shows 21% of hemicellulose, 40% of cellulose, 19% of lignin and 20% of other protein/minerals. The  
 222 hemp is mainly composed of cellulose. For the rest of the constituents: hemicellulose, lignin and other  
 223 minerals, they are at almost equal amounts. **These results are in agreement with the composition of**  
 224 **hemp shives presented in the literature. The percentages of cellulose vary between 12 to 37% for**  
 225 **hemicellulose, 34 to 60% for cellulose, 15 to 30% for lignin and 4 to 20% for remainder compounds**

226 (other proteins/minerals) (Belinda, 2005; Delannoy, 2019; Evrard and Erde, 2015; Jami et al., 2019;  
 227 Vignon and Dupeyre, 1995).  
 228



229  
 230 **Fig. 3** Chemical composition (%) of RHS and THS at different temperatures as a function of time  
 231

232 The results show that the vapothermal treatment caused a decrease in the hemicellulose percentage  
 233 from 21 % for RHS, to 12% for THS at 150°C for 2 hours. This percentage continued to decrease by  
 234 increasing the temperature of the vapothermal treatment until it reaches a value of 0.4% for an 8 hours  
 235 cure at 230°C. This can be explained by the fact that hemicelluloses are the first structural compounds  
 236 to be thermally affected because of their amorphous nature, even at low temperatures (Kocaeffe et al.,  
 237 2008; Rousset et al., 2009; Tumuluru et al., 2011; Yildiz et al., 2006). Degradation begins with  
 238 deacetylation of hemicellulose and depolymerization by random cleavage of the glyosidic bonds. The  
 239 released acetic acid acts as a catalyst that promotes the decomposition of polysaccharides (Esteves and  
 240 Pereira, 2008). Acid-catalyzed degradation leads to the formation of formaldehyde, furfural and other  
 241 aldehydes. Furfural and hydroxymethylfurfural are degradation products of pentoses and hexoses,  
 242 respectively. At the same time, hemicelluloses undergo dehydration reactions with decreasing  
 243 hydroxyl groups (Esteves and Pereira, 2008). The results are compared with observations after  
 244 hydrothermal curing because the lack of information for vapothermal treatment.

245  
 246 For cellulose, vapothermal curing caused an increase in the content from 40% for RHS to 43% for a 2  
 247 hours treatment at 150°C. This percentage continued to increase to reach values around 50% for cures  
 248 up to 210°C. At 230°C, the amount of cellulose dropped to an average of 1% for an 8 hours treatment.



249 Due to the crystalline nature of cellulose, this latter is difficult to degrade (Maniscalco et al., 2020) and  
250 starts its decomposition above 210°C. In other studies (Olszewski et al., 2020; Volpe et al., 2020), a  
251 complete decomposition of the cellulose was reported at 260°C (Maniscalco et al., 2020). Cellulose  
252 can be broken down into water-soluble, lower molecular weight compounds (oligomers) and then into  
253 glucose (monomers), which is partially isomerized to fructose. The products of decomposition then  
254 undergo a series of isomerization, dehydration and fragmentation (ring opening and C-C bond  
255 cleavage), producing intermediates products, 5-HMF or furfural, and their derivatives. These  
256 intermediates undergo further polymerization and condensation reactions that lead to the formation of  
257 hydrochar (Wang et al., 2018).

258  
259 The Klason lignin content decreased from 19% to 17% after a vapothermal cure at 150°C for 2 hours.  
260 After this slight decrease, this percentage increased to 84% (230°C for 8 hours). This behavior was  
261 observed in some studies where they also found that the lignin content decreases slightly at  
262 temperature of 160°C, while it increases at higher temperatures (Výbohová et al., 2018). According to  
263 the literature, significant lignin reactions are observed at temperatures above 205°C. These are  
264 depolymerization and condensation reactions (Sivonen et al., 2002). Lignin is depolymerized mainly  
265 by cleavage of the ether bonds. The cleavage of these bonds is accompanied by an increase in phenolic  
266 hydroxyl groups and carbonyl groups (Nuopponen et al., 2004), which are responsible for cross-  
267 linking via the formation of methylene bridges (Tjeerdsma et al., 1998; Tjeerdsma and Militz, 2005)  
268 and a decrease in aliphatic hydroxyl groups (Tjeerdsma and Militz, 2005). The methoxyl content  
269 decreases and new reactive sites on the aromatic ring can lead to further condensation reactions  
270 (Wikberg and Maunu, 2004). **At low vapothermal temperatures (150-170°C), decreasing percentages**  
271 **are explained by depolymerization and degradation reactions. However, with increasing process**  
272 **severity, the rate of carbohydrate degradation (hemicellulose, cellulose) had probably surpassed that of**  
273 **decomposition of lignin, resulting in high mass loss values and explains the increased content of**  
274 **Klason lignin as seen in other works (Assor et al., 2009; El Hage, 2010; Hochegger et al., 2019;**  
275 **Windeisen et al., 2007). The possibility that the lignin content is overestimated by the Klason method**  
276 **if such treatment induces some recondensation reactions between polysaccharides (or between**  
277 **polysaccharide degradation products) and lignins cannot be excluded (Rousset et al., 2009).**

278  
279 As for the rest of the proteins (calculated as the remainder percentage after subtracting the sum of the  
280 percentages of cellulose, hemicellulose and lignin), an increase of the percentage from 20% for RSH  
281 to 28% for a cure of 2 hours at 150°C. Then, a progressive decrease is observed with the increase of  
282 the cure temperature to almost 5% at 210°C (8 hours) explained by the polysaccharides degradation.  
283 After this, an increase to 15% is noted at 230°C (8 hours). Most extractives degrade during heat  
284 treatment, especially the most volatile ones (Esteves and Pereira, 2008; Maniscalco et al., 2020;  
285 Sharma et al., 2020; Yeoh et al., 2018). However, new compounds resulting from the degradation of

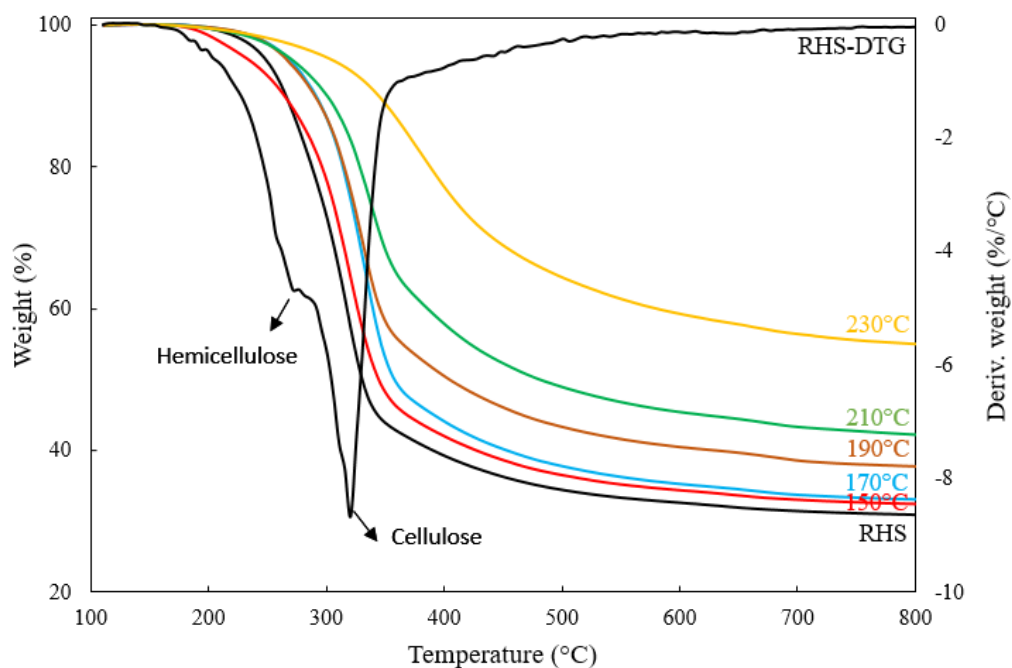
286 structural components of the cell wall can also be formed in the form of extracted waxes,  
 287 carbohydrates, tannins and resins (Esteves and Pereira, 2008). The evolution of the proteins/minerals  
 288 depends on the balance between the phenomenon of degradation of polysaccharides and the  
 289 phenomenon of condensation of certain products such as lignin. The respective rates of these 2  
 290 phenomena play a role on the protein and mineral content. **The eventual overestimation of lignin**  
 291 **explained in the previous section, may cause an underestimation of the remaining proteins/minerals.**

292  
 293 The temperature of 150°C seems to change slightly the chemical structure of hemp shives without  
 294 denaturing them. The three main constituents (hemicellulose, cellulose and lignin) are preserved at  
 295 percentages similar to those found for RHS.

296  
 297 3.2.2. Thermal decomposition

298 **Fig. 4** shows the thermogravimetry TG and differential thermogravimetry DTG curves of RHS and  
 299 TG curves for THS at different temperatures for 6 hours.

300



301  
 302 **Fig. 4** DTG (%/°C) curve of RHS and TG (%) curves of RHS and THS at different temperatures for 6  
 303 hours

304  
 305 In the DTG curves, for RHS, the first decomposition shoulder peak at about 180-300°C corresponds  
 306 probably to thermal depolymerisation of hemicelluloses or pectin (mass loss 27.5%) and the maximum  
 307 mass loss rate is observed at 270°C. In the literature, the first component that is affected by the  
 308 vapothermal curing is hemicellulose (Esteves et al., 2008; Esteves and Pereira, 2008) due to its  
 309 hydrophilic, amorphous and crosslinked (H-bonds) nature (Farhat, 2018). The decomposition of

310 hemicelluloses vary in the range 180-320°C (Libra et al., 2011; Ouajai and Shanks, 2005; Padilla et  
311 al., 2019; Výbohová et al., 2018; Yang et al., 2007). The major second decomposition peak is at about  
312 300-360°C (mass loss 29.8%). The maximum mass loss rate was observed at 330°C. In the literature,  
313 cellulose decomposition ranges from 315 to 400°C (Ouajai and Shanks, 2005; Padilla et al., 2019;  
314 Sevilla and Fuertes, 2009; Yang et al., 2007). Among the three major components, lignin was the most  
315 difficult to decompose. It decomposes slowly, over a wide range of temperature from 100 to 900°C  
316 (Yang et al., 2007). Some other studies specify that lignin decomposes gradually in a temperature  
317 interval of 250-500°C (Fred Shafizadeh, 1985; Khelfa, 2009). Lignin remains degrading even when  
318 cellulose and hemicellulose have been completely degraded (Padilla et al., 2019). The complexity of  
319 the lignins and the diversity of their structure come from the association of the three monolignols by  
320 different chemical bonds without orderly or repetitive character to form an amorphous and  
321 hydrophobic polymer (Xun, 2015).

322 Other components, especially extractives, which include monosaccharides (glucose and fructose) and  
323 various aldehydic alcohols, aliphatic acids, oligomeric sugars, and phenolic glycosides, are highly  
324 reactive in hydrothermal media (Krylova and Zaitchenko, 2018).

325 It should be noted also that the mass loss curve for hems shives treated at 150°C closely resembles to  
326 that of the RHS showing that the shives keep their basic chemical structure despite the vapothermal  
327 treatment at 150°C.

328  
329 Thermal degradation of lignocellulosic biomass is often described by the sum of the thermal behavior  
330 of its constituents (Khelfa, 2009). Since the temperature range for the degradation of the constituents  
331 is relatively narrow, a high heating rate causes the different maxima in the derived curve to overlap  
332 and the temperatures of the characteristic processes tend to become progressively higher. Furthermore,  
333 if the temperatures are sufficiently high, significant degradation rates are then simultaneously achieved  
334 by all constituents. In other words, although one constituent can be identified respectively as  
335 hemicellulose, cellulose and lignin for each zone, the simultaneous participation of the other  
336 constituents cannot be avoided (Khelfa, 2009).

337  
338 **Table. 3** presents the mass losses noted at the different temperature ranges 180-300°C, 300-360°C and  
339 360-900°C. These results are only indicative due to the overlapping of the different mass loss peaks of  
340 the 3 main constituents of hemp shives. However, they can give an indication of the evolution of the  
341 degradation of the phases.

342  
343 **Table. 3** Loss of mass (%) between different temperature ranges for RSH and THS at different curing  
344 temperatures for 6 hours

Mass losses (%)	Decomposition T (°C)		
Vapothermal T (°C)	180-300	300-360	360-900
RHS	28	30	12
150	22	31	14
170	14	27	16
190	14	30	18
210	11	25	23
230	5	9	32

346

347 The results show that for RHS, that has not undergone vapothermal treatment, the mass loss between  
 348 180 and 300°C (considered to be due to the decomposition of hemicellulose) is 28%, between 300 and  
 349 360°C, is 30% (considered to be responsible for the degradation of cellulose) and between 360 and  
 350 900°C, is 12% (considered to be at the origin of the decomposition of lignin).

351 Following the increase of the temperature of the vapothermal treatment from 150 to 230°C, the  
 352 percentage of mass loss corresponding to the decomposition of hemicellulose decreases to 5%,  
 353 showing once again the degradation of hemicellulose by increasing the temperature of the cure.

354 For cellulose, the percentage of mass loss remains around 30% up to 190°C. From 210°C, the mass  
 355 losses decrease to a percentage of 9% showing a significant degradation of the cellulose that appears at  
 356 temperatures above 210°C.

357 For lignin, mass loss percentages increase progressively up to a value of 32.4% for a vapothermal  
 358 treatment at 230°C. If we consider that the percentage of mass loss between 360 and 900°C is an  
 359 indication of the evolution of the presence of lignin or recondensation products of lignin in hemp  
 360 shives, these increasing percentages can show that the vapothermal treatment allows the  
 361 recondensation of lignin products, a phenomena described in literature (Rousset et al., 2009).

362 Mass losses at 150°C demonstrate that this treatment does not denature completely the treated hemp  
 363 shives. Indeed, the observed mass losses are of the same order as those noted for the RHS.

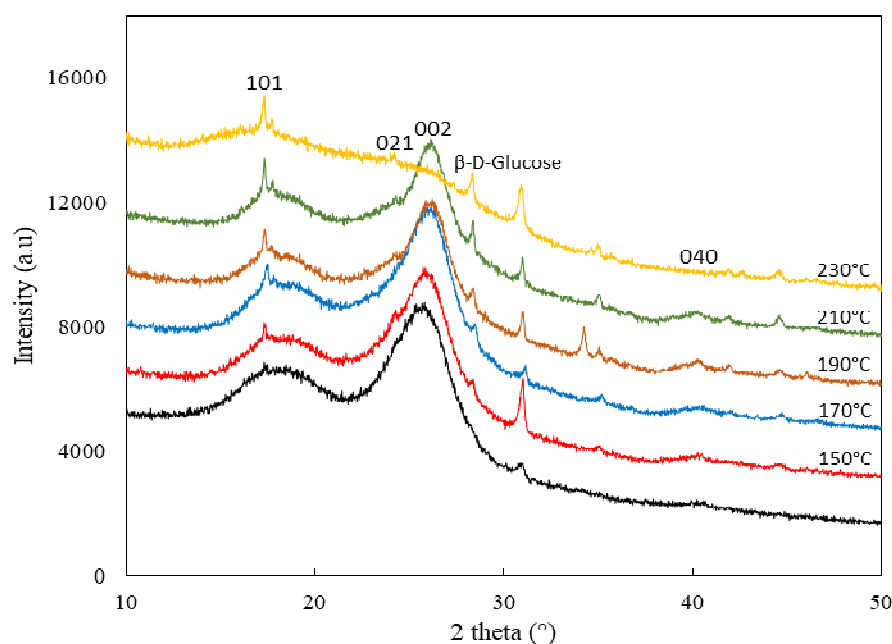
364 All of these results (**Table .3**) are in agreement with the chemical compositions of the different THS  
 365 (**Fig .3**), that show that the hemicellulose starts to degrade after the treatment at 150°C, while the  
 366 decomposition of the cellulose only takes place at temperatures of 210°C and finally the lignin, the  
 367 most difficult component to degrade, does not show signs of degradation at least up to temperatures of  
 368 230°C, however the latter can show signs of condensation reactions.

369

### 370 3.2.3. Mineralogical composition

371 For XRD analysis, as the patterns are similar for the different vapothermal treatment times, only  
 372 results of treatments for 6 hours are presented (**Fig. 5**). For temperatures below 210°C, it can be

373 observed that XRD pattern for THS are similar to that of RHS, indicating that the crystalline structure  
374 has been preserved. Patterns show the following peaks:  $\sim 16^\circ(101)$ ,  $\sim 19^\circ(101)$ ,  $\sim 24^\circ(021)$ ,  $\sim 26^\circ(002)$ ,  
375 and  $\sim 40^\circ(040)$ . These signatures are characteristic of cellulose I (Dash et al., 2020; Roumeli et al.,  
376 2015; Sevilla and Fuertes, 2009; Udoetok et al., 2018). Among the main constituents of hemp shives,  
377 cellulose is the only molecule that have a crystalline nature that can be detected by XRD.  
378 In addition to the peaks of cellulose, two other peaks around  $28^\circ$  and  $31^\circ$  appear for THS at all cure  
379 temperatures. These two peaks are identified as peaks corresponding to the presence of  $\beta$ -D-Glucose.  
380



381  
382 **Fig. 5** XRD patterns of RHS and THS at different temperatures for 6 hours  
383

384 The crystallinity of the cellulose depends on the temperature of the hydrothermal cure (Esteves and  
385 Pereira, 2008; Michiel Boonstra, 2008). Up to temperatures of  $210^\circ\text{C}$ , the crystallinity increases due to  
386 the degradation of the less ordered parts of the cellulose (Michiel Boonstra, 2008). The hydroxyl  
387 groups of cellulose degrade in the following order: amorphous, semi-crystalline and crystalline  
388 (Wikberg and Maunu, 2004). On the other hand, pattern obtained at temperature of  $230^\circ\text{C}$  is no longer  
389 crystalline, as can be inferred from the absence of reflections in the X-ray pattern, according with  
390 literature (Sevilla and Fuertes, 2009). The crystallinity of cellulose increases due to the degradation of  
391 amorphous cellulose, leading to a decrease in the accessibility of hydroxyl groups to water molecules,  
392 which contributes to a decrease in the hydrophilic character of the plant aggregates (Esteves and  
393 Pereira, 2008).

394  
395 As for Glucose peaks, their presence can be explained by the fact that hemicellulose and cellulose  
396 degradations (even at the amorphous parts), proceed via cleavage of mainly  $\beta$ -(1-4) glycosidic bonds

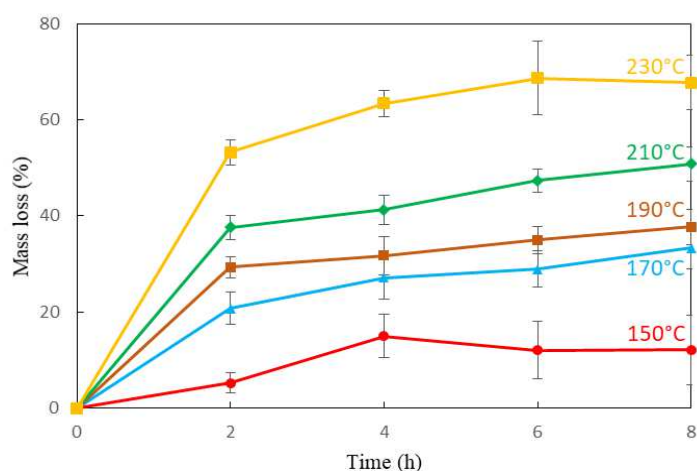
397 and cause the release of glucose monomers (Esteves and Pereira, 2008; Krylova and Zaitchenko,  
398 2018).

399

### 400 **3.3. Physical modification of hems shives by vapothermal treatment**

#### 401 3.3.1. Mass loss

402 **Fig. 6** summarizes the yield results of mass loss calculations (four hemp samples of 10g for each  
403 temperature and time curing) at different temperatures in function of time. As mentioned before, at  
404 temperatures above 190°C the hemp becomes crumbly and causes a very slight loss of material in the  
405 autoclave. As a result, the mass losses noted for temperatures of 210°C and 230°C may be less  
406 accurate, but can still be indicative.



407

408 **Fig. 6** Mass losses (%) of THS at different temperatures as a function of time

409

410 At a fixed time of curing, the percentages of mass loss increase with increasing temperature. For  
411 example, after 2 hours of curing, the loss of mass passes from 5.2% at T=150°C to 29.3% at T=190°C  
412 and reaches 53.3% at 230°C. These percentages increase also with the treatment time duration. The  
413 mass loss percentage at 190°C passes from 29.3% at 2 hours to 37.7% after 8 hours of treatment.

414 According to the results obtained, the average loss of mass of the hemp increases as the temperature of  
415 the cure increases, which is in accordance with the conclusions of previous studies showing the loss of  
416 mass of hydrothermal treated biomass in function of the temperature used (Wang et al., 2018; Zhang  
417 et al., 2020). Different types of plants (rapeseed straw, oil palm biomass...) have been treated under  
418 hydrothermal curing from 170 to 230°C (Díaz et al., 2010; Zakaria et al., 2015).

419 These mass losses confirm the presence of chemical transformations that occur under the effect of the  
420 increase in temperature and pressure and that may include removal of volatiles (Esteves and Pereira,  
421 2008; Maniscalco et al., 2020; Sharma et al., 2020; Yeoh et al., 2018). Unlike the visual aspect which  
422 does not change according to the duration of the treatment, mass losses increase from 2 to 8 hours of  
423 treatment at all temperature curing.

424

425 3.3.2. Water absorption

426 Water absorption for RHS is 335%. **Table. 4** presents the results of the quantities of water absorbed  
 427 (%) at 48 hours by the hemp following the different vapothermal treatments.

428

429 **Table. 4** Water content (%) at 48 hours of THS at different temperatures as a function of time

T (°C)	Time (h)			
	2	4	6	8
150	319 ± 1	325 ± 4	314 ± 6	328 ± 2
170	265 ± 4	282 ± 7	269 ± 2	274 ± 4
190	249 ± 5	234 ± 2	218 ± 7	240 ± 5

430

431 Based on these results, it can be seen that the absorption coefficient decreases after vapothermal  
 432 treatments. It passes from 335% without treatment, to 314% for a cure at 150°C showing an absorption  
 433 decrease of 6.3%. Absorption coefficient continues to decrease in function of temperature until it  
 434 reaches 218% at 190°C (a decrease of 34.9%). For this test, absorptions at 210°C and 230°C were not  
 435 measured as the hemp shives turned to a carbonized crumbly state.

436 Vapothermal treatment causes a decrease in water absorption due to a chemical change in the structure  
 437 of the hemp during the vapothermal cure. In literature, after hydrothermal curing, this fact was  
 438 explained by the increased crystallinity of the cellulose due to the degradation or to the crystallization  
 439 of amorphous cellulose (or both) (Michiel Boonstra, 2008), causing decreased accessibility of  
 440 hydroxyl groups to water molecules (Esteves and Pereira, 2008). The decrease in water absorption can  
 441 also be explained by the cross-linking of lignin caused after hydrothermal treatment that may also play  
 442 a role in the decrease of the amount of water absorbed by the hemp, which improves the  
 443 hydrophobicity of THS (Pejic et al., 2008; Sivonen et al., 2002).

444

445 3.3.3. Specific gravity

446 Specific gravity of RHS is 1.5. **Table. 5** shows the specific gravities of hemp treated under different  
 447 conditions. The values for the THS do not differ much from each other (1.43-1.49). The values  
 448 obtained show that the vapothermal cure causes a decrease in the specific gravity of the hemp shives.  
 449 The results for temperatures above 190°C will not be presented for the same reason cited before.

450

451 **Table. 5** Specific gravities of THS at different temperatures as a function of time

T (°C)	Time (h)			
	2	4	6	8
150	1.49	1.46	1.49	1.43
170	1.44	1.45	1.43	1.42

190	1.49	1.43	1.44	1.44
-----	------	------	------	------

452

453 The decrease in the specific gravity can be explained by the loss of mass (degradation reactions of  
 454 different constituents of hemp shives into volatile products) of THS seen after the vapothermal  
 455 treatment (**Fig. 6**).

456

457 All these physical changes are the result of modifications and transformations in the composition of  
 458 the treated hemp shives.

459

#### 460 **4. Conclusions**

461 The main objective of the work was the evaluation of the effect of vapothermal curing **on the chemical**  
 462 **(composition in cellulose, hemicellulose and lignin)** and physical **properties** (mass loss, absorption  
 463 coefficient and specific gravity) of hemp shives, **as aggregates that can enter in the production of**  
 464 **structural vegetal concrete. The idea of the production of vapothermal treated vegetal concrete is**  
 465 **totally innovative, and can make it possible to overcome of the compatibility problem with**  
 466 **cementitious matrix (improvement of mechanical performances in a perspective of development of**  
 467 **green and structural building materials).**

468 As a result, hemp **shives** underwent different vapothermal cures at temperatures of 150°, 170°, 190°,  
 469 210° and 230°C.

470 The main conclusions drawn are:

471 -The color of the hemp shives becomes darker and go through a progressive carbonization, and the  
 472 loss of mass increases as the temperature of the vapothermal cure increases.

473 -The water absorption coefficient decreases with the temperature of the cure, but still not enough for a  
 474 good compatibility in cement interaction, while the specific gravity decreases after the vapothermal  
 475 treatment and remains unchanged with increasing cure temperature.

476 -These physical changes during a vapothermal treatment are associated with chemical transformations  
 477 that take place into the structure of the treated hemp, thus changing the chemical composition of the  
 478 hemp.

479 These changes can be summarized by:

480 -The depolymerization of hemicellulose, which is the first component that starts to be affected by the  
 481 cure at low temperatures (150°C)

482 -The increase in the crystallinity of the cellulose accompanied by a decrease in the hydrophilic sites  
 483 and leading to a drop in the absorption coefficient even at low curing temperatures (<210°C). Towards  
 484 higher temperatures (>210°C), cellulose no longer resists to degradation.

485 -As for lignin, it depolymerizes at temperatures close to 190°C. However, condensation reactions of  
 486 degradation products can occur.

487



488 This study that determined the effect of vapothermal curing on the physicochemical properties of  
489 hemp shives, constitutes the first step in the approach of the formulation of autoclaved structural hemp  
490 concrete for civil engineering applications. Therefore, a vapothermal treatment at 150°C seems to be  
491 the curing process that allows to preserve the chemical structure of the hemp shives.

492

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