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Published in:
ACS Sustainable Chemistry and Engineering

DOI:
[10.1021/acssuschemeng.2c02954](https://doi.org/10.1021/acssuschemeng.2c02954)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2022

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Citation for published version (APA):

Wang, Z., Liu, Y., Barta, K., & Deuss, P. J. (2022). The Effect of Acidic Ternary Deep Eutectic Solvent Treatment on Native Lignin. *ACS Sustainable Chemistry and Engineering*, 10(38), 12569-12579. <https://doi.org/10.1021/acssuschemeng.2c02954>

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The Effect of Acidic Ternary Deep Eutectic Solvent Treatment on Native Lignin

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Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 12569–12579

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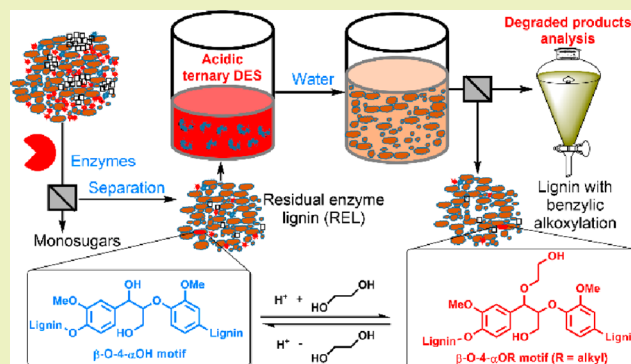
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Supporting Information

ABSTRACT: Ternary deep eutectic solvents (DESs) are gaining increased attention to serve as a cheap green alternative medium for the processing of lignocellulosic biomass. For example, mixtures of choline chloride (ChCl), ethylene glycol (EG), and oxalic acid (OA) were recently explored for the fractionation of lignocellulosic biomass into its main components. Interestingly, during this processing, the recovered lignin was structurally modified by incorporation of EG, which altered its solubility properties and led to the need for different lignin recovery strategies. This offers an excellent starting point for a deeper investigation of the effect of acidic DES systems on the structure of lignin. In particular, native-like residual enzyme lignins (RELs) that are hard to completely dissolve in organic solvents are specifically suitable for this task. Here, a ternary DES is used consisting of ChCl/EG with OA or trifluoromethanesulfonic acid (HOTf) as a third component. The results showed that both solvent systems led to high EG incorporation into REL. The HOTf system showed a lesser extent of lignin depolymerization at similar modification levels as it already induced modification at lower temperature (25–30 °C). Low recovery yields from typical acidic precipitation were observed for treatment with both acidic DES systems. Analysis of THF and DCM extracts showed that the products in the water phase included small EG modified lignin fragments and aromatic monomers released from lignin aryl ether linkage cleavage. This analysis details the types of other products that can be expected and where these will end up during fractionation. These results show that the treatment of lignin with acidic DES in the presence of alcohols leads to low- and high-molecular-weight products that are not effectively recovered by typical precipitation procedures.

KEYWORDS: biomass, lignin, deep eutectic solvents, acid catalysis, 2D HSQC NMR, benzylic alkoxylation



INTRODUCTION

Lignin, the only aromatic main component in lignocellulosic biomass, is mainly composed by syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units linked together via aryl ether motifs (β -O-4) as some other minor linkages such as the β - β and β -5 motifs.^{1–4} Quantities of the aromatic units and linkages are influenced by plant species, growing environment, and stage, cell types, and wall layers.^{4–6} The aromatic character and widespread and abundant availability in waste streams make lignin a promising renewable alternative resource for the production of high-value aromatic chemicals and materials.^{7,8} However, the high molecular weight, diverse unit constituents, and labile inter-unit linkages of lignin significantly hamper efficient isolation and modification, which greatly restrict development toward its use in high-value applications.^{9,10}

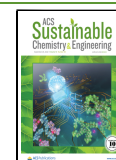
To efficiently utilize lignin, effective and mild fractionation from the lignocellulosic matrix is essential.^{11–13} For this, an efficient solvent system that allows for dissolution and recovery of the lignin constituent while limiting intensive aryl ether cleavage and subsequent condensation is sought after.

Recently, deep eutectic solvents (DESs) have been intensively studied for the upgrading of biomass.^{14–17} Here, the use of DES is found attractive due to its low volatility, abundant hydrogen bonding network that can interact with the polar biopolymers, low toxicity, general biocompatibility, and typical good recyclability.^{18–22} In contrast to ionic liquids that share some of these advantages, DESs are more easily prepared from widely available and inexpensive components and thus have a higher potential to be used for processing biomass on a large scale.^{15,23,24} A typical DES is composed of two or more components serving either as hydrogen-bond acceptors (HBA), such as quaternary ammonium salts, or as hydrogen-bond donors (HBD), such as alcohols and carboxylic acids.

Received: May 19, 2022

Revised: August 24, 2022

Published: September 12, 2022



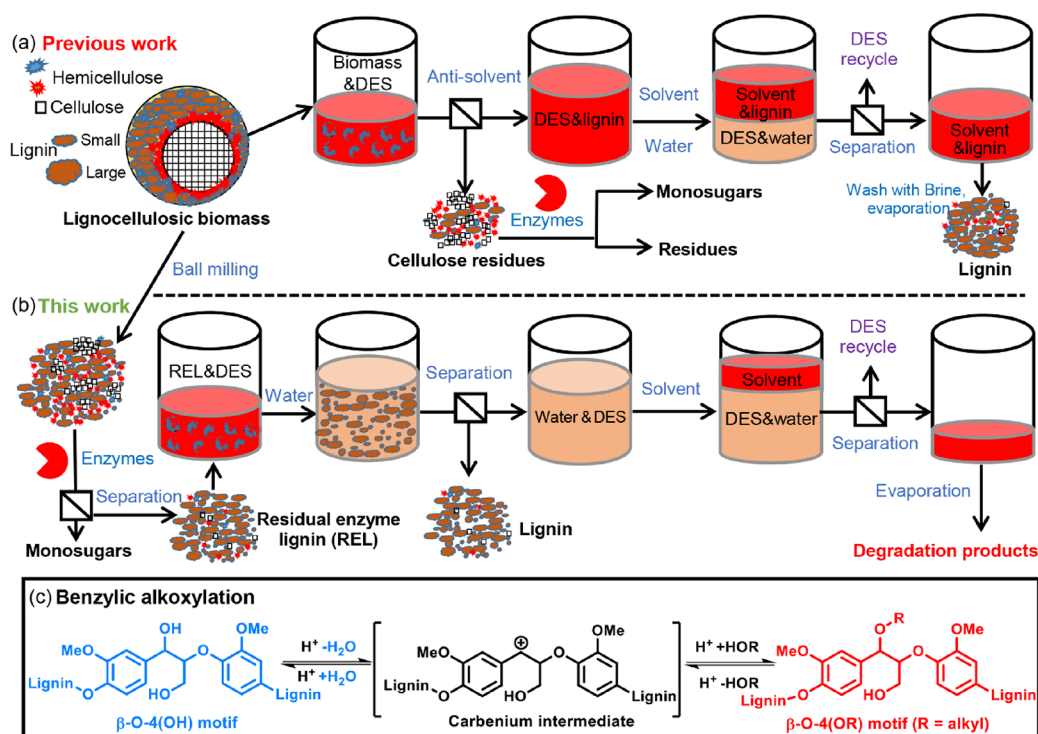


Figure 1. Treatment of lignocellulosic biomass or lignin in DES. (a) Previous lignin isolation from ChCl/EG/OA. In this procedure, after treating lignocellulosic biomass, cellulose-rich residues are obtained by filtration, and lignin is recovered by THF extraction. (b) This work treats isolated native-like lignin (REL), obtained by enzymatic removal of carbohydrates and milling, with ChCl/EG/(OA and HOTf), and then lignin is precipitated from DES by the addition of acidic water. The products in the liquid fraction are extracted by organic solvents (THF and DCM) to track the degradation products. (c) Schematic overview of benzylic alkoxylation of the lignin β -O-4 motif (with EG in this work).

Several binary and ternary DES systems have been confirmed to have high efficacy for lignin extraction.^{24–27} For instance, we previously reported a tunable ternary choline chloride (ChCl)/ethylene glycol (EG)/oxalic acid (OA) system (Figure 1a) that was able to efficiently fractionate biomass to yield cellulose-rich residues suitable for high-yield fermentable sugar production and in parallel isolate lignin with a relatively intact structure suitable for subsequent depolymerization.²⁸

Benzylic alkoxylation of lignin with EG occurs during this fractionation (Figure 1c), which can significantly suppress repolymerization, providing lignin with enhanced chemical stability and new functionality.^{28–30} Furthermore, the modification leads to increased solubility of such fully or partially modified lignin in common (organic) solvents, making it particularly suitable for further processing and upgrading.^{29,31–35} This endows lignin with tunable properties and higher recalcitrance toward harsh reaction condition for more applications such as directly serving as building blocks or filling material for the production of functional polymers and composites.³⁶ In addition, the normal aryl ether linking motif can be recovered from the alkoxyated lignin via a mild acidic hydrolysis.^{29,32} For further application, fundamental understanding of the consequences of such modifications on lignin isolation is required to understand where different modified lignin fragments end up in the process and to improve fractionation.

Tracking the reaction paths and stability of lignin in the DES systems plays a vital role in guiding the valorization of lignin. However, the complexity of lignocellulosic biomass makes the elucidation of the degradation and derivatization routes a challenge. In addition, the results obtained from simplified

dimeric model compounds show discrepancies when compared to those from lignin.³⁷ Therefore, residual enzyme lignin (REL) obtained from ball milling and subsequent enzymatic polysaccharide hydrolysis provides a promising model lignin for such studies. In contrast to some typical native-like lignins such as milled wood lignin (MWL), REL isolation conserves the majority of the native linkage structure and high molecular weight as no extraction step is applied.^{38,39} This does mean that such lignin is insoluble in common organic solvents and water. However, DES systems are particularly suitable to dissolve such materials. In this study (Figure 1b), four REL samples obtained from birch, pine, reed, and walnut shell representing lignin from hard wood, soft wood, herbaceous biomass, and non-wood biomass, respectively, were isolated as native-like model lignins to study how the lignin structure changes in the ternary DES systems of ChCl/EG acidified by OA or HOTf. The products obtained from treating REL in ChCl/EG with different acids were comprehensively studied by tracking the degree of lignin benzylic alkoxylation and characterization of products from depolymerization and their fate during fractionation. Overall, the intention is to provide some solid insights for understanding the transformation of lignin in the ChCl/EG system under different acids to guide the efficient delignification and subsequent utilization of lignin from ChCl/EG biomass treatment.

EXPERIMENTAL SECTION

See the Supporting Information (SI) for the materials used as well as procedures for the isolation of residual enzyme lignin, carbohydrate content analysis, and reductive catalytic hydrogenolysis of DES-fractionated lignins. For a detailed description of the procedures used

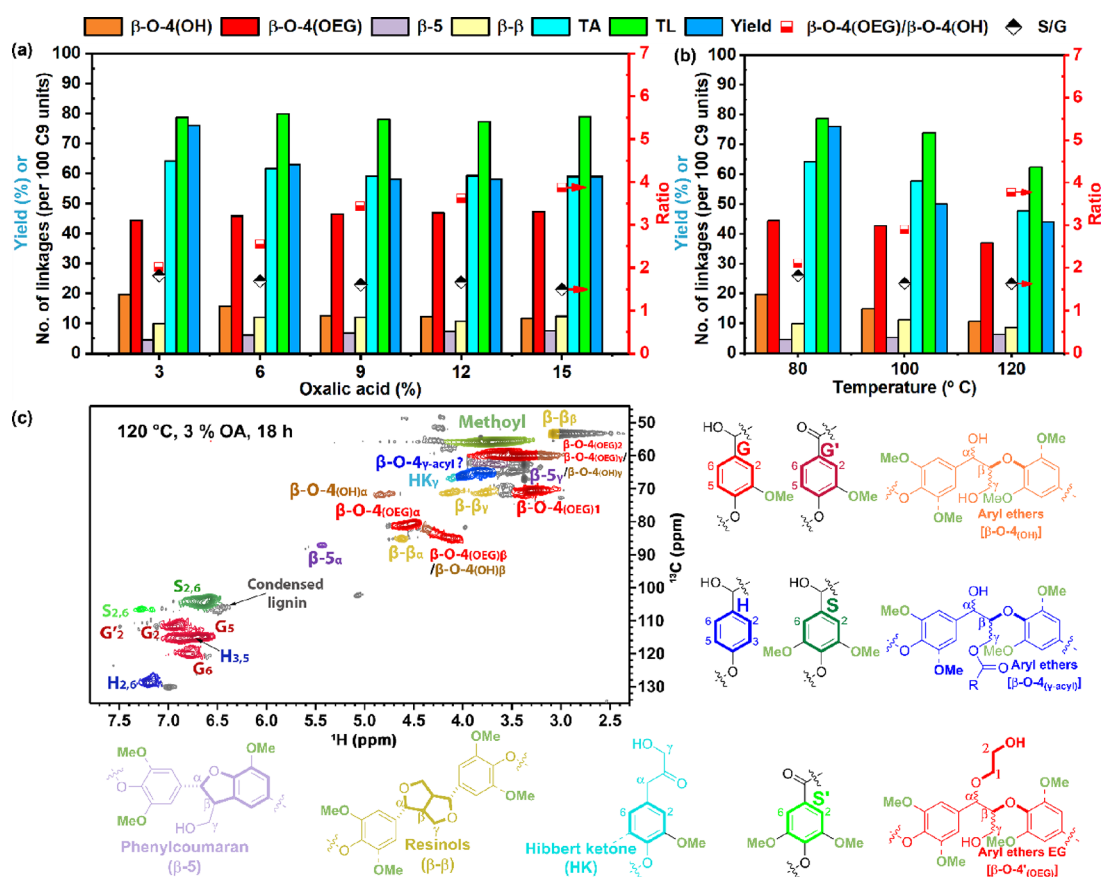


Figure 2. The main linkages (semi-quantification from 2D HSQC NMR; see the detailed calculation in Eq.S1 in the SI), S/G ratios, and recovery yields of lignins obtained from treating REL_Walnut with ChCl/EG/OA (1 : 2 mol ratio with 3–15% of OA based on the total weight of ChCl and EG) using different acid dosages and different temperatures; β -O-4(OH), aryl-alkyl ether, β -O-4(OEG), aryl-alkyl ether with EG incorporation at the α position, β -5, phenylcoumaran, β - β , resinols, TA, total aryl ether linkage [β -O-4(OH) + β -O-4(OEG)], TL, total linkage (TA + β -5 + β - β); reaction conditions: (a) 4.2 g of ChCl, 3.6 g of EG, 100 mg of REL_Walnut, and different percentages of OA (based on the total mass of ChCl and EG) at 80 °C for 18 h (see the original spectra in Figures S4–S8 and detailed data in Table S1). The yield was calculated by dividing the weight of the freeze-dried lignins to the weight of starting materials (eq 1). (b) 4.2 g (30 mmol) of ChCl, 3.6 g (60 mmol) of EG, 100 mg of REL_Walnut, and 0.234 g of OA (3%, based on the total weight of ChCl and EG) at different temperatures for 18 h (see the original spectra in Figures S9 and S10 and detailed data in Table S2). The yield was calculated by dividing the weight of the freeze-dried lignins to the weight of starting materials (eq 1). (c) Example of an assigned 2D HSQC NMR spectrum of the recovered lignin material after treatment with 3% OA at 120 °C for 18 h, indicating the appearance of condensed S units indicative of lignin degradation and condensation.

for characterization in this work, please see the general characterization section of the SI.

Preparation of DESs. DESs were prepared by simply mixing ChCl with EG in a mol ratio of 1:2. A clear transparent liquid was obtained after vigorous stirring for 30 min and heating (around 50 °C). The acidified DES was prepared right before use by adding acid to ChCl/EG according to the pre-designated amount (see below).

Representative Treatment of RELs in DESs. For the ChCl/EG/OA system, DESs were first prepared by weighing a mixture of ChCl/EG [4.2 g (30 mmol) of ChCl and 3.6 g (60 mmol) of EG with a mol ratio of 1:2] in a 20 mL glass pressure tube, and then the desired amount of OA (0.234–1.17 g, 3–15%, based on the total weight of ChCl and EG) was added into the liquid under stirring, followed by the addition of 100 mg of REL_Walnut. For the ChCl/EG/HOTf system, DES was prepared by weighing a mixture of ChCl/EG [2.1 g (15 mmol) of ChCl and 1.8 g (30 mmol) of EG with a mol ratio of 1:2], and dropwise trifluoromethanesulfonic acid (0.39–1.95 g, 5–25%, based on the total weight of ChCl and EG) was added into the liquid, followed by the addition of 100 mg of REL_Birch. The mixture was vigorously mixed before heating in a preheated oil bath. After reaching the pre-designated reaction time, the vial was cooled down using an ice bath and then subjected to precipitation by the addition of 20 times the volume of acidic water (pH = 2, acidified with HCl). The precipitate was recovered by

centrifugation (15,000 rpm, Thermo Scientific Sorvall Legend X1R Centrifuge) and freeze-dried (ALPHA 2-4 LD, Appropriate Technical Resources) to yield a powder that was designated as the recovered solid. The recovered yield was determined based on gravimetric analysis by eq 1 below:

$$\text{Yield}(\%) = \frac{\text{Weight of residual lignin}}{\text{Weight of starting material}} \quad (1)$$

The recovered lignin was characterized by 2D HSQC and gel permeation chromatography (GPC).

Larger-Scale Treatment of REL from Four Representative Biomasses in ChCl/EG/OA and Degradation Products Extracted by DCM and THF. After treating 0.3 g of REL from birch, pine, reed, and walnut shell in ChCl/EG/OA [mol ratio of 1:2 for ChCl and EG, 12.6 g (90 mmol) of ChCl, 10.8 g (180 mmol) of EG, and 2.11 g of OA (9%, based on the total weight of ChCl and EG)] at 80 °C for 36 h. The cooled mixture was poured into 20 volume times of acidic water (120 mL, pH = 2, acidified with HCl) under vigorous stirring. The precipitate was collected by centrifugation and washed three times with acidic water. The recovered product yield was determined by gravimetric analysis after freeze-drying and used for reductive catalytic hydrogenolysis. The liquid phases collected from the separation and washing steps were combined (around 200 mL) and extracted by DCM (40 mL \times 3 times). The DCM in the

combined organic phases was carefully removed by an airflow in the fume hood to collect the DCM_Oil. The oil products were subjected to GC–MS analysis.

For THF extraction, 0.5 g of REL_Walnut was treated under ChCl/EG/OA [mol ratio of 1:2 for ChCl and EG, 21 g (0.15 mol) of ChCl, 18 g (0.3 mol) of EG, and 3.51 g of OA (9%, based on the total weight of ChCl and EG)] under 80 °C for 36 h, and the combined liquid phase from the separation and washing steps (400 mL) was extracted by THF (100 mL \times 3 times), and brine was used to help the separation of THF and water phase (keep adding 30 mL of brine several times). The combined THF phase was further dried by anhydrous MgSO₄, and THF was removed by a rotary evaporator. A black oil was obtained and the lignin fragments were recovered by precipitation in diethyl ether. The final precipitate was carefully dried under a nitrogen flow overnight and subjected to 2D HSQC NMR and GPC analysis.

RESULTS AND DISCUSSION

The ChCl/EG/OA System. Previously, the DES system composed by ChCl and OA or ChCl/EG with minor amount of H₂SO₄ was studied for the pretreatment of biomass to extract lignin and enhance the enzymatic hydrolysis of cellulose for high fermentation sugar recovery.^{40,41} But the effect of such treatments on the lignin structure was not studied in a lot of detail due to the challenges in the analysis of the complex product mixture that originate from the lignin and hemicellulose decomposition. A previous study did give detailed lignin structural transformations related to a binary DES system in terms of molecular weight and hydroxyl groups.²² However, no study has thus far focused on revealing selective benzylic alkoxylation from our described ternary DES.²⁸ However, when using this system to fractionate lignin from lignocellulosic biomass, the recovered lignin was lower than the actual delignification of the raw material.²⁸ Possible explanations included the depolymerization of lignin and its loss during fractionation steps that could be due to increased water solubility because of EG incorporation observed in the recovered material and dimeric model compounds. Thus, a further study was deemed necessary to track the loss of lignin during fractionation. In another study, we developed a method for the isolation of REL with a native-like structure (high β -O-4 content and high molecular weight), which can serve an ideal native-like model lignin.³⁸ The structural changes in this native-like lignin in the ChCl/EG/OA system would lead to the understanding of changes to the lignin structure during DES fractionation.

REL isolated from walnut shells was first used for studying the ChCl/EG/OA system at 80 °C and the optimal conditions for fractionation found in our previous work.²⁸ At the initial stage of the reaction (Figure S1), lignin did not fully dissolve in the mixture, leading to a suspension. After an 18 h reaction, the final viscous reaction mixture was almost completely homogeneous, which is hard to attain in the treatment in common organic solvent systems and water without serious alteration of the lignin structure in terms of molecular weight reduction and condensation. Importantly, the treatment with the ternary DES system would allow for better structural elucidation of the obtained “protected” lignins, thereby providing useful information regarding the structure of the parent native lignin, which is difficult to attain due to its insolubility in common organic solvents. The effect of the dosage of OA was evaluated by tracking the lignin recovery after water addition and the structure in terms of linkage content from 2D HSQC NMR (Figure 2a). The recovered

materials were all high in aryl ether content (combination of regular β -O-4(OH) and modified β -O-4(OEG)), showing that this DES system is indeed suitable for processing native-like lignin without severe cleavage of aryl ether linkages. Up to 9% dosage of OA, the β -O-4(OEG)/ β -O-4(OH) ratio gradually increased from 2 to 4, and at the same time, the recovered yield of lignin decreased from 86 to 59%. The mass loss linked to the increased dosage of OA was anticipated to be due to the enhanced water solubility of lignin with the increased of the amount of EG incorporation and the increased cleavage of aryl ether linkages (see the reaction mechanism in Scheme S1).⁴²

After a further increase of the OA dosage, both the EG incorporation and lignin recovery yield leveled off. In the recovered lignin at these higher OA loadings, all the main linkages [β -O-4(OEG), β -O-4(OH), β - β , and β -5] showed no big differences. Furthermore, the S/G values of the recovered lignins were stable. These results indicated that extra loading of OA did not have any further significant effects on the lignin structure. Overall, this could indicate that the incorporation of EG is indeed linked to a more stable lignin structure. With this data in hand, we further studied the influence of temperature on the structure of lignin and the recovery yield (Figure 2b). Although the β -O-4(OEG)/ β -O-4(OH) ratio kept increasing with an increase in temperature up to 120 °C, the recovered lignin yield decreased. The total linkage content, in particular the aryl ether linkage, seriously declined, and obvious signals for condensation appeared in the aromatic region of the 2D HSQC NMR spectra (Figure 2c). This indicated that a necessary balance between reaction temperature and EG incorporation needs to be considered in terms of linkage preservation and lignin recovery yield. Additionally, the dosage of EG was lowered and the reaction time was prolonged to 36 h with a 9% OA loading at 80 °C and it was found that the incorporation of EG was only slightly increased (Table S1, entry Ec). This might be due to the prolongation of the reaction time that only slightly contributed to the increase of benzylic alkoxylation of residual enzyme lignin from the walnut shell with EG in the ChCl/EG/OA system possibly due to the β -O-4(OEG) and the regular β -O-4(OH) being in equilibrium.^{30,43} However, the yield of lignin was lower (55% down from 36 h) than that of lignin obtained from an 18 h reaction (58%). Thus, the loss of lignin fragments with lower molecular weight or higher EG incorporation in the water fraction might also have contributed to the low increase of EG incorporation found in the recovered lignin. From these results, it is clearly seen that the balance between high EG incorporation of lignin without a serious decrease of the main linkages in high recovered yield and reaction parameters such as temperature and OA dosage of ChCl/EG/OA was hard to establish.

The ChCl/EG/HOTf System. In the above studies of REL_Walnut in the ChCl/EG/OA system, it was found that the acid dosage played an important role in achieving a high yield of benzylic alkoxylation of lignin but that lignin recovery was very sensitive to the elevated reaction temperature. If the reaction temperature could be decreased by carefully tuning the constituents of DES, a high modification degree with minor depolymerization might be achieved. ChCl has an excellent compatibility with different acids. Among them, trifluoromethanesulfonic acid (HOTf), a HBD previously reported,⁴⁴ with strong acidity had an excellent performance on the acidolysis of lignin with EG as a protecting reagent for tracking the active products to increase product yields and selectivity.^{45,46} Our

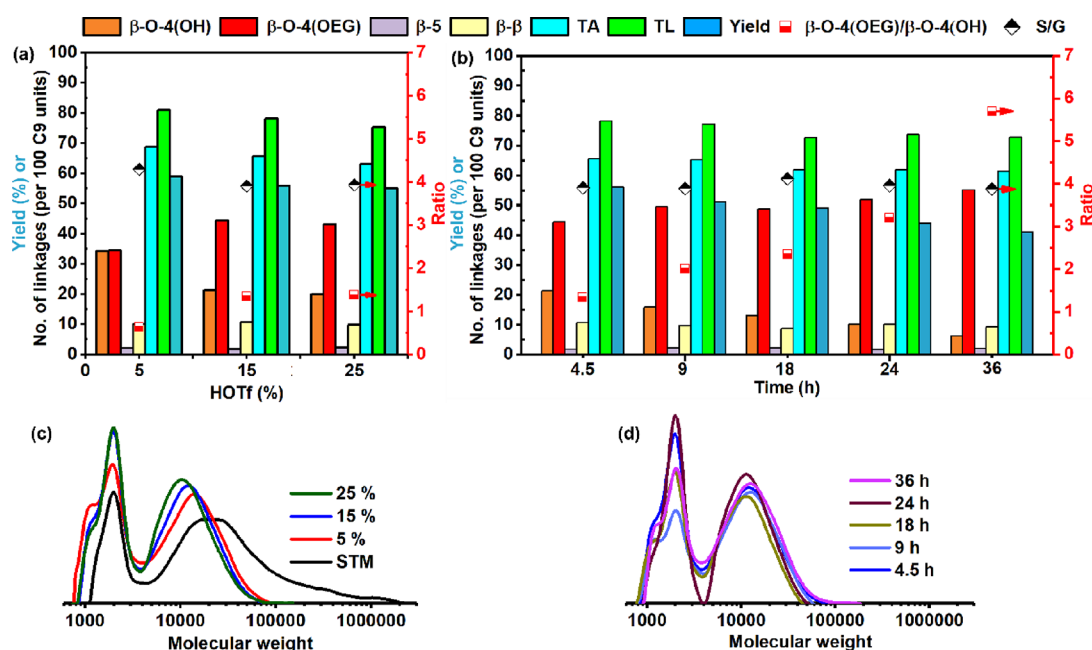


Figure 3. The main linkages, S/G ratios (semi-quantification from 2D HSQC NMR; see the detailed calculation in Eq.S1 in the SI), recovery yield, and molecular weight distribution of lignins obtained from treating REL_Birch with ChCl/EG/HOTf (1 : 2 mol ratio with 5–25% of HOTf based on the total weight of ChCl and EG) containing different acid dosages and reaction times. β -O-4(OH), aryl ether, β -O-4(OEG), aryl ether with EG incorporation at the α position, β -5, phenylcoumaran, β - β , resinols, TA, total aryl ether linkage [β -O-4(OH) + β -O-4(OEG)], TL, total linkage (TA + β -5 + β - β); (a) the main linkage of lignin obtained from treating REL_Birch with different amounts of HOTf (%), reaction condition: (a) 2.1 g (15 mmol) of ChCl, 1.8 g (30 mmol) of EG, 100 mg of REL_Birch, and different percentages of HOTf (based on the total mass of ChCl and EG) at room temperature (30 °C) for 4.5 h (see the original spectra in Figures S12–S14 and detailed data in Table S3). The yield was calculated by dividing the weight of the freeze-dried lignins to the weight of starting materials (eq 1). (b) The main linkage of lignin obtained from treating REL_Birch for different reaction times (see the original spectra in Figures S15–S18 and detailed data in Table S4), reaction condition: 2.1 g (15 mmol) of ChCl, 1.8 g (30 mmol) of EG, 100 mg of REL_Walnut, and 0.59 g of HOTf (15%, based on the total weight of ChCl and EG) at different reaction times at room temperature (30 °C). The yield was calculated by dividing the weight of the freeze-dried lignins to the weight of starting materials (eq 1). (c) The molecular weight distribution of lignin obtained from treating REL_Birch with different amounts of HOTf (%) (see the detailed molecular weight values in Table S3). (d) The molecular weight distribution of lignin obtained from treating REL_Birch for different times (see the detailed molecular weight values in Table S3).

previous study with an acidic HOTf-based ionic liquid showed an excellent performance on achieving benzylic alkoxylation of lignin isolated from different biomasses at ambient temperature.³⁰ Thus, we thought that a HOTf DES might allow to decrease the reaction condition and avoid intensive degradation of lignin. To test this assumption, our attention was switched from OA to HOTf, targeting high EG incorporation and lower degradation of lignin by controlling the reaction under milder conditions. Here, we switched from walnut shell to birch, since its lignin contains high aryl ether linkage and has relatively high solubility after DES treatment according to our previous experience, enabling also the analysis of the MW before and after the treatment. In addition, the mass ratio between REL and DES was doubled and was confirmed to not induce significant structural variations (Figure S27 and Table S4). The loading of HOTf for treating REL_Birch was first tested (Figure 3a). A lower β -O-4(OEG)/ β -O-4(OH) ratio comparable to that of the OA system was observed but now at near to room temperature (30 °C). Also, here, the trend of an increase in the β -O-4(OEG)/ β -O-4(OH) ratio was accompanied with a decrease in the lignin recovery yield. Nevertheless, even though the β -O-4 content remained high, lignin was found to be only slightly degraded by looking at molecular weight distribution (Figure 3c). This might be due to the instability of the unmodified aryl ether linkages under strong acidic conditions. This was similar to the results observed in

the ChCl/EG/OA system and illustrated that high EG incorporation is hard to achieve by simply increasing the dosage of acid without also inducing undesired reactions.

Reaction time is another key parameter that needs to be carefully evaluated. Therefore, REL_Birch was further treated under different reaction times (Figure 3b). The data showed that the EG incorporation was significantly increased by simple prolongation of the reaction time. Among them, in a 36 h reaction, lignin had a 5.7 ratio of β -O-4(OEG)/ β -O-4(OH) that is much higher than the maximum ratio obtained from tuning the dosage of acid and did not lead to a significant decrease in the recovery yield. The aryl ether linkage content of the recovered lignin and in particular the molecular weight (Figure 3d) showed that only minimal further chain cleavage occurred at these mild conditions even at extended reaction time. When the temperature was increased to 80 °C, almost no linkage signals were observed on 2D HSQC NMR (Figure S28). This indicates that lignin with benzylic alkoxylation has a relatively higher stability to the acidic reaction medium at such a lower temperature and that mass losses must also be linked to the formation of smaller fragments that are more soluble. In total, the ChCl/EG/HOTf system showed more potential to serve as a ternary DES system compared ChCl/EG/OA to achieve high EG incorporation of lignin without a serious decrease of the main linkages at a much lower temperature and a relatively longer reaction time.

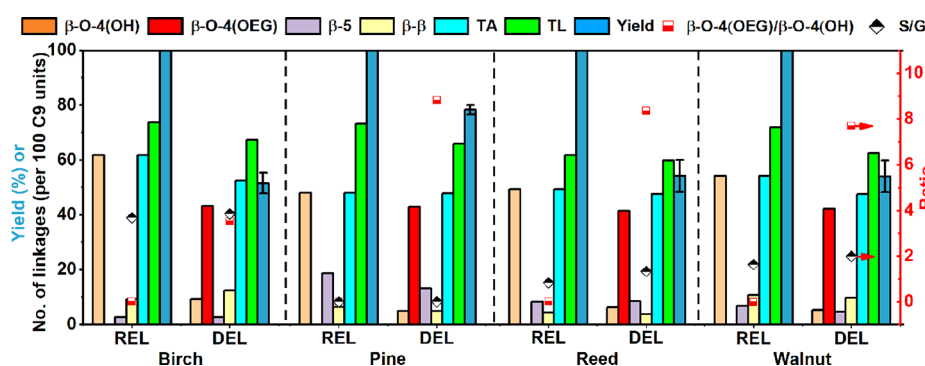


Figure 4. The main linkages and S/G ratios (calculated from semi-quantification of 2D HSQC NMR; see the detailed calculation in Eq.S1 in the SI) and yields of lignin obtained from treating REL from birch, pine, reed, and walnut shell with ChCl/EG/OA (1:2, 9%) at a 300 mg scale; REL, residual enzyme lignin; DEL, REL recovered from the treatment with ChCl/EG/OA; DES reaction condition: 12.6 g (90 mmol) of ChCl, 10.8 g (180 mmol) of EG, 300 mg of REL (from four biomasses), and 2.11 g of OA (9%, based on the total mass of ChCl and EG) at 80 °C for 36 h; β -O-4(OH), aryl ether, β -O-4(OEG), aryl ether with EG incorporation at the α position, β -5, phenylcoumaran, β - β , resins (see the original spectra in Figures S19–S26 and detailed data in Table S6). The yield was calculated by dividing the weight of the freeze-dried lignins to the weight of starting materials (eq 1).

Recyclability is vital for the application of DES to be used for lignin valorization. A high recovery yield without loss of reactivity can significantly decrease the cost of the process. We previously discussed the recyclability of the ChCl/EG/OA system.²⁸ Here, we recycled the ChCl/EG/HOTf system three times. As shown in Table S10, more than 90% recycling of DES was achieved, while the loss might be due to the consumption of EG for lignin modification and the losing during water removal and the transferring process at this relatively small scale. The loss of EG was confirmed by ¹H NMR (Figure S30). Changes to the EG signal that could indicate self-polymerization of EG were also observed by ¹H NMR. This loss of EG affected the incorporation of EG in REL_Birch, as a slight decrease in the ratio of β -O-4(OEG)/ β -O-4(OH) was observed (Figure S31 and Table S9). Overall, the ChCl/EG/HOTf system also showed the potential to be recyclable.

Scale-Up of Treating REL from Different Biomasses in the ChCl/EG/OA System. For both ChCl/EG systems with the addition of OA and HOTf, structural alteration and significant amounts of the starting material were lost upon treatment and lignin recovery. To track the mass loss more accurately and look at unrecovered products, the treatment of REL from different biomasses was scaled up to 0.3 g in the cheaper ChCl/EG/OA system for 36 h at 80 °C. The OA system was selected because it is easier to handle and likely more suitable for scale-up in contrast to DES with HOTf. As lignin from different biomasses has different percentages of the main linkages, in particular the content of the aryl ether linkage, four REL samples from birch, pine, reed, and walnut shell were used here to also see how general the structural modification and linkage cleavage were. The mass loss upon treatment showed differences for the REL samples from the four different feedstocks. The mass loss for REL followed the sequence of birch (48.4%) > walnut shell (45.8%) \approx reed (45.8%) > pine (21.7%). 2D HSQC NMR (Figure 4 and Table S6) revealed that the aryl ether linkage presented the highest percentage and followed an order of REL_Birch (61.9%) > REL_Walnut (54.4%) > REL_Reed (49.3%) \approx REL_Pine (48.1%). Nevertheless, the ratio of β -O-4(OEG)/ β -O-4(OH) ranked as DEL_Pine (8.8) > DEL_Reed (8.3) > DEL_Walnut (7.7) > DEL_Birch (3.5). It seemed that the mass loss was mainly linked to the total aryl ether content of the lignin

starting material. Lignin with a high percentage of aryl ether linkages contains more potential cleavage sites and EG modification sites that might lead to the release of more highly soluble fragments that are not readily recovered by precipitation. This could also be revealed by the slightly enhanced lowering of the linkage content after ChCl/EG/OA treatment, in particular for lignin with a higher β -O-4 linkage. Furthermore, the higher β -O-4 content also meant that more water is released from the benzylic alkoxylation that might inhibit the incorporation of EG (see Figure 1c and Scheme S1). From the 2D HSQC NMR analysis, it was found that lignin from different biomasses had different degrees of structural alteration and EG incorporation in the same DES systems. Lignin with a higher benzylic alkoxylation ratio had a relatively higher recalcitrance toward structural alteration under such acidic conditions. Overall, the results indicate that lignin with different linkage constituents needs a separate optimization of the parameters for efficient fractionation and recovery with a limited decrease of the main linkages.

After looking at the different levels of modification, the trends in the mass loss upon lignin recovery were studied in more detail. The REL samples contain different amounts of saccharide impurities such as minor amount of residual cellulose and hemicellulose components from enzymatic saccharification. Thus, the difference in mass loss might partially be caused by the removal of the saccharide impurities upon water precipitation. To investigate this, the saccharide impurities before and after DES treatment were determined and are depicted in Figure 5 (see the detailed data in Table S5). After DES treatment, the total saccharide content had significantly reduced, as observed in a previous publication,⁴⁷ but samples from birch and walnut shell still contained relatively high saccharide impurities after treatment. This revealed the saccharide removal yield (Table S5) of different RELs (based on the initial amount of saccharide impurity), followed an order of REL_Pine (82.1%) > REL_Reed (81.4%) > REL_Birch (55.9%) > REL_Walnut (51.3%). The relative percentage of cellulose in DEL was all increased except for DEL_Pine, confirming that the hemicellulose constituents degrade easier in the DES system in contrast to the cellulose components. This observation correlates to our previous study when this DES was applied on the fractionation of lignocellulosic biomass.²⁸ The correction of the saccharide

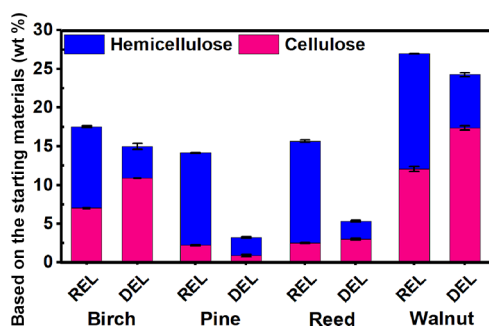


Figure 5. The carbohydrate impurities before and after treating REL from birch, pine, reed, and walnut shell with ChCl/EG/OA (1:2, 9%) in a 300 mg scale; REL, residual enzyme lignin; DEL, REL recovered from the treatment with ChCl/EG/OA; DES reaction condition: 12.6 g (90 mmol) of ChCl, 10.8 g (180 mmol) of EG, 300 mg of REL (from four biomasses), and 2.11 g of OA (9%, based on the total mass of ChCl and EG) at 80 °C for 36 h. Hemicellulose was determined by measuring the total amount of xylan and arabinan, and cellulose was calculated by the glucan content, all determined by monosaccharide analysis after hydrolysis (see the detailed procedures in the SI).

degradation for the total mass loss followed an order of REL_Walnut (13.9%) > REL_Reed (12.8%) > REL_Pine (11.6%) > REL_Birch (9.8%). The detailed data and calculation are listed in Table S5.

Overall, the loss of carbohydrate components contributed to some of the mass loss (around 10%) for lignin recovered after ChCl/EG/OA treatment. However, the mass loss of lignin after DES treatment for REL from birch, pine, reed, and walnut shell was 20–50% (Table S6). Some degraded products are expected to remain in the liquid fraction after precipitation and can potentially reveal the origin of the remainder of the mass loss. Thus, all the filtrates were extracted by DCM. The relative yields of the oil obtained from DCM extraction were in an order of birch (16.1%) > walnut shell (7.8%) \approx reed (6.6%) > pine (5.2%) that correlated with the order of mass loss and the β -O-4 content of the lignin starting material (Table S6).

The oil was analyzed by GC–MS, and of the many components observed, more than 15 compounds were identified with significant certainty (Figure 6, and mass spectra in Section S2 in the SI). The main found compounds contain aromatic acetals resulting from reaction between aldehyde

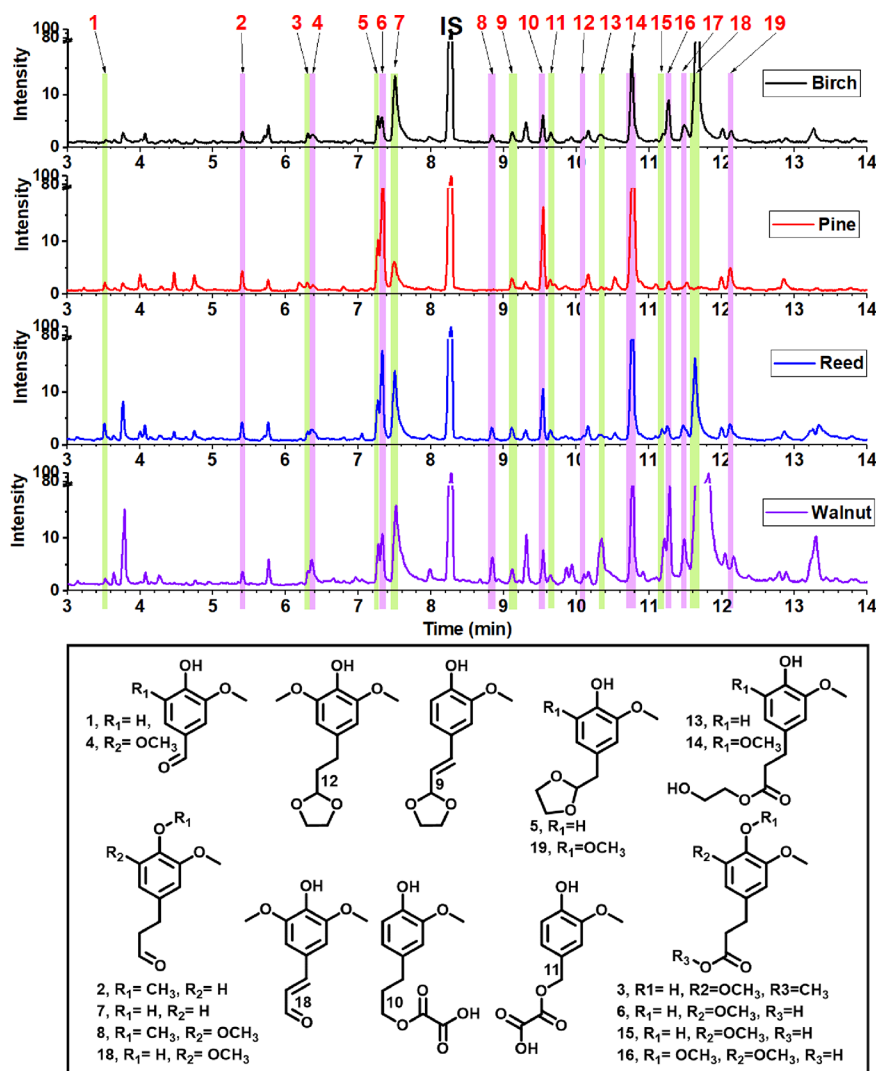


Figure 6. The GC–MS spectra of the oil extracted by DCM from the filtrate after precipitation; DES reaction condition: 0.3 g of REL from birch, pine, reed, and walnut shell under 12.6 g (90 mmol) of ChCl, 10.8 g (180 mmol) of EG, 300 mg of REL (from four biomasses), and 2.11 g of OA (9%, based on the total mass of ChCl and EG) at 80 °C for 36 h. See the original MS spectra in Section S2 in the SI.

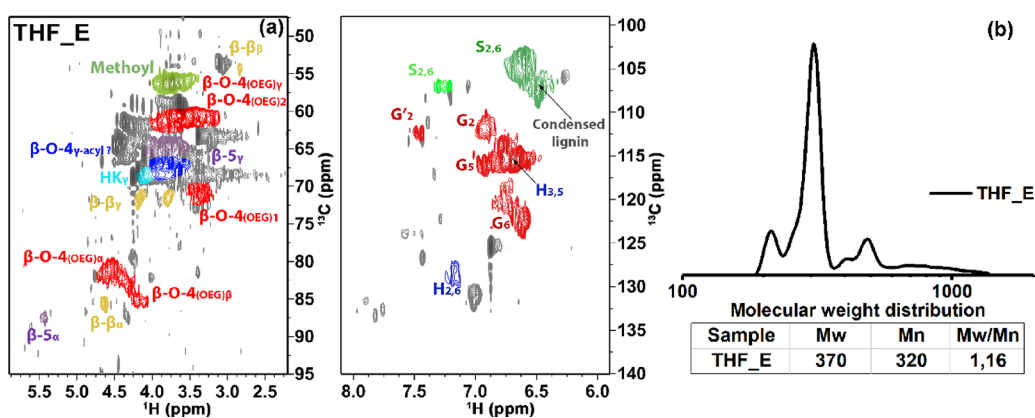


Figure 7. 2D HSQC NMR and molecular weight distribution of the oil obtained from THF extraction of the filtrate obtained after precipitation. (a) 2D HSQC NMR (see the detailed semi-quantification data in Table S8). (b) The molecular weight distribution; DES reaction condition: 0.5 g of Walnut_REL, 21 g (0.15 mol) of ChCl, 18 g (0.3 mol) of EG, and 3.51 g of OA (9%, based on the total weight of ChCl and EG) under 80 °C for 36 h.

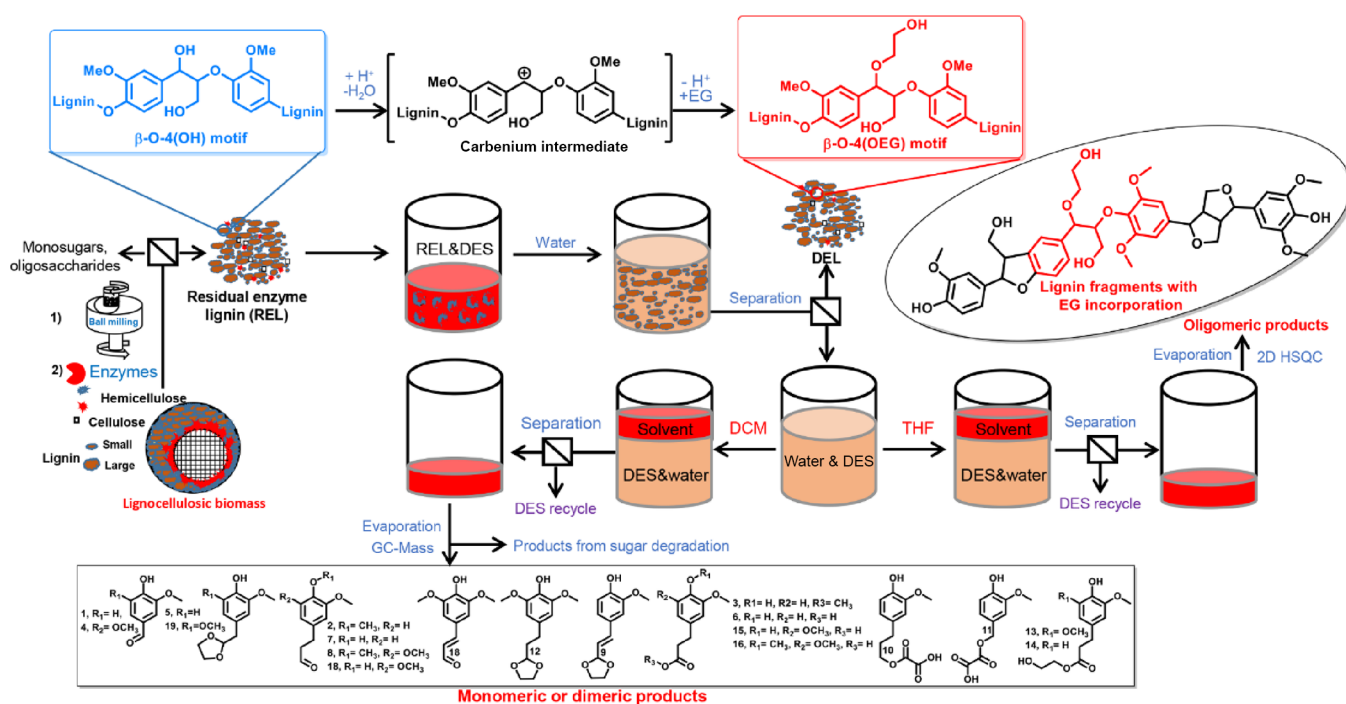


Figure 8. Schematic illustration of acidic ternary deep eutectic solvent treatment of native-like lignin.

fragments and EG, such as products 5 and 9. These two products were the main products released from the acidolysis of lignin in the presence of EG, which has been widely investigated.^{45–47} Other products such as 1, 4, 7, and 18 were observed in a previous study using acidic DES without EG present.²⁴ These indicated that the oil mainly consists of aromatic monomers released from the acid-mediated cleavage of the lignin aryl ether linkages and subsequent reaction with EG. In addition, the distribution of the products corresponded well to the parent biomass. For instance, only the G-type aromatic monomers were found in the products obtained from REL_Pine, which was due to lignin from pine wood mainly consisting of G-type lignin. These analyses confirmed the contribution of mass loss from lignin depolymerization by cleavage of aryl ether linkages.

From the above analysis, it was found that both the removal of saccharides and partial depolymerization of lignin resulted in

a higher mass loss of starting materials from the treatment of ChCl/EG/OA. Taking into account the saccharide removal and oil yield from DCM extraction, the mass losses that can be traced back from these two parts are 77.6, 53.5, 47.3, and 42.4% for REL from pine, birch, walnut shell, and reed, respectively (Table S5). Still, more than 20% mass loss was missing. This might be due to the presence of soluble lignin oligomers that were not precipitated with water. To investigate the influence of the EG incorporation on solubility, the liquid fraction obtained from treating 0.5 g of REL_Walnut in ChCl/EG/OA (mol ratio of 1:2 with 9% OA) was extracted with THF. After extraction and solvent removal, 2D HSQC NMR of these oils revealed EG-incorporated lignin fragments (Figure 7a). The molecular weight distribution obtained by GPC confirmed that these fragments were small oligomers (Figure 7b). In addition, we also scaled up the processing of REL_Walnut shell in the ChCl/EG/HOTf system and

extracted the liquid fraction with THF in the same way; clear signals from EG-incorporated lignin were observed (Figure S29 and Table S8). In contrast to lignin extracted from the ChCl/EG/OA system, the extracted lignin from ChCl/EG/HOTf has lower condensation and a higher percentage of aryl ether linkages related to the milder reaction conditions. Thus, overall, these analyses revealed that lignin treated in ChCl/EG/OA in a relatively large scale has a higher mass loss. This is mainly caused by the partial degradation of lignin and losses of saccharide impurities as well as the higher solubility of the small oligomers with higher EG incorporation.

Overview of the Fractions of REL Treated from the Acidified DES. The main fractions characterized from the treatment of REL with ChCl/EG/OA were tracked from the scaled-up experiment. Based on this a general scheme of this whole process is illustrated in Figure 8. The ChCl/EG acidified by OA could facilitate the incorporation of EG to the β -O-4 aryl ether motif, which increased not only the stability of the modified lignin but also its solubility, which could increase the loss of small lignin fragments during the purification steps as verified by the analysis of THF extraction. 2D HSQC NMR and reductive catalytic hydrogenolysis of lignin (Figure S2) before and after ChCl/EG/OA treatment clearly showed that the EG incorporation led to the lower total monomer yield (15.0–36.6 to 11.0–24.3%) even at a similar β -O-4 content of the starting material (48.1–61.9 to 47.7–52.5%). High aromatic monomers still could be obtained from DEL, even though they were lower than that of REL. This might be caused by the increased recalcitrance of EG-incorporated lignin toward reductive cleavage or by other cleavage pathways. Our previous work showed that the addition of free EG for the reductive hydrogenolysis of lignin did not influence the monomer yield and distribution; thus, the lower monomer yields were specifically caused by the EG incorporation.³⁰ These results indicated that the incorporation of EG lowered the monomer yield from reductive hydrogenolysis, making this pretreatment less suitable for this particular method of upgrading. A temperature of 80 °C and the acidic reaction conditions still induced some degradation of lignin such as the cleavage of aryl ether linkages, followed by EG-involved side reaction. This was shown by the analysis of the oil products obtained from DCM extraction. These reaction conditions also caused the removal of the saccharide impurities (hemicellulose and cellulose) as revealed by the carbohydrate analysis. All these factors influence the distribution of components in different fractions from the treatment of REL in ChCl/EG/OA. A rough mass balance was profiled in Figure S3; the fractions that could not be recovered from the acid water showed various amounts for different biomasses. Among them, REL_Birch showed the highest amount of products that dissolved in the liquid fraction, followed by REL_Reed and REL_Walnut. The least amount was calculated for REL_Pine. A detailed analysis of the products that were tracked by carbohydrate analysis and DCM extraction showed that the amount of the extracts follows a similar trend as that in the liquid fractions. This amount has a rough correlation with the amount of aryl ether linkages, further indicating that apart from carbohydrate removal, the partial depolymerization and EG modification of lignin also contributed a large proportion of mass losses, but still a higher proportion of the components that dissolved in the liquid fractions was unknown. Only THF and DCM were used to extract the liquid fractions obtained from the ChCl/EG/OA system; thus, degradation products

that do not dissolve in these two solvents or have a higher solubility in water were not traced. Therefore, the materials that are not recovered are likely fragments that are more hydrophilic with, for example, even more extensive EG modification. Further precise studies are required to track these unknown products in detailed ways.

CONCLUSIONS

The reactivity of REL in the ChCl/EG solvent system with OA and HOTf was evaluated under different reaction conditions. Both systems led to a high EG incorporation percentage of 80–85% and relatively high linkage content (60–80% of aryl ether linkages) in the recovered lignin fragments. In contrast to the OA system, the HOTf system achieved a high EG incorporation percentage of 85% at low temperature with relatively long reaction time and showed higher conversion of the main linkages. Both systems had a higher mass loss of the starting material recovered by precipitation from the treatment under the studied DES when acid loading, temperature, or time was increased. By a detailed analysis of the different fractions, the contribution to the mass loss was traced back in order of contribution to (1) the EG-incorporated oligomeric lignin fragments that have increased water solubility, (2) the partial depolymerization of lignin to monomers and other low-molecular-weight compounds, and (3) the removal of saccharide impurities. Overall, this study shows that the ternary DESs of ChCl/EG with organic acids are indeed a promising reaction media for processing native-like lignin with a high molecular weight, and the data presented in this work provides valuable insights for understanding how these systems affect the lignin structure during fractionation of lignocellulosic biomass.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02954>.

Supplementary experiment sections, results and discussion, raw 2D HSQC NMR spectra, mass spectra of the identified compounds, and other supplementary tables and figures (PDF)

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Author Contributions

Z.W. and P.J.D. were involved in conceptualization, investigation, and writing of the original draft. Z.W. and Y.L. were involved in methodology. Z.W., Y.L., and P.J.D. were involved in funding acquisition and resources. Z.W., Y.L., K.B., and P.J.D. were involved in writing, review, and editing. K.B. and P.J.D. were involved in supervision.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Z.W. and Y.L. acknowledge the China Scholarship Council for funding (grant nos. 201706300138 (Z.W.) and 201706600008 (Y.L.)). Y.L. acknowledges the National Natural Science Foundation of China (grant no. 32001280). The authors would like to acknowledge Johanna H. L. Kaelen and Lambert J. Deuss for providing the walnut shells, A. Bakker, Harkstede, for providing birch wood, and Prof. Gert Jan Euverink for providing reed for lignin isolation. Analytical support was provided by Leon Rohrbach, Johan Kemmink, Gert-Jan Boer, and Pieter van der Meulen.

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