

Article

Choline Chloride-Based Deep Eutectic Solvent-Treated Wood

Ahmet Can ^{1,*}, İsmail Özlüsoylu ¹, Petar Antov ^{2,*} and Seng Hua Lee ^{3,4}¹ Faculty of Forestry, Bartın University, Bartın 74100, Türkiye² Faculty of Forest Industry, University of Forestry, 1797 Sofia, Bulgaria³ Department of Wood Industry, Faculty of Applied Sciences, Universiti Teknologi MARA Jengka (UiTM), Cawangan Pahang Kampus, Bandar Tun Razak 26400, Pahang, Malaysia⁴ Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia (UPM), Serdang 43400, Selangor, Malaysia

* Correspondence: acan@bartin.edu.tr (A.C.); p.antov@ltu.bg (P.A.)

Abstract: Due to their adaptability and low preparation costs, deep eutectic solvents (DESs) have been widely used in a variety of applications. For some potential industrial applications, developing new low-cost DESs is critical. Oxalic acid (OA), acetic acid (AA), urea (Ur), and glycerol (GL) were mixed in various molar ratios to make DES solutions, with choline chloride (ChCL) acting as the hydrogen bond acceptor (HBA). In this work, DES solutions were applied to wood samples of Oriental spruce (*Picea orientalis*) at 150 °C. The chemical structures of wood samples were significantly altered after impregnation with DES solutions, as revealed by Fourier transform infrared spectroscopy (FTIR). The hemicellulose and cellulose peaks increased around 1700 cm⁻¹, while the lignin peak disappeared completely around 1500 cm⁻¹. After the decay test, mass losses were lower than in the control samples. The decay tests revealed that the leached wood samples were more resistant to decay. DES-treated wood samples, on the other hand, decomposed at lower temperatures.

Keywords: deep eutectic solvents; spruce wood; wood impregnation; decay tests



Citation: Can, A.; Özlüsoylu, İ.; Antov, P.; Lee, S.H. Choline Chloride-Based Deep Eutectic Solvent-Treated Wood. *Forests* **2023**, *14*, 569. <https://doi.org/10.3390/f14030569>

Academic Editor: Miklós Bak

Received: 20 February 2023

Revised: 8 March 2023

Accepted: 10 March 2023

Published: 13 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Green technology is currently one of the most important issues in all fields because it attempts to protect the environment and reduce the negative effects of human activity. The adoption of novel green solvents is the most critical issue, and deep eutectic solvents (DESs) have grown in popularity due to their strong association with ionic liquids (IL). Due to their unique properties, such as ease of synthesis, renewable resources, and low-cost raw materials, DESs have attracted significant scientific and industrial interest [1].

Ionic liquids are salts that are liquid at or near room temperature and are composed of organic cations and of inorganic or organic anions. They have several distinct properties that make them appealing for a variety of applications, including a low vapor pressure, high ionic conductivity, non-flammability, recyclability, catalytic activity, and chemical stability [2–4]. However, there are some disadvantages associated with the use of ionic liquids. One significant issue is that they are frequently non-biodegradable, which means that they can persist in the environment for an extended period of time. Furthermore, many ionic liquids have a high thermal stability, making them difficult to degrade or recycle. Finally, some ionic liquids are toxic to humans or the environment, so they must be handled with caution [5]. Given the drawbacks of IL, it is recommended to use DES systems formed by combining two types of compounds based on other liquid solvent systems [6]. DESs have the following advantages: a thermal and chemical stability, low vapor pressure, high dissolution rate, non-flammability, adaptability, and low melting point. Furthermore, DESs can be produced in a straightforward and cost-effective manner by combining and heating natural and/or widely available substances. As a result, DESs are less expensive, often biodegradable and water-neutral, and possess low or non-toxic

characteristics [7]. In general, DESs are composed of hydrogen bond donors (HBD), such as amines, amides, carboxylic acids, polyols, and quaternary ammonium salts [8,9]. Choline chloride (ChCl) is a common ingredient in the manufacture of dietary supplements. It is inexpensive, biodegradable, and non-toxic. ChCl may be used in all species without restriction, according to Council Directive 70/524/EEC [10]. DESs are used in a variety of processes, including synthesis, electrochemistry, metal-catalyzed organic reactions, fossil fuels, nanomaterials, fermentation, biochemistry, separation, bio-industrial chemistry, and the processing and analysis of lignocellulosic biomass. DES research has grown significantly in recent years [11–17].

Some reviews of the treatment of lignocellulosic materials with DESs are available [18–20]. These studies, however, concentrated on cellulose delignification, isolation, modification [21–25] and lignin extraction [26–28]. Many specific characteristics of DESs are required for their industrial utilization. The biodegradation and ecotoxic effects of DES solvents used in green technology processes are not fully understood. Therefore, DESs must be thoroughly and critically evaluated before they can be mass-produced on a large scale. The available data on the biomaterial toxicity of DES constituents support the assumption that DESs are safe. However, the possibility of DESs having a synergistic effect with the substance used is not considered. DESs excel in a wide range of applications. Significantly, their wider industrial application is still very limited due to a lack of data on their corrosivity, biodegradability, and toxicity.

A few research works focusing on the antibacterial and antimicrobial activities of DESs have been reported [29–32]. However, no studies on the antifungal effects of DESs on wood have been conducted. This study looked into the potential synergistic antifungal action of four commonly used ChCl-based DESs that contained oxalic acid (OA), acetic acid (AA), urea (Ur), and glycerol (GL) as hydrogen donors. The information gathered could be used to forecast the impact of DESs on human health and the environment, as well as to fill knowledge gaps regarding their potential environmental impact.

2. Materials and Methods

2.1. Materials

Oriental spruce (*Picea orientalis*) sapwood with a density of 0.39 g/cm³ was used in this study. Samples with dimensions of 5 mm (radial, R) × 15 mm (tangential, T) × 30 mm (longitudinal, L) were prepared. Chlorine chloride (CL) (99%, 139.62 g/mol, Acros), oxalic acid (OA) (126.07 g/mol, Merck), acetic acid (AA) (60.05 g/mol, Merck), urea (Ur) (60.06 g/mol, Merck), and glycerol (GL) (92.09 g/mol, Sigma) with no further purification were used.

2.2. Preparing DESs

Several DESs were created by combining OA, AA, Ur, and GL with CL. The components were weighed using the appropriate molar ratios (Table 1). To improve dissolution, the mixtures were agitated in a water bath with a magnetic stirrer at various temperatures and air pressures (Table 1). After cooling to room temperature, none of the mixes precipitated, as previously reported for ChCl-based DESs using different acids. Instead, all mixtures resulted in clear, homogeneous solutions [33,34]. Table 1 lists the molar ratios and acids used to make the DESs.

2.3. Pretreatment of Wood with DESs

Spruce wood samples with dimensions of 5 × 15 × 30 mm³ were put into a separate beaker with 50 g of DESs and heated to 80 °C for an hour while under vacuum. During this process, no mixing was used. The wood samples were soaked in DESs for three hours at atmospheric pressure after the 1-h vacuum time. The untreated control samples were subjected to the same thermal stress, which consisted of keeping them at 80 °C under vacuum for 1 h. The samples were then kept at 80 °C until reaching a fully dry weight to calculate their weight gain. After over-drying, the DES-impregnated wood was referred to as DESsW. The weight percentage gain (WPG) achieved for DES1, DES2, DES3, and DES4, WPG was 97.63, 109.25, 73.13 and 81.01%, respectively. After the atmospheric pressure treatment, the

samples were conditioned for 3 weeks, and the mass was recorded prior to performing the leaching test at 65% relative humidity and 20 °C in an air-conditioning cabinet.

Table 1. The molar ratios, temperatures, and physicochemical property data for DES hydrogen bond donors (HBDs) and acceptors (HBAs).

DESs	HBA	HBD	Molar Ratio	Temperature (°C)	Density (g/cm ³)	Viscosity (Pa.s) 25 °C
DES1 (Ur-ChCL)	Urea	ChCL	2:1	110	1.24	0.584
DES2 (GL-ChCL)	Glycerol		1:1	80	1.22	0.310
DES3 (OA-ChCL)	Oxalic acid		1:1.5	90	1.29	0.120
DES4 (AA-ChCL)	Acetic acid		2:1	70	1.21	0.045

2.4. Leaching and Decay Test

Prior to the decay test, half of the samples were subjected to a 14-day leaching test in accordance with the EN 84 standard to assess any reduction in the efficacy of decay resistance. A significant amount of DES leaching was observed from the wood samples after the leaching test. WPG values of wood samples after leaching were obtained as 1.82%, 2.67, 13.53 and 12.14% for DES1, DES2, DES3, and DES4, respectively. This demonstrates that DES materials do not chemically bond with wood and are removed by leaching with water.

The decay test was carried out in accordance with the EN 113 procedures, with minor adjustments to the sample diameters, Kolle flasks, and overall test duration. The study involved the cultivation of two fungal species, *Trametes versicolor* (white rot fungus) and *Coniophora puteana* (brown rot fungus), on a sterile malt-extract agar medium in petri dishes. The samples (leached (L) and unleached (UL)) were placed on the growing mycelium and incubated for 12 weeks at 20 °C and 70% relative humidity. The weight loss was determined by comparing the oven-dry weights before and after the decay test.

2.5. FTIR Analysis

The Bruker Optics Tensor 37 instrument was used to perform FTIR analyses on each sample group. A minimum of two measurements from the same surface area were taken with the ATR unit from the wood surface. The wave number range is 400–4000 cm⁻¹, and the spectrum resolution is 4 cm⁻¹ (Bruker Optics GmbH, Ettlingen, Germany).

2.6. TGA Analysis

The thermal stability of the PCM and PCMW was evaluated by a thermogravimetric analyzer (Perkin Elmer Pyris™ 1 TGA) at a scanning rate of 10 °C·min⁻¹ in the temperature range of 20–500 °C under a sustained stream of nitrogen atmosphere. The graphics of the TG and DTG were drawn with the Origin 2019b program.

3. Results and Discussion

FTIR spectra of Spruce wood, Ur-ChCL (DES1), DES1-treated wood, GL-ChCL (DES2), DES2-treated wood, OA-ChCL (DES3), DES3-treated wood, and AA-ChCL (DES4), DES4-treated wood are depicted in Figures 1–4, with the distinctive bands and their corresponding vibrational assignments.

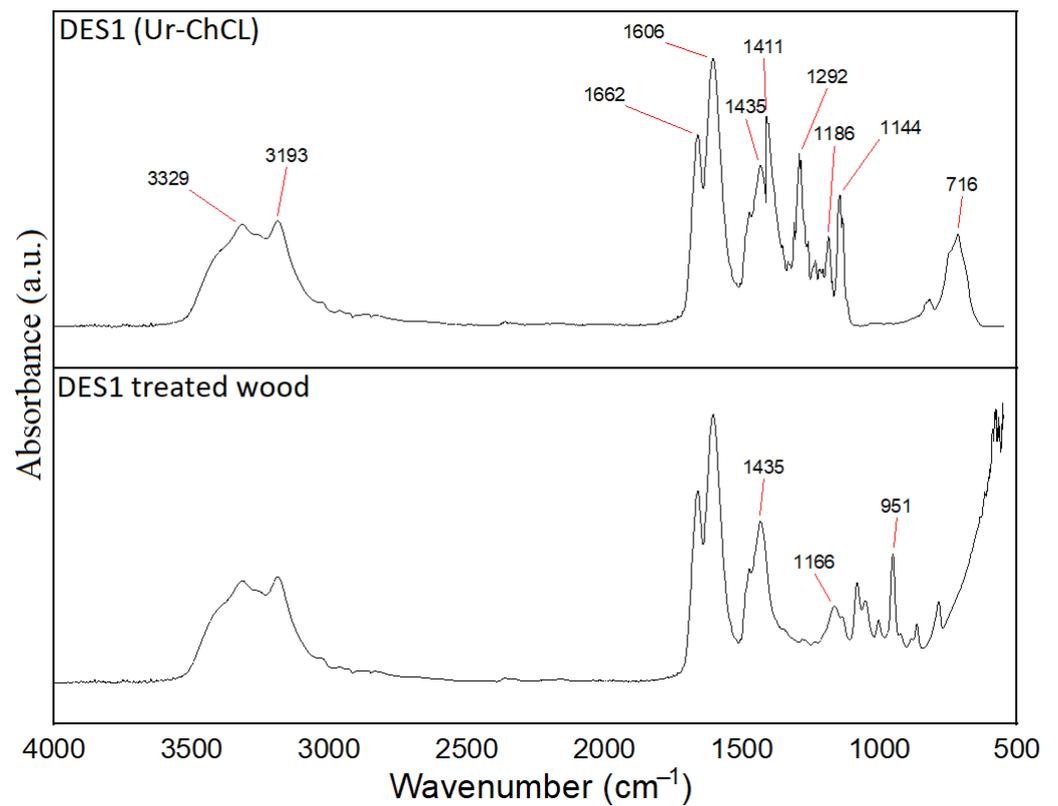


Figure 1. FTIR-ATR spectra of the DES1 (Ur:ChCL) and DES1-impregnated wood.

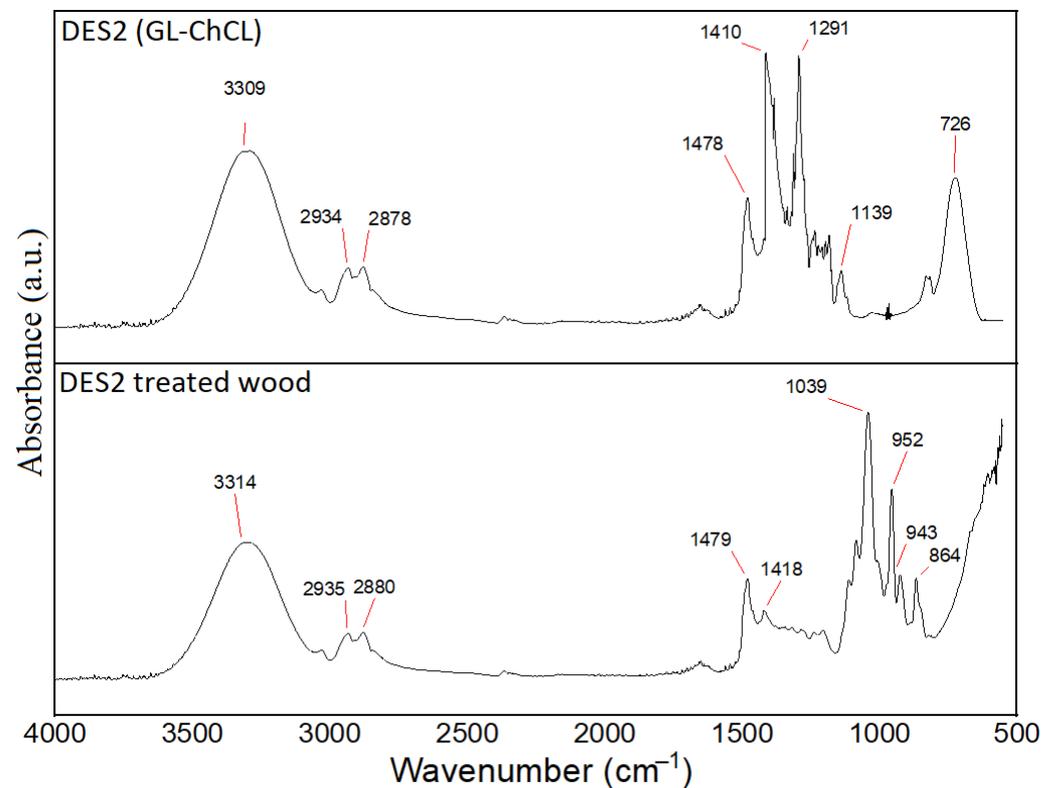


Figure 2. FTIR-ATR spectra of the DES2 (GL:ChCL) and DES2-impregnated wood.

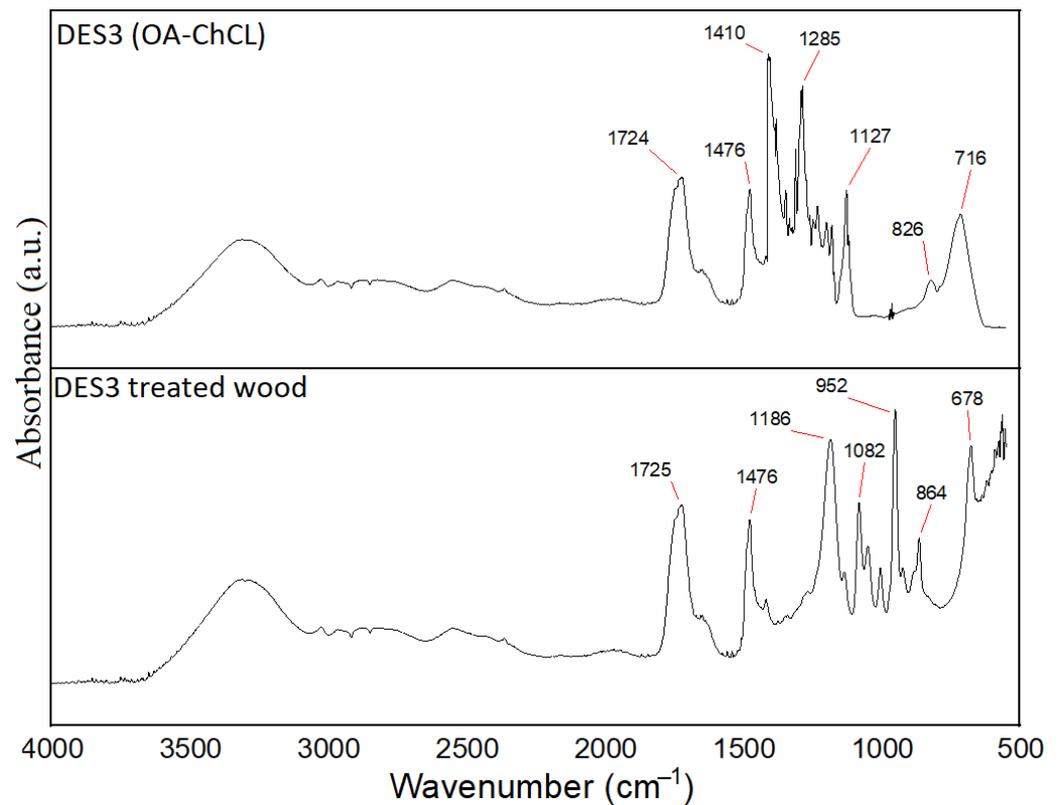


Figure 3. FTIR-ATR spectra of the DES3 (OA:ChCL) and DES3-impregnated wood.

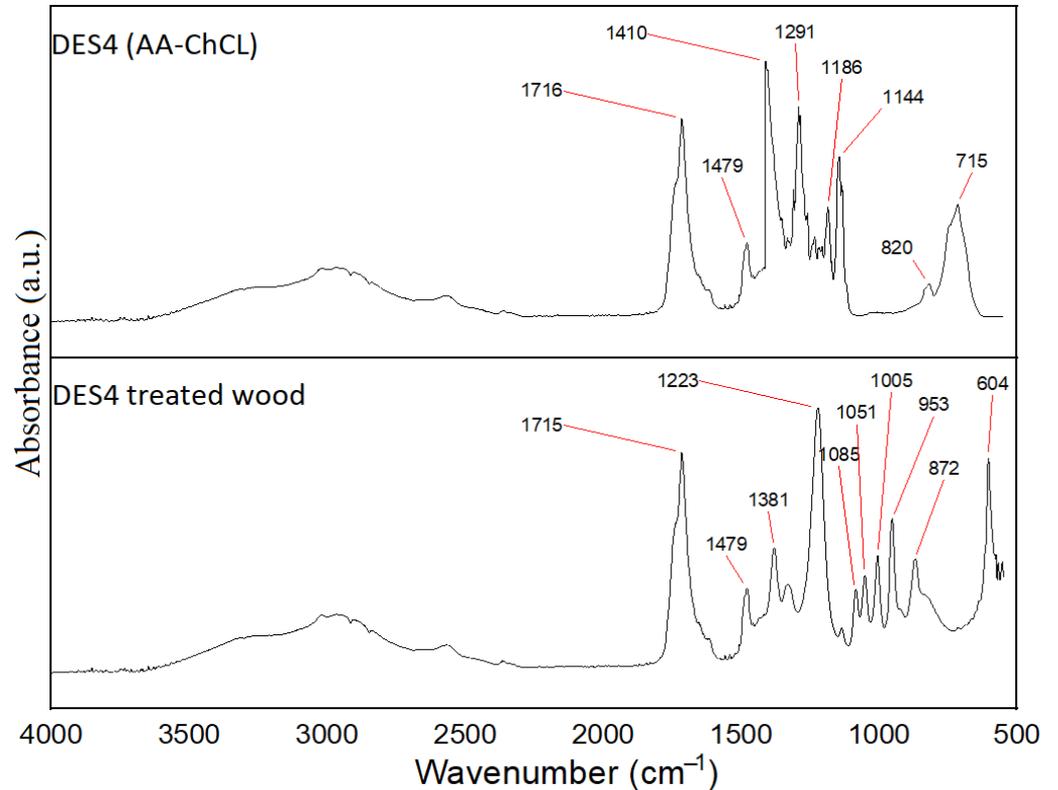


Figure 4. FTIR-ATR spectra of the DES4 (AA:ChCL) and DES4-impregnated wood.

The vibrational bands at 3329 and 3193 cm^{-1} corresponded to the stretching symmetric vibration of NH_2 and the bending symmetric vibration of NH_2 for DES1, indicating hydrogen bonding between choline and urea. Because urea and ChCL intermolecular

hydrogen interactions are formed, the stretching vibration of NH_2 at 1662 cm^{-1} and the asymmetric vibration of NH_2 at 1606 cm^{-1} in the FTIR spectra of urea shifted to 1663 and 1623 cm^{-1} , respectively, in the FTIR spectra of ChCL–urea DES [35–37]. The band at 1435 cm^{-1} of the DES1 that corresponded to CH_3 was associated with ChCL [38]. In addition, the band located at 716 cm^{-1} was ascribed to the weak stretching of $\text{C}=\text{O}$, while 1144 cm^{-1} corresponded to the stretching asymmetric vibration of CN. According to the reference, H-bonds specifically occur between NH_2 of urea and CL- of ChCL and between OH of ChCL and $-\text{C}=\text{O}$ of urea, generating $\text{N-H}\dots\text{Cl}$ and $\text{O-H}\dots\text{O}$ [39]. The structure of the impregnated wood samples was completely changed. All the characteristic bonds of wood were lost, and new bonds were formed. No change was observed in the peak values of 3329 , 3193 , 1662 , and 1606 cm^{-1} ; the peaks at 1411 and 1292 cm^{-1} disappeared, the peaks at 716 cm^{-1} decreased, and a new peak was formed at 1166 and 951 cm^{-1} in the impregnated wood samples.

In the case of the compound GL-ChCL, vibrational bands at 3314 cm^{-1} belonged to O-H stretching hydroxyl groups in the neat components, indicating the creation of intermolecular oxygen and chlorine H-bonds. The incorporation of ChCL by the surrounding glycerol molecules may be the cause of the DESs' structure [36]. Vibrational bands at 2935 and 2880 cm^{-1} referred to a C-H stretching, 1478 cm^{-1} to the CH_2 bending of an alkyl group, and 1410 cm^{-1} to a C-H deformation. Meanwhile, the peaks at around 1139 and 726 cm^{-1} corresponded to C-C-O asymmetric stretching and C-O symmetric stretching, respectively. Additional bands corresponding to C-O-H bending appeared at 1291 cm^{-1} . After treatment of wood samples with DES2, new peaks were formed at 1039 , 952 , 943 and 864 cm^{-1} , which were C-O vibrations in hemicellulose and cellulose, a C-H deformation in cellulose, and out-of-plane C-H out-of-plane aromatic lignin peaks, respectively.

According to Figure 3, the peaks at 1478 , 1410 , 1285 , 1127 and 713 cm^{-1} were associated with ChCL, while peaks at 1724 and 826 cm^{-1} were from OA. This peak was attributed to the stretching vibration of the $\text{C}=\text{O}$ group, which might have resulted from the esterification reaction between the oxalic acid and wood during the DESs' treatment. Compared with DESs, a new band at 1186 and 952 cm^{-1} appeared in the DES3-treated wood spectra. The peaks denoted a C-O-C vibration in hemicellulose and cellulose, as well as a C-H deformation in the cellulose, respectively. Similar research using ramie fibers, cotton, and cellulose pulp processed by DES based on choline chloride and oxalic acid dihydrate has been reported [35,40].

Figure 4 compares the FTIR spectra of DES4 and DES4-treated wood. A double bond or carbon and oxygen monomer is shown for acidic acid: choline chloride at 1716 cm^{-1} . There was no difference between the modified wood samples and the DES4 samples. Modified samples had similar peaks to DES4. A strong peak appeared at 1223 cm^{-1} in wood impregnated with DES4. The 1223 cm^{-1} band was assigned to C-O vibrations.

The spruce wood FTIR-ATR spectrum exhibited the same fundamental structure as wood samples (Figure 5). Strong primary OH stretching can be seen in peaks measuring 3342 cm^{-1} , while C-H stretching in methyl and methylene groups can be seen in peaks measuring 2800 to 3000 cm^{-1} . Another characteristic peak at 1735 cm^{-1} , including acetyl groups in xylan and other non-conjugated carbonyls, a $\text{C}=\text{O}$ stretch in xylan (hemicelluloses), a lignin aromatic skeletal vibration at 1508 cm^{-1} , a lignin aromatic skeletal vibration at 1427 cm^{-1} with a C-H deformation at 1365 cm^{-1} , and carbohydrates at 897 cm^{-1} were observed. The peak at 1265 cm^{-1} indicated C-O stretching of the lignin ring in guaiacyl units, and the peak at 1026 cm^{-1} denoted a C-O vibration of cellulose and hemicellulose.

The mass loss of untreated (control) spruce specimens was determined to be 42.8% for *T. versicolor* attack and 40.8% for *C. puteana* attack, respectively (Figure 6). *T. versicolor* attack resulted in weight loss of 17.14 – 11.82% , 31.79 – 10.92% , 32.05 – 7.44% and 12.00 – 7.44% for leached and non-leached Ur:CL-, OA:CL-, AA:CL-, and GL:CL-treated wood specimens, respectively. Meanwhile, after being exposed to *C. puteana*, leached and non-leached Ur:CL-, OA:CL-, AA:CL-, and GL:CL-treated wood specimens experienced a mass loss of 13.06 – 1.97% , 23.29 – 1.91% , 8.99 – 4.82% and 17.28 – 15.53% , respectively. Wood samples

modified with DES solutions yielded WPG values ranging from 81.01 to 109.25%. The UL samples had significant chemical leaching during the decay test, resulting in a significant mass loss. Leached samples of *T. versicolor* and *C. puteana* had lower weight losses. The low weight losses in the leached samples suggest that the remaining wood material is sufficient to protect it from fungi attacks.

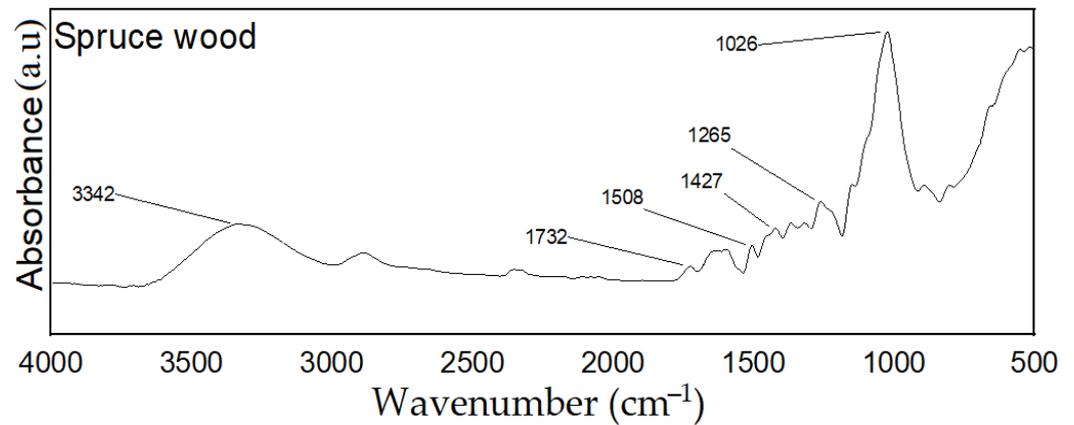


Figure 5. Spruce wood's FTIR-ATR spectrum (Control).

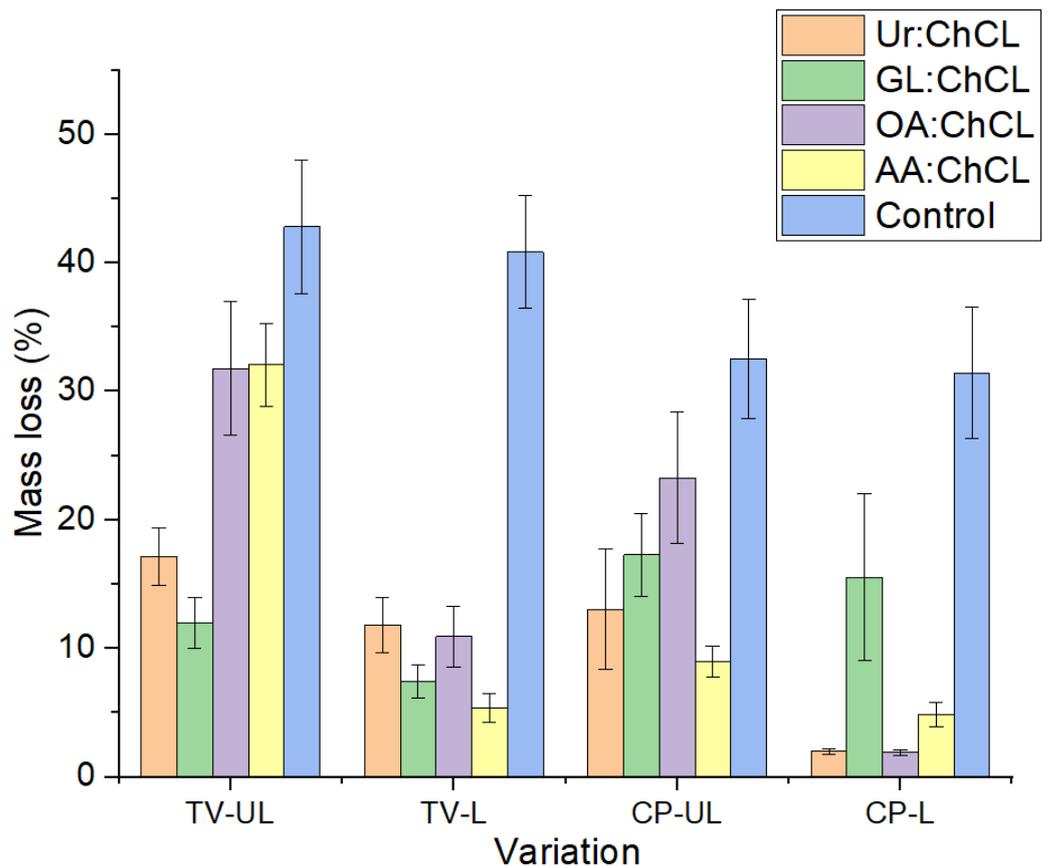


Figure 6. Mass loss (%) of control and DES-treated wood after 8 weeks of exposure to fungi.

Figures 7 and 8 present the TGA and DTG thermograms of DESs, while Figures 9 and 10 show the TGA and DTG thermograms of spruce wood and DES-treated wood. The thermal decomposition of DESs occurred in two main stages for DES1 and DES4, three main stages for DES3 and one main stage for DES2. All DESs exhibited different thermal stabilities. The initial mass loss of DES1 before 223 °C was 34.47%, that of DES3 before 197 °C was 4.4 and 13.53%, that of DES4 before 253 °C was 38.96%, and DES2 lost about 99.64% of its weight at

283–290 °C. The volatility or breakdown of HBD (Ur, OA, GL, and AA) and pyrolysis of ChCL, as well as their combination, cause the decomposition of DESs to occur mainly in the temperature range of 200–315 °C. The temperatures at which DESs completely decomposed (272, 283, 313, and 299 °C) are comparable to the complete decomposition temperature of neat ChCL, which is 302 °C. The sublimation temperatures of urea (132.9 °C), glycerol (219 °C), oxalic acid (125 °C), and acetic acid were greater than the initial decomposition temperatures of Ur: ChCL (223 °C), GL: ChCL (283 °C), OA: ChCL (197 °C), and AA: ChCL (253 °C) [39,41,42].

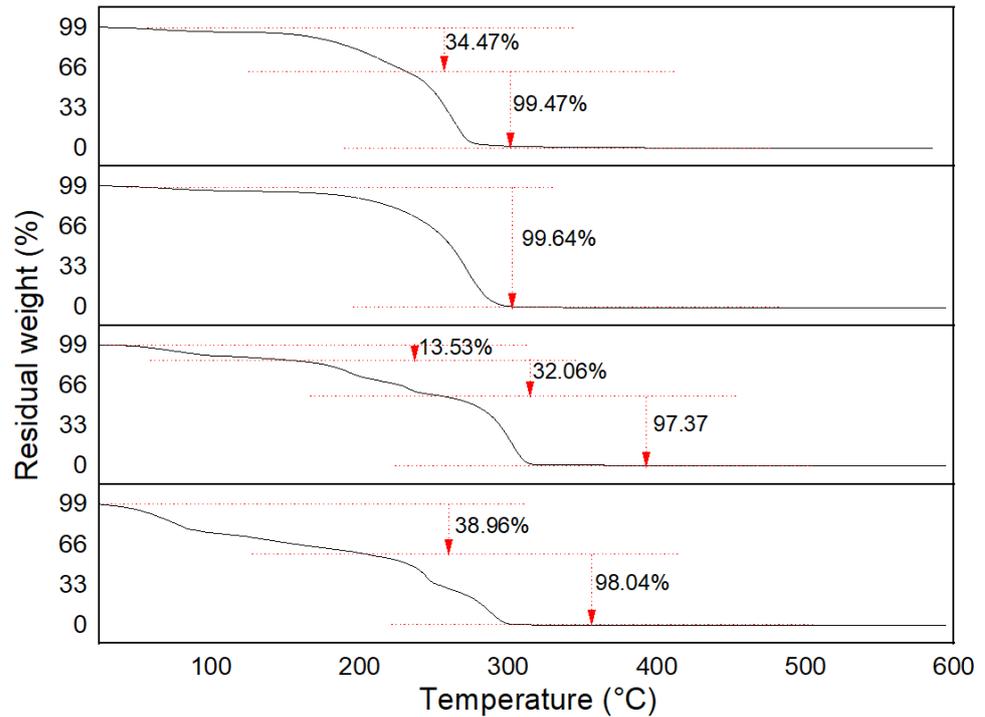


Figure 7. The DESs' TGA curves.

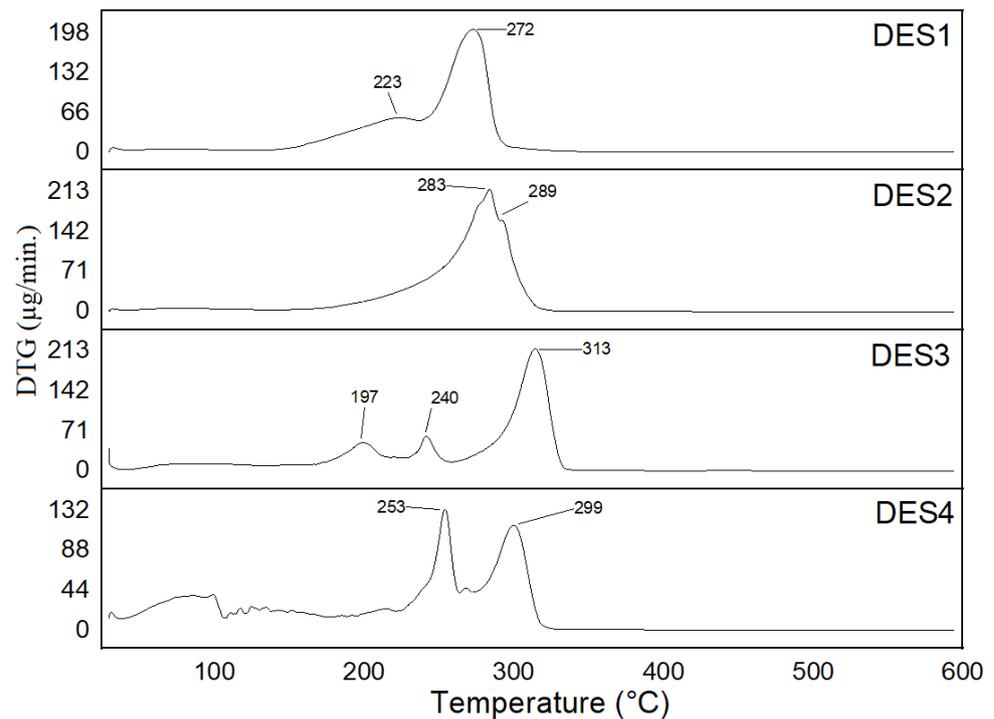


Figure 8. DTG curves of the DESs.

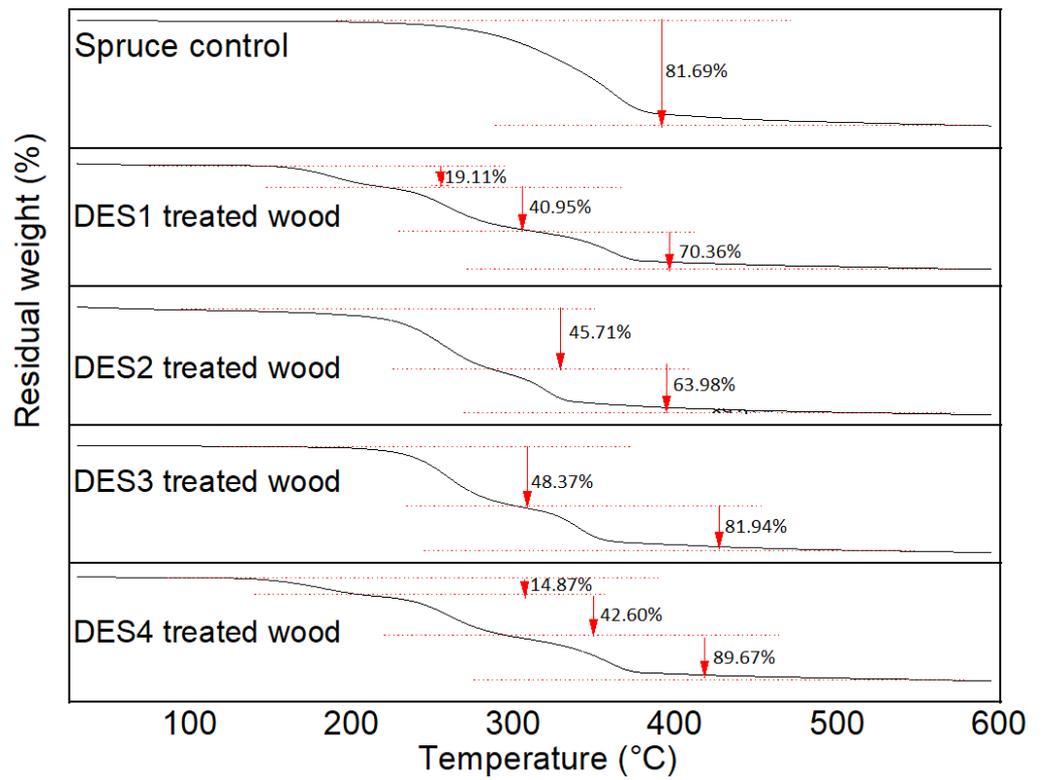


Figure 9. TGA curves of the DES-impregnated wood.

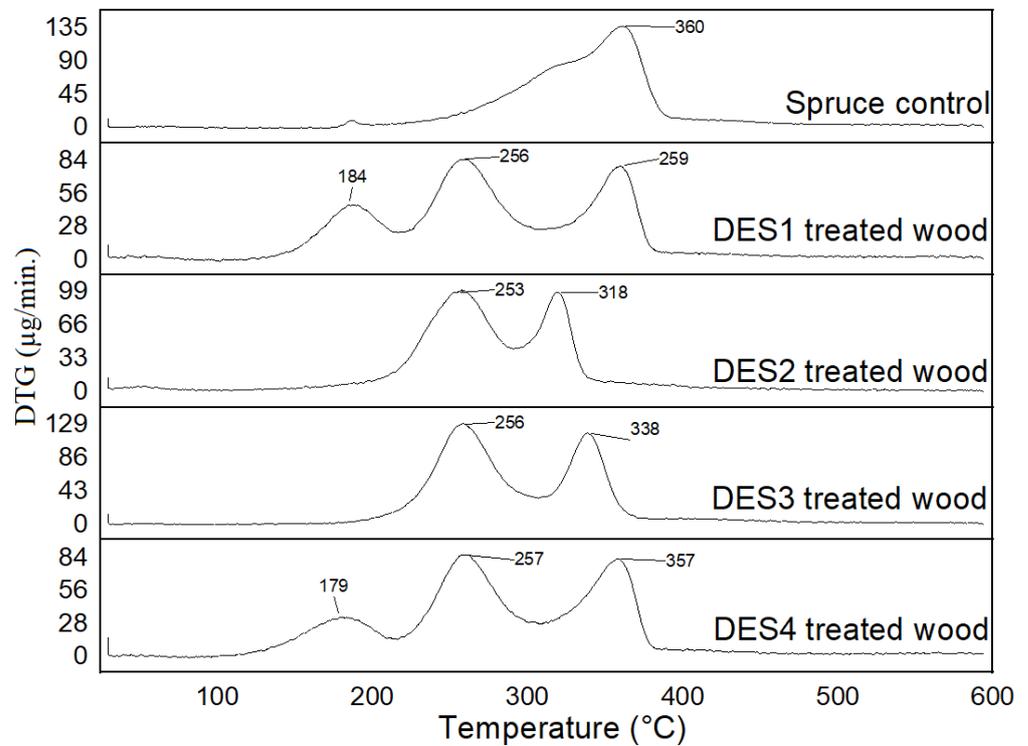


Figure 10. DTG curves of the DES-impregnated wood.

Wood thermal decomposition occurred in one main stage for DES1- and DES4-treated wood and in two main stages for DES2- and DES3-treated wood (Figure 10). The initial mass loss of DES1-treated wood before 184 °C was 19.11% and it was 45.71% for DES2-treated wood before 253 °C, 48.37% for DES3-treated wood before 256 °C and 14.87% for DES4-treated wood before 179 °C. At approximately 250 °C, DES2- and DES3-treated wood

samples lost half of their weight. At 350 °C, spruce wood samples lost 81.69% of their weight. DES-treated wood samples degraded faster than control spruce samples. This is due to the fact that DES chemicals decompose at low temperatures.

4. Conclusions

Choline chloride (ChCl)-based DESs were prepared by mixing oxalic acid (OA), acetic acid (AA), urea (Ur), and glycerol (GL) as the hydrogen bond donor (HBD). Oriental spruce wood samples were exposed to these solutions at 150 °C. Then, some properties of wood were examined. Significant changes were observed in the chemical structures of wood samples impregnated with DES solutions. Significantly, an increase in hemicellulose and cellulose peaks around 1700 cm⁻¹ was determined, while the lignin peak around 1500 cm⁻¹ disappeared completely. Mass losses were reduced compared to the control samples after the decay test. However, high mass losses were observed in the unleached samples compared to the leached wood samples. This indicates that the DES solution was leached from the wood during the decay test. Samples treated with DESs provided significant resistance to the CP fungus. The weight losses observed in the leached samples of these DES solutions were 1.97 and 1.91%, respectively. These values are lower than the 3% weight loss required by the EN113 standard. While DES3 from the prepared DES samples was degraded in three stages, the other DES solutions were degraded in two stages. The initial decomposition temperature of the DES3 solution was 197 °C. While spruce wood reached a maximum weight loss at 350 °C in a single step, samples modified with DES solutions decomposed in two or three stages. DES1- and DES4-treated wood degraded in three stages. The findings indicate that ChCl-based DESs have a high potential as a low-cost, environmentally friendly wood-treatment agent.

Author Contributions: Writing—review & editing, A.C., İ.Ö., S.H.L. and P.A.; Writing—original draft, A.C.; Visualization, A.C.; Validation, P.A.; Resources, A.C.; Methodology, A.C.; Investigation, A.C.; Formal analysis, A.C. and S.H.L.; Data curation, A.C. and İ.Ö.; Conceptualization, P.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

Acknowledgments: The authors would like to thank Bursa Technical University, Faculty of Forestry Dean's Office for the use of the FTIR device.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Qu, Q.; Lv, Y.; Liu, L.; Row, K.H.; Zhu, T. Synthesis and characterization of deep eutectic solvents (five hydrophilic and three hydrophobic), and hydrophobic application for microextraction of environmental water samples. *Anal. Bioanal. Chem.* **2019**, *411*, 7489–7498. [[CrossRef](#)] [[PubMed](#)]
2. Seoud, O.A.; Koschella, A.; Fidale, L.C.; Dorn, S.; Heinze, T. Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules* **2007**, *8*, 2629–2647. [[CrossRef](#)] [[PubMed](#)]
3. Wilpiszewska, K.; Szychaj, T. Ionic liquids: Media for starch dissolution, plasticization and modification. *Carbohydr. Polym.* **2011**, *86*, 424–428. [[CrossRef](#)]
4. Kudlak, B.; Owczarek, K.; Namieśnik, J. Selected issues related to the toxicity of ionic liquids and deep eutectic solvents—A review. *Environ. Sci. Pollut. Res.* **2015**, *22*, 11975–11992. [[CrossRef](#)]
5. Radošević, K.; Bubalo, M.C.; Srček, V.G.; Grgas, D.; Dragičević, T.L.; Redovniković, I.R. Evaluation of toxicity and biodegradability of choline chloride based deep eutectic solvents. *Ecotoxicol. Environ. Saf.* **2015**, *112*, 46–53. [[CrossRef](#)]
6. Abbott, A.P.; Capper, G.; Davies, D.L.; Rasheed, R.K.; Tambyrajah, V. Novel solvent properties of choline chloride/urea mixtures. *Chem. Comm.* **2003**, *1*, 70–71. [[CrossRef](#)]
7. Zdanowicz, M.; Wilpiszewska, K.; Szychaj, T. Deep eutectic solvents for polysaccharides processing. A review. *Carbohydr. Polym.* **2018**, *200*, 361–380. [[CrossRef](#)]

8. Trivedi, T.J.; Lee, J.H.; Lee, H.J.; Jeong, Y.K.; Choi, J.W. Deep eutectic solvents as attractive media for CO₂ capture. *Green Chem.* **2016**, *18*, 2834–2842. [[CrossRef](#)]
9. Germani, R.; Orlandini, M.; Tiecco, M.; Del Giacco, T. Novel low viscous, green and amphiphilic N-oxides/phenylacetic acid based Deep Eutectic Solvents. *J. Mol. Liq.* **2017**, *240*, 233–239. [[CrossRef](#)]
10. EFSA Panel on Additives and Products or Substances used in Animal Feed (FEEDAP). Scientific Opinion on safety and efficacy of choline chloride as a feed additive for all animal species. *EFSA J.* **2011**, *9*, 2353.
11. Liu, P.; Hao, J.W.; Mo, L.P.; Zhang, Z.H. Recent advances in the application of deep eutectic solvents as sustainable media as well as catalysts in organic reactions. *RSC Adv.* **2015**, *5*, 48675–48704. [[CrossRef](#)]
12. Abbott, A.P.; El Ttaib, K.; Frisch, G.; Ryder, K.S.; Weston, D. The electrodeposition of silver composites using deep eutectic solvents. *Phys. Chem.* **2012**, *14*, 2443–2449. [[CrossRef](#)]
13. Morrison, H.G.; Sun, C.C.; Neervannan, S. Characterization of thermal behavior of deep eutectic solvents and their potential as drug solubilization vehicles. *Int. J. Pharm.* **2009**, *378*, 136–139. [[CrossRef](#)]
14. Shishov, A.; Bulatov, A.; Locatelli, M. Carradori, S. Andruch, V. Application of deep eutectic solvents in analytical chemistry. A review. *Microchem. J.* **2017**, *135*, 33–38. [[CrossRef](#)]
15. Fu, N.; Lv, R.; Guo, Z.; Guo, Y.; You, X.; Tang, B.; Han, D.; Yan, H.; Row, K.H. Environmentally friendly and nonpolluting solvent pretreatment of palm samples for polyphenol analysis using choline chloride deep eutectic solvents. *J. Chromatogr. A* **2017**, *1492*, 1–11. [[CrossRef](#)]
16. Sattlewal, A.; Agrawal, R.; Bhagia, S.; Sangoro, J.; Ragauskas, A.J. Natural deep eutectic solvents for lignocellulosic biomass pretreatment: Recent developments, challenges and novel opportunities. *Biotechnol. Adv.* **2018**, *36*, 2032–2050. [[CrossRef](#)]
17. Posada, E.; Roldán-Ruiz, M.J.; Riobóo, R.J.J.; Gutiérrez, M.C.; Ferrer, M.L.; del Monte, F. Nanophase separation in aqueous dilutions of a ternary DES as revealed by Brillouin and NMR spectroscopy. *J. Mol. Liq.* **2019**, *276*, 196–203. [[CrossRef](#)]
18. Tang, X.; Zuo, M.; Li, Z.; Liu, H.; Xiong, C.; Zeng, X.; Sun, Y.; Hu, L.; Liu, S.; Lei, T.; et al. Green processing of lignocellulosic biomass and its derivatives in deep eutectic solvents. *ChemSusChem* **2017**, *10*, 2696–2706. [[CrossRef](#)]
19. Osch van, D.J.G.P.; Kollau, L.J.B.M.; Bruinhorst van der, A.; Asikainen, S.; Rocha, M.A.A.; Kroon, M.C. Ionic liquids and deep eutectic solvents for lignocellulosic biomass fractionation. *Phys. Chem. Chem. Phys.* **2017**, *19*, 2636–2665. [[CrossRef](#)]
20. Loow, Y.L.; New, E.K.; Yang, G.H.; Ang, L.Y.; Foo, L.Y.W.; Wu, T.Y. Potential use of deep eutectic solvents to facilitate lignocellulosic biomass utilization and conversion. *Cellulose* **2017**, *24*, 3591–3618. [[CrossRef](#)]
21. Alvarez-Vasco, C.; Ma, R.; Quintero, M.; Guo, M.; Geleynse, S.; Ramasamy, K.K.; Wolcott, M.; Zhang, X. Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): A source of lignin for valorization. *Green Chem.* **2016**, *18*, 5133–5141. [[CrossRef](#)]
22. Draman, S.F.S.; Daik, R.; Mohd, N. Eco-friendly extraction and characterization of cellulose from the lignocellulosic fiber. *ARPJ J. Eng. Appl. Sci.* **2016**, *11*, 9591–9595.
23. Fang, C.; Thomsen, M.H.; Frankær, G.; Brudecki, G.P.; Schmidt, J.E.; AlNashef, I.M. Reviving pretreatment effectiveness of deep eutectic solvents on lignocellulosic date palm residues by prior recalcitrance reduction. *Ind. Eng. Chem. Res.* **2017**, *56*, 3167–3174. [[CrossRef](#)]
24. Abdulmalek, E.; Zulkefli, S.; Rahman, M.B.A. Deep eutectic solvent as a media in swelling and dissolution of oil palm trunk. *Malays. J. Anal. Sci.* **2017**, *21*, 20–26.
25. Chen, Z.; Wan, C. Ultrafast fractionation of lignocellulosic biomass by microwave-assisted deep eutectic solvent pretreatment. *Biores. Technol.* **2018**, *250*, 532–537. [[CrossRef](#)]
26. Zhang, L.; Yu, H. Conversion of xylan and xylose into furfural in biorenewable deep eutectic solvent with trivalent metal chloride added. *BioResources* **2013**, *8*, 6014–6025. [[CrossRef](#)]
27. Zhang, L.S.; Gao, S.P.; Huang, Y.P.; Li, Z.-S. Green synthesis of polymer monoliths incorporated with carbon nanotubes in room temperature ionic liquid and deep eutectic solvents. *Talanta* **2016**, *154*, 335–340. [[CrossRef](#)]
28. Morais, E.S.; Mendonça, P.V.; Coelho, J.F.J.; Freire, M.G.; Freire, C.S.R.; Coutinho, J.A.P.; Silvestre, A.J.D. Deep eutectic solvent aqueous solutions as efficient media for the solubilization of hardwood xylans. *ChemSusChem* **2018**, *11*, 753–762. [[CrossRef](#)]
29. Hayyan, M.; Hashim, M.A.; Hayyan, A.; Al-Saadi, M.A.; AlNashef, I.M.; Mirghani, M.E.; Saheed, O.K. Are deep eutectic solvents benign or toxic? *Chemosphere* **2013**, *90*, 2193–2195. [[CrossRef](#)]
30. Hayyan, M.; Looi, C.Y.; Hayyan, A.; Wong, W.F.; Hashim, M.A. In vitro and in vivo toxicity profiling of ammonium-based deep eutectic solvents. *PLoS ONE* **2015**, *10*, e0117934. [[CrossRef](#)]
31. Jalil, A.; Asim, M.H.; Akkus, Z.B.; Schoenthaler, M.; Matuszczak, B.; Bernkop-Schnürch, A. Self-emulsifying drug delivery systems comprising chlorhexidine and alkyl-EDTA: A novel approach for augmented antimicrobial activity. *J. Mol. Liq.* **2019**, *295*, 111649. [[CrossRef](#)]
32. Al-Akayleh, F.; Khalid, R.M.; Hawash, D.; Al-Kaissi, E.; Al-Adham, I.S.; Al-Muhtaseb, N.; Jaber, N.; Al-Remawi, M.; Collier, P.J. Antimicrobial potential of natural deep eutectic solvents. *Lett. App. Microbiol.* **2022**, *75*, 607–615. [[CrossRef](#)]
33. Craveiro, R.; Aroso, I.; Flammia, V.; Carvalho, T.; Viciosa, M.T.; Dionísio, M.; Barreiros, S.; Reis, R.L.; Duarte, A.R.C.; Paiva, A. Properties and thermal behavior of natural deep eutectic solvents. *J. Mol. Liq.* **2016**, *215*, 534–540. [[CrossRef](#)]
34. Fernandes, P.M.V.; Campina, J.M.; Pereira, N.M.; Pereira, C.M.; Silva, F. Biodegradable deep-eutectic mixtures as electrolytes for the electrochemical synthesis of conducting polymers. *J. Appl. Electrochem.* **2012**, *42*, 997–1003. [[CrossRef](#)]

35. Yue, D.Y.; Jia, Y.Z.; Yao, Y.; Sun, J.H.; Jing, Y. Structure and electrochemical behavior of ionic liquid analog based on choline chloride and urea. *Electrochimica Acta* **2012**, *65*, 30–36. [[CrossRef](#)]
36. Delgado-Mellado, N.; Larriba, M.; Navarro, P.; Rigual, V.; Ayuso, M.; García, J.; Rodríguez, F. Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR–ATR analysis. *J. Mol. Liq.* **2018**, *260*, 37–43. [[CrossRef](#)]
37. Li, Y.; Li, Y.; Li, H.; Fan, X.; Yan, H.; Cai, M.; Xu, X.; Zhu, M. Insights into the tribological behavior of choline chloride-urea and choline chloride-thiourea deep eutectic solvents. *Friction* **2022**, *11*, 76–92. [[CrossRef](#)]
38. Yuan, C.S.; Zhang, X.; Ren, Y.F.; Feng, S.Q.; Liu, J.B.; Wang, J.; Su, L. Temperature- and pressure-induced phase transitions of choline chloride–urea deep eutectic solvent. *J. Mol. Liq.* **2019**, *291*, 111343. [[CrossRef](#)]
39. Zhu, J.; Shao, H.; Feng, L.; Lu, Y.; Meng, H.; Li, C. Absorptive separation of HCl gas by choline chloride-based deep eutectic solvents. *J. Mol. Liq.* **2021**, *341*, 116928. [[CrossRef](#)]
40. Sirvio, J.A.; Visanko, M.; Liimatainen, H. Acidic deep eutectic solvents as hydrolytic media for cellulose nanocrystal production. *Biomacromolecules* **2016**, *17*, 3025–3032. [[CrossRef](#)]
41. Fadzallah, I.A.; Majid, S.R.; Careem, M.A.; Arof, A.K. A study on ionic interactions in chitosan–oxalic acid polymer electrolyte membranes. *J. Membr. Sci.* **2014**, *463*, 65–72. [[CrossRef](#)]
42. Gómez-Siurana, A.; Marcilla, A.; Beltrán, M.; Berenguer, D.; Martínez-Castellanos, I.; Menargues, S. TGA/FTIR study of tobacco and glycerol–tobacco mixtures. *Thermochim. Acta* **2013**, *573*, 146–157. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.