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## Microwave-assisted extraction of high-molecular-weight hemicelluloses from spruce wood

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1                   **MICROWAVE ASSISTED EXTRACTION OF HIGH MOLECULAR WEIGHT**  
2                   **HEMICELLULOSES FROM SPRUCE WOOD**  
3                   **EXTRACTION ASSISTEE PAR MICRO-ONDES DES HEMICELLULOSES DE HAUTS**  
4                   **POIDS MOLECULAIRES A PARTIR D'EPICEA DE BOIS**

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26

27 **Abbreviations**

28	<b>Ac-GGM</b>	Acetyl-Galactoglucomannan
29	<b>ARX</b>	Arabinoglucoronoxylan
30	<b>DW</b>	Dry wood
31	<b>kDa</b>	kilo Dalton
32	<b>FTIR</b>	Fourier Transform InfraRed
33	<b>GGM</b>	Galactoglucomannans
34	<b>HMF</b>	Hydroxymethylfurfural
35	<b>HPLC</b>	High performance liquid chromatography
36	<b>M</b>	Mole
37	<b>MAE</b>	Microwave Assisted Extraction
38	<b>Mw</b>	Molecular weight average
39	<b>NREL/TP</b>	National Renewable Energy Laboratory/ Technical Report
40	<b>PD</b>	Polymerization degree
41	<b>W</b>	Watts
42	<b>PDI</b>	Polydispersity index

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48 **Abstract**

49 Microwave assisted extraction (MAE) at atmospheric pressure has been demonstrated as an efficient  
50 technology for the extraction of polymeric hemicelluloses from spruce sawdust. This technology was  
51 shown to be more efficient than conventional extraction. MAE leads to a high solubilization of wood  
52 and a selective extraction of hemicelluloses polymers with high molecular weights. To optimize MAE,  
53 different treatments power (125-573W) for a period of 60 min of a pre-soaked spruce sawdust in water  
54 and 1M sodium hydroxide solution were tested. The yield of hemicellulose extraction increased with  
55 the microwave power in both mediums, but with a clear advantage for pre-soaked samples in basic  
56 medium. The characterization of extracted hemicelluloses has shown a high extraction selectivity  
57 depending on the medium of impregnation of sawdust before MAE: high molecular mass acetylated  
58 galactoglucomannans ( $M_w \sim 41$  kDa) were isolated after a pre-soaking in water and higher molecular  
59 mass arabinoglucoronoxylans ( $M_w \sim 66$  kDa) in basic medium.

60 **Key words:** Wood, spruce, microwave-assisted extraction, hemicelluloses, polymers

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72 **Résumé**

73 Le traitement par microondes (MAE) à pression atmosphérique a montré son efficacité pour  
74 l'extraction des polymères d'hémicelluloses à partir de la sciure du bois d'épicéa. Cette technologie de  
75 traitement s'est avérée plus efficace qu'un traitement thermique conventionnel. Le traitement  
76 microondes a conduit à une solubilisation élevée du bois et une extraction sélective des polymères  
77 d'hémicelluloses de poids moléculaires élevés. Pour optimiser le traitement MAE, différentes  
78 puissances de traitements (125-573W pendant 60 minutes) ont été testées sur la sciure de bois  
79 imprégnée soit dans de l'eau, soit dans une solution de NaOH à 1 mol/L. Les résultats ont montré que  
80 le rendement d'extraction d'hémicelluloses augmentait avec l'augmentation de la puissance des micro-  
81 ondes dans les deux milieux étudiés, avec un avantage pour la sciure imprégnée dans la solution  
82 basique. La caractérisation des hémicelluloses extraites a montré une sélectivité d'extraction  
83 importante en fonction du milieu d'imprégnation de la sciure de bois avant MAE: des  
84 Galactoglucomannanes de masse moléculaire élevée ( $M_w \sim 41$  kDa) ont été obtenus après  
85 imprégnation dans l'eau et des arabinoglucoronoxylyanes de masse moléculaire élevée ( $M_w \sim 66$  kDa)  
86 en milieu de basique.

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88 **Mots clés :** Bois, épicéa, extraction assistée par micro-ondes, hémicelluloses, polymères

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## 1. Introduction

98 Non cellulosic wood polysaccharides are of great interest because of their structural diversity and  
99 functionality. The potential for application of polymeric hemicelluloses has been demonstrated by  
100 several authors [1–5]. As a result, new utilizations of hemicellulosic polysaccharides are emerging in  
101 the fields of bioactive polymers, hydrocolloids, papermaking additive, or coating films [6,7].  
102 Softwood hemicelluloses are mainly constituted of galactoglucomannans (GGM), approximately 14–  
103 20% of the wood [8] and arabinoglucuronoxylans (7–10% of the wood). Softwood xylans are not  
104 acetylated, but the xylan backbone is substituted at carbon 2 and 3 with 4-*O*-methyl- $\alpha$ -D-glucuronic  
105 acid and  $\alpha$ -L-arabinofuranosyl residues, respectively. Softwood xylan has a relatively low DP of about  
106 100 [9]. GGM have been described to have an approximate degree of polymerisation of 100–150,  
107 matching to a molar mass of 16–24 kDa [9]. The potential applications of spruce GGM in biomaterials  
108 and hydrocolloids, such as barriers in food packaging, bioactive polysaccharides, hydrogels and fibers,  
109 and health-promoting agents, have been studied [3,5,10–14].

110 The extraction of polymeric hemicelluloses has been investigated for years. Extraction of softwood  
111 hemicelluloses has been studied by hydrothermal treatment at high temperatures ( $\geq 170$  °C) [15,16], by  
112 chemical extraction (alkaline) [17–20] and ionic liquids [21], by pressured hot water [22,23], and by  
113 microwave heat-fractionation ( $> 180$  °C) ([24–26].

114 The fractionation of wood at high temperatures leads to high solubilization of all macromolecules,  
115 including hemicelluloses. However, the extraction at high temperatures for long reaction times led to a  
116 low pH level, causing hydrolytic cleavages. As a result, GGMs extracted using these conditions are  
117 generally highly deacylated and exhibit low molecular mass. Chemical treatments, especially alkaline  
118 extractions are described to produce higher molecular weight hemicelluloses. Nevertheless, alkaline  
119 extraction of hemicelluloses has some disadvantages. In addition to causing saponification of  
120 polysaccharides, extraction with high concentrated alkaline solutions for long times can lead to peeling  
121 reactions [27].

122 Nowadays, new process of extraction have been developed in order to reduce the amount of chemical  
123 solvents, treatment time and temperature as well as energy consumption, hence improving the  
124 recovery of valuable compounds with lower costs [28]. Microwave-assisted extraction is one of the  
125 advantageous green extraction methods based on electromagnetic radiations with a frequency from 0.3  
126 to 300 GHz. In this process, microwave irradiations are used to extract biomolecules. Unlike  
127 conventional heat treatment where the energy is transferred to the material by convection, conduction  
128 or radiation from the surface of the material, microwave energy is delivered directly to the material  
129 through a molecular interaction with the electromagnetic field [29]. This interaction allows the heating  
130 of the material and a transfer of energy from the inside to the outside of the cell [30].

131 Several studies have been carried out on the effect of microwaves on the extraction of hemicelluloses  
132 from lignocellulosic materials. Microwave heating was shown to be efficient for the extraction of  
133 softwood hemicelluloses [26,31,32]. In 2014, Panthapulakkal has observed a slightly higher xylans  
134 extraction yield from wood fibers using microwave-assisted extraction (58 % of xylans) compared to  
135 conventional extraction (54 %) [33]. Similar results have been reported in pretreatment of maize cane  
136 using water and acid [34], alkaline pretreatment of *Panicum virgatum* [35]. Free sugars are generally  
137 released from the degradation of polysaccharides during the extraction process [36]. Most of the  
138 published works are carried out at temperature above 100 °C and at pressure above atmospheric  
139 pressure, these conditions leading to a degradation and a depolymerization of hemicellulose chains.

140 In the current work, microwave heating at atmospheric pressure was carried out for the extraction of  
141 polymeric hemicelluloses in mild conditions (temperature < 100 °C) in order to limit any possible  
142 degradation and depolymerization. The effect of MAE was compared with a conventional treatment at  
143 the same temperature. The effect of different conditions (power and/or temperature, pH of extraction)  
144 on the yield and the physicochemical properties of extracted hemicelluloses was assessed.

## 145 **2. Material and method**

### 146 **2.1. Raw material**

147 Spruce sawdust was produced from a spruce tree from the Lorraine region of France with a particle  
148 size of (1-5 mm) and stored at room temperature in a sealed polyethylene bags in the dark until use.

149 The average moisture content of the raw material was 10% w/w. The hemicelluloses content of the  
150 sawdust was approximately 30 % w/w dry biomass. Carbohydrate composition of sawdust includes 72  
151 % glucan, 7.5 % xylan, and 16.3 % of mannan and other sugars.

## 152 **2.2. Impregnation**

153 For each experiment, a mass of 20 g of spruce sawdust was soaked with a solution of 1M sodium  
154 hydroxide (ratio solid/liquid = 1:7) or water (ratio solid/liquid = 1:7). The sawdust was left for 15  
155 hours before treatment at room temperature.

## 156 **2.3. Experimental methodology of extraction**

### 157 **2.3.1. Microwave activation**

158 The microwave assisted extraction (MAE) experiments for the extraction of hemicelluloses from  
159 spruce sawdust were carried out using a microwave laboratory system (230V-50 Hz, NEOS-GR,  
160 Milestone, Italy). This mono-mode apparatus operates at 2.45 GHz with maximum delivered power of  
161 900 W regulated in 10 Watt increments with a temperature and power feedback/control. This  
162 instrument is equipped with time controller. The experiments were performed at atmospheric pressure  
163 and time, power were controlled and followed by the software. The MAE experiments were conducted  
164 in a glass extraction vessel. The samples were treated for 1h using different selected powers. Indeed,  
165 the effect of microwave irradiation, nature of solvent and consumed energy were studied. The liquid-  
166 to-solid ratio was fixed at 7 during microwave treatment.

167 The power values presented in all figures correspond to the effective power received by the sample  
168 ( $P_{effective}$ ) which was calculated by the following equations:

$$169 P_{effective} = P_{input} \times Y_{MW}$$

170 (1)

$$171 Y_{MW} = \frac{m \times C_p \times \Delta T(373 K - T_i)}{P_{input} \times t}$$

172 (2)



173 with  $P_{input}$  is the power immitted by microwave apparatus (Watts),  $Y_{MW}$  is the yield of microwave,  
174  $m$  is the weight of water (kg),  $T_i$  is the initial temperature of water (K),  $t$  is the necessary time of  
175 treatment to increase temperature from  $T_i$  to  $T_f$ ,  $C_p$  is the specific heat of water ( 4181.3 J/kg/K )

### 176 **2.3.2. Diffusion**

177 After microwave treatment, supplementary diffusion step was done by a heating under reflux at low  
178 temperature to avoid degradation of polymeric chains (70 °C for 3 h). The liquid-to-solid ratio was  
179 fixed at 15 (w/w).

180 For comparison, conventional extraction, without microwave treatment, from impregnated spruce  
181 sawdust was treated in similar extraction vessel heated with a water bath at 100 °C for one hour (to  
182 highlight the effect of microwave, the time to reach 100 °C for conventional extraction is not included)  
183 and then followed by 3 hours of extraction at 70 °C.

### 184 **2.3.3. Separation of extracted hemicelluloses**

185 After each experiment, the extract was filtered on qualitative filter paper with retention particle size of  
186 5–13  $\mu\text{m}$  (VWR International, Fontenay-sous-Bois, France). The volume and end-pH of the extract  
187 solutions were measured at room temperature shortly after the extraction. The liquid fraction from 1M  
188 NaOH impregnated sawdust was neutralized to a pH of 5.5-6 by a solution of 72%  $\text{H}_2\text{SO}_4$ . 10 mL  
189 were taken from the filtered extract for analyses. The extract solution was concentrated by vacuum  
190 evaporation (BUCHI, France) using a water bath at 50 °C. To precipitate high-molecular weight  
191 hemicelluloses, four volumes of 95% ethanol were added to the liquid extracts. The liquid phase was  
192 separated from the precipitated hemicelluloses by settling at room temperature and decantation.  
193 Hemicelluloses were further separated from the remaining liquid by centrifugation at 4000 rpm for 10  
194 min at room temperature. The precipitated hemicelluloses were re-dissolved in distilled water and  
195 dialyzed with a dialysis membrane with a cut-off of 3.4 kDa (Spectrum Laboratories, USA). Finally,  
196 dialyzed hemicelluloses solutions were freeze-dried. Fig.1. shows the experimental procedure of  
197 extraction and separation from spruce sawdust.

198 **Fig. 1.** Scheme for extraction and separation of hemicelluloses from spruce sawdust using microwave  
199 assisted extraction and conventional extraction.

#### 200           **2.4. Measurement of monosaccharides and uronic acids using HAPE-PAD**

201   The monosaccharide content of the soluble fraction was analyzed according to [37] method. The sugar  
202   concentrations were measured by HAPE-PAD (ICS-3000 Dionex, Dionex Corp., Sunnyvale, USA)  
203   equipped with a Dionex CarboPac™ PA-20 (3 × 150 mm) analytical column. Filtered samples (20 µL)  
204   were eluted at 35 °C and at 0.4 mL/min with the following composition: pure water 99.2%/250 mM  
205   NaOH 0.8%: 0–20 min; pure water 75%/250 mM NaOH 20%/ NaOCOCH<sub>3</sub>(1 M)- NaOH (20 mM) 5%  
206   20–37 min; and pure water 40%/250 mM NaOH 20%/NaOCOCH<sub>3</sub> (1 M)- NaOH (20 mM) 40% 37–41  
207   min. Each elution was followed by a wash and subsequent equilibration step. External sugar and  
208   uronic acid standards were used for calibration (7 points per curve). The reagents and standards are  
209   provided by Sigma-Aldrich and Fisher Scientific.

#### 210           **2.5. Degradation products**

211   Degradation products of hemicelluloses (furfural, HMF, formic acid and levulinic acid) are analyzed  
212   according to [38] procedure. All the products are quantified with an Ultimate 3000 HPLC system. The  
213   components are separated in 45 min on a Agilent Hi-Plex H column at 55° C with an isocratic flow  
214   rate of 0.4 mL·min<sup>-1</sup> of sulfuric acid (5. 10<sup>-3</sup> M). Acids were detected by UV at 210 nm, while HMF  
215   and furfural are detected by UV at 280 nm. An external calibration is performed with six calibration  
216   points per standard. Reagents and standards are provided by Sigma-Aldrich.

#### 217           **2.6. Acetyl content**

218   Acetyl content of extracted hemicelluloses was calculated by measuring the acetic acid concentration  
219   of hemicelluloses after a saponification reaction. Acid acetic was measured following the same  
220   procedure as degradation products with an UV detection at 210 nm instead of 280 nm.

#### 221           **2.7. Size-exclusion chromatography (SEC)**

222   A Shimadzu Prominence HPLC system is used to determine molecular weight distribution of  
223   hemicelluloses by gel filtration chromatography. The stationary phase is a Phenomenex Polysep GFC-  
224   P guard column (7.8 x 35 mm), Phenomenex Polysep GFC-P3000 and GFC-P2000 analytical

225 columns (7.8 x 300 mm). The mobile phase is 0.25 M aqueous NaNO<sub>3</sub>. Samples are filtered with a  
226 0.45 μm membrane and 20 μL are injected. Samples are separated at 30 °C with a 0.5 mL min<sup>-1</sup> flow  
227 and detection is done with a Refractive Index Detector (Shimadzu RID-20A). Each analysis runs for  
228 70 min. aqueous solutions (1 mg/mL) of dextran standards with molecular weights of 1000–80,000  
229 were used to prepare the calibration curve.

## 230 **2.8. FTIR**

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

## 236 **2.9. 2D 13C–1H HSQC NMR spectroscopy**

237 <sup>1</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  
238 spectrometer equipped with a 5-mm BBFO probe. Experiment was conducted with 20 mg sample  
239 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  
240 relaxation of 1.5- and 256-time increments were recorded in <sup>13</sup>C-dimension. HSQC spectra were  
241 taken at room temperature.

242

## 243 **2.10. Soluble lignin**

244 The acid-soluble lignin (ASL) content was determined from absorbance values at 205 nm according to  
245 the laboratory analytical procedure (LAP) provided by the National Renewable Energy Laboratory  
246 [37].

$$247 \quad \% \text{ ASL} = \frac{(Abs_{205 \text{ nm}} * V_t * 100)}{(DM_i)} \quad (3)$$

248 where V<sub>t</sub> is the total volume of sample (L); DM<sub>i</sub> is the initial dry matter (g).

## 249 **2.11. Wood solubilization**

250 Wood solubilization (WS) was presented as the ratio of the wood dissolved to the weight of the wood  
251 used for extraction as expressed in the Eq. (4):

$$252 \quad WS = \frac{\text{Weight of DW before extraction} - \text{Weight of DW after extraction}}{\text{Weight of DW before extraction}} \quad (4)$$

253 where DW stand for the term dry wood.

254

### 255 **3. Results and discussion**

#### 256 **3.1 Wood solubilization**

257 Prior to microwave activation, spruce sawdust was impregnated in a solution of distilled water (neutral  
258 medium) or 1 M NaOH (basic medium) for one night. The aim of the impregnation step is to open the  
259 wood structure and to enhance the accessibility of hemicelluloses during the microwave extraction  
260 [39–41]. After microwave treatment, a diffusion step was carried out during 3h at 70°C. The effect of  
261 impregnation and diffusion steps on hemicelluloses yields in neutral medium (+ 19 % and 2.5 %  
262 respectively) and (+ 16.4 % and +30 % respectively) in basic medium. See (**Fig. S1**) in SD section.  
263 The temperature profiles for conventional extraction and for MAE at different power are also given in  
264 SD section (**Fig. S2**).

265 Solubilization of wood was calculated using Eq.(3). As expected, the solubilization of wood is  
266 significantly higher in basic medium (**Fig.3**). The microwave assisted extraction increase notably the  
267 effect of sodium hydroxide (+81% for 573W). The advantage of MAE over conventional extraction  
268 could be explained by the rapid and the selective heating of wood that lead to destabilization and  
269 structural damage of wood matrix, thus improving biomolecules extraction, and also the heat and mass  
270 transfer which act in the same direction. Furthermore, the effect of MAE is not only related to the fast  
271 increase of temperature, but also to the power transmitted to the wood matrix which destabilizes and  
272 weakens structural linkages between lignin and carbohydrates. In conventional extraction, heat  
273 transfer and mass transfer had opposite directions [42].

274 Wood solubilization steadily increased with the increase of microwave power. The solubilization of  
275 sawdust is mainly affected by microwave power which is the main parameter affecting the irradiation

276 strength and the rate of temperature increase (**Fig.2**). For basic impregnation, alkaline solutions  
277 increase the water absorption capacity, swell up cellulosic fibers and decrease their crystallinity, and  
278 thus increase the specific surface area [43]. Based on previous reports, the mechanism of action is due  
279 to the decrease of intermolecular hydrogen bonds by solvation [44] as well as lignin- hemicelluloses  
280 bonds scissions.

281 **Fig.2.** Solubilization of wood after MAE and conventional extractions (1 h under  
282 MW, 3h diffusion)

### 283 3.2 Hemicellulose extraction

284 Polymeric hemicelluloses extracted in the liquid fraction were quantified by subtracting the amount of  
285 monomeric sugars (determined by ionic chromatography) from the total sugars content in the liquid  
286 fraction obtained after extraction. As expected, **Fig.3 (A and B)** shows that the extraction of  
287 hemicelluloses highly depends on the pH of the impregnation step, as it affects the hydrolysis of the  
288 hemicelluloses-lignin linkages. In fact, at maximum power (573 Watts) when sodium hydroxide was  
289 used as solvent, the effect of microwave on the extraction yield was higher as compared to the  
290 conventional extraction (32.3 and 22.5 mg/ g of dry wood respectively). On the other hand, lower  
291 extraction yields were observed using water as solvent. To explain the effect of MAE on wood,  
292 **Panthapulakkal et al., (2015)** have suggested that the disruption of wood structure and the rupture of  
293 wood fibers are due to the selective interaction of the microwaves with the inhomogeneous  
294 lignocellulosic materials [35, 45] have found that microwave treatment improves surface disruption  
295 and breaking of lignin structures in alkaline treated switch grass, while in conventional heating, the  
296 fibers remain intact.

297 The composition of the liquid fraction in terms of monomeric sugars (after acid hydrolysis) at different  
298 conditions of microwave extraction are also given in the **Fig.3 (A and B)**. Polysaccharides extracted in  
299 neutral medium are mainly composed of mannose (33%), glucose (18%) and galactose (20%). As a  
300 result we can assume that the hemicellulosic extract is mainly composed of galactoglucomannans [9].  
301 On the other hand, in the basic medium the high contents in xylose (57%) and arabinose (10%)  
302 suggests the dominant extraction of arabinoxylans. This selectivity of extraction as a function of the

303 pH of the medium is in accordance with previous reports. It has been described that in neutral or mild  
304 acid medium (pH  $\approx$  5), hemicelluloses extracted from softwood are rich in mannose, acetyled  
305 glucomannans exhibiting a relatively high water solubility [9,32]. In basic medium, the high xylose  
306 content can be rationalized by the dominant extraction of arabinoglucuronoxylans. In fact,  
307 arabinoglucuronoxylans are substituted with methyl-glucuronic acid and arabinose moiety which  
308 affect their solubility [46]. Thornton **et al., (1994)** have found from the Norway spruce wood that at  
309 pH values greater than 10, the concentration of extracted arabinose and xylose units increase,  
310 suggesting the release of arabino-(4-*O*-methylglucurono)xylans [47].

311 **Fig.3.** Yield and sugar composition of extracted hemicelluloses polymers in neutral medium (A) and  
312 basic medium (B)

313 The oligo- and polymeric fraction of the extracted hemicelluloses were calculated by subtracting the  
314 amount of monomeric sugars from the total sugars content in the extracts. The monomer proportion is  
315 very low (< 2%) whatever the extraction conditions, the mild conditions used in this study (T<100°C,  
316 pH>5) limiting the hydrolytic cleavage of hemicelluloses. Based on literature data, the hydrolysis of  
317 hemicellulose into monomeric sugars is promoted by extraction at higher temperatures for longer  
318 times and lower pH level [48].

319 Solubilization of lignin during the extraction of hemicelluloses is expected especially in basic medium.  
320 As shown in (**Fig.4.B**) the amount of soluble lignin increased after MW sawdust irradiation. A  
321 significant difference was observed for MAE at high power input (4.8% and 0.49% at 573 W for 1h  
322 compared to 3.3 % and 0.3 % at 100 °C for 1h at basic and neutral medium respectively). Acetic,  
323 uronic, formic and levulinic acids have also been detected in the liquid effluents. The carboxylic acids  
324 contents were relatively important in basic medium (**Fig.4. A**). Acetic and formic acids are the major  
325 carboxylic acids formed (6 and 1.7 g/l respectively). Levulinic acid present the lowest concentration  
326 accounting for 0.3 g/l. The peeling reactions occurring during alkaline treatments lead to endwise  
327 degradation of polysaccharides with formation of formic acid and different dihydroxy and  
328 dicarboxylic acid [49]. Acetic acid is released from the hemicellulosic backbone by saponification of  
329 acetate groups.

330 **Fig.4.** Degradation products in the liquid fraction in basic medium (A) and ASL (%) (B)

### 331 **3.3 composition of the recovered hemicelluloses powder**

332 The sugar composition of polymeric hemicelluloses recovered after precipitation and dialyze is similar  
333 to the sugar composition of the liquid fraction (**Fig.5**). Galactoglucomannans and arabinoxylans are  
334 the main polysaccharides extracted in neutral and basic medium respectively. In neutral medium,  
335 MAE promotes the extraction of arabinose and galactose compared to conventional extraction. In fact,  
336 hemicelluloses obtained from neutral medium are accounting for 24% and 19.5 % of galactose, for  
337 10.5 % and 5% of arabinose for MW (573W) and conventional extraction respectively. The advantage  
338 of MAE seems to be not only due to the temperature, but also owed to the physicochemical  
339 interactions induced by microwave heating of the wood matrix.

340 **Fig.5.** Sugar composition of recovered hemicelluloses by MAE and conventional extraction

341 In native softwood, mannopyranosyl units are acetylated at C-2 or C-3 with a degree of acetylation of  
342 about 0.5 [17,9]. In our study, the precipitated hemicelluloses recovered from a neutral medium had a  
343 lower degree of acetylation, in the range of 0.10-0.15. In basic medium, the acetyl groups have been  
344 totally released from the hemicellulosic backbone by saponification.

345 These results have been confirmed by a FTIR study. In the **Fig. 6** two weak absorbances at 1735 and  
346 1247  $\text{cm}^{-1}$  due to acetyl groups attached to the hemicelluloses chains were observed for the fractions  
347 extracted in neutral media but not for the basic extracts. Moreover, the absorption at 1515  $\text{cm}^{-1}$   
348 observed in all the hemicellulosic fractions was assigned to lignin's aromatic skeletal vibrations [50].  
349 The higher intensity of this signal for the fractions isolated from basic media confirms the higher  
350 lignin contamination for hemicelluloses obtained in basic medium compared to those obtained in  
351 neutral medium previously observed (**Fig. 4.B**).

352 **Fig.6.** FTIR spectra of extracted hemicelluloses

353 2D  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra clearly shows the typical signal spots expected for the hemicellulosic  
354 moieties. In basic medium (**Fig 7. B**),  $\beta$ -D-xylopyranoside units are specified by these signals at  
355  $\delta\text{C}/\delta\text{H}$  60/3.4; 62/4; 72/4.3; 72.5/3.2; 74/3.5; 72.5/3.7. The signals at 72/ 3.5 is assigned to  $\alpha$ -D-

356 xylopyranoside of xylans reducing end and at 62/3.3 and 71/3.5 for  $\beta$ -D-xylopyranoside of xylans non  
357 reducing end. In neutral medium (**Fig 7. A**), the signals at 3.4/74; 3.5/74; 3.8/76; 4.2/70 are attributed  
358 to  $\beta$ -D-mannopyranoside. The same results were found by [51]. The signal in neutral medium at  
359 5.45/72 was assigned to 6-*O*-acetyl  $\beta$ -D-mannopyranoside. In fact, as confirmed by the FTIR analysis,  
360 the extraction in neutral medium preserved some of the acetyl groups of the backbone units of GGM.  
361 These results are in close agreement to those obtained by [47] who found that deacetylation of the *O*-  
362 acetyl-galactoglucomannans appeared to begin at pH values above 8. The presence of acetyl residues  
363 is critical for the water-solubility of GGM. The acetyl moieties are generally cleaved during the  
364 extraction at high temperatures leading to the release of acetic acid. The signals at 98/5.25 and 82/3.1  
365 are assigned to 4-*O*-methyl- $\alpha$ -D-glucuronic acids that are spotted only in basic medium which  
366 confirms the extraction of arabinoglucuronoxylans in these conditions.

367 **Fig.7.** HSQC spectra of extracted hemicelluloses (A) in neutral medium; (B) in basic medium

368 Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, as well as the polydispersity index  
369 (PDI) were determined by gel-permeation chromatography. The results in Table 2 show that  
370 hemicellulose fractions isolated from microwave irradiation display higher molecular mass as  
371 compared to the conventionally extracted fractions (for conventional extraction,  $M_w$  ~38000 and  
372 ~56000 g.mol<sup>-1</sup> in neutral and basic medium respectively and ~42000 and ~67000 g mol<sup>-1</sup> for  
373 hemicelluloses extracted with microwave activation in neutral and basic medium respectively). It can  
374 be also observed that the hemicelluloses extracted in neutral medium had much lower molecular  
375 weights than those isolated in basic medium. These results were in close agreement to those reported  
376 by [52] who found that increasing the alkali concentration during extraction increased the  $M_w$  of  
377 extracted hemicelluloses by 46%. They suggested that the extraction of high  $M_w$  hemicelluloses was  
378 owed to the increase of the co-extraction of lignin-carbohydrates complexes. Considering the sugar  
379 composition given in **Fig.5**, it can be concluded that the neutral medium released relatively low  
380 molecular-weight GGM, while basic extraction allowed the recovery of high molecular mass xylans.



381 **Table 1.** Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, polydispersity  
382 index (PDI) and the polymerization degree (PD) of the hemicellulosic fractions obtained with  
383 MAE at 573 W and conventional extraction  
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#### 388 **4. Conclusion**

389  
390 In this study the extraction of the hemicelluloses polymers by MAE at atmospheric pressure was  
391 investigated. The highest amount of hemicelluloses extracted was 27.5 mg/g of dry wood from pre-  
392 soaked wood in 1M NaOH solution using microwave treatment at 573 W for 1 h over. At this  
393 condition, the  $M_w$  of extracted hemicellulose chains was 66 kDa. At the same conditions, i.e.,  
394 temperature and time, the yield and the  $M_w$  were lower using a conventional heating than microwave,  
395 which highlights the efficacy of MAE for extraction of hemicelluloses chains from spruce sawdust.  
396 Pre-soaking in sodium hydroxide improves the solubilization of wood and hence the extraction of high  
397 molecular weight hemicelluloses. However, pre-soaking in water preserve acetyl groups in the  
398 hemicellulose chains which could be advantageous in various polymer applications. High extraction  
399 selectivity was observed as a function of the pre-soaking medium: acetylated galactoglucomannans  
400 were isolated after pre-soaking in neutral medium and high molecular mass arabinoglucoronoxylans in  
401 basic medium. MAE at atmospheric pressure and mild conditions (temperature < 100°C and pH 5) has  
402 shown its effectiveness to extract high molecular weight hemicelluloses chains from spruce wood with  
403 less depolymerization and degradation. This technology has a great potential as an alternative method  
404 to autohydrolysis and hydrothermal treatments of wood in the aspects of molecular weight of extracted  
405 hemicelluloses.

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**Conflict of interest**

The authors have no conflict of interest.

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606 **Figure captions:**

607 **Fig. 1.** Scheme for extraction and separation of hemicelluloses from spruce sawdust using microwave  
608 assisted extraction and conventional extraction.

609 **Fig.2.** Solubilization of wood after MAE and conventional extractions (1 h under MW, 3h diffusion)

610 **Fig.3.** Yield and sugar composition of extracted hemicelluloses polymers in neutral medium (A) and  
611 basic medium (B)

612 **Fig.4.** Degradation products in the liquid fraction in basic medium (A) and ASL (%) (B)

613 **Fig.5.** Sugar composition of recovered hemicelluloses by MAE and conventional extraction

614 **Fig.6.** FTIR spectra of extracted hemicelluloses

615 **Fig.7.** HSQC spectra of extracted hemicelluloses (A) in neutral medium; (B) in basic medium

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620 **Supplementary data:**

621 **S1.** Effect of the impregnation and the diffusion on the yield of extracted hemicelluloses by MAE at

622 573 Watts in neutral and basic mediums

623 **S2.** Temperature profile during MAE and conventional extraction

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625 **Table caption:**

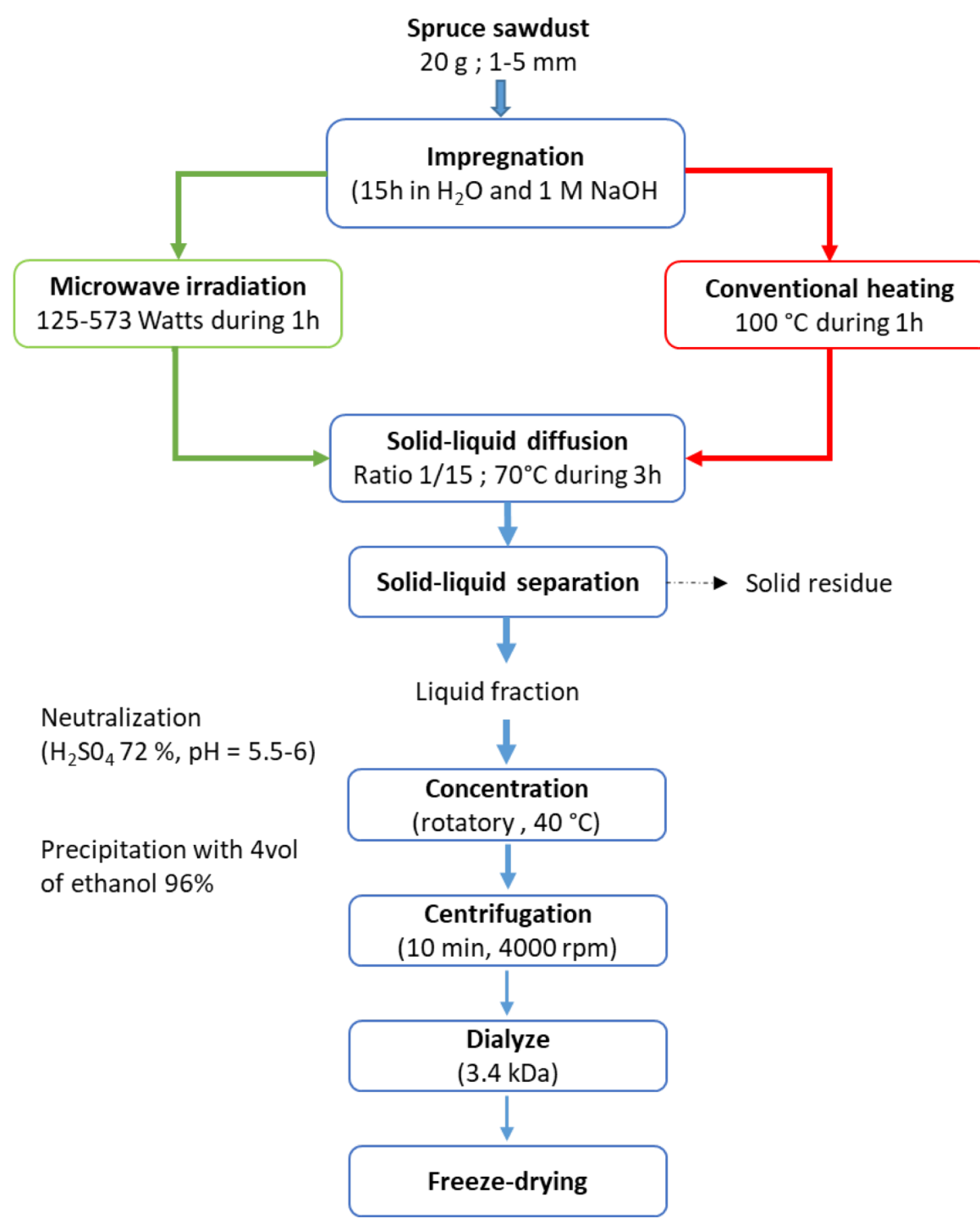
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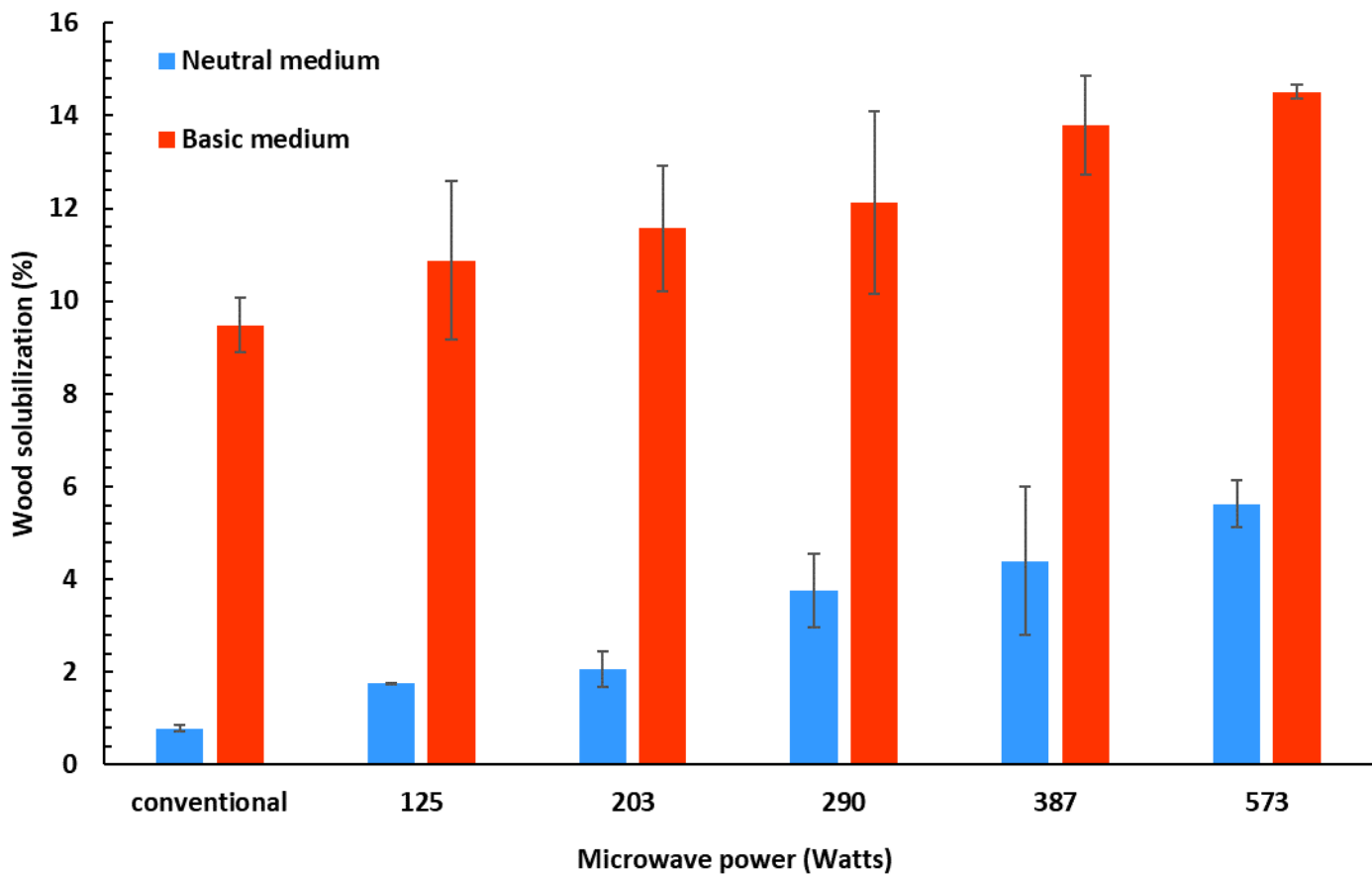
627 **Table 1.** Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, polydispersity  
628 index (PDI) and the polymerization degree (PD) of the hemicellulosic fractions obtained with  
629 MAE at 573 W and conventional extraction

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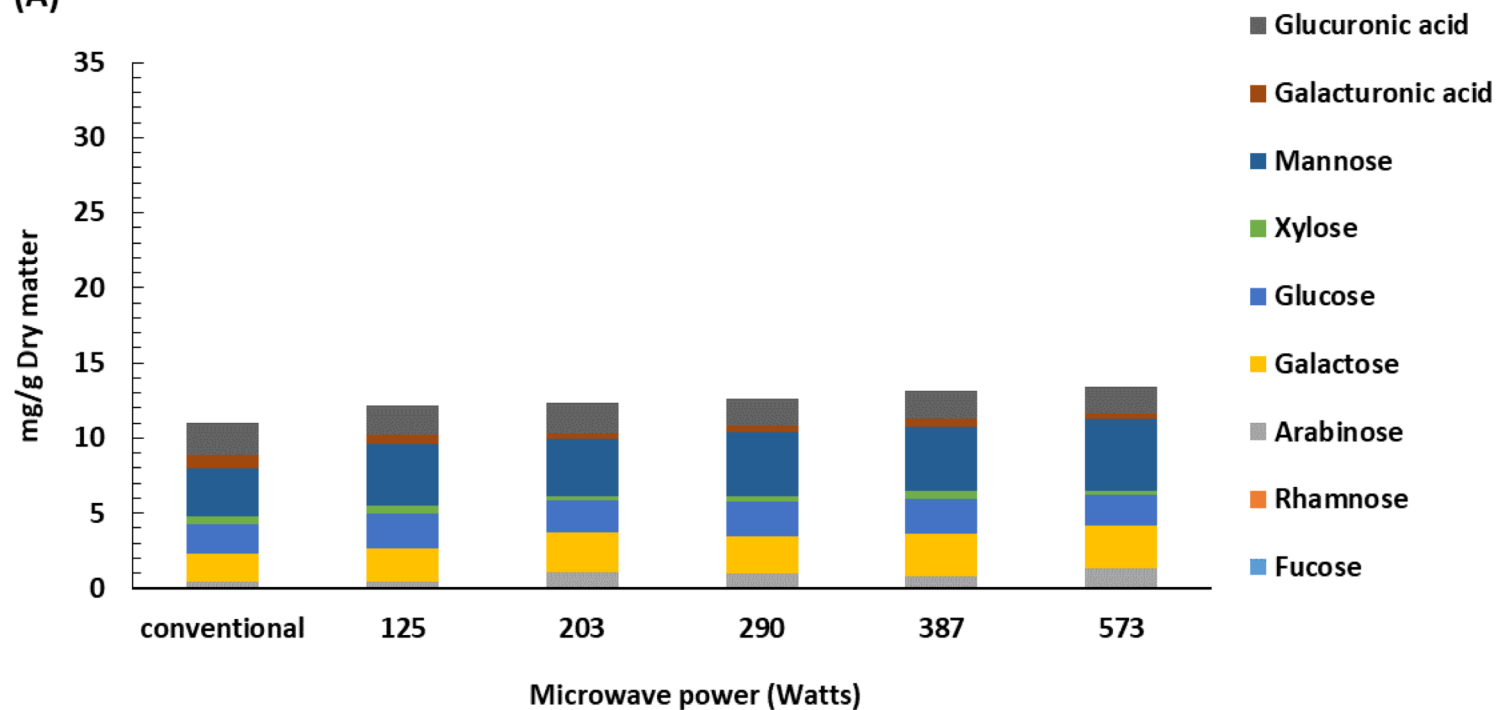
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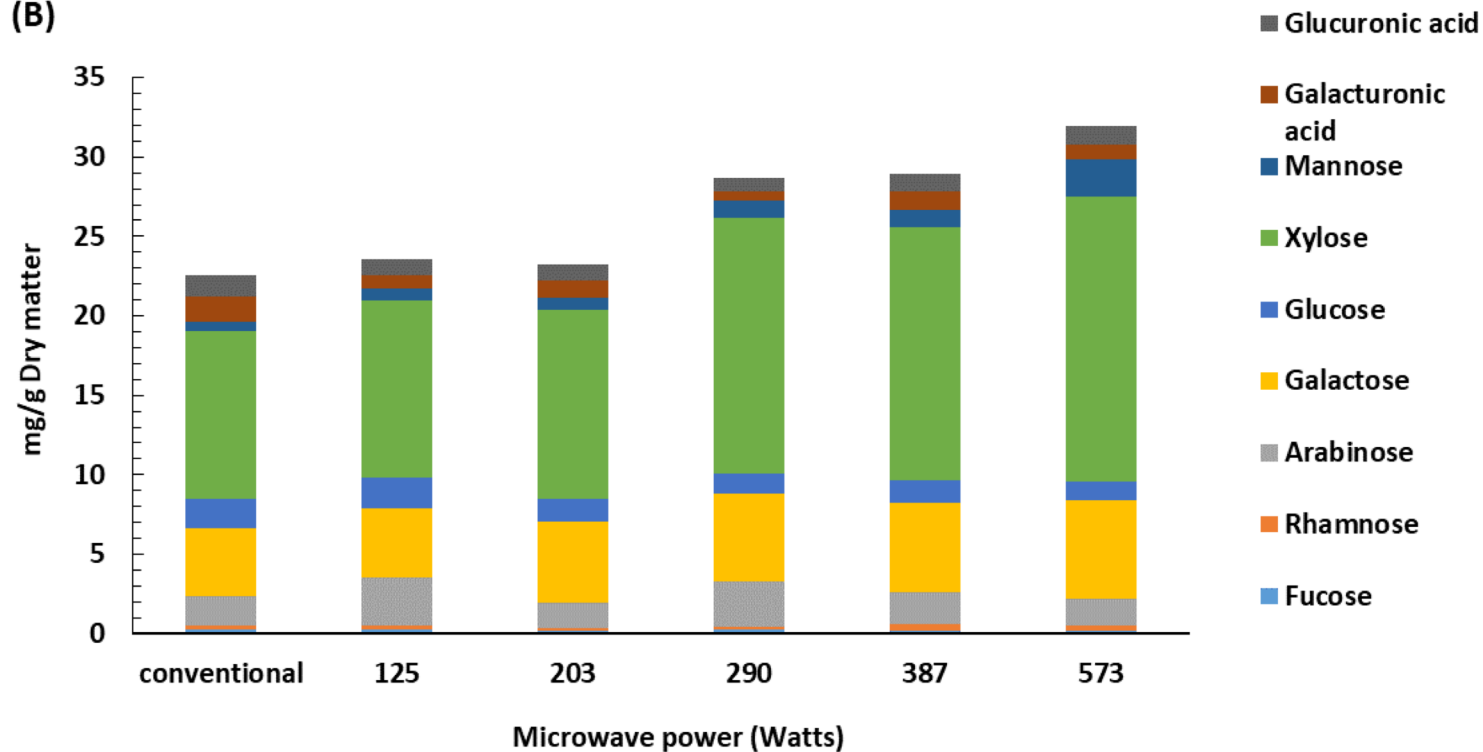


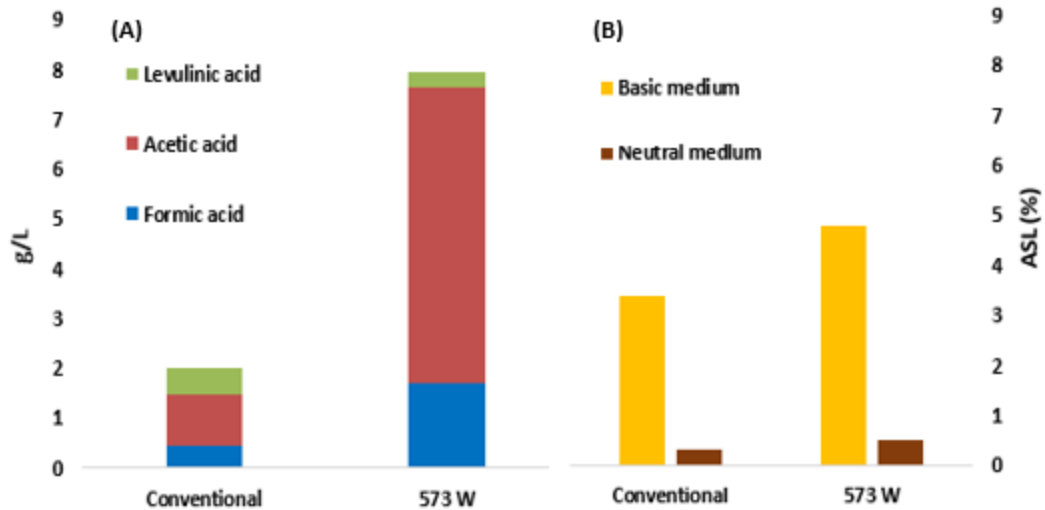


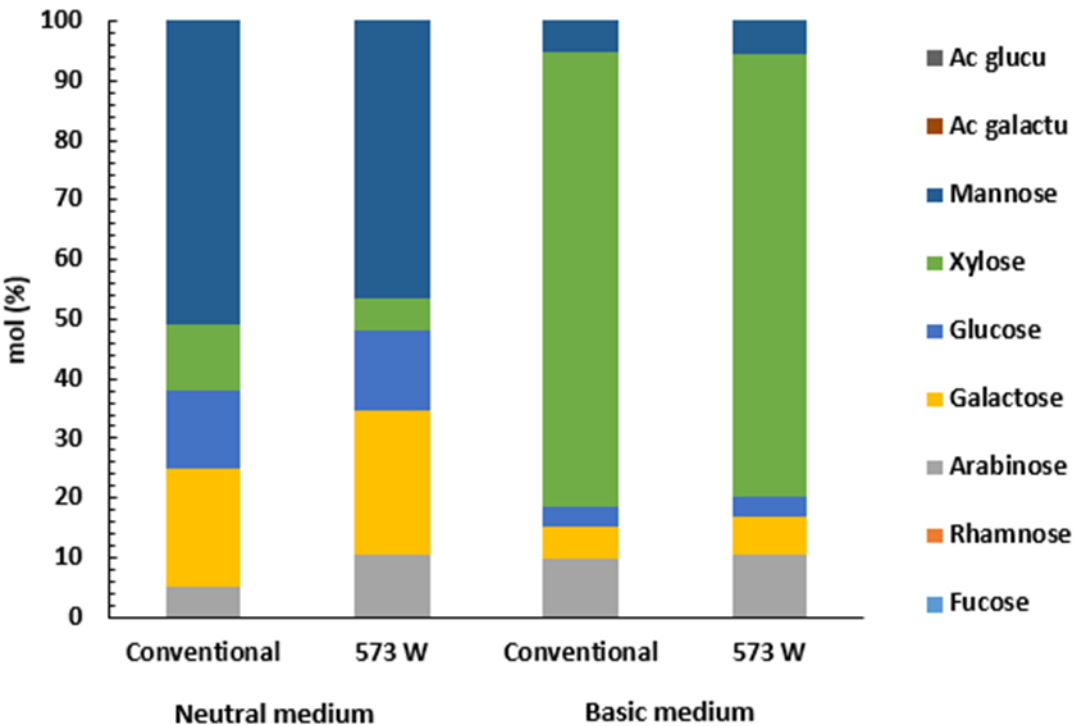
(A)

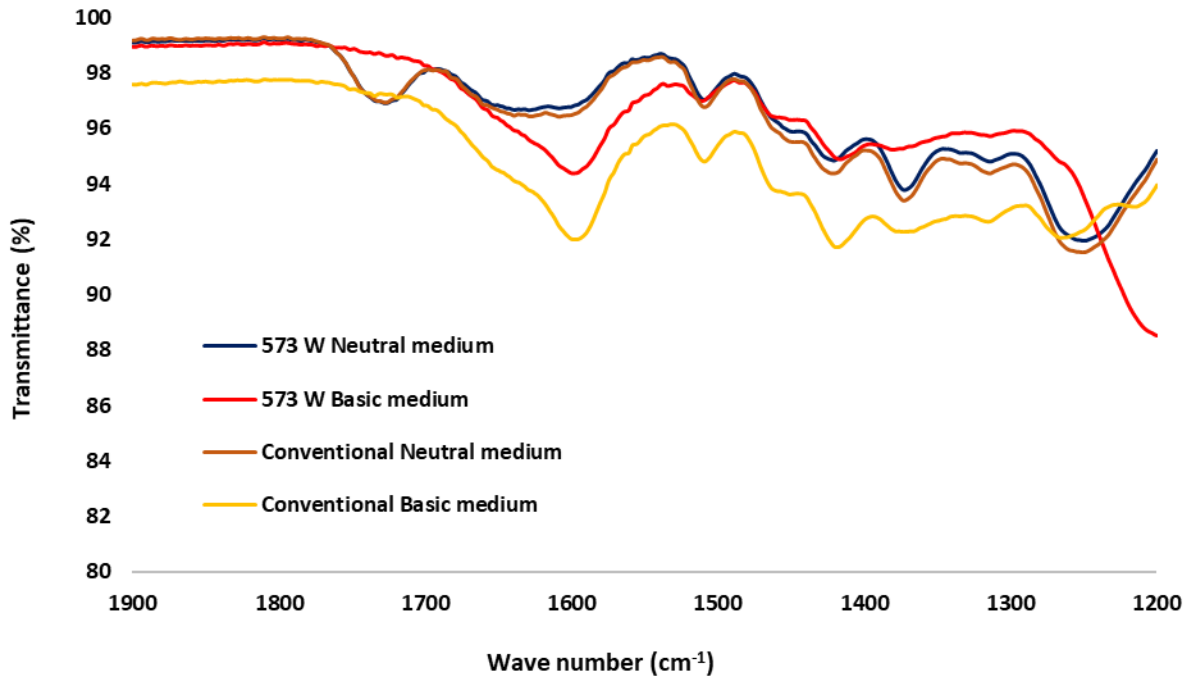


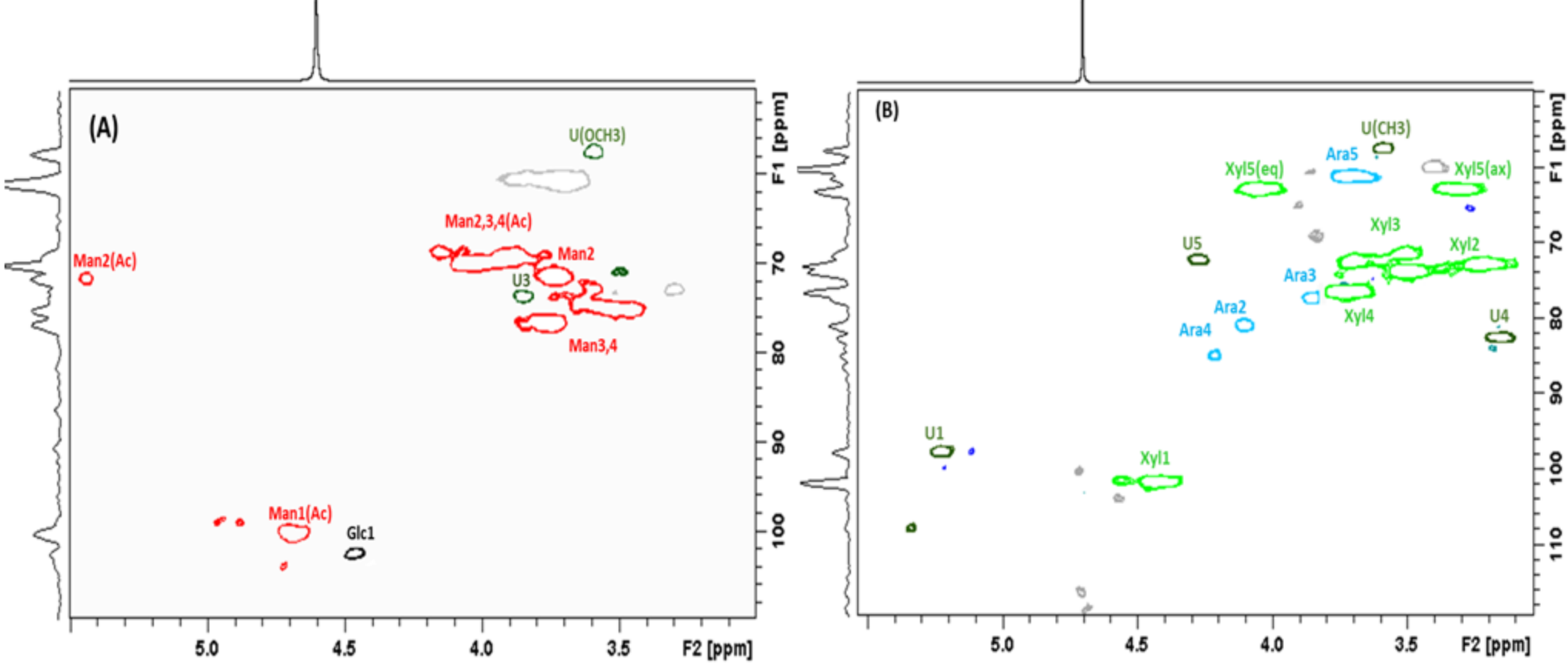
(B)











**Table 1.** Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights, polydispersity index (PDI) and the polymerization degree (PD) of the hemicellulosic fractions obtained with MAE at 573 W and conventional extraction

	Basic medium				Neutral Medium			
	$M_n$	$M_w$	PDI	PD	$M_n$	$M_w$	PDI	PD
Conventional	27266	56298	2.06	351	20730	37870	1.82	236
MAE 573 W	54227	66564	1.22	416	23875	41589	1.74	259