



# Conversion of Lignin into Phenolic Monomer and Low Molecular Weight Bio-oil in Different Supercritical Solvent System

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## Abstract

High-value utilization of lignin is crucial in further developing biomass refining processes and producing biofuels. In this work, lignin depolymerization was examined in different supercritical systems. The effects of reaction temperature and reaction time on various lignin depolymerization products were investigated in detail. Among them, in the supercritical ethanol/water system (50% ethanol), the  $\beta$ -O-4 aryl ether bonds of lignin were depolymerized into phenolic hydroxyl groups, alcoholic hydroxyl groups and alkyl groups through hydrogenation and hydrolysis reactions. The lignin intermediate fragments produced by depolymerization undergo further hydrocracking to form more low molecular weight products such as 4-alkylguaiacols. In addition, low molecular weight lignin intermediates also produced lignin oligomers and carbon solid residues (SR) through repolymerization reactions. When the reaction temperature was higher than 360 °C, the repolymerization reaction between the highly active lignin depolymerization intermediates could be promoted to form more SR products. All in all, when the reaction temperature was 300 °C, lignin was more suitable for depolymerization into phenolic monomer products during the supercritical ethanol/water system (1/1, v/v).

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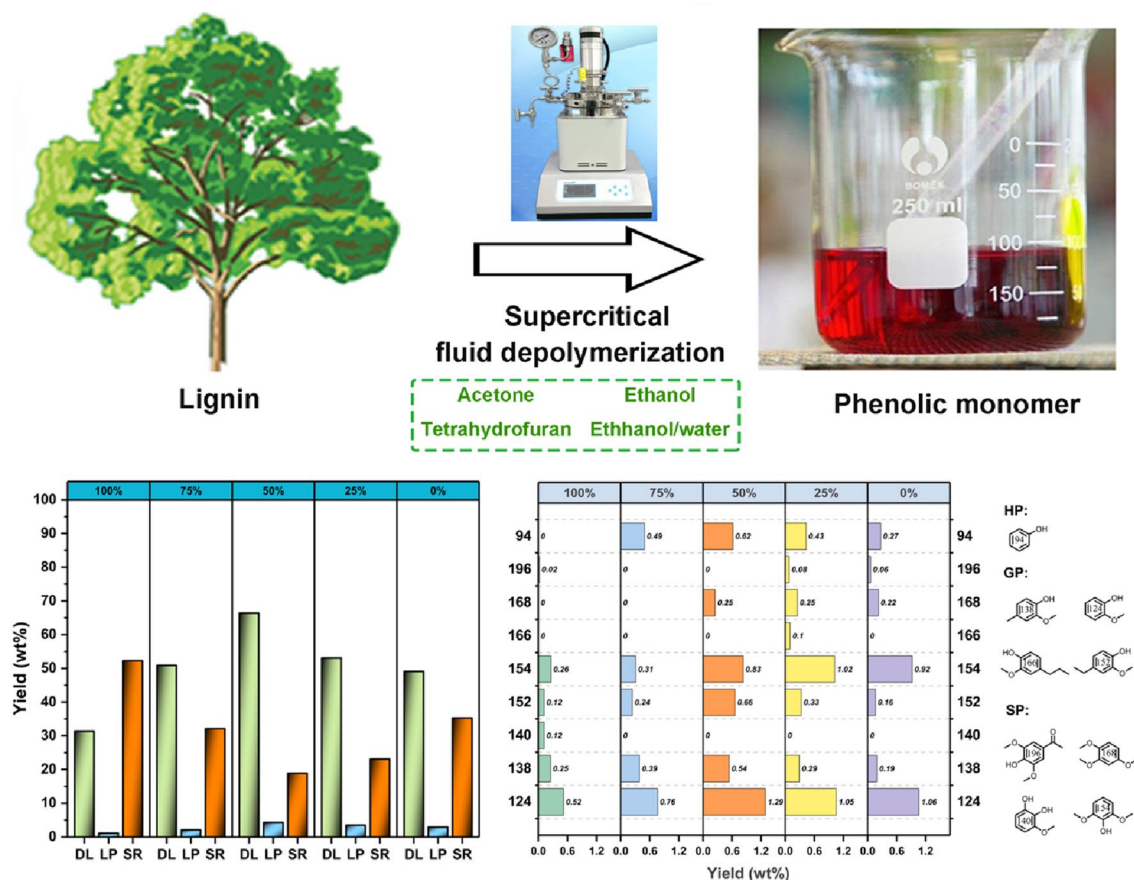
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## Graphical Abstract



**Keywords** Lignin · Depolymerization · Supercritical solvent system · Phenolic monomer · Bio-oil

## Statement of Novelty

Depolymerization of lignin is an important step to obtain a lignin monomer for the synthesis of functional chemicals. In the context of more lignin produced from biomass and pulp industry, converting real lignin with low purity is still required more studies. In this work, the lignin depolymerization was examined in different supercritical systems. The effects of reaction temperature and reaction time on various lignin depolymerization products were investigated in detail. Results showed that the maximum ethyl acetate-soluble depolymerization products of 67.32% and the minimum solid residue yield of 19.27% was under the condition of 300 °C, 300 min, and ethanol 50%.

## Introduction

Recently, the problem of fossil energy is the driving force for global search for new alternative sources of energy and chemicals [1, 2]. Biomass, as the only carbon-neutral renewable energy source, can be considered as a promising potential substitute for fossil fuels since it can be used to synthesize liquid oils and other correlative high value-added chemicals [3, 4]. As the typical and major component of lignocellulosic biomass, lignin is the most abundant natural phenolic polymer and a particularly promising resource in the world [5, 6]. It is made up of three major units, such as syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H), which connects together through C–C and C–O bonds [7, 8]. Therefore, high-calorific liquid fuels and aromatic monomers that extracted from lignin by breaking the C–C and C–O bonds, will greatly increase the supply of power and chemicals and then improve biomass utilization.

To date, kinds of methods for lignin conversion have been explored in plentiful studies, including biochemical transformation, catalytic depolymerization, pyrolysis and enzyme catalyzed photocatalytic [5, 6, 9–15]. Nevertheless, most of these methods are difficult to inhibit the repolymerization reaction and with low product yield and selectivity [16, 17]. Thus, it is necessary to find an efficient method for lignin conversion. At present, supercritical fluids have found applications for the chemical conversion of lignin due to their unique properties [18, 19]. It possess unique transport properties (gas-like diffusivity and liquid-like density), and also have the ability to dissolve materials not normally soluble in either the liquid or gaseous phase of the solvent and, hence, promote the gasification/liquefaction reactions [17, 20]. Meanwhile, during the whole reaction process, by regulating the temperature and pressure of the supercritical fluid, not only the conditions of the polymerization reaction are adjusted, but also the physical and thermochemical properties of the fluid are changed, thereby the better depolymerization effect can be achieved without adding catalyst or less number of catalyst [17, 21]. Particularly, under the near supercritical or supercritical conditions, the reaction fluid solvents are extremely active and can also provide abundant ions or free radicals for the catalytic system, such as water, methanol, ethanol and acetone etc. [22–27]. For example, Saisu et al. and Okuda et al. studied the depolymerization of lignin in supercritical water and water/phenol, they preliminatively discussed the influence mechanism of the presence of phenol on the depolymerization of lignin [28, 29]. Meanwhile, it was believed that the hydrolysis reaction and dealkylation reaction of lignin in supercritical water could be generated low molecular weight lignin fragments and mixtures, such as eugenol, guaiacol and catechins. Bata et al. used copper porous metal oxides as catalysts to depolymerize organic solvent lignin in supercritical methanol [30]. They believed that hydrogen radicals on methanol would cause phenyl ether bond cleavage and aromatic epoxidation by transferring to lignin. Yong et al. studied the chemical kinetics models of the main decomposition pathways of simple model substances such as benzene and phenol in supercritical water in order to clarify the initial mechanism of lignin depolymerization to form carbonates and gases in supercritical water [31]. In addition, Tang et al. found the catalytic hydrolysis of lignin in supercritical methanol, mainly observing that the catalyst Ru could be catalyzed the depolymerization of lignin into liquid fuel and detecting that its composition was mainly phenolic, anisole, ester, ketones, and alcohols [32]. They believed that lignin depolymerization route in the supercritical ethanol depolymerization pathway was speculated through comprehensive analysis of phenolic products and coke products. Despite the apparent promise of different organic solvent for lignin supercritical fluid depolymerization, there is a lack of

detailed knowledge about its role in obtaining high product yield. Thus, understanding the influences of different solvent effects on the lignin depolymerization products are highly desirable to rationally design supercritical systems for the high-valorization of lignin.

Herein, the aim was to screen the effect of yield and distribution of phenolic monomer products during lignin depolymerization with different solvents. The yield and distribution changes of various depolymerization products were studied in detailed to determine the supercritical reaction solvent and reaction conditions for the preparation of high yields of phenolic monomer and low molecular weight of lignin bio-oil. In summary, the research can provide theoretical basis for the production of phenol-rich bio-oil from lignin during the supercritical organic solvent system and have important significance for promoting the high value utilization of lignin.

## Materials and Methods

### Materials

The raw material was poplar wood chips, provided by Yue Yang Paper Co., Ltd. The wood chips were 40–60 mm, long and 20–30 mm wide. After being manual selected and dusted off, they were put into sealed bags to balance water content. All chemical reagents used were analytical grade.

### Extraction of Lignin

The extraction condition of lignin from poplar ethanol pulping black liquor were as follows: ethanol concentration 60%, liquid ratio 1:10, maximum temperature 205 °C, holding time 150 min and adding the black liquor to pH 2. After standing overnight, lignin was separated by centrifugation and collected. Finally, lignin was frozen in a refrigerator and dried in a freeze dryer. The obtained lignin was named as ethanol lignin.

### Characterization of Lignin

The purity of lignin was determined by National Renewable Energy laboratory's (NREL) standard analytical procedure [33, 34]. The monomeric sugar in two-step hydrolysis liquid were measured by ionic chromatography (Waters e2695, USA) [35]. Crude lignin of about 0.1 g was weighed and placed in 150 mL conical flask, and 1.5 mL 72% concentrated H<sub>2</sub>SO<sub>4</sub> was accurately added. After the mixture was evenly mixed, the lignin was placed in 20 °C constant temperature shaker for 2 h, and 42 mL was added when reaction time came. Deionized water was hydrolyzed in 121 °C constant temperature oil bath for 1 h and then filtered by G3

glass crucible to collect filtrate. Dilute hydrolysate ten times and filter with 0.45  $\mu\text{m}$  water filter headed. The filtrate was detected ion chromatograph of Diane Corporation.

The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ , PDI) of lignin were determined by GPC analysis [36, 37]. The specific test condition was as follows: 1 mg lignin was dissolved in 0.5 mL chromatographic tetrahydrofuran (THF), and the dissolved liquid was filtered by an organic filter with three chromatographic columns. The styragel column was used in series with mobile phase THF at flow rate of 1.0 mL/min and test temperature of 30 °C. Polystyrene was used as standard sample.

### Solvent Depolymerization of Lignin

A certain amount of lignin was dissolved in organic solvent (acetone, THF, ethanol and ethanol/water) in a 100 mL high temperature and high pressure reaction kettle (Model RT100, Jiangsu). The mass ratio of lignin to organic solvent was 1:20, set the reaction temperature and time as required by experiment. When the reaction reached the required time and temperature, took out the reaction kettle quickly and putted it in cold water to cool down rapidly. When it reached room temperature, opened the reaction kettle and collected the depolymerization products. The separation process of liquid and solid products after depolymerization with different supercritical solvents was shown in Fig. 1. In supercritical organic solvent system, acetone had good solubility in unreacted lignin. At the end, all the unreacted lignin and lignin oligomer were dissolved by acetone, and solid residue (SR) was separated through filtration. The liquid phase product of the solvent was re-dissolved with deionized water after removing the organic solvent by rotary evaporation. After centrifugation, water-soluble phase product was obtained and lignin-phenolic monomer (LP) was obtained after extraction with ethyl acetate. Since ethyl acetate did not dissolve unreacted and condensed lignin, the solid

product in the insoluble phase was dissolved in water for separation with ethyl acetate to obtain ethyl acetate-soluble depolymerization products (DL) and ethyl acetate-insoluble solid products (mainly residual and condensed lignin, IDL), respectively.

### Analysis of Liquid Phase Monomer Products

The composition of liquid phase products after depolymerization of lignin with organic solvent was determined by GC-MS. SCION 456 GC-TQ Gas chromatography-Triple quadrupole mass spectrometer (Bruker, USA) was used. The column was DB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). Injector temperature 250 °C. Flow rate was 1 mL/min and split ratio was 50:1. The initial temperature was 50 °C and kept for 2 min. The temperature was raised to 250 °C at 5 °C/min and kept for 20 min. Total analysis time was 62 min. The sample dilution procedure for compound similarity was compared with database NIST11 as follows: ethyl acetate phase products obtained in accordance with the separation process in Fig. 1 were injected in a 50 mL volumetric flask with this solution as the sample. GC-FID was used for the quantitative detection of each component in the liquid product. The quantitative method was Effective Carbon Number method (ECN) to determine the relative response factor (RF), and *n*-dodecane was used as the internal standard for RF correction.

The yield of lignin monomer from residual lignin carbon residue was calculated as follows:

$$\text{Yield of LP(wt\%)} = \frac{\text{wt. of monomer (calc. from GC-FID)}}{\text{wt. of starting protobind lignin}} \times 100\%$$

$$\text{Yield of DL(wt\%)} = \frac{\text{wt. of DL}}{\text{wt. of starting protobind lignin}} \times 100\%$$

$$\text{Yield of SR(wt\%)} = \frac{\text{wt. of SR}}{\text{wt. of starting protobind lignin}} \times 100\%$$

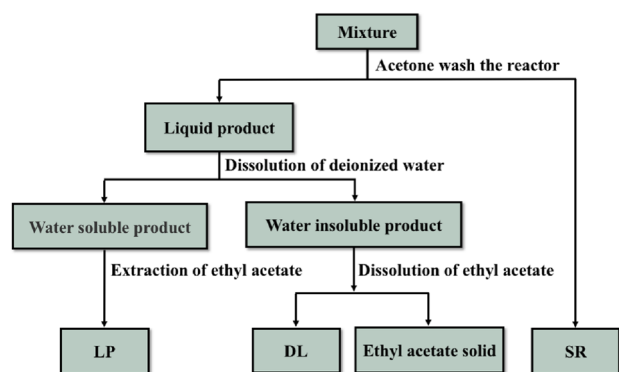


Fig. 1 Separation processes of lignin depolymerization products

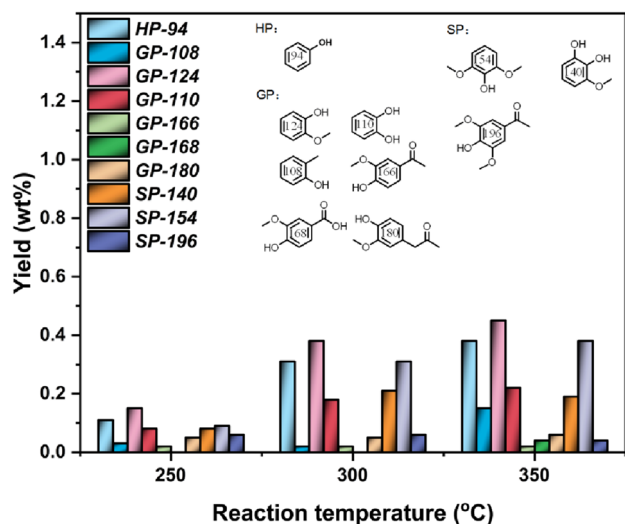
## Results and Discussion

### Purity and Molecular Weight Analysis of Lignin

The contents of ash and sugar impurities of lignin are shown in Table 1. Clearly, the contents of ash and total sugar in extracted lignin are 0.56% and 1.27%, respectively. Among them, the sugars contained in lignin are mainly xylose and glucose, which may be LCC structure formed by lignin and carbohydrates. In general, the content of sugar impurity is

**Table 1** Purity and molecular weight of lignin

Sample	Ash (%)	Sugar (%)						$M_w$ (g/mol)	$M_n$ (g/mol)	PDI
		Ara	Gal	Glu	Xyl	Man	Total			
Lignin	0.56	0.02	0.05	0.17	0.96	9.97	1.27	4270	2880	1.48

**Fig. 2** Effect of reaction temperature on the product distribution of lignin depolymerization at supercritical acetone solvent

small in total lignin, and the error caused by subsequent analysis of lignin depolymerization product is small, which basically meets the experimental requirements. In addition, the molecular weight of lignin is also shown in Table 1. Apparently, the  $M_w$  of lignin is 4270 g/mol, and the PDI of lignin is 1.48.

### Distribution of Lignin Depolymerization Products in Supercritical Acetone Solvent

In the process of supercritical solvent depolymerization of lignin, the supercritical temperature of the reaction solvent is an important factor for the distribution of lignin depolymerization products in organic solvents. Increasing the reaction temperature can not only promote the thermochemical depolymerization of lignin intermolecular bond, but also promote the active repolymerization reaction between the intermediate of lignin depolymerization.

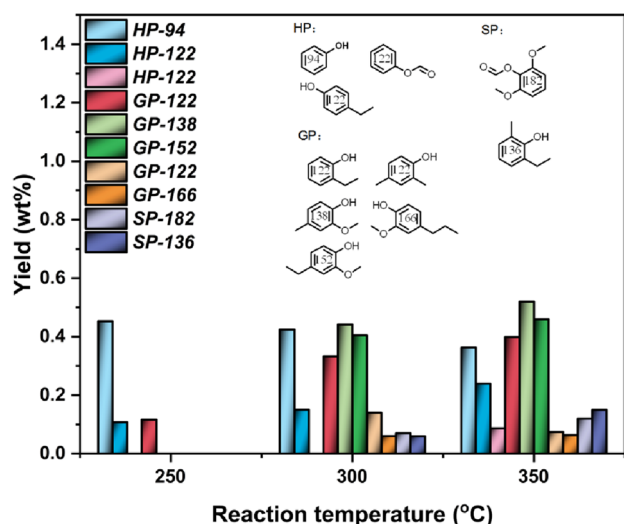
After lignin depolymerization reaction with supercritical acetone solvent, the depolymerization product is separated according to the separation process shown in Fig. 1. The isolated phenolic monomer products are detected by GC-MS and GC-FID and the yield is calculated. As shown in Fig. 2, it is the structure and yield distribution of depolymerization products. The phenolic monomers comprising lignin are mainly divided into three categories: Guaiacyl-type (G-type), Syringyl-type (S-type) and *p*-hydroxyphenyl-type

(H-type) structural monomers [38, 39]. Simultaneously, according to the structural characteristics of LP products, the products are also divided into guaiac-based monomer derived phenols (GP) and syringyl monomer derived phenols (SP) and *p*-hydroxyphenyl monomer derived phenols (HP). In Fig. 2, the product distribution of lignin depolymerization product in supercritical acetone at different temperatures shows that when the reaction temperature is lower than 250 °C, the monomer products are very few. It indicates that the intramolecular bond fracture of lignin, such as  $\beta$ -*O*-4,  $\alpha$ -*O*-4 aryl ether bonds, is less at this temperature and has not reached the condition of forming monomer products. When the temperature reaches 300 and 350 °C, the LP products are increased significantly, mainly guaiacol eugenol, while a small amount of cresol and catechol products are appeared, indicating that in supercritical acetone solvent, in addition to ether bond hydrolysis, alkylation demethoxylation and demethylation reactions occur. In particular, the  $\beta$ -*O*-4 ether bond between guaiac-based syringyl and other basic connecting units in lignin is broken by hydrolysis reaction, resulting in the formation of guaiacol and eugenol, followed by further demethylation reaction to form phenol-cresol and catechol. Besides, as the reaction temperature increases, the LP products yields of guaiacol (124) and eugenol (154) gradually increase, indicating that high temperature in supercritical acetone solvent is conducive to improving the degree of ether bond hydrothermal depolymerization in lignin. By comparing the yield of guaiacol and eugenol monomers at various temperatures, it can be found that the yield of guaiacol monomer is greater than that of eugenol monomer, and there is no obvious LP with *p*-hydroxyphenyl structure in the product. On the one hand, the structural units of poplar lignin are mainly G-type and S-type, but no H-type. On the other hand, the source of phenol in LP products may be caused by  $\beta$ -*O*-4 ether bond fracture and G-type demethoxylation.

### Distribution of Lignin Depolymerization Products in Supercritical Tetrahydrofuran Solvent

The LP products are also separated according to the process shown in Fig. 1 after supercritical tetrahydrofuran solvent depolymerization. It can be seen from the LP product distribution of lignin-dissociated monomer in supercritical tetrahydrofuran at different temperatures in Fig. 3 that when the reaction temperature is lower than 250 °C, HP is the main product, and phenol has the highest yield, indicating



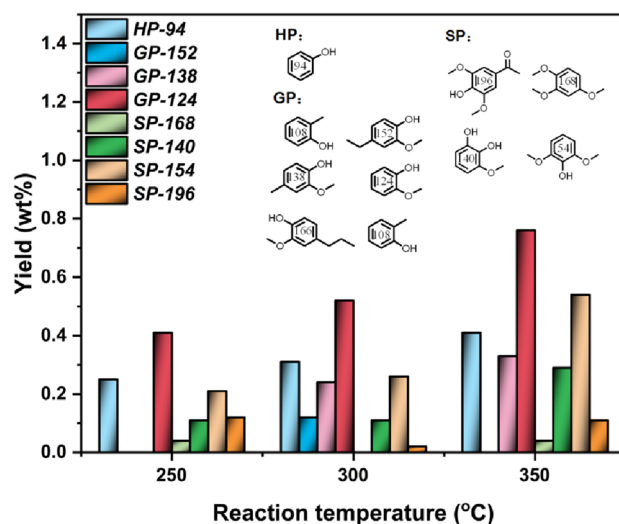


**Fig. 3** Effect of reaction temperature on the product distribution of lignin depolymerization at supercritical tetrahydrofuran solvent

that lignin in THF solvent at 250 °C has been synthesized, and the production of phenol may be part of it. Subsequently, the formation of  $\alpha$ -O-4 ether bond after further demethoxide fracture. When the temperature reaches 300 and 350 °C, the LP products increase significantly, mainly GP products, and no guaiacol and eugenol are found. However, the products 122 and 136 formed after demethoxidation and alkylation of methoxyl on guaiacol and eugenol have higher yields. Thus, it indicates that demethoxidation and alkylation are more likely to occur in supercritical tetrahydrofuran solvent. In addition, as shown in Fig. 3, 4-aliphatic guaiacols, such as 4-methyl guaiacol (138) 4-ethyl guaiacol (152) and 4-propyl guaiacol, are formed by demethoxide of 4-aliphatic guaiacol. At the same time, the 4-aliphatic phenol is also detected. As compared with the supercritical acetone solvent in Fig. 2,  $\alpha$  carbonyl and  $\beta$  carbonyl phenol products are almost not found in supercritical tetrahydrofuran system. The  $\alpha$  carbonyl and  $\beta$  carbonyl mainly come from the oxidation of  $\alpha$  and  $\beta$  hydroxyl groups in the process of lignin depolymerization, while  $\alpha$  and  $\beta$  hydroxyl groups in supercritical tetrahydrofuran system tend to undergo elimination reactions to form corresponding hydrocarbons.

### Distribution of Lignin Depolymerization Products in Supercritical Ethanol Solvent

The distribution of LP products in supercritical ethanol solvent at different temperatures is shown in Fig. 4. When the reaction temperature is below 250 °C, the LP products are mainly phenol (94) guaiacol (124) and eugenol (154), meanwhile, the demethylated eugenol product 140 is also found. Particularly, the  $\alpha$  carbonyl phenol product (196) is found at the lower reaction temperature, which may be due



**Fig. 4** Effect of reaction temperature on the product distribution of lignin depolymerization at supercritical ethanol solvent

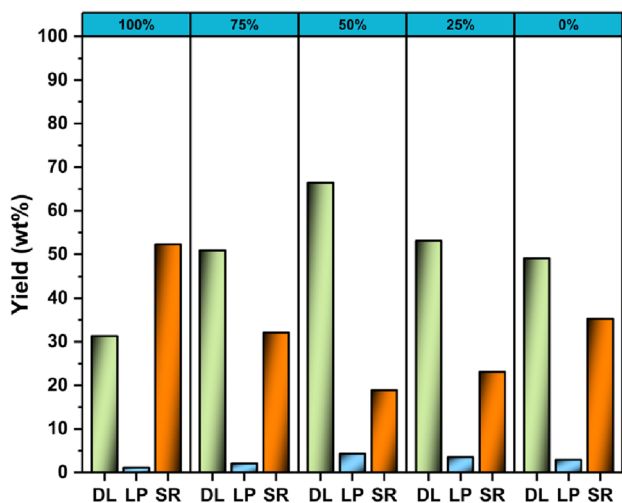
to the oxidation of  $\alpha$  hydroxyl groups to carbonyl groups during the extraction of lignin raw materials. Moreover, the  $\beta$ -O-4 ether bond is also broken during the depolymerization process, forming the corresponding product 196. With the increase of reaction temperature, product 196 containing carbonyl group disappears basically, mainly because ethanol depolymerized into acetaldehyde under high temperature conditions to release hydrogen [40]. Hydroreduction of  $\alpha$  carbonyl group leads to  $\alpha$  hydroxyl group, which is then depolymerized at high temperature into corresponding monomer derivatives, such as eugenol product (154). At the same time, with the increase of reaction temperature, the yield of demethylated eugenol product 140 is also increased significantly, possibly because high temperature improve ethanol dehydrogenation, and the increase of hydrogen supply in the system is contributed to the hydrogenation reaction of aryl methyl ether bond to form corresponding hydroxyl and alkane [41]. Relative to the supercritical of acetone and THF system, not only as a supercritical ethanol solvent, but the dehydrogenation reaction to produce hydrogen gas at high temperatures, which as a hydrogen source of lignin depolymerization system directly involved in the depolymerization reaction, thus reduce exogenous hydrogen addition amount and reduce the risk of high temperature and high pressure reaction, for the subsequent lignin of hydrogenation catalysts has important research and development meaning.

### Distribution of Lignin Depolymerization Products in Supercritical Ethanol/Water Solvent

Based on the above study and analysis of the distribution of LP products in supercritical acetone, THF and ethanol system, the supercritical ethanol is comprehensively considered

as a reaction solvent in this work. On one hand, supercritical ethanol can be used as a hydrogen source to promote the hydrogenation reaction process in the system [42]. On the other hand, ethanol has the advantages of low toxicity, low boiling point and wide application, which is helpful to promote the development of green process of lignin depolymerization [3]. However, it has been shown that when co-blended solvents were used, the depolymerization result was more active than that of a single solvent. Cheng et al. studied that co-solvent of water/ethanol was much more reactive than either pure ethanol or water, leading to much higher lignin conversion and bio-oil yields (up to 65 wt%) [43]. Wang et al. investigated the effect of different HZSM-5 zeolite on the catalytic activity for the conversion of lignin to phenol under supercritical ethanol/water conditions [44]. When the reaction conditions of 350 °C and 4 h, nano-HZSM-5 zeolite had the highest lignin conversion and LP products selectivity. Among these studies, the supercritical water has a lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility, and an enhanced solubility for organic compounds than ambient liquid water [42, 45]. Meanwhile, it also has been found very effective for promoting ionic, polar non-ionic, and free-radical reactions, which make it a promising reaction medium for biomass direct [42, 45]. Therefore, ethanol and water are mixed in a certain proportion for lignin depolymerization, and the influence of ethanol/water system on lignin depolymerization behavior is further investigated in this work.

Figure 5 shows the yield distribution of DL, LP and SR in different ethanol concentration systems at 300 °C and 300 min. It can be found that when the concentration of ethanol is 50%, the yield of DL is the highest (67%), while the yield of SR is the lowest of 19%. Similar results were



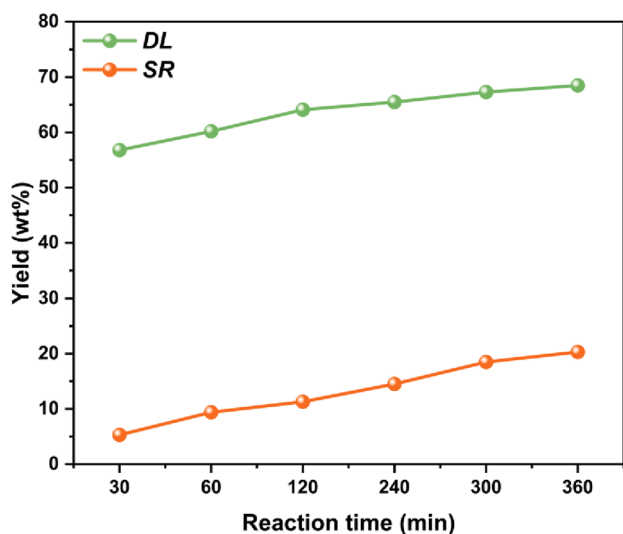
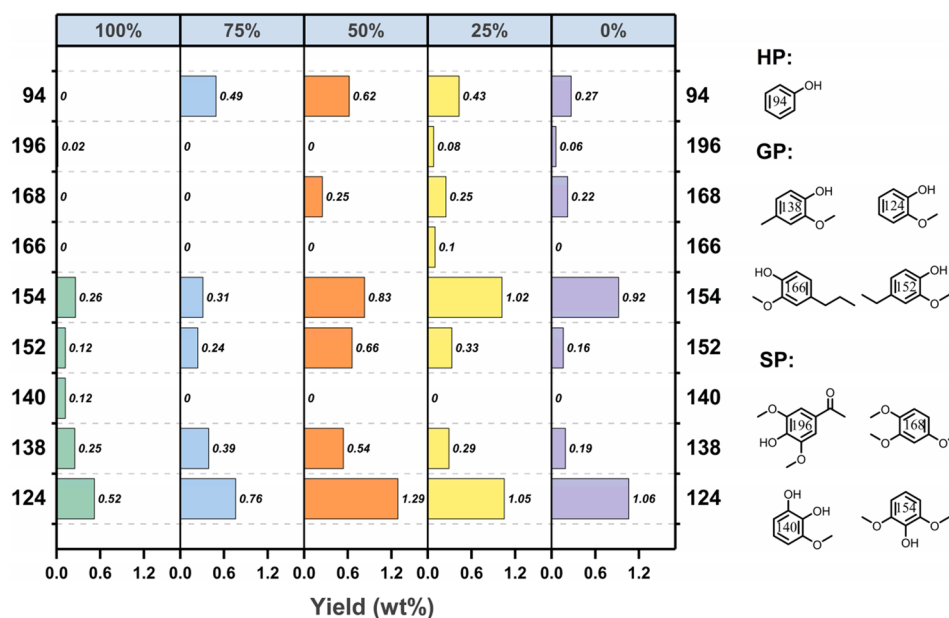
**Fig. 5** Yield of DL, LP and SR after lignin depolymerization with different ethanol content

found in the study by Cheng et al. [43]. As compared with this concentration, the yield of DL in pure ethanol system is 30% lower, and the yield of SR is 50% higher. However, in pure water system, the yield of DL is higher than that in pure ethanol system, and the yield of SR is lower than that in pure ethanol system, mainly because hydrothermal degradation reactions including ion reaction and free radical reaction can occur in high temperature and high pressure water system, such as nucleophilic hydrolysis reaction, electrophilic hydrolysis reaction, pyrolysis and thermal decomposition reaction [42, 46]. The yield of DL in pure ethanol system is lower than that in pure water system, which may be due to the difficulty of hydrolysis in pure ethanol system [42]. As shown in Fig. 6, lignin causes intramolecular ether bond fracture through hydrolysis reaction, forming a large number of LP derived from G-type and S-type lignin structural monomer. Among them, the LP products are mainly guaiacol and eugenol, and there are also guaiacol 4-position aliphatic hydrocarbon replacement products, such as 4-methyl guaiacol (138), 4-ethyl guaiacol (152) and 4-propyl Guaiacol (166). Especially, when the ethanol concentration is 50%, the yield of guaiacol (124), 4-aliphatic hydrocarbon substituents (138 and 152) and phenol (94) is the highest, which may be due to the hydrolysis reaction of  $\beta$ -O-4 and  $\alpha$ -O-4 in lignin, thereby, small molecular monomers such as LP, DL and SR are synthesized after fracture at different ethanol concentrations. Thus, the yield can be determined to enhance the solvation and hydrolysis reaction of lignin when the water is used as cosolvent in ethanol system [47].

Figures 7 and S1 shows the yield of DL and SR products in 50% ethanol system at 300 °C for different reaction time (15–360 min). It is found that reaction time has minimal influence on the yield of lignin depolymerization products (from 48 to 65%). Similar situations were found in the studies of Meier et al. and Kim et al. [48, 49]. However, for SR, the yield of SR is close to 5% when the reaction time is shorter (less than 30 min). When the reaction time is extended to 60–360 min, the yield of SR is increased significantly. It indicates that the long reaction time can promote the occurrence of the repolymerization reaction, which further improves the yield of SR.

When the system is 50% ethanol solvent, the  $M_w$  and PDI of DL obtained at different reaction times (15–360 min) are shown in Fig. 8 and Table S1. When the reaction time is 15–120 min, the  $M_w$  distribution of DL is 900–1100 g/mol. When the reaction time is 240–360 min, the  $M_w$  distribution of DL is 1300–1900 g/mol. Apparently, the  $M_w$  of DL is improved with the increase of the reaction time. It can be explained to the repolymerization reaction that occurs between the active intermediates produced by the depolymerization of lignin and LP, resulting in the increase in  $M_w$  of DL. This is also similar to the reason shown in Fig. 7 that long-term high temperature promotes the repolymerization

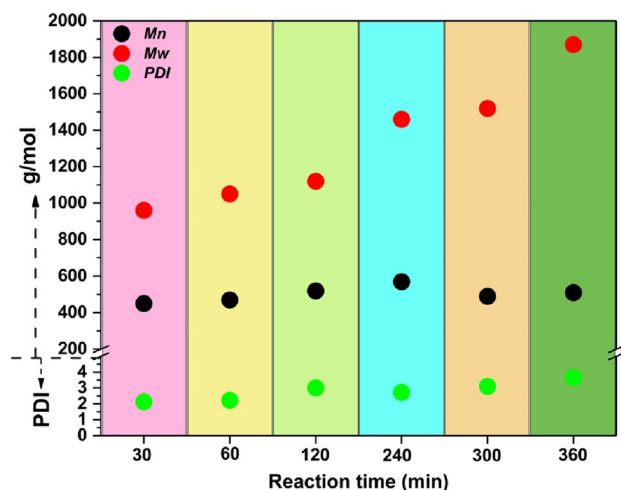
**Fig. 6** The distribution and yield of lignin monomer products with different ethanol content



**Fig. 7** Yield of DL and SR after lignin depolymerization with different reaction time during 50% ethanol content

reaction to produce more SR. This phenomenon is similar to Yuan et al., such as their research on alkali lignin hydrolytic reaction time in the water/ethanol were found that the shorter reaction time, and the system of large amounts of water could inhibit the activity of lignin sealing side reaction intermediates and phenolic compounds, made segments of small  $M_w$  of lignin content increased [47]. Therefore, when the high temperature reaction time extension, lignin active intermediates and sealing side reaction between phenolic compounds violent, resulting in large  $M_w$  of DL is increased.

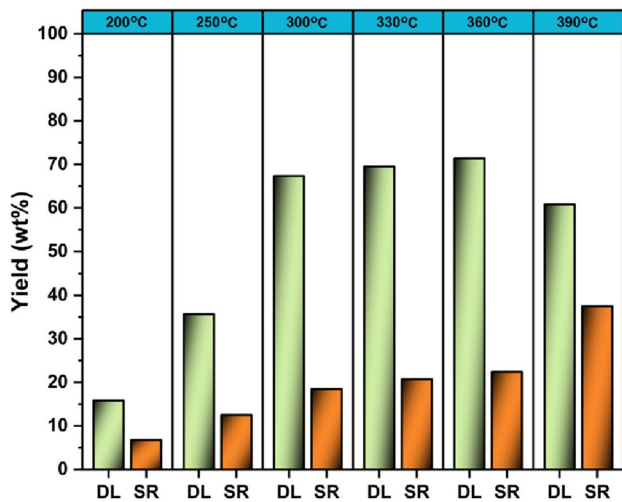
In order to further confirm the relationship between the yield of DL and SR and reaction temperature and reaction



**Fig. 8** GPC results of DL after lignin depolymerization with different reaction time during 50% ethanol content

time, when the reaction time is fixed for 300 min and the reaction temperature is prolonged, the yields distributions of various depolymerization products are shown in Fig. 9. When the reaction temperature is lower than 250 °C, the yield of DL and SR is lower. It may be that the lignin re-polymerization reaction is smaller. When the temperature is lower, and the coking polymer produced is less, leading to the low yields of SR and DL. At this time, it is mainly the depolymerized lignin, including the oligomer and LP. Meanwhile, the depolymerization reaction also occurs lightly at low temperature, and its yield is low. When the temperature is between 300 and 330 °C, the yield of DL is significantly higher than that of 250 °C, while the yield of SR continues to increase, which may be due to the fact

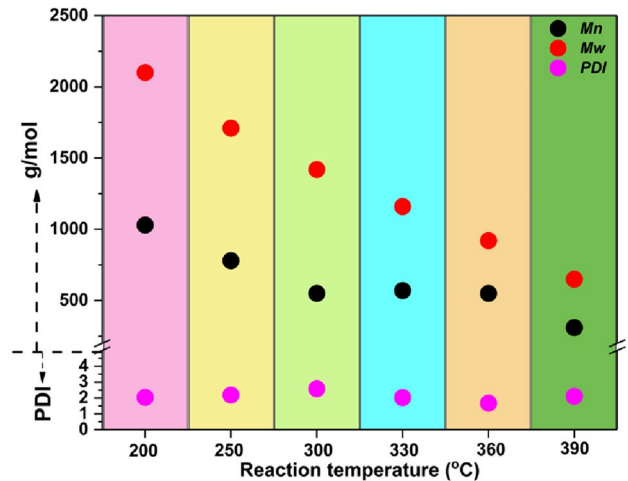




**Fig. 9** Yield of DL and SR after lignin depolymerization with different reaction temperature during 50% ethanol content

that high temperature promotes lignin depolymerization and the repolymerization reaction is also strengthened. Thus, the amount of coked lignin produced by high temperature coking increases, which leads to an increase in SR yield. Subsequently, the yield of lignin oligomers and LP products generated after enhanced depolymerization are dissolved in ethyl acetate and separated as DL phase products, resulting in a significant increase in yield. As the temperature continues to rise to 390 °C, the yield of DL decreases and the yield of SR continues to increase. As compared with the yield of LP products at 200 and 250 °C, the SR is dominated by carbon residue, which may be because the high temperature promotes the further occurrence of lignin repolymerization reaction. The carbon residue generated by high polymer and repolymerization reaction of lignin remains in SR, while the low  $M_w$  substance generated by depolymerization of lignin is dissolved in ethyl acetate as part of DL. The analysis of  $M_w$  of lignin in DL is shown in Fig. 10. With the increase of reaction temperature, the  $M_w$  of DL is gradually decreased. Combined with the yields of DL and SR products, it can be found that reaction temperature is promoted the lignin to low  $M_w$  product (lignin oligomer). Furthermore, high temperature and long reaction time can both affect the yields of DL and SR, and high temperature has a more obvious effect on the yields of DL and SR, especially on the yield of SR.

Generally, lignin is mainly composed of three phenylpropanol structural units connected by aryl ether bond ( $\beta$ -O-4 and  $\alpha$ -O-4) [6]. Among them,  $\beta$ -O-4 and  $\alpha$ -O-4 ether bonds are easy to fracture in different depolymerization solvents, and the general fracture temperature is 200–300 °C [5]. However, aryl ether bonds are relatively stable, generally requiring the use of catalysts and under the high temperature conditions (more than 400 °C), while the C–C bonds

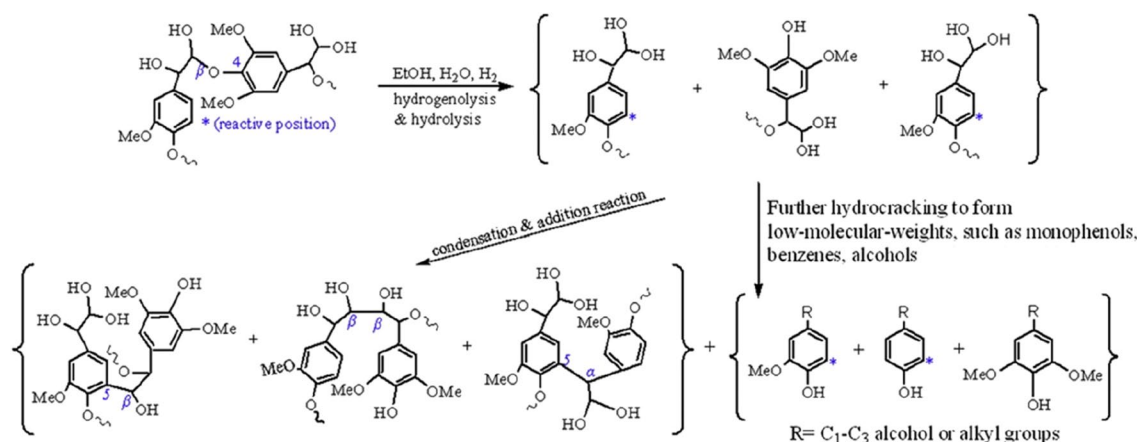


**Fig. 10** GPC results of DL after lignin depolymerization with different reaction temperature during 50% ethanol content

are more difficult to depolymerize. Based on the influence of various conditions on lignin depolymerization under the above supercritical ethanol/water system, the possible lignin depolymerization mechanism is shown in Fig. 11. In supercritical ethanol/water system, aryl ether bonds in lignin are depolymerized to phenolic hydroxyl alcohol and alkyl by hydrogenation and hydrolysis [40, 50]. At the same time, lignin intermediate fragment produced by depolymerization is further hydrolysed to form more low  $M_w$  products, such as 4-lipid hydrocarbon-based guaiacol products (Fig. 6) [51]. In addition, low  $M_w$  of lignin intermediates can further produce lignin oligomer coking and carbon through repolymerization reaction, especially when supercritical ethanol/water temperature is higher than 360 °C, which can promote the repolymerization reaction between highly active lignin depolymerization intermediates to form more SR [51, 52]. Thus, the optimal reaction temperature of the target product of lignin depolymerization into LP products in supercritical ethanol/water (50% ethanol solvent) system is about 300 °C.

## Conclusion

In this work, we performed lignin depolymerization under different supercritical systems, including supercritical acetone, supercritical tetrahydrofuran, supercritical ethanol, and supercritical ethanol/water. The effects of reaction temperature and reaction time on various lignin depolymerization products were investigated in detail. Among them, the supercritical ethanol/water system was the best reaction system. When the ethanol concentration was 50%, the reaction temperature was 300 °C and the reaction time was 300 min, DL had the highest yield of 67.32%, while SR had the lowest yield of 19.27%. In particular, the  $\beta$ -O-4 aryl ether bonds of lignin



**Fig. 11** Possible lignin depolymerization mechanism in supercritical ethanol/water solvent

were depolymerized into phenolic hydroxyl groups, alcoholic hydroxyl groups and alkyl groups through hydrogenation and hydrolysis reactions. Then, lignin intermediate fragments produced by depolymerization undergo further hydrocracking to form more low  $M_w$  products such as 4-alkylguaiacols. In addition, low  $M_w$  of lignin intermediates could further produce lignin oligomers, and carbon residues through repolymerization reactions. When the reaction temperature was higher than 360 °C, the repolymerization reaction between the highly active lignin depolymerization intermediates could be promoted to form more SR products.

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**Author Contributions** YB: Investigation and methodology. BD: Writing-original draft. ZP: Visualization and Investigation. JX: Software and Validation. QW: Project administration. XW: Conceptualization and Writing review & editing. JZ: Supervision and Resources.

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## Declarations

**Competing Interests** 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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