Biointerface Research in Applied Chemistry
Open-Access Journal (ISSN: 2069-5837)

Review
Volume 13, Issue 3, 2023, 261
https://doi.org/10.33263/BRIAC133.261

Fractionation of Biomass using Green Solvents

Veronika Jancikova [1,*], Michal Jablonsky [1]

[1] Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava SK-812 37, Slovakia
* Correspondence: veronika.jancikova@stuba.sk (V.J.);

Scopus Author ID 8670030600
Received: 2.12.2021; Accepted: 30.12.2021; Published: 11.06.2022

Abstract: Green solvents show several favorable features to be used as extraction and fractionation solvents, such as their ease of preparation and lower cost, and they can be both non-toxic and biodegradable when prepared with natural compounds. Due to their properties, green solvents' application in biomass fractionation has been extensively studied during the past years. The presented work describes the application of several possible combinations to create deep eutectic solvents with the potential to be used in processing different types of biomass. The results of studies suggest that deep eutectic solvents may have an important ability to dissolve lignin molecules from plants and can realize a mild catalytic mechanism (acid-base) that will activate the checked cleavage of non-stable ether linkages between phenylpropane units.

Keywords: biomass; green solvents; fractionation; lignin; green technology.

1. Introduction

Solvents determine an essential part of the chemical industry's environmental properties and impact the health, safety, and cost of processes. The idea of "green" solvents interprets the goal of minimizing the impact on the environment and humans resulting from using solvents in chemical production [1]. The concept of “green” solvent was proposed in the early 2000s and derived from the concepts of green chemistry described by Anastas and Kirchhoff [2]. For a solvent to be considered green, it should meet most of the 12 fundamental principles of green chemistry [3]. These principles summarize the rational and methodological use of chemicals, with a preference for using renewable feedstock or innocuous substances that will not remain in the environment [2]. Solvents occupy a strategic place in the world of green chemistry. The solvent must meet strict requirements regarding its less-toxicity, biodegradability, recyclability, sustainability, availability, and, of course, low cost to qualifying as a green solvent [3].

In harmony with the principles of green chemistry [4-6], the development of ecological extraction methods (shorter extraction time and lower solvent consumption) is currently required. In recent years, green technology has focused on deep eutectic solvents (DESs), new solvents emerging as promising and greener alternatives to conventional organic solvents [7-10].

DESs are formed by combining a halide salt or another hydrogen bond acceptor (HBA) and one or two hydrogen bond donors (HBD). The most common DES are formed by choline chloride with cheap and safe HBD. The most popular ones are urea, ethylene glycol, and glycerol, but other alcohols, amino acids, carboxylic acids, and sugars have also been

commonly used [11]. Based on the work of Abbott and colleagues and reflecting the nature of the starting materials, DES is classified into five types: type I (quaternary salt and metal halide), type II (quaternary salt and hydrated metal halide), type III (donor of quaternary salts and hydrogen bond) type IV (metal halide and hydrogen bond donor) and type V (non-ionic DES composed only of molecular substances) [12].

To increase the number of candidates for ionic liquids and DESs and to expand their applications, attention has focused, in addition to synthetic compounds, on natural products, such as organic acids, amino acids, sugars, choline, and urea. When combined in a certain composition, these compounds, mainly sugars, organic acids, choline derivates, or urea, form a new deep eutectic solvent referred to as natural deep eutectic solvents (NADES) [13].

Natural low-temperature transition mixtures (LTTM) can be used as promising green solvents for biomass pretreatment. The variety of possible combinations of starting materials provides a powerful tool for controlling the physical properties and phase behavior of LTTM, and their ability to dissolve numerous soluble substances of various natures. Application methods include LTTM extractions for biomass destruction, biofuel processing, or solids and liquids separation [14].

2. Fractionation of Lignocellulosic Materials using DES (Removal of Lignin from Biomass)

Lignocellulosic biomass is mostly composed of cellulose, hemicelluloses, and lignin, which are bound to each other into a fixed and strong matrix, which is difficult to process and fractionate. The solution involves thermochemical, biological, or chemical processing processes, which allows further fractionation and conversion to the desired products. However, conventional processes require high temperatures, non-ecological, and toxic and harmful agents that directly impact economic viability and are contrary to environmental guidelines [15]. Due to this problem, new and efficient methods or processes of fractionation and biomass extraction have been sought. "Green" solvents have proven to be a promising technology. Several studies have focused on the influence of deep-eutectic solvents in the biomass pretreatment process and on their final composition. Eutectic mixtures were used to dissolve parts of the biomass [16].

The use of DES in the valorization of biomass and lignocellulosic materials has proven to be a promising approach to achieving efficient and ecological fractionation of biomass. In biomass processing, it is possible to combine the amount of DES. It is very important to find suitable DES combinations that will be able to dissolve the main biomass components, namely cellulose, hemicelluloses, and lignin is highly required [17].

Light and pure fractionation of basic raw materials is an important operation for all processes involving the recovery of other products. A unique raw material can be obtained if the various components can be easily separated. The obtained raw material can be further used as a starting material for new materials, fibers, biopolymers, and also for the production of chemicals [16].

Due to their properties, DESs are used in the fractionation of biomass, and their efficiency has been extensively monitored and studied in recent years. Several articles have described the delignification of different types of biomass using DES. The authors tested the delignification of different types of wood (pine [18], pine wood meal [19], (*Pinus bungeana Zucc)* [20], pine wood sawdust (*Pinus pinaster Ait.)* [21], poplar wood meal *(Populus ussuriensis)* [22-28], wood meal (*Douglas fir)* [24], poplar wood chips [26], willow wood meal

(*Salix matsudana cv. Zhuliu*) [29], willow chips [30], ground beech chips [31], beech wood sawdust (*Fagus silvatica)* [32], birch wood meal [33], spruce sawdust [34], spruce wood meal (*Picea alba)* [35], balsa wood *(Ochroma pyramidale)* [36], bamboo wood meal *(Dendrocalamus yunnanicus)* [37], mesh dewaxed *(Eucalyptus globulus*) wood [38], wood sawdust (*Eucalyptus camaldulensis)* [39], wood meal *(Eucalyptus globulus*) [40] milled pulp from *Eucalyptus urograndis* [34]), fractionation of annual plants and herbs (grinded corncobs [41], raw corncob [42], knife-milled corn stover [43], corn stover meal [30,44], milled corn stalk [45], rice husk [46], grinded rice straw and rice husk [47-53], rice straw meal [48], rice straw [49-52], milled wheat straw [16,18,31,45, 47, 53,54], shredded wheat straw [34], grass fractionation, meal wood (*Miscanthus)* [33,44,55], and delignification of other lignocellulosic materials (castor stalk [56], oil palm empty fruit bunch [57,76], oil palm fronds [58], date palm [59], watermelon rind [60], curcuminoids from *Curcuma longa* [61], oil palm trunk [62], milled rapeseed stem residues [45], pulp [63-67], olive leaves [68], (ground switchgrass (*Panicum virgatum L.)* [44,69], peach *(Prunus persica*) and walnut (*Juglans nigra*) endocarp [70], sugarcane bagasse [71, 73, 78]), herb residues (*Akebia*) [72]),moso bamboo [74], *paddy* husks [76], moso bamboo *(Phyllostachys pubescens)* [77].

2.1. Fractionation of wood.

In 2013, De Dios [18] tested the delignification of pine wood. Five different DESs are choline chloride and lactic acid; oxalic acid; malic acid, and lactic acid and 2-chloroethyltrimethylammonium chloride and [N(Me)4]Cl were used when applied to pine wood in various ratios. Content of lignin after delignification ranged from 0.6-7.8%. The author found that for a solvent system of lactic acid and choline chloride, the solubility of lignin increases with increasing relative lactic acid ratio.

Biomass deconstruction and depolymerization of lignin were performed using three DESs. Various temperature (110 °C, 130 °C, and 150 °C) and time (1 min, 5 min, 10 min, and 15 min) conditions were tested in a 2450 MHz microwave reactor. In this study [19], pinewood sawdust was dried in a convection oven for 24 h at 103 °C. The binary mixtures were prepared with a molar ratio of 1:1 for choline chloride/lactic acid and choline chloride/formic acid, and 2:1 for choline chloride/formic acid. 5% of biomass was mixed with 30 g DES. The mixture was then heated in a microwave system (1.6 kW, 2450 MHz). The depolymerization was carried out using oxalic acid/choline chloride DES at 130 °C for 15 min and formic acid/choline chloride DES at 150 °C for 15 min. Lignin depolymerization and biomass deconstruction were carried out in a conventional oil bath compared with microwave heating. Oxalic acid DES (130 °C, 15 min) and formic acid DES (150 °C, 15 min) gave the highest yield of lignin.

The author tested the subcellular dissolution of lignin to enhance enzymatic hydrolysis of a microwave-assisted DES that pretreated the *Pinus bungeana Zucc.* Pine wood was used for the experiment, ground to a powder, then dried and weighed. The synthesis of DES was performed by mixing choline chloride and lactic acid in a molar ratio of 1:10 at 60 °C to form a homogeneous liquid. 3 g of wood powder were mixed with 48 ml of DES and added to a 75 ml glass reactor. The mixtures were maintained at 120 °C with magnetic stirring for 4 h or heated under microwave irradiation with 800 W. DES pretreatment showed higher lignin removal of 66.59% than that of microwave-DES (42.81%). These results were consistent with previous research that DES has high lignin selectivity and solubility for the separation of lignin and cellulose fractions [20].

In this document [21], acidic DESs were produced and applied to the extraction of lignin from pine (*Pinus pinaster Ait.).* Several DES were prepared to combine different carboxylic acids with choline chloride, betaine, or urea. The components were weighed according to the respective molar ratios, and the mixtures were stirred with a magnetic stirrer in an oil bath at 80 °C for 1 h, except for those prepared from two solid compounds (citric and tartaric acid with choline chloride), where a temperature of 100 °C was used to improve dissolution. 1 g of pine sawdust was placed in a round-bottom flask containing the DES of interest (solute to solvent ratio of 1:10) and stirred in reflux in an oil bath at 150 °C for 2 h. To obtain the lignin from the solution, water was used as an antisolvent to drive lignin precipitation. The prepared DES lactic acid/tartaric acid/choline chloride, in a molar ratio of 4:1:1, is the most efficient DES for selective lignin extraction and recovery. Extraction temperature and time were also optimized for this process, revealing that 1 h at 175 °C allowed the recovery of 95% of the total lignin present in pine with a purity of 89%. The novel DES prepared in this work proved highly efficient and selective for lignin extraction from pine sawdust. Considering the favorable "green" features of this new solvent system and the remarkable extraction capacity and selectivity for lignin (even after being recycled), one can consider this process highly appealing for future applications (large-scale), thus contributing to valorizing lignin.

A process for the delignification of poplar wood using lactic acid-based DESs with different HBAs (choline chloride, glycine) was studied [22]. The effects of operating parameters, chemical composition, and extent of delignification were monitored with respect to several factors, such as the types of HBA, reaction temperature, and time. Air-dried poplar wood *(Populus ussuriensis)* was used for the experiment. The main components of the starting materials were as follows: 49.6% cellulose, 25.7% hemicelluloses, 23.8% lignin, and 0.9% extractives. Lactic acid/choline chloride with a molar ratio of 10:1 and lactic acid/glycine with a molar ratio of 9:1 was added to closed glass vials, and the mixtures were magnetic stirred under 60 °C until a clear liquid was formed. Five percent mass fraction of wood in DESs was prepared by adding 0.75 g of oven-dry wood fiber into 15 g of preheated DES and then stirred at temperatures of 90 °C, 100 °C, 110 °C, 120 °C (oil bath) for 3 h, 6 h, 9 h, and 12 h. It is well known that the nature and conditions of the process affect the effectiveness of delignification. The extraction process was found to be high temperature and time-dependent for both DES used. The maximum delignification extent of approximately 90.4% was achieved with lactic acid/choline chloride DES at 120 °C for 12 h. However, only about 58.4% of lignin was removed with lactic acid/glycine DES under the same reaction condition.

This study [23] applies DES to the selective extraction of lignin from poplar. This work aimed to find the most efficient DES for the selective dissolution of lignin and to investigate the effect of temperature and time on the lignin delignification. Poplar wood meal contained 27.69% lignin, 41.22% cellulose, and 20.47% hemicellulose. Choline chloride and lactic acid (urea, glycerol, citric acid monohydrate, glycol, succinic acid, and acetamide) were used to prepare DES. 2 g of the oven-dry wood meal and 98 g of the DES composed of lactic acid/choline chloride were mixed. The temperatures were 100 °C, 110 °C, 120 °C, and 130 °C and the dissolving times were 3 h and 6 h. The solubility of biomass in lactic acid/choline chloride is higher than that for other DES, which is more than 50%, thereby suggesting that lactic acid/choline chloride is the optimal DES solvent for woody biomass dissolution among these DESs. The solubility of poplar wood meal increased with the lactic acid/choline chloride molar ratio (from 1:1 to 9:1), and lactic acid/choline chloride (9:1) exhibited the best dissolving

capacity for poplar wood meal, which demonstrated lactic acid plays a positive role in the solubility of the poplar wood meal. If the lactic acid/choline chloride molar ratio is 9:1 (at 120 °C for 6 h), up to 95% dissolution capacity can be achieved, and the purity of DES lignin will be 98.1%. The lignin removal rate can be improved by increasing the temperature and time.

For the research on the valorization of lignin from biomass in this work [24], the types of softwood (*Douglas fir*) and hardwood (poplar wood) were selected. The lignin content of the untreated sample was 27.7±0.8% in *Douglas fir* and 26.3± 0.3% in poplar wood. Four DES mixtures were prepared using choline chloride as an HBA with four HBDs: acetic acid, lactic acid, levulinic acid, and glycerol. The results show that treatment with choline chloride/glycerol did not help to remove wood components under all conditions from the samples. Removal of lignin and hemicelluloses by other DES was more significant and increased with treatment time. After raising the temperature to 145 °C, all three DESs extracted more than 70% of the lignin originally found in the poplar. The amount of lignin extracted from *Douglas fir* increased with increasing temperature up to 145 °C. Maximum lignin yields were observed at 145 °C from all DES. Choline chloride/lactic acid again appeared to be the best DES for lignin extraction, with a 58.2% lignin yield.

A new choline-based DES with low halogen content, namely choline lactate/lactic acid, was prepared by replacing the chloride anion with lactate anion in choline chloride/lactic acid. Both choline lactate/lactic acid and choline chloride/lactic acid were used to selectively separate lignin from poplar for evaluating the extraction efficiency of choline lactate/lactic acid and choline chloride/lactic acid. The poplar chips were ground, the dry wood powder was used as the lignocellulosic raw material for the experiment, and its chemical composition was measured. The raw hardwood poplar sample contains 25.62% lignin. Choline chloride/lactic acid and choline lactate/lactic acid used in this work were synthesized by mixing lactic acid with choline chloride and choline lactate. 1.5 g of dried biomass and 45 g of DES were used in this experiment, which was mixed and incubated at 80-160 °C for 4-14 h. Optimal DES processing conditions were obtained in a ratio of 1:10 with an operation of 140 ºC for 12 h. The prepared DES was shown to be effective in fractionating poplar wood samples. In the choline chloride/lactic acid treatment process, 22.04% of the native lignin was extracted into the choline chloride/lactic acid lignin mixture. Choline lactate/lactic acid treatment has also been found to represent a higher fractionation, e.g., a higher amount of lignin present in choline chloride/lactic acid (23.09%). Choline lactate/lactic acid appears to be a beneficial solution to achieving selective separation of lignin from biomass. It has been clearly shown that replacing the chloride anion with lactate in DES promoted separation selectivity during DES treatment of lignocellulosic biomass, which increased the lignin extraction rate from 86.02% (choline chloride/lactic acid lignin) to 90.13% (choline lactate/acid dairy lignin). The replacement of the chloride anion in choline chloride/lactic acid with the lactate anion facilitated the fractionation of biomass by extracting more lignin into DES and leaving more carbohydrates in the solid residue [25].

This work [26] was focused on a two-stage pretreatment, i.e., extraction with liquid hot water and subsequent treatment with acidic DES. This was used to fractionate lignocellulosic biomass while increasing cellulose reactivity selectively. This two-step fractionation route could provide a high-quality lignin fraction product and a high purity cellulose fraction for further use. Pretreatment with liquid hot water uses water in the liquid state at elevated temperature (160-240 ºC) as an extraction medium. This work used DES, composed of choline chloride with three natural and cheap acids (lactic acid, acetic acid, and formic acid) with

considerable ability to provide hydrogen and extract lignin from biomass. Poplar wood shavings were used in the experiment, which were first extracted with hot water using an autoclave reactor. The temperature for hot water extraction was chosen to be 170 °C (40 min). DESs were synthesized by mixing with a molar ratio of 1:2. To 120 g of acidic DES was added 6 g of pretreated poplar substrate and stirred at 130 °C for 3 h. The chemical composition of the substrates was determined according to the Klason protocol and the standard method. The results showed that after the extraction of poplar shavings, the solids yield was 79.8%, and 54.4% removal of hemicelluloses was observed, corresponding to almost 100% cellulose retention. The solids yield was greater than 52% for all applied acidic DES pretreatments, and the three acidic systems showed similar delignification ability.

In this study [27], the authors investigated and analyzed the character of the complex molecular interactions between choline chloride and glycerol in a molar ratio of 1:2. Due to the absence of active protons and acidic sites, DES was not able to fractionate ether bonds in biomass. Accordingly, the authors prepared and applied three constituent DESs by coordinating $AlCl_3 \times 6H_2O$ in choline chloride/glycerol to cleave the lignin-saccharide complex and lignin fractionation. Poplar wood powder was treated with the DESs by heating in an oil bath at 110, 120, and 130 °C for 4 h to verify their lignin fractionation efficiency. $AlCl_3 \times 6H_2O$ as an anion donor and active acid site holder was introduced into choline chloride/glycerol. DES was prepared by mixing choline chloride, glycerol, and $AlCl_3 \times 6H_2O$ in specific molar ratios and the conditions. The results show that the lignin extraction rate changes with increasing $AlCl_3 \times 6H_2O$ and increasing temperature. The yield of lignin increases from 0.69±0.21% (using choline chloride/glycerol at 120 °C and for 4 h) to 18.2±0.72% (using choline chloride/glycerol/$AlCl_3 \times 6H_2O$ at 120 °C and for 4 h), which represents 95.46±0.82% of the lignin content of the untreated wood. The purity of lignin extracted with choline chloride/glycerol/$AlCl_3 \times 6H_2O$ reached 94±0.45%.

In this work [28], the choline chloride and oxalic acid dihydrate system was investigated for delignification and characterization of lignin from poplar flour. The DES was stirred in an oil bath at 80 °C under reduced pressure for 1 h. A 1:1 molar ratio was verified as a priority in this experiment. DES-based on choline chloride/oxalic acid dihydrate in a weight ratio of 1:20 was used to fractionate lignin from poplar flour. DES was treated using an oil bath heating mode (80 ºC and 110 ºC, 9 h) and microwave heating (80 ºC, microwave power 800 W). The results revealed that DES with choline chloride/oxalic acid dihydrate has the highest acid value of the hydrogen bond, which leads to the breaking of the lignocellulosic matrix in the wood. The results further showed that DES dissolved visible amounts of xylan and lignin at room temperature, but the solubility of microcrystalline cellulose was poor. At 80 °C in an oil bath, the dissolution of lignin and xylan was more remarkable, and the solubility of the cellulose increased slightly. These results suggest a good potential for the use of this DES for the selective fractionation of hemicellulose and lignin from wood biomass. The combination of microwave radiation and DES appears to be effective in fractionating lignin from lignocellulosic materials. The higher temperature was shown to contribute to lignin separation, and approximately 17.5% (90% initial lignin) was separated when the oil bath temperature was raised to 110 °C. Microwave DES treatment also showed good delignification efficiency. By treating the DES with a microwave oven for 3 min, 15.4% of the lignin fraction was extracted.

Three different DESs were used in this work [29], and the effects of treatment time and temperature of the optimal DES on the extraction of lignin from willow were investigated. DES prepared from choline chloride and three HBDs: lactic acid, glycerol, and urea, were evaluated

for isolation of willow (*Salix matsudana cv. Zhuliu*) lignin. It has been shown that negligible amounts of lignin have been removed by the action of choline chloride/glycerol and choline chloride/urea. It is noteworthy that the application of choline chloride/lactic acid had an important effect on the isolation of lignin. DES types, the molar ratio of choline chloride to hydrogen bond donors, extraction temperature, and yield time of fractionated DES lignin showed that the optimal yield of DES lignin (91.8%, based on the initial lignin in the willow) with a high purity of 94.5% was reached a molar ratio of choline chloride/lactic acid (1:10), an extraction temperature of 120 ºC and a time of 12 h.

Eutectic mixtures of lactic acid/alanine (9:1), lactic acid/betaine (2:1), lactic acid/glycine (9:1), choline chloride/glycolic acid (1:3), and choline chloride/ethylene glycol (1:2) were tested and used as delignifying agents on beech wood sawdust samples to examine behavior and effectiveness. The solutions were mixed in a water bath (70 °C) to give a homogeneous liquid. In the case of beech sawdust samples, the most effective eutectic solvents were lactic acid/alanine, which removed 14.4% of lignin from the sample, and choline chloride/glycolic acid, which removed 15.4% of lignin [31].

This work [30] compares the effectivity of DES (lactic acid/betaine) with a hydrotrope, p-toluenesulfonic acid (p-TsOH), depending on their ability to cleave lignin molecules after a mechanical pretreatment process applied to corn stover and willow. DES was prepared by mixing lactic acid and betaine (2:1). The mixture was kept in an oven at 60 °C for 2 h. The p-TsOH solution was prepared by dissolving the p-TsOH in deionized water at a concentration of 80%. Corn stover and willow were mixed with the DES (20:1 loading on biomass). The mixture was heated in an oil bath at 50 °C, 80 °C, 110 °C, and 140 °C. For the p-TsOH treatment, 80% p-TsOH was added with willow/corn stover at a liquid to solids loading of 20:1. The treatment was conducted at either 50 °C, 80 °C, 110 °C, and 140 °C for 30 min. The hydrotropes and DES both showed the ability to remove lignin. DES treatment removed lignin with greater selectivity and allowed increased cellulose and hemicellulose recovery at a pretreatment temperature of 140 °C. p-TsOH could efficiently remove 51-96% lignin at relatively low temperatures (50-80 °C).

Different DESs were prepared and used to delignify miscanthus and birchwood crude, including monocarboxylic acid/choline chloride, dicarboxylic acid/choline chloride, and polyalcohol/choline chloride. The efficiency of delignification was evaluated in terms of the nature of HBD and the acid strength of DES. Both the feedstocks were fine grind using a hammer mill. These feedstocks were selected because of the presence of different types of subunits in lignin. The compositional analysis results indicated that miscanthus and birchwood feedstocks had 12.97% and 11.13% of lignin, respectively. Choline chloride was used as an HBA and mixed with six different kinds of HBDs (lactic acid, formic acid, acetic acid, oxalic acid, malic acid, and glycerol). The mixtures were heated to 60 °C and stirred in screw-cap bottles until a transparent liquid formed. The delignification of biomass was performed in a microwave reactor. The biomass with the DES was loaded into microwave vials (5 mL) using a 10% solid loading of biomass (0.3 g of biomass and 3 g of DES). The reaction conditions used for different DES treatments are a temperature of 130 °C for 60 min and pre-stirring at 300 rpm for 10 min. Formic acid and oxalic acid-based DES were found to be promising solvents with the highest lignin extraction yields for both feedstocks. The results showed that the extent of delignification and the composition of extracted lignin depends on the type of HBD used to prepare DESs and the properties of the feedstocks used. The results showed an

increase in lignin extraction with increasing temperature from 60 °C to 130 °C. The optimal reaction time was different, 30 min for miscanthus and 60 min for birchwood [33].

In order to develop an efficient, simple, and environmentally friendly water-oil separation method, DES was applied to remove lignin and hemicellulose from bulk balsa wood partially. This resulted in delignified wood further modified by hydrophobic coating to transform it into an oil absorbent wood. The composition, morphology, and wettability of the oil absorbent wood were examined, and its oil absorption property was subsequently evaluated. Balsa wood samples were dried at 103 °C for 4 h before use. The delignified wood was produced with three different methods using NaOH-Na_2SO_3, $NaClO_2$, and choline chloride/oxalic acid DES treatment. As for the DES delignified wood, DES was made by 1:1 (molar ratio) mixing choline chloride and oxalic acid at 100 °C for 1 h to create a transparent and homogeneous solution. Afterward, the wood sample was dipped into DES for 2 h at 80 °C. The DES approach partially removed lignin and hemicellulose in balsa wood to form highly compressible tubular structures for potential use in oil-water separation [36].

Herein, an acidic biomass-derived DES (choline chloride/oxalic acid) pretreatment was developed to deconstruct the structure of bamboo for enhanced lignin fractionation and valorization. DES preparation was carried out by mixing choline chloride/oxalic acid with a molar ratio of 1:1 in a round flask. The mixture was melted at 60 °C for 2 h using a water bath and stirred continuously during this period until a homogeneous transparent solution was formed. The pretreatment was carried out using a biomass concentration of 10% (4 g dry bamboo and 40 g DES) in a glass pressure vessel reactor. Subsequently, the mixtures were heated at a target temperature for 4 h with constantly stirred. In summary, this work demonstrates that acidic DES assisted biomass delignification and promoted the cleavage of β-O-4 linkages at the elevated temperature of the reaction, which led to an increase in the sustained rise of phenolic OH groups and lower molecular weights. [37].

A biomass-derived DES pretreatment was developed to fractionate the structure of eucalyptus for cellulose enzymatic hydrolysis and lignin valorization. The DES consisted of biomass-derived chemicals (lactic acid and choline chloride). The pretreatments were carried out using a biomass concentration of 10% (2 g of dry biomass and 20 g of DES or lactic acid) in reaction vessels. In this study, *Eucalyptus camaldulensis* biomass was pretreated with DES solutions at a sample to DES ratio of 1:10 solid loading and a temperature of 90 °C, 100 °C, 110 °C, 120 °C, and 130 °C for 6 h. The composition of eucalyptus sawdust was 43.5% cellulose, 17.1% hemicelluloses, 26.3% of Klason lignin, and 3.9% of acetyl groups in terms of dry weight. Lignin and hemicelluloses were largely removed during pretreatment with DES, and biomass resistance was significantly reduced [39].

In this study [77], an environmentally benign extraction method via hydrothermal-DESs was proposed to separate hemicelluloses and high purity of lignin simultaneously from *moso* bamboo, with most of the cellulose retained in the residues. First, hydrothermal pretreatment was carried out to selectively remove hemicelluloses and result in the cleavage of lignin-carbohydrate linkages, which would facilitate the lignin extraction and reduce the biomass recalcitrance. Subsequently, two typical DESs, namely, choline chloride/lactic acid and betaine/lactic acid, were employed to extract lignin in the following process stage.

After thorough drying, the raw moso bamboo samples were chopped, milled, and then sieved. The binary mixtures were carried out using a water bath kettle at 60 ℃ with continuous stirring (350 rpm) until the solid parts disappeared. 50 g of loaded feedstock was mixed with 500 ml of deionized water in the vessel, followed by filling with certain amounts of carbon

dioxide, which will form into carbonic acid. The reaction temperature was heated up to 200 ℃ and maintained for 10 min to achieve maximum removal of hemicellulose. For DESs treatment, 1.0 g solid residues (after hydrothermal pretreatment) were mixed with 20 g DESs in a 50 mL round-bottom flask. The treatments were conducted at the temperature of 100 ℃, 120 ℃, and 140 ℃ for 6 h. Notably, 98.2% of hemicelluloses were degraded and mainly converted into pentose. Meanwhile, 80.1% of delignification was achieved under the optimum condition (lactic acid/choline chloride 140 ℃, 6 h), followed by up to 99.49% lignin purity. The mass balance evaluation demonstrated that the combined hydrothermal-DESs pretreatment is a potential method for efficient fractionation of lignocellulose.

2.2. Fractionation of annual plants, grasses, and herbs.

The objective of this present study [41] was to test three different DESs for the pretreatment of the corncob. The selected DES were choline chloride and glycerol, chlorine chloride and urea, and imidazole. Two different anti-solvents (water and ethanol) were tested to improve the biomass recovery after pretreatment, and all samples were characterized in light of lignin content. Corncobs were cleaned, ground and dried to the material's mass fraction of 0.08 water. Biomass was isolated by adding water or ethanol as an antisolvent, followed by separation of the solid. Recoveries larger than 80% were achieved for choline chloride/glycerol and choline chloride/urea at 80°C and 115°C, while 55% was achieved with choline chloride/glycerol at 150°C. Pre-treatment with choline chloride/imidazole appears to be highly effective in lignin removal. The pretreatment temperature, like the DES system, strongly affects the enzymatic conversion. Choline chloride/imidazole was the most effective DES tested and can be applied at relatively low temperatures (80°C), while temperatures of 150°C were required to achieve similar results for choline chloride/glycerol. DES pretreatment of biomass can enhance enzymatic saccharification by lignin removal and via a reduction of the cellulose crystallinity.

In this work [42], three DESs were used in the pretreatment of corncob, including monocarboxylic acid/choline chloride, dicarboxylic acid/choline chloride, and polyalcohol/choline chloride. The HBDs were lactic acid, glycolic acid, levulinic acid, malonic acid, glutaric acid, oxalic acid, malic acid, ethylene glycol, and glycerol. The prepared mixture of DES and corncob was stirred on a magnetic stirrer at a specific temperature and time. It has been observed that the extent of delignification and the efficiency of enzymatic hydrolysis were significant after pre-treatment. As for the lactic acid/choline chloride, with the molar ratio of lactic acid to choline chloride increasing from 2:1 to 15:1, the lignin extractability increased drastically (64.7–93.1%). It indicated that a larger amount of acid in the DES can facilitate the extensive delignification of corncob, resulting in fewer residues recovery. The acid amount and HBAs´ nature greatly influenced the pretreatment results. The consistency of characterization results indicated that the DES deconstructed corncob structures by removing the hemicellulose and lignin. The optimal pretreatment temperature and time showed to be 24 h and 90°C.

The pretreatment in this study [44] was conducted for 45 s with microwave irradiation at 800 W using a DES composed of choline chloride and lactic acid. In this study, three biomass feedstocks, corn stover, switchgrass, and miscanthus, were subjected to ultrafast DES pretreatment assisted by microwave. Three feedstocks were air-dried, ground, and stored in plastic bags. The compositional change of biomass in response to the pretreatment was investigated. Lignin recoverability and purity were also studied. The results showed that the

microwave-assisted DES pretreatment was highly effective for fractionating all the tested feedstocks. Among three feedstocks, corn stover showed the highest lignin removal (about 80%). Switchgrass and miscanthus also removed more than 65% lignin during the pretreatment. In the present study, the microwave was proven to enhance choline chloride/lactic acid pretreatment efficiency. Thus, microwaves can significantly shorten the reaction time for DES pretreatment while achieving a similar or even higher degree of effectiveness compared to DES pretreatment alone. All the recovered lignin had relatively high purity (85-87%), which is advantageous to further lignin valorization.

Six different DESs treatments: five acidic (natural organic acid/choline chloride) and one alkaline (K_2CO_3/glycerol), were compared in delignification and nanofibrillation of agricultural by-products from wheat straw, corn stalk, and rapeseed stem in this study [45]. The wheat straw, corn stalk, and rapeseed stem samples were oven-dried to a constant weight and then milled to a particle size of one millimeter and used as such. 3 g of wheat, corn, or rapeseed was added to the suspension with 5 g of water, and the suspension (3%) was allowed to stir at 100 °C for 8 or 16 h, or at 80 °C for 24 h. The samples initially contained 19-24% lignin, 27–40% cellulose, and 11–18% hemicelluloses. The gravimetric yield of lignin from DES treatment varied from 1.0-9.5% for wheat, 0.8-8.5% for corn, and 0.8–11.8% for rapeseed stem. The results show that acidic (lactic acid/choline chloride, 5:1) resulted in the highest lignin yield among the different DES with all biomasses. The 16 h reaction at 100 °C was the optimum condition for lignin removal with lactic acid/choline chloride (5:1), 8.5% for wheat, 9.5% for corn, and 11.8% for rapeseed and other acidic DES treatments. Evaporation was not observed with other acids nor with glycerol. Despite the evaporation, the lactic acid DES had the highest delignification efficiency. The lignin yield with the alkaline DES treatment was from 0.8 to 5.7% and was comparable to acidic DES with wheat and rapeseed and lowered with corn. However, the lignin content measured from solid fractions was generally only slightly lower with glycerol/K_2CO_3, thus indicating similar delignification efficiency to that of lactic acid/choline chloride (1:2) and lactic acid/choline chloride (5:1). This result may be attributed to incomplete lignin precipitation from alkaline DES, which is seen as a low lignin recovery.

The goal of this work [48] was to develop DES based on carbohydrates and evaluate their ability to dissolve biomass. For this purpose, mixtures of different HBAs such as choline chloride, acetylcholine chloride, benzyldimethyl(2-hydroxyethyl)ammonium chloride, and several natural carbohydrates such as xylose, mannose, fructose, glucose, and ribose. 10% water was added to all prepared DES to mimic the prepared DES in contact with the atmosphere. The results of rice straw dissolution have been shown to depend on the HBAs, and HBDs used. It was also possible to observe that they were present in all carbohydrates; higher dissolution rates were observed using choline chloride. The highest limit solubility of rice straw (6.5 mg / 1 g DES) was achieved for choline chloride/fructose.

Authors have demonstrated [49] choline chloride/urea pretreatment on rice straw, which is abundant, renewable, and available worldwide. To better evaluate the transformation mechanism during choline chloride/urea pretreatment on rice straw biomass fractionation, the chemical fractions of holocellulose, α-cellulose, and acid-insoluble-lignin were isolated from rice straw. These isolated chemical fractions were further pretreated with choline chloride/urea. Rice straws were collected, prepared with the screening system, and dried at 105°C to constant weight. Holocellulose (60.80%), α-cellulose (34.15%), and acid-insoluble lignin (11.10%) were isolated from rice straw. The eutectic mixture was prepared by combining choline chloride/and urea at the molar ratio of 1:2 at 80°C with a magnetic stirrer using an oil bath until

a clear homogeneous, colorless, and viscous solution was obtained. For comparison, the oven-dried holocellulose, α-cellulose and acid-insoluble-lignin isolated from rice straw were also treated with choline chloride/urea at 130°C for 4h. The lignin content decreased from 14.84% to 8.20%-10.08%. The lignin content decreased significantly by 32–45% within all chemical compositions, which further proves that choline chloride/urea has a higher selective solubility for lignin. Lignin exhibited an efficient solubility during choline chloride/urea pretreatment.

Rice straw pretreatment mediated by choline chloride or lactic acid sequences DESs was investigated in this work [50]. HBAs and HBDs proved to be both important for DES pretreatment efficiency. A group of DES, the series of polyols and acid amides-based DES with different HBA (choline chloride and lactic acid), and choline chloride-based DES with various HBD (diols, monocarboxylic acids, dicarboxylic acids) were synthesized and used to pretreat rice straw to investigate the roles of HBD and HBA on the effectiveness of rice straw pretreatment. The xylan and total lignin contents in native rice straw are 20.6% and 21.5%. Both HBD and HBA had non-negligible effects on the pretreatment efficiency of DES. HBD containing more hydroxyl or amino groups always had detrimental impacts on the pretreatment efficiency, while the presence of strong electron-with drawing groups in the HBD enhanced the DES performance. In addition, a temperature-dependent negative relationship between xylan removal and pKa values of the HBD was observed, and DES with strong acidity could remove excessive xylan and significantly enhance cellulose enzymatic digestion. This work is useful for understanding the mechanism of DES pretreatment and for designing effective DES for biomass deconstruction.

In a certain line of research, a new group of systems has emerged as solvents of the 21st century, named natural deep eutectic solvents (NADES). The efficiency of delignification using NADES depends on the type of biomass and structural variations of lignins. The current study [51] details the technical assessment of an integrated biorefinery process using NADES pretreated rice straw, recovery of high purity lignin using lactic acid/choline chloride/water (9:1:0,11) based NADES reagent. The tested conditions were biomass pretreatment at 5% solids loading and enzymatic saccharification at 10% solids loading; biomass pretreatment at 5% solids loading and enzymatic saccharification at 25% solids loading; biomass pretreatment at 10% solids loading and enzymatic saccharification at 10% solids loading; biomass pretreatment at 10% solids loading and enzymatic saccharification at 25% solids loading. The residual lignin content in the NADES pretreated biomass of 4.3%, 4.1%, 3.9% and 3.5%. The % of lignin in the NADES pretreated liquid extract was 62.2%; 63.5%; 71.9% and 72.3%.

In this study [52], four DESs have been used as “greener” alternatives to ionic liquids to form microemulsions. The cellulose, hemicellulose, and lignin contents of rice straw were 35.84%, 31.71%, and 24.45%. The DES was synthesized by mixing the two or three constituents in an available molar ratio. The mixtures were heated at 70–80 °C until a clear solution was obtained. The phase diagrams were constructed based on the isotropic properties of the DES, surfactant (Tween 20), cosurfactant (methanol), and cyclohexane by direct visual observation. The mass ratio of Tween 20 and methanol was 3:1. According to the phase diagrams, all the systems at the mass ratio of DES: Tween 20/methanol:cyclohexane = 0.1:0.8:0.1 are microemulsions at 70 °C. The microemulsion pretreatments facilitated the rice straw dissolution and delignification. DES/Tween20/methanol/cyclohexane were successfully used as alternative pretreatment solvents for rice straw. It has been found that microemulsions can selectively dissolve rice straw at 70 ºC, and this treatment removed 54.3% of lignin.

A novel ternary system consisting of a DES-alcohol mixture was developed for the effective valorization of biomass. Optimization studies included selecting suitable co-solvent (n-butanol, n-propanol, and ethyl acetate) for treating biomass (rice husk, rice straw, and wheat straw), altering the DES to alcohol ratio (2:1, 1:1, and 1:2) as well as the reaction temperature (50 °C, 80 °C, and 120 °C). The biomass samples were ground and oven-dried at 105 °C until constant weight. DES was prepared by mixing choline chloride and oxalic acid. Lignin removal was observed to be in the range of 23–31% for all the tested biomass samples with DES, which is in contrast with DES-alcohol, where ~50% delignification was observed for all the tested biomass samples. The results indicated the use of the combination DES and n-butanol achieved the best results among the tested mixtures of organic solvents. Thus, the highest delignification, 50%, was observed using DES choline chloride/oxalic acid with n-butanol in a ratio of 2:1 at 120 °C in a 60 min reaction [53].

This work [16] tries to contribute to the yield and selectivity investigation regarding the delignification of wheat straw using different types of DES. The goal of the work was to estimate the effectiveness of delignification in removing lignin, as well as the selectivity of the process. Samples of wheat straw were cleaned, ground and dried. Before delignification, the wheat straw was extracted and analyzed to determine the content of lignin. The lignin content in the original wheat straw sample was 17.3 ± 1.0%. The yield ranged from 59.1% to 94.9%. The results showed that each of the DES was able to dissolve lignin from a given sample of wheat straw. The amount of dissolved lignin varied depending on the components of each DES. The highest amount of lignin (57,9%) was removed using choline chloride and oxalic acid dihydrate. From the point of view of the selectivity of lignin removal from wheat straw, the best results were obtained using choline chloride/lactic acid in a molar ratio of 1:10. This work showed that the DES used did not act selectively. Along with lignin, other biomass components (holocellulose) passed to DES.

Recent studies show that choline chloride and lactic acid-based DES are effective in extracting and removing lignin from woods and plants. In addition, it has been speculated that an adequate amount of water existing in the biomass may facilitate the formation of a hydrogen bond between DES and biomass by improving the solubilization capacity of DES for biomass. This study [54] was focused on optimizing lignin extraction from wheat straw using DES (choline chloride and lactic acid). A sample of wheat straw was composed of 6.6±0.05% water, 22.4±0.1% lignin, 38.1±0.6% cellulose, 27.3±0.2% hemicellulose, and 3.4±0.1% ash. DES-based on choline chloride and lactic acid was prepared in a molar ratio of 1:2. 3 g of wheat straw sample and 30 g of DES were used. Two types of wheat straw samples were used, air-dried, containing 6.6±0.05% water, and samples which have been dried in an oven at 105 ºC for 3 h (0% water). Effects of processing temperature and reaction time in lignin extraction by DES treatment were examined at three temperatures (90 ºC, 120 ºC, and 150 ºC) and at different reaction times (6 h, 12 h, and 24 h). Wheat straw was treated with DES at 90 ºC and 168 h. After choline chloride/lactic acid-based DES treatment, the wheat straw was divided into three fractions: solid residues, isolated lignin, and solutes in DES. It was found that the DES used could extract high purity lignin (94.8%) in high yield (81.5% of samples dried on air and 85.9% of oven-dried samples) of wheat straw. The extraction temperature, reaction time, and water content of wheat straw significantly affected the properties of lignin. Temperature and time processing significantly affects the yield and purity of lignin.

Recent research has focused on the behavior and effectiveness of a DES for the fractionation of wheat straw. Five eutectic mixtures were prepared and used as delignifying

agents for samples of ground wheat straw. The sample must be extracted first, and the content of lignin, ash, and holocellulose is determined. The work aimed to achieve the highest possible removal of lignin at atmospheric pressure and to use solvents at temperatures below 100 ºC. The results show that the most effective eutectic mixture for the delignification of wheat straw appears to be lactic acid and alanine, which achieved a delignification efficiency of 23.7% and the lignin content decreased to 12.3%. A mixture of choline chloride/glycolic acid proved to be another effective solvent, the delignification reached 16.6%, and the lignin content decreased to 13.4%. The use of other DES was ineffective; lignin was only marginally reduced after delignification, or the lignin content did not change. Many attempts have been made to remove lignin from wheat straw using various mixtures of substances and solvents. The application of choline chloride/lactic acid appears to be most effective in removing lignin, regardless of biomass source [31].

Three environmentally friendly heteropoly acids (phosphotungstic, phosphomolybdic, and silicotungstic acids) were used as catalysts. These acids were used as catalysts to remove hemicellulose and lignin of *Miscanthus x giganteus* in the choline chloride/glycerol system. DES (choline chloride/glycerol at a molar ratio of 1:2) was synthesized at 60 °C for 1 h. *Miscanthus x giganteus* (2 g) and heteropoly acid (0,5 g) were suspended in 40 mL of choline chloride/glycerol DES. The mixture was heated at 120 °C for 3 h. The untreated material mainly included cellulose (40.7%), xylan (20.0%), and lignin (24.8%). The choline chloride/glycerol pretreatment had less effective for the removal of lignin (1.6%) and hemicellulose (5.3%). After the choline chloride/glycerol with heteropoly acids pretreatment, it was observed that the content of cellulose was enhanced to 64.7–75.3%, which was attributed to the that the systems were capable of prominent solubilizing lignin (56.5–89.5%) and hemicellulose (44.0-58.5%). Overall, the results suggested that the neutral DES with heteropoly acids had a unique capability for selective lignin and hemicellulose removal from bioenergy crops while preserving most cellulose under mild conditions [55].

Ternary DESs were developed to enable rapid biomass pretreatment. Six ternary DESs mixed with choline chloride or guanidine hydrochloride as an HBA, ethylene glycol, propylene glycol, and glycerin as a polyol-based HBD, and p-toluenesulfonic acid as an acidic HBD. Switchgrass was used as a feedstock for all the experiments. Switchgrass was air-dried, ground, and stored. To synthesize ternary DESs, HBA/polyol/p-toluenesulfonic acid was mixed at a molar ratio of 1:1.94:0.06 in a glass bottle. Next, the mixture was heated at 80 °C for 2 h until a transparent liquid was formed. Guanidine hydrochloride/ethylene glycol/p-toluenesulfonic acid was the most effective, evidenced by 79% xylan and 82% lignin removal in only 6 min at 120 °C and 10% solid loading. Even at 35% solid loading, both guanidine hydrochloride/ethylene glycol/p-toluenesulfonic acid and choline chloride/ethylene glycol/p-toluenesulfonic acid still removed more than 60% xylan and lignin in 30 min. This study [69] demonstrated a novel and high-performance ternary DESs for effective lignocellulose delignification.

2.3. Fractionation of other lignocellulosic materials.

Guanidine hydrochloride-based DES was applied using a microwave oven for efficient pretreatment of castor stalk. The focus of this research [56] was to explore the microwave-assisted multiple DES systems deconstructing castor stalk in a single step. An experimental field provided the raw castor stalk, and then it was pulverized and then crushed through a screen. Guanidine hydrochloride and choline chloride were used as the HBAs in DES synthesis.

Lactic acid, glycerol, and urea were employed as the HBDs. DES-lignin yield was calculated based on the Klason lignin content of the raw castor stalk. The chemical composition of raw castor stalk was 41.45% glucan, 18.31% xylan, and 19.49% Klason lignin. The microwave-assisted DES pretreatment effectively deconstructed the castor stalk. The solid recovery was affected by the dissolution of xylan (23.31-77.56%) and lignin (26.27-92.02%) in each DES. Guanidine hydrochloride/urea DES retained 92.18% glucan and removed 26.06% xylan and 28.21% lignin. Glucan loss among four DES pretreatments was similar (5.10–11.31%), while guanidine hydrochloride/lactic acid DES significantly removed xylan and lignin, 77.56% and 92.02%. These results indicated that guanidine hydrochloride can replace choline chloride as the HBA and promote the DES pretreatment performance with lactic acid. DES pretreatment process removed 26–93% of lignin from the castor stalk. The lignin recovery from the guanidine hydrochloride/lactic acid was up to ~ 32%, while 3–17% was obtained from the other DES. Under the same pretreatment condition, guanidine hydrochloride/lactic acid DES resulted in the highest lignin recovery (32.07%), which is 2-10 times higher than the yields with the other DES (3.34–16.52%). The increase in microwave temperature (100–140 °C) enhanced the removal of the xylan and lignin from castor stalk. A large portion of lignin (32.77%–95.14%) in the castor stalk was dissolved in the pretreatment process. Lignin yield ranged from 5.85% to 34.58% at 100–140 °C. The microwave-assisted guanidine hydrochloride-based DES pretreatment was effective for castor stalk fractionation and biological conversion. DES synthesized with guanidine hydrochloride and lactic acid effectively delignified (92.02%) the biomass within 30 min. This resulted in a 96.3% cellulose saccharification yield. The regenerated lignin exhibited a high purity of up to 98%, conducting a promising feedstock for bio-based materials without additional purification. Therefore, this study demonstrated a novel process for low-cost and efficient biomass deconstruction.

The oil palm frond is one of the most abundant lignocellulosic biomass wastes found in the palm oil industry. Oil palm frond was subjected to ultrasound-assisted sodium hydroxide (NaOH)-aqueous DES pretreatment in this study [58] to increase delignification and enhance enzymatic saccharification. Fresh oil palm frond without leaflets was obtained from an oil palm plantation. The ground and dried petioles were termed oil palm fronds and used throughout this study. Oil palm frond mainly consists of cellulose (glucan 41.25%), hemicellulose (xylan 21.51% and arabinan 2.44%), and lignin (18.42%). Choline chloride/urea DES was synthesized at a molar ratio of 1:2. The mixture was synthesized at a temperature of 60 °C to form a clear homogenous liquid. Aqueous DES was then prepared by mixing distilled water and DES at a ratio of 1:4, followed by the addition of NaOH to obtain solvents with overall concentrations of 0.1, 0.5,1.5,2.5, and 3.5 wt% NaOH-aqueous DES. Pure DES and a 0% NaOH aqueous-DES solvent were prepared as reference pretreatments for the study. Various amplitudes (50%, 60%, and 70%) and ultrasonic durations (10 min, 20 min, 30 min, 40 min, and 50 min) were explored. A higher concentration of NaOH solution (up to 2.5%) was found to yield a greater extent of delignification. The result was expected as a higher alkali concentration could enhance the degradation of ester bonds and cleave glycosidic linkages. The recommended NaOH concentration to be combined with DES was found to be 2.5%. The lignin removal obtained by pure DES and the aqueous DES pretreatment was found to be 18.05% and 29.79%, respectively. The use of an aqueous DES solvent during ultrasonic pretreatment was able to increase lignin removal significantly. The increase in lignin removal was likely due to the generation of microjets within the solvent, which was able to disrupt the surface of the oil palm frond to enhance delignification.

Sequential delignification of watermelon rind using ultrasonication and DES pretreatment methods was demonstrated in this study [60]. The watermelon rinds were dried at 80 °C for 24 h, after which they were ground and mesh-screened. Raw watermelon rind contains 10.63% lignin, 39.67% cellulose, and 23.21% hemicellulose. Ultrasonication pretreatment was conducted in a water medium, followed by DES pretreatment. The ultrasonic pretreatment was performed using a multi-frequency ultrasound equipped with a generator (300 W). A biomass sample and distilled water were added to a Schott bottle. The mixture in the Schott bottle was fully submerged in the treatment chamber of the ultrasound equipment to allow the transmission of ultrasound. Dried ultrasound pretreated watermelon rind solid residue was stored and kept in a desiccator before DES pretreatment. Choline chloride and lactic acids were the HBA and HBD. The DES was placed in a round-bottom flask and was continually stirred magnetically for 2 h at a temperature of 80 °C when a clear transparent solvent was obtained. The significant factors were further investigated, and maximum lignin removal of 43.56% was achieved at ultrasonication power 180 W, ultrasonication frequency 60 kHz, ultrasonication time 40 min, reaction temperature 120 °C, and reaction time 180 min.

This report [62] aims to study the alternative method or media for the pretreatment of biomass with an environmentally friendly process. Herein, we studied the potential of five DESs for the pretreatment solvent and oil palm trunk as the raw material. Oil palm trunk was shredded and refined into the loose fiber. The fiber was then sieved and dried to a constant weight prior to use. All DES were prepared by mixing ammonium salt and HBD in a molar ratio (1:2). The mixture was stirred and heated at 80 °C for 1 h or until a homogenous and colorless liquid was obtained. All DES pretreated biomass showed a reduced lignin content with choline chloride/glycerol treated oil palm trunk, recording the least lignin content (49% lignin removal) after pretreatment. However, ethylammonium chloride/ethylene glycol showed the worst performance in lignin removal with only 36% after pretreatment.

The microwave has recently been applied in extraction due to its advantages, such as shorter extraction and lower solvent consumption. The authors used NADES and microwave activation to extract phenol compounds from plant biomass. Olives were used as biomass, washed with distilled water, dried, and ground. NADES were made by mixing choline chloride with different HBD. 20% water was added to the NADES, then 2 g of the sample was mixed with 5 ml of NADES in a vessel, and microwave radiation was applied to this mixture (100 W, 30 or 10 min at 80 °C). Six different HBD in combination with choline chloride (combination with urea (1:2), glycerol (1:1), lactic acid (1:1), ethylene glycol (1:1), and citric acid (1:1) were selected to form NADES. The result of the work was that green solvents and microwave extraction are effective methods for recovering phenolic compounds from olive oil processing [68].

The structural properties of peach and walnut endocarp cells have been studied in this work [70]. Peach (*Prunus persica*) and nut shells (*Juglans nigra*) endocarps were dried, ground, and used for the experiment. The DES synthesis included mixing choline chloride and lactic acid (1:2). Endocarp biomass has different properties (high lignin content, bulk density, and hardness) than other plant materials. The lignins were extracted in high yields of 64.3% for walnut and 70.2% for peach endocarps, with a purity of more than 92%.

2.4. Delignification (fractionation) of pulp.

In this study [63], the authors delignified pulp by applying DES (choline chloride and 3 organic acids, alanine, and lactic acid). The hardwood kraft pulp was mixed at 60 ° C for 2

hours and treated with DES. The sample was washed, filtered, and air-dried. The lignin content of the biomass (pulp) was expressed using the kappa number. The efficiency of delignification was expressed as a decrease in kappa number on the unit change of the initial kappa number of pulp in all articles in this subchapter. Pulps (initial kappa numbers: 21.7 and 14.3) were used. The results showed that pulp with a higher initial lignin content will have a better and greater fraction of easily removable lignin fragments, and the type of DES influenced the mechanical properties (tensile, burst and tear indices, tensile length, and stiffness) of delignified pulp and the pulp with a higher initial lignin content underwent a more efficient delignification when pre-treated by DESs.

In this work [64], the potential of selected DES in delignification of unbleached pulp was investigated. Unbleached beech pulp was used as a raw material for delignification (initial Kappa number 15 ± 0.6 with an average degree of polymerization of 609 ± 7). The results showed that the most effective DES (lignin removal aspect) was (malonic acid/choline chloride propanediol), with the kappa number falling from 15 to about 9 (39.8% efficiency). It is known from various studies that among the most important properties of DES are its viscosity and density (with increasing density, it is more difficult to penetrate the fiber structure). It has been found that the addition of alcohol to the DES composition leads to a reduction in both density and viscosity. In contrast, the addition of an organic acid causes them to increase.

In the following experiment, the authors used the kraft pulp as an initial pulp. The pulp was treated with two different DES systems based on choline chloride/lactic acid (1:9) and system alanine/lactic acid (1:9). This study [65] was conducted to investigate the effects of DES treatment on the physical and chemical properties of delignified pulp. DESs were prepared by the heating method. The heating method is based on mixing the two components, which are then heated at 70 °C under constant stirring until a homogeneous liquid is formed. The raw pulp had a kappa number of 21.7. After delignification using DES, the kappa number decreased to 13.5 for the choline chloride/lactic acid system and to 12.3 for alanine/lactic acid.The delignification efficiency growth: choline chloride/lactic acid (37.8%) > alanine/lactic acid (43.3%). Obtained results showed that the type of DES influenced on mechanical properties of delignified pulp. The results indicate that the application of DESs might be an interesting alternative to oxygen delignification of pulp following kraft cooks.

This study [66] aimed to understand the effect of initial lignin content in hardwood kraft pulps on delignification of pulp by DES. The authors used the kappa number of the concerned pulp and the efficiency of delignification as the parameters of the effect. The biomass (pulp) was processed with four different DESs systems based on choline chloride with lactic acid (1:9), oxalic acid (1:1), malic acid (1:1), and system alanine/lactic acid (1:9); the results were compared to those reached by oxygen delignification. In this work, pulp with different initial kappa numbers: 21.7, 11.8, and 14.3 were used (degree of polymerization: 1.157; 805; 1.258). The pulp with Kappa number 21.7 subjected to oxygen delignification reached kappa number 11,8. This means that the efficiency of delignification was 45.6%.

Fifteen ternaries DESs were prepared and tested as solvents suitable for the delignification of unbleached pulp. In this work [67], unbleached beech pulp (initial kappa number of 13.9 and an average degree of polymerization of 1.034) was used. Mixtures with the required molar ratio were heated in a spherical glass flask and stirred by a vacuum rotary evaporator in water at the appropriate temperature (70-90 °C) and atmospheric pressure. The sample, after delignification, was washed using hot water to a neutral pH, filtered, and air-dried. The most suitable solvent for pulp delignification appeared to be DES (malonic acid,

choline chloride, and 1,3-propanediol, in a molar ratio of 1:1:3). This DES reached a lignin removal efficiency of 28.06%. The lignin removal efficiency of the other DESs is relatively lower (15.83% to 1.44%).

Table 1. Delignification of different types of biomass using green solvents.

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Lactic acid/$[N(Me)_4]Cl$	Pine wood	1:3	0,5 g sample, 10 g DES, 14 h, 60 ºC	12.6 %	[18]
Lactic acid/$[N(Me)_4]Cl$	Pine wood	1:2	0,5 g sample, 10 g DES, 14 h, 60 ºC	8.3 %	[18]
Choline chloride/Oxalic acid	Pine wood	1:1	0,5 g sample, 10 g DES, 14 h, 85 ºC	9.7 %	[18]
Choline chloride/Lactic acid	Pine wood	1:9	0,5 g sample, 10 g DES, 14 h, 60 ºC	9.7 %	[18]
Choline chloride/Lactic acid	Pine wood	1:2	0,5 g sample, 10 g DES, 14 h, 60 ºC	4.9 %	[18]
Choline chloride/Malic acid	Pine wood	1:1	0,5 g sample, 10 g DES, 14 h, 85 ºC	1.7 %	[18]
Lactic acid/2-chloroethyl trimethylammonium chloride	Pine wood	1:5	0,5 g sample, 10 g DES, 14 h, 60 ºC	22.3 %	[18]
Lactic acid/2-chloroethyl trimethylammonium chloride	Pine wood	1:2	0,5 g sample, 10 g DES, 14 h, 60 ºC	9.1 %	[18]
Choline chloride/Lactic acid	Pine wood *(Pinus bungeana Zucc.)*	1:10	3 g sample, 48 ml DES, 120 ºC, 4 h	33.95 %	[20]
Choline chloride/Lactic acid	Pine wood *(Pinus bungeana Zucc.)*	1:10	3 g sample, 48 ml DES, 120 ºC, 4 h, microwave (800 W)	12.52 %	[20]
Lactic acid/Choline chloride	Pine wood (*Pinus pinaster Ait.*).	5:1	1 g sample, 10 g DES, 150 ºC, 2 h	81.3 ± 7.1 %	[21]
Lactic acid/Choline chloride	Pine wood (*Pinus pinaster Ait.*).	2:1	1 g sample, 10 g DES, 150 ºC, 2 h	76.7 ± 0.9 %	[21]
Lactic acid/Tartaric acid/ Choline chloride	Pine wood (*Pinus pinaster Ait.*).	4:1:1	1 g sample, 10 g DES, 150 ºC, 2 h	86.2 ± 5.0 %	[21]
Lactic acid/Tartaric acid/ Choline chloride	Pine wood (*Pinus pinaster Ait.*).	4:1:1	1 g sample, 10 g DES, 175 ºC, 1 h	94,9 ± 3,3 %	[21]
Choline chloride/Lactic acid	Poplar wood	-	0,6 g sample, 6 g DES, 90 ºC, 6 h; 120 ºC, 3 h; 145 ºC, 69 h; 180 ºC, 0,5 h	25.2 % (90 ºC) 72.1 % (120 ºC) 78.5 % (145 ºC)	[24]
Choline chloride/Acetic acid Choline chloride /Glycerol	Poplar wood	-	0,6 g sample, 6 g DES, 90 ºC, 6 h; 120 ºC, 3 h; 145 ºC, 69 h; 180 ºC, 0,5 h	18.1 % (90 ºC)	[24]
Choline chloride/Levulinic acid	Poplar wood	-	0,6 g sample, 6 g DES, 90 ºC, 6 h; 120 ºC,3 h; 145 ºC, 69 h; 180 ºC, 0,5 h	21.3 % (90 ºC)	[24]
Choline chloride/Lactic acid	Poplar wood *(Douglas fir)*	-	0,6 g sample, 6 g DES90 ºC, 6 h; 120 ºC, 3 h; 145 ºC, 69 h; 180 ºC, 0,5 h	58.2 % (145ºC)	[24]
Choline chloride/Glycerol	Poplar wood	1:2	1 g sample, 20 g DES, 4 h, 110, 120, 130 ºC	0 % 0.04 % 0.04 %	[27]
Cholinechloride/Glycerol/ $AlCl_3 \times 6H_2O$	Poplar wood	1:2:0,1	1 g sample, 20 g DES, 4 h, 110, 120, 130 ºC	61.29 % 75.15 % 89.22 %	[27]
Choline chloride/Glycerol/		1:2:0,13	1 g sample, 20 g DES,	66.44 %	[27]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
$AlCl_3 \times 6H_2O$	Poplar wood		4 h, 110, 120, 130 ºC	87.83 % 98.45 %	
Choline chloride/Glycerol/ $AlCl_3 \times 6H_2O$	Poplar wood	1:2:0,2	1 g sample, 20 g DES, 4 h, 110, 120, 130 ºC	79.07 % 93.40 % 105. 0%	[27]
Choline chloride/Glycerol/ $AlCl_3 \times 6H_2O$	Poplar wood	1:2:0,28	1 g sample, 20 g DES, 4 h, 110, 120, 130 ºC	83.66 % 95.46 % 105.21 %	[27]
Choline chloride/Glycerol/ $AlCl_3 \times 6H_2O$	Poplar wood	1:2:0,33	1 g sample, 20 g DES, 4 h, 110, 120, 130 ºC	83.57 % 95.11 % 105.26 %	[27]
Choline chloride/Oxalic acid dihydrate	Poplar wood	1:1	0,5 g sample, 10 g DES, oil bath (80 ºC, 110 ºC, 9h)	90.6 % (110 ºC)	[28]
Choline chloride/Oxalic acid dihydrate	Poplar wood	1:1	0,5 g sample, 10 g DES, microwave (800 W,80 ºC) retention 1,3 a 8 min	81.8 % (3 min) 78.2 % (8 min)	[28]
Choline chloride/Lactic acid	Willow wood (*Salix matsudana cv. Zhuliu*)	1:2, 1:4 1:6, 1:8 1:10 1:12	2,5 g sample, solvent to solid ratio 1:30, 90-120 ºC, 6-42 h	91.82 % (1:10, 120 ºC, 12 h) 94.20 % (42 h)	[29]
Choline chloride/Glycerol	Willow wood (*Salix matsudana cv. Zhuliu*)	1:2	2,5 g sample, solvent to solid ratio 1:30, 90-120 ºC, 6 h	52.43 % ,(120ºC)	[29]
Choline chloride/Urea	Willow wood (*Salix matsudana cv. Zhuliu*)	1:2	2,5 g sample, solvent to solid ratio 1:30, 90-120 ºC, 6 h	2.5 % (120 ºC)	[29]
Choline chloride/Lactic acid	Willow wood (*Salix matsudana cv. Zhuliu*)	1:2	2,5 g sample, solvent to solid ratio 1:30, 90-120 ºC, 6 h	7 % (120 ºC)	[29]
Lactic acid/Alanine	Beech wood	9:1	10 g sample, 200 g DES, 60 ºC, 24 h	14.4 %	[31]
Lactic acid/Betaine	Beech wood	2:1	10 g sample, 200 g DES, 60 ºC, 24 h	11.6 %	[31]
Lactic acid/Glycine	Beech wood	9:1	10 g sample, 200 g DES, 60 ºC, 24 h	6.4 %	[31]
Choline chloride/Ethylene glycol	Beech wood	1:2	10 g sample, 200 g DES, 60 ºC, 24 h	4.9 %	[31]
Lactic acid/Choline chloride	Moso bamboo	10:1	1 g sample, 20 g DES, 100 ºC, 6 h	46.6 %	[74]
Lactic acid/Choline chloride	Moso bamboo	10:1	1 g sample, 20 g DES, 120 ºC, 6 h	50.4 %	[74]
Lactic acid/Choline chloride	Moso bamboo	10:1	1 g sample, 20 g DES, 140 ºC, 6 h	80.1 %	[74]
Lactic acid/betaine	Moso bamboo	2:1	1 g sample, 20 g DES, 100 ºC, 6 h	45.5 %	[74]
Lactic acid/betaine	Moso bamboo	2:1	1 g sample, 20 g DES, 120 ºC, 6 h	46.9 %	[74]
Lactic acid/betaine	Moso bamboo	2:1	1 g sample, 20 g DES, 140 ºC, 6 h	54.5 %	[74]
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:15, 100 ºC, 2 h	61.47 %	[77]
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:20, 100 ºC, 3 h	72.39 %	[77]
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:25, 110 ºC, 3 h	89.35 %	[77]
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:25, 120 ºC, 2 h	91.52 %	[77]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:15, 120 ºC, 3 h	87.04 %	[77]
Choline chloride/Lactic acid	Moso bamboo *(Phyllostachys pubescens)*	1:9	3 g sample, DES solid to liquid ratio 1:20, 120 ºC, 4 h	91.42 %	[78]
Choline chloride/Imidazole	Corncob	3:7	solvent to solid ratio 16:1, 15 h, 80, 115 and 150 ºC	43.1 % 70.8 % 88.3 %	[41]
Choline chloride/Glycerol	Corncob	1:2	solvent to solid ratio 16:1, 15 h, 80, 115 and 150 ºC	4.3 % 8.8 % 24.8 %	[41]
Choline chloride/Urea	Corncob	1:2	solvent to solid ratio 16:1, 15 h, 80, 115 and 150 ºC	8.0 % 24.8 %	[41]
Choline chloride/Oxalic acid	Corncob	1:1	0,3 g sample, 6 g DES, 24 h, 90 ºC	98.5 %	[42]
Choline chloride/Lactic acid	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 70, 80, 90, 100, 110 ºC	11.8 %, 31.1 %, 42.7 %, 65.8 %, 95.5 %	[42]
Choline chloride/Lactic acid	Corncob	1:15	0,3 g sample, 6 g DES, 24 h, 90 ºC	93.1 %	[42]
Choline chloride/	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 90 ºC	87.6 %	[42]
Choline chloride/Lactic acid	Corncob	1:10	0,3 g sample, 6 g DES, 24 h, 90 ºC	86.1 %	[42]
Choline chloride/Lactic acid	Corncob	1:5	0,3 g sample, 6 g DES, 24 h, 90 ºC	77.9 %	[42]
Choline chloride/Glycerol	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 90 ºC	71.3 %	[42]
Choline chloride/Lactic acid	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 90 ºC	64.7 %	[42]
Choline chloride/Malonic acid	Corncob	1:1	0,3 g sample, 6 g DES, 24 h, 90 ºC	56.5 %	[42]
Choline chloride/Glycolic acid	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 90 ºC	56.4 %	[42]
Choline chloride/Lactic acid	Corncob	1:2	0,3 g sample, 6 g DES, 90 ºC, 1, 5, 3, 6, 12, 24 and 36 h	8.6 %, 15.7%, 20.9 %, 25.7 %, 42.7 %, 48.5 %	[42]
Choline chloride/Levulinic acid	Corncob	1:2	0,3 g sample, 6 g DES, 24 h, 90 ºC	43 %	[42]
Choline chloride/Glutaric acid	Corncob	1:1	0,3 g sample, 6 g DES, 24 h, 90 ºC	34.3 %	[42]
Choline chloride/Malic acid	Corncob	1:1	0,3 g sample, 6 g DES, 24 h, 90 ºC	22.4 %	[42]
Choline chloride/Lactic acid	Corn stover Switchgrass Miscanthus	1:2	2,5 g sample, 25 g DES, microwave (45 s, 800 W)	79.6 % 72.23 % 65.8%	[44]
Choline chloride/Urea	Rice straw	1:2	10 g sample, 200 g DES, magnetic stirrer (130 ºC, 4, 6, 8 h)	35.7 % 43.2 % 44.7 %	[49]
Choline chloride/Urea	Rice straw	1:2	10 g sample, 200 g DES, magnetic stirrer, (110 ºC, 4, 6, 8 h)	41.2 % 32.1 % 33.3 %	[49]
Choline chloride/Oxalic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	9.3 %	[50]
Choline chloride/ Chloropropionic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	13 %	[50]
Choline chloride/Lactic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	25.4 %	[50]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/ Ethyleneglycol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	28.7 %	[50]
Choline chloride/ 1,2-propanediol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	32.1 %	[50]
Choline chloride/ 1,3-propanediol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	34.2 %	[50]
Choline chloride/Glycolic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3 h	36.9 %	[50]
Choline chloride/Xylitol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	20.6 %	[50]
Choline chloride/Glycerol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 3	24.1 %	[50]
Choline chloride/ Ethyleneglycol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	26.2 %	[50]
Lactic acid/Xylitol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux,120 ºC, 6 h	27.9 %	[50]
Lactic acid/Urea	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux,120 ºC, 6 h	28.8 %	[50]
Lactic acid/Glycerol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux,120 ºC, 6	30.7 %	[50]
Choline chloride/ Guanidine.hydrochloric acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux,120 ºC, 6 h	36.6 %	[50]
Lactic acid/Ethyleneglycol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	41.4 %	[50]
Choline chloride/Formamide	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux,120 ºC, 6 h	45.8 %	[50]
Lactic acid/Formamide	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	46.4 %	[50]
Choline chloride/Urea	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	48.5 %	[50]
Lactic acid/ Guanidine.hydrochloric acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 120 ºC, 6 h	61 %	[50]
Choline chloride/ 1,2-propanediol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80ºC, 6 h	26.5 %	[50]
Choline chloride/ 1,3-propanediol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	29.2 %	[50]
Choline chloride/Glycolic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	33.2 %	[50]
Choline chloride/Oxalic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	36.8 %	[50]
Choline chloride/Malonic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	51.3 %	[50]
Choline chloride/Lactic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	51.4 %	[50]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/ Chloropropionic acid	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	52 %	[50]
Choline chloride/ Ethyleneglycol	Rice straw	1:1	0,3 g sample, 6 g DES, stirring and reflux, 80 ºC, 6 h	21.9 %	[50]
Lactic acid/Glucose/Water	Rice straw	5:1:3	5 g sample, 100 ml of microemulsions, 70 ºC, 12 h	54.3 ± 0.3 %	[52]
Lactic acid/Fructose/Water	Rice straw	5:1:3	5 g sample, 100 ml of microemulsions, 70 ºC, 12 h	46.5 ± 1.8 %	[52]
Choline chloride/Glycerol	Rice straw	1:3	5 g sample, 100 ml of microemulsions, 70 ºC, 12 h	24.3 ± 0.5 %	[52]
L-Proline/Glycerol	Rice straw	1:3	5 g sample, 100 ml of microemulsions, 70 ºC, 12 h	10,8 ± 0.6 %	[52]
Choline chloride/Oxalic acid DES/n-butanol	Rice straw Rice husk Wheat straw	2:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	49 % 48 % 49%	[53]
Choline chloride/Oxalic acid DES/n-butanol	Straw	2:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	49%	[53]
Choline chloride/Oxalic acid, DES/n-propanol	Straw	2:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	41 %	[53]
Choline chloride/Oxalic acid DES/n-butanol	Rice straw Rice husk Wheat straw	1:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	21.5 % 20 % 23 %	[53]
Choline chloride/Oxalic acid DES/n-butanol	Rice straw Rice husk Wheat straw	2:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	21 % 20 % 23 %	[53]
Choline chloride/Oxalic acid DES/n-butanol	Rice straw Rice husk Wheat straw	1:2	2,25 g sample, 15 ml DES, 1 h, 120 ºC	18.2 % 17 % 14 %	[53]
Choline chloride/Oxalic acid, DES/Ethyl acetate	Straw	2:1	2,25 g sample, 15 ml DES, 1 h, 120 ºC	15 %	[53]
Choline chloride/Oxalic acid DES/n-butanol	Rice straw Rice husk Wheat straw	2:1	2,25 g sample, 15 ml DES, 1 h, 50 ºC	11 % 9 % 12 %	[53]
Ethylene glycol/Citric acid	*Paddy* husks	1:1	biomass to DES ratio of 10 %, 16 h, 90 ºC,	47.10 %	[76]
Ethylene glycol/Citric acid	*Paddy* husks	1:2	biomass to DES ratio of 10 %, 16 h, 90 ºC,	52.35 %	[76]
Ethylene glycol/Citric acid	*Paddy* husks	2:1	biomass to DES ratio of 10 %,1 6 h, 90 ºC,	51.17 %	[76]
Ethylene glycol/Citric acid	*Paddy* husks	1:1	biomass to DES ratio of 10 %, 4 h, 120 ºC,	57.33 %	[76]
Choline chloride/Oxalic acid dihydrate	Wheat straw	1:1	2,5 g sample, 50 g DES, 24 h, 60 ºC	57.9 %	[16]
Choline chloride/Lactic acid	Wheat straw	1:10	2,5 g sample, 50 g DES, 24 h, 60 ºC	29.1 %	[16]
Choline chloride/Malic acid	Wheat straw	1:1	2,5 g sample, 50 g DES,24 h, 80 ºC	21.6 %	[16]
Choline chloride/Malonic acid	Wheat straw	1:1	2,5 g sample, 50 g DES,24 h, 60 ºC	3.8 %	[16]
Choline chloride/Malic acid	Wheat straw	1:2	2,5 g sample, 50 g DES, 24 h, 80 ºC	1.3 %	[16]
Choline chloride/Urea	Wheat straw	1:9	2,5 g sample, 50 g DES, 24 h, 60 ºC	14.6 %	[16]
Lactic acid/Alanine	Wheat straw	9:1	10 g sample, 200 g DES, 24 h, 60 ºC	23.7 %	[47]
Lactic acid/Betaine	Wheat straw	2:1	10 g sample, 200 g DES,24 h, 60 ºC	0 %	[47]
Choline chloride/Glycolic acid	Wheat straw	1:3	10 g sample, 200 g DES, 24 h, 60 ºC	16.6 %	[47]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Lactic acid/Glycine	Wheat straw	9:1	10 g sample, 200 g DES, 24 h, 60 ºC	0 %	[47]
Choline chloride/ Ethyleneglycol	Wheat straw	1:2	10 g sample, 200 g DES, 24 h, 60 ºC	0 %	[47]
Lactic acid/$[N(Me)_4]Cl$	Wheat straw	1:3	0,5 g sample, 10 g DES, 14 h, 60 ºC	25 %	[18]
Lactic acid/$[N(Me)_4]Cl$	Wheat straw	1:2	0,5 g sample, 10 g DES, 14 h, 60 ºC	19.2 %	[18]
Choline chloride/Oxalic acid	Wheat straw	1:1	0,5 g sample, 10 g DES, 14 h, 60 ºC	18.7 %	[18]
Choline chloride/Lactic acid	Wheat straw	1:9	0,5 g sample, 10 g DES, 14 h, 60 ºC	7.9 %	[18]
Choline chloride/Lactic acid	Wheat straw	1:2	0,5 g sample, 10 g DES, 14 h, 60 ºC	3.9 %	[18]
Choline chloride/Malic acid	Wheat straw	1:1	0,5 g sample, 10 g DES, 14 h, 85 ºC	2.9 %	[18]
Lactic acid/2-chloroethyl trimethyl-ammonium chloride	Wheat straw	1:2	0,5 g sample, 10 g DES,14 h, 60 ºC	15 %	[18]
Lactic acid/2-chloroethyl trimethyl-ammonium chloride	Wheat straw	1:5	0,5 g sample, 10 g DES, 14 h, 60 ºC	1.6 %	[18]
Lactic acid/Alanine	Wheat straw	9:1	10 g sample, 200 g DES, 24 h, 60 ºC	23.7 %	[31]
Lactic acid/Betaine	Wheat straw	2:1	10 g sample, 200 g DES, 24 h, 60 ºC	0 %	[31]
Choline chloride/Glycolic acid	Wheat straw	1:3	10 g sample, 200 g DES, 24 h, 60 ºC	16.6 %	[31]
Lactic acid/Glycine	Wheat straw	9:1	10 g sample, 200 g DES, 24 h, 60 ºC	0 %	[31]
Choline chloride/Ethylene glycol	Wheat straw	1:2	10 g sample, 200 g DES, 24 h, 60 ºC	0 %	[31]
Guanidine hydrochloride/ Propylene glycol/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	79.68 ± 0.14 %	[69]
Guanidine hydrochloride/ Ethylene glycol/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	82.07 ± 0.03 %	[69]
Guanidine hydrochloride/ Glycerin/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	9.06 ± 0.25 %	[69]
Choline chloride/Propylene glycol/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	64.35 ± 2.56 %	[69]
Choline chloride/Ethylene glycol/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	74.77 ± 0.89 %	[69]
Choline chloride/Glycerin/*p*-toluene sulfonic acid-10 %	Switchgrass	1:1,94:0,06	1,5 g sample, 13,5 g DES, 120 ºC, 6 min, 200 rpm	30.06 ± 1.45 %	[69]
Guanidine hydrochloride/ Ethylene glycol/*p*-toluene sulfonic acid-30 %	Switchgrass	1:1,94:0,06	10 g sample, 23,33 g DES, 120 ºC, 20 min, 200 rpm	76.07 ± 0.41 %	[69]
Choline chloride/Ethylene glycol/*p*-toluene sulfonic acid-30 %	Switchgrass	1:1,94:0,06	10 g sample, 23,33 g DES, 120 ºC, 20 min, 200 rpm	65.42 ± 1.35 %	[69]
Guanidine hydrochloride/ Ethylene glycol/*p*-toluene sulfonic acid-35 %	Switchgrass	1:1,94:0,06	10 g sample, 18,57 g DES, 120 ºC, 30 min, 200 rpm	65.39 ± 1.22 %	[69]
Choline chloride/Ethylene glycol/*p*-toluene sulfonic acid-35 %	Switchgrass	1:1,94:0,06	10 g sample, 18,57 g DES, 120 ºC, 30 min, 200 rpm	59.10 ± 2.62 %	[69]
Choline chloride/Formic acid	Herb residues (*Akebia)*	1:2	solid to liquid ratio of 1:10, 120 ºC, 8 h	40.7 %	[72]
Choline chloride/Acetic acid	Herb residues (*Akebia)*	1:6	solid to liquid ratio of 1:10, 100 ºC, 8 h	33.8 %	[72]
Choline chloride/Glycolic acid	Herb residues (*Akebia)*	1:4	solid to liquid ratio of 1:10, 120 ºC, 8 h	58.4 %	[72]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/Levulinic acid	Herb residues (*Akebia)*	1:4	solid to liquid ratio of 1:10, 120 ºC, 8 h	20.2 %	[72]
Choline chloride/Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 130 ºC, microwave (400 W)	16.52 ± 1.91 %	[56]
Guanidine hydrochloride/ Glycerol	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 130 ºC, microwave (400 W)	3.34 ± 0.32 %	[56]
Guanidine hydrochloride/ Urea	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 130 ºC, microwave (400 W)	8.80 ± 0.99 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 130 ºC, microwave (400 W)	32.07 ± 2.18 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 100 ºC, microwave e (400 W)	5.85 ± 0.56 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 110 ºC, microwave (400 W)	9.47 ± 0.11 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 120 ºC, microwave (400 W)	23.07 ± 0.18 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 30 min, 140 ºC, microwave (400 W)	34.58 ± 0.97 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 5 min, 130 ºC, microwave (400 W)	14.58 ± 1.01 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 10 min, 130 ºC, microwave (400 W)	24.19 ± 2.10 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 15 min, 130 ºC, microwave (400 W)	26.83 ± 1.00 %	[56]
Guanidine hydrochloride/ Lactic acid	Castor stalk	1:2	2 g sample, 40 g DES, 20 min, 130 ºC, microwave (400 W)	27.12 ± 0.75 %	[56]
0,0 % NaOH + pure DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 mL DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	18.05 ± 0.14 %	[58]
0,0 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	29.79 ± 1.28 %	[58]
0,1 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	31.01 ± 0.12 %	[58]
0,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	34.36 ± 0.23 %	[58]
1,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	39.06 ± 0.64 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz,	43.40 ±0.85 %	[58]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
			amplitude 70 %, 30 min)		
3,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	41.41 ± 0.69 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 50 %, 10 min)	31.51 ± 0.38 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 50 %, 20 min)	37.65 ± 0.04 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 50 %, 30 min)	37.48 ± 0.81 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 50 %, 40 min)	38.48 ± 0.16 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 50 %, 50 min)	35.28 ± 1.75 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h , ultrasound (20 kHz, amplitude 60 %, 10 min	35.28 ± 1.75 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 10 min)	38.35 ± 0.06 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 20 min)	40.35 ± 0.44 %	[58]
0,0 % NaOH + pure DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	17.05 ± 1.19 %	[58]
0,0 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	27.54 ± 1.66 %	[58]
0,1 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	27.95 ± 1.23 %	[58]
0,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	32.25 ± 0.34 %	[58]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
0,0 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	27.54 ± 1.66 %	[58]
1,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	37.49 ± 0.91 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	47.00 ± 0.16 %	[58]
3,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 30 min)	45.92 ± 2.48 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 40 min)	40.32 ± 0.76 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 60 %, 50 min)	34.96 ± 0.23 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 10 min)	34.06± 0.59 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 20 min)	38.74 ± 0.40 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 30 min)	43.40 ± 0.85 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound (20 kHz, amplitude 70 %, 40 min)	38.78 ± 2.23 %	[58]
2,5 % NaOH + aqueous DES Choline chloride/Urea	Oil palm frond	1:2	1 g sample, 10 ml DES, 120 ºC, 4 h, ultrasound: (20 kHz, amplitude 70 %, 50 min)	36.19 ± 0.10 %	[58]
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:20, 140 ºC, 120 min, ultrasound (solid/liquid ratio 1:10, 60 W, 80 ºC, 60 kHz, 60 min)	41.50 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:20, 140 ºC, 240 min, ultrasound (solid to liquid ratio 1:20, 60 W, 80 ºC, 20 kHz, 20 min)	19.89 %	[60]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:20, 140 ºC, 120 min, ultrasound (solid to liquid ratio 1:10, 300 W, 40 ºC, 20 kHz, 20 min)	34.55 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:20, 100 ºC, 120 min, ultrasound (solid to liquid ratio 1:20, 300 W, 40 ºC, 60 kHz, 60 min)	42.24 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:6	DES solid to liquid ratio 1:15, 120 ºC, 180 min, ultrasound (solid to liquid ratio 1:15, 180 W, 60 ºC, 40 kHz, 40 min)	25.50 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:15, 120 ºC, 180 min, ultrasound (solid to liquid ratio 1:15, 180 W, 60 ºC, 40 kHz, 40 min)	26.62 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:10, 100 ºC, 120 min, ultrasound (solid to liquid ratio 1:10, 60 W, 40 ºC, 20 kHz, 20 min)	37.22 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:10, 140 ºC, 240 min, ultrasound (solid to liquid ratio 1:20, 300 W, 40 ºC, 60 kHz, 20 min)	27.76 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:10, 100 ºC, 120 min, ultrasound (solid to liquid ratio 1:20, 60 W, 80 ºC, 60 kHz, 20 min)	26.03 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:20, 100 ºC, 240 min, ultrasound (solid to liquid ratio 1:10, 300 W, 80 ºC, 60 kHz, 20 min)	35.70 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:10, 140 ºC, 240 min, ultrasound (solid to liquid ratio 1:10, 60 W, 40 ºC, 60 kHz, 60 min)	22.92 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:10	DES solid to liquid ratio 1:20, 100 ºC, 240 min ultrasound (solid to liquid ratio 1:20, 60 W, 40 ºC, 20 kHz, 60 min)	38.21 %	[60]
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:10, 140 ºC, 120 min, ultrasound (solid to liquid ratio 1:20, 300 W, 80 ºC, 60 kHz, 60 min)	31.63 %	[60]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/Lactic acid	Watermelon rind	1:1	DES solid to liquid ratio 1:10, 100 ºC, 240 min, ultrasound (solid/liquid ratio 1:10, 300 W, 80 ºC, 20 kHz, 60 min)	34.55 %	[60]
Choline chloride/Glycerol	Oil palm trunk	1:2	0,5 g sample, 9,5 g DES, oil bath (100 ºC, 48 h)	48.35 %	[62]
Choline chloride/Ethylene glycol	Oil palm trunk	1:2	0,5 g sample, 9,5 g DES, oil bath (100 ºC, 48 h)	47.57 %	[62]
Ethylammonium chloride/Glycerol	Oil palm trunk	1:2	0,5 g sample, 9,5 g DES, oil bath (100 ºC, 48 h)	47.25 %	[62]
Ethylammonium chloride/Ethylene glycol	Oil palm trunk	1:2	0,5 g sample, 9,5 g DES, oil bath (100 ºC, 48 h)	35.64 %	[62]
Choline chloride/Urea	Oil palm trunk	1:2	0,5 g sample, 9,5 g DES, oil bath (100 ºC, 48 h)	43.38 %	[62]
Choline chloride/Lactic acid	Oil palm empty fruit bunch	1:5	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	88 %	[75]
Glucose/Lactic acid	Oil palm empty fruit bunch	1:5	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	55 %	[75]
Choline chloride/Glucose	Oil palm empty fruit bunch	1:1	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	22 %	[75]
Choline chloride/Glycerol	Oil palm empty fruit bunch	1:2	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	17 %	[75]
Choline chloride/Urea	Oil palm empty fruit bunch	1:2	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	34 %	[75]
Potassssium carbonate/Glycerol	Oil palm empty fruit bunch	1:6	0,45 g sample, 4,5 g DES, 120 ºC, 8 h	51 %	[75]
Choline chloride/Lactic acid	Peach endocarp	1:2	2 g sample, 18 g DES, 145 ± 2 ºC, 6 h	70.2 %	[70]
Choline chloride/Lactic acid	Walnut endocarp	1:2	2 g sample, 18 g DES, 145 ± 2 ºC, 6 h	64.3 %	[70]
Choline chloride/Lactic acid	Sugarcane bagasse	1:5	5 % sample loading 80 ±2 ºC, 12 h	50.6 ± 0.2 %	[71]
Choline chloride/Glycerol	Sugarcane bagasse	1:2	5 % sample loading 80 ±2 ºC, 12 h	21.4 ± 0.2 %	[71]
Choline chloride/Imidazol	Sugarcane bagasse	3:7	5 % sample loading 80 ±2 ºC, 12 h	29.9 ±0.2 %	[71]
Choline chloride/Lactic acid	Sugarcane bagasse	1:2	solid to liquid 1:10, 120 ºC, 3 h	78.35 ±1.01 %	[73]
Choline chloride/Lactic acid	Sugarcane bagasse	1:2	solid to liquid 1:10, 120 ºC, 3 h,ultrasound (28 kHz, 60 min, 600 W, 30ºC)	83.81 ± 2.04 %	[73]
Choline chloride/Lactic acid	Sugarcane bagasse	1:2	solid to liquid 1:10, 120 ºC, 3 h,ultrasound (40 kHz, 60 min, 600 W, 30ºC)	80.13 ± 0.93 %	[73]
Choline chloride/Lactic acid	Sugarcane bagasse	1:2	solid to liquid 1:10, 120 ºC, 3 h,ultrasound (68 kHz, 60 min, 600 W, 30ºC)	85.74 ±0.47 %	[73]
Choline chloride/Lactic acid	Sugarcane bagasse	1:2	solid to liquid 1:10, 120 ºC, 3 h ultrasound (68 kHz, 90 min, 600 W, 30ºC)	86.82 ±2.10 %	[73]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
Choline chloride/Glycerol/ $FeCl_3 \times 6H_2o$	Sugarcane bagasse	1:1:0.3	2 g sample, 20 g DES, 120 ºC, 3 h,ultrasound (room temperature, 100 % ethanol, 20+28+40 kHz, 240 W, 60 min)	86.39 %	[78]
Choline chloride/Oxalic acid dihydrate	Hardwood kraft pulp	1:1	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	38.7 %	[63]
Choline chloride/Malic acid	Hardwood kraft pulp	1:1	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	39.2 %	[63]
Choline chloride/Lactic acid	Hardwood kraft pulp	1:9	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	37.8 %	[63]
Alanine/Lactic acid	Hardwood kraft pulp	1:9	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	43.3 %	[63]
Choline chloride/Oxalic acid dihydrate	Hardwood kraft pulp	1:1	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	22.4 %	[63]
Choline chloride/Malic acid	Hardwood kraft pulp	1:1	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	14.0 %	[63]
Choline chloride/Lactic acid	Hardwood kraft pulp	1:9	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	17.5 %	[63]
Alanine/Lactic acid	Hardwood kraft pulp	1:9	50 g absolute dry weight sample, 115 ml water, 200 g DES, 60 ºC, 2 h	21.7 %	[63]
Betaine/Ethylene glycol/ Glycerol Betaine/Ethylene glycol/ Lactic acid Alanine/Lactic acid/Citric acid Choline chloride/Ethylene glycol/Lactic acid	Unbleached beech pulp	1:2:2 1:1:1 1:3:1 1:2:1	10 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 2 h	6.07 % 7.40 % 6.47 % 9.27 %	[64]
Betaine/Glycerol/Citric acid Proline/Lactic acid/Citric acid Proline/Glycerol/Citric acid Malic acid/Proline/Lactic acid Choline chloride/Urea/Lactic acid	Unbleached beech pulp	1:2:1 1:3:1 1:4:1 1:2:4 1:2:3	10 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 2 h	8.13 % 7.93 % 6.67 % 34.60 % 9.13 %	[64]
Malic acid/Alanine/Lactic acid Betaine/Propanediol/Lactic acid Betaine/Urea/Glycerol Choline chloride/ Acetamide/Lactic acid	Unbleached beech pulp	1:1:3 1:3:1 1:2:3 1:2:3	10 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 2 h	6.93 % 36.53 % 5.80 % 33.80 %	[64]
Malonic acid/Choline chloride/Propanediol Urea/Acetamide/Glycerol	Unbleached beech pulp	1:1:3 1:2:3	10 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 2 h	39.80 % 31.73 %	[64]
Choline chloride/Lactic acid	Kraft beech pulp	1:9	50 g absolute dry weight sample, 115 ml	37.8 % 14.4 %	[66]

Solvent	Sample	Molar ratio	Delignification conditions	Efficiency of delignification (%)	Ref.
	Oxygen delignified beech pulp Kraft beech pulp		water into DES (1:20), 60 ºC, 1 h	 17.5 %	
Choline chloride/Oxalic acid	Kraft beech pulp Oxygen delignified beech pulp Kraft beech pulp	1:1	50 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 1 h	38.7 % 0.8 % 22.4 %	[66]
Choline chloride/Malic acid	Kraft beech pulp Oxygen delignified beech pulp Kraft beech pulp	1:1	50 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 1 h	39.2 % 11.9 % 14.0 %	[66]
Alanine/Lactic acid	Kraft beech pulp Oxygen delignified beech pulp Kraft beech pulp	1:9	50 g absolute dry weight sample, 115 ml water into DES (1:20), 60 ºC, 1 h	43.3 % 11.9 % 21.7 %	[66]
Betaine/Ethylene glycol/ Glycerol Betaine/Ethylene glycol/Lactic acid Alanine/Lactic acid/Citric acid Choline chloride/ Ethylene glycol /Lactic acid Betaine/Glycerol/Citric acid	Unbleached beech pulp	1:2:2 1:1:1 1:3:1 1:2:1 1:2:1	10 g absolute dry weight sample, 33 g water, 200 g DES, 60 ºC, 2 h	9.35 % 14.75 % 12.95 % 15.47 % 12.59 %	[67]
Proline/Lactic acid/Citric acid Proline/Glycerol/Citric acid Malic acid/Proline/Lactic acid Choline chloride/Urea/Lactic acid Malic acid/Alanine/Lactic acid	Unbleached beech pulp	1:3:1 1:4:1 1:2:4 1:2:3 1:1:3	10 g absolute dry weight sample, 33 g water, 200 g DES, 60 ºC, 2 h	15.83 % 20.86 % 21.58 % 23.38 % 21.94 %	[67]
Betaine/Propanediol/Lactic acid Betaine/Urea/Glycerol Choline chloride/Acetamide/ Lactic acid Malonic acid/Choline chloride/1,3-Propanediol Urea/Acetamide/Glycerol	Unbleached beech pulp	1:3:1 1:2:3 1:2:3 1:1:3 1:2:3	10 g absolute dry weight sample, 33 g water, 200 g DES, 60 ºC, 2 h	23.02 % 21.22 % 26.62 % 28.06 % 1.44 %	[67]

3. Mechanism of DES Action on the Lignin Removal Process

Lignocellulosic biomass is one of the most renewable bioresources on the earth and is promising to replace fossil fuels to produce biofuels, chemicals, and biopower [79]. Biochemically, lignocellulosic biomass is composed of a mixture of cellulose, hemicellulose, and lignin, which are interconnected with each other for the formation of a typical complicated network through several chemical bonds. After cellulose, lignin is the second most abundant

biomaterial available on the earth, which is made up of repetitive units of phenyl polymers, namely, p-coumaryl, coniferyl, and sinapyl alcohols. Primarily, lignin supports plant biomass by forming a layer of different polymeric units of alcohol interlinked with each other through several chemical bonds, such as carbon-carbon and aryl ether linkages. The interconnection of lignin, and cellulose is mediated through the participation of covalent bonds with hemicelluloses [80]. Lignin is a renewable aromatic biopolymer and accounts for 10–35% of higher plants. It is usually composed of three units: p-hydroxyphenyl, guaiacyl, and syringyl unit. These units are linked by aryl-alkyl ether bonds (β-O-4, α-O-4, 4-O-5) and interunit carbon-carbon bonds (β-β, β-5, β-1, and 5–5) without any rule [80].

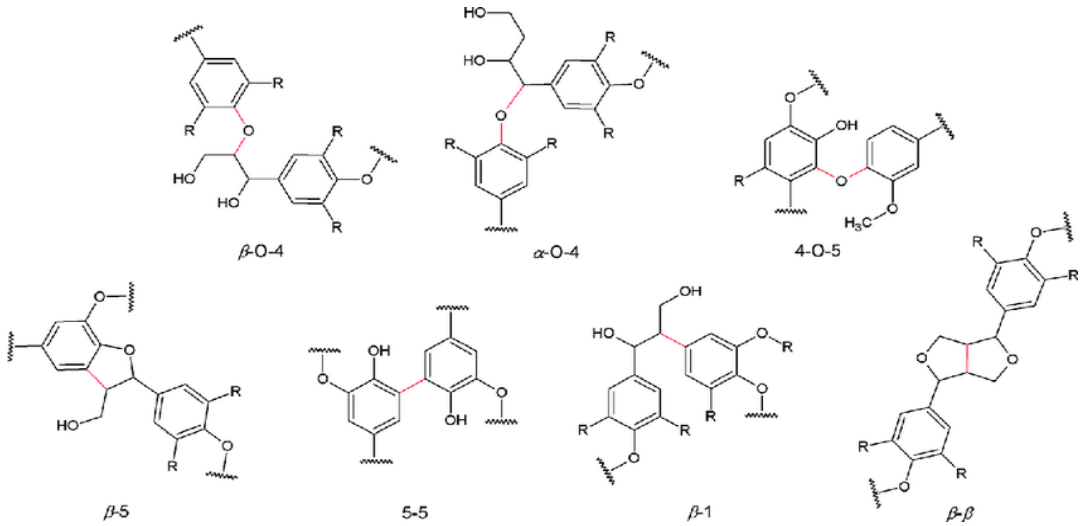

Figure 1. Characteristic bonds occur in the structure of lignin.

DES, a new generation of readily synthesized and low-cost green solvent, has been considered a promising solvent for lignocellulose pretreatment. In this study [79], alkaline choline chloride-based DESs, namely choline chloride/imidazole (3:7) and choline chloride/urea (1:2), were used to isolate lignin from *Populus deltoides.* The samples were treated under stirring at 115 °C and 150 °C for 15 h. The yield of lignin recovered from choline chloride/imidazole was higher than that of choline chloride/urea at 115 °C, suggesting that the stronger alkaline condition of DES contributed to improving the recovery of lignin. It indicated that alkaline choline chloride-based DES can extract lignin with high purity. A quantitative ^{31}P NMR method was employed to determine the types and amount of OH groups in DES-lignin. The aliphatic OH contents in DES-lignin were decreased, which may be ascribed to the dehydration reaction induced by β-O-4 ether breakage. In addition, the carboxyl content in choline chloride/urea (115 °C) was higher than that in choline chloride/imidazole (115 °C), revealing that a more drastic oxidation reaction occurred during chloride/urea DES treatment, which was consistent with FT-IR analysis. The chemical structure of lignin fractions from Populus was further investigated via 2D HSQC NMR. The results indicate that a demethylation reaction occurred during alkaline choline chloride-based DES pretreatment. It indicated that 72.2%–77.4% of β-O-4 linkage was preserved under a drastic condition during alkaline choline chloride-based DES pretreatment. Results indicated that guaiacyl units of lignin fractions were degraded more preferentially than syringyl units during pretreatment. The molecular weight was analyzed by GPC, and the results confirmed the depolymerization of lignin macromolecules during alkaline DES pretreatment.

In this context, a comprehensive study [81] revealing new insights on the mechanisms of β-O-4 ether bond cleavage mediated by acidic DES is herein provided. In this respect, the

cleavage of a model compound of lignin, *2-phenoxy-1-phenylethanol* (PPE), by three different DES, namely lactic acid/choline chloride (10:1), propionic acid/urea (2:1), and p-toluene sulphonic acid/choline chloride (1:1) was examined. The reactions were performed at 80 °C or 120 °C for 8 h. Propionic acid/urea (2:1) has been shown to dissolve lignin but is not able to fractionate β-O-4 ether bonds in PPE. On the other hand, lactic acid/choline chloride (10:1), allowed the cleavage of PPE, but esterification between PPE and lactic acid was found, as well as oligomerization of the acid dairy. Among the solvents examined, p-toluene sulfonic/choline chloride (1:1) showed the highest efficiency in the cleavage of PPE, although the high acidity of this system led to the condensation of the cleavage products over time. Although water reduces the efficacy of DES on the ether bond cleavage by diluting DES and decreasing its acidity, the extension of the reaction may be enough to achieve lignin extraction from biomass while simultaneously preventing undesired side reactions. Among several investigated DES with different molar ratios, they revealed propionic acid/urea (2:1) and p-toluenesulfonic acid/choline chloride (1:1) as the highest solubility values for lignin monomer compounds syringaldehyde and technical lignins (Kraft and Organosolv). This study determined a rough correlation between DES acidity and its ability to cleave the β-O-4 ether bond. The more acidic the hydrogen donor, the higher the cleavage of the PPE ether bond.

This work [23] carried out the use of DES for the selective fractionation of lignin from poplar. The temperatures were 100 °C, 110 °C, 120 °C, and 130 °C, and the times were 3 h and 6 h. The yields of cellulose after the DES (choline chloride) dissolving treatment decreased gradually with the increase of the temperature. Increasing temperature can maximize ionic characteristics and increase the molecular polarity of DES, causing the intramolecular network of hydrogen bonds to break and increasing the solubility of lignin and hemicellulose. The results show that DES treatment can destroy the double bond in the alpha lignin position and destroy the conjugated structure. Oxidation and alkaline products from poplar wood after nitrobenzene oxidation were vanillin, vanillic acid, syringaldehyde, syringic acid, 4-hydroxybenzaldehyde, and acid 4-hydroxybenzoic acid. The main bonds of poplar lignin are non-condensable bonds (α-O-4, β-O-4) and condensable connections (β-5, 5–5, β-1, 4-O-5). Yields of nitrobenzene oxidation products of isolated lignin have been significantly reduced, which is attributed to the cleavage of a large number of non-condensed lignin bonds, such as α-aryl, alkyl, and β-aryl ether bonds. Compared with MWL, the change of the DES-lignin signals in the aromatic region suggested that the side chains of lignin, especially the etherified structures, were damaged significantly after the DES treatment.

To explain the mechanisms of biomass fractionation (switchgrass) and lignin extraction by DES, lignin was prepared and characterized by efficient pretreatment of four DES. The β-0-4 interunit bond is dominant in the native lignin (aliphatic region), while β-5 and β-β linkages were minor. For guanidine hydrochloride/ethylene glycol/p-toluenesulfonic acid and guanidine hydrochloride/propylene glycol/p-toluenesulfonic acid lignins, no β-O-4, β-5, and β-β linkages were detected. When guanidine hydrochloride was replaced by choline chloride in the ternany DESs, the recovered lignin had partially preserved interunit linkages. Choline chloride/ethylene glycol/p-toluenesulfonic acid lignin showed 2.3% β-O-4 interunit linkage but no peaks for β-5 and β-β. In the aromatic regions for native lignin, the dominant peaks were assigned to syringyl unit, guaiacyl unit, p-coumarat, and ferulate. The lignin extracted by guanidine hydrochloride/ethylene glycol/p-toluenesulfonic acid and guanidine hydrochloride/propylene glycol/p-toluenesulfonic acid had increased syringyl/guaiacyl ratios (1.6 and 1.4, relative to 0.7 in native lignin), suggesting that guaiacyl unit is more prone to

degradation than syringyl unit. The difference in ferulate contents in the recovered lignin corroborated the degree of fractionation. All these results suggested that the ternary DESs fractionate switchgrass via cleaving the ether and ester bonds linked by ferulate, and the solubilized lignin experiences further depolymerization and repolymerization upon the cleavage of β-O-4 interunit linkages benzylic carbon cation. The carbon cation can directly react with the electron-rich aromatic ring (syringyl, guaiacyl units) on the 2-, 5-, -6 positions, or undergo the cleavage of ether bonds to form C3 ketone or C2 aldehyde via different routes. The formed C3 ketone and C2 aldehyde can also react with each other to produce more condensed lignin [69].

In this study [82] authors made a comparison of the delignification capacities of some chemicals (p-TsOH hydrotrope, ionic liquids, and DESs) under mild conditions (80 °C) to understand their behaviors of lignin dissolution. The obtained lignin samples were analyzed and characterized by FT-IR, TGA, ^{31}P NMR, and 2D HSQC NMR to evaluate their structural properties. At the initial stage of decomposition (≤ 200 °C), the weakest C–O bonds in β-O-4 linkages are cleaved. Subsequently, aryl ether bond linkages cleavage occurs when the temperature is up to 200-350 °C. Afterward, the increased decomposition rate is closely related to the lignin oxidation, such as chain dehydrogenation and the oxidation of the aliphatic hydroxyl group to carbonylation or carboxylation, within a temperature range of 350-400 °C. As the temperature rises to 400 °C above, the C–C bonds, mainly the 5-5 (biphenyl) linkages, and the aromatic rings are decomposed, releasing H_2O, CO_2, and CO. Compared with the β-O-4 linkages content of 91.68% in native lignin, both DES-lignin and p-TsOH lignin retained high ethyl ester bond contents of 83.75% and 78.51%, suggesting slight modifications of the extracted lignin. The fewer β-O-4 linkages in p-TsOH lignin supported the hypothesis about the cleavage of β-O-4 bonds during lignin extraction. To better understand the interactions between lignin and solvent molecules, a lignin model compound was employed for simulation calculations. The intramolecular H-bonds interactions were more prominent than the π-π stacking interactions. Both two noncovalent interactions simultaneously contributed to the poor solubility of lignin in most traditional organic solvents. Therefore, disrupting the two interactions may improve lignin solubility in solvents and further facilitate the lignin extraction from lignocellulosic biomass.

The present study [73] investigates the synergy part of DESs with ultrasound in the fractionation of sugarcane bagasse. To explore DES preprocessing conditions, sugarcane bagasse and DES (choline chloride/glycerol, choline chloride/lactic acid, choline chloride/oxalic acid, choline chloride/acetic acid, and choline chloride/glycerol were mixed (1:10) and incubated at 90–130 °C in an oil bath for 0.5–5 h. The ultrasound pretreated sugarcane bagasse and DES (1:10) were mixed and heated at 120 °C for 3 h. The ultrasonic action causes the liquid's tiny bubbles (cavitation nuclei) to vibrate, grow, and accumulate tremendous energy continuously. When the energy reaches a limit, the cavitation bubbles collapse sharply, releasing huge energy accompanied by micro-jet and accompanied by local high temperature and high pressure. Due to the strong effect of micro-jets, the cell wall of the biomass is broken, and the lignin matrix outside the cell wall begins to crack. The hydrogen and chemical bonds in the lignocellulose structure begin to be destroyed.

Most lignin and hemicellulose began to separate from cellulose. Cl^- forms hydrogen bonds with hydroxyl groups in lignin, thereby promoting the cleavage of ether or ester bonds between the polysaccharide and lignin. The stronger the hydrogen bond strength, the stronger the proton dissociation ability of DES; therefore, the stronger the lignin removal ability. Most

importantly, the hydrogen bond between Cl^- and the lignin aromatic ring can extract aromatic rings and dissolve lignin. The DES pretreatment based on choline chloride/lactic acid firstly cleaves the effective bonds between phenylpropane units and then selectively extracts the cleaved lignin. The existence of hydrogen bonds between DES and lignin is important for the smooth progress. In addition, the strong acid DES (choline chloride/oxalic acid has a good effect on the removal of xylan during the pretreatment process. In this study, the hydroxyl groups of lactic acid in choline chloride/lactic acid can increase the polarity of DES, coupled with the US effect, thereby promoting the interaction of hydrogen bonding with the biomass matrix, which ultimately led to a large lignin removal.

An acidic biomass-derived DES (choline chloride/oxalic acid) pretreatment was developed to deconstruct the structure of bamboo for enhanced lignin fractionation. In this work [83], bamboo *Dendrocalamus yunnanicus* was pretreated with choline chloride and oxalic acid at 80−120 °C for 4 h. After fractionation treatment, the lignin samples resulting from the DES solutions were regenerated and analyzed in detail with enzymatic mild acidolysis lignin as the control to illustrate the structural changes of lignins during the acidic DES delignification process. It can be seen that both lignin yield and delignification ratio increased with elevated pretreatment temperature. The enhanced yield of lignin obtained under harsher reaction conditions was due to the significant destruction of hydrogen bonds of the plant cell wall at higher temperatures, enabling the lignin macromolecules to be cleaved into small lignin fragments in the proposed DES system. After acidic DES pretreatment, the 2D HSQC NMR spectra of the regenerated DES lignin samples revealed significant degradation of the lignin side chain and the aromatic units with increasing pretreatment temperatures as compared to that of enzymatic mild acidolysis lignin. The contents of β-O-4 in enzymatic mild acidolysis lignin were 49.20%, while it drastically decreased to 12.2% in DES pretreatment (80 °C) and completely disappeared when the temperature reached 100 °C, suggesting the effective depolymerization reaction for the cleavage of β-aryl-ethers during the acidic DES pretreatment.

Additionally, it was found that the depolymerization rate of β-O-4 linked to syringyl units was faster than that of β-O-4 linked to guaiacyl units. Apart from the cleavage of β-O-4 linkages, other C-C linkages (such as β-5 and β-β) also occurred partial degradation compared with those of enzymatic mild acidolysis lignin. The elevated syringyl/guaiacyl ratio suggested that guaiacyl-type lignin units were preferentially degraded or removed in the current acidic DES system. The regenerated DES lignin samples showed decreased signal intensities of C-O aromatics and β-O-4 linkages compared to those of enzymatic mild acidolysis lignin. Those results support that the acidic DES system promoted bamboo delignification and degradation of lignin macromolecular through the C-O bond cleavage. The content of− OCH_3 slightly decreased in enzymatic mild acidolysis lignin, implying the demethoxylation reaction occurred during the acidic DES delignification process. After the acidic DES pretreatment, it was found that aliphatic -OH content reduced under severe pretreatment temperature and finally dramatically decreased. The decreased aliphatic -OH content is due to the dehydration reaction, while the increased phenolic -OH content is attributed to the cleavage of β-O-4 linkages. Typically, the degradation temperature of lignin can be divided into three stages. The first stage appeared at around 130 °C due to the evaporation of free water and bound water in the lignin samples. The second stage is in the range of 130 and 280 °C, which can be attributed to the decomposition of the low molecular weight lignin polymers and the release of CO, CO_2, and H_2O during the decomposition of the lignin macromolecule side chain. At the third stage of 280−600 °C, the mass loss of lignin accounts for 30-40% of the original weight, which is the

main weightlessness stage of lignin. The regenerated DES lignin samples in the present work are consistent with a proposed 3-stage behavior (lignin solubilization, lignin depolymerization, and lignin condensation).

In this work [29], three different DESs were used, and the effects of treatment time and temperature of the optimal DESs on the extraction of lignin from willow were investigated. To examine the activity of different DES and temperature on the extraction of willow lignin, three DES mixtures with the same mole ratio of choline chloride to three HBDs (molar ratio 1:2): glycerol, urea, and lactic acid (molar ratio 1:2, 1:4, 1:6, 1:8, 1:10, 1:12) were prepared and used. The treatment of willow by each DES was conducted at four different temperatures: 90 °C, 100 °C, 110 °C, and 120 °C over 6 h. Compared with the initial sample, the intensity of the bands at 1600 cm^{-1}, 1510 cm^{-1}, 1270 cm^{-1}, 1120 cm^{-1}, and 835 cm^{-1} in the solid residue was significantly reduced, which indicated that most of the lignin was removed from willow after choline chloride/lactic acid (1:10) treatment. The bands at 1600 cm^{-1} and 1510 cm^{-1} indicated that the benzene ring skeleton of lignin was left intact. The entity of the β-O-4 ether and β-β linkage was indicated (57-61 ppm, 52-54 ppm). Another striking observation was the high level of phenolic hydroxyl groups (171-174 ppm) in DES-Lignin. The DES-Lignin extracted from willow could be recognized as guaiacyl/p-hydroxyphenyl/syringyl lignin, and the guaiacyl/p-hydroxyphenyl/syringyl ratio was 2.59:1:4.73. The syringyl unit was dominant in DES-Lignin, which was consistent with the typical structure of hardwood lignin. Results showed that willow lignin extracted by choline chloride/lactic acid was mainly composed of syringyl and guaiacyl units.

The aim of this work [84] was to improve the enzymatic hydrolysis and extraction of lignin from wheat straw after pre-treatment with DES (triethylbenzyl ammonium chloride/lactic acid). The solid fraction was characterized by scanning electron microscopy (SEM). The surface of untreated wheat straw is smooth and without apparent damage. Wrinkles appeared after DES (triethylbenzyl ammonium chloride/lactic acid) treatment and holes in the surface of the pretreated wheat straw. This is due to the fact that DES removed lignin and hemicelluloses and exposed cellulose molecules. The major structures identified in regenerated lignin were resinol structures β-β, α-O-γ,and γ-O-α bonds, phenylcoumaran structures formed by β-5 and α-O-4 bonds, Hibbert ketone, β-coumaroylated substructures formed by Cα-Hα, guajacyl and syringyl unit, and (S'a S") oxidized syringyl units with a Cα ketone or a Cα carboxyl group.

The results of the works [24] and [85] show that after preliminary treatments of lignocellulosic materials using DES, most of the carbon-carbon bonds were retained, and these remained the main bonds in lignin samples, while the presence of ether bonds has decreased significantly, therefore ether bonds more susceptible to damage than carbon-carbon bonds. The action of DES induces the cleavage of β-O-4 bonds in lignin, thereby degrading the lignin macromolecule into smaller molecules, which facilitates the fractionation of lignocellulosic biomass. The typical response to cleavage of β-O-4 bonds in lignin is in which the formation of protonated intermediates.

In the present examination [86], the purity, morphology, and structural characteristics of DES-lignin samples (willow lignin) after DES treatment (choline chloride/lactic acid, 1:10) at 120 °C for varied times, were investigated. The purity of all lignin samples was >90%. The purity increased from 90.0% to 95.4% with the extension of treatment time. With extraction time, the content of oxygen in the separated DES-lignin samples gradually decreased from 35.87% (6 h) to 33.26% (24 h). The hydrogen content increased from 4.22% (6 h) to 6.90%

(24 h), which means such as the methoxy group and aryl ether bond in willow lignin, were eliminated during DES treatment. DES may provide a mild acid-base catalysis mechanism that would be favorable for cleavage of labile ether linkages and thus lead to the generation of a low molecular weight lignin fragment. This chemistry may affect the elemental composition of the isolated lignin. NMR spectra indicated lignin-linked functional groups were present and were not severely impaired during DES treatment. Correlations for syringyl β-aryl ether and guajacyl were missing β-aryl ether, indicating that β-aryl ether bonds in willow lignin were eliminated during DES treatment. The correlation for guajacyl disappeared in the DES lignin spectrum compared to the spectrum EMAL, indicating that some of the guajacyl in willow lignin was eliminated during DES treatment.

The hydrothermal-deep eutectic solvents pretreatment method was proposed to selectively degrade hemicellulose and lignin from moso bamboo, with the residue rich in cellulose. Subsequently, two typical DESs, choline chloride/lactic acid and betaine/ lactic acid, were employed to extract lignin in the following process stage. The lignin yields were increased when the temperature was raised from 100 °C to 140 °C. The results might be ascribed to the fact that higher temperatures caused more lignin decomposition. After choline chloride/lactic acid treatment at 140 °C, the yield of the lignin fraction reached 86.9%. All the lignin samples included small amounts of bound carbohydrates. The sugar content might result from destroying the chemical bonds between lignin carbohydrates complexes. The values of molecular weight of lignin samples were evaluated via GPC analysis. The results might be attributed to choline chloride/lactic acid treatment bringing about more serious cleavage of intermolecular linkages of lignin. For more insight into the structural information of the extracted lignin fractions, HSQC analysis technique was further conducted to examine the detailed chemical compositions. The results revealed that the β-O-4 linkage of lignin fractions was more impressionable to cleavage during the choline chloride/lactic acid treatment processing, achieving a high rate of delignification. The lignin product contained guaiacyl and syringyl lignin units and exhibited a representative structure of β-O-4 linkage. Moreover, almost all cellulose was retained with a purity as high as 92.7% [74].

Authors used enzymatic mild acidolysis lignin (EMAL), derived from the Eucalyptus tree (as dimeric and polymeric β-O-4 lignin models), to undergo the treatment of choline chloride/lactic acid DES.. 2D HSQC NMR spectra analysis indicated this EMAL featured abundant β-O-4 linkages (64%), as well as less β-β (3%) and β-5 (10%) substructures, being kin to native lignin in biomass. The detailed structural changes to the EMAL were then assessed by GC-MS, GPC, and NMR spectroscopy. The abundance of aliphatic OH tapered off with the increase in reaction temperature and time because the cleavage of β-O-4 linkages resulted in the loss of C_α-OH moiety. A decline of β-O-4 linkage (46%) was observed after DES treatment at 80 °C for 1 h, being lower than that from EMAL (64%). The lessening of β-O-4 linkage corresponded to the rise of phenolic hydroxyl groups. In the case of carbon-carbon linkages (β-β and β-5), partial degradation was detected by comparison with those from EMAL. The cleavage of β-O-4 linkage occurred preferentially in the DES treatment process. Cross signals for Hibbert's ketone were also detected in the regenerated lignin samples, consistent with the conclusion that the DES treatment process is acid-catalyzed. The increased syringyl/guaiacyl ratio values were detected after DES treatment by comparison with unreacted EMAL. The high ratios of syringyl/guaiacyl in regenerated lignin indicated that more guaiacyl subunits had been solubilized in fragmented lignin. Based on the results acquired from realistic lignin and model compounds, a plausible reaction pathway for the DES-treated lignin was proposed. β-O-4 units

in lignin should be efficiently cleaved through an acid-catalyzed process during DES. The reaction starts from a hydrogen ion attack on the α-hydroxyl group, which gives a carbocation species via the release of one molecular unit of H_2O. The elimination reaction between α positive charge and β-H results in an enol ether intermediate, together with regeneration of a hydrogen ion. Following hydrolysis leads to the cleavage of the C-O bond, thus affording Hibbert's ketone moiety. Allylic rearrangement forms isomeric enol ether and can also be generated from the rearrangement reaction under acidic conditions. The isomerization of intermediate gives probably via an enediol, and an equilibrium is proposed. An oxidoreduction of the mixture leads to the formation of monotone and diketone. Experiments have shown the rapid formation of oligomers (when DES is applied), which means that repolymerization occurs rather than depolymerization. [87].

4. Properties and characterization of isolated lignin by DES

In the work Yue *et al.* [91], lignin fractions were isolated from wheat straw using alkaline and acidic DESs. Alkaline DES (K_2CO_3/glycerol) was prepared by mixing potassium carbonate and glycerol at a molar ratio of 1:5, while acidic DES (lactic acid/choline chloride) was prepared by mixing lactic acid and choline chloride at a molar ratio of 2:1. The reaction was stopped with the addition of ethanol. The DES, which contained the dissolved lignin, was separated from the solid fraction by filtration, and deionized water was then added to the mixture to precipitate lignin at room temperature. The alkaline DES filtrate was acidified to pH 3 using HCl before adding deionized water. The precipitated lignin was centrifuged and washed twice with ethanol/water solution (1:10). The total lignin content and purity of lignin fraction (74.8%) from alkaline treatment was lower than that (83.5%) from acidic treatment in the used conditions. In addition, alkaline DES lignin contained more carbohydrates than acidic DES lignin, with the overall carbohydrate content being still relatively low (<3.5%) and is mainly derived from sugars associated with hemicelluloses (d-xylose, l-arabinose, and l-galactose). The polydispersity index of alkaline DES lignin (4.08) was higher than that of acidic DES lignin (3.09), indicating the molecular weight of alkaline DES lignin was more heterogeneous. Both the weight-average and number-average molecular weights of alkaline DES lignin were higher than that of acidic DES lignin, revealing more effective depolymerization and fragmentation of the macromolecular structure of lignin under acidic conditions. In addition, both alkaline and acidic DES lignins showed higher molecular weight dispersion (PDI).

In another work [25], a novel choline-based DES, namely, choline lactate/lactic acid, was synthesized by replacing the chloride anion in choline chloride/lactic acid. Both choline lactate/lactic acid and choline chloride/lactic acid were used to separate lignin from poplar selectively. The reaction was terminated by adding a large amount of ethanol. Deionized water was added to the filtrate to precipitate the extracted lignin by DES treatment (DES lignin). Lignin extracted by choline lactate/lactic acid and choline chloride/lactic acid treatments were of high purity (>85%), with only a trace of glucose and no detectable hemicellulose residues. Lignin extracted by choline chloride/lactic acid was of 88.82% purity, with only 0.35% of glucose, while lignin extracted by choline lactate/lactic acid presented a higher purity (91.17%) with only 0.21% of glucose detected. In comparison with the milled wood lignin, DES extraction significantly reduced the M_w and M_n value of lignin. M_w and M_n of choline chloride/lactic acid lignin decreased from 10.000 and 4166 to 4416 and 2349 g/mol. At the same time, M_w and M_n of the choline lactate/lactic acid lignin could further reduce to 1805 and

971 g/mol. This indicated that both DES treatments could make the cleavage of the lignin linkage facile.

Wang *et al.* [92] characterized the properties of lignin isolated from hybrid *Pennisetum* using the ternary mixtures composed of choline chloride/glycerol/lewis acid ($AlCl_3.6H_2O$, $CuCl_2$, $FeCl_3.6H_2O$; 62:124:1). After the reaction, the suspension was transferred to a 50% acetone/water mixture. Then, the suspension was filtrated with a 50% acetone/water mixture to form a cellulose-rich fraction and a DES-soluble fraction. Then, the acetone in the DES-soluble fraction was evaporated using a rotary evaporator at 60 °C, and the solution was vacuum-filtered to obtain the regenerated lignin. The $FeCl_3$-catalyzed DES pretreatment produced high-purity (49%) lignin. During this DES pretreatment, xylose and glucose were identified as the major sugar components of all of the regenerated lignins, while arabinose, glucose, galactose, and mannose were the minor sugar constituents. During this pretreatment, the content of the associated polysaccharides of the lignin was low and only reached 3.15%. Compared to double enzymatic mild lignin, the molecular weights of the regenerated lignins decreased significantly. Additionally, the polydispersity index of the regenerated lignins increased, indicating that this pretreatment can yield heterogeneous lignin. The resulting properties of isolated lignin were: purity of 49% (choline chloride/glycerol/$FeCl_3.6H_2O$) and less than 49% for other treatments, polydispersity index from 1.81 to 2.18.

In the work of Lyu *et al.* [86], purity, morphology, and structural characterization of synthesized DES lignins extracted from willow (*Salix matsudana* cv. Zhuliu) after treatment with a 1:10 molar ratio of choline chloride and the lactic acid at 120 °C for 6, 9 h were carried out. The DES soluble fractions and solid residues were separated by filtration. The deionized water and ethanol were added to the mixture to precipitate lignin. The purity of all lignin samples was >90%, and with an extension of treatment time, the purity increased from 90.02% to 92.37%. Based on lignin properties analyzes, it was found that 1.12% of glucose, 0.96% of xylose, 0.12% arabinose, and 0.05% mannose were present in the DES-lignin sample (6h, 120 °C) and 0,77% of glucose and 0,56% of xylose were present in DES-lignin sample (9h, 120 °C). The polydispersity value of DES-lignin samples decreased from 1.34 (6h, 120 °C) to 1.20 (9h, 120 °C), which indicated that the distribution of DES-lignin gradually concentrated with treatment time. The DES-lignin had low molecular weights and small particle sizes and was reduced with the extension of the extraction time. The lignin nanoparticles extracted from willow by DES treatment had smooth surfaces and diameters of 200 – 420 nm. The total phenolic hydroxyl content and total hydroxyl content reached their highest values (2.05 and 3.42 $mmol \cdot g^{-1}$ (6h, 120 °C).

This work [93] developed several representative green processes to extract the DESs isolated lignin from corn straw. Two DESs (choline chloride/lactic acid and betaine/lactic acid, molar ratio 1:2) were applied for isolating lignin. The solid residues were completely cleaned with deionized water and ethanol (9:1). All filtrates were combined and then added into deionized water to precipitate lignin. The precipitated lignin was collected by centrifuge and washed with a deionized water/ethanol mixture (9:1). The isolated lignin had a purity range from 88.19±2.53 to 89.15±2.12%. Furthermore, this lignin was characterized by the fact that the main composition percentages of DESs isolated lignin were 1.56 ± 0.17 of glucan and 0.30 ± 0.04 of xylan (choline chloride/lactic acid) and 6.40 ± 0.16 of glucan and 3.40 ± 0.09 of xylan (betaine/lactic acid), the polydispersity index was 2.02 (choline chloride/lactic acid) and 2.31 (betaine/lactic acid).

In various works, the authors characterized and analyzed the properties of the lignin fraction, which were isolated by DES from different types of biomass. Some works focus on determining the chemical composition and purity of lignin fractions after the application of DESs. The variation of weight average molecular weight (Mw), average molecular weight (Mn), and the polydispersity index (PDI) during DES treatment of lignin samples were measured using gel permeation chromatography. Table 2 summarizes the properties of lignins isolated from plant biomass using DES. Based on the results of the works [25,86,91-93], the purity of acquired lignins obtained after applying green solvents (DES, NADES, LTTMs) ranges approximately from 49-92.37 %, and the polydispersity index ranges from 1.20 to 4.08.

Table 2. Properties of isolated lignin by DES.

DES lignin samples	Lignin purity (%)	Glucose, Xylose,Arabinose, Galactose, Mannose (%)	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	Ref.
K_2CO_3/Glycerol	74,8	0,65 ± 0,01;1,14 ±0,02; 0,67±0,01;0,52±0,01;0,1	5696	1396	4,08	[91]
Lactic acid/ Choline chloride	83,5	0,77 ± 0,01; 1,02 ± 0,01; 0,75 ± 0,05; <0,10;<0,10	3215	1042	3,09	[91]
Choline chloride/ Lactic acid	88,82	0,35± 0,1 of glucose	4416	2349	1,88	[25]
Choline lactate/ Lactic acid	91,17	0, 21± 0,1 of glucose	1805	971	1,86	[25]
Choline chloride/ Glycerol/$FeCl_3.6H_2O$	49	3,15; 6,12; 0,21; 0,17; 0,19	1910	875	2,18	[92]
Choline chloride/ Glycerol/$CuCl_2$	<49	2,12; 3,91; - ; 0,09; 0,08	1900	1050	1,81	[92]
Choline chloride/ Glycerol/$AlCl_3.6H_2O$	<49	1,19; 3,81; - ; 0,03; 0,15	1440	760	1,89	[92]
Choline chloride/ Lactic acid	90,02	1,12; 0,96; 0,12; 0,05; -	1806,7	1348,1	1,34	[86]
Choline chloride/ Lactic acid	92,37	0,77; 0,56; - ; - ; -	1454,2	1213,3	1,20	[86]
Choline chloride/ Lactic acid	89,15 ± 2,12	1,56 ±0,17 of glucan and 0,30 ± 0,04 of xylan		979	2,02	[93]
Betaine/Lactic acid	88,19 ± 2,53	6,40 ±0,16 of glucan and 3,40 ± 0,09 of xylan	1985	858	2,31	[93]

5. Recycling of DES

The current research trends suggest that DESs could be utilized in eco-friendly and efficient catalysis and organic synthetic processes. The important features associated with the DES performance are convenient and selective extraction of products, pH tunability, dissolution of a wide range of materials such as organic, inorganic salts, transition metal complexes, and nanoparticles, and efficient recycling, which is the most promising benefit of DES systems [89]. Recyclability of a solvent is desirable to achieve an economically and environmentally sustainable material extraction or pretreatment process. This usually involves recovery or separation and, if necessary, purification of the solvent, followed by reusing or recycling it. It has been shown that the recycling of DES depends on the product's physicochemical, reactive properties conditions, and properties [89].

Many studies have looked into different recovery methods (anti-solvent addition, crystallization, solid-liquid extraction, liquid-liquid extraction, supercritical fluid extraction, separation due to density, and viscosity differences) for recycling DESs. Water, ethanol, and acetone are the most frequently tested anti-solvents. They could be used alone or sequentially to separate different portions of the dissolved biomass [90].

In this work [40], the authors took the first step in determining whether the concept of delignification based on DES has the potential to become industrially viable or not. Part of this work was to optimize the process for energy use. Energy consumption is a very important parameter not only from an environmental point of view but also for the operating costs of the process. The results showed that the heat intensity of the proposed DES process is 28% lower than the sulfate process. Washing with other solvents, such as ethanol instead of water, can further reduce the energy consumption of the process. DES delignification offers potential advantages over the current sulfate process in terms of the 12 principles of Green Chemistry. This process is less destructive for lignin, so obtaining lignin at a higher yield is possible. It seems that all operations are possible carried out using easily accessible technology, and no pressure equipment is required. That means that the process can have very low capital expenditures. In addition, there is energy consumption proposed process is very low, which is not only favorable for operating costs but also because the investment costs of chemical processes are usually dictated by energy losses, which is also favorable for the investment costs of the proposed process. The biggest opportunity for DES-based products is their valorization. In addition to the cellulose produced, they can produce lignins, and the process can be modified to produce valuable hemicelluloses products. The supported delignification process based on DES shows a large economic potential.

6. Conclusions

To achieve greater defensibility than conventional processes, the evolution of innovative technologies for efficient but ecological delignification of biomass is needed. In this context, the use of DES for the delignification process of plant biomass meets these requirements and is now a promising alternative. DES are green solvents that are rapidly evolving and are used as alternative solvent systems for processing lignocellulosic materials. Due to their properties, DES is used in biomass fractionation, and its effectiveness has been extensively studied in recent years. DESs have been reported for the delignification of various types of lignocellulose (softwoods, pulps, grasses, annual plants and herbs, and other lignocellulosic materials). DES has the ability to cleave ether bonds without affecting C-C bonds in lignin selectively. The main mechanism is the cleavage of ether bonds, which leads to the depolymerization of lignin, which facilitates lignin extraction from biomass. DES can provide a mild acid-base catalytic mechanism to initiate controlled cleavage labile ether linkages between phenylpropane units. The separation processes should be selected based on the characteristic of DES, the amount of DES that could be recovered, the nature of the process, the properties of the target compound/product, toxic substances usage, the amount of energy required, and the equipment cost.

Funding

This publication was supported by the Slovak Scientific Grant Agency contract VEGA 1/0403/19 (80%) and by the generous support under the Operational Program Integrated Infrastructure for the project: “Strategic research in the field of SMART monitoring, treatment and preventive protection against coronavirus (SARS-CoV-2),” Project no. 313011ASS8, co-financed by the European Regional Development Fund (20%).

Acknowledgments

The authors would like to acknowledge the financial support of the Slovak Scientific Grant Agency (80%) and the support for infrastructure equipment provided by the Operation Program Integrated Infrastructure (20%).

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Capello, C.; Fischer, U.; Hungerbühler, K. What is a green solvent? A comprehensive framework for the environmental assessment of solvents. *Green Chemistry* **2007**, *9*, 927-934, http://dx.doi.org/10.1039/b617536h.
2. Anastas, P.T.; Kirchhoff, M.M. Origins, current status, and future challenges of green chemistry. *Accounts of Chemical Research* **2002,** *35*, 686-694, http://dx.doi.org/10.1021/ar010065m.
3. Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R.L.; Duarte, A.R.C. Natural deep eutectic solvents - Solvents for the 21st century. *ACS Sustainable Chemistry and Engineering* **2014**, *2*, 1063-1071, http://dx.doi.org/10.1021/sc500096j.
4. Cravotto, G.; Vian, M.A.; Chemat, F. Green extraction of natural products:concept and principles. *International Journal of Molecular Sciences* **2012**, *13*, 8615-8627, https://doi.org/10.3390/ijms13078615.
5. Chemat, F.; Vian, M.A.; Fabiano-Tixier, A.S.; Nutrizio, M.; Jambrak, A.R.; Munekata, P.E.S.; Lorenzo, J.M.; Barba, F.J.; Binello, A.; Cravotto, G. A review of sustainable and intensified techniques for extraction of food and natural products. *Green Chemistry.* **2020,** *22*, 2325-2353, http://dx.doi.org/10.1039/C9GC03878G.
6. Bubalo, M.C.; Vidović, S.; Redovniković, I.R.; Jokić, S. Green solvents for green technologies. *Journal of Chemical Technology and Biotechnology* **2015**, *90*, 1631-1639, http://dx.doi.org/10.1002/jctb.4668.
7. Di Gioia, M.L.; Cassano, R.; Costanzo, P.; Cano, N.H.; Maiuolo, L.; Nardi, M.; Nicoletta, F.P.; Oliverio, M.; Procopio, A. Green synthesis of privileged benzimidazole scaffolds usinf active deep eutectic solvent. *Molecules* **2019**, *24*, 2885, https://doi.org/10.3390/molecules24162885.
8. Di Gioia, M.L.; Nardi, M.; Costanzo, P.; De Nino, A.; Maiuolo, L.; Oliverio, M.; Procopio, A. Biorenewable deep eutectic solvent for selective and scalable conversion of furfural into cyclopentenone derivatives. *Molecules* **2018**, *23*, 1891, https://doi.org/10.3390/molecules23081891.
9. Di Gioia, M.L.; Costanzo, P.; Maiuolo, L.; Nardi, M.; Olivito, F.; Procopio, A.; De Nino, A. Simple and efficient Fmoc removal in ionic liquid. *Royal Society of Chemistry* **2017**, *7*, 36482-36491, http://dx.doi.org/10.1039/C7RA04425A.
10. Perna, F.M.; Vitale, P.; Capriati, V. Deep eutectic solvents and their applications as green solvents. *Current Opinion in Green and Sustainable Chemistry* **2020**, *21*, 27-33, https://doi.org/10.1016/j.cogsc.2019.09.004.
11. Ruesgas-Ramón, M.; Figueroa-Espinoza, M.C.; Durand, E. Application od deep eutectic solvents (DES) for phenolic compounds extraction: overview, challenges,and opportunities. *Journal od Agricultural and Food Chemistry* **2017**, *65*, 3591-3601, http://dx.doi.org/10.1021/acs.jafc.7b01054.
12. Abranches, D.O.; Martins, M.A.R; Silvia, L.P.; Schaeffer, N.; Pinho, S.P.; Coutinho, J.A.P .Phenolic hydrogen bond donors in the formation of non-ionic deep eutectic solvents: the quest for type V DES. *Chemical Communications* **2019**, *55*, 10253-10256, http://dx.doi.org/10.1039/C9CC04846D.
13. Radošević, K.; Ćurko, N.; Srček, V.G.; Bubalo, M.C.; Redovniković, I.R.; Tomašević, M.; Ganić, K.K. Natural deep eutectic solvents as beneficial extractants for enhancement of plant extracts bioactivity. *LWT-Food Science and Technology* **2016**, *73*, 45-51, https://doi.org/10.1016/j.lwt.2016.05.037.
14. Kovács, A.; Cornet, I.; Wijnants, M.; Neyts, E.C.; Billen, P. Modeling of physicochemical properties of natural deep eutectic solvents - a review. *Chemistry Sustainability Energy Materials* **2020,** *13*, 3789-3804, https://doi.org/10.1002/cssc.202000286.
15. Humbird, D.; Davis, R.; Tao, L. *et al.* Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: Dilute-acid pretreatment and enyzmatic hydrolysis of corn stover. *National Renewable Energy Laboratory United States* **2011**, http://dx.doi.org/10.2172/1013269.
16. Jablonský, M.; Škulcová, A.B.; Kamenská, L.; Vrška, M.; Šima, J. Deep eutectic solvents:fractionation of wheat straw. *Bioresources* **2015**, *10*, 8039-8047, http://dx.doi.org/10.15376/biores.10.4.8039-8047.

17. Sosa, F.H.B.; Dias, R.M.; da Costa Lopes, A.M.; Coutinho, J.A.P.; da Costa, M.C. Fast and efficient method to evaluate the potential of eutectic solvents todissolve lignocellulosic components. *Sustainability* **2020**, *12*, 3358, https://doi.org/10.3390/su12083358.
18. Lago Garcia de Dios, S. Phase equilibria for extraction processes with designer solvents. *PhD. Dissertation, University of Santiago de Compostela* **2013**, Santiago, Spain, http://hdl.handle.net/10347/9570.
19. Muley, P.D.; Mobley, J.K.; Tong, X.; Novak, B.; Stevens, J.; Moldovan, D.; Shi, J.; Boldor, D. Rapid microwave-assisted biomass delignification and lignin depolymerization in deep eutectic solvents. *Energy Conversion and Management* **2019**, *196*, 1080-1088, https://doi.org/10.1016/j.enconman.2019.06.070.
20. Li, P.; Zhang, Q.; Zhang, X.; Zhang, X.; Pan, X.; Xu, F. Subcellular dissolution of xylan and lignin for enhancing enzymatic hydrolysis of microwave assisted deep eutectic solvent pretreated *Pinus bungeana* Zucc. *Bioresource Technology* **2019**, *288*, 121475, https://doi.org/10.1016/j.biortech.2019.121475.
21. Fernandes, C.; Melro, E.; Alves, L. *et al.* New deep eutectic solvent assisted extraction of highly pure lignin from maritime pine sawdust (*Pinus pinaster* Ait.). *International Journal of Biological Macromolecules* **2021**, 177, 294-305, https://doi.org/10.1016/j.ijbiomac.2021.02.088.
22. Li, L.; Yu, L.; Wu, Z.; Hu,Y. Delignification of poplar wood with lactic acid-based deep eutectic solvents. *Wood Research* **2019**, *64*, 499-514.
23. Chen, Y.; Zhang, L.; Yu, J.; Lu, Y.; Jiang, B.; Fan, Y.; Wang, Z. High-purity lignin isolated from poplar wood meal through dissolving treatment with deep eutectic solvents. *Royal society open science* **2019**, *6*, 181757, http://dx.doi.org/10.1098/rsos.181757.
24. Alvarez-Vasco, C.; Ma, R.; Quintero, M. *et al.* Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization. *Green Chemistry* **2016**, *18*, 5133-5141, http://dx.doi.org/10.1039/C6GC01007E.
25. Liu, J.; Qi, L.; Yang, G.; Xue, Y.; He, M.; Lucia, L.A.; Chen, J. Enhancement of Lignin Extraction of Poplar by Treatment of Deep Eutectic Solvent with Low Halogen Content. *Polymers* **2020**, *12*, 1599, https://doi.org/10.3390/polym12071599.
26. Tian, D.; Guo, Y.; Hu, J. *et al.* Acidic deep eutectic solvents pretreatment for selective lignocellulosic biomass fractionation with enhanced cellulose reactivity. *International Journal of Biological Macromolecules* **2020**, *142*, 288-297, https://doi.org/10.1016/j.ijbiomac.2019.09.100.
27. Xia, Q.; Liu, Y.; Meng, J.; Cheng, W.; Chen, W.; Liu, S.; Liu, Y.; Li, J.; Yu, H. Multiple hydrogen bond coordination in three-constituent deep eutectic solvents enhances lignin fractionation from biomass. *Green Chemistry* **2018**, *20*, 2711-2721, http://dx.doi.org/10.1039/C8GC00900G.
28. Liu, Y.; Chen, W.; Xia, Q. *et al.* Efficient cleavage of lignin-carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass using microwave-assisted deep eutectic solvent treatment. *Chemistry Sustainability Energy Materials* **2017**, *10*, 1692-1700, https://doi.org/10.1002/cssc.201601795.
29. Li, T.; Lyu, G.; Liu, Y.; Lou, R.; Lucia, L.A.; Yang, G.; Chen, J.; Saeed, H.A.M. Deep Eutectic Solvents (DESs) for the Isolation of Willow Lignin (*Salix matsudana cv. Zhuliu*). *International Journal of Molecular Sciences* **2017**, *18*, 2266, https://doi.org/10.3390/ijms18112266.
30. Song, Y.; Chandra, R.P.; Zhang , X.; Tan, T.; Saddler, J.N. Comparing a deep eutectic solvent (DES) to a hydrotrope for their ability to enhance the fractionation and enzymatic hydrolysis of willow and corn stover. *Sustainable Energy and Fuels* **2019**, *3*, 1329-1337, https://doi.org/10.1039/C8SE00617B.
31. Jablonský, M.; Ház, A.; Majová, V. Assessing the opportunities for applying deep eutectic solvents for fractionation of beech wood and wheat straw. *Cellulose* **2019**, *26*, 7675-7684, https://link.springer.com/article/10.1007/s10570-019-02629-0.
32. Mamilla, J.L.K.; Novak, U.; Grilc, M.; Likozar, B. Natural deep eutectic solvents (DES) for fractionation of waste lignocellulosic biomass and its cascade conversion to value-added bio-based chemicals. *Biomass and Bioenergy* **2019**, *120*, 417-425, https://doi.org/10.1016/j.biombioe.2018.12.002.
33. Kohli, K.; Katuwal, S.; Biswas, A.; Sharma, B.K. Effective delignification of lignocellulosic biomass by microwave assisted deep eutectic solvents. *Bioresource Technology* **2020**, *303*, 122897, https://doi.org/10.1016/j.biortech.2020.122897.
34. Wahlström, R.; Hitunen, J.; Sirkka, M.P.de S.N.; Vuoti, S.; Kruus, K. Comparison of three deep eutectic solvents and 1-ethyl-3-methylimidazolium acetate in the pretreatment of lignocellulose: effect on enzyme stability, lignocellulose digestibility and one-pot hydrolysis. *RSC Advances* **2016**, *6*, 68100-68110, http://dx.doi.org/10.1039/C6RA11719H.

35. Schäfer, T.; Eisenlauer, M.; Teipel, U. Extraction of Spruce Lignin with a Deep Eutectic Solvent in Dependence of the Particle Size. *Chemie Ingenieur Technik* **2018**, *90*, 507-512**,** http://dx.doi.org/10.1002/cite.201700104.
36. Yang, R.; Cao, Q.; Liang, Y. *et al.* High capacity oil absorbent wood prepared through eco-friendly deep eutectic solvent delignification. *Chemical Engineering Journal* **2020**, *401*, 126150**,** https://doi.org/10.1016/j.cej.2020.126150.
37. Li, W.X.; Xiao, W.Z.; Yang, Y.Q *et al.* Insights into bamboo delignification with acidic deep eutectic solvents pretreatment for enhanced lignin fractionation and valorization. *Industrial Crops and Products* **2021**, *170*, 113692, https://doi.org/10.1016/j.indcrop.2021.113692.
38. Liang, X.; Fu, Y.; Chang, J. Effective separation, recovery and recycling of deep eutectic solvent after biomass fractionation with membrane-based methodology. *Separation and Purification Technology* **2019**, *210*, 409-416, https://doi.org/10.1016/j.seppur.2018.08.021.
39. Shen, X.J.; Wen, J.L.; Mei, Q.Q.; Chen, Xu.; Sun, D.; Yuan, T.Q.; Sun, R.C. Facile fractionation of lignocelluloses by biomass-derived deep eutectic solvent (DES) pretreatment for cellulose enzymatic hydrolysis and lignin valorization. *Green Chemistry* **2019**, *21*, 275-283, http://dx.doi.org/10.1039/C8GC03064B.
40. Smink, D.; Kersten, S.R.A.; Schuur, B. Process development for biomass delignification using deep eutectic solvents. Conceptual design supported by experiments. *Chemical Engineering Research and Design* **2020**, *164*, 86-101, https://doi.org/10.1016/j.cherd.2020.09.018.
41. Procentese, A.; Johnson, E.; Orr, V. *et al.* Deep eutectic solvent pretreatment and subsequent saccharification of corncob. *Bioresource Technology* **2015**, *192*, 31-36, https://doi.org/10.1016/j.biortech.2015.05.053.
42. Zhang, C.W.; Xia, S.Q.; Ma, P.S. Facile pretreatment of lignocellulosic biomass using deep eutectic solvents. *Bioresource Technology* **2016**, *219*, 1-5, https://doi.org/10.1016/j.biortech.2016.07.026.
43. Xu, G.C.; Ding, J.C.; Han, R.Z.; Dong, J.J.; Ni, Y. Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation. *Bioresource Technology* **2016**, *203*, 364-369, https://doi.org/10.1016/j.biortech.2015.11.002.
44. Chen, Z.; Wan, C. Ultrafast fractionation of lignocellulosic biomass by microwave-assisted deep eutectic solvent pretreatment. *Bioresource Technology* **2018**, *250*, 5321-537, https://doi.org/10.1016/j.biortech.2017.11.066.
45. Suopajärvi, T.; Ricci, P.; Karvonen, V.; Ottolina, G.; Liimatainen, H. Acidic and alkaline deep eutectic solvents in delignification and nanofibrillation of corn stalk, wheat straw, and rapeseed stem residues. *Industrial Crops and Products* **2020**, *145*, 111956, https://doi.org/10.1016/j.indcrop.2019.111956.
46. Gunny, A.A.N.; Arbain, D.; Nashef, E.M.; Jamal, P. Applicability evaluation of Deep Eutectic Solvents–Cellulase system for lignocellulose hydrolysis. *Bioresource Technology* **2015**, *181*, 297-302, https://doi.org/10.1016/j.biortech.2015.01.057.
47. Kumar, A.K.; Parikh, B.S.; Shah, E.; Liu, L.Z.; Cotta, M.A. Cellulosic ethanol production from green solvent-pretreated rice straw. *Biocatalysis and Agricultural Biotechnology* **2016**, *7*, 14-23**,** https://doi.org/10.1016/j.bcab.2016.04.008.
48. Florindo, C.; Oliveira, M.M.; Branco, L.C.; Marrucho, I.M. Carbohydrates-based deep eutectic solvents: Thermophysical properties and rice straw dissolution. *Journal of Molecular Liquids* **2017**, *247*, 441-447, https://doi.org/10.1016/j.molliq.2017.09.026.
49. Pan, M.; Zhao, G.; Ding, C.; Wu, B.; Lian, Z.; Lian, H. Physicochemical transformation of rice straw after pretreatment with a deep eutectic solvent of choline chloride/urea. *Carbohydrate Polymers* **2017**, *176*, 307-314, https://doi.org/10.1016/j.carbpol.2017.08.088.
50. Hou, X.D.; Li, A.L.; Lin, K.P.; Wang, Y.Y.; Kuang, Z.Y.; Cao, S.L. Insight into the structure-function relationships of deep eutectic solvents during rice straw pretreatment. *Bioresource Technology* **2018**, *249*, 261-267, https://doi.org/10.1016/j.biortech.2017.10.019.
51. Kumar, A.K.; Sharma, S.; Shah, E.; Patel, A. Technical assessment of natural deep eutectic solvent (NADES) mediated biorefinery process: A case study. *Journal of Molecular Liquids* **2018**, *260*, 313-322**,** https://doi.org/10.1016/j.molliq.2018.03.107.
52. Gao, J.; Chen, C.; Lin, Y.; Zhang, L.; Ji, H.; Liu, S. Enhanced enzymatic hydrolysis of rice straw via pretreatment with deep eutectic solvents-based microemulsions. *Bioresource Technology Reports* **2020**, *10*, 100404, https://doi.org/10.1016/j.biteb.2020.100404.

53. Kandanelli**,** R.; Thulluri, C.; Mangala, R. *et al.* A novel ternary combination of deep eutectic solvent-alcohol (*DES-OL*) system for synergistic and efficient delignification of biomass. *Bioresource Technology* **2018**, *265*, 573-576, https://doi.org/10.1016/j.biortech.2018.06.002.
54. Lou, R.; Ma, R.; Lin, K.T.; Ahamed, A.; Zhang, X. Facile Extraction of Wheat Straw by Deep Eutectic Solvent (DES) to Produce Lignin Nanoparticles. *ACS Sustainable Chemistry and Engineering* **2019**, *7*, 10248-10256, https://doi.org/10.1021/acssuschemeng.8b05816.
55. Guo, Z.; Zhang, Q.; You, T. *et al.* Heteropoly acids enhanced neutral deep eutectic solvent pretreatment for enzymatic hydrolysis and ethanol fermentation of *Miscanthus x giganteus* under mild conditions. *Bioresource Technology* **2019**, *293*, 122036**,** https://doi.org/10.1016/j.biortech.2019.122036.
56. Zhong, L.; Wang, C.; Yang, G. *et al.* Rapid and efficient microwave-assisted guanidine hydrochloride deep eutectic solvent pretreatment for biological conversion of castor stalk. *Bioresource Technology* **2022**, *343*, 126022, https://doi.org/10.1016/j.biortech.2021.126022.
57. Nor, N.A.M.; Mustapha, W.A.W.; Hassan, O. Deep Eutectic Solvent (DES) as a Pretreatment for Oil Palm Empty Fruit Bunch (OPEFB) in Sugar Production. *Procedia Chemistry* **2016**, *18*, 147-154, http://dx.doi.org/10.1016/j.proche.2016.01.023.
58. Ong, V.Z.; Wu, T.Y.; Chu, K.K.L.; Sun, W.Y.; Shak, K.P.Y. A combined pretreatment with ultrasound-assisted alkaline solution and aqueous deep eutectic solvent for enhancing delignification and enzymatic hydrolysis from oil palm fronds. *Industrial Crops and Products* **2021**, *160*, 112974, https://doi.org/10.1016/j.indcrop.2020.112974.
59. Fang, C.; Thomsen, M.H.; Frankaer, C.G.; Brudecki, G.; Schmidt, J.E.; Alnashef, I. Reviving Pretreatment Effectiveness of Deep Eutectic Solvents (DESs) on Lignocellulosic Date Palm Residues by Prior Recalcitrance Reduction. *Industrial and Engineering Chemistry Research* **2017**, *56*, 3167-3174, https://doi.org/10.1021/acs.iecr.6b04733.
60. Fakayode, O.A.; Aboagarib, E.A.A.; Yan, D. *et al.* Novel two-pot approach ultrasonication and deep eutectic solvent pretreatments for watermelon rind delignification: Parametric screening and optimization via response surface methodology. *Energy* **2020**, *203*, 117872, https://doi.org/10.1016/j.energy.2020.117872.
61. Patil, S.S.; Pathak, A.; Rathod, V.K. Optimization and kinetic study of ultrasound assisted deep eutectic solvent based extraction: A greener route for extraction of curcuminoids from *Curcuma longa*. *Ultrasonics Sonochemistry* **2021**, *70*, 105267, https://doi.org/10.1016/j.ultsonch.2020.105267.
62. Zulkefli, S.; Abdulmalek, E.; Abdul Rahman, M.B. Pretreatment of oil palm trunk in deep eutectic solvent and optimization of enzymatic hydrolysis of pretreated oil palm trunk. *Renewable Energy* **2017**, *107*, 36-41, https://doi.org/10.1016/j.renene.2017.01.037.
63. Škulcová, A.B.; Majová, V.; Šima, J.; Jablonský, M. Mechanical Properties of Pulp Delignified by Deep Eutectic Solvents. *Bioresources* **2017**, *12*, 7479-7486.
64. Jablonský, M.; Majová, V.; Ondrigová, K.; Šima, J. Mechanical Preparation and characterization of physicochemical properties and application of novel ternary deep eutectic solvents. *Cellulose* **2019**, *26*, 3031-3045, https://link.springer.com/article/10.1007/s10570-019-02322-2.
65. Jablonský, M.; Majová, V.; Škulcová, A.B.; Ház, A. Delignification of pulp using deep eutectic solvents. *Journal of Hygienic Engineering and Design* **2018,** *22*, 76-81.
66. Majová, V.; Horanová, S.; Škulcová, A.B.; Šima, J.; Jablonský, M. Deep Eutectic Solvent Delignification: Impact of Initial Lignin. *Bioresources* **2017**, *12*, 7301-7310, http://dx.doi.org/10.15376/biores.12.4.7301-7310.
67. Majová,V.; Jablonský, M.; Lelovský, M. Delignification of unbleached pulp by ternary deep eutectic solvents. *Green Processing and Synthesis* **2021**, *10*, 666-676, https://doi.org/10.1515/gps-2021-0066.
68. Bonacci, S.; Di Gioia, M.L.; Costanzo, P.; Maiuolo, L.; Tallarico, S ; Nardi, M. Natural Deep Eutectic Solvent as Extraction Media for the Main Phenolic Compounds from Olive Oil Processing Wastes. *Antioxidants* **2020**, *9*, 513, https://doi.org/10.3390/antiox9060513.
69. Chen, Z.; Jacoby, W.; Wan, C. Ternary deep eutectic solvents for effective biomass deconstruction at high solids and low enzyme loadings. *Bioresource technology* **2019**, 279, 281-286, https://doi.org/10.1016/j.biortech.2019.01.126.
70. Li, W.; Amos, K.; Li, M.; Pu, Y.; Debolt, S.; Ragauskas, A.J.; Shi, J. Fractionation and characterization of lignin streams from unique high-lignin content endocarp feedstocks. *Biotechnology for Biofuels* **2018**, *11*, 304, https://doi.org/10.1186/s13068-018-1305-7.

71. Satlewal, A.; Agrawal, R.; Das, P. *et al.* Accesing the facile pretreatments of bagasse for efficient enzymatic conversion and their impacts on structrural and chemical properties. *ACS Sustainable Chemistry and Engineering* **2019**, *7*, 1095-1104, https://doi.org/10.1021/acssuschemeng.8b04773.
72. Yu, Q.; Zhang, A.; Wang, W. *et al.* Deep eutectic solvents from hemicellulose-derived acids for the cellulosic ethanol refining of Akebia´ herbal residues. *Bioresource Technology* **2018**, *247*, 705-710, https://doi.org/10.1016/j.biortech.2017.09.159.
73. Ji, Q.; Yu, X.; Yagoub, A.E.A. *et al.* Synergism of sweeping frequency ultrasound and deep eutectic solvents pretreatment for fractionation of sugarcane bagasse and enhancing enzymatic hydrolysis. *Ultrasonics Sonochemistry* **2021**, *73*, 105470, https://doi.org/10.1016/j.ultsonch.2021.105470.
74. Wang, R.; Wang, K.; Zhou, M.; Xu, J.; Jiang, J. Efficient fractionation of *moso* bamboo by synergistic hydrothermal-deep eutectic solvents pretreatment. *Bioresource Technology* **2021**, *328*, 124873, https://doi.org/10.1016/j.biortech.2021.124873.
75. Tan, Y.T.; Ngoh, G.C.; Chua, A.S.M. Evaluation of fractionation and delignification efficiencies of deep eutectic solvents on oil palm empty fruit bunch. *Industrial Crops and Products* **2018**, *123*, 271-277, http://doi.org/10.1016/j.indcrop.2018.06.091.
76. Okur, M.; Koyuncu, D.D.E. Investigation of pretreatment parameters in the delignification of paddy husks with deep eutectic solvents. *Biomass and Bioenergy* **2020**, *142*, 105811, https://doi.org/10.1016/j.biombioe.2020.105811.
77. Liu, Q.; Yuan, T.; Fu, Q.J.; Bai, Y.Y.; Peng, F.; Yao, C.L. Choline chloride-lactic acid deep eutectic solvent for delignification and nanocellulose production of moso bamboo. *Cellulose* **2019**, *26*, 9447-9462, https://link.springer.com/article/10.1007/s10570-019-02726-0.
78. Ji, Q.; Yu, X.; Yagoub, A.B.A.; Chen, L.; Mustapha, A.T.; Zhou, C. Enhancement of lignin removal and enzymolysis of sugarcane bagasse by ultrasound-assisted ethanol synergized deep eutectic solvent pretreatment. *Renewable Energy* **2021**, *172*, 304-316, https://doi.org/10.1016/j.renene.2021.03.050.
79. Li, H.; Li, X.; You, T.; Li, D.; Nawaz, H.; Zhang, X.; Xu, F. Insights into alkaline choline chloride-based deep eutectic solvents pretreatment for *Populus deltoides*: Lignin structural features and modification mechanism. *International Journal of Biological Macromolecules.* **2021**, 193, 319-327, https://doi.org/10.1016/j.ijbiomac.2021.10.134.
80. Haldar, D.; Purkait, M.K. A review on the environment-friendly emerging techniques for pretreatment of lignocellulosic biomass: Mechanistic insight and advancements. *Chemosphere* **2021**, *264*, 128523, https://doi.org/10.1016/j.chemosphere.2020.128523.
81. Da Costa Lopes, A.M.; Gomes, J.R.B.; Coutinho, J.A.P.; Silvestre, A.J.D. Novel insights into biomass delignification with acidic deep eutectic solvents: a mechanistic study of β-O-4 ether bond cleavage and the role of the halide counterion in the catalytic performance. *Green Chemistry* **2020**, *22*, 2474-2487, http://dx.doi.org/10.1039/C9GC02569C.
82. Ji, H.; Lv, P. Mechanistic insights into the lignin dissolution behaviors of a recyclable acid hydrotrope, deep eutectic solvent (DES), and ionic liquid (IL). *Green Chemistry* **2020,** *22*, 1378-1387, https://doi.org/10.1039/C9GC02760B.
83. Li, W.X.; Xiao, W.Z.; Yang, Y.Q.; Wang, Q.; Chen, X.; Xiao, L.P.; Sun, R.C. Insights into bamboo delignification with acidic deep eutectic solvents pretreatment for enhanced lignin fractionation and valorization. *Industrial Crops and Products* **2021**, *170*, 113692, https://doi.org/10.1016/j.indcrop.2021.113692.
84. Liu, Y.; Zheng, J.; Xiao, J. *et al.* Enhanced Enzymatic Hydrolysis and Lignin Extraction of Wheat Straw by Triethylbenzyl Ammonium Chloride/Lactic Acid-Based Deep Eutectic Solvent Pretreatment. *ACS Omega* **2019**, *4*, 19829-19839, https://doi.org/10.1021/acsomega.9b02709.
85. De Gregorio, G.F.; Weber, C.C.; Gräsvik, J.; Welton, T.; Brandt, A.; Hallett, J.P. Mechanistic insights into lignin depolymerisation in acidic ionic liquids. *Green Chemistry* **2016**, *18*, 5456-5465, https://doi.org/10.1039/C6GC01295G.
86. Lyu, G.; Li, T.; Ji, X.; Yang, G.; Liu, Y.; Lucia, L.A.; Chen, J. Characterization of Lignin Extracted from Willow by Deep Eutectic Solvent Treatments. *Polymers* **2018**, *10*, 869, https://doi.org/10.3390/polym10080869.
87. Wang, S.; Li, H.; Xiao, L.P.; Song, G. Unraveling the Structural Transformation of Wood Lignin During Deep Eutectic Solvent Treatment. *Frontiers in Energy Research* **2020**, *8*, 48, http://dx.doi.org/10.3389/fenrg.2020.00048.

88. Elgharbawy, A.A.M.; Hayyan, M.; Hayyan, A.; Basirun,W.J.; Salleh, H.M.; Mirghani, M.E.S. A grand avenue to integrate deep eutectic solvents into biomass processing. *Biomass and Bioenergy* **2020**, *137*, 105550, https://doi.org/10.1016/j.biombioe.2020.105550.
89. Kalhor, P.; Ghandi, K. Deep Eutectic Solvents for Pretreatment, Extraction, and Catalysis of Biomass and Food Waste. *Molecules* **2019**, *24*, 4012, https://doi.org/10.3390/molecules24224012.
90. Isci, A.; Kaltschmitt, M. Recovery and recycling of deep eutectic solvents in biomass conversions: a review. *Biomass Conversion and Biorefinery* **2021**, https://link.springer.com/article/10.1007%2Fs13399-021-01860-9.
91. Yue, X.; Suopajärvi, T.; Mankinen, O. *et al.* Comparison of Lignin Fractions Isolated from Wheat Straw Using Alkaline and Acidic Deep Eutectic Solvents. *Journal of agricultural and Food Chemistry* **2020**, *68*, 15074-15084, https://doi.org/10.1021/acs.jafc.0c04981.
92. Wang, Z.K.; Wen, J.L.; Hong, S. *et al.* Lewis Acid-Facilitated Deep Eutectic Solvent (DES) Pretreatment for Producing High-Purity and Antioxidative Lignin. *ACS Sustainable Chemistry and Engineering* **2020**, *8*, 1050-1057, https://doi.org/10.1021/acssuschemeng.9b05846.
93. Liu, X.; Li, T.; Wu,S.; Ma, H.; Yin, Y. Structural characterization and comparison of enzymatic and deep eutectic solvents isolated lignin from various green processes: Toward lignin valorization. *Bioresource Technology* **2020**, *310*, 123460, https://doi.org/10.1016/j.biortech.2020.123460.