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Morad Chadni, N. Grimi, Isabelle Ziegler-Devin, Nicolas Brosse, Olivier Bals. High voltage electric discharges treatment for high molecular weight hemicelluloses extraction from spruce. *Carbohydrate Polymers*, 2019, 222, pp.115019. 10.1016/j.carbpol.2019.115019 . hal-02290577

HAL Id: hal-02290577

<https://hal.univ-lorraine.fr/hal-02290577>

Submitted on 17 Sep 2019

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1 **High voltage electric discharges treatment for high molecular**
2 **weight hemicelluloses extraction from spruce**

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4

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26 **Abbreviations**

27 **HVED** : High voltage electrical discharge

28 **Mw** Molecular weights (g/mol)

29 **GGM** Galactoglucomannans

30 **Mn** Number average molecular weights (g/mol)

31 **PI** Polydispersity index

32 **IR** Infrared

33 **UV** Ultraviolet

34 **AD** Acetylation degree

35 **AcGGM** Acetylated galactoglucomannan

36 **DM** Dry matter

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47 **1. Introduction**

48 Polymeric hemicelluloses are polysaccharides with an important structural diversity and
49 functionality. Although cellulose is the most widely used polysaccharide, the potential of application
50 of polymeric hemicelluloses has been demonstrated by several authors (Bai, Hu, and Xu 2012;
51 Lindqvist et al. 2013; Mikkonen and Tenkanen 2012; Alvira et al. 2010; Hartman, Albertsson, and
52 Sjöberg 2006). The physicochemical properties of hemicelluloses have made them today an
53 important untapped resource that can be used in several fields.

54 Spruce hemicelluloses are mainly composed of acetylated galactoglucomannan (AcGGM). AcGGM
55 has a backbone of β -D-(1 \rightarrow 4) -glucopyranosyl and β -D-(1 \rightarrow 4)-mannopyranosyl units in a linear or
56 slightly branched chain. Single α -D-galactopyranose units are attached to the main chain by (1 \rightarrow 6)-
57 bonds. The mannopyranosyl units are acetylated at C-2 or C-3 with a degree of acetylation of about
58 0.5 (Capek et al. 2000). An approximate ratio of galactose-to-glucose-to-mannose is around 0.5–
59 1.1:1:3.5–4.5 for water-soluble AcGGM (Timell 1967). The average weight molar mass M_w of
60 native AcGGM has been reported to be between 20 and 50 kDa and the degree of polymerization
61 varies from 100 to 400 (Timell 1967; Willför et al. 2008).

62 GGMs have the potential to become high added-value products with various applications in food,
63 health, papermaking, textile and cosmetic industries (Mikkonen et al. 2012, 2010). Different
64 applications request GGMs in different forms (different molar masses). High molecular masses
65 GGMs can be used as such or mixed with other polysaccharides to form a raw material for
66 biodegradable films with promising oxygen barrier properties (Hartman et al. 2006).

67 The extraction of spruce hemicelluloses in general has been investigated for years. The common
68 studies were focused on the extraction of monomeric form of wood polysaccharides for ethanol
69 bioconversion. However, due to the discovery of the high potential of application of polymeric
70 hemicelluloses, many authors have investigated the extraction of the polymeric form of
71 hemicelluloses from wood. Extraction of softwood hemicelluloses has been studied by hydrothermal
72 treatment at high temperatures (≥ 170 °C) (Krogell et al. 2013; Song, Pranovich, and Holmbom
73 2012), by chemical extraction (alkaline) (Capek et al. 2000; Curling, Fowler, and Hill 2007; Alvarez-
74 Vasco and Zhang 2013), ionic liquids (Anugwom et al. 2012), by pressured hot water (Song et al.

75 2008; Gallina et al. 2017), and by microwave heat-fractionation ($> 180\text{ }^{\circ}\text{C}$) (Gulbrandsen et al.
76 2015; Palm and Zacchi 2003; Lundqvist et al. 2002).

77 The fractionation of wood at high temperatures leads to high solubilization of all macromolecules,
78 including hemicelluloses. However, the extraction at higher temperatures led to a lower pH level,
79 causing deacetylation and partly hydrolytic cleavage of GGMs, and consequently, decreasing the
80 solubility, the yield and the molar mass of extracted GGMs.

81 Nowadays, electrical pretreatments that provoke electroporation and cell walls destabilization have
82 also been used for biomolecules extraction (Grimi et al. 2009; Boussetta, 2010; Boussetta et al. 2009;
83 Loginova et al. 2010). High voltage electric discharges (HVED) have shown very interesting results
84 for the biomolecules extraction from biomass. HVED showed its effectiveness for polyphenols
85 extraction from vine shoots (Rajha et al. 2014) and grape pomace (Boussetta et al. 2009; Boussetta et
86 al. 2012) lignin from rapeseed straw (Brahim et al. 2016), flavonoids from peanut shells based (Yan
87 et al. 2018), polyphenol and protein extraction from sesame cake (Sarkis et al. 2015), polyphenols
88 and lignans from flaxseed cake (Boussetta et al. 2013) and sugars from orange peels (El Kantar et al.
89 2018). Indeed, when applied in a liquid medium, HVED have physical features leading to the
90 extraction of biomolecules from raw materials located inside the cell walls. The main effect of
91 HVED is the fragmentation and destruction of raw materials. This destruction occurs through a
92 certain number of physical phenomena, which will be discussed later. These physical phenomena are
93 complex and the way they lead to extraction of raw material is insufficiently delighted.

94 There are numerous phenomena that could lead to the fragmentation of biomass during the
95 application of HVED in liquid medium. Such as electrical breakdown which occurs when the
96 streamer crosses the two electrodes, the breakdown induces the formation of a powerful shock wave
97 (hundreds of MPa) in only a few micro- or nanoseconds. Shock waves are known to be responsible
98 of mechanical cell membrane damages (Boussetta et al. 2009). Directly after shock waves, the
99 apparition and the collapse of microcavitation bubbles create an intense and very localized shock
100 waves that can lead to the fragmentation of raw material. The electric arc also emits high-intensity
101 UV light and induces a large variety of chemical reactions like radical formation, radical molecule
102 reaction, photochemical reaction, ozone molecules reaction and aqueous electron reaction etc. (Adda

103 et al. 2016). UV light in the range of 200–400 nm is mutagenic to cells (Boussetta and Vorobiev
104 2014) and hydroxyl radicals lead to oxidative cell damage.

105 To our knowledge, the HVED have not yet been applied to the extraction of hemicelluloses from
106 sawdust wood. The originality of this study is to suggest an original method to extract high
107 molecular weight hemicelluloses and reducing the severity of conventional treatments by combining
108 HVED with chemical and thermal treatment. The main objective of this work is to extract high
109 molecular weight hemicelluloses at mild conditions (low temperature and suitable pH). Mild
110 conditions were achieved by combining HVED with chemical extraction and autohydrolysis.

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131 **2. Materials and methods**

132 The objective of this study is to evaluate the effect of HVED pretreatment on the extraction of high
133 molecular weight hemicelluloses from spruce sawdust. For this purpose, numerous pretreatments at
134 different impulsions (0-4 ms) were carried out in two different mediums (1M NaOH and water). The
135 temperature generated during HVED pretreatment was between 40 and 50 °C.

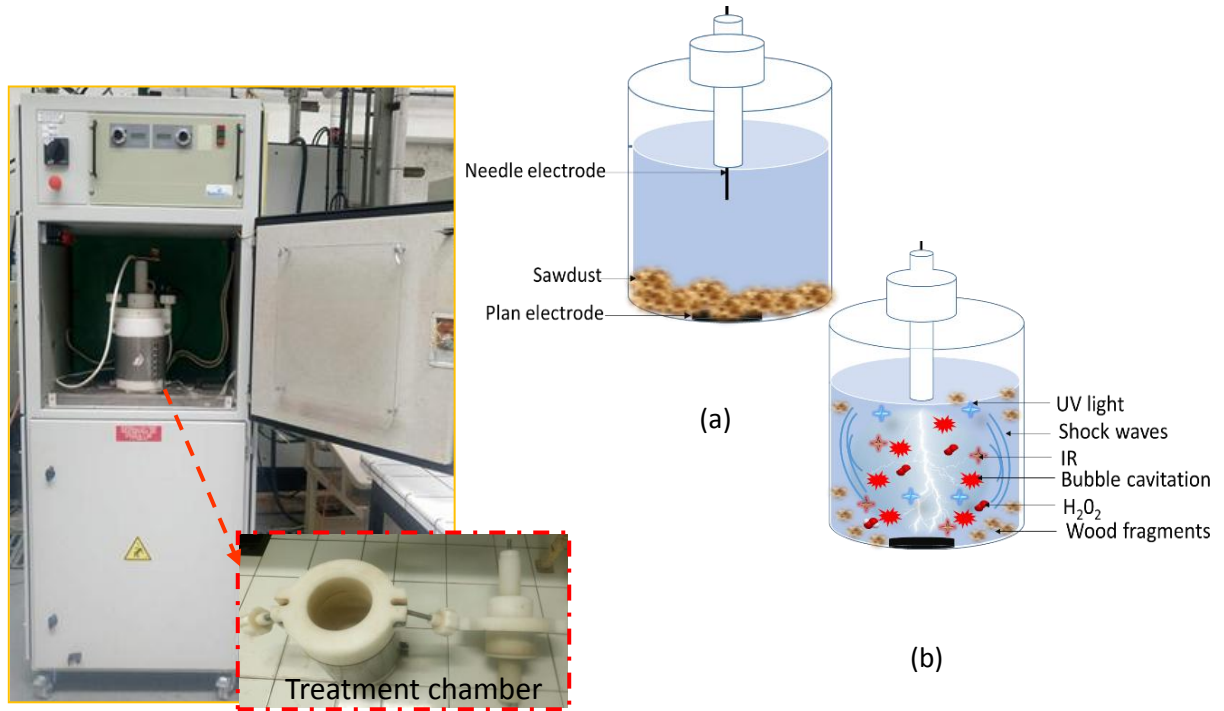
136 **2.1 Raw material**

137 Spruce sawdust with a particle size of (1-5 mm) was produced from a spruce tree from the Lorraine
138 region in France and stored at room temperature in a sealed polyethylene bags in the dark until
139 extraction. The average moisture content of the raw material was 10% w/w. The hemicellulose content
140 of the sawdust (~30 % w/w dry biomass) was calculated by analyzing no-cellulosic monosaccharides
141 of spruce wood according to NREL/TP-510-42618 method. Carbohydrate composition of sawdust
142 includes 72 % glucan, 7,5 % xylan, and 16,3 % of mannan and other sugars.

143 **2.2 Extraction procedure**

144 **2.2.1 HVED pretreatment**

145 HVED pretreatment was carried out using a high voltage pulsed power 40 kV-10 kA generator (Basis,
146 Saint Quentin, France), 1-liter cylindrical batch treatment chamber. The HVED treatment chamber
147 was equipped with needle-plate geometry electrodes. The diameters of stainless-steel needle and the
148 grounded disk electrodes were 10 and 35 mm, respectively. The distance between the electrodes was
149 10 mm. The energy was stored in a set of low-inductance capacitors, which were charged by the high-
150 voltage power supply. The electrical discharges were generated by electrical breakdown in the
151 medium of extraction (liquid) at the peak pulse voltage (U) of 40 kV.



152

153 **Fig. 1.** HVED setup and treatment chamber: (a) before HVED pretreatment; (b) during HVED
 154 pretreatment

155 In all experiments the liquid-to-solid ratio was fixed at 15 (w/w). The HVED generator (40 kV,
 156 10 kA) provided pulses of an exponential form with a pulse repetition rate of 0.5 Hz. The effective
 157 time (t_{HVED}) of HVED treatment was calculated:

158
$$t_{HVED} = n \cdot t_p \quad (1)$$

159 Where n ($=1-400$) is the number of pulses and t_p ($\approx 10 \pm 1 \mu s$) is the pulse duration.

160 The specific energy input W (kJ/kg) was obtained from Eq. (2):

161
$$W = \frac{\sum_{n=1}^n W_{HVED}}{m} \quad (2)$$

162 Where

163 W_{HVED} is the pulse energy (kJ/pulse) and m is sawdust mass (kg). W_{HVED} is determined from
 164 Eq. (3).

165
$$W_{HVED} = \int_0^n U I dt \quad (3)$$

166 Where U is the voltage (V) and I is the current strength (A)

167 **1.2.2 Diffusion**

168 The goal of the diffusion step is to facilitate the transfer of hemicelluloses chains from wood matrix to
169 the extracellular medium. Temperature during HVED treatment was between 40 and 50 °C. In order to
170 maintain mild conditions of extraction (low temperature, low decrease of pH), the diffusion was done
171 under reflux at 50°C during 3 h with agitation.

172 **1.2.3 Separation of extracted hemicelluloses**

173 After each experiment, the extract was filtered on qualitative filter paper with retention particle size of
174 5–13 µm (VWR International, Fontenay-sous-Bois, France). The volume and end-pH of the extract
175 solutions were measured at room temperature shortly after the extraction. The liquid fraction from 1M
176 NaOH impregnated sawdust was neutralized to a pH of 5.5-6 by a solution of 72% H₂SO₄. 10 mL
177 were taken from the filtered extract for analyses. The extract solution was concentrated by vacuum
178 evaporation using a water bath at 50 °C. To precipitate high-molecular weight hemicelluloses, four
179 volumes of 95% ethanol were added to the liquid extracts. The liquid phase was separated from the
180 precipitated hemicelluloses by settling at room temperature and decantation. Hemicelluloses were
181 further separated from the remaining liquid by centrifugation at 4000 rpm for 10 min at room
182 temperature. The precipitated hemicelluloses were re-dissolved in distilled water and dialyzed with a
183 dialysis membrane with a cut-off of 3.4 kDa (Spectrum Laboratories, Inc., Rancho Dominguez, CA,
184 USA). Finally, dialyzed hemicelluloses solutions were freeze-dried.

185 **1.3 Measurement of monosaccharides and uronic acids using HAPE-PAD**

186 The monosaccharide content of the soluble fraction was analyzed according to NREL/TP-510-42618
187 method. The sugar concentrations were measured by HAPE-PAD (ICS-3000 Dionex, Dionex Corp.,
188 Sunnyvale, USA) equipped with a Dionex CarboPacTM PA-20 (3 × 150 mm) analytical column.
189 Filtered samples (20 µL) were eluted at 35 °C and at 0.4 mL/min with the following composition: pure
190 water 99.2%/250 mM NaOH 0.8%: 0–20 min; pure water 75%/250 mM NaOH 20%/ NaOCOCH₃ (1
191 M)- NaOH (20 mM) 5% 20–37 min; and pure water 40%/250 mM NaOH 20%/NaOCOCH₃ (1 M)-

192 NaOH (20 mM) 40% 37–41 min. Each elution was followed by a wash and subsequent equilibration
193 step. External sugar and uronic acid standards were used for calibration (7 points per curve). The
194 reagents and standards are provided by Sigma-Aldrich and Fisher Scientific.

195 **1.4 Size-exclusion chromatography (SEC)**

196 A Shimadzu Prominence HPLC system is used to determine molecular weight distribution of
197 hemicelluloses by gel filtration chromatography. The stationary phase is composed of two columns
198 linked in series: Phenomenex Polysep GFC-P as a guard column (7.8 x 35 mm), Phenomenex Polysep
199 GFC-P3000 and GFC-P2000 analytical columns (7.8 x 300 mm). Sodium nitrate (0.25 M) is used as
200 an eluent with a 0.5 mL.min⁻¹ flow rate. Samples are filtered with a 0.45 µm membrane and 20 µL are
201 injected. Samples are separated at 30 °C and detection is done with a Refractive Index
202 Detector (Shimadzu RID-20A). Each analysis runs for 70 min. aqueous solutions (1 mg/mL) of
203 dextran standards with molecular weights of 1000; 5000; 12000; 24000; 50000 and 80,000 Da were
204 used to prepare the calibration curve.

205 **1.5 FTIR**

206 FTIR analysis for extracted hemicelluloses were performed by a FTIR spectrophotometer (Thermo
207 Scientific iD3ZnSe ATR—Nicolet iS 5 FTIR Spectrometer unit). Hemicelluloses powder was placed
208 on a ZnSe crystal plate. Each IR spectrum was obtained over the wave number range of 400–
209 4000 cm⁻¹ with eight scans at resolution of 4 cm⁻¹. The spectra were analyzed using ThermoScientific
210 OMNIC software.

211

212 **1.6 2D ¹³C–¹H HSQC NMR spectroscopy**

213 ²H NMR and ¹H–¹³C correlation 2D NMR (HSQC) spectra were recorded on a Bruker III 400
214 MHz spectrometer equipped with a 5-mm BBFO probe. Experiment was conducted with 20 mg
215 sample dissolved in 1 ml D₂O. The number of collected complex points was 1024 for the ¹H-
216 dimension with a relaxation of 1.5- and 256-time increments were recorded in ¹³C-dimension.
217 HSQC spectra were taken at room temperature.

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2.2 Thermal gravimetric analysis (TGA)

The thermal behavior of extracted hemicelluloses was investigated by TGA (Thermal Gravimetric Analysis) (Setaram Setsys). The samples were dried before thermal analysis. The heating rate in the experiments was 10 C.min⁻¹ up to 600 C. A platinum cup was used in these tests. The weight of the sample was recorded during the temperature rise under azote flow (30 ml / min).

2.3 Scanning microscopy

The surface morphology of sawdust fibers was studied by scanning electron microscopy (SEM). An environmental high-resolution electron scanning microscope QUANTA 250 FEG (FEI Company) was used in low-vacuum mode.

244

245 **3 Results and discussion**

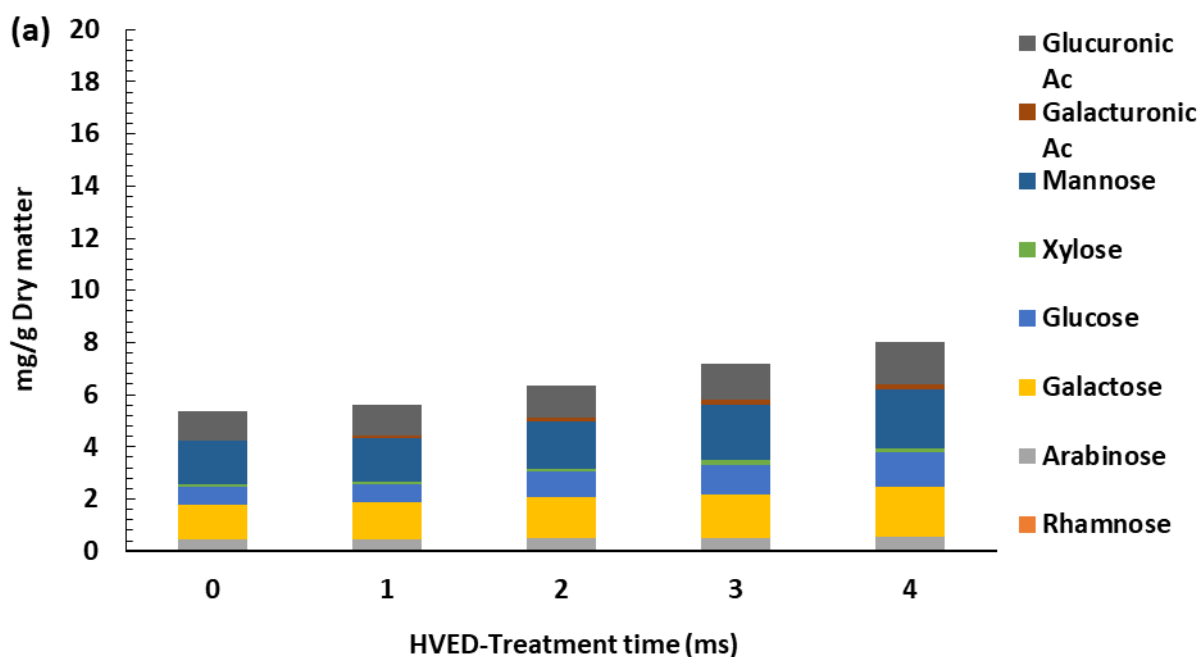
246 **3.1 Yield of hemicellulose extraction**

247 **Fig. 2 (A and B)**, shows the yield of extraction of non-monomeric hemicellulose chains from spruce
248 sawdust in the liquid fraction in distilled water and in basic media (1M NaOH) respectively. As
249 expected higher hemicelluloses yields were obtained in basic conditions ($\approx + 80 \%$). This observation
250 is be explained by the fact that alkaline solutions increase the water absorption capacity, swell up
251 cellulosic fibers and decrease their crystallinity, and thus increase the specific surface area by
252 increasing the volume of the solid (Wen et al. 1988). HVED pretreatments increase significantly the
253 yield of extraction in both media. In water, at 4 ms of HVED pretreatment (376 J/g DM), the yield of
254 extraction was increased by 38 % compared to the extraction without HVED activation (0 ms) (5.8
255 mg/g of DM for 0 ms pretreatment and 8 for 4 ms pretreatment). In basic medium, the advantage of
256 HVED pretreatment step was also apparent. The yield was about 15.8 and 19.7 mg/g of dry wood for 0
257 and 4 ms of pretreatment respectively.

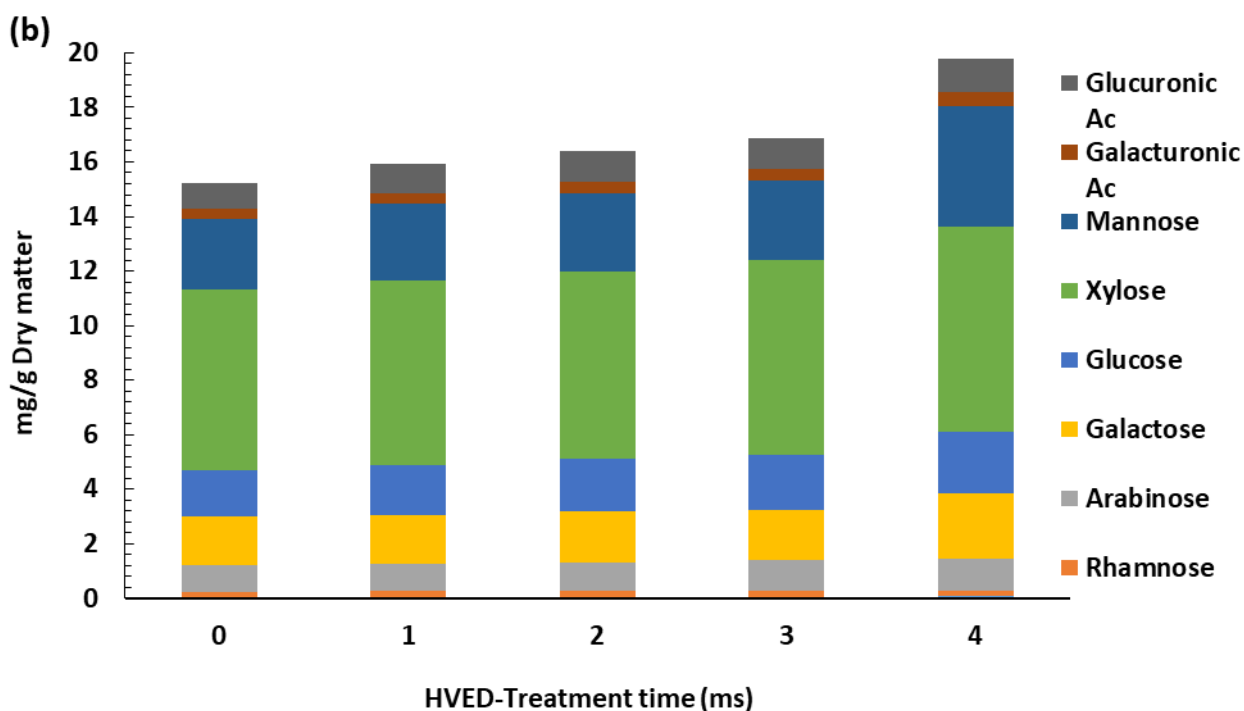
258 The application of HVED-treatment results in generation of shock waves. These shockwaves may play
259 an important role in the raw material fragmentation, thus facilitating hemicelluloses extraction. The
260 formation of the shock waves in liquid medium is often followed by the apparition of cavitation
261 bubbles. The combined effect of shock waves and cavitation bubbles may improve the disruption and
262 the destabilization of cell walls (Boussetta and Vorobiev 2014; Sarkis et al. 2015; Boussetta 2010).
263 The pH of extraction is also an important parameter for the extraction of hemicelluloses chains. After
264 extraction, the final pH of the suspension treated in water had dropped from 7 to 6.1 for untreated
265 sawdust (0 ms) and from 7 to 5.2-5.3 for HVED pretreated sawdust. The drop of pH in the suspension
266 treated in water is due to the release of carboxylic acids, mainly acetic acid from GGMs (Casebier,
267 Hamilton, and Hergert 1969). Acetic acid released in the suspension treated in 1M NaOH solution are
268 neutralized by hydroxide anions and pH remains stable at 13.5 for both untreated and HVED-treated
269 samples.

270 **Fig.2 (A and B)** show also the composition of the extracted hemicelluloses in water and 1M NaOH
 271 solution respectively. Polysaccharides extracted in water are composed of mannose (28%), glucose
 272 (16%), galactose (23%) xylose (2.1 %), arabinose (6.5%), galacturonic acid (2.25 %) and glucuronic
 273 acid (20%). The relative sugar composition of these polysaccharides is the same as for a typical GGM
 274 (Timell 1967). Indeed, in water 64 % of extracted sugars are GGMs. In 1M NaOH, the sugar
 275 composition of liquid extract is as follows: mannose (22%), glucose (11.3%), galactose (12%), xylose
 276 (38%), arabinose (10%) galacturonic acid (2.25 %) and glucuronic acid (20%). The increase in
 277 concentration of arabinose and xylose units at pH 13 suggests the release of arabino-(4-O-
 278 methylglucurono)xylans (ARX). Indeed, in 1M NaOH solution, approximately 50 % of extracted
 279 hemicelluloses are ARX and 35% of galactose-poor GGM. These results were in close agreement with
 280 those found by Thornton et al. 1994 who have found that at pH values above 10, arabino-(4-0-
 281 methylglucurono) xylans began to dissolve from the Norway spruce.

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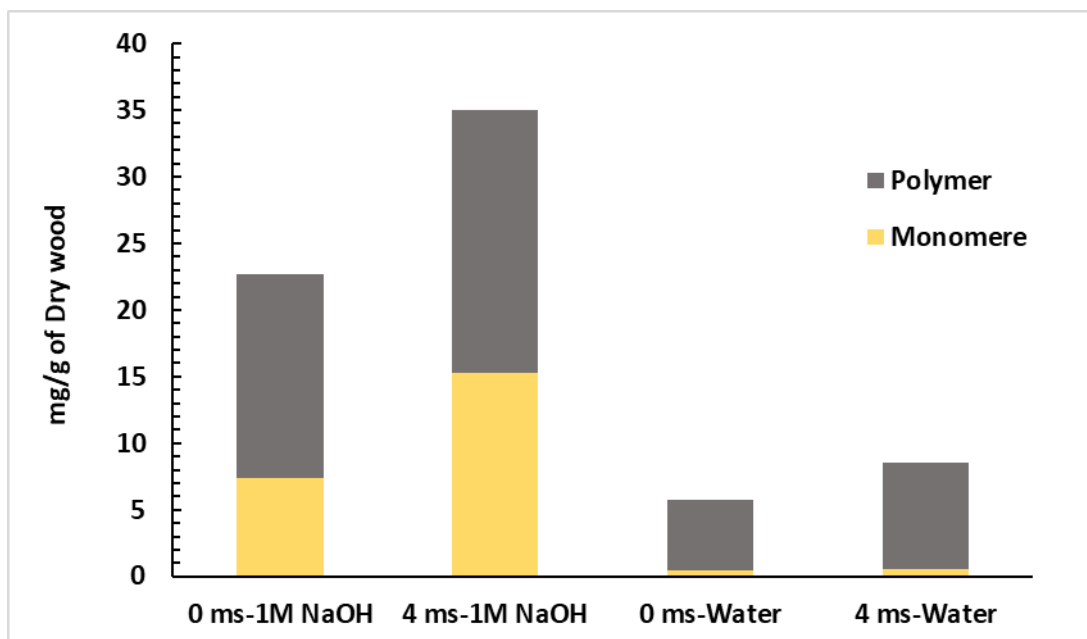
283



284 Fig. 2. Yield of extraction and sugar composition of extracted hemicelluloses versus HVED treatment
 285 time in (a) water and (b) 1M NaOH
 286

287 3.2 Extracted polymers

288 Fig.4 show the amount of polymers and monomers extracted in water and 1M NaOH solutions. About
 289 95% of extracted hemicelluloses in water are oligomers and polymers. It can be observed that the
 290 amount of monomers increased slightly when the HVED treatment duration increased. Extraction in
 291 1M NaOH shows an increase of the amount of monomers compared to the extraction in water. Indeed,
 292 about 70 % of the extracted hemicelluloses are polymers. The increase of the amount of monomers is
 293 assumed to be due to the depolymerization of hemicelluloses chains under alkaline conditions,
 294 especially by peeling reactions and saponification. The mild extraction conditions induced by HVED
 295 (temperature around 50 °C) limited the depolymerization of hemicelluloses chains.

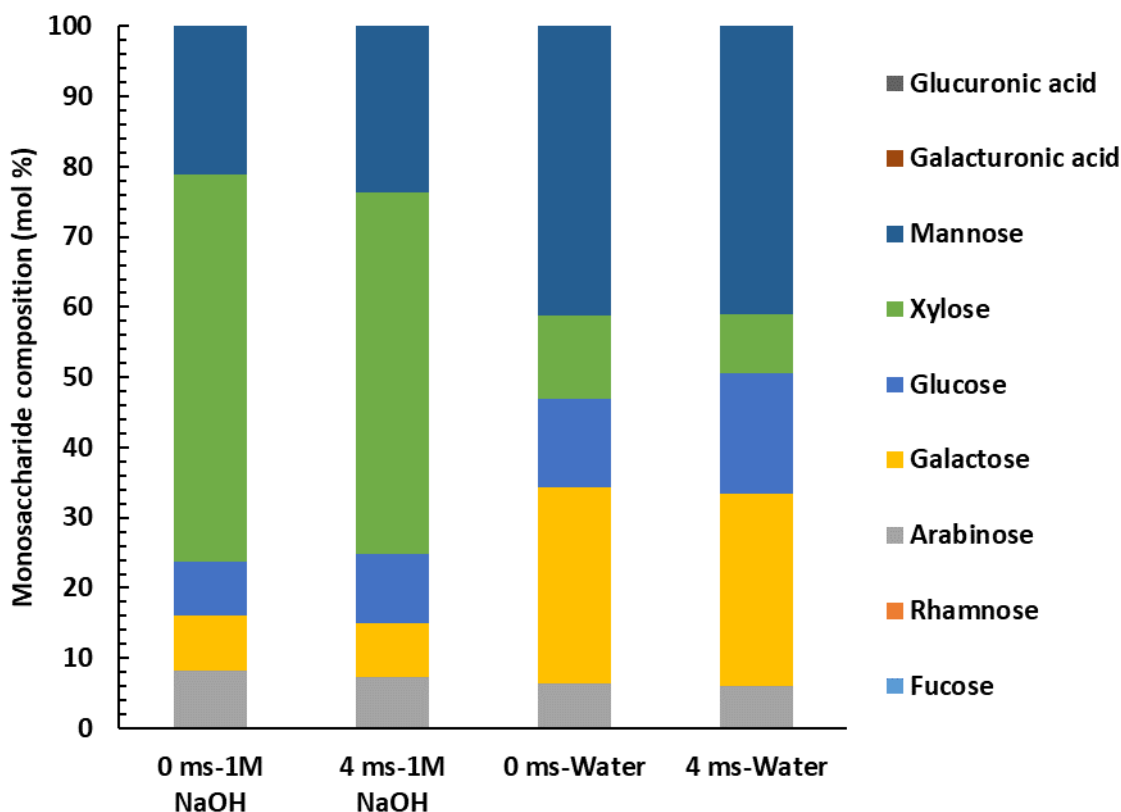


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297 **Fig.3.** Total monomers and polymers extracted versus HVED-treatment time in (a) water and (b) 1M
 298 NaOH solutions

299 **3.3 Characterization of the recovered hemicelluloses**

300 **Fig. 4** shows the sugar composition of hemicellulose powder obtained after precipitation of
 301 hemicellulose chains in water and 1M NaOH solution. As expected from the analyze of the liquid
 302 fraction, hemicelluloses extracted in 1M NaOH are rich with xylose ($\approx 60\%$), mannose ($\approx 20\%$) and
 303 arabinose ($\approx 8\%$). The fraction extracted in water is reach in mannose, galactose and glucose (40 %,
 304 27 % and 13 % respectively). The relative sugar composition of these polysaccharides is the same as
 305 for a spruce galactoglucomannans (Timell 1967). On the other hand, hemicelluloses extracted in 1M
 306 NaOH solution seem to be mainly composed of arabinoxylans. From these results, it is remarkable to
 307 note that the medium of extraction (pH) strongly affects the selectivity of the extraction (solubilization
 308 of hemicelluloses).



309

310 **Fig. 4.** Sugar composition of hemicellulose chains recovered in water and 1 M NaOH.

311 The average molecular weight (Mw) and molecular weight distribution of extracted hemicelluloses
 312 were determined by gel permeation chromatography (Table 1). With increasing the time of
 313 pretreatment by HVED, the average molecular weight of high molecular weight hemicelluloses
 314 increased. Pretreatment for 4 ms by HVED gave the highest Mw (55 kDa and 47 kDa in 1M NaOH
 315 solution and water respectively). As expected, the Mw of the extracted carbohydrates clearly increased
 316 with 1M NaOH solution compared to extraction in water.

317 The polydispersity index (PI) of hemicelluloses is also given in table 1. As shown in table 1, all
 318 hemicelluloses fractions show a moderate low polydispersity index (1.5-2.8), suggesting a chemical
 319 and structural homogeneity.

320

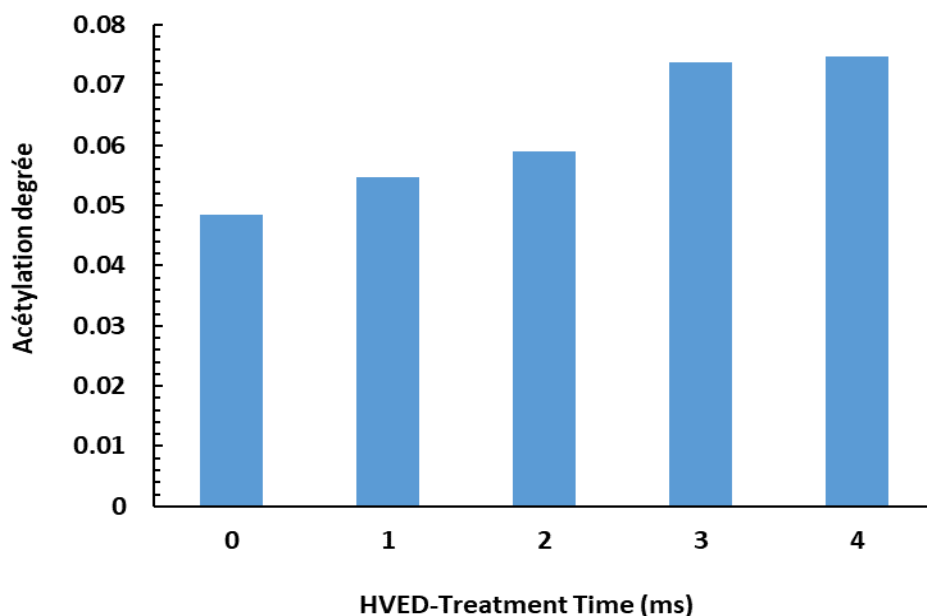
321

322 **Table.1** molecular weight distribution of recovered hemicelluloses

Time of HVED pretreatment	1M NaOH			Water		
	Mn (kDa)	Mw (kDa)	PI	Mn (kDa)	Mw (kDa)	PI
0 ms	28219	44775	1.58	16164	32959	2.03
1 ms	29289	50808	1.73	20700	36034	1.74
2 ms	27343	51808	1.89	19096	36950	1.93
3 ms	18411	51852	2.81	21041	42807	2.03
4 ms	21429	55464	2.58	24788	47662	1.92

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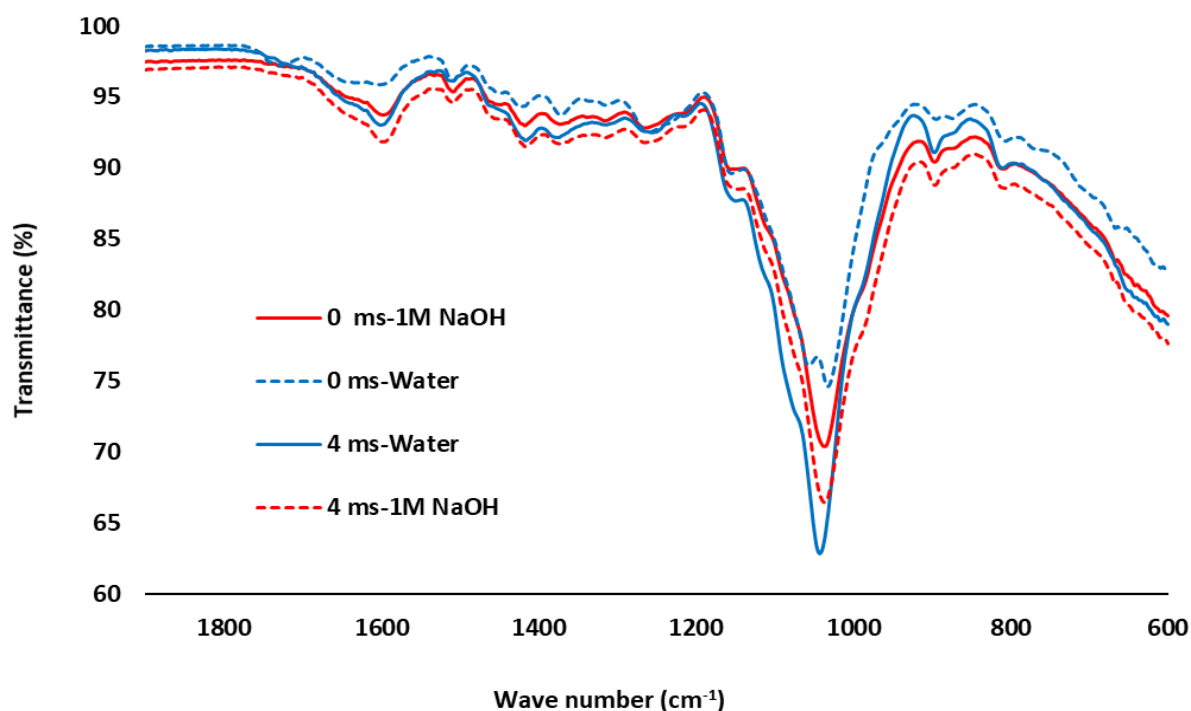
324 Deacetylation of hemicelluloses occurs principally during hot-water extraction (Song, Pranovich, and
325 Holmbom 2011) and by saponification during the extraction in basic solutions. At higher pH levels
326 Song et al., 2011 have found that deacetylation was very fast, thus decreasing the extraction of GGM.
327 The degree of acetylation is calculated as the molar Ac/Man ratio. As shown in **Fig. 6**, all extracted
328 hemicelluloses in water exhibited an acetylation degree (AD) in the range of 0.05-0.08, lower
329 compared to that of native GGM in spruce wood (0.45 -0.50) (Timell 1967). It can be observed from
330 Fig x that the AD increased with the increase of HVED pretreatment time. This observation can be
331 rationalized by a fragmentation and destruction of sawdust fibers induced by HVED pretreatment
332 promoting the extraction of acetyl-GGM. As expected, the AD is very low in hemicelluloses extracted
333 in 1M NaOH due to deacetylation by saponification reactions.



334

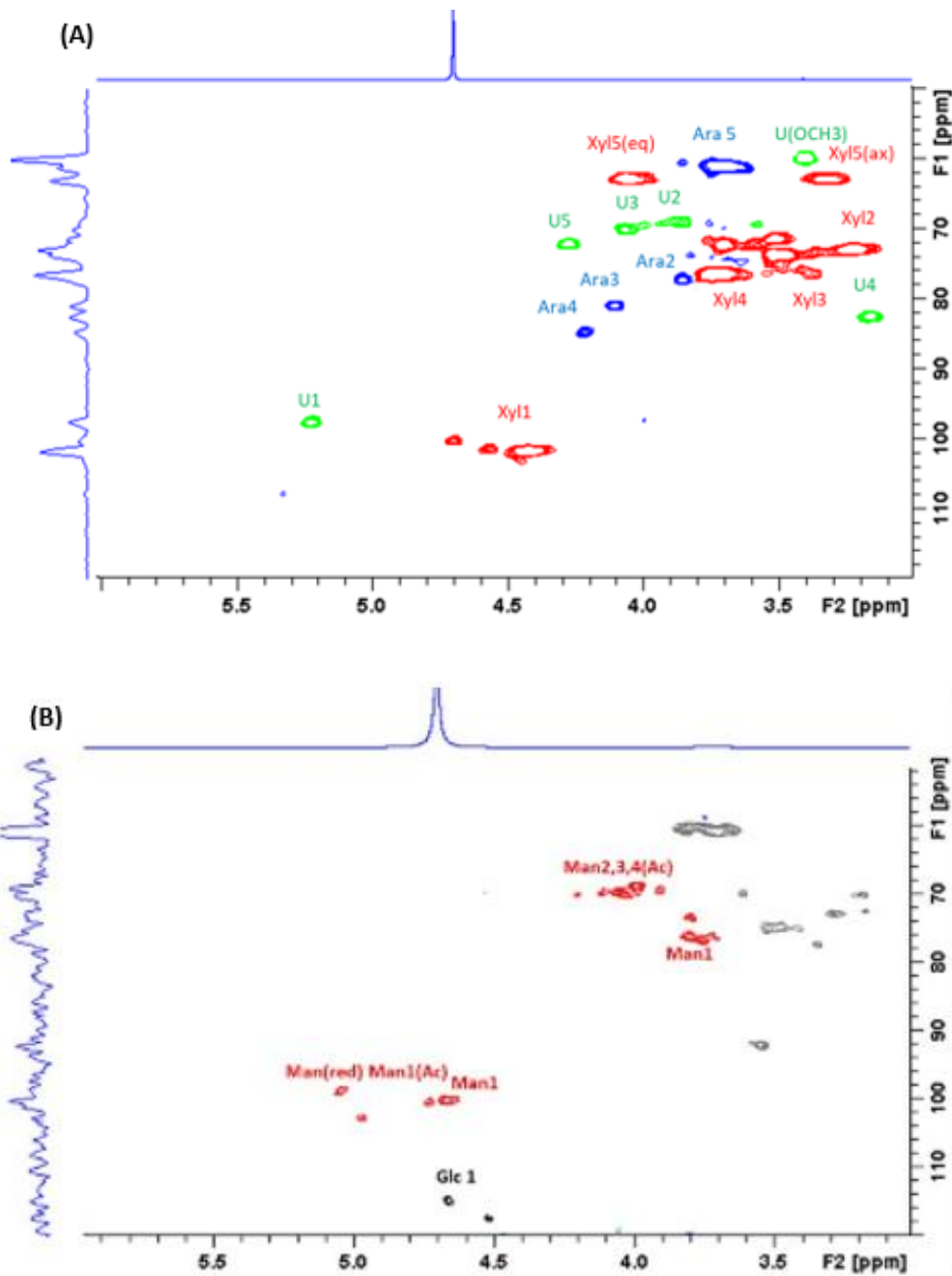
335 **Fig. 5.** Acetylation degree of extracted hemicelluloses in water after HVED pretreatment

336 The FTIR spectra of the extracted hemicelluloses shown in the **Fig. 6.** are in accordance to previous
 337 papers (Peng et al. 2009). The absorption at 1025 cm^{-1} , which is assigned to the C-O and C C
 338 stretching vibration and the glycosidic linkage (C-O-C) contributions in hemicelluloses (Peng et al.
 339 2009). The weak absorbances at 1735 and 1247 cm^{-1} are due to some acetyl groups attached to the
 340 hemicelluloses, particularly for 0 ms-Water and 4 ms-Water. These pics are absent in the fractions
 341 obtained in 1M NaOH solution (0 ms-1M NaOH and 4 ms-1M NaOH) confirming the deacetylation of
 342 hemicelluloses in basic media previously observed. Furthermore, the presense of the signal at 1506
 343 cm^{-1} in hemicellulosic fractions obtained in 1M NaOH is originated from the phenolic ring absorbance
 344 of lignin.



345
346 **Fig. 6.** FTIR spectra of extracted hemicelluloses in different conditions

347 ¹H-¹³C HSQC spectra clearly shows the typical signal pattern expected for the hemicellulosic moiety.
 348 The analysis confirms the extraction of arabinoxylans and acetyl-galactoglucomannans (**Figure 7 (A)**
 349 **and (B)** respectively). **In figure 7, (A)** The xylopyranosyl units of the hemicellulosic extract
 350 preparation (H3) produce signals at $\delta C/\delta H$ 102.2/4.33 (C1H), 63.6/3.94 and 3.23 (C5H2), 75.9/3.57
 351 (C4H), 74.4/3.31(C3H) and 73.1/3.10 (C2H) in the HSQC NMR spectrum, in which the two chemical
 352 shifts of 4 and 3.3 ppm are assigned to the equatorial and axial protons linked at C5, respectively.
 353 Xylan and arabinan signals, reveals that arabinoxylan was the major hemicellulose extracted in 1M
 354 NaOH solution. **In figure 7 (B)**, H1/C1 cross peaks assigned to galactose, glucose and mannose units
 355 are detected at 4.96/98.9 ppm, 4.58/104.4 ppm and 4.68/100.2 ppm respectively. Signals assigned to
 356 2-O-acetylated- β - Manp units are clearly observed at 4.87/99.0 ppm (H1/C1), 5.44/71.6 ppm (H2/C2),
 357 and the presence of 3-O-acetylated- β - Manp units is confirmed by correlation at 5.03/73.2 ppm
 358 (H3/C3), 4.75/99.9 ppm (H1/C1). These results confirm the previous conclusions drawn from the
 359 sugar composition of the recovered hemicelluloses powder and the liquid fraction (**Fig 2 and 4**
 360 **respectively**) about the high selectivity of extraction of hemicelluloses as a function of the pH of
 361 extraction.



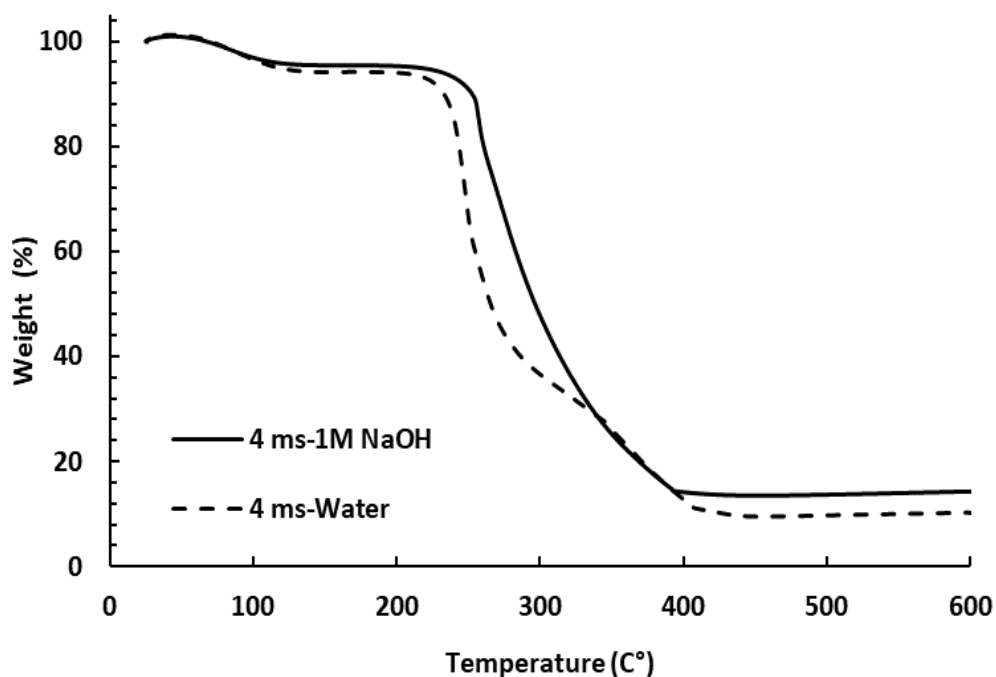
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364 **Fig. 7.** 2D HSQC NMR spectral analysis of extracted hemicelluloses in 1M NaOH (A) and Water (B)

365 TGA curves of hemicellulose fractions 4 ms-Water and 4 ms -1M NaOH are shown in Figure 8. As
 366 can be seen, the thermal decomposition of hemicelluloses can be divided into four phases. At the first
 367 step, the weight loss observed below 100 °C was attributed to moisture. At the second phase, 4 ms-
 368 Water began to decompose, and the maximum rate of weight loss was observed from 217 to 330 °C.
 369 Compared to 4 ms -1M NaOH, the weight loss mainly occurred between 250 and 335 °C. It was
 370 concluded that 4 ms-1M NaOH was thermally more stable at this phase. This higher thermal stability

371 can be attributed to their higher molecular weights (see table 1). Outstandingly, this thermal
372 decomposition process can be attributed to the cracking and abscission of C-C and C-O bonds
373 connected with the main branch of hemicelluloses, and the decarboxylation and decarbonylation may
374 also occur (Sun et al. 2013). The third phase involved a gradual loss in weight at temperature above
375 350 °C, which may be attributed to decomposition of cellulose and continued up to 400 °C. Since the
376 thermal and chemical condition during extraction of hemicelluloses are so mild??? (low temperature,
377 low decrease of pH). The presence of a very small quantities of cellulose in the extracted
378 hemicelluloses owing to the physical and electrical effect of HVED on the wood matrix. Which could
379 be due to the propagation of high-energy shock waves which could provoke the cleavage of the β -
380 glycosidic linkage. This observation is in accordance with Brahim et al. 2017, who found that HVED
381 induced a fragmentation of cellulose macromolecules from rapeseed straw mostly when HVED is
382 associated to the soda treatment. The fourth phase exhibited weight loss at a temperature above 400 °C
383 resulted from the decomposition of lignin. It is observed that a higher lignin content was co-extracted
384 in basic conditions (4 ms -1M NaOH).



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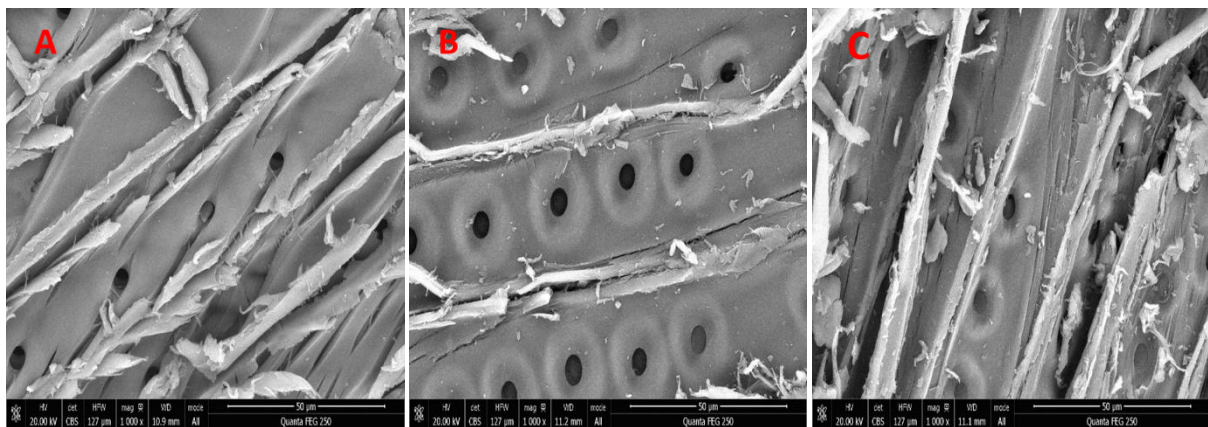
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Fig.8. Thermograms of hemicellulosic fractions

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388 **3.4 Scanning electron microscopy**

389 Fig. 9 shows the scanning electron micrographs of spruce sawdust pretreated by HVED which were
390 associated to the highest extraction yields. Fig. 9 (A and C) shows that the spruce fibers became
391 ragged and full of cracks due to the structural damage induced HVED. The surface images also
392 revealed a notable effect of sodium hydroxide on sawdust surface (Fig. 9. (C)), mainly due to the
393 removal of lignin and its precipitation. Therefore, the hemicellulose extraction increased with the
394 increase of HVED pretreatment time due to a better breakdown of polysaccharides-lignin matrix and
395 better accessibility to solvents. Similar observations have been reported in previous works by (Brahim
396 et al. 2016) who have associated enhancement in material accessibility to higher porosity degree
397 induced by to the propagation of shock waves and explosion of cavitation bubbles under HVED.



398
399 **Fig.9.** Scanning electron microscopy images of sawdust submitted to HVED pretreatment: (A) in 1M
400 NaOH solution, (C) in Water. And (b) untreated sawdust

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407 **4 Conclusion**

408 The extraction of high molecular weight hemicelluloses polymers from spruce sawdust induced by
409 HVED pretreatment was evaluated. The results have shown that HVED could be used as an alternative
410 technology for the extraction of hemicelluloses polymers. HVED have electrical and mechanical
411 effects on spruce sawdust caused by shock waves, which can disrupt the cellular walls, reduce the
412 particle size of wood and increase the overall mass transfer of the intracellular content. The effect of
413 HVED pretreatment could be enhanced by pH of extraction. The damage caused by HVED on spruce
414 sawdust fibers increases the accessibility and the penetration of the water into the wood matrix
415 promoting the hemicelluloses extraction at low temperature. These conditions prevent the decrease of
416 pH which is responsible for depolymerization of hemicelluloses chains and the degradation of
417 polysaccharides.

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430 **Acknowledgment**

431 This work was financially supported by SOFREN Company and ANRT “Agence National de la
432 Recherche et de la Technologie”. The authors appreciate the financial support from SOFREN and
433 ANRT. LERMAB is supported by the French National Research Agency through the Laboratory of
434 Excellence ARBRE (ANR-12- LABXARBRE-01).

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