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

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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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## 1. Introduction

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

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

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

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

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

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

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

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

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

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

## **2. Materials and methods**

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

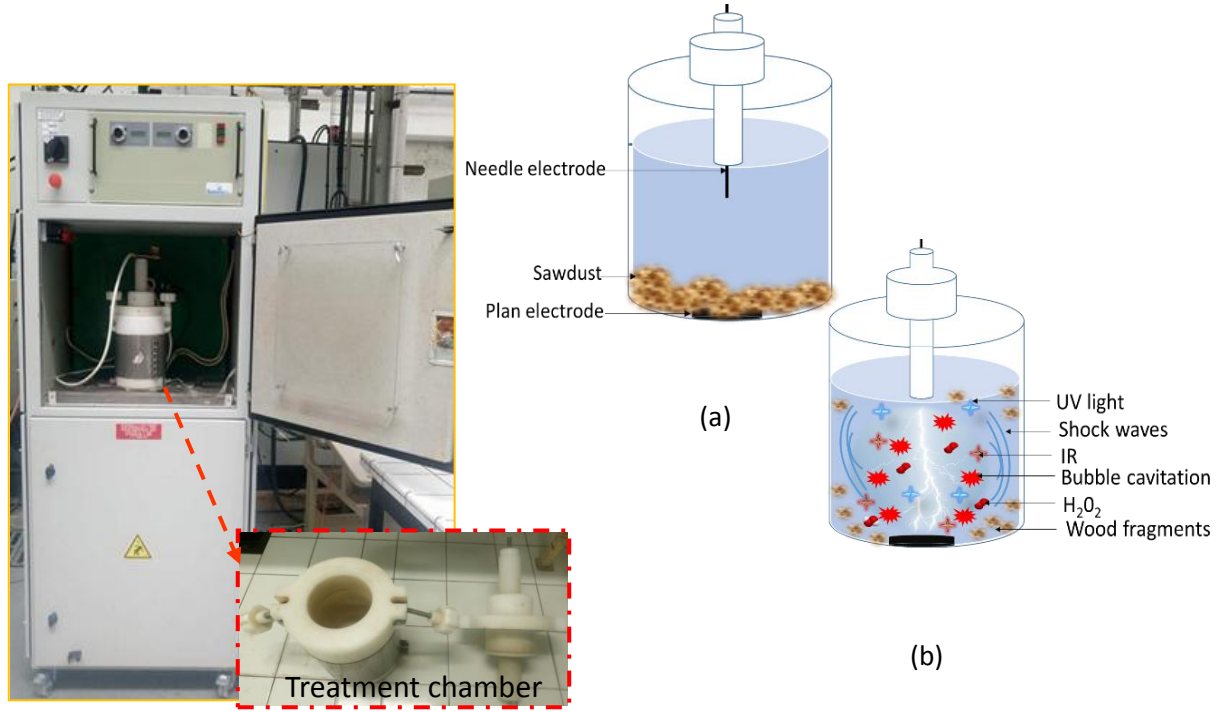
### **2.1 Raw material**

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

### **2.2 Extraction procedure**

#### **2.2.1 HVED pretreatment**

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



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

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

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

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

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

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

Where

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

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



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

### 1.2.2 Diffusion

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

### 1.2.3 Separation of extracted hemicelluloses

After each experiment, the extract was filtered on qualitative filter paper with retention particle size of 5–13 µm (VWR International, Fontenay-sous-Bois, France). The volume and end-pH of the extract solutions were measured at room temperature shortly after the extraction. The liquid fraction from 1M NaOH impregnated sawdust was neutralized to a pH of 5.5-6 by a solution of 72% H<sub>2</sub>SO<sub>4</sub>. 10 mL were taken from the filtered extract for analyses. The extract solution was concentrated by vacuum evaporation using a water bath at 50 °C. To precipitate high-molecular weight hemicelluloses, four volumes of 95% ethanol were added to the liquid extracts. The liquid phase was separated from the precipitated hemicelluloses by settling at room temperature and decantation. Hemicelluloses were further separated from the remaining liquid by centrifugation at 4000 rpm for 10 min at room temperature. The precipitated hemicelluloses were re-dissolved in distilled water and dialyzed with a dialysis membrane with a cut-off of 3.4 kDa (Spectrum Laboratories, Inc., Rancho Dominguez, CA, USA). Finally, dialyzed hemicelluloses solutions were freeze-dried.

## 1.3 Measurement of monosaccharides and uronic acids using HAPE-PAD

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

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

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

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

#### **1.5 FTIR**

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

#### **1.6 2D <sup>13</sup>C–<sup>1</sup>H HSQC NMR spectroscopy**

<sup>2</sup> H NMR and <sup>1</sup> H-<sup>13</sup>C correlation 2D NMR (HSQC) spectra were recorded on a Bruker III 400 MHz spectrometer equipped with a 5-mm BBFO probe. Experiment was conducted with 20 mg sample dissolved in 1 ml D<sub>2</sub>O. The number of collected complex points was 1024 for the <sup>1</sup>H-dimension with a relaxation of 1.5- and 256-time increments were recorded in <sup>13</sup>C-dimension. 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<sup>-1</sup> 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.

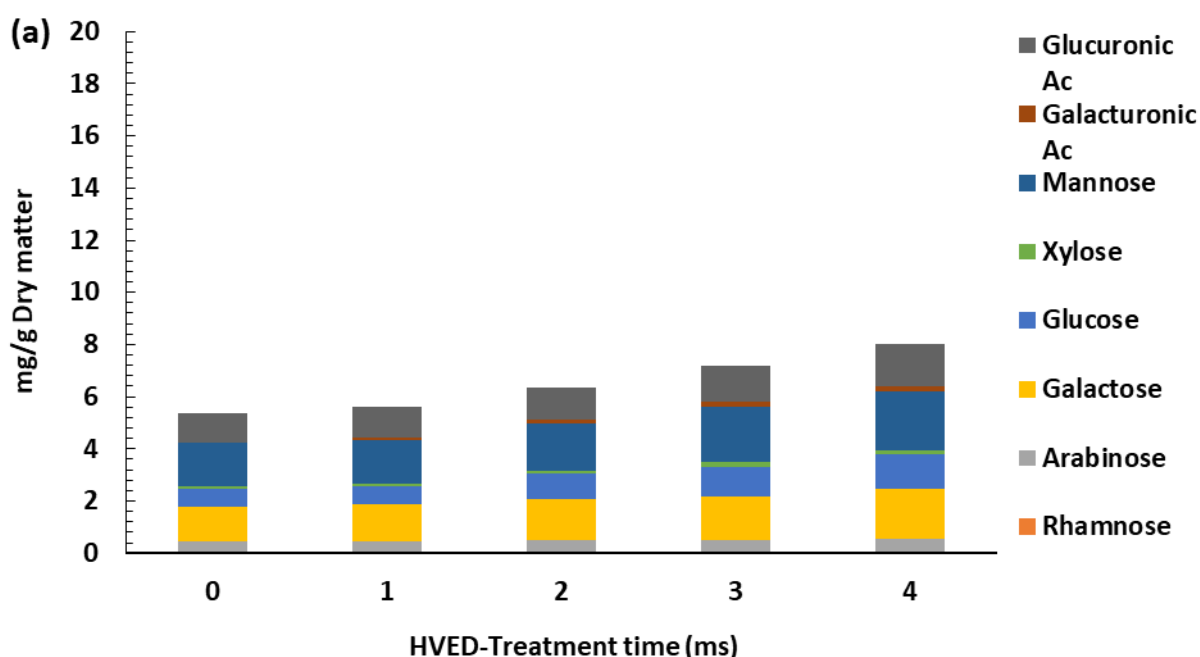
### 3 Results and discussion

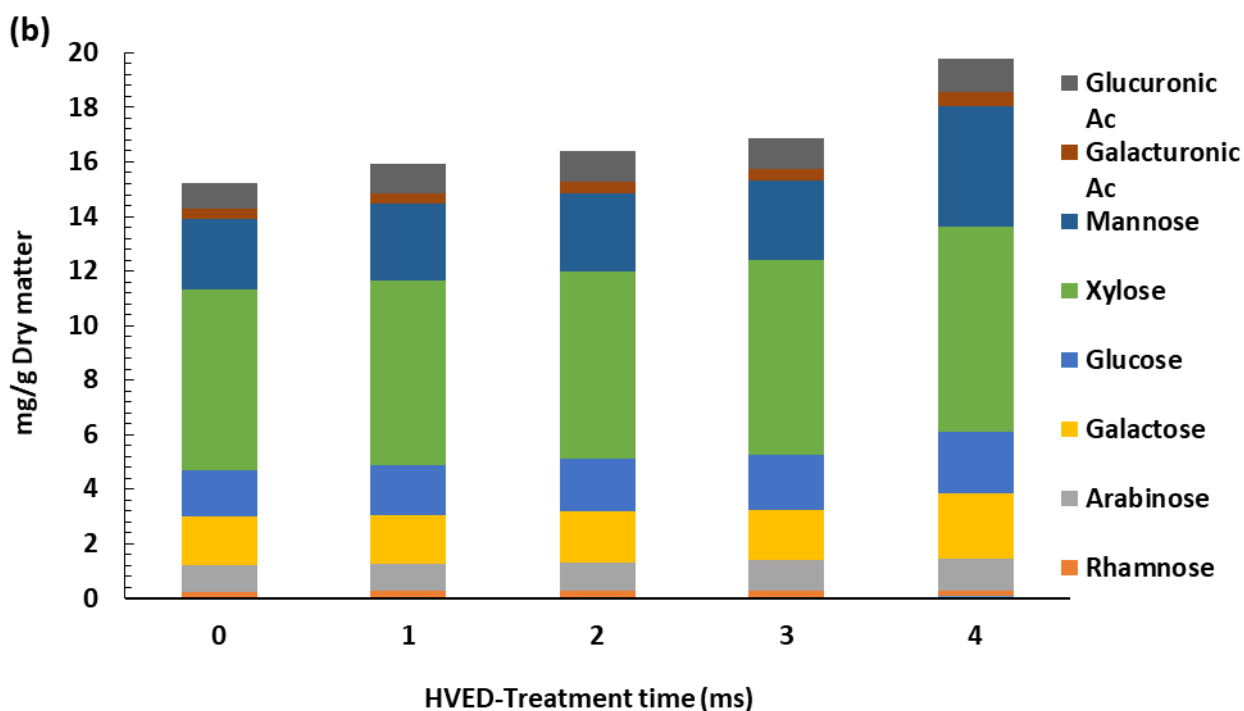
#### 3.1 Yield of hemicellulose extraction

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

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

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

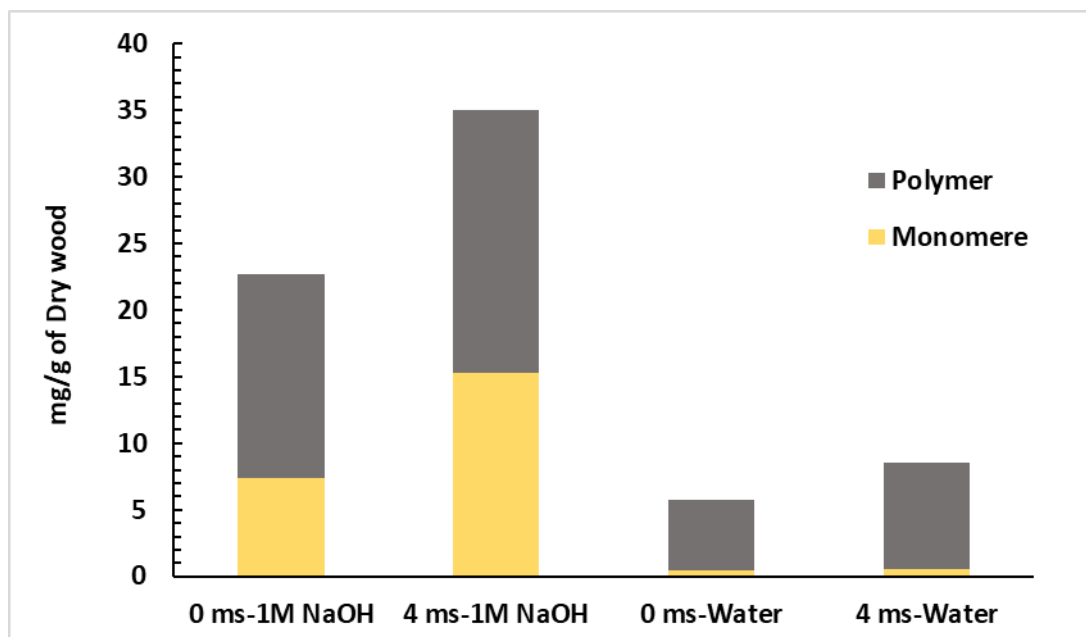




**Fig. 2.** Yield of extraction and sugar composition of extracted hemicelluloses versus HVED treatment time in (a) water and (b) 1M NaOH

### 3.2 Extracted polymers

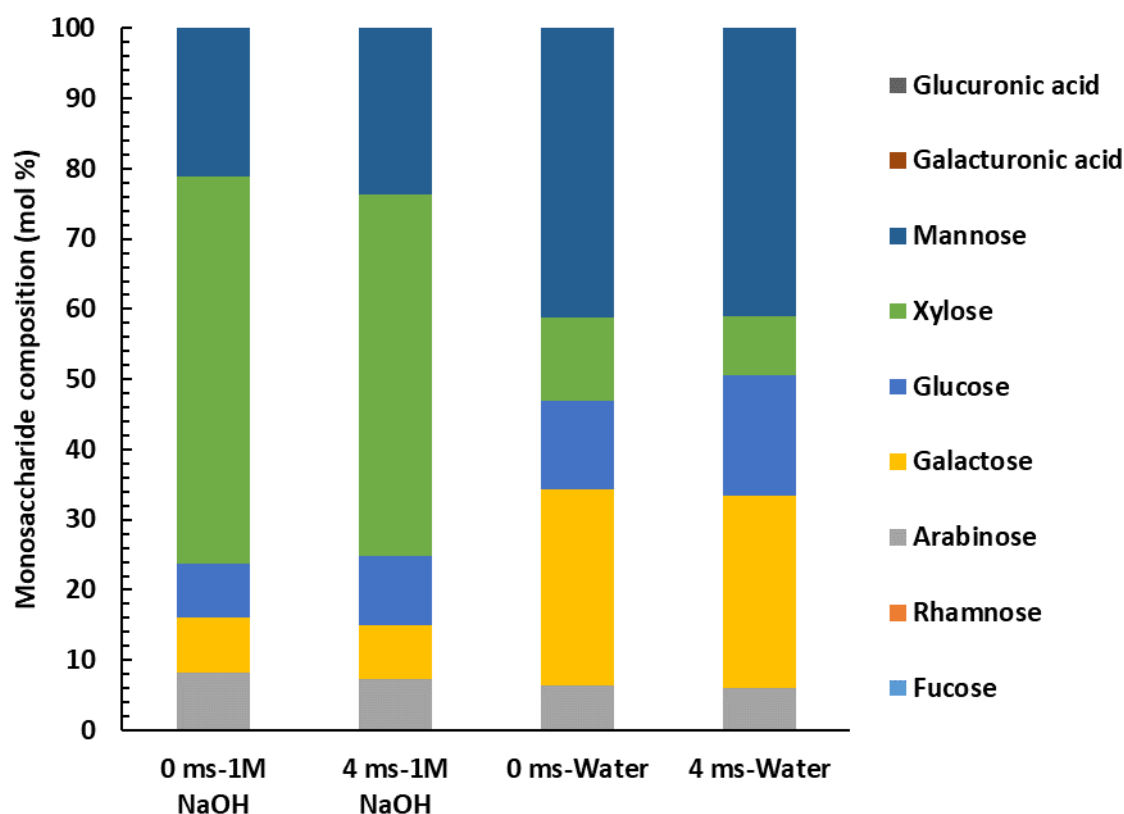
Fig.4 show the amount of polymers and monomers extracted in water and 1M NaOH solutions. About 95% of extracted hemicelluloses in water are oligomers and polymers ,. It can be observed that the amount of monomers increased slightly when the HVED treatment duration increased. Extraction in 1M NaOH shows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



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

### 3.3 Characterization of the recovered hemicelluloses

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



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

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

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

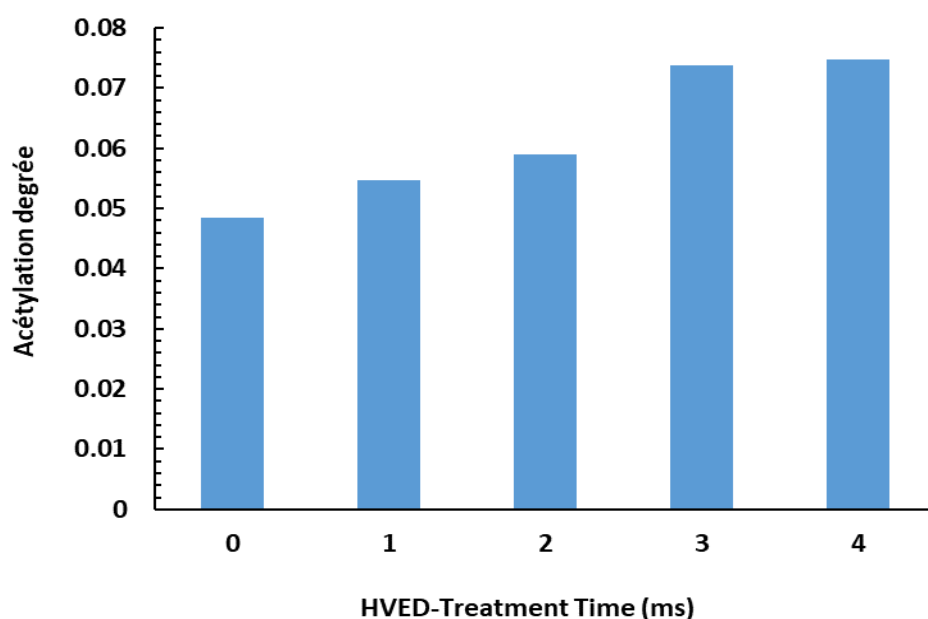
**Table.1** molecular weight distribution of recovered hemicelluloses



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

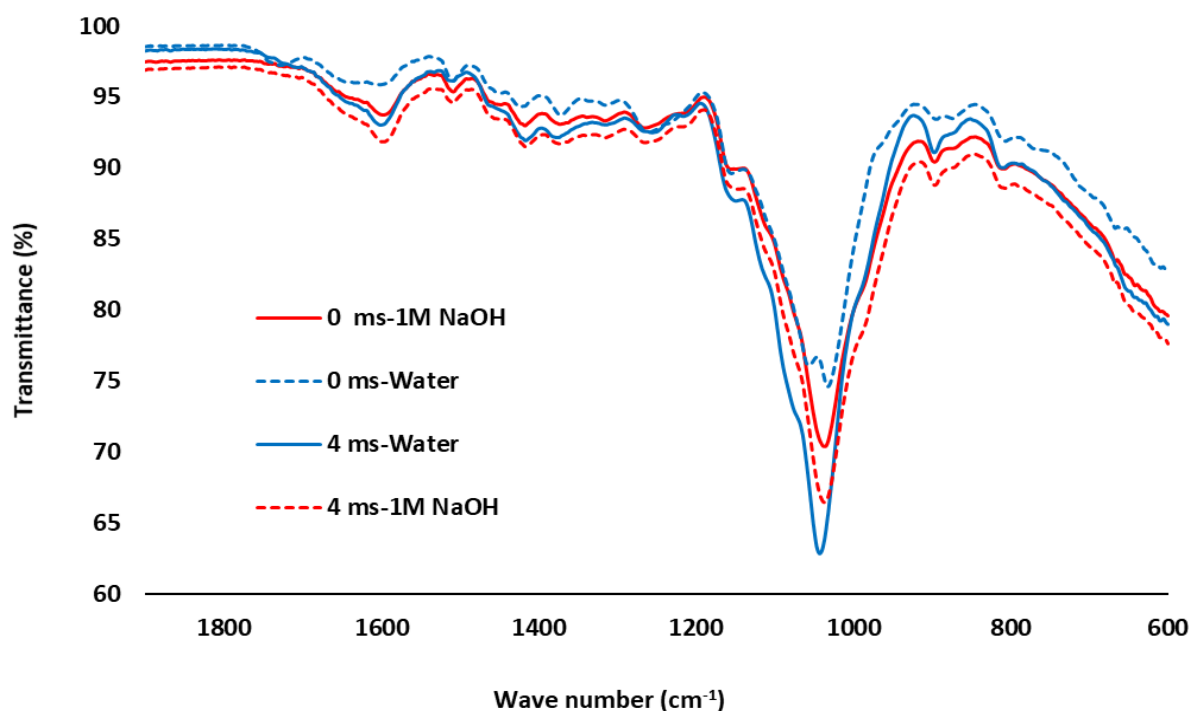
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324 Deacetylation of hemicelluloses occurs principally during hot-water extraction (Song, Pranovich, and  
325 Holmbom 2011) and by saponification during the extraction in basic solutions. At higher pH levels  
326 Song et al., 2011 have found that 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.



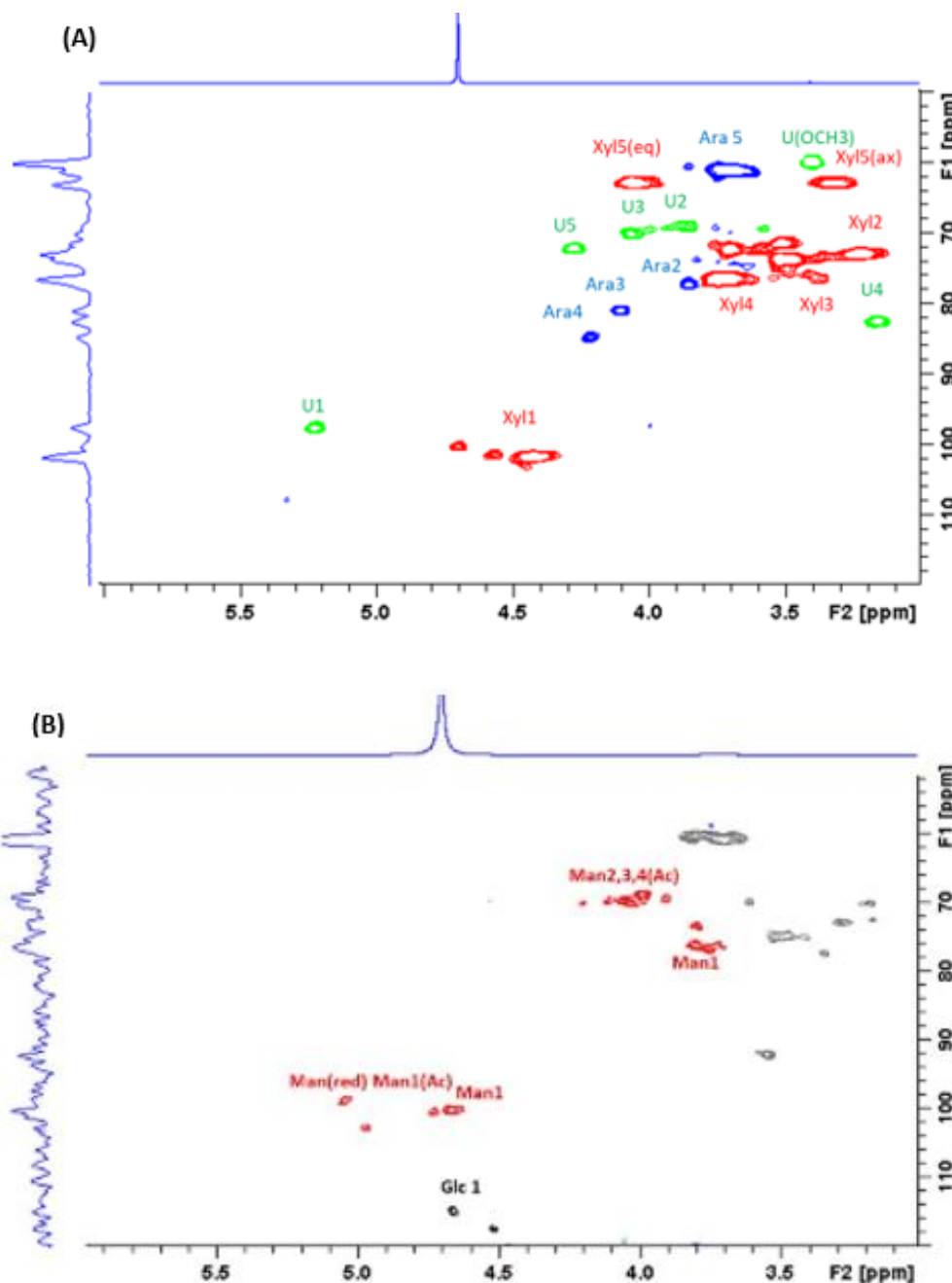
**Fig. 5.** Acetylation degree of extracted hemicelluloses in water after HVED pretreatment

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



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

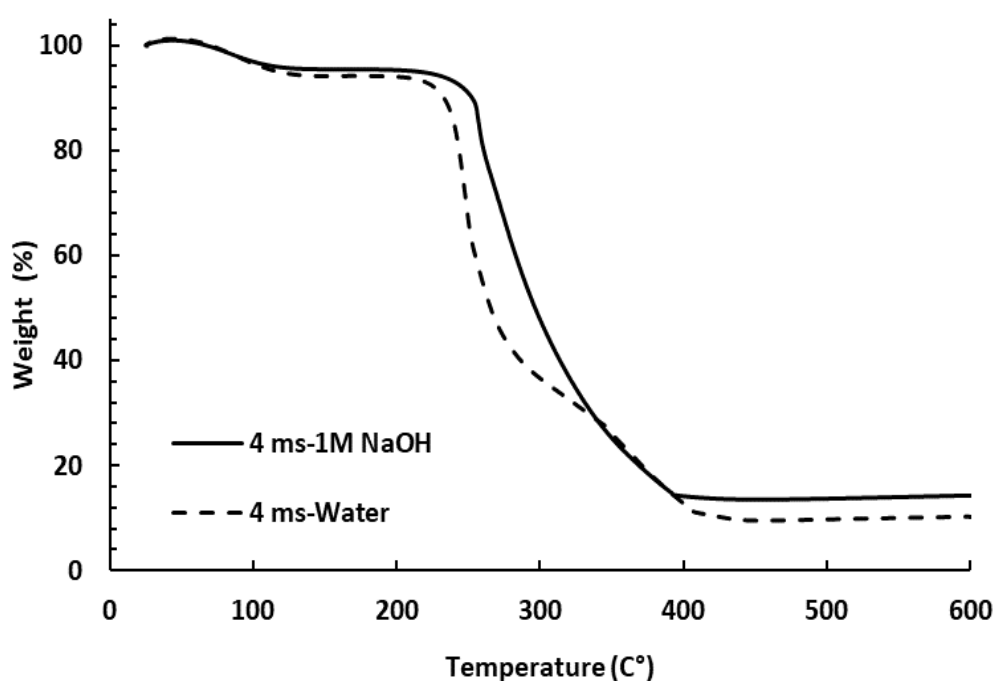
<sup>1</sup>H-<sup>13</sup>C HSQC spectra clearly shows the typical signal pattern expected for the hemicellulosic moiety. The analysis confirms the extraction of arabinoxylans and acetyl-galactoglucomannans (**Figure 7 (A) and (B)** respectively). In **figure 7, (A)** The xylopyranosyl units of the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



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

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

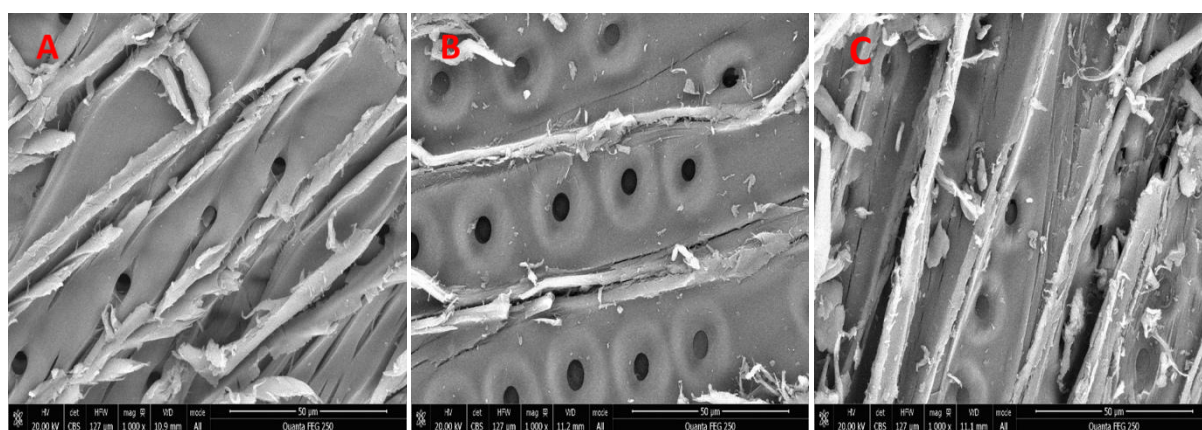
can be attributed to their higher molecular weights (see table 1). Outstandingly, this thermal decomposition process can be attributed to the cracking and abscission of C-C and C-O bonds connected with the main branch of hemicelluloses, and the decarboxylation and decarbonylation may also occur (Sun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



**Fig.8.** Thermograms of hemicellulosic fractions

### 3.4 Scanning electron microscopy

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



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

#### 4 Conclusion

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

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## References:

- Adda, P., N. Boussetta, O. Lesaint, and E. Vorobiev. 2016. "High-Voltage Electrical Discharge Assisted Extraction of Phenolic Compounds from Grape Seeds." *Handbook of Electroporation*, 1–26.
- Alvarez-Vasco, Carlos, and Xiao Zhang. 2013. "Alkaline Hydrogen Peroxide Pretreatment of Softwood: Hemicellulose Degradation Pathways." *Bioresource Technology* 150 (December): 321–27. <https://doi.org/10.1016/j.biortech.2013.10.020>.
- Alvira, P., E. Tomás-Pejó, M. Ballesteros, and M. J. Negro. 2010. "Pretreatment Technologies for an Efficient Bioethanol Production Process Based on Enzymatic Hydrolysis: A Review." *Bioresource Technology*, Special Issue on Lignocellulosic Bioethanol: Current Status and Perspectives, 101 (13): 4851–61. <https://doi.org/10.1016/j.biortech.2009.11.093>.
- Anugwom, I., P. Mäki-Arvela, P. Virtanen, S. Willför, R. Sjöholm, and J. -P. Mikkola. 2012. "Selective Extraction of Hemicelluloses from Spruce Using Switchable Ionic Liquids." *Carbohydrate Polymers* 87 (3): 2005–11. <https://doi.org/10.1016/j.carbpol.2011.10.006>.
- Bai, Likun, Hui ren Hu, and Jianfeng Xu. 2012. "Influences of Configuration and Molecular Weight of Hemicelluloses on Their Paper-Strengthening Effects." *Carbohydrate Polymers* 88 (4): 1258–63. <https://doi.org/10.1016/j.carbpol.2012.02.002>.
- Boussetta, N., M. Turk, C. De Taeye, Y. Larondelle, J. L. Lanoisellé, and E. Vorobiev. 2013. "Effect of High Voltage Electrical Discharges, Heating and Ethanol Concentration on the Extraction of Total Polyphenols and Lignans from Flaxseed Cake." *Industrial Crops and Products* 49 (August): 690–96. <https://doi.org/10.1016/j.indcrop.2013.06.004>.
- Boussetta, N., E. Vorobiev, T. Reess, A. De Ferron, L. Pecastaing, R. Ruscassié, and J. -L. Lanoisellé. 2012. "Scale-up of High Voltage Electrical Discharges for Polyphenols Extraction from Grape Pomace: Effect of the Dynamic Shock Waves." *Innovative Food Science & Emerging Technologies* 16 (October): 129–36. <https://doi.org/10.1016/j.ifset.2012.05.004>.
- Boussetta, Nadia. 2010. *Intensification de l'extraction Des Polyphénols Par Électrotechnologies Pour La Valorisation Des Marcs de Champagne*. Compiègne. <http://www.theses.fr/2010COMP1899>.

478 Boussetta, Nadia, Jean-Louis Lanoisellé, Catherine Bedel-Cloutour, and Eugène Vorobiev. 2009.  
 479 “Extraction of Soluble Matter from Grape Pomace by High Voltage Electrical Discharges for  
 480 Polyphenol Recovery: Effect of Sulphur Dioxide and Thermal Treatments.” *Journal of Food*  
 481 *Engineering* 95 (1): 192–98. <https://doi.org/10.1016/j.jfoodeng.2009.04.030>.

482 Boussetta, Nadia, and Eugène Vorobiev. 2014. “Extraction of Valuable Biocompounds Assisted by  
 483 High Voltage Electrical Discharges: A Review.” *Comptes Rendus Chimie, Green extraction of*  
 484 *natural products (GENP2013)*, 17 (3): 197–203. <https://doi.org/10.1016/j.crci.2013.11.011>.

485 Brahim, M., B. L. Checa Fernandez, O. Regnier, N. Boussetta, N. Grimi, C. Sarazin, E. Husson, E.  
 486 Vorobiev, and N. Brosse. 2017. “Impact of Ultrasounds and High Voltage Electrical  
 487 Discharges on Physico-Chemical Properties of Rapeseed Straw’s Lignin and Pulps.”  
 488 *Bioresource Technology*, 1st International Conference on Bioresource Technology for  
 489 *Bioenergy, Bioproducts & Environmental Sustainability (BIORESTEC)*, 237 (August): 11–  
 490 19. <https://doi.org/10.1016/j.biortech.2017.04.003>.

491 Brahim, M., S. El Kantar, N. Boussetta, N. Grimi, N. Brosse, and E. Vorobiev. 2016. “Delignification  
 492 of Rapeseed Straw Using Innovative Chemo-Physical Pretreatments.” *Biomass and Bioenergy*  
 493 95 (December): 92–98. <https://doi.org/10.1016/j.biombioe.2016.09.019>.

494 Capek, P., M. Kubacková, J. Alföldi, L. Bilisics, D. Lisková, and D. Kákoniová. 2000.  
 495 “Galactoglucomannan from the Secondary Cell Wall of *Picea Abies* L. Karst.” *Carbohydrate*  
 496 *Research* 329 (3): 635–45.

497 Casebier, R. L., J. K. Hamilton, and H. L. Hergert. 1969. “Chemistry and Mechanism of Water  
 498 Prehydrolysis on Southern Pine Wood.” *Tappi Tech Ass Pulp Pap Indus.*  
 499 <http://agris.fao.org/agris-search/search.do?recordID=US201301228941>.

500 Curling, S. F., P. A. Fowler, and C. A. S. Hill. 2007. “Development of a Method for the Production of  
 501 Hemicellulosic Gels from Sitka Spruce.” *Carbohydrate Polymers* 69 (4): 673–77.  
 502 <https://doi.org/10.1016/j.carbpol.2007.02.003>.

503 El Kantar, Sally, Nadia Boussetta, Hiba N. Rajha, Richard G. Maroun, Nicolas Louka, and Eugène  
 504 Vorobiev. 2018. “High Voltage Electrical Discharges Combined with Enzymatic Hydrolysis

for Extraction of Polyphenols and Fermentable Sugars from Orange Peels.” *Food Research International* 107 (May): 755–62. <https://doi.org/10.1016/j.foodres.2018.01.070>.

Gabrielii, I, P Gatenholm, W. G Glasser, R. K Jain, and L Kenne. 2000. “Separation, Characterization and Hydrogel-Formation of Hemicellulose from Aspen Wood.” *Carbohydrate Polymers* 43 (4): 367–74. [https://doi.org/10.1016/S0144-8617\(00\)00181-8](https://doi.org/10.1016/S0144-8617(00)00181-8).

Gallina, Gianluca, Álvaro Cabeza, Henrik Grénman, Pierdomenico Biasi, Juan García-Serna, and Tapio Salmi. 2017. “Hemicellulose Extraction by Hot Pressurized Water Pretreatment at 160oC for 10 Different Woods: Yield and Molecular Weight.” *The Journal of Supercritical Fluids*, October. <https://doi.org/10.1016/j.supflu.2017.10.001>.

Grimi, N., N. I. Lebovka, E. Vorobiev, and J. Vaxelaire. 2009. “Effect of a Pulsed Electric Field Treatment on Expression Behavior and Juice Quality of Chardonnay Grape.” *Food Biophysics* 4 (3): 191–98.

Gulbrandsen, Torea A., Ingvild A. Johnsen, Mihaela Tanase Opedal, Kai Toven, K. Øyaas, Andrey Pranovich, Jyri-Pekka Mikkola, and Bard H. Hoff. 2015. “Extracting Hemicelluloses from Softwood and Bagasse as Oligosaccharides Using Pure Water and Microwave Heating.” *Cell. Chem. Tech* 49 (2): 117–126.

Hartman, Jonas, Ann-Christine Albertsson, Margaretha Söderqvist Lindblad, and John Sjöberg. 2006. “Oxygen Barrier Materials from Renewable Sources: Material Properties of Softwood Hemicellulose-Based Films.” *Journal of Applied Polymer Science* 100 (4): 2985–91. <https://doi.org/10.1002/app.22958>.

Hartman, Jonas, Ann-Christine Albertsson, and John Sjöberg. 2006. “Surface- and Bulk-Modified Galactoglucomannan Hemicellulose Films and Film Laminates for Versatile Oxygen Barriers.” *Biomacromolecules* 7 (6): 1983–89. <https://doi.org/10.1021/bm060129m>.

Krogell, Jens, Ekaterina Korotkova, Kari Eränen, Andrey Pranovich, Tapio Salmi, Dmitry Murzin, and Stefan Willför. 2013. “Intensification of Hemicellulose Hot-Water Extraction from Spruce Wood in a Batch Extractor – Effects of Wood Particle Size.” *Bioresource Technology* 143 (Supplement C): 212–20. <https://doi.org/10.1016/j.biortech.2013.05.110>.

532 Lindqvist, Hanna, Jessica Holmback, Ari Rosling, Kristian Salminen, Bjarne Holmbom, Markku Auer,  
 533 and Anna Sundberg. 2013. "Galactoglucomannan Derivatives and Their Application in  
 534 Papermaking." *BioResources* 8 (1): 994–1010. <https://doi.org/10.15376/biores.8.1.994-1010>.  
 535 Loginova, K. V., M. V. Shynkaryk, N. I. Lebovka, and E. Vorobiev. 2010. "Acceleration of Soluble  
 536 Matter Extraction from Chicory with Pulsed Electric Fields." *Journal of Food Engineering* 96  
 537 (3): 374–79. <https://doi.org/10.1016/j.jfoodeng.2009.08.009>.  
 538 Lundqvist, Jon, Anita Teleman, Linda Junel, Guido Zacchi, Olof Dahlman, Folke Tjerneld, and Henrik  
 539 Stålbrand. 2002. "Isolation and Characterization of Galactoglucomannan from Spruce (*Picea*  
 540 *Abies*)." *Carbohydrate Polymers* 48 (1): 29–39. [https://doi.org/10.1016/S0144-](https://doi.org/10.1016/S0144-8617(01)00210-7)  
 541 [8617\(01\)00210-7](https://doi.org/10.1016/S0144-8617(01)00210-7).  
 542 Mikkonen, Kirsi S., Heikkilä, Mari I., Willf, Stefan M. R., Maija Tenkanen, Kirsi S.  
 543 Mikkonen, et al. 2012. "Films from Glyoxal-Crosslinked Spruce Galactoglucomannans  
 544 Plasticized with Sorbitol, Films from Glyoxal-Crosslinked Spruce Galactoglucomannans  
 545 Plasticized with Sorbitol." *International Journal of Polymer Science, International Journal of*  
 546 *Polymer Science* 2012, 2012 (January): e482810. <https://doi.org/10.1155/2012/482810>,  
 547 [10.1155/2012/482810](https://doi.org/10.1155/2012/482810).  
 548 Mikkonen, Kirsi S., Mari I. Heikkilä, Harry Helén, Lea Hyvönen, and Maija Tenkanen. 2010. "Spruce  
 549 Galactoglucomannan Films Show Promising Barrier Properties." *Carbohydrate Polymers* 79  
 550 (4): 1107–12. <https://doi.org/10.1016/j.carbpol.2009.10.049>.  
 551 Mikkonen, Kirsi S., and Maija Tenkanen. 2012. "Sustainable Food-Packaging Materials Based on  
 552 Future Biorefinery Products: Xylans and Mannans." *Trends in Food Science & Technology*,  
 553 Special Section: Food Integrity and Traceability, 28 (2): 90–102.  
 554 <https://doi.org/10.1016/j.tifs.2012.06.012>.  
 555 NREL/TP-510-42618, B. Hames, R. Ruiz-Peinado, C. Scarlata, W. J. Sluiter, D. Templaton, A. D.  
 556 Crocker, and M. D. Sluiter. 2010. "Determination of Structural Carbohydrates and Lignin in  
 557 Biomass, Technical Report NREL/TP-510-42618, National Renewable Energy Laboratory,  
 558 Golden, CO," January. [https://www.scienceopen.com/document?vid=a3e04a5d-b049-4506-](https://www.scienceopen.com/document?vid=a3e04a5d-b049-4506-9739-b0c71a39b992)  
 559 [9739-b0c71a39b992](https://www.scienceopen.com/document?vid=a3e04a5d-b049-4506-9739-b0c71a39b992).

560 Palm, Magnus, and Guido Zacchi. 2003. "Extraction of Hemicellulosic Oligosaccharides from Spruce  
561 Using Microwave Oven or Steam Treatment." *Biomacromolecules* 4 (3): 617–23.  
562 <https://doi.org/10.1021/bm020112d>.

563 Peng, Feng, Jun-Li Ren, Feng Xu, Jing Bian, Pai Peng, and Run-Cang Sun. 2009. "Comparative Study  
564 of Hemicelluloses Obtained by Graded Ethanol Precipitation from Sugarcane Bagasse." *Journal of Agricultural and Food Chemistry* 57 (14): 6305–17.  
565 <https://doi.org/10.1021/jf900986b>.

567 Rajha, Hiba N., Nadia Boussetta, Nicolas Louka, Richard G. Maroun, and Eugene Vorobiev. 2014. "A  
568 Comparative Study of Physical Pretreatments for the Extraction of Polyphenols and Proteins  
569 from Vine Shoots." *Food Research International, Recovery and Utilization of Valuable  
570 Compounds from Food Processing By-products*, 65 (November): 462–68.  
571 <https://doi.org/10.1016/j.foodres.2014.04.024>.

572 Sarkis, Júlia Ribeiro, Nadia Boussetta, Christelle Blouet, Isabel Cristina Tessaro, Ligia Damasceno  
573 Ferreira Marczak, and Eugène Vorobiev. 2015. "Effect of Pulsed Electric Fields and High  
574 Voltage Electrical Discharges on Polyphenol and Protein Extraction from Sesame Cake." *Innovative Food Science & Emerging Technologies, APPLICATIONS OF PEF FOR FOOD  
575 PROCESSING*, 29 (May): 170–77. <https://doi.org/10.1016/j.ifset.2015.02.011>.

577 Song, Tao, Andrey Pranovich, and Bjarne Holmbom. 2011. "Effects of PH Control with Phthalate  
578 Buffers on Hot-Water Extraction of Hemicelluloses from Spruce Wood." *Bioresource  
579 Technology* 102 (22): 10518–23. <https://doi.org/10.1016/j.biortech.2011.08.093>.

580 ———. 2012. "HOT-WATER EXTRACTION OF GROUND SPRUCE WOOD OF DIFFERENT  
581 PARTICLE SIZE." *BioResources* 7 (3): 4214–25. [https://doi.org/10.15376/biores.7.3.4214-  
582 4225](https://doi.org/10.15376/biores.7.3.4214-4225).

583 Song, Tao, Andrey Pranovich, Ivan Sumerskiy, and Bjarne Holmbom. 2008. "Extraction of  
584 Galactoglucomannan from Spruce Wood with Pressurised Hot Water." *Holzforschung* 62 (6):  
585 659–666. <https://doi.org/10.1515/HF.2008.131>.

- Sun, Shao-Long, Jia-Long Wen, Ming-Guo Ma, and Run-Cang Sun. 2013. "Successive Alkali Extraction and Structural Characterization of Hemicelluloses from Sweet Sorghum Stem." *Carbohydrate Polymers* 92 (2): 2224–31. <https://doi.org/10.1016/j.carbpol.2012.11.098>.
- Timell, T. E. 1967. "Recent Progress in the Chemistry of Wood Hemicelluloses." *Wood Science and Technology* 1 (1): 45–70. <https://doi.org/10.1007/BF00592255>.
- Wen, L.f., K.c. Chang, G. Brown, and D.d. Gallaher. 1988. "Isolation and Characterization of Hemicellulose and Cellulose from Sugar Beet Pulp." *Journal of Food Science* 53 (3): 826–29. <https://doi.org/10.1111/j.1365-2621.1988.tb08963.x>.
- Willför, Stefan, Kenneth Sundberg, Maija Tenkanen, and Bjarne Holmbom. 2008. "Spruce-Derived Mannans – A Potential Raw Material for Hydrocolloids and Novel Advanced Natural Materials." *Carbohydrate Polymers* 72 (2): 197–210. <https://doi.org/10.1016/j.carbpol.2007.08.006>.
- Yan, Liang-Gong, Yong Deng, Ting Ju, Kejiang Wu, and Jun Xi. 2018. "Continuous High Voltage Electrical Discharge Extraction of Flavonoids from Peanut Shells Based on 'Annular Gap Type' Treatment Chamber." *Food Chemistry* 256 (August): 350–57. <https://doi.org/10.1016/j.foodchem.2018.02.129>.