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1	Vapothermal curing of hemp shives: influence on some chemical and physical properties
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0 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	

1. Introduction

35

36 The building sector is known to be responsible for one of the world's main sources of CO_2 emissions, 37 through the production of building materials and the energy consumption of buildings in the operating phase: heating, ventilation and air conditioning (United Nations Environment Programme, 2009). In France, this sector represents 44% of the energy consumed, i.e. more than 120 million tons of CO_2 each year (Commissariat Général au Développement Durable, 2020). Particularly, the cement industry is responsible of large volumes of CO_2 emitted during the manufacture of Portland cement clinker (Gartner, 2004). Today, most research efforts are focused on the production of building materials that 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 CO₂ 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 vegetable aggregates and thus of the vegetal concretes. So, a lot of researches were carried out to 68 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

Among the different approaches used generally for energy recovery from biomass, can be found the hydrothermal treatment (Funke et al., 2013; Huang and Yuan, 2016; Rulkens, 2008; Shafie et al., 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 vapothermal 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 vapothermal 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 vapothermal 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, vapothermal 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 materials 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). Vapothermal 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 vapothermal curing on the hardening of other types of concrete. 105 Hence the idea of combining the production of vegetal concrete with vapothermal 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 vapothermal 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 approach of production of a structural vegetal concrete based on hemp shives and lime (lower carbon footprint than cement). The vapothermal treatment is a "green" solution (cure at temperatures below 230°C) that will be used for the hardening of the binder. This experimental investigation is the first step that provides important informations on the degree of transformation of the hemp under vapothermal curing. Beyond the modified physical properties of the hemp shives following the different curing conditions, this project is mainly focused on the evolution of the chemical composition 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 ³)	110 133
Water retention capacity (ml/l) EN-13041	370 ¹³⁴
pH in suspension at 10%	6.7 – ¹ 7 .2
Thermal conductivity (W/mK)	0.048
Specific gravity (Helium pycnometer)	1.5

- 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 vapothermal 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

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

147



148

149 Fig. 2 Hemps shives in the tea ball, tea ball on the gridded support, tea balls in the autoclave, the150 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 "Retsch156 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 H₂SO₄. 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

linear gradient of 8 mM NaOH to 1 mM NaOH from 6 to 23 min. At 23.1 min, the gradient wasincreased 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 acid169 medium that hydrolyzes and dissolves the other parietal constituents (cellulose and hemicelluloses) is

170 used (Hochegger et al., 2019). 72% of H_2SO_4 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 \pm 1°C while being stirred frequently. Water is added in order to dilute the solution (3% of H₂SO₄). 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 $105 \pm 3^{\circ}$ 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 α : $\lambda = 1,74$ Å).
- Loss of mass was determined by mass weighing of the samples (non-grinded) before and after the treatment. Each weighing at a given temperature and time was carried out on four hemp samples of 10g each. Water absorption was carried out after drying the aggregates and then calculating their absorption coefficient at 48 hours according to the technical recommendations of RILEM TC 236-BBM (Amziane et al., 2017). Specific gravity (grinded samples) was measured using the Helium
- 189 pycnometer "micromeritics AccuPyc 1330".
- 190

1913. Results and discussion

3.1. Visual aspect of hemps shives after vapothermal treatment

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



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



202

The change in color of THS as a function of temperature can therefore be explained by a series of chemical transformations that the material has undergone between 180 and 250°C, the range commonly used for the heat treatment of biomass (Esteves and Pereira, 2008). The increase in temperature and pressure in the autoclave has an effect on the structure of the hemp and modifies its chemical composition by degrading the cell wall compounds and extractives (Esteves and Pereira, 2008; Sauvageon, 2017). The chemical modifications due to high temperatures depend on the duration 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).
- The crumbly state observed above 190°C is explained by the fact that the hemp passes gradually by a progressive carbonization that alters the hemp shives structure.
- 216

3.2. Chemical, thermal and mineralogical modifications of hemps shives by vapothermal treatment

219 3.2.1. Chemical composition

Fig. 3 shows the chemical composition of RHS and vapothermal THS. The composition of RHS shows 21% of hemicellulose, 40% of cellulose, 19% of lignin and 20% of other protein/minerals. The hemp is mainly composed of cellulose. For the rest of the constituents: hemicellulose, lignin and other minerals, they are at almost equal amounts. These results are in agreement with the composition of hemps shives presented in the literature. The percentages of cellulose vary between 12 to 37% for 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



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

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 (Kocaefe 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

For cellulose, vapothermal curing caused an increase in the content from 40% for RHS to 43% for a 2 hours treatment at 150°C. This percentage continued to increase to reach values around 50% for cures 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 undergo a series of isomerization, dehydration and fragmentation (ring opening and C-C bond 254 cleavage), producing intermediates products, 5-HMF or furfural, and their derivatives. These 255 256 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

As for the rest of the proteins (calculated as the remainder percentage after subtracting the sum of the percentages of cellulose, hemicellulose and lignin), an increase of the percentage from 20% for RSH to 28% for a cure of 2 hours at 150°C. Then, a progressive decrease is observed with the increase of the cure temperature to almost 5% at 210°C (8 hours) explained by the polysaccharides degradation. After this, an increase to 15% is noted at 230°C (8 hours). Most extractives degrade during heat treatment, especially the most volatile ones (Esteves and Pereira, 2008; Maniscalco et al., 2020; Sharma et al., 2020; Yeoh et al., 2018). However, new compounds resulting from the degradation of structural components of the cell wall can also be formed in the form of extracted waxes, carbohydrates, tannins and resins (Esteves and Pereira, 2008). The evolution of the proteins/minerals depends on the balance between the phenomenon of degradation of polysaccharides and the phenomenon of condensation of certain products such as lignin. The respective rates of these 2 phenomena play a role on the protein and mineral content. The eventual overestimation of lignin explained in the previous section, may cause an underestimation of the remaining proteins/minerals.

292

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

296

297 3.2.2. Thermal decomposition

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

300





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

In the DTG curves, for RHS, the first decomposition shoulder peak at about 180-300°C corresponds probably to thermal depolymerisation of hemicelluloses or pectin (mass loss 27.5%) and the maximum mass loss rate is observed at 270°C. In the literature, the first component that is affected by the vapothermal curing is hemicellulose (Esteves et al., 2008; Esteves and Pereira, 2008) due to its 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 difficult to decompose. It decomposes slowly, over a wide range of temperature from 100 to 900°C 315 316 (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).

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

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

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

Table. 3 Loss of mass (%) between different temperature ranges for RSH and THS at different curing
 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

345

346

The results show that for RHS, that has not undergone vapothermal treatment, the mass loss between and 300°C (considered to be due to the decomposition of hemicellulose) is 28%, between 300 and 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).

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

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

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

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

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

369

370 3.2.3. Mineralogical composition

For XRD analysis, as the patterns are similar for the different vapothermal treatment times, only 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° and 31° appear for THS at all cure
- 379 temperatures. These two peaks are identified as peaks corresponding to the presence of β -D-Glucose.
- 380



381



383

384 The crystallinity of the cellulose depends on the temperature of the hydrothermal cure (Esteves and Pereira, 2008; Michiel Boonstra, 2008). Up to temperatures of 210°C, the crystallinity increases due to 385 386 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°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 β -(1-4) glycosidic bonds and cause the release of glucose monomers (Esteves and Pereira, 2008; Krylova and Zaitchenko,2018).

- 399
- 400

3.3. Physical modification of hemps 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.





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

409

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

According to the results obtained, the average loss of mass of the hemp increases as the temperature of the cure increases, which is in accordance with the conclusions of previous studies showing the loss of mass of hydrothermal treated biomass in function of the temperature used (Wang et al., 2018; Zhang 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).

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

- 425 3.3.2. Water absorption
- Water absorption for RHS is 335%. Table. 4 presents the results of the quantities of water absorbed
 (%) at 48 hours by the hemp following the different vapothermal treatments.
- 428

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			

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

430

Based on these results, it can be seen that the absorption coefficient decreases after vapothermal treatments. It passes from 335% without treatment, to 314% for a cure at 150°C showing an absorption decrease of 6.3%. Absorption coefficient continues to decrease in function of temperature until it reaches 218% at 190°C (a decrease of 34.9%). For this test, absorptions at 210°C and 230°C were not 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 explained by the increased crystallinity of the cellulose due to the degradation or to the crystallization 438 439 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.

451	Table. 5	5 Specific	gravities	of THS a	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			

	19	0	1.49	1.43	1.44	1.44		
452							l	
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	treatmen	t (Fi	g. 6).					
456								
457	All these	e phy	viscal changes are the	e result of modificati	ons and transformation	ons in the compositio	on of	
458	the treate	ed he	mp shives.					
459								
460	4. (Conc	lusions					
461	The main	n obj	ective of the work wa	as the evaluation of th	ne effect of vapothern	nal curing on the chen	nical	
462	(compos	ition	in cellulose, hemice	ellulose and lignin) a	and physical properti	es (mass loss, absorp	otion	
463	coefficie	ent ar	nd specific gravity)	of hemp shives, as a	ggregates that can e	nter in the productio	n of	
464	structura	ıl veg	getal concrete. The	idea of the production	on of vapothermal tr	reated vegetal concre	te is	
465	totally i	innov	ative, and can ma	ke it possible to o	vercome of the cor	npatibility problem	with	
466	cementit	tious	matrix (improvemen	nt of mechanical perf	formances in a persp	ective of developmer	nt of	
467	green an	d stru	ctural building mate	rials).				
468	As a res	ult, h	emp shives underwe	ent different vapother	mal cures at tempera	tures of 150°, 170°, 1	.90°,	
469	210° and	1 230	°C.					
470	The main	n con	clusions drawn are:					
471	-The col	lor of	the hemp shives be	ecomes darker and go	o through a progressi	ve carbonization, and	1 the	
472	loss of m	nass i	ncreases as the temp	erature of the vapothe	rmal cure increases.			
473	-The wat	ter ab	osorption coefficient	decreases with the ter	nperature of the cure	, but still not enough f	for a	
474	good con	mpati	ibility in cement inte	eraction, while the sp	ecific gravity decrea	ses after the vapother	rmal	
475	treatmen	it and	remains unchanged	with increasing cure	emperature.			
476	-These p	hysic	cal changes during a	vapothermal treatment	nt are associated with	chemical transformat	tions	
477	that take	e plac	e into the structure	of the treated hemp,	hus changing the che	emical composition of	f the	
478	hemp.							
479	These ch	nange	s can be summarized	l by:				
480	-The dep	oolyn	nerization of hemicel	llulose, which is the f	irst component that s	tarts to be affected by	y the	
481	cure at lo	ow te	mperatures (150°C)					
482	-The inc	rease	in the crystallinity	of the cellulose accord	mpanied by a decreas	se in the hydrophilic	sites	
483	and lead	ing to	o a drop in the absorp	ption coefficient even	at low curing temper	atures (<210°C). Tow	vards	
484	higher te	emper	ratures (>210°C), cel	lulose no longer resis	ts to degradation.			
485	-As for lignin, it depolymerizes at temperatures close to 190°C. However, condensation reactions of							
486	degradat	tion p	roducts can occur.					

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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