

Efficient Extraction and Structural Characterization of *Eucalyptus* Lignin with Deep Eutectic Solvents

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Effects of deep eutectic solvents (DES) type and pretreatment time were evaluated relative to lignin extraction efficiency. Three major indicators, including lignin yield, solid residue proportion, and lignin purity, were investigated in detail at fixed molar ratios (1:8 and 1:8:1) and temperature (120 °C). The lignin yield gradually increased over 2 to 10 h, reaching 78.9% at 6 h in the choline chloride (ChCl)-formic acid (Fa)-oxalic acid (OA) system. The solid residue proportion continuously decreased to 36.4%, while maintaining lignin purity above 90% without significant variation. According to the lignin structure analysis, the basic aromatic structure of lignin, comprising syringyl (S) and guaiacyl (G) units, remained unchanged after treatment with the ternary DES system. The C/O ratio of carbon-rich macromolecular structures gradually increased with reaction time, and the carbon content of the samples exceeded 60%. This study provides a new approach to optimizing lignin extraction.

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Keywords: Deep eutectic Solvents; Lignin; Structure analysis; Carbon-rich

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INTRODUCTION

Lignocellulose constitutes the predominant component of biomass and a significant renewable resource on Earth. Lignin is the only renewable naturally occurring aromatic biomass component, and it comprises 15 to 30% of the mass fraction of lignocellulose (Wang *et al.* 2021). It is composed of phenol structural units, syringyl structures (s), guaiacyl structures (g), and p-hydroxyphenyl (H) units (Zou *et al.* 2024). As a natural aromatic polymer, lignin's complex and rich unsaturated groups have drawn a lot of interest. Its high carbon content and abundance of active functional groups have made it a critical raw material for producing high-performance carbon fiber, bio oil, vanillin, phenolic resin, and other high-value-added products (Lobato-Peralta *et al.* 2021). Compared to carbohydrates, it has been demonstrated to have a more intricate structure and bonding. The structural complexity and diversity of lignin can be determined by the abundance of benzene rings and unsaturated groups. The basic structural units of plant lignin are comprised of the following bonds: β -O-4, α -O-4, α -O- γ , 4-O-5, β - β , and 5-5 (Lobato-Peralta *et al.* 2021).

Recently, the exploration of the biorefinery process has primarily focused on the transformation of cellulose components, whereas lignin is regarded as waste/by-product, resulting in some resource waste (Zhang and Naebe 2021). The high-value utilization of lignin, as an important part of lignocellulosic biomass, can achieve the complete usage of

lignocellulosic biomass and implement the development concept of energy conservation and emission reduction (Yao *et al.* 2022). Structural variations and differences were observed in lignin extracted using physical and chemical methods across all separation and extraction processes. The effective separation and extraction of lignin is fundamental for the utilization of lignin-based chemicals and materials with high added value.

It is important to investigate pretreatment methods that lead to good chemical reaction activity, high purity, and low molecular weight. Native lignin generally retains intact molecular structures and has a strong potential for additional high-value conversion due to its comparatively high chemical reactivity (Wang and Deuss 2023). Moreover, the inherent structure and chemical reactivity of lignin further affect the development of lignin byproducts. It is essential to lower condensation and degradation of lignin in a traditional biorefinery to achieve optimal carbohydrate retention and to obtain lignin in high yield and purity. The extraction process relies on the treatment's final objective, the type and quantity of biomass. Deep eutectic solvent (DES), a low-melting-point mixed liquid medium, is made by melting at least one hydrogen bond donor and at least one receptor under mild conditions. It has the basic characteristics of good solubility and high stability of ionic liquids (Li *et al.* 2021). This approach has attracted significant attention due to its cost-effectiveness, simple operation, non-toxicity, and recyclability (Wang *et al.* 2023).

Lignin isolation is commonly performed using binary DES systems composed of choline chloride and a single hydrogen-bond donor, such as an organic acid. Although binary DES systems have been widely applied for lignocellulosic biomass fractionation, their performance can be limited by insufficient tunability of solvent properties, including acidity, viscosity, hydrogen-bonding capacity, and lignin dissolution ability. The central hypothesis of this study is that introducing a second organic acid into a binary ChCl–organic acid DES can provide a more flexible hydrogen-bonding network and adjustable acid-catalytic environment, thereby enhancing lignin solubilization and biomass delignification. In this ternary system, formic acid may contribute to biomass penetration and lignin dissolution, while oxalic acid or p-toluenesulfonic acid may strengthen acidity and promote cleavage of lignin–carbohydrate linkages and ether bonds. Therefore, the ternary DES system was designed to improve lignin extraction efficiency while maintaining high lignin purity and structural integrity.

This study used a ternary DES system to isolate lignin from biomass and explore the effects of different DES types on lignin yield, thereby revealing the mechanism underlying the enhancement of lignin removal ability by this system and its impact on lignin structure. The isolated lignin was comprehensively analyzed using a series of analytical instruments, including Fourier infrared spectroscopy (FTIR), gel permeation chromatography (GPC), 2D nuclear magnetic resonance (2D-NMR), thermogravimetric analysis (TGA), and elemental analysis (EA), to provide a deeper understanding of the pretreatment process in DES.

EXPERIMENTAL

Materials

The eucalyptus wood was obtained from a local factory in Weifang City, Shandong Province. The raw material was thoroughly washed to remove surface impurities and subsequently cooled naturally before pretreatment (Bai *et al.* 2020; Hong *et al.* 2022). The wood chips were cut into small pieces, ground into a 40 to 60 mesh powder, then extracted

with absolute ethanol at 100 °C for 12 h to remove the interference of lipid in raw materials. The mixed solvent was removed by filtration, through filtration, followed by vacuum drying of the filter cake at 80 °C for 12 h until a constant weight was achieved. Formic acid was acquired from Shanghai Hushi Reagent Co., Ltd., and all other chemical reagents were obtained from Shanghai McLean Biochemical Co., Ltd. Based on dry weight, the chemical composition of eucalyptus wood comprised 45.3% cellulose, 25.6% hemicellulose, 24.7% acid-soluble lignin, 2.6% acid-insoluble lignin, 1.1% extractives, and 0.5% ash.

Synthesis of DES

Choline chloride (ChCL)/formic acid (Fa), choline chloride (ChCL)/formic acid/oxalic acid (OA), and choline chloride/formic acid/p-toluenesulfonic acid (Ta) type eutectic solvents were prepared using the heating and stirring procedure (Gómez-Cruz *et al.* 2024). The hydrogen-bond acceptor and donor were accurately weighed according to the molar ratios (1:8, 1:8:1, and 1:8:1) (Liang *et al.* 2023), and then added to a round-bottom flask equipped with a stopper. The mixture was placed on a constant-temperature magnetic stirrer and stirred at 500 rpm in an oil bath at 80 °C until a uniform, transparent, stable, and colorless liquid was obtained (Lynam *et al.* 2017), indicating successful synthesis of the solvent. No water was intentionally introduced during DES preparation. After cooling to room temperature, the synthesized DES was sealed and stored as an anhydrous system until use.

DES Treatment

Prior to DES treatment, the eucalyptus wood powder was dried to constant weight and was therefore regarded as oven-dried biomass with negligible moisture content. The dried wood powder (2.0 g) and pre-prepared DES (40 g) were added to the flask, heated in an oil bath at 120 °C (Hong *et al.* 2022), and magnetically stirred at 300 rpm for a specific time. Upon completion, the flask was placed in an ice-water bath to terminate the reaction. Afterwards, an ethanol-water mixture (1:9, v/v, 50 mL) was added to decrease the viscosity of the system, followed by stirring to provide uniform dispersion of the dissolved substances. After dilution with the ethanol–water mixture and stirring, no visible sediment or large suspended particles were observed, indicating that the lignin-containing fraction was uniformly dispersed in the liquid phase. However, this observation does not necessarily indicate complete molecular dissolution of lignin; therefore, the lignin-containing liquid phase was regarded as a mixed system containing dissolved lignin molecules and possibly colloidal lignin particles. The mixture was then centrifuged at 8000 rpm for 10 min to separate the residue from the black liquor, after which the residue was washed thrice with an ethanol-water mixture (1:9, v/v) and centrifuged to collect supernatant. To recover the dissolved lignin in the supernatant, deionized water (800 mL) was added as the antisolvent to precipitate lignin, and the resulting sediment was collected by centrifugation for 10 min at 8000 rpm (He *et al.* 2024). Finally, the washed lignin was placed in a Petri dish and dried at 50 °C for 24 h until a constant weight was achieved, yielding a dark brown powdered lignin sample.

Based on the hydrogen-bond donor used, the lignin samples were categorized and designated after extraction with choline chloride/formic acid (Fa) (1:8), choline chloride/Fa/oxalic acid (OA) (1:8:1, 6 h), and choline chloride/Fa/p-toluenesulfonic acid (Ta) (1:8:1, 6 h) as DES-F, DES-F-O, and DES-F-T, respectively.

The DES lignin yield and solid residue yield were calculated using different reference bases. The DES lignin yield was defined as the mass of recovered DES lignin

relative to the lignin mass originally present in the raw woody biomass, whereas the solid residue yield was defined as the mass of the remaining solid residue relative to the initial dry woody biomass mass. Therefore, these two values should not be directly summed as a mass balance of the pretreatment process. To measure the lignin content present in Elm, both acid-soluble lignin (ASL) and acid-insoluble lignin (AIL) were determined according to the NREL standard procedure. (Liu *et al.* 2023).

The calculation formulas are shown as follows:

$$\text{DES lignin yield (\%)} = \frac{\text{recovered DES lignin mass}}{\text{lignin mass in raw woody biomass}} \times 100 \quad (2-1)$$

$$\text{Solid residue yield (\%)} = \frac{\text{solid residue mass}}{\text{initial dry woody biomass mass}} \times 100 \quad (2-2)$$

$$\text{Lignin purity (\%)} = \frac{\text{AILweight} + \text{ASLweight}}{\text{Ligninweight}} \times 100 \quad (2-3)$$

Characterization of Lignin

In this study, the term “lignin solution” refers to the lignin-containing liquid phase obtained after DES treatment and ethanol–water dilution, rather than a confirmed true molecular solution. The apparent homogeneity of this phase was evaluated visually based on the absence of visible sediment or large suspended particles after stirring. Because lignin can exist as colloidal particles in aqueous or ethanol–water media, the liquid phase was considered to potentially contain both dissolved lignin molecules and colloidal lignin particles.

A Fourier transform infrared spectrometer (Thermo Fisher, Waltham, Massachusetts, USA) was used to analyze the functional groups in lignin samples within a spectral wavelength between 400 and 4000 cm^{-1} . Each component was made by pressing tablets of potassium bromide (mass ratio 1:100). The molecular weight distribution of lignin components was investigated using GPC (Agilent, Santa Clara, CA, USA). Acetylated lignin (50 mg) was prepared following a lignin acetylation reaction in a 1:1 v/v ratio of acetic anhydride and pyridine solution for 24 h at room temperature. After complete dissolution in tetrahydrofuran, the acetylated lignin (2 mg) was filtered via a 0.22 μm filter. The aromatic group and side chain properties of lignin were examined by 2D-NMR. The lignin component (80 mg) was completely dissolved in deuterated dimethyl sulfoxide (d_6 -DMSO, 0.5 mL) and syringe-transferred to the NMR tube to record the NMR spectra on a 400 MHz spectrometer at 25 $^{\circ}\text{C}$ (AVIII400, Bruker, Germany), and scanned for 12 h. A synchronous thermal analyzer (DTG-60, Shimadzu, Japan) was used to analyze the thermal stability of lignin in an alumina crucible from ambient temperature to 800 $^{\circ}\text{C}$ under a nitrogen environment at the rate of 10 $^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The effects of DES type and pretreatment time on lignin extraction were thoroughly investigated at constant molar ratios and temperature, namely 1:8 for ChCl-Fa , 1:8:1 for the ternary DES systems, and 120 $^{\circ}\text{C}$. Figure 1 shows the lignin yield, solid residue yield, and lignin purity. As shown in Fig. 1a, the lignin yield increased gradually with increasing pretreatment time in the ChCl-Fa system, while the solid residue yield decreased and lignin

purity remained high throughout the treatment period. In Fig. 1b, the ChCl-Fa-Ta system exhibited a more pronounced delignification effect, with lignin yield increasing from the early to later stages and solid residue decreasing correspondingly. In Fig. 1c, the ChCl-Fa-OA system showed the highest lignin yield and the lowest solid residue among the three systems at comparable reaction times, indicating a slightly better fractionation performance than ChCl-Fa-Ta.

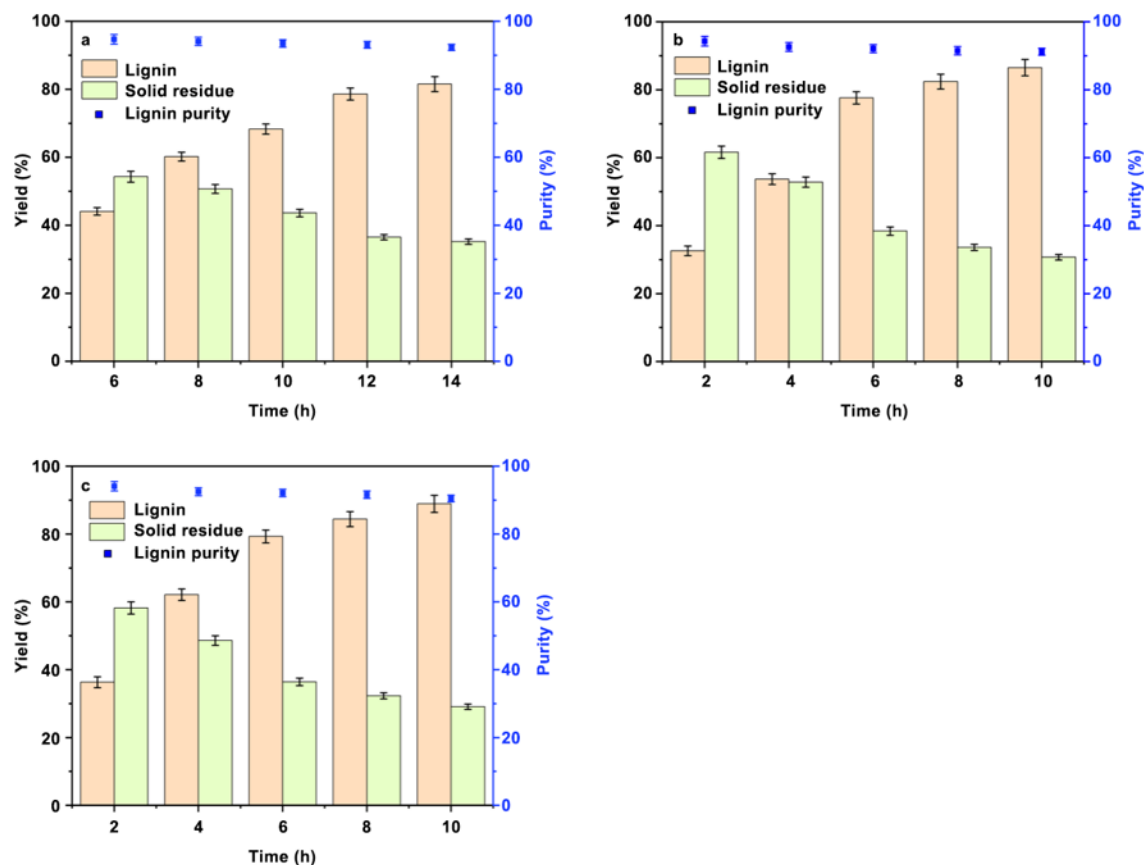


Fig. 1. DES system-treated lignin yield, solid residue, and purity, (a): ChCl: Fa, 1: 8, (b): ChCl: Fa: Ta, 1: 8: 1, (c): ChCl: Fa:Oa, 1: 8: 1.

Overall, both ternary DES systems outperformed the binary ChCl-Fa system, and ChCl-Fa-OA was slightly more effective than ChCl-Fa-Ta in promoting lignin release. The lignin yield was initially increased and then stabilized as the reaction time increased from 6 to 14 h in the ChCl-Fa system (Fig. 1a). The lignin yield was 68.13% at 10 h. The proportion of solid residue gradually decreased with time, reaching 43.35% at 10 h. The purity of lignin remained high and relatively stable at all-time points. As shown in Fig. 1b, within the time range of 2 to 10 h, the lignin yield considerably increased with time, attaining a high level of 77.3% lignin yield at 6 h in the ChCl-Fa-Ta system. The proportion of solid residue considerably decreased, reaching 38.09% at 6 h. In Fig. 1c, the ChCl: Fa:Oa system displayed a gradual increase in the lignin yield from 2 h to 10 h, attaining a 78.9% lignin yield after 6 h. The proportion of solid residue considerably decreased, reaching 36.4% at 6 h. Lignin's purity was consistently above 90% and did not significantly change. Appropriately prolonging the reaction time can lead to increased lignin yield, decreased solid residue to a certain extent, and maintained high purity of lignin.

FT-IR Analysis

The infrared spectra of the three samples had a similar shape, suggesting comparable basic chemical structures or functional group compositions. However, the position, intensity, and width of the absorbance peaks showed some variations, suggesting slight changes in the environment or chemical structure between the samples. FT-IR absorbance band assignment and spectra of DES-F-T, DES-F-O, and DES-F lignin samples are presented in Fig. 2. All samples showed a characteristic peak at 1591 cm^{-1} corresponding to aromatic skeletal vibrations (Barbosa *et al.* 2022). The samples showed characteristic absorbance peaks for aromatic groups at 1611 cm^{-1} , 1523 cm^{-1} , and 1425 cm^{-1} . The band at 1459 cm^{-1} was ascribed to C-H bending and C-C stretching of methoxyl (Cheng *et al.* 2023). The results showed that the aromatic structure of lignin was essentially unchanged, suggesting that the ternary DES system pretreatment of biomass can successfully maintain lignin's integral structure. All samples displayed strong absorbance bands at 1121 , 1267 , and 1332 cm^{-1} , corresponding to the syringyl and guaiacy units vibration. Meanwhile, the small absorption peaks at 916 cm^{-1} correspond to the C-H out-of-plane deformation (Gomide *et al.* 2020).

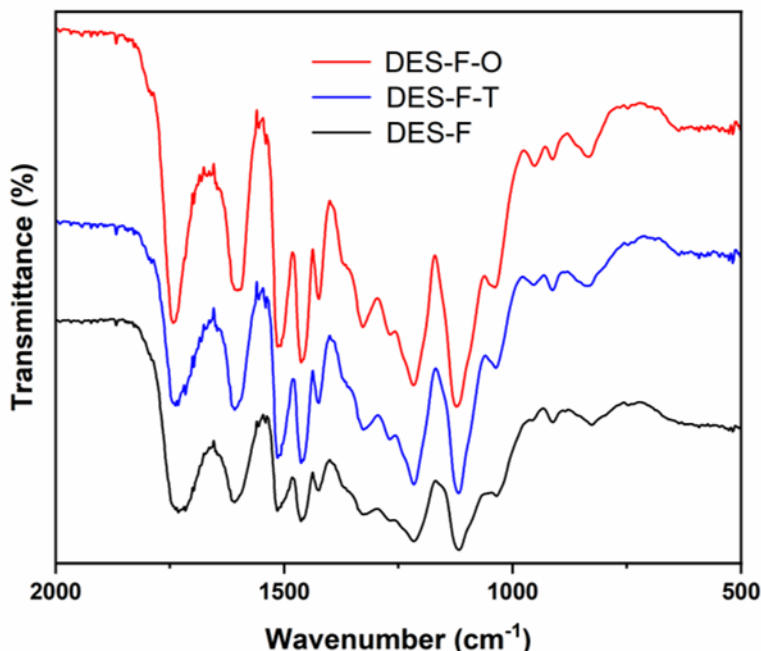


Fig. 2. FT-IR spectra of the DES lignin fractions

Molecular Weight Analysis

The depolymerization and repolymerization reactions of lignin were monitored through changes in its molecular weight, as presented in Fig. 3. DES-F-O demonstrated a weight average molecular weight (M_w) of 2843 g/mol , a number average molecular weight (M_n) of 1579 g/mol , and the calculated polymer dispersion index (PDI) of 1.8, indicating its broad molecular weight distribution. DES-F-T showed the corresponding values of 2361 g/mol , 1476 g/mol , and 1.6. The DES-F-T displayed a slightly lower PDI value compared to DES-F-O. The DES-F showed M_w , M_n , and PDI values of 2186 g/mol , 1361 g/mol , and 1.6. Both DES-F-T and DES-F indicated similar PDI values, thus suggesting similar molecular weight distribution patterns. However, M_w and M_n decreased gradually from

DES-F-O to DES-F, suggesting that the molecular weight of the lignin decreased as the treatment conditions were aggravated.

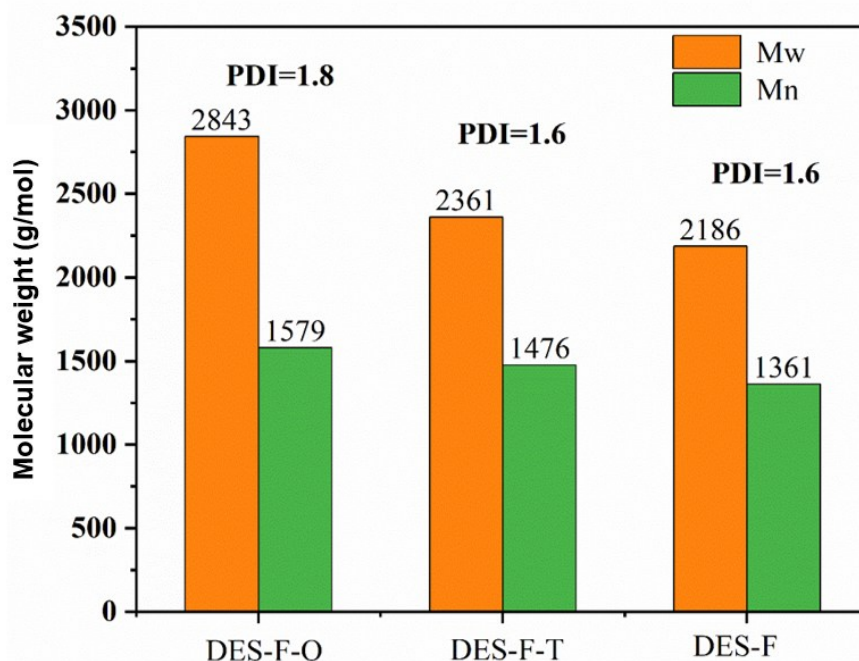


Fig. 3. Mw, Mn, and PDI of the DES lignin fractions

Elemental Analysis

In terms of elemental composition, DES-F showed the highest carbon (C), reaching 63.9 wt%, whereas DES-F-O demonstrated the lowest C content at 60.8 wt%. All samples demonstrated comparable hydrogen (H) contents, with slightly higher DES-F-O content of 6.53 wt%. The trend of oxygen (O) content was DES-F-O > DES-F-T > DES-F, with the following values: 32.3 wt%, 31.3 wt%, and 29.9 wt%. All samples demonstrated low nitrogen (N) and sulfur (S), with the DES-F-O showing slightly higher contents of 0.27 wt% and 0.13 wt%. In terms of the C/O ratio, DES-F exhibited the highest C/O value of 2.14. DES-F-O displayed the lowest value of 1.8, indicating a higher degree of carbon oxidation (or a relatively lower oxidation state) of DES-F compared to the other two samples, and that DES-F-O may have a higher oxidation degree. The increase in the C/O ratio with prolonged DES treatment can be attributed to several possible chemical pathways during acidic DES pretreatment. According to previous research, acidic DES systems can promote the cleavage of oxygen-containing ether linkages, especially β -O-4 bonds, and may also disrupt lignin-carbohydrate complex linkages, thereby promoting lignin depolymerization and fractionation (He *et al.* 2024). With increasing reaction time, oxygen-rich side-chain fragments and carbohydrate-derived impurities may be progressively removed from the recovered lignin fraction, resulting in an apparent increase in carbon content. In addition, dehydration of aliphatic hydroxyl groups, decarboxylation or decarbonylation of oxidized side-chain groups, and limited condensation/aromatization reactions under acidic conditions may further decrease the relative oxygen content and enrich carbon-rich macromolecular structures. Therefore, the gradual increase in C/O ratio is likely caused by the combined effects of oxygen-containing group removal, side-chain cleavage, dehydration, and partial condensation/aromatization during DES pretreatment.

Table 1. Elemental Analysis of Lignin Fractions

Sample	Elemental composition (wt%)					C/O
	C	H	O	N	S	
DES-F	63.91	5.98	29.93	0.13	0.05	2.14
DES-F-T	62.04	6.39	31.28	0.21	0.08	1.98
DES-F-O	60.78	6.53	32.29	0.27	0.13	1.88

2D-NMR Analysis

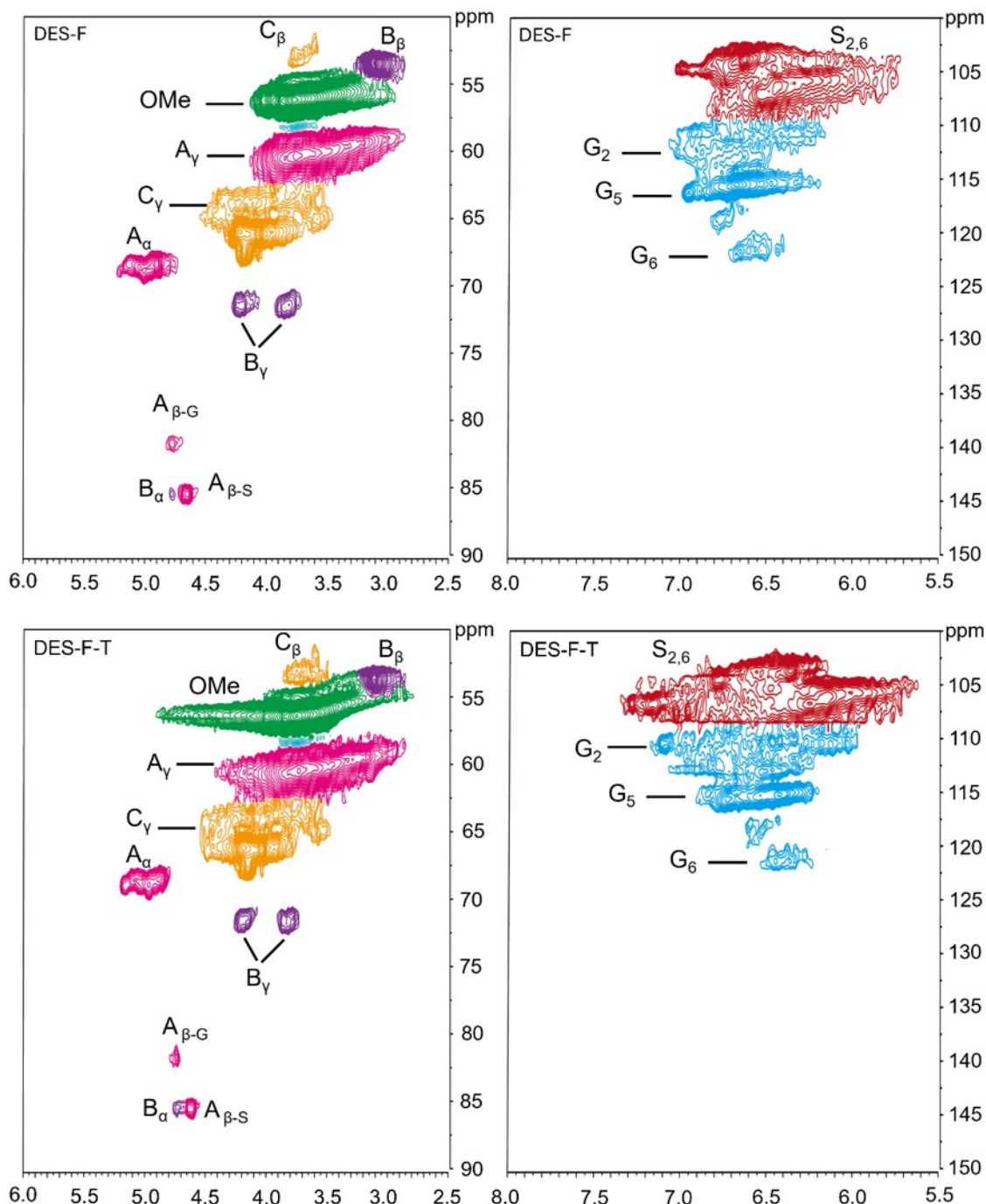
Based on lignin structure, the side chain ($\delta\text{C}/\delta\text{H}$ 50-90/2.5-6.0) and aromatic regions ($\delta\text{C}/\delta\text{H}$ 90-150/6.0-8.0) NMR spectra of DES-F, DES-F-T, and DES-F-O are displayed in Fig. 4.

The sidechain region comprised the main structures, including β -aryl-ether (A and A', β -O-4), resinol (B, β - β), and phenylcoumaran (C, β -5) of lignin. All samples demonstrated signals corresponding to side-chain regions ($\delta\text{C}/\delta\text{H}$ 50-90/2.5-6.0) and methoxyl groups ($\delta\text{C}/\delta\text{H}$ 55.9/3.73), indicating syringyl and guaiacyl units in the lignin (Lu *et al.* 2022). The samples showed β -O-4 linkages (A' γ) signals at $\delta\text{C}/\delta\text{H}$ 63.6/4.36, which can be attributed to the acylation of lactic acid on lignin side chains, in line with the previously published findings (Wu *et al.* 2024; Zhai *et al.* 2020). Furthermore, signals associated with $\text{C}_\alpha\text{-H}_\alpha$, $\text{C}_\beta\text{-H}_\beta$, and $\text{C}_\gamma\text{-H}_\gamma$ correlations in β - β substructures were identified with slight differences at $\delta\text{C}/\delta\text{H}$ 84.9/4.69, 53.7/3.05, and 71.3/3.91 (Yao *et al.* 2022). The samples erased the $\text{C}_\alpha\text{-H}_\alpha$ correlation signals at $\delta\text{C}/\delta\text{H}$ 86.8/5.49 in the β -5 substructure, with no carbohydrate signals, in line with the previously discussed compositional analysis results (Giummarella *et al.* 2020).

In the aromatic region of the 2D-HSQC spectra ($\delta\text{C}/\delta\text{H}$ 100.0-150.0/5.5-8.00), clear and distinct signals corresponding to syringyl (S) and guaiacyl (G) lignin units were observed. The G units showed pronounced correlations for $\text{C}_2\text{-H}_2$ ($\delta\text{C}/\delta\text{H}$ 112.6/6.89, G2), $\text{C}_5\text{-H}_5$ ($\delta\text{C}/\delta\text{H}$ 116.6/6.75, G5), and $\text{C}_6\text{-H}_6$ ($\delta\text{C}/\delta\text{H}$ 122.1/6.76, G6), indicating their structural integrity (Teo *et al.* 2024).

According to previous studies, the extent of lignin condensation during pretreatment can be evaluated qualitatively or semi-quantitatively using 2D HSQC NMR spectroscopy by examining the appearance of new cross-peaks corresponding to condensed linkages and by comparing the relative integral intensities of typical inter-unit structures, such as β -O-4, β - β , and β -5 linkages (Wang and Deuss, 2023; Mansfield *et al.* 2012; Xiao *et al.* 2023). Typical condensed motifs, including 5-5', β -5', and β - β' structures, may give characteristic cross-peaks in both the side-chain and aromatic regions of the HSQC spectra, and changes in the relative abundance of these signals are often used to assess condensation reactions in lignin during chemical pretreatment (Wang and Deuss 2023; Xiao *et al.* 2023). In the present work, the HSQC spectra of all lignin samples did not show newly generated cross-peaks that could be assigned to condensed structures.

Meanwhile, the relative integral intensities of the major native lignin linkages remained essentially unchanged among the different DES pretreatments. These observations indicate that only slight condensation reactions occurred during DES treatment and that the overall degree of condensation of the isolated lignin was very low.



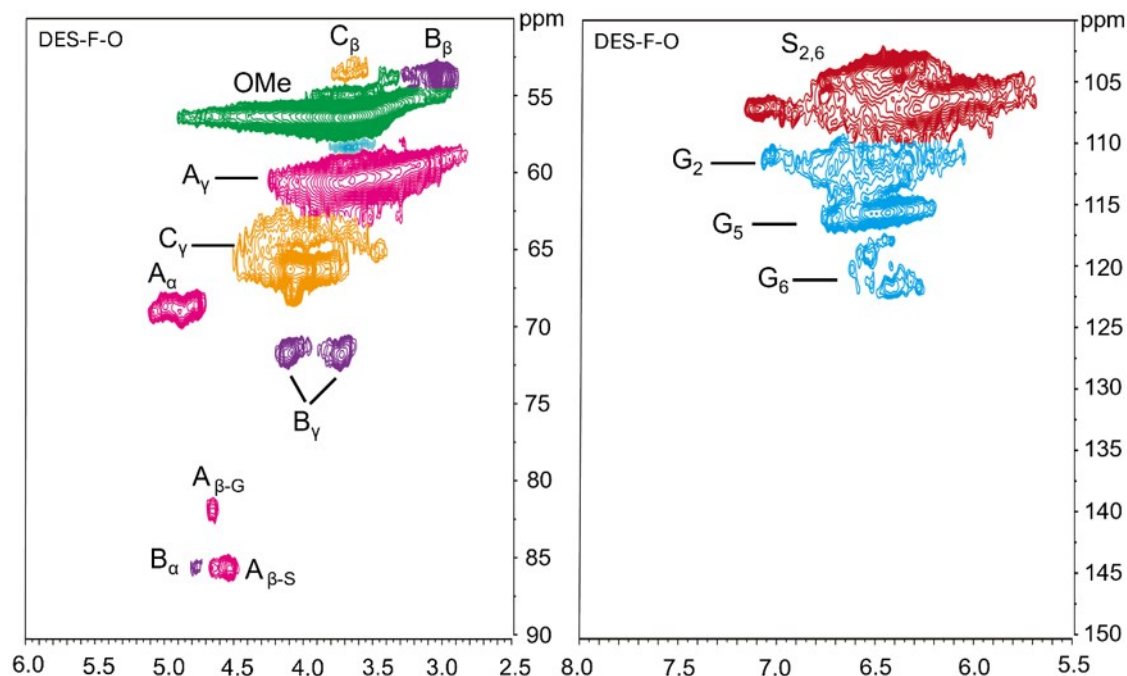


Fig. 4. 2D-HSQC spectra of the DES lignin fractions

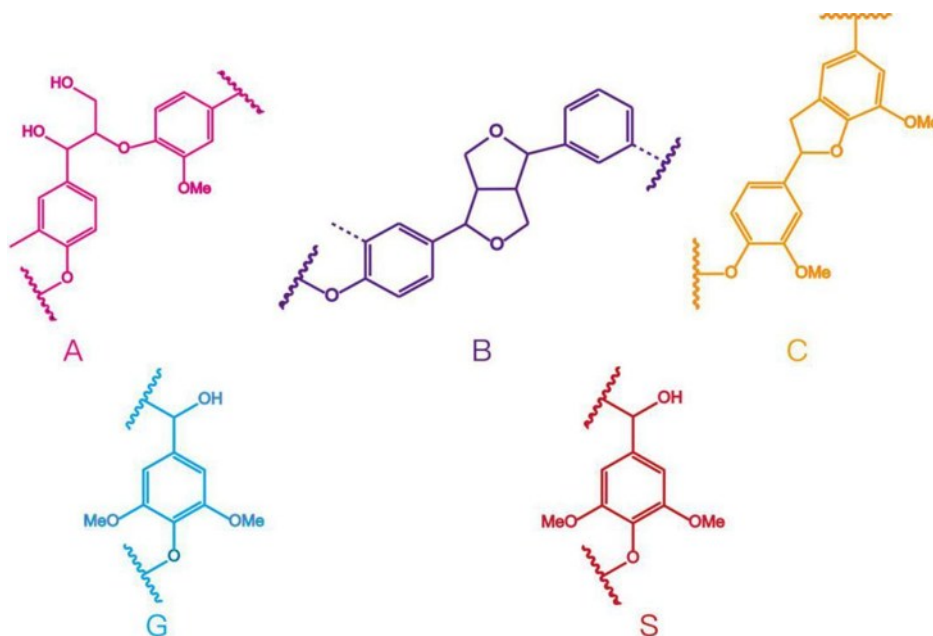


Fig. 5. Main structures observed in lignin fractions

Thermal Analysis

According to the thermogravimetric analysis (TGA) curve, the mass of all samples gradually decreased as the temperature increased. The mass loss was relatively gentle in the lower temperature range (around 0 to 200 °C), which can be attributed to the evaporation of volatile small molecules or adsorbed water (Kim and Um 2020). The rate of mass loss increased with temperature, with a high stage of mass decline from 300 to 500 °C, corresponding to the decomposition of the main components in the sample (Ortega-Sanhueza *et al.* 2024). In the high-temperature range (500 to 800 °C), the mass loss

plateaued and stabilized, indicating decomposition into stable residues (Yuan *et al.* 2025). Distinct variations in thermal behavior were observed among the three lignin samples upon further comparison. A more detailed comparison revealed that DES-F exhibited a lower onset decomposition temperature than DES-F-O and DES-F-T, indicating that its structure contained a higher proportion of thermally labile linkages, such as β -O-4 ether bonds and side-chain functionalities, which are more susceptible to cleavage at relatively low temperatures. In contrast, the ternary DES systems, particularly DES-F-O, appear to have promoted the formation or preservation of slightly more condensed or oxidized structures, which enhance thermal resistance and delay initial degradation. Regarding char formation, DES-F produced less residual char at approximately 400 °C and at high temperatures. Char yield during pyrolysis is generally associated with the presence of condensed aromatic structures and cross-linked C-C frameworks, which favor carbonization rather than volatilization. Conversely, DES-F-O and DES-F-T exhibited relatively higher residual char, suggesting a slightly higher degree of structural condensation or cross-linking that promotes carbonaceous residue formation. In addition, the elemental analysis showed that DES-F had a higher C/O ratio compared with DES-F-O, which may also influence thermal degradation pathways. Lignin fractions with higher oxygen content (lower C/O ratio) can undergo dehydration and cross-linking reactions during heating, contributing to enhanced char formation in DES-F-O and DES-F-T. DES-F demonstrated a lower onset decomposition temperature and retained less residual char at around 400 °C compared to DES-F-O and DES-F-T, probably because its molecular structure contains abundant thermally labile chemical bonds and side-chain groups susceptible to breakage under heating. Combined with the 2D HSQC NMR results, DES-F contained fewer condensed structures and rigid cross-linked frameworks. As condensed structures significantly promoted char formation during pyrolysis, the lack of such frameworks resulted in extensive thermal degradation and lower char residue at high temperatures. At 800 °C, the commercial lignin residue and three different dosages of DES-F-O, DES-F-T, and DES-F demonstrated residual rates of 40.01%, 37.26%, and 31.71%, highlighting the good thermal stability of the lignin extracted from DES.

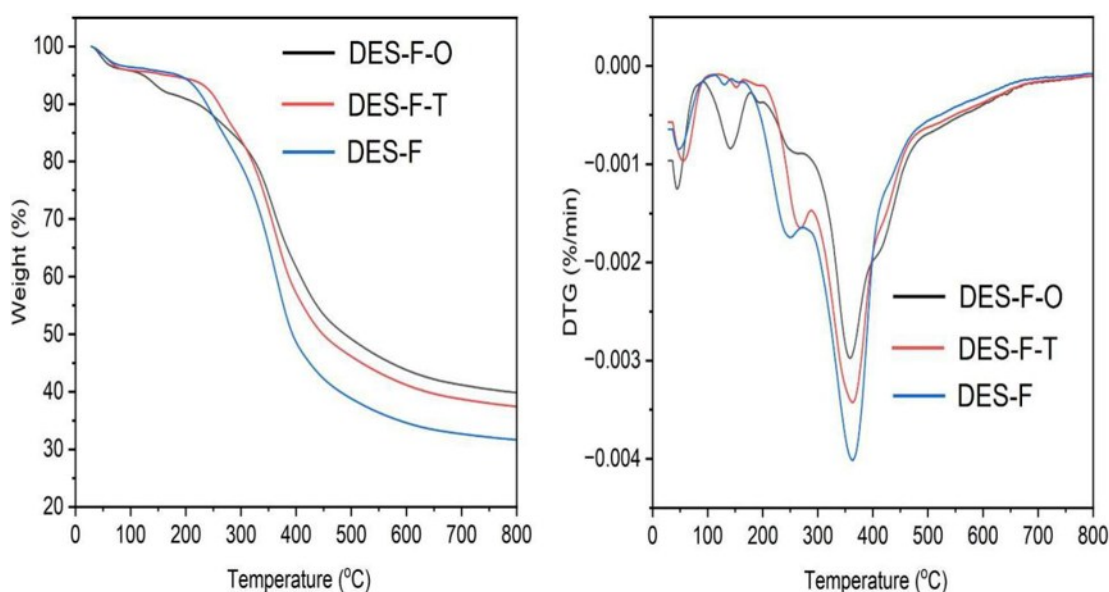


Fig. 6. TGA and DTG curves of the DES lignin fractions

CONCLUSIONS

1. The choline chloride – formic acid – oxalic acid (ChCl-Fa-Oa) deep eutectic solvent (DES) system showed a gradual increase in the lignin yield between 2 and 10 h, reaching 78.9% at 6 h. It showed a continuous decrease in the proportion of solid residue to 36.4%, along with the lignin purity exceeding 90% with no significant variation at fixed molar ratios (1:8 and 1:8:1) and temperature (120 °C).
2. The basic aromatic structure of lignin, consisting mainly of syringyl (S) and guaiacyl (G) units, remained intact following treatment with the ternary DES system.
3. Elemental analysis showed that the recovered DES lignin fractions possessed carbon-rich macromolecular structures, with carbon contents exceeding 60%. The increase or variation in C/O ratio may be associated with acid-catalyzed cleavage of oxygen-containing linkages, removal of oxygen-rich carbohydrate impurities, dehydration, decarboxylation/decarbonylation, and limited condensation or aromatization during DES pretreatment.
4. The extracted DES lignin showed high stability. The DES-F-O sample had the greatest residual carbon at 40.0% during the quality decrease stage between 300 and 500 °C.

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Credit Authorship Contribution Statement

Wenxiu Huang: Writing-review & editing, Writing-original draft, Validation, Methodology, Data curation, Project administration. Yinglong Wu: Methodology, Conceptualization, Data curation, Validation. Guangyan Du: Resources, Funding acquisition. Jing Zheng: Resources. Yueying An: Funding acquisition. Xiangyu Wei: Investigation.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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