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# Urea-Formaldehyde Resin Removal in Medium-Density Fiberboards by Steam Explosion: Developing Nondestructive Analytical Tools

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1 Urea-formaldehyde resin removal in medium density  
2 fiberboards by steam explosion: developing non-  
3 destructive analytical tools

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10

11 KEYWORDS

12 MDF waste, medium density fiberboards, UF resin removal, near-infrared spectroscopy,  
13 correlative microscopy, fiber recovery

14

15 ABSTRACT

16 The cascading recycling of wood waste is currently a hot topic. Medium density fiberboard  
17 (MDF) is a material whose consumption has been increasing worldwide for several decades.  
18 However, current wood waste treatment processes do not allow for efficient recycling. The  
19 potential of steam explosion (SE) treatment was investigated for stripping off the urea-  
20 formaldehyde (UF) resin and the production of clean fibers from MDF. Hot liquid water during  
21 the hydrothermal stage and water expansion during the decompression stage of SE provoked (1)  
22 the hydrolytic breakdown of UF and the removal of > 80% of the resin from the fibers and (2)  
23 efficient defibration of MDF producing  $\approx 67\%$  of fibers with similar morphological features  
24 when compared with MDF fibers. Near infrared spectroscopy (NIRS), nitrogen quantification  
25 and confocal laser scanning microscopy/ scanning electron microscopy-wavelength dispersive  
26 spectroscopy were used to evaluate the SE effect on UF removal from MDF fibers. The sample  
27 clusters obtained by principal component analysis of NIRS spectra were correlated with nitrogen  
28 content and processing conditions used. This work brings versatile solutions based on  
29 hydrothermal treatments, namely SE, for diverse low environmental impact and valorization  
30 routes of MDF waste. We showed that MDF processing treatment must be chosen wisely  
31 according to the future valorization of the MDF targeted.

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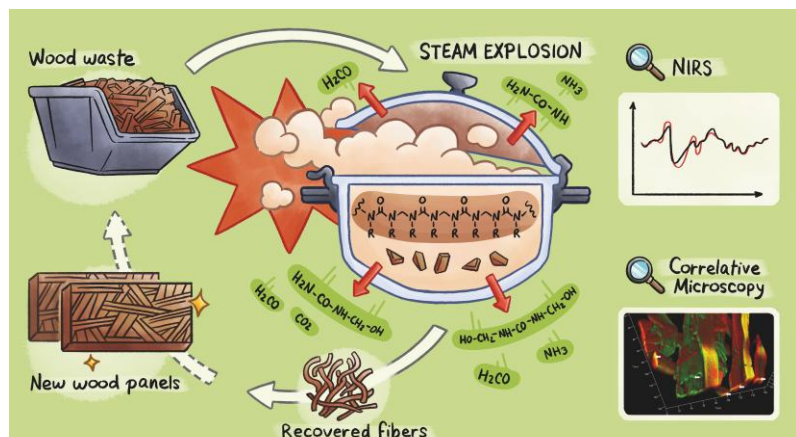
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37 GRAPHICAL ABSTRACT



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40

## 41 INTRODUCTION

42 Wood is a renewable material with valuable properties including recyclability. Current  
43 consumption trends are leading to ever increasing volumes of waste wood, which may constitute  
44 a feedstock for the cascade production of new products.<sup>1</sup> Among wood-based manufactured  
45 products, medium density fiberboard (MDF) has been used since 1965 to produce a core stock  
46 for the furniture industry.<sup>2</sup> Over the last few decades, household consumption habits have  
47 changed as the lifespan of interior furniture has decreased. As a result, the world production of  
48 fiberboard was multiplied by 4 between 2000 and 2020 and since 2015, the global production is  
49 over 100 million m<sup>3</sup>.<sup>3</sup> These evolutions have led to a sharp increase in waste furniture. For MDF  
50 alone, the volume of waste generated in the last five years worldwide is estimated at 220 million  
51 m<sup>3</sup> and growing.<sup>4</sup> However, unlike other wood products, there is no industrial scale process for  
52 the recovery or recycling of MDF and most of the panels are currently incinerated or landfilled.  
53 Recycling wood waste and especially MDF is challenging because of the presence of cured  
54 residual adhesive on the surface of the fibers. The poor end-of-life management of MDF panels  
55 has a negative environmental impact including the generation of hazardous gases during thermal  
56 treatment and pollutants can be released into the environment.<sup>5,6</sup> Recycling MDF is therefore a  
57 major issue for the furniture industry and the wood sector in general.<sup>1</sup>

58 Urea-formaldehyde (UF) resins are the most widely used in the wood sector because of their  
59 high reactivity, good performance and low price.<sup>7</sup> It has been shown in previous studies that the  
60 presence of residual cured UF resin on the surface of the wood fibers negatively impacts the  
61 properties of the panels formed from recycled wood.<sup>8,9</sup> Cured UF resins have a relatively low  
62 water resistance and can be degraded by hydrolysis.<sup>10</sup> As a result, hydrolytic strategies have been

63 proposed for UF removal prior to the reuse of wood-based panels.<sup>11</sup> Neutral and acidic  
64 hydrolysis can removed ~ 50% and ~ 70% respectively of UF resin from MDF fibers.<sup>12</sup>  
65 Hydrothermal treatment led to a reduction in resin content but it also resulted in a reduction in  
66 the average length and width of the fibers, thus reducing the potential for further fiber  
67 recovery.<sup>13,14</sup>

68 The steam explosion (SE) technology is both energy efficient and versatile. The technology was  
69 initially developed to manufacture chipboard panels<sup>15,16</sup> and is particularly mature for cellulosic  
70 bioethanol<sup>1,17,18</sup>. This process was also recently described for biomolecules and biopolymers  
71 extraction or the valorization of biomass from phytotechnology.<sup>19-22</sup> Several studies examined  
72 the importance of water content in hydrolytic processes during SE pretreatments.<sup>23,24</sup> However,  
73 these phenomena are still largely unknown. The utilization of SE as a pretreatment for MDF  
74 recovery was reported in the literature<sup>25</sup> but due to technical limitations, this study was carried  
75 out at a relatively low pressure/temperature (0.16 MPa, 113°C). More recently, hydrolysis of UF  
76 resin from wood waste during SE was studied.<sup>13</sup> Temperature and steam ratio improved the UF  
77 removal from waste, but neither the treatment homogeneity nor clear correlation could be  
78 established between ammonia and formaldehyde emissions.

79 Processes for removing resin from wood must be coupled with effective technologies for  
80 quantifying resin in the bulk and at the fiber scale. The cured resin is opaque and therefore  
81 difficult to identify. Near-infrared spectroscopy (NIRS) is a promising non-destructive and  
82 contactless method for waste wood sorting because it can distinguish treated wood from  
83 untreated waste wood.<sup>26,27</sup> Confocal laser scanning microscopy (CLSM) has been developed to  
84 detect or visualize UF resin.<sup>28</sup> The combination of the localization of the region of interest by

85 CLSM and the morphology by scanning electron microscopy (SEM) is valuable to perform *in-*  
86 *situ* analysis on the fibers. The elemental mapping analysis of nitrogen can be performed by  
87 SEM coupled with energy dispersive spectroscopy (EDS) and its quantification achieved by  
88 wavelength dispersive spectroscopy (WDS).<sup>29</sup>

89 This work aims to examine and optimize the effect of SE processes performed at high pressure,  
90 namely 0.9-1.9 MPa, on MDF waste. For an efficient recovery of MDF, two effects are sought:  
91 the elimination of the glue on the surface of the fibers and the recovery of long (0.5 mm - 14  
92 mm) wood fibers with a good yield. The impact of the treatment parameters on the fiber's  
93 composition and the role of the water states in the hydrolytic degradation of the resin were  
94 investigated. The study focused on a multi-processes approach that optimized resin removal,  
95 maximized defibration and minimized the use of water to recover MDF fibers for future  
96 recycling.

## 97 MATERIALS AND METHOD

### 98 **MDF characterization**

99 Because we wanted here to evaluate the UF removal potential of SE and decrease the variability  
100 associated with the material, we used newly manufactured MDF. Standard MDF panels were  
101 purchased from EGGGER (EGGER Brilon GmbH & Co, Germany). The MDF samples were sawn  
102 into cubes of side 20 mm to obtain sample sizes comparable to industrially ground waste wood  
103 panels for recycling. The moisture content of the MDF samples was 6%.

### 104 **Resin removal and MDF fragmentation**

105 The experiments were carried out in two different reactors to optimize the resin removal and  
106 MDF fragmentation.

107 The resin removal was optimized by a standard hydrothermal treatment. MDF samples were  
108 treated by Hot Pressurized Water treatment (HPW) in a 10 L Parr reactor with a Parr 4842  
109 temperature controller (Parr Instrument Company, Moline, IL, USA) at medium pressure (1  
110 MPa) at 180°C for 15 minutes. Distilled water was in excess in the process to ensure the highest  
111 resin removal rate. The ratio biomass/water was 1/25.

112 To optimize the fragmentation of the material and the water consumption, MDF samples were  
113 treated by SE. Technically, the SE prototype used in this study (ADF, France) consists of a  
114 steam generator that feeds the pressurized reactor containing the MDF to reach and maintain the  
115 set temperature. The biomass was introduced horizontally in a 4.8 liters reactor and additional  
116 water was injected into the pressurized SE reactor. Saturated steam at high pressure (1.6 MPa)  
117 was injected in the reactor at 180°C for 15 minutes. The opening of a pneumatic valve dropped  
118 the pressure in the reactor and the exploded biomass was released into the discharge tank (Figure  
119 S1). The samples were treated by SE with additional water (SEW) with a ratio biomass/water  
120 from 1/1 to 1/10.

121 To reduce the water consumption, SE experiments were carried out without the injection of  
122 additional water with different retention times (from 5 to 20 minutes) and pressures (from 1.6 to  
123 2.3 MPa). The results of the preliminary study were used to select the experimental conditions.

124 **Fibers drying**



125 As the SE generates effluents, the fibers had to be separated from the effluents and dried. The  
126 fibers were separated from the liquid products by centrifugation at 7000 RPM for 10 min at room  
127 temperature (Thermo Scientific Multifuge X4R Pro, USA). Supernatant was removed and kept  
128 for subsequent analysis and fiber pellets were dried at 80°C for 24h and pressurized by air pulse.  
129 Finally, fibers were sieved (300-850  $\mu\text{m}$  mesh) and fiber size repartition was analyzed. The  
130 complete process is depicted in Figure 1.



132 **Figure 1.** Process flowchart

### 133 **Pollutants quantification**

134 To determine the rate of UF-resin removal in different SE conditions, nitrogen and formaldehyde  
135 were measured on the fibers. An elemental combustion analysis was performed on a Thermo  
136 Scientific Flash EA 112 (USA) to determine the percentage of nitrogen on the fibers. The  
137 samples were grounded into a homogeneous powder. The combustion of the samples was  
138 performed at 950°C in the presence of copper oxide under oxygen flow for 15 seconds and  
139 produces  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{NO}_x$  which were reduced to nitrogen by copper. The combustion  
140 products were then measured by gas chromatography under the conditions determined by the  
141 manufacturer. The results were recorded and analyzed by the software Eager 300.

142 Formaldehyde emissions were measured according to the perforator method EN ISO 12460-5  
143 (AFNOR, 2016) and a high-performance liquid chromatography (HPLC) method was used to  
144 quantify the formaldehyde content on fibers after hydrothermal extraction. Previous works  
145 showed UF resin can be efficiently extracted by hydrothermal treatment.<sup>14,30</sup> Thus, the fibers

146 were autoclaved at 121°C for 20 min to extract the formaldehyde. Before the analysis, the  
147 samples were derivatized with a solution of 2,4 dinitrophenylhydrazine (2,4 DNPH). 500 mg of  
148 2,4 DNPH and 0.5 mL of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) 85% were dissolved in 49.5 mL of  
149 acetonitrile. The pH of the samples was adjusted to 5. One milliliter of the sample was  
150 centrifuged at 12 000 RPM for 10 min and the supernatant was passed through a 0.45 diameter  
151 nylon filter. 20 µL of the sample, 30 µL of 2,4 DNPH solution and 950 µL of acetonitrile were  
152 mixed in a 1.5 mL vial and injected into the HPLC. Formaldehyde analyses were performed on a  
153 C18 Luna column (50 mm × 2.1 mm, 1.7 µm particle size) (Acquity, UPLC, Waters, USA) using  
154 a HPLC (Thermo Scientific, Dionex Ultimate 3000, USA). The wavelength was set to 365 nm.  
155 Separation was achieved with a mixture of water/acetonitrile (40:60, v/v). The flow rate was 0.3  
156 mL/min and the injection volume was 1 µL. The total run time was 12 min.

## 157 **NIRS**

158 The measurements were performed on a Perkin Elmer NIRS spectrometer (USA) equipped with  
159 an InGaAs detector and a CaF<sub>2</sub> beam splitter. Three samples of 5 g from each condition were  
160 analyzed and five spectra for each sample were recorded from 10,000 to 4,000 cm<sup>-1</sup> with a 2 cm<sup>-1</sup>  
161 resolution. As described previously, only the spectral region between 6950 and 5500 cm<sup>-1</sup> was  
162 further considered for analysis.<sup>31</sup> The log<sub>10</sub> (1/R) of the spectral data was calculated. This  
163 process is typically used for quantitative analysis.<sup>32</sup> Then second derivative was calculated as  
164 previously described.<sup>33</sup> In lab developed scripts based on RStudio and the plugin Chemospec  
165 were used to analyze the raw data.<sup>34</sup> Principal component analysis (PCA) was performed to  
166 analyze a limited set of independent and significant variables. The chemical differences of the  
167 samples were visualized in a scatter plot and the loadings were analyzed to identify the main  
168 contributive variables.

169 **CLEM**

170 In-situ analysis were performed by Correlative Light and Electron Spectroscopy (CLEM) to  
171 observe the removal of the resin on the fibers by combining images from a CLSM and a SEM.  
172 The sample were mounted on a stub accommodated on a specific holder (shuttle and find holder  
173 for material sciences, Zeiss GmbH, Germany). The holder has three L-shaped registration  
174 markers defining a coordinate system that can be quickly located and calibrated semi-  
175 automatically in the "Shuttle & Find" module of Zen software (Zeiss GmbH, Germany) on both  
176 CLSM and SEM microscopes. The areas of interest were first identified under a confocal  
177 microscope and the images were saved including the "shuttle and find" coordinate system. Then  
178 the same areas of interest were recovered under the SEM (Sigma HDVP and EVO 15, Zeiss  
179 GmbH, Germany) to perform electronic imaging and microanalysis with an EDS (SDD X max  
180 80mm<sup>2</sup>, Oxford instrument, UK) and a WDS detector (IncaWave 600, Oxford instrument, UK).  
181 To perform spectral deconvolution, samples were stained in 0.1% aqueous safranin O (Merck)  
182 for 5 min and rinsed until the water became clear. They were mounted onto SEM specimen stubs  
183 and observed on a confocal LSM 780 r (Zeiss GmbH, Germany) equipped with a spectral  
184 deconvolution mode. The settings were optimized to ensure maximum distinction between  
185 stained resin and fibers into green and red emission light, respectively. Uncoated-control fibers,  
186 UF coated-control fibers and UF-resin were used as references and were compared to SE treated  
187 samples.

188 After the observation on the confocal microscope and prior to the observations on the SEM, the  
189 samples were coated under a high vacuum mode with 2 nm of platinum (ACE600 metallizer,  
190 LEICA, Germany).

191 **EDS and WDS analyses**

192 The field of observation was relocated to a FE-SEM (Sigma HDVP, Zeiss GmbH, Germany) to  
193 perform EDS analysis and then under an EVO15-SEM equipped with a WDS detector (Zeiss  
194 GmbH, Germany). The WDS is an INCA Wave that can accommodate six crystals and is  
195 equipped with a crystal optimized for nitrogen analysis LSM80E (Oxford Instruments, UK).  
196 Surface images for the selection of sites of interest were acquired from a high definition back-  
197 scattered detector (HDBSD) (Zeiss GmbH, Germany).

198 The working distance on the EVO15 was 9 mm. The acceleration voltage and the beam current  
199 were set to 10 Kv and 5 nA respectively for the nitrogen measurements performed on the fibers.  
200 The specific peaks of nitrogen were acquired and deconvoluted with the Energy+ 250 interface  
201 of the INCA software. The calibration and the optimization of the detection of the nitrogen peak  
202 were carried out under the conditions of acquisition starting from a pellet of glue powder with  
203 the WAVE interface of the INCA software suite (Oxford Instruments). For each sample, the  
204 relative elemental percentage of nitrogen was measured on 9 pellets of 8 mm diameter and 0.5  
205 mm thickness. The reference used for nitrogen content was cured UF resin.

206 **X-ray tomography**

207 One cube of side 20 mm was scanned on a 39 Watt Tomograph (RX Solution, France) with a  
208 high tension of 0–130 kW and an anode current of 0–300  $\mu$ A. The voxel size was 10.67  $\mu$ m. A  
209 subsample of 500 slices amongst the 1131 slices was selected for the 3D reconstruction using  
210 Fiji software<sup>35</sup>.

211

212 RESULTS AND DISCUSSION

213 **Hot Pressurized Water treatment (HPW)**

214 In a first attempt, the effect of a standard hydrothermal treatment (i.e without decompressive  
215 explosion) was experimented by treating MDF samples by HPW in a closed high-pressure  
216 reactor at 180°C for 15 min (Table 1, run 1). Perforator extraction coupled with HPLC analysis  
217 showed a total removal of formaldehyde emissions after treatment (2.4 mg/100 g of dry mass  
218 MDF before treatment to non-detectable after HPW). Hydrolysis of UF resin was reported to  
219 produce mainly urea, ammonia and formaldehyde.<sup>13</sup> Quantification of nitrogen by the Kjeldahl  
220 method was used as an indicator of resin removal performance. HPW led to a 91% ( $\pm$  1%)  
221 reduction in nitrogen content (Table 1) and to a 94 % reduction in formaldehyde content ( $\pm$  1%)  
222 in the fiber.

223 In order to analyze the effect of the treatment on the fragmentation of the sample, a defibration  
224 class (dc) was defined as followed: 0 = unaltered sample, 1 = sample swelling, 2 = partial  
225 defibration and 3 = total defibration. As shown in Table 1 and Figure 2, HPW treatment of MDF  
226 led to a swelling of the sample without disruption of MDF ultra-structure (defibration class = 1,  
227 Table 1). However, the fragmentation of the material can be required for the future use of the  
228 recovered fibers.



230 **Figure 2.** Effect of the treatment on the MDF fragmentation and defibration class definition, 0 =  
 231 unaltered sample, 1 = sample swelling, 2 = partial defibration, 3 = total defibration.

232

233 **Steam explosion treatment (SE and SEW)**

234 MDF was treated by SE using 4 temperatures and 4 residence times as summarized in Table 1  
 235 (runs 2-10). The condition sets used in this study were selected considering a visual effect of the  
 236 material. Technically, the SE pilot consists of a steam generator that feeds the pressurized reactor  
 237 containing the MDF to reach and maintain the set temperature. During the explosive discharge,  
 238 the fibers are recovered in the explosion tank with condensed water. For the runs 11-15 (SEW),  
 239 the water content was increased by injection of additional water in the pressurized SE reactor  
 240 before heating by steam injection.

241 **Table 1.** HPW, SE and SEW with reaction conditions and nitrogen content.

Run	Process	Pressure (MPa)	T (°C)	t (min)	S/L	N (% of total elements)	N removal (%)	Defibration class
MDF						4.15 ± 0.03		0
1	HPW	1.6	180	15	1/25	0.40 ± 0.03	-92%	1
2	SE	1.6	180	10		1.00 ± 0.01	-76%	2
3	SE	1.6	180	15		1.27 ± 0.01	-69%	3
4	SE	1.6	180	20		0.70 ± 0.02	-83%	3
5	SE	1.9	190	5		0.83 ± 0.01	-80%	3

6	SE	1.9	190	10		$0.91 \pm 0.01$	-78%	3
7	SE	1.9	190	20		$1.02 \pm 0.05$	-75%	3
8	SE	2.3	200	5		$1.65 \pm 0.01$	-65%	3
9	SE	2.3	200	10		$1.09 \pm 0.03$	-74%	3
10	SE	2.8	210	5		$1.88 \pm 0.04$	-55%	3
<hr/>								
11	SEW	1.6	180	15	1/1	$0.78 \pm 0.04$	-81%	3
12	SEW	1.6	180	15	1/2	$0.80 \pm 0.03$	-81%	3
13	SEW	1.6	180	15	1/6	$0.60 \pm 0.02$	-86%	3
14	SEW	1.6	180	15	1/8	$0.64 \pm 0.01$	-85%	3
15	SEW	1.6	180	15	1/10	$0.59 \pm 0.01$	-86%	3

242  
243 Standardized analysis (see Materials and Method section) showed that formaldehyde emissions  
244 from all SE and SEW treated fibers were below the detection limit. Regarding the evaluation of  
245 the efficiency of the resin removal, nitrogen quantifications were carried out. As seen in Table 1,  
246 SE treatment (runs 2-10) allowed the removal of 55 %-83 % of the resin from the fibers. For run  
247 2, performed at the lowest SE severity a partial defibration of MDF was observed (see Fig. 2). In  
248 contrast, runs 3-10 allowed total defibration (Fig. 2.) probably because of the explosive  
249 decompression step, involving a well-known water expansion. As previously proposed in a study  
250 aiming at the defibration of bast fibers, the high-speed extrusion of MDF from the reactor to the

251 cyclone during the explosive decompression could also induce a high mechanical stress to the  
252 material causing its total disruption<sup>36</sup>.

253 Interestingly, it was observed that a decrease of the ratio solid: liquid improved the removal of  
254 the resin. A comparison of run 3 and runs 11-15 showed that a SEW carried out with the same  
255 severity but with a higher water content resulted in a significant decrease in N%, from  $\approx 1.3\%$  to  
256  $\approx 0.6-0.8\%$  which correspond to the removal of  $\approx 85\%$  of the resin. This observation is in line  
257 with previous works dealing with the SE pre-treatment of lignocellulosic biomass. These studies  
258 have shown that an increase in condensed water content during the cooking step of SE could  
259 promote hydrolysis reactions through autohydrolysis mechanisms.<sup>23</sup> However, Table 1 shows  
260 that resin removal reached a limit and that from a 1: 6 ratio onwards, increasing the volume of  
261 water did not significantly improve adhesive removal (runs 14 and 15). Increasing the severity  
262 of steam treatments allowed a gradual removal of resin up to 80% and that a further increase of  
263 severity did not improve the resin removal.<sup>14</sup> In accordance with this work, it appeared from our  
264 study that  $\approx 15-20\%$  of the UF is strongly linked to the fibers and is highly recalcitrant.

## 265 **NIRS characterization**

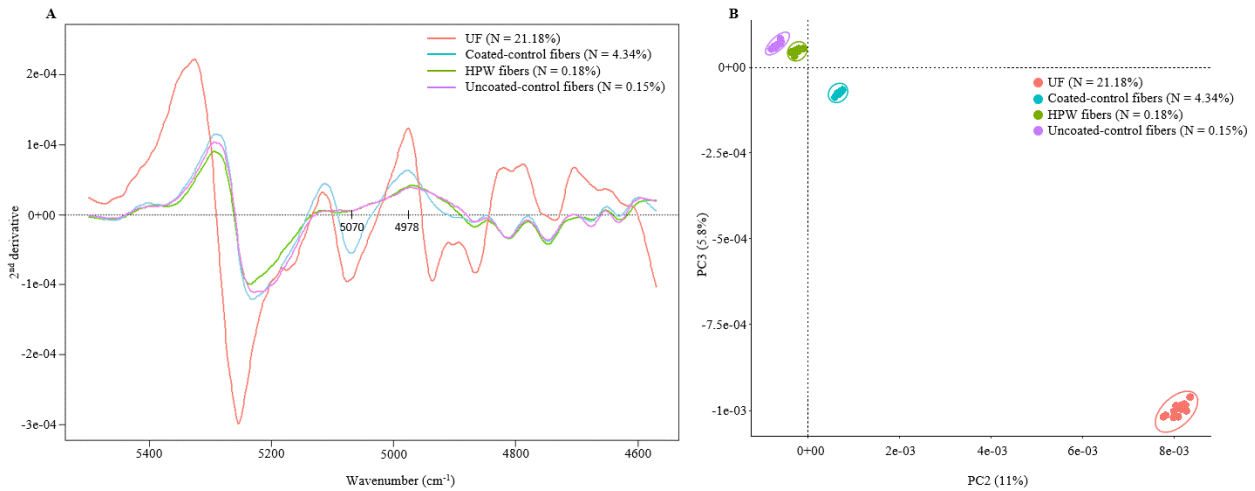
266 NIRS which was successfully used to describe UF synthesis was experimented in this work as a  
267 non-destructive technique to characterize samples subjected to HPW and SE treatments.<sup>37</sup> NIRS  
268 acquisition (n = 15) were first performed on uncoated-control fibers, coated-control fibers  
269 (containing UF resin) and treated by HPW (positive control of the resin removal) and compared  
270 with cured UF resin. A PCA was performed on the second derivative spectra. Based on the signal  
271 to noise ratio of the spectra, spectral region of interest was selected between  $7000\text{ cm}^{-1}$  and  $4500$   
272  $\text{cm}^{-1}$  (Figure S2). The variability analysis showed three spectral regions with high variability: one



273 between 6858  $\text{cm}^{-1}$  and 6630  $\text{cm}^{-1}$ , another one between 5978  $\text{cm}^{-1}$  and 5726  $\text{cm}^{-1}$  and the last  
274 one between 5500  $\text{cm}^{-1}$  and 4570  $\text{cm}^{-1}$  (Figure S3).

275 In order to determine the best conditions for analysis, PCA was performed on each subregion.  
276 Plotting of PCA of the components 1 and 2 performed on the region between 5500  $\text{cm}^{-1}$  and  
277 4570  $\text{cm}^{-1}$  allowed the best discrimination between wood and resin materials (Figure S4) but the  
278 best correlation between NIRS samples clusters and nitrogen content was obtained for the area  
279 between 5500  $\text{cm}^{-1}$  and 4570  $\text{cm}^{-1}$  (Fig. 3A) with components 2 and 3 plotted. This subregion has  
280 thus been selected for subsequent analysis. As shown on figure 3B, after PCA samples fall in  
281 significant distinct clusters that were correlated with their relative nitrogen content.

282



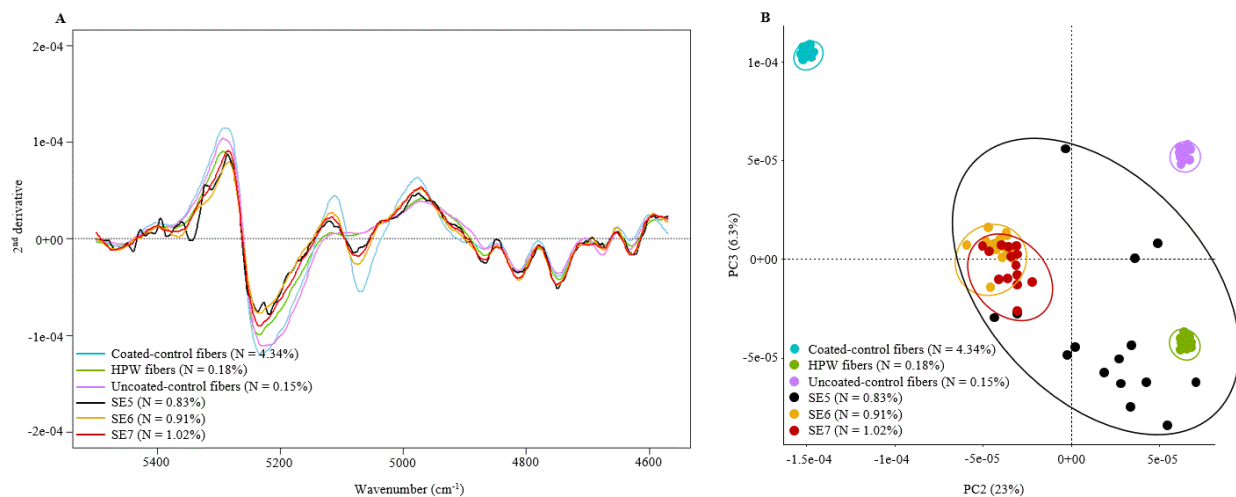
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284 **Figure 3.** NIRS detection of UF resin in MDF samples. A) Mean second derivative of cured UF  
285 (red), coated-control fibers (blue), HPW (green) and uncoated-control fibers (violet). The mean  
286 second derivative was calculated between 5500  $\text{cm}^{-1}$  and 4570  $\text{cm}^{-1}$ ; n=15. B) PCA of cured UF,  
287 coated-control fibers, HPW and uncoated-control fibers. The plot shows PC2-PC3 scores.

288 Variability analysis of the mean second derivative spectra and loadings analysis showed that the  
289 bands at  $5070\text{ cm}^{-1}$  and  $4978\text{ cm}^{-1}$  were found to be present in cured UF and in coated-control  
290 fibers but not in uncoated-control fibers (Fig. 3A and S5). These bands were found to be  
291 significant contributors to the variance explained on principal components 2 and 3 (Figure S5).  
292 These bands have thus been used as a marker of UF resin in subsequent analysis.

293 NIRS analysis was then performed on fibers treated by SE. Combining variability analysis and  
294 loadings analysis from PCA allowed to validate the attribution of the bands  $5070\text{ cm}^{-1}$  and  $4978$   
295  $\text{cm}^{-1}$  to the resin (Figure S6). The plotting of the spectral region (Fig. 4A) showed clearly a  
296 decrease of the amplitude of UF resin marker bands in all samples proceed by SE.

297 Plotting of PCA of the components 2 and 3 (Fig. 4B) confirmed trends observed on second  
298 derivative spectra (Fig. 4A). NIRS allowed discrimination of samples in clusters according to the  
299 treatment parameters. HPW fibers were really closed to uncoated-control fibers and SE fibers fall  
300 in an intermediate cluster between coated-control fibers and HPW. The fibers treated by SE at  
301  $190^{\circ}\text{C}$  for 10 and 20 min are not discriminated. The high dispersion of the fibers treated by SE at  
302  $190^{\circ}\text{C}$  for 5 min reflected the high variability of the treatment. Interestingly, the variability of the  
303 sample (95% CI ellipses) was decreasing with the increase of the residence time in the reactor.  
304 The tighter the scatter plot, the more homogeneous the treatment. Thus, increasing the retention  
305 time from 5 to 10 minutes allowed to improve the homogeneity of the treatment without  
306 decreasing thermohydrolysis efficiency of UF resin. Taking together, treating the fibers at  $190^{\circ}\text{C}$   
307 for 10 min allowed to obtain a good compromise between the retention time, the homogeneity of  
308 the treatment, the resin removal and the defibration of the material.



309  
 310 **Figure 4.** NIRS monitoring of SE effect on MDF fibers. A) Second derivative, B) PCA of  
 311 coated-control fibers, HPW, uncoated-control fibers, SE5, SE6 and SE7 fibers. The mean second  
 312 derivative was calculated between 5500 cm<sup>-1</sup> and 4500 cm<sup>-1</sup> (n=15). The plot shows PC2 and  
 313 PC3 scores. For each cluster the nitrogen content is indicated.

### 314 **Fibers yield, morphology and resin mapping**

315 Hydrothermal treatments previously described in the literature on MDF recycling lead to a fiber  
 316 shortening of ~ 30%<sup>11</sup>. Steam refining performed in comparable conditions lead to a fiber yield  
 317 of ~ 75%<sup>14</sup>. In this study, regardless of the experimental SE or SEW conditions considered  
 318 (Table 1, runs 2-15), a comparable fiber yield of 80% w/w (± 2 %) was achieved. Regarding the  
 319 fibers morphology, fibers resulting from run 6 were further analyzed. The fiber size distribution  
 320 is reported in Table 2. The size of the wood fibers used in the manufacture of MDF panels is  
 321 between 0.5 and 6 mm depending on the wood species and the manufacturing process used<sup>38</sup>. A  
 322 picture of the three fiber fractions obtained after SE 6 is given in Figure S7. For comparison, X-  
 323 ray tomography of the wood fibers in the MDF panel board was done (Fig S7A). Interestingly, in  
 324 these conditions SE allowed the recovery of more than 67% of the fibers with a length above 300

325  $\mu\text{m}$  without visible alteration of the fiber morphology. The different fiber fractions could be  
326 reused in different applications such as new panels or bio based composite materials.

327 **Table 2.** Particle size distribution of MDF fibers treated by SE (run SE6)

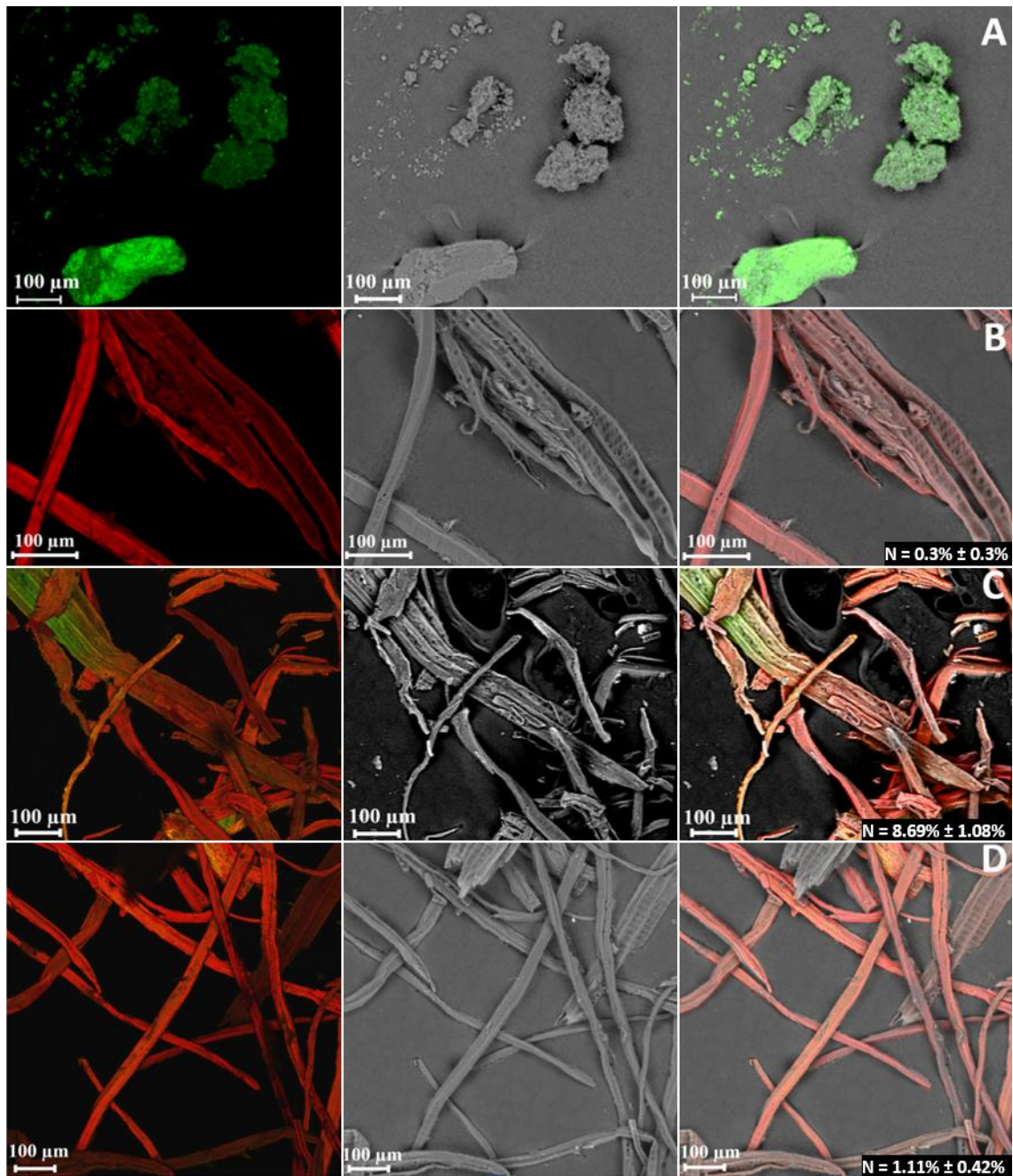
Sieve Mesh	Fraction type	Material captured
$> 850 \mu\text{m}$	Coarse fibers (a)	$28\% \pm 3\%$
$300 \mu\text{m} - 800 \mu\text{m}$	Medium coarse fibers (b)	$35\% \pm 3\%$
$< 300 \mu\text{m}$	Fines (c)	$37\% \pm 7\%$

328

329 To map the UF resin on the fibers, optical fluorescence microscopy was used. A preliminary  
330 study was carried out to validate the staining method using safranin. Safranin-stained unresinated  
331 fibers and UF resin were observed under a confocal microscope to acquire specific fluorescence  
332 emission spectra. The maxima emission of the resin and the wood being distinct, it is possible to  
333 apply a spectral deconvolution at any pixel of the microscope image in order to attribute a signal  
334 to the resin (green) (Fig. 5A) and to the wood (red) (Fig. 5B). Indeed, after staining, the cell  
335 walls of wood containing cellulose and lignin produced a red fluorescence.<sup>39</sup> The fiber staining  
336 method made it possible to visualize the distribution of resin on MDF fibers with high sensitivity  
337 and specificity.<sup>40</sup> It is therefore suitable for comparing non-treated MDF fibers with a high  
338 amount of UF resin and treated MDF fibers (run SE6) with a residual amount of UF resin.

339 The images on Figure 5 are representative of the observed phenomenon. coated-control fibers  
340 (Fig. 5C) showed green patches on wood fiber in red. This patchy distribution of UF resin was  
341 observed previously.<sup>41,42</sup> In order to validate that green signal was resulting from UF resin  
342 occurrence, correlative CLSM-SEM microscopy coupled to WDS analysis was carried out.

343 Briefly, after observation of fields of interest with CLSM, these fields could be relocated under  
344 the SEM and an overlay of the two images could be obtained. Then EDS and WDS spectral  
345 acquisition could be done on specific region of interest on fibers or fiber pellets. CLEM-EDS and  
346 WDS microanalysis confirmed the localization of nitrogen coming from UF in the green areas  
347 (Figure S8, S9). These observations validate the methodology. Treated fibers (SE6, Fig. 5D)  
348 displayed a strong decrease of the green fluorescence linked to the resin and instead showed a  
349 yellow orange fluorescence. Three dimensional reconstructions showed the intrinsic embedding  
350 of the UF resin in the fiber making its total removal impossible without destroying the fibers  
351 (Figure S10) and are in agreement with the previous reports of UF resin penetration into the  
352 fibers leading to its recalcitrance<sup>14,43</sup>. These images confirmed an efficient resin removal from  
353 the steam exploded fibers.



354

355 **Figure 5.** From left to right, CLSM (maximal intensity projection), SEM and CLEM images of

356 A) UF resin B) Uncoated-control fibers C) Coated-control fibers and D) Treated MDF fibers

357 SE6, stained by safranin. Relative nitrogen percentage determined by WDS on fibers pellets,

358 mean of 15 acquisitions are given on CLEM images. Error values are 95% CI.

359 CLEM-EDS allowed the UF mapping on fibers but is not quantitative. Thus, SEM-WDS  
360 quantification was performed on pellets of milled fibers. Relative nitrogen quantifications are  
361 indicated in Figure 5. Interestingly, fibers resulting from SE6 treatment differed significantly  
362 from coated-control fibers but not from uncoated-control fibers (ANOVA,  $P = 0.81$ ). This non-  
363 destructive *in-situ* semi-quantitative analysis estimated a relative resin removal on the fibers  
364 treated by SE of about 88% which is in the same range as the bulk elemental combustion  
365 analysis.

## 366 CONCLUSION

367 Compared to hot pressurized water treatment, steam explosion is a very promising process for  
368 the recovery of MDF fibers, allowing 83% of the resin removal accompanied with an efficient  
369 fragmentation in a very short time and a water consumption divided by 3. MDF waste must be  
370 treated according to its future recovery to choose the most suitable treatment. A detailed analysis  
371 of the fibers was conducted to characterize the fibers. PCA performed on NIRS data has great  
372 potential for distinguishing waste MDF and recovered fibers. The loadings analysis confirmed  
373 the decrease of the resin on recovered fibers. Combining CLSM and SEM allowed the  
374 observation and *in situ* quantification of the reduction of UF resin coverage on MDF fibers. The  
375 work that we are currently carrying out in the perspective of industrial developments aim to (1)  
376 validate the results obtained on real MDF waste; (2) take interest in the decontamination of the  
377 aqueous effluents of the process which were not addressed in this article; (3) transfer the batch  
378 process into a continuous process. We hope that these prospects will pave the way for industrial  
379 recycling of MDF with a better environmental impact than its current end-of-life management.

## 380 ASSOCIATED CONTENT

381 **Supporting information.** The supporting information is available free of charge on the ACS  
382 Publication website.

383 Steam explosion schematic view. Determination of the informative region of second derivative  
384 spectra. Variability analysis on second derivative spectra calculated between 7000 cm<sup>-1</sup> and  
385 4500 cm<sup>-1</sup> and identification of the three sub regions of interest. PCA analysis with PC1 and  
386 PC2. Variability and loadings analysis for UF bands identification between 5500 cm<sup>-1</sup> and 4570  
387 cm<sup>-1</sup>. Variability and loadings analysis on SE and HPW samples between 5500 cm<sup>-1</sup> and 4570  
388 cm<sup>-1</sup>. Fibers treated by SE6. CLEM-EDS analysis of UF-resin on wood fibers. CLEM-EDS  
389 analysis of UF-resin on wood fibers with EDS nitrogen mapping. CLSM 3D reconstruction of  
390 MDF fibers.

391

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396

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398 **Author Contributions**

399 Sarah Troilo: Investigation and Conceptualization. Arnaud Besserer: Methodology. Analysis.

400 Investigation. Christophe Rose: Investigation and analysis. Safwan Saker: technical assistance.

401 Lucas Soufflet: Project administration and funding. Nicolas Brosse: Project administration and

402 supervision.

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#### 417 ABBREVIATIONS

418 CLEM, correlative light electron microscopy; CLSM, confocal laser scanning microscopy; EDS,  
419 energy dispersive spectroscopy; HPLC, high-performance liquid chromatography; HPW, hot  
420 pressurized water treatment; MDF, medium density fiberboard; NIRS, near-infrared  
421 spectroscopy PCA, principal component analysis; SE, steam explosion; SEM, scanning electron  
422 microscopy, SEW, steam explosion with additional water; UF, urea-formaldehyde; WDS,  
423 wavelength-dispersive spectroscopy.

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- 559  
560

## 561 SYNOPSIS

562 This work presents an ecological solution for the recovery of MDF waste, a non-recyclable and  
563 environmentally harmful material.

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