Investigating the Depolymerization Behavior of Structurally Modified Kraft Lignin in Deep Eutectic Solvents

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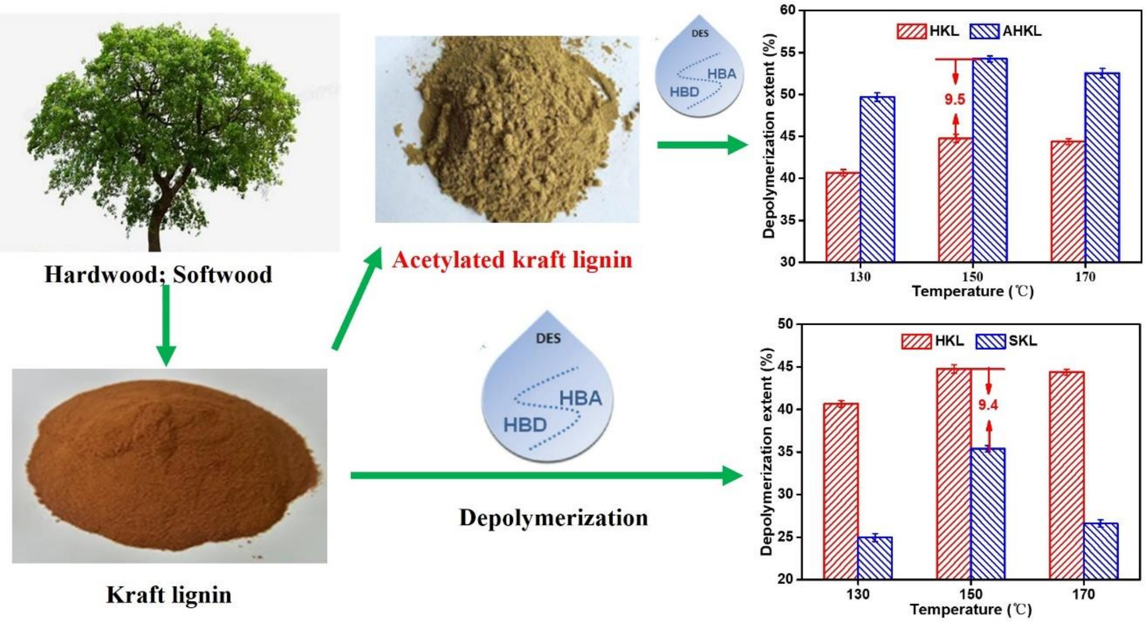
DOI: 10.15376/biores.20.1.219-234

GRAPHICAL ABSTRACT



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Deep eutectic-like solvents (DESs) are ideal green solvents for achieving depolymerization of kraft lignin under mild conditions. In this study, the impact of changes in chemical structures in hardwood kraft lignin (HKL), softwood kraft lignin (SKL), hydroxypropyl-modified hardwood kraft lignin (PHKL), and acetylated hardwood kraft lignin (AHKL) on depolymerization was investigated. The results indicated that structural modification can effectively adjust the depolymerization reaction of lignin. Under the depolymerization conditions (150 °C, 3 h, CHCl:p-TSOH), the depolymerization extent of HKL was 44.8%, which was 9.4% higher than that of SKL (35.4%). It was found that after hydroxypropyl modification of phenolic hydroxyl in HKL, the depolymerization extent of PHKL decreased to 29.5%, confirming that phenolic hydroxyl was the key functional group promoting lignin depolymerization. Acetylation modification of HKL can effectively increase the lignin depolymerization extent from 44.8% to 54.2%. The experimental results of lignin model compound addition confirmed that acetylation modification can effectively inhibit condensation reactions. The GPC analysis showed that the average molecular weight (M_w) of depolymerized oil was less than 800 g/mol and had a narrow polydispersity index ($M_w/M_n < 1.2$), making it an important precursor for high-value applications such as the preparation of aviation fuel.

DOI: 10.15376/biores.20.1.219-234

Keywords: Lignin depolymerization; DESs; Structural modification; Kraft lignin; Modification of kraft lignin

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INTRODUCTION

Degradation of industrial lignin into small molecular weight compounds is an effective way to achieve its high-value utilization. However, the kraft lignin with extremely abundant reserves currently undergoes harsh reaction conditions, resulting in ether bond cleavage to form stable carbon-carbon bonds. The complex and irregular structure of kraft lignin complicates depolymerization, and known depolymerization methods typically provide unclear products with low yields (Du *et al*. 2022). Depolymerization is an important starting point for kraft lignin value-added strategies, as it can generate valuable aromatic chemicals or provide a source of low molecular weight raw materials suitable for downstream processing (Li *et al*. 2024). How to improve the depolymerization of kraft lignin has become an urgent problem that needs to be solved.

At present, the depolymerization of kraft lignin mainly includes acid-base catalysis (Feng *et al*. 2021), pyrolysis (Yue *et al*. 2023), hydrogenolysis (Shen *et al*. 2022), and oxidative degradation (Zhu *et al*. 2018), which usually involve high temperature and high-pressure reaction conditions. It is urgent to develop an environmentally friendly and low-cost lignin depolymerization process. Deep eutectic-like solvents (DESs), as green solvent systems, have been successfully applied in the depolymerization of lignin in recent years. The term "eutectic-like" is used here as a reminder that such mixtures are seldom prepared at their true eutectic points. The acid-base properties of DESs can effectively promote cleavage of ether bonds of lignin units, making it an ideal solvent for achieving efficient depolymerization under mild conditions. Ong *et al*. (2023) found that lignin can be effectively depolymerized in the DESs system (ChCl: urea), and the yield of aromatic monomers can reach 69.8 mg/g. Li *et al*. (2023) studied the degradation of alkaline lignin in ChCl:FA, and the results showed that the phenolic hydroxyl of regenerated lignin residue increased, the M_w decreased, and high-value phenolic monomers were detected in depolymerization oil. The residual lignin (RL) obtained from DESs depolymerization has also received widespread attention in material preparation due to its structural characteristics (Hong *et al*. 2016). The above analysis indicates that lignin can be depolymerized in DESs. However, the reported DESs system currently has a low lignin depolymerization extent, and there are serious condensation problems that limit the acquisition of high-yield monomers. Therefore, how to effectively improve the depolymerization of lignin in DESs has become a difficult problem. The factors affecting lignin depolymerization mainly depend on several parameters, including reaction conditions (DESs properties, depolymerization temperature, depolymerization time, and catalyst) and the structural characteristics of lignin. Current research indicates that reaction conditions are the key factors affecting lignin depolymerization (Li *et al*. 2022). The depolymerization behavior of industrial lignin with different chemical structures in DESs is less studied. The content of alkyl aryl ether bonds between the structural units of kraft lignin is low, so how to improve its depolymerization efficiency in DES solvents is a significant and challenging topic. There are many active functional groups in the structure of lignin, including methoxy, phenolic hydroxyl, alcohol hydroxyl groups, *etc*. The presence of these groups endows lignin with good chemical activity. Previous study by the research team has shown that the structural modification of lignin have a significant impact on the distribution of pyrolysis products (Du *et al*. 2024). However, depolymerization and product formation of kraft lignin with different chemical structure in DESs are rarely reported. The aim of this study is to reveal the relationship between lignin structure and depolymerization behavior, to achieve efficient depolymerization of kraft lignin in the DESs.

Therefore, in this study, based on previous research, different methods were used to modify kraft lignin. Thereafter, the structural characteristics of modified lignin were further investigated with elemental analysis, Fourier transform infrared (FTIR), and thermogravimetric (TG) analysis. Finally, the depolymerization of lignin with different structures in DESs was studied, and the depolymerization oil was analyzed and characterized.

EXPERIMENTAL

Materials

The hardwood kraft lignin (HKL) and softwood kraft lignin (SKL) were obtained from two paper mills in Guangdong and Shangdong provinces, respectively (Chen *et al*. 2020; Du *et al*. 2024). The lignin samples were then further purified. Choline chloride

(ChCl), *p*-toluenesulfonic acid (*p*-TSOH), ethyl acetate (EA), and 2-methyltetrahydrofuran were supplied by the Aladdin Chemical Reagent Company (China).

Preparation of DESs

ChCl and *p*-TSOH were mixed to form DESs. The mixture was heated at 65 ℃ under continuous stirring for 2 h. After cooling down, the DESs were stored in a dry flask.

Lignin Modification

Hydroxypropyl modification of hardwood kraft lignin

About 1 g of hardwood kraft lignin (HKL) was completely dissolved in 10 mL of 0.5 M NaOH. A certain amount of 1,2-epoxypropane was added, and it was allowed to react at 40 ℃ for 18 h. After the reaction was completed, NaOH was neutralized with H_2SO_4, centrifuged, and washed multiple times. The as-obtained hydroxypropyl-modified hardwood kraft lignin was designated as PHKL.

Acetylation modification of HKL

About 1 g of HKL was placed in a flask containing 6 g DESs (choline chloride/acetic anhydride (1/5, w/w)) and heated to 120 ℃ for 60 min. After the reaction was complete, cooled the reactants, added 10 mL of anhydrous ethanol and 40 mL of water to deposit the lignin. The mixture was centrifuged and washed multiple times, then vacuum dried at 40 ℃ for 48 h. The acetylated-modified hardwood kraft lignin was designated as AHKL.

Depolymerization of Lignin with DESs

A total of 0.5 g lignin and 10.0 g DESs were mixed in a 100-mL flask, heated to the desired temperature (130, 150, 170 ℃) and reacted for 3 h. After the reaction was completed, the flask was cooled by cold water, and 100 mL acidic water (pH = 2) was added to the flask to precipitate the residual lignin (RL). The RL was washed multiple times with deionized water, vacuum dried, and weighed as m_1. The supernatant was extracted and subjected to rotary evaporation to obtain the depolymerization oil. Its weight was determined as m_2. The depolymerization extent was obtained using Eq. 1, the oil yield was calculated by Eq 2,

$$\text{Depolymerization extent } = \left(1-\frac{m_1}{m_{Raw}}\right)\times 100\% \tag{1}$$

$$\text{Oil yield} = \frac{m_2}{m_{Raw}}\times 100\% \tag{2}$$

where m_{Raw}, m_1, and m_2 denote the mass of lignin before degradation (g), RL (g), and lignin depolymerization oil (g), respectively.

Analytical Methods

FTIR analysis

The functional groups of lignin, modified lignin, and RL were analyzed by FTIR (Nicolet iS50, Thermo Scientific Company, USA). The wavenumber scanning range used was 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, and the scanning times were 32.

GPC analysis

The column temperature was set at 30 ℃, and the mobile phase used was tetrahydrofuran. Approximately 3 mg lignin sample was added to 3 mL THF, the solution was filtered using a 0.22-µm filter, and then injected into the column at a flow rate of 1 mL /min (Agilent Technologies Inc., Santa Clara, CA, USA).

TG analysis

TG experiments were performed with a TA Instruments Q50 thermogravimetric analyzer. Lignin, modified lignin, and RL were heated from room temperature to 800 ℃ under N_2 atmosphere at a heating rate of 10 °C/min.

Elemental analysis

The content of major elements in lignin and modified lignin was measured using a German Vario E elemental analyzer. The oxygen content in lignin was quantified by differential subtraction method.

RESULTS AND DISCUSSION

Effect of Lignin Modification on the Lignin Structure

The O–H stretching vibration of DESs depends on their intermolecular interactions between the ChCl and HBD. Fig. 1 (a) shows the FTIR analysis of prepared DESs and p-TSOH. The DESs had strong broad bands ranging from 3200 to 3600 cm^{-1}, implying the presence of hydrogen bonds between ChCl and p-TSOH. Fig. 1 (b) shows the FTIR analysis of lignin before and after modifications, The peaks at 1217 and 1115 cm^{-1} indicated that HKL was mainly composed of guaiacyl-type (G), and syringyl-type (S) units, which are consistent with the characteristics of hardwood lignin.

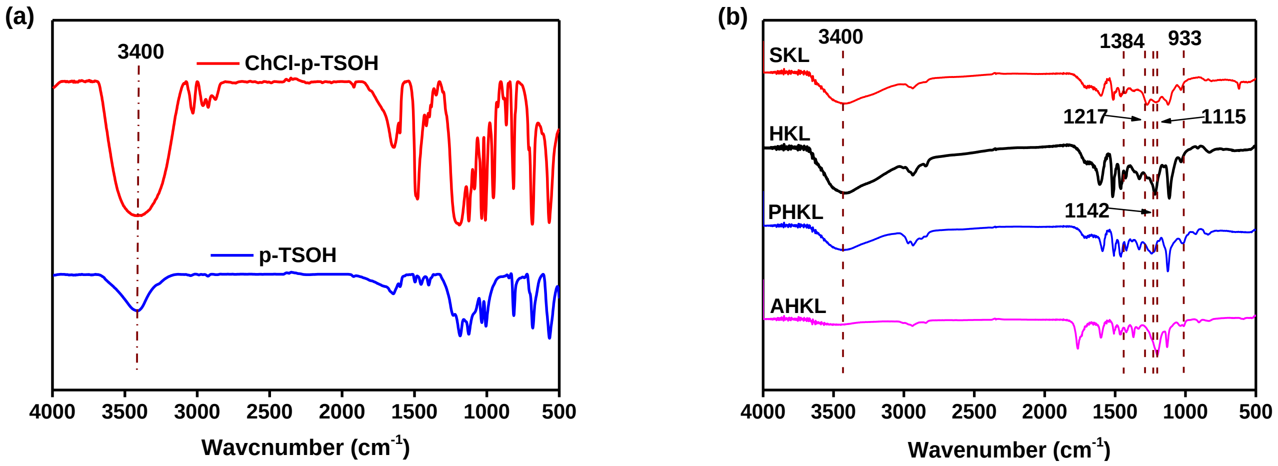

Fig. 1. FTIR spectral analysis of (a) DESs, (b) lignin before and after modifications

Compared with HKL, PHKL samples exhibited new absorbance peaks at 1142 and 933 cm^{-1}, which can be attributed to C-OH and -CH_2 bonds, respectively (Li *et al*. 2020). This result indicated that PHKL was successfully prepared through propylene oxide treatment. The broad peak at 3500 to 3300 cm^{-1} was attributed to hydroxyl groups, which were much weaker in the AHKL spectrum than in the HKL, as most hydroxyl groups in the lignin structure were shielded by acetylation modification. Acetylation has a good shielding effect on both phenolic and aliphatic hydroxyls (Li *et al*. 2020). The AHKL showed a new strong carbonyl band at 1740 cm^{-1} associated with ester bonds (C=O). This new peak was due to the esterification reaction, which reportedly leads to a sharp decrease in the OH absorption band. The absorbance peak of acetyl -C-O at 1210 cm^{-1} and acetate -C-H at 1384 cm^{-1} in AHKL indicated that the acetylation reaction was successful. The peaks of 1423, 1504, and 1593 cm^{-1} could be detected obviously in PHKL and AHKL, indicating that due to the mild modification conditions, the aromatic structure of lignin was still retained. In addition, the reference spectrum indicates that the chemical bond between PHKL and AHKL had not undergone significant changes (Du *et al*. 2024).

The elemental analyses of HKL before and after modifications are shown in Table 1. After hydroxypropyl modification, the ratio of hydrogen and carbon increased, which was due to the introduction of oxy-propyl structures. After acetylation modification, the carbon content remarkably increased from 59.9% to 62.0%, while the hydrogen and oxygen contents showed a decreasing trend.

Table 1. Elemental Compositions of Lignin Before and After Modifications

Sample	Elemental Composition (wt%)					C_9 Formula [b]
	C	H	O [a]	S	N	
HKL	59.88	5.58	31.35	2.89	0.30	$C_9H_{10.06}O_{3.53}$
PHKL	61.57	6.73	30.21	1.27	0.22	$C_9H_{11.81}O_{3.31}$
AHKL	62.03	5.29	30.56	1.84	0.28	$C_9H_{9.21}O_{3.32}$

[a] The oxygen content was quantified by differential subtraction method

[b] The C_9 formula was obtained from the results of elemental analysis

The thermal stability of modified lignin and RL was analyzed by TG. As shown in Fig. 2, the main weight loss temperature of lignin was between 200 to 500 °C. Compared with HKL, the T_{max} of AHKL and PHKL slightly increased, indicating that the modification had improved the thermal stability of HKL.

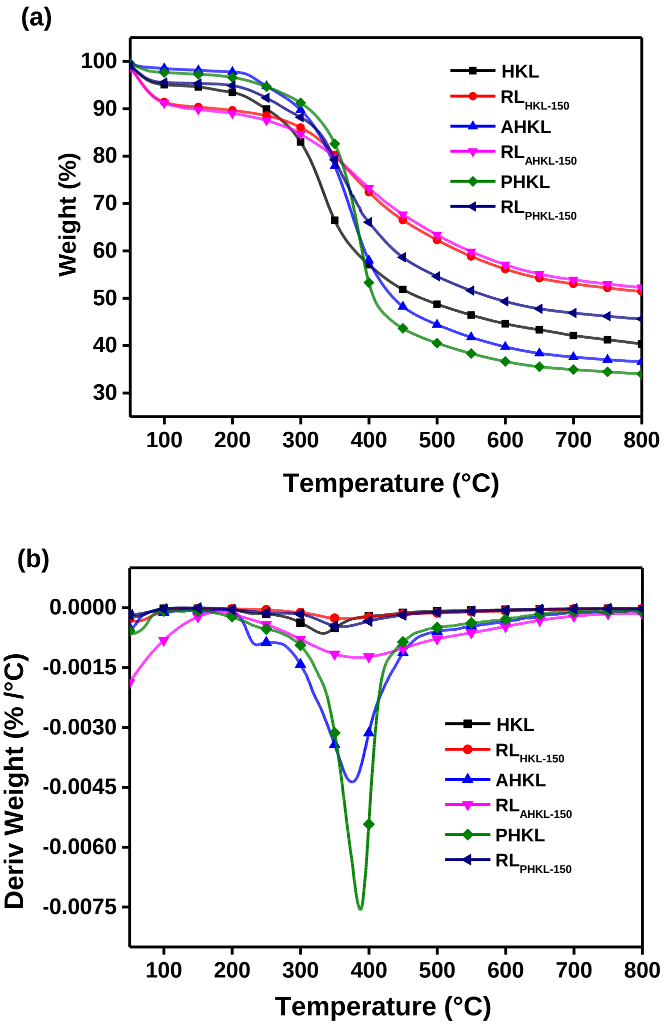

Fig. 2. TGA (a) and DTG (b) curves of lignin and RL

The results showed that the amount of pyrolysis residue after modification was lower than that of HKL, which means that more volatiles were released from AHKL and PHKL during the pyrolysis process. At the same time, it was found that the RL exhibited high thermal stability and a high amount of pyrolysis residue. The reason is that in the depolymerization process of DESs, small molecular lignin fragments were converted into depolymerization oil, and the RL was mainly composed of highly condensed macromolecular structures connected by carbon-carbon bonds. Research has shown that the depolymerization of lignin fractions was the dominant reaction during DESs pretreatment, accompanied by partial condensation reactions. The RL has high phenolic hydroxyl content, narrow dispersion coefficient, and high thermal stability. Therefore, it has the potential to prepare high-value functional materials (Hong *et al*. 2016, Wang *et al*. 2020).

The structural modification of lignin can affect the chemical bonding energy of lignin macromolecules; therefore, the mild depolymerization of modified lignin in DESs was studied.

Effect of Lignin Species on the Depolymerization

The depolymerization behavior of SKL and HKL at different reaction temperatures was investigated in the ChCl:*p*-TSOH system. The reaction time was 3 h, and reaction temperatures were 130, 150, and 170 °C. As shown in Fig. 3, compared to SKL, HKL had a higher depolymerization extent. This confirms that lignin's structure is a key factor affecting its depolymerization in DESs. The present study indicated that lignin follows an acid catalyzed depolymerization mechanism in acidic DESs. Lignin ether bonds were broken under the catalysis of acidic protons to generate small molecular lignin fragments, and the depolymerization reaction was accompanied by condensation reactions (Hong *et al*. 2020). The reasons for the higher depolymerization extent of HKL compared with SKL may be as follows: more ether bonds cleavage in the HKL or because the fragments obtained from HKL depolymerization undergo less condensation reaction. According to Table 2, due to the harsh preparation conditions, many ether bonds in the lignin structure were broken, resulting in lower ether bond content in kraft lignin (Chen *et al*. 2020; Du *et al*. 2024). Therefore, the effect of ether bond cleavage on the depolymerization extent was relatively small. At the same time, Shioya *et al*. (2017) used lignin model compounds to detect the rate of benzyl cation intermediate formation under acid hydrolysis conditions for hydroxyphenyl (H), guaiacyl (G), or syringyl (S) units. The rate was in the order of H > G > S. Therefore, it was inferred that the noticeable difference in depolymerization extent observed between the two kraft lignins in the DESs may be due to differences in product condensations. Alvarez-Vasco *et al*. (2016) found that compared with acidolysis, the condensation reaction of lignin in acidic DESs was remarkably reduced. Choline chloride in DESs can bind with lignin phenolic structures, and compared with softwood, the binding effect between hardwood phenolic structures and choline chloride was more substantial. Therefore, the small molecule phenolic fragments generated by HKL during DESs depolymerization may bind with choline chloride, inhibiting the generation of RL with high molecular weight.

Table 2. Quantitative Analysis of Internal Chemical Bonds in Lignin

Sample	β-O-4[a]	β-5[a]	β-β[a]
HKL	3.7	1.2	5.4
SKL	7.0	2.9	8.5

[a] Based on 100 aromatic ring units (Chen *et al*. 2020; Du *et al*. 2024)

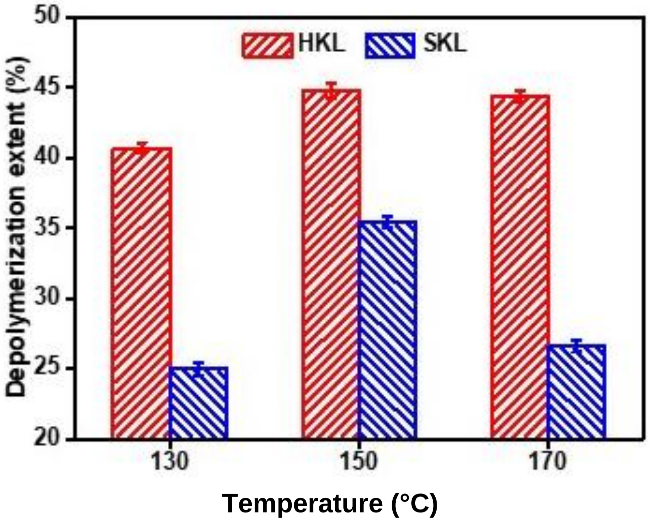

Fig. 3. Depolymerization extent of HKL and SKL at different temperatures

It is well known that lignin undergoes acid catalyzed depolymerization in the DESs, and ether bonds break to form small molecular fragments that dissolve in the DESs. Components with higher molecular weights can be precipitated by adding water. Currently, the use of larger molecular weight components as raw materials for the preparation of functional materials has been widely studied. However, there is relatively little research on small molecular fragments dissolved in DESs. In this study, EA and 2-methyltetrahydrofuran were selected as the extraction solvents to extract small molecular fragments. The molecular weight distribution of the depolymerization oil was studied by GPC analysis, and the results are shown in Table 3 and Fig. 4.

There were noticeable differences in the yield and molecular weight of the depolymerization oil at different temperatures. When the reaction temperature was 150 ℃, the yield of depolymerization oil was the highest, reaching 37.8%. As the temperature was further increased, the yield of depolymerized oil decreased to 28%. It can be seen that when the reaction temperature increased from 130 to 150 ℃, the M_w increased from 564 g/mol to 678 g/mol. This shows that as the temperature was increased, more unstable chemical bonds were broken, leading to the dissolution of larger molecular weight fragments in DESs and an increase in the molecular weight of the depolymerized oil. As the temperature was further increased, the condensation reaction intensified, some lignin fragments were polymerized to form RL, the M_w decreased to 514 g/mol.

The above analysis confirmed the depolymerization extent in Fig. 3. These results were consistent with the report by Cox and Ekerdt (2012). Compared with HKL, the yield of depolymerization oil obtained by depolymerization of SKL at 150 ℃ was 23.8%, a decrease of 14.0% in depolymerization oil yield, and a smaller M_w of only 373 g/mol. The possible reason was that the condensation reaction during the SKL depolymerization was more intense, and some larger molecular weight fragments were recondensed into RL, which is very similar to the reaction situation of HKL at 170 ℃. In addition, the presence of methoxy groups in the HKL structure leads to significant steric hindrance, hindering the condensation between polymer fragments (Gao *et al*. 2023).

Table 3. Molecular Weight and Polydispersity Coefficient of Lignin Oil

Lignin Species	Temperature (°C)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	Oil Yield (%)
HKL	130	564	515	1.10	33.68
HKL	150	678	603	1.12	37.80
HKL	170	514	474	1.08	28.00
SKL	150	373	332	1.07	23.76

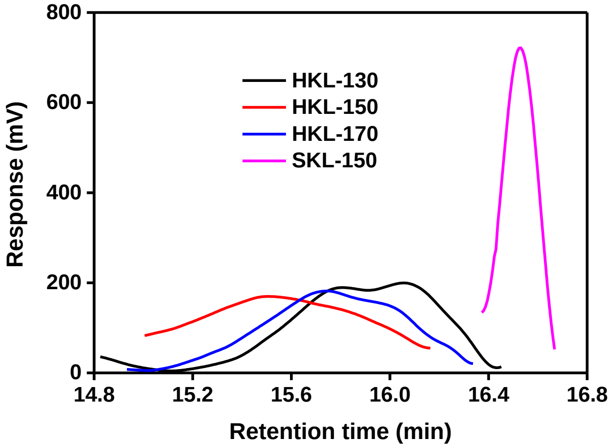

Fig. 4. Molecular weight distribution of lignin oil

Based on the above analysis, it can be concluded that the structural differences between HKL and SKL remarkably affect their depolymerization behavior in DESs. At the same time, it was found that increasing the depolymerization temperature did not further promote the increase of the depolymerization extent. In contrast, severe condensation behavior will lead to a decrease in the yield of depolymerization oil. Therefore, based on the authors' previous proposal of a "two-step" pyrolysis method for lignin, a new approach has been developed to achieve high yields of pyrolysis oil and product control. In the DESs depolymerization process, the lignin structure was first selectively modified through physical or chemical means, and then the chemically modified lignin was depolymerized under optimized depolymerization conditions to achieve the goal of regulating depolymerization products and producing high-quality chemicals. The above analysis showed that the depolymerization extent of HKL was relatively high. Therefore, HKL was chosen for further study on the effect of modification on depolymerization. Sturgeon *et al.* (2014) used model compounds to investigate the acid-catalyzed depolymerization mechanism of β-O-4 ether bonds. The study showed that the extent of acid-catalyzed β-O-4 cleavage in dimers having a phenolic hydroxyl group was 2 orders of magnitude faster than in non-phenolic dimers. Due to the presence of electron withdrawing hydroxyl groups, the benzylic carbocation was delocalized onto the hydroxyl group, promoting the stability of the carbocation intermediate. In addition, it has been shown that the hydrogen bonds between lignin and DESs can facilitate the cleavage of ether bonds (Wang *et al.* 2022; Ong *et al.* 2023). Based on the cited work, hydroxyl groups in lignin structure may be the key factor affecting lignin depolymerization. Therefore, hydroxypropyl modification and acetylation modification were chosen to investigate the depolymerization behavior of modified lignin in DESs.

The hydroxypropyl modification of the phenolic hydroxyl in HKL was carried out using 1,2-epoxypropane, and the effect of the presence of phenolic hydroxyl group on depolymerization in an acidic DESs was investigated. Fig. 5 shows the depolymerization extent and oil yield of HKL at different temperatures before and after hydroxypropyl modification. It can be seen that the depolymerization extent and oil yield of HKL decreased after hydroxypropyl modification. When the reaction temperature was 150 °C, the depolymerization extent decreased from 44.8% to 29.5%, and the oil yield decreased from 37.8% to 20.3%. Further increasing the reaction temperature did not increase the depolymerization extent, consistent with the result of Sturgeon *et al*. (2014). This confirmed that phenolic hydroxyl groups can effectively promote the cleavage of ether bonds during acid catalysis process. Table 4 and Fig. 6 show the GPC analysis of the depolymerized oil at 150 °C. It can be observed that the M_w of PHKL depolymerized oil decreased. During the acidic DESs depolymerization process of lignin, the active protons in the acidic solvent attack the C_α-OH to obtain carbocations. Unstable carbocations can be deprotonated to form enol ether structures. On the one hand, it may further degrade into small molecular fragments, and on the other hand, it may undergo repolymerization reactions with active fragments. Due to the presence of carbocations and enol ether structures, repolymerization reactions are prone to occur. The possible reason was that the presence of hydroxypropyl groups leads to the timely stabilization of the active intermediates that promote repolymerization (Li *et al*. 2020). In addition, the shielding of phenolic hydroxyl groups may also be one of the reasons for inhibiting product condensation (Zhu *et al*. 2016). This inference explains the experimental results that when the reaction temperature increased to 170 °C, HKL had undergone severe condensation, resulting in a decrease in depolymerization oil yield, while PHKL depolymerization oil yield further increased.

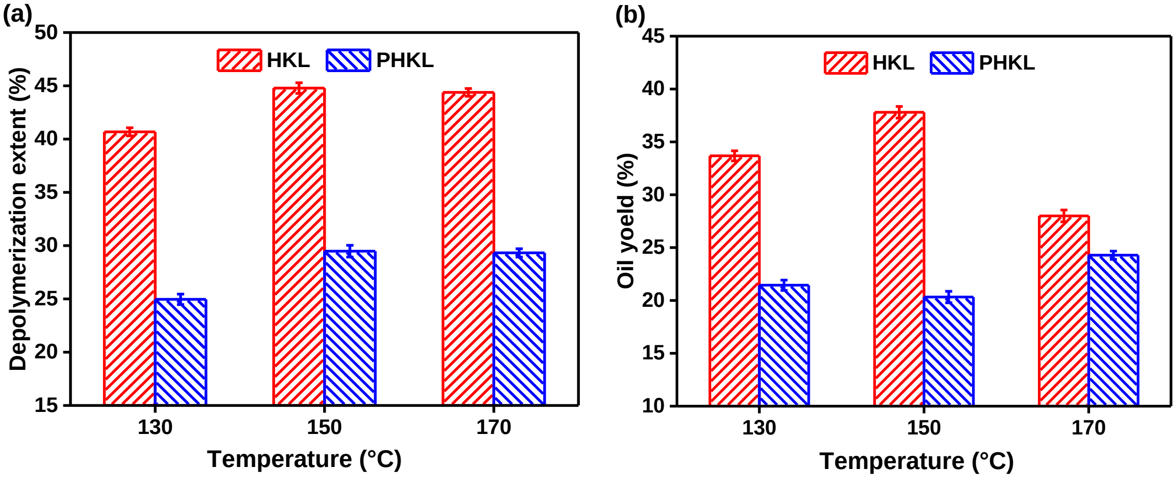

Fig. 5. Lignin depolymerization extent (a); and oil yield (b) before and after hydroxypropyl modification at different temperatures

Table 4. Molecular Weight and Polydispersity Coefficient of Lignin Oil

Lignin Species	M_w (g/mol)	M_n (g/mol)	M_w/M_n
HKL	678	603	1.12
PHKL	457	412	1.11

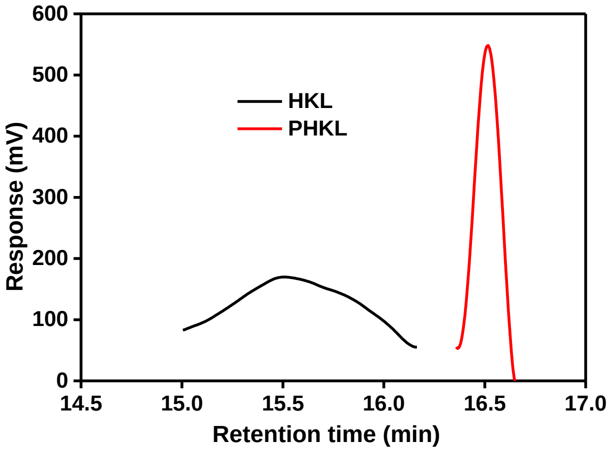

Fig. 6. Molecular weight distribution of lignin oil

Intrinsically, the efficient depolymerization of lignin and the obtaining of low molecular phenolic compounds with high yield mainly depend on the competition between ether bond cleavage and condensation of depolymerization intermediates. Therefore, the key point of lignin depolymerization process is how to effectively inhibit the condensation reaction during lignin depolymerization process. Numerous scholars have studied the effect of adding novel capping agents on the products, and the results showed that the addition of novel capping agents effectively improves the yield and quality of depolymerized oil (Qi *et al*. 2020). From the perspective of the structure of lignin, there is relatively little research on the effect of lignin structure on product condensation through pretreatment of lignin. Studies have shown that acetylation of phenolic monomers during lignin depolymerization can inhibit further condensation (Nandiwale *et al*. 2019). Shuai *et al*. (2016) reported that under acid conditions, formaldehyde (FA) reacts with 1,3-diols (and their α- and γ-hydroxyl groups) on lignin side-chains to form a stable six-membered 1,3-dioxane structure, blocking the formation of phenyl cations. Zhu *et al*. (2018) predicted the depolymerization of veratrylglycerol-β-guaiacyl ether (VG) in acidic ionic liquids through calculations. Adding formaldehyde can prevent the depolymerization of VG without remarkably changing the mechanism of depolymerization. Therefore, in this study, the hydroxyl groups in the lignin structure were acetylated and the impact of acetylation modification on lignin depolymerization in DESs was investigated.

The depolymerization extents of HKL at different temperatures before and after acetylation modification are shown in Fig. 7. It can be seen that after acetylation modification, the depolymerization extent of lignin in acidic DESs was increased. The depolymerization extent was increased from 44.8% to 54.2% at 150 °C. At the same time, as the temperature further increased to 170 °C, the depolymerization extent was 52.5%, which did not noticeably decrease, indicating that the condensation of lignin active fragments was inhibited after acetylation modification. In addition, Fig. 2 shows that the amount of $RL_{\mathrm{AHKL\text{-}150}}$ pyrolysis residue obtained was relatively low, further confirming that the condensation reaction of AHKL in DESs was inhibited. It can be observed that the yield of depolymerized oil can be improved after acetylation modification. At a depolymerization temperature of 150 °C, the yield of depolymerized oil increased from 37.8% to 41.4%, an increase of about 3.6%. According to Table 4 and Fig. 8, the depolymerized oil obtained after acetylation modification had a smaller molecular weight

(< 800 g/mol) and a narrow molecular weight dispersion. Therefore, there is potential for upgrading to aviation fuel through mild hydrogenation deoxygenation (Peng *et al*. 2023)

Deuss *et al*. (2015) have shown that unstable C2 aldehydes participate in the re-condensation process during lignin acidolysis, which is an important factor leading to the generation of high molecular weight by-products. To confirm the conclusion that acetylation modification can effectively inhibit product condensation, phenylacetaldehyde was selected as an additive, and the effect of phenylacetaldehyde addition on depolymerization was investigated. As shown in Fig. 9, the addition of phenylacetaldehyde remarkably reduced the depolymerization extent, and the depolymerization extent of HKL decreased from 44.8% to 10.8%, a decrease of 33.9%. It has been confirmed that during the acidolysis process, phenylacetaldehyde can condense with depolymerization active intermediates to generate high molecular weight by-products. Compared with HKL, adding the same proportion of phenylacetaldehyde to AHKL reduced the lignin depolymerization extent from 54.2% to 22.9%, a decrease of 31.3%. It has been confirmed that the condensation effect of unstable C2 aldehydes on lignin is inhibited after acetylation modification.

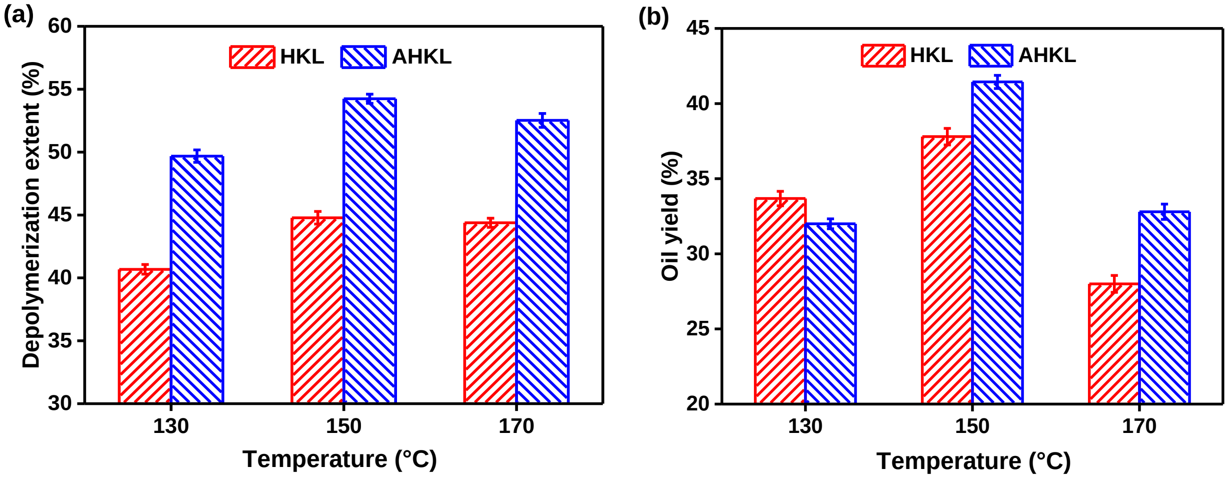

Fig. 7. Lignin depolymerization extent (a); and oil yield (b) before and after acetylation modification at different temperatures

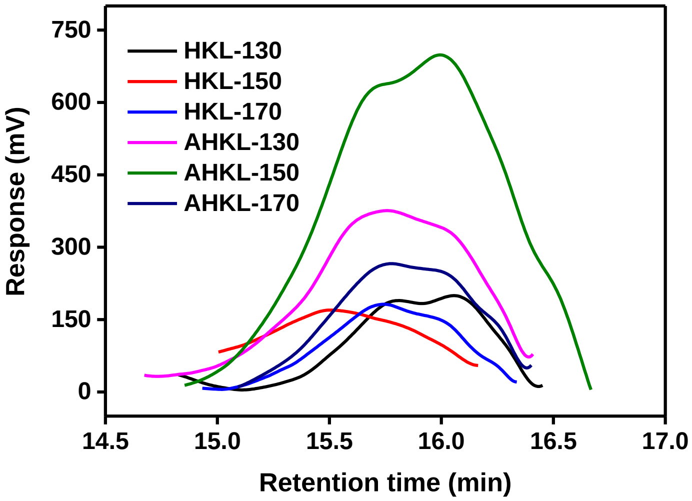

Fig. 8. Molecular Weight distribution of lignin oil

Table 5. Molecular Weight and Polydispersity Coefficient of Lignin Oil

Lignin Species	Temperature (ºC)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
HKL	130	564	515	1.10
HKL	150	678	603	1.12
HKL	170	514	474	1.08
AHKL	130	598	543	1.10
AHKL	150	537	501	1.07
AHKL	170	536	482	1.11

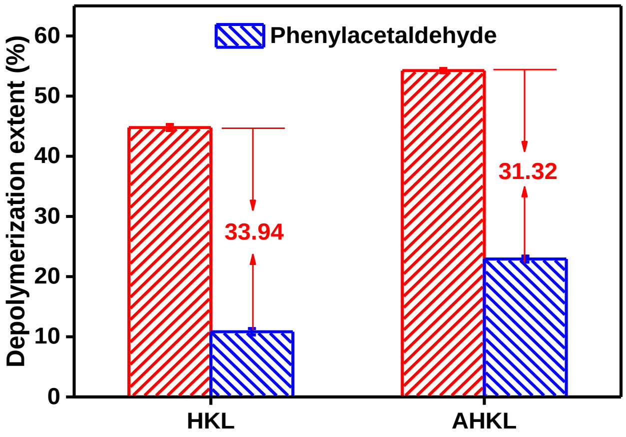

Fig. 9. The depolymerization extent of adding phenylacetaldehyde in HKL and AHKL

CONCLUSIONS

The structural modification can effectively adjust the depolymerization reaction of kraft lignin.

1. Hardwood kraft lignin exhibited a higher depolymerization extent compared to softwood kraft lignin.
2. Phenolic hydroxyl groups can effectively increase the depolymerization extent in acidic DESs. Under acidolysis conditions, unstable C2 aldehyde fragments are the main cause of condensation reactions. Acetylation modification can effectively inhibit the condensation reaction, and the lignin depolymerization extent can be increased by 9.5%.
3. Research showed that lignin modification can provide a new pathway for achieving mild degradation and production of low molecular weight chemicals in DESs systems.

ACKNOWLEDGMENTS

This work is partly funded by the National Natural Science Foundation of China (32271807), and the Guangdong Basic and Applied Basic Research Foundation (2024A1515011941).

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Article submitted: August 17, 2024; Peer review completed: October 5, 2024; Revised version received: October 30, 2024; Accepted: October 31, 2024; Published: November 11, 2024.
DOI: 10.15376/biores.20.1.219-234