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

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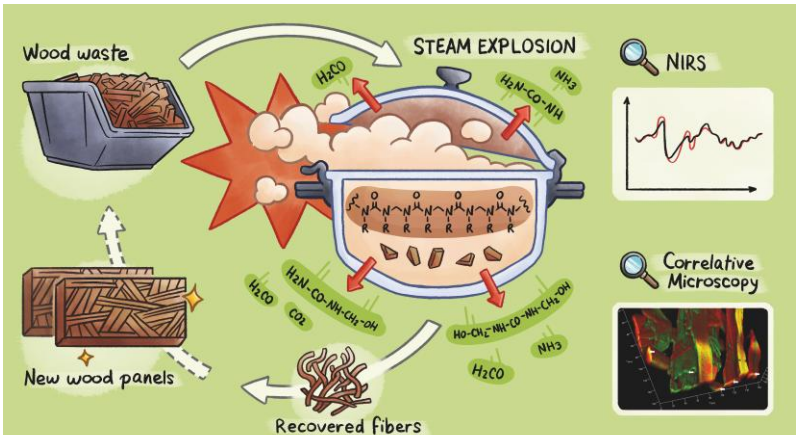
KEYWORDS

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

ABSTRACT

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

GRAPHICAL ABSTRACT



INTRODUCTION

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

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

63 proposed for UF removal prior to the reuse of wood-based panels.[11] Neutral and acidic
64 hydrolysis can removed ~ 50% and ~ 70% respectively of UF resin from MDF fibers.[12]
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.[13,14]

68 The steam explosion (SE) technology is both energy efficient and versatile. The technology was
69 initially developed to manufacture chipboard panels[15,16] and is particularly mature for cellulosic
70 bioethanol[1,17,18]. This process was also recently described for biomolecules and biopolymers
71 extraction or the valorization of biomass from phytotechnology.[19–22] Several studies examined
72 the importance of water content in hydrolytic processes during SE pretreatments.[23,24] However,
73 these phenomena are still largely unknown. The utilization of SE as a pretreatment for MDF
74 recovery was reported in the literature[25] 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.[13] 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. [26,27] Confocal laser scanning microscopy (CLSM) has been developed to
84 detect or visualize UF resin.[28] The combination of the localization of the region of interest by

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

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

MATERIALS AND METHOD

MDF characterization

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

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**

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

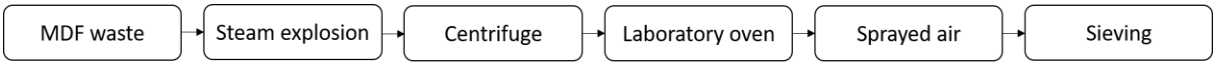


Figure 1. Process flowchart

Pollutants quantification

To determine the rate of UF-resin removal in different SE conditions, nitrogen and formaldehyde were measured on the fibers. An elemental combustion analysis was performed on a Thermo Scientific Flash EA 112 (USA) to determine the percentage of nitrogen on the fibers. The samples were grounded into a homogeneous powder. The combustion of the samples was performed at 950°C in the presence of copper oxide under oxygen flow for 15 seconds and produces CO_2, H_2O, SO_2 and NO_x which were reduced to nitrogen by copper. The combustion products were then measured by gas chromatography under the conditions determined by the manufacturer. The results were recorded and analyzed by the software Eager 300.

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

were autoclaved at 121°C for 20 min to extract the formaldehyde. Before the analysis, the samples were derivatized with a solution of 2,4 dinitrophenylhydrazine (2,4 DNPH). 500 mg of 2,4 DNPH and 0.5 mL of phosphoric acid (H_3PO_4) 85% were dissolved in 49.5 mL of acetonitrile. The pH of the samples was adjusted to 5. One milliliter of the sample was centrifuged at 12 000 RPM for 10 min and the supernatant was passed through a 0.45 diameter nylon filter. 20 µL of the sample, 30 µL of 2,4 DNPH solution and 950 µL of acetonitrile were mixed in a 1.5 mL vial and injected into the HPLC. Formaldehyde analyses were performed on a C18 Luna column (50 mm × 2.1 mm, 1.7 µm particle size) (Acquity, UPLC, Waters, USA) using a HPLC (Thermo Scientific, Dionex Ultimate 3000, USA). The wavelength was set to 365 nm. Separation was achieved with a mixture of water/acetonitrile (40:60, v/v). The flow rate was 0.3 mL/min and the injection volume was 1 µL. The total run time was 12 min.

NIRS

The measurements were performed on a Perkin Elmer NIRS spectrometer (USA) equipped with an IngaAs detector and a CaF2 beam splitter. Three samples of 5 g from each condition were analyzed and five spectra for each sample were recorded from 10,000 to 4,000 cm^{-1} with a 2 cm^{-1} resolution. As described previously, only the spectral region between 6950 and 5500 cm^{-1} was further considered for analysis.[31] The log10 (1/R) of the spectral data was calculated. This process is typically used for quantitative analysis.[32] Then second derivative was calculated as previously described.[33] In lab developed scripts based on RStudio and the plugin Chemospec were used to analyze the raw data.[34] Principal component analysis (PCA) was performed to analyze a limited set of independent and significant variables. The chemical differences of the samples were visualized in a scatter plot and the loadings were analyzed to identify the main contributive variables.

CLEM

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

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

EDS and WDS analyses

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

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

X-ray tomography

One cube of side 20 mm was scanned on a 39 Watt Tomograph (RX Solution, France) with a high tension of 0–130 kW and an anode current of 0–300 µA. The voxel size was 10.67 µm. A subsample of 500 slices amongst the 1131 slices was selected for the 3D reconstruction using Fiji software[35].

RESULTS AND DISCUSSION

Hot Pressurized Water treatment (HPW)

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

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

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

Steam explosion treatment (SE and SEW)

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

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

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

cyclone during the explosive decompression could also induce a high mechanical stress to the material causing its total disruption [36].

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

NIRS characterization

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

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

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

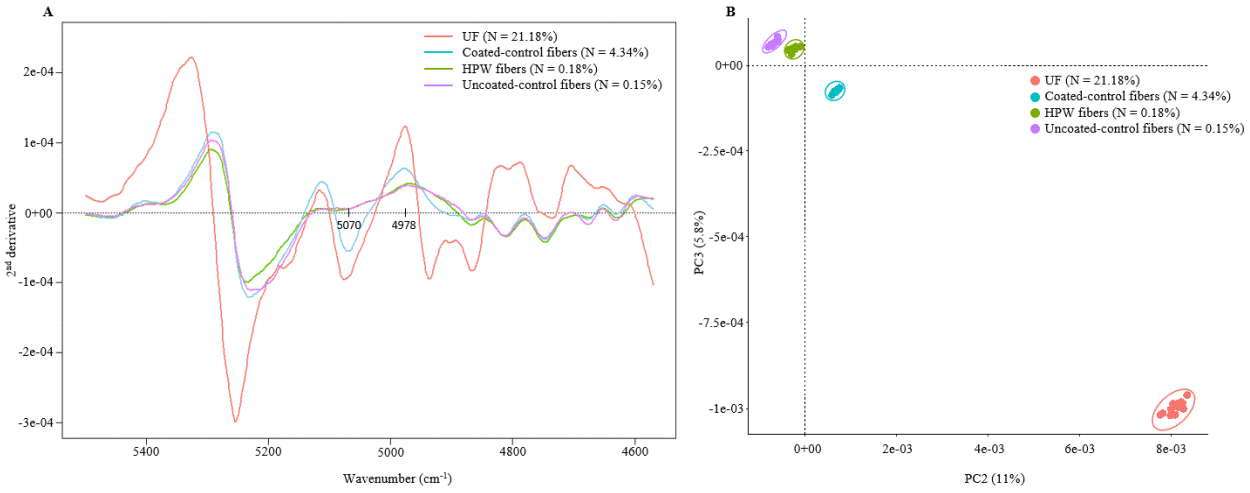


Figure 3. NIRS detection of UF resin in MDF samples. A) Mean second derivative of cured UF (red), coated-control fibers (blue), HPW (green) and uncoated-control fibers (violet). The mean second derivative was calculated between 5500 cm^{-1} and 4570 cm^{-1}; n=15. B) PCA of cured UF, coated-control fibers,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

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

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

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

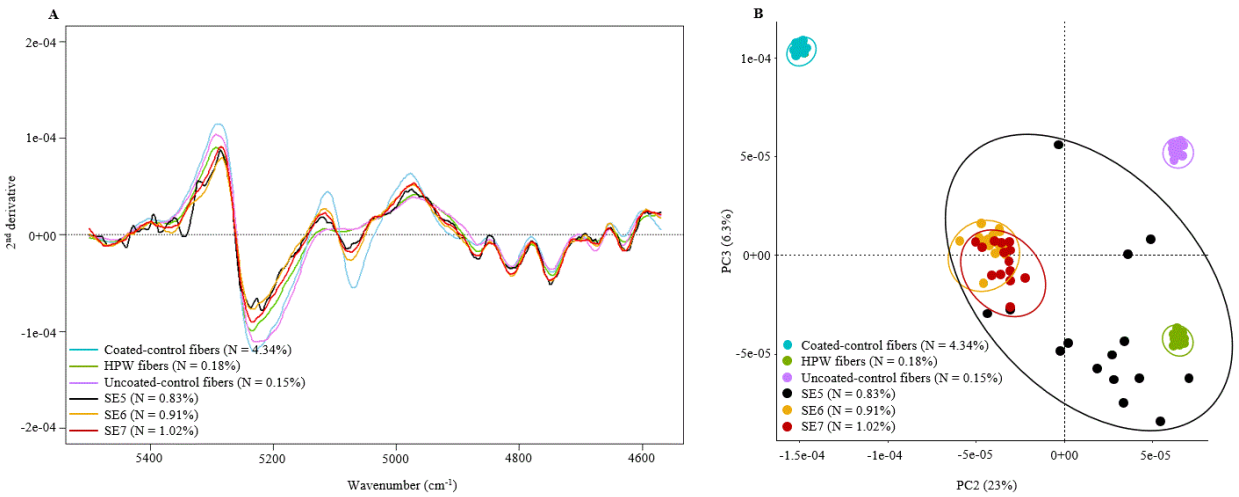


Figure 4. NIRS monitoring of SE effect on MDF fibers. A) Second derivative, B) PCA of coated-control fibers, HPW, uncoated-control fibers, SE5, SE6 and SE7 fibers. The mean second derivative was calculated between 5500 cm^{-1} and 4500 cm^{-1} (n=15). The plot shows PC2 and PC3 scores. For each cluster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

Fibers yield, morphology and resin mapping

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

325 µm 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 µm	Coarse fibers (a)	28% ± 3%
300 µm – 800 µm	Medium coarse fibers (b)	35% ± 3%
< 300 µm	Fines (c)	37% ± 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.[39] The fiber staining
336 method made it possible to visualize the distribution of resin on MDF fibers with high sensitivity
337 and specificity.[40] 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.[41,42] 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.

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

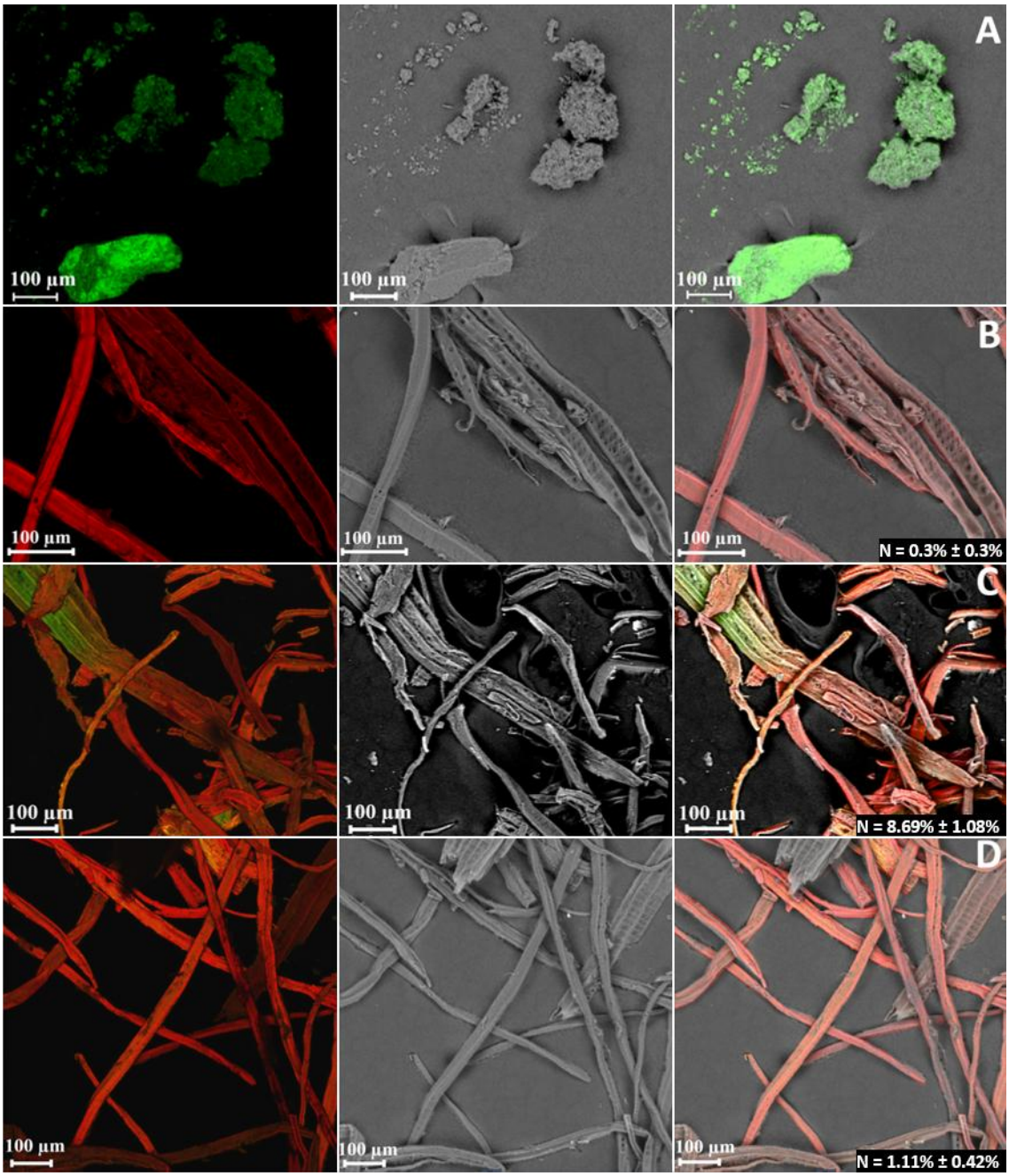


Figure 5. From left to right, CLSM (maximal intensity projection), SEM and CLEM images of A) UF resin B) Uncoated-control fibers C) Coated-control fibers and D) Treated MDF fibers SE6, stained by safranin. Relative nitrogen percentage determined by WDS on fibers pellets, mean of 15 acquisitions are given on CLEM images. Error values are 95% CI.

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

CONCLUSION

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

ASSOCIATED CONTENT

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

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

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Notes

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ABBREVIATIONS

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

REFERENCES

(1) Besserer, A.; Troilo, S.; Girods, P.; Rogaume, Y.; Brosse, N. Cascading Recycling of Wood Waste: A Review. *Polymers* **2021**, *13* (11), 1752. https://doi.org/10.3390/polym13111752.
(2) Suchsland, O. *Fiberboard Manufacturing Practices in the United States*; U.S. Department of Agriculture, Forest Service, 1987; Vol. 640.
(3) FAOSTAT. *Forestry Production and Trade*. http://www.fao.org/faostat/en/#data/FO (accessed 2021-10-05).

(4) Irle, M.; Privat, F.; Couret, L.; Belloncle, C.; Déroubaix, G.; Bonnin, E.; Cathala, B. Advanced Recycling of Post-Consumer Solid Wood and MDF. *Wood Material Science & Engineering* **2019**, *14* (1), 19–23. https://doi.org/10.1080/17480272.2018.1427144.
(5) Girods, P.; Rogaume, Y.; Dufour, A.; Rogaume, C.; Zoulalian, A. Low-Temperature Pyrolysis of Wood Waste Containing Urea–Formaldehyde Resin. *Renewable Energy* **2008**, *33* (4), 648–654. https://doi.org/10.1016/j.renene.2007.03.026.
(6) Lee, M.; Prewitt, L.; Mun, S. P. Formaldehyde Release from Medium Density Fiberboard in Simulated Landfills for Recycling. *Journal of the Korean Wood Science and Technology* **2014**, *42* (5), 597–604. https://doi.org/10.5658/WOOD.2014.42.5.597.
(7) Dunky, M. Urea–Formaldehyde (UF) Adhesive Resins for Wood. *International Journal of Adhesion and Adhesives* **1998**, *18* (2), 95–107. https://doi.org/10.1016/S0143-7496(97)00054-7.
(8) Moezzipour, B.; Ahmadi, M.; Abdolkhani, A.; Doosthoseini, K. Chemical Changes of Wood Fibers after Hydrothermal Recycling of MDF Wastes. *J Indian Acad Wood Sci* **2017**, *14* (2), 133–138. https://doi.org/10.1007/s13196-017-0198-6.
(9) Zhong, R.; Gu, J.; Gao, Z.; Tu, D.; Hu, C. Impacts of Urea-Formaldehyde Resin Residue on Recycling and Reconstitution of Wood-Based Panels. *International Journal of Adhesion and Adhesives* **2017**, *78*, 60–66. https://doi.org/10.1016/j.ijadhadh.2017.06.019.
(10) Fleischer, O.; Marutzky, R. Hydrolyse von Harnstoff-Formaldehyd-Harzen: AufloÈsung des SpangefuÈges in Holzwerkstoffen durch hydrolytischen Abbau der Leimfuge. *Holz Als Roh Und Werkstoff* **2000**, 6.
(11) Lubis, M. A. R.; Manohar, S. Y.; Laksana, R. P. B.; Fatriasari, W.; Ismayati, M.; Falah, F.; Solihat, N. N.; Sari, F. P.; Hidayat, W. The Removal of Cured Urea-Formaldehyde Adhesive towards Sustainable Medium Density Fiberboard Production: A Review. *JSL* **2021**, *9* (1), 23. https://doi.org/10.23960/jsl1923-44.
(12) Lubis, M. A. R.; Hong, M.-K.; Park, B.-D. Hydrolytic Removal of Cured Urea–Formaldehyde Resins in Medium-Density Fiberboard for Recycling. *Journal of Wood Chemistry and Technology* **2018**, *38* (1), 1–14. https://doi.org/10.1080/02773813.2017.1316741.
(13) Gibier, M.; Sadeghisadeghabad, M.; Girods, P.; Zoulalian, A.; Rogaume, Y. Furniture Wood Waste Depollution through Hydrolysis under Pressurized Water Steam: Experimental Work and Kinetic Modelization. *Journal of Hazardous Materials* **2022**, *436*, 129126. https://doi.org/10.1016/j.jhazmat.2022.129126.
(14) Hagel, S.; Saake, B. Fractionation of Waste MDF by Steam Refining. *Molecules* **2020**, *25* (9), 2165. https://doi.org/10.3390/molecules25092165.
(15) Mason, W. H. Process and Apparatus for Disintegration of Wood and the Like, 1926. https://patentimages.storage.googleapis.com/0a/31/f4/551e24519451f0/US1578609.pdf (accessed 2020-07-20).
(16) Ziegler-Devin, I.; Chrusciel, L.; Brosse, N. Steam Explosion Pretreatment of Lignocellulosic Biomass: A Mini-Review of Theorical and Experimental Approaches. *Frontiers in Chemistry* **2021**, *9*, 860. https://doi.org/10.3389/fchem.2021.705358.
(17) Fernandes, M. C.; Ferro, M. D.; Paulino, A. F. C.; Mendes, J. A. S.; Gravitis, J.; Evtuguin, D. V.; Xavier, A. M. R. B. Enzymatic Saccharification and Bioethanol Production from Cynara Cardunculus Pretreated by Steam Explosion. *Bioresource Technology* **2015**, *186*, 309–315. https://doi.org/10.1016/j.biortech.2015.03.037.

(18) Chen, W.-H.; Pen, B.-L.; Yu, C.-T.; Hwang, W.-S. Pretreatment Efficiency and Structural Characterization of Rice Straw by an Integrated Process of Dilute-Acid and Steam Explosion for Bioethanol Production. *Bioresource Technology* **2011**, *102* (3), 2916–2924. https://doi.org/10.1016/j.biortech.2010.11.052.
(19) Chadni, M.; Grimi, N.; Bals, O.; Ziegler-Devin, I.; Brosse, N. Steam Explosion Process for the Selective Extraction of Hemicelluloses Polymers from Spruce Sawdust. *Industrial Crops and Products* **2019**, *141*, 111757. https://doi.org/10.1016/j.indcrop.2019.111757.
(20) He, Q.; Ziegler-Devin, I.; Chrusciel, L.; Obame, S. N.; Hong, L.; Lu, X.; Brosse, N. Lignin-First Integrated Steam Explosion Process for Green Wood Adhesive Application. *ACS Sustainable Chem. Eng.* **2020**, *8* (13), 5380–5392. https://doi.org/10.1021/acssuschemeng.0c01065.
(21) Mougnala Moukagni, E.; Ziegler-Devin, I.; Safou-Tchima, R.; Brosse, N. Extraction of Acetylated Glucuronoxylans and Glucomannans from Okoume (Aucoumea Klaineana Pierre) Sapwood and Heartwood by Steam Explosion. *Industrial Crops and Products* **2021**, *166*, 113466. https://doi.org/10.1016/j.indcrop.2021.113466.
(22) Simangunsong, E.; Ziegler-Devin, I.; Chrusciel, L.; Girods, P.; Wistara, N.; Brosse, N. Steam Explosion of Beech Wood: Effect of the Particle Size on the Xylans Recovery | EndNote Click. **2020**.
(23) Sui, W.; Chen, H. Effects of Water States on Steam Explosion of Lignocellulosic Biomass. **2016**.
(24) Liu, L.-Y.; Qin, J.-C.; Li, K.; Mehmood, M. A.; Liu, C.-G. Impact of Moisture Content on Instant Catapult Steam Explosion Pretreatment of Sweet Potato Vine. **2017**. https://doi.org/10.14288/1.0360749.
(25) Wan, H.; Wang, X.-M.; Barry, A.; Shen, J. Recycling Wood Composite Panels: Characterizing Recycled Materials. *BioResources* **2014**, *9*. https://doi.org/10.15376/biores.9.4.7554-7565.
(26) Mauruschat, D.; Plinke, B.; Aderhold, J.; Gunschera, J.; Meinlschmidt, P.; Salthammer, T. Application of Near-Infrared Spectroscopy for the Fast Detection and Sorting of Wood–Plastic Composites and Waste Wood Treated with Wood Preservatives. *Wood Sci Technol* **2016**, *50* (2), 313–331. https://doi.org/10.1007/s00226-015-0785-x.
(27) So, C.-L.; Lebow, S. T.; Groom, L. H.; Rials, T. G. The Application of near Infrared (NIR) Spectroscopy to Inorganic Preservative-Treated Wood. *Wood and Fiber Science* **2004**, *36(3)*, 329–336.
(28) Pakdel, H.; Cyr, P.-L.; Riedl, B.; Deng, J. Quantification of Urea Formaldehyde Resin in Wood Fibers Using X-Ray Photoelectron Spectroscopy and Confocal Laser Scanning Microscopy. *Wood Sci Technol* **2008**, *42* (2), 133–148. https://doi.org/10.1007/s00226-007-0155-4.
(29) Tessier, F. Determining the Nitrogen Content in (Oxy)Nitride Materials. *Materials* **2018**, *11* (8), 1331. https://doi.org/10.3390/ma11081331.
(30) Ren, T.; Wang, Y.; Wu, N.; Qing, Y.; Li, X.; Wu, Y.; Liu, M. Degradation of Urea-Formaldehyde Resin Residues by a Hydrothermal Oxidation Method into Recyclable Small Molecular Organics. *Journal of Hazardous Materials* **2022**, *426*, 127783. https://doi.org/10.1016/j.jhazmat.2021.127783.
(31) Fackler, K.; Schwanninger, M.; Gradinger, C.; Srebotnik, E.; Hinterstoisser, B.; Messner, K. Fungal Decay of Spruce and Beech Wood Assessed by Near-Infrared Spectroscopy in

Combination with Uni- and Multivariate Data Analysis. *Holzforschung* **2007**, *61* (6), 680–687. https://doi.org/10.1515/HF.2007.098.
(32) Schwanninger, M.; Rodrigues, J. C.; Fackler, K. A Review of Band Assignments in near Infrared Spectra of Wood and Wood Components. *Journal of Near Infrared Spectroscopy* **2011**, *19* (5), 287–308. https://doi.org/10.1255/jnirs.955.
(33) Sandak, A.; Sandak, J.; Zborowska, M.; Prądzyński, W. Near Infrared Spectroscopy as a Tool for Archaeological Wood Characterization. *Journal of Archaeological Science* **2010**, *37* (9), 2093–2101. https://doi.org/10.1016/j.jas.2010.02.005.
(34) Hanson, B. A. ChemoSpec: An R Package for Chemometric Analysis of Spectroscopic Data (Package Version 4.4.97), 2017. https://bryanhanson.github.io/ChemoSpec/ (accessed 2012-09-15).
(35) Schindelin, J.; Arganda-Carreras, I.; Frise, E.; Kaynig, V.; Longair, M.; Pietzsch, T.; Preibisch, S.; Rueden, C.; Saalfeld, S.; Schmid, B.; Tinevez, J.-Y.; White, D. J.; Hartenstein, V.; Eliceiri, K.; Tomancak, P.; Cardona, A. Fiji: An Open-Source Platform for Biological-Image Analysis. *Nature Methods* **2012**, *9* (7), 676–682. https://doi.org/10.1038/nmeth.2019.
(36) Kessler, R. W.; Becker, U.; Kohler, R.; Goth, B. Steam Explosion of Flax - a Superior Technique for Upgrading Fibre Value. *Biomass and Bioenergy* **1998**, *14* (3), 237–249.
(37) Minopoulou, E.; Dessipri, E.; Chryssikos, G. D.; Gionis, V.; Paipetis, A.; Panayiotou, C. Use of NIR for Structural Characterization of Urea–Formaldehyde Resins. *International Journal of Adhesion and Adhesives* **2003**, *23* (6), 473–484. https://doi.org/10.1016/S0143-7496(03)00089-7.
(38) Benthien, J. T.; Heldner, S.; Ohlmeyer, M. Investigation of the Interrelations between Defibration Conditions, Fiber Size and Medium-Density Fiberboard (MDF) Properties. *Eur. J. Wood Prod.* **2017**, *75* (2), 215–232. https://doi.org/10.1007/s00107-016-1094-2.
(39) Bond, J.; Donaldson, L.; Hill, S.; Hitchcock, K. Safranine Fluorescent Staining of Wood Cell Walls. *Biotechnic & Histochemistry* **2008**, *83* (3–4), 161–171. https://doi.org/10.1080/10520290802373354.
(40) Grigsby, W. J.; Thumm, A.; Kamke, F. A. Determination of Resin Distribution and Coverage in MDF by Fiber Staining. *WOOD AND FIBER SCIENCE* **2003**, *37*, 12.
(41) Loxton, C.; Thumm, A.; Grigsby, W. J.; Adams, T. A.; Ede, R. M. Resin Distribition in Medium Density Fiberboard. Quantification of UF Resin Distribution on Blowline-and Dry-Blended MDF Fiber and Panels. *Wood and Fiber Science* **2003**, *35*, 11.
(42) Thumm, A.; McDonald, A. G.; Donaldson, L. A. Visualisation of UF Resin in MDF by Cathodoluminescence/ Scanning Electron Microscopy. *Holz als Roh- und Werkstoff* **2001**, *59* (3), 215–216. https://doi.org/10.1007/s001070100196.
(43) Xing, C.; Riedl, B.; Cloutier, A.; Shaler, S. M. Characterization of Urea–Formaldehyde Resin Penetration into Medium Density Fiberboard Fibers. *Wood Sci Technol* **2005**, *39* (5), 374–384. https://doi.org/10.1007/s00226-005-0294-4.

SYNOPSIS

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

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