



# Microwave-Assisted Treatment of Waste Wood Biomass with Deep Eutectic Solvents

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Deep eutectic solvents (DESs) are new sustainable and cheap reaction media combining the features of both ionic liquids and organic solvents. They are made up by association of hydrogen-bond donors and hydrogen-bond acceptors, and they can promote the hydrolysis of lignocellulosic bonds. Herein the microwave-assisted treatment of waste wood flours with a DES constituted by choline chloride and oxalic acid to get a cellulosic residue separated from lignin degradation products is reported. The insoluble deposit is characterized by SEM, TGA, DSC, FTIR-ATR, and  $^1\text{H}$ - $^{13}\text{C}$  CP/MAS NMR techniques and can be available for further uses such as nanocellulose production.

biofuels, chemicals, and other value-added products, commonly obtained from petroleum. Recently, numerous protocols for processing lignocellulosic biomass of selected plants have been reported. However, developing an environment-friendly method is still a big goal. This challenge becomes more interesting if lignocellulosic biomass coming from wood wastes could be efficiently treated. Deep eutectic solvents (DESs) are innovative and sustainable solvents consisting of a hydrogen bond donor and a hydrogen bond acceptor, having similar features of ionic liquids. DESs have a lower melting point than that of the respective components, preventing them from

crystallizing.<sup>[2]</sup> Many studies have been made on lignocellulosic biomass treatment with DES,<sup>[3]</sup> but in any case, the kind of wood source seems to play a key-role.<sup>[4]</sup> To the best of our knowledge, simple carpentry waste wood flours have never been considered before. Herein, we report on the microwave-assisted treatment of waste wood flours with DES formed by choline chloride and oxalic acid to get a cellulosic residue separated from lignin degradation products. The insoluble deposit was characterized by SEM, TGA, DSC, FTIR-ATR, and  $^1\text{H}$ - $^{13}\text{C}$  CP/MAS NMR techniques and could be available for further uses such as nanocellulose production.

## 1. Introduction

The increasing depletion of fossil feeds and the environmental concerns linked to the use of traditional energy sources have stimulated both academic and industrial communities in exploiting new sustainable and renewable suppliers of raw materials.<sup>[1]</sup> In this framework, lignocellulosic biomass can play an important role, acting as the starting material of a biorefinery leading to

## 2. Results and Discussion

On the base of the experiments carried out by Yu's research group<sup>[5]</sup> on poplar lignocellulosic biomass, we decided to treat our WWF with acidic DES composed by  $\text{ChCl}$ /oxalic acid in 1:1 molar ratio, being partially suitable to break the well-known biomass recalcitrance caused by the presence of lignin-carbohydrate complexes in wood feedstock. As this behavior can be enhanced under heating conditions, we decided to carry out the DES treatment of WWF under microwave irradiation, that ensures a uniform temperature distribution throughout the system. The WWF biomass was treated with DES, as summarized in **Figure 1**.

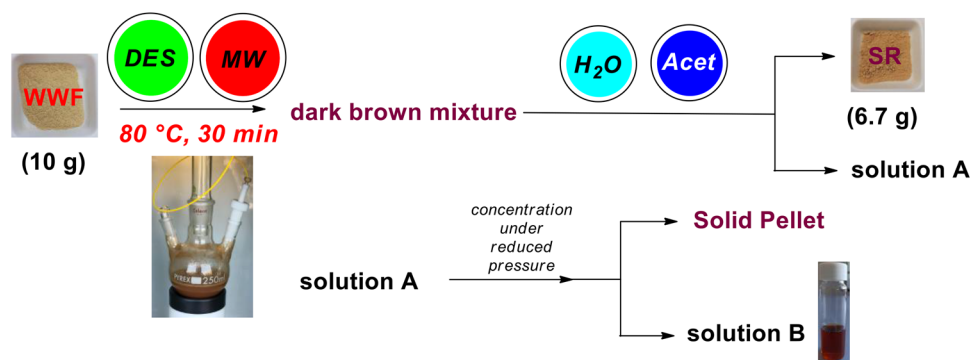
As depicted in **Figure 1**, after microwave assisted DES treatment of WWF, a solution of water and acetone was added to the dark brown formed mixture, giving a pale brown solid residue (SR) and a solution A, which was in turn concentrated under reduced pressure, causing the precipitation of a solid pellet (100 mg) from the remaining solution B. The transformation of the starting WWF material was analyzed by FT-IR spectroscopy (**Figure 2**).

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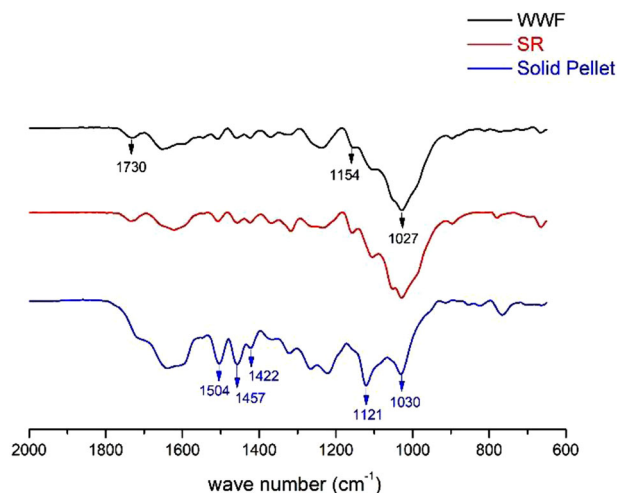
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**Figure 1.** Schematic representation of the DES treatment of WWF. DES indicates deep eutectic solvent; WWF, waste wood flour.

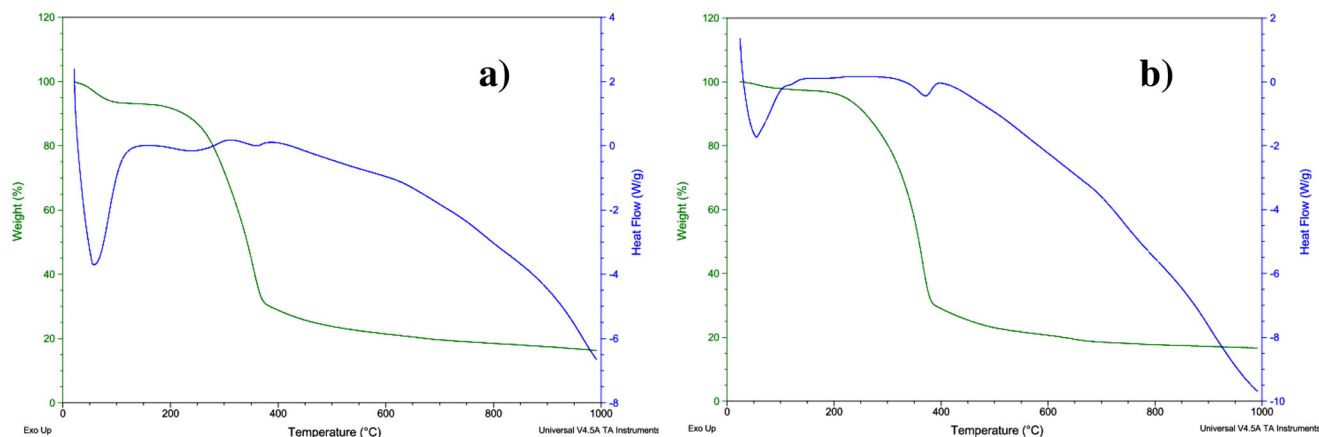


**Figure 2.** FT-IR spectra of WWF (black), SR (red), and solid pellet (blue). WWF indicates waste wood flour.

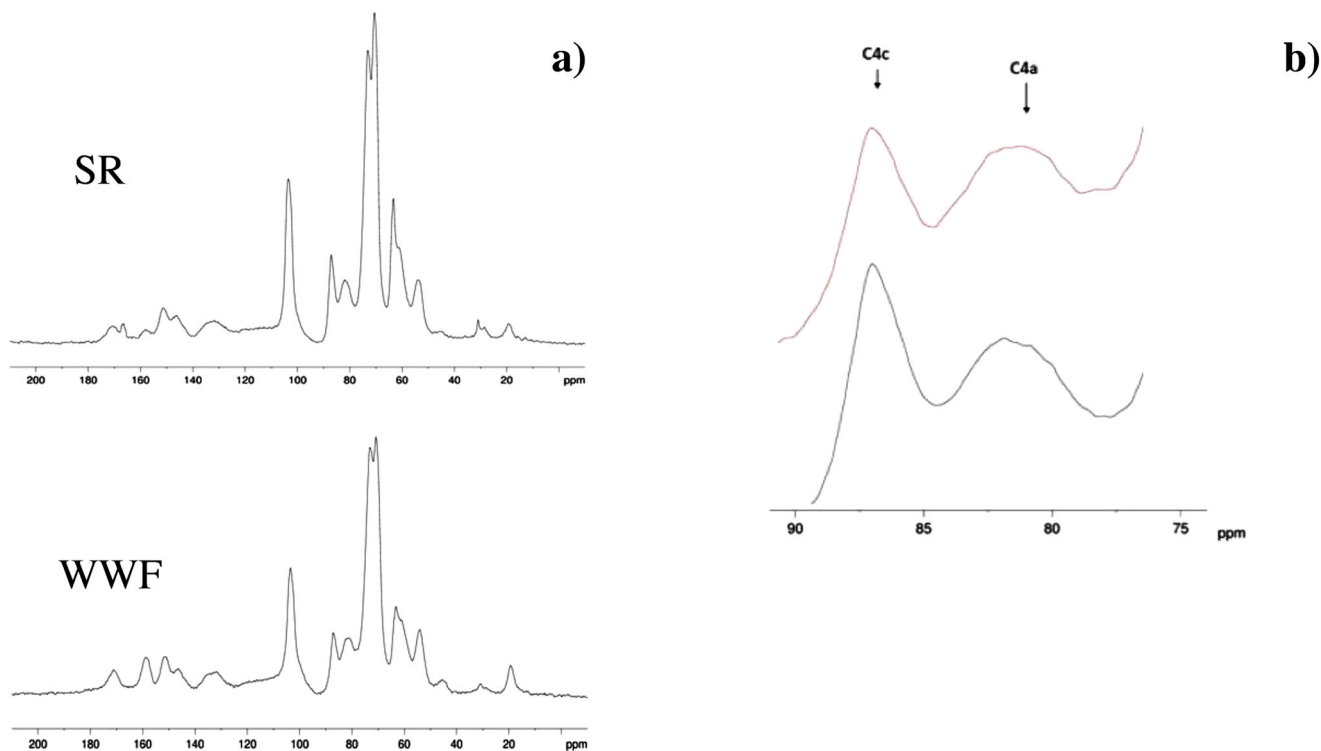
Lignocellulosic biomass, such as WWF, is constituted by cellulose (50% ca.), hemicellulose (30% ca.), and lignin (20% ca.). FT-IR spectra of WWF and SR (Figure 2) shows that both materials have similar structures, being the typical cellulose (and hemicellulose) peak at  $1027\text{ cm}^{-1}$  (due to the asymmetric stretching of C—O—C) the most intense band. In addition, in both

spectra the absorption bands at  $1730$  and  $1154\text{ cm}^{-1}$  belonging to C = O stretching in unconjugated ketone and carboxyl groups and C—O stretching in ester groups, respectively, are perceptible. The peaks in the region  $1510\text{--}1420\text{ cm}^{-1}$  due to aromatic skeletal vibrations are very intense in solid pellet spectrum, and visible (with low intensity) also in WWF and SR spectra (Figure 2), while the very intense bands at  $1030$  and  $1121\text{ cm}^{-1}$  are detectable only in the IR spectrum of the solid pellet. These occurrences strongly suggest that the solid pellet is constituted by lignin oligomers. In fact, the last bands belong to aromatic C—H in plane deformation for guaiacyl (G) and syringyl (S) type lignin units, respectively.<sup>[5]</sup> On the base of the FT-IR analyses, we can argue that part of lignin was extracted from biomass starting material through the microwave assisted treatment, and lignin oligomers solubilized in DES. The total amount of SR and solid pellet did not reach the initial mass of WWF employed, because many saccharides deriving from cellulose and hemicellulose hydrolysis and many lignin degradation products remained in the final solution B (Figure 1). TGA and DSC graphics of WWF (Figure 3a) and SR (Figure 3b) show that the thermal stability of SR resembles that of the original cellulose feedstock, suggesting that the DES-derived residue might be a promising source to generate cellulosic nanomaterials.

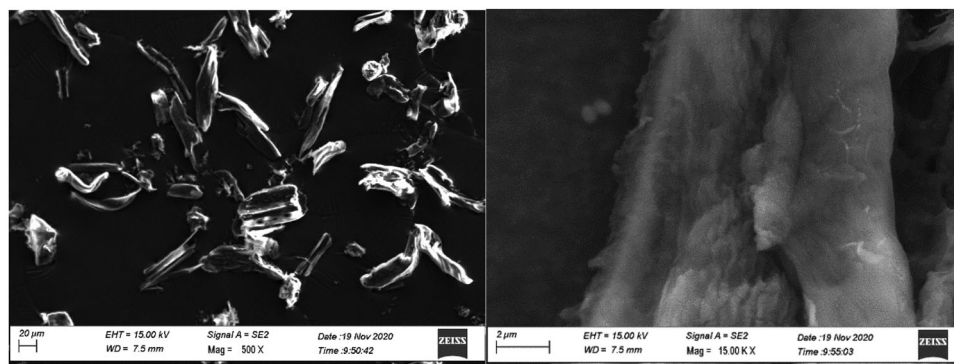
Figure 4 displays the  $^{13}\text{C}$  NMR spectra of WWF and SR. The three peaks at  $152.7$ ,  $147.1$ , and  $54.2$  ppm, belonging to syringyl (S), guaiacyl (G), and methoxyl group in lignin, respectively,



**Figure 3.** TG and DSC curves of: a) WWF and b) SR. DSC indicates Differential Scanning Calorimetry; WWF, waste wood flour.



**Figure 4.** a)  $^{13}\text{C}$  NMR spectra of WWF (down) and SR (up) and b) expansion of  $\text{C}^4$  region. SR indicates solid residue; WWF, waste wood flour.



**Figure 5.** SEM images of SR at different magnifications. SEM indicates Scanning Electron Microscopy; SR, solid residue.

slightly decreased on passing from WWF to SR, indicating the removal of some lignin. However, the peak at 174.8 ppm assigned to ester groups is detectable in both  $^{13}\text{C}$  NMR spectra, suggesting that the delignification process was not quantitative. Moreover, the two peaks around 85–90 and 77–85 ppm, corresponding to crystalline and noncrystalline  $\text{C}^4$  cellulose carbon, allowed to calculate the crystallinity index (CI),<sup>[6]</sup> which was 0.62 and 0.64 for WWF and SR, respectively, indicating the retaining of the crystallinity degree in the obtained SR after the fractionation process.

Finally, SEM micrograph of SR showed that this material was composed by microfibrils with a length of 80–100  $\mu\text{m}$  and a thickness of about 10  $\mu\text{m}$ , confirming the efficiency of the microwave assisted DES treatment in giving a microstructure morphology to the final residue (**Figure 5**).

### 3. Conclusion

Microwave assisted DES treatment of waste wood flours was applied to extract cellulose from lignocellulosic biomass. DES composed by choline chloride and oxalic acid turned to be able to cleave covalent bonds of lignin carbohydrate complexes. In fact, at the end of the process, lignin oligomers and saccharides coming from cellulose and hemicellulose hydrolysis were found in DES phase, while cellulose was recovered as insoluble residue. SEM analyses revealed the microstructure morphology (microfibrils) of the extracted cellulose, whose crystallinity index (0.64) was retained during DES treatment. In conclusion, microwave assisted DES treatment of wood flours acted as a promising biorefinery process.



## 4. Experimental Section

**Materials and Methods:** Sieved (80 mesh) carpentry waste wood flour (WWF) was used as starting material for cellulose extraction. Choline chloride (ChCl) and oxalic acid dihydrate were purchased from Scharlab S.L. (Barcelona, Spain) and used without further purification for the preparation of DES. All chemicals were of analytical purity and used as received from commercial sources. Tap water was deionized by ionic exchange resins (Millipore) before use. Microwave-assisted heating was conducted with an ETHOS E-TOUCH Milestone Microwave reaction system. FT-IR spectra were recorded with a Jasco FT-IR 4200 spectrophotometer in the attenuated total reflectance (ATR) mode. 600–4000  $\text{cm}^{-1}$  was selected as wavenumber range. Each spectrum was performed in absorbance mode collecting 32 scans per analysis with a resolution of 4  $\text{cm}^{-1}$ . Scanning Electron Microscopy (SEM) analyses were carried out by employing a FESEM Zeiss Sigma 300 VP (Zeiss Oberkochen, Germany) to observe the surface morphology of the samples at 15 kV. A droplet of diluted sample suspension in deionized water was deposited on the carbon-covered electron microscopy specimen holder. The system was let standing at room temperature for a couple of hours until water evaporated. Before SEM analysis, all samples were coated with gold under vacuum to enhance image sharpness.

Thermogravimetric (TG) analyses were conducted using a TA instruments SDT Q600 thermal analyzer to simultaneously perform Thermogravimetric (TGA) and Differential Scanning Calorimetry (DSC) analyses. The measurements were accomplished in nitrogen flow from 30 to 1000 °C with a heating rate of 10 °C  $\text{min}^{-1}$ .  $^1\text{H}$ - $^{13}\text{C}$  CP/MAS NMR analyses were carried out at room temperature with a Bruker Avance-400 (Rheinstetten, Germany) spectrometer. Spectra were acquired with a 4 mm MAS probe using a combination of CP, MAS, and high-power proton decoupling methods. A total of 4096 scans were accumulated for each sample using 10 kHz of MAS spinning speed, 3 ms of CP contact time, and 6 s of recycle delay. The crystallinity index (CI) of cellulose was calculated by dividing the area of the crystalline peak (integrating the peak from 85 to 90 ppm) by the total area assigned to the  $\text{C}^4$  peaks (integrating the region from 77 to 90 ppm).

**Treatment with DES:** ChCl and oxalic acid dihydrate (1:1 molar ratio) were placed in a round bottom flask. The binary mixture was heated at 80 °C under reduced pressure for the time necessary to obtain a clear liquid (about 1 h). The so obtained DES was allowed to cool down to room temperature. Waste wood flour (10 g) was added to DES (100 g), and the temperature was raised from room temperature to 80 °C for 2 min and held for 28 min in an ETHOS E-TOUCH Milestone oven. After heating, a mixture of deionized water/acetone (100 mL 100 mL $^{-1}$ ) was added, and

the mixture was filtered. The solid residue (SR) was washed with deionized water (250 mL x 2) and then oven-dried overnight. Yield = 6.7 g.

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The author's name "Piero Mastrorilli" was updated on October 21, 2022.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Data available on request from the authors.

## Keywords

biorefinery, deep eutectic solvents, lignocellulose treatment, microwave, wood biomass

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