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Effect of switching solvent type and extraction parameters on lignin structure and selectivity of pyrolyzed oil phenolic products from corn stover

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SUMMARY: *Degradation of lignin by means of catalytic depolymerization for the preparation of monophenolic compounds, and then obtaining high value-added platform chemicals as well as liquid fuels, is of great significance for alleviating energy problems and environmental pollution. In this paper, we carried out a study on the structure of corn stover lignin and pyrolysis of oleophenolic products, selected a variety of* CO_2*-switching solvents, and explored the mechanism of the influence of solvent type and extraction parameters on the selectivity of oleophenolic products. The results showed that the lipophilicity of the switching solvent, the extraction time, the particle size of lignin, the material-liquid ratio and the ultrasonic time all had important effects on the extraction of the oleophenolic products at room temperature and normal pressure, and the optimal extraction conditions were as follows: DMCHA as the solvent, the material-liquid ratio of 1:4, the particle size of the lignin was less than 0.30 mm, the extraction time was 80 min, and the ultrasonic time was 25 min. Meanwhile, in the case of β-O-4 bond content is low in corn stover lignin (CSL), the extraction capacity of the solvent is favorable to obtain and stabilize the monophenolic compounds. Whereas, when the content of β-O-4 bonds was high, other characteristics of the solvent would affect the depolymerization of lignin and the selectivity of the products. In addition, there is a solvent effect between the phenolic compounds in the lignin pyrolysis products and the switching solvent.*

KEYWORDS: CO_2 *switching solvent; corn stover lignin; pyrolysis; product selectivity*

1 Introduction

Lignocellulose is one of the richest renewable biomass resources on earth. It is the main component of plant cell walls and contains three major components: cellulose, lignin and hemicellulose. For graminaceous plants such as corn stover, lignin is connected to the arabinosyl and xylosyl structures of hemicellulose through ester bonds and aryl ethers, and different varieties and growth conditions can lead to the three component ratios not being exactly the same [1, 2]. Lignocellulosic biomass produced by photosynthesis amounts to more than 100 billion tons per year, however, only a small portion of the biomass is effectively utilized [3, 4]. In the utilization process of lignocellulose, the structure of the existence of the "stubborn resistance" has become a major obstacle to the efficient use of lignocellulose, due to the lignin in the three major components as a "glue" role, making it difficult to separate the three major components to reduce the efficiency of the utilization of lignocellulose. Lignocellulose utilization efficiency [5-7]. Therefore, in the utilization of wood resources, how

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to reduce the recalcitrance of biomass through pretreatment has become a key issue.

The choice of pretreatment methods and parameter conditions not only affects the subsequent enzymatic saccharification, but also the equipment requirements and size of the reactor, enzymatic and fermentation efficiency, wastewater treatment, and the design of the cogeneration process [8, 9]. In recent years, solvent pretreatment is one of the most promising pretreatment methods to improve enzymatic saccharification of biomass by enhancing solvent permeability and biomass solubilization. Most studies have proved that the nature, concentration and pH of the solvent together determine the degree and rate of lignin solubilization, depolymerization and condensation, which in turn affects the lignin separation effect. Kanani and Rusdi empirically found that under the action of sodium hydroxide solvent and ultrasound (60 °C, 40 kHz), when the ratio of sodium hydroxide to aluminum oxide was 1:2, the lignin residue in treated cellulose was the was the lowest, only 12%, which effectively improved the separation efficiency of cellulose [10]. Xie et al. In this study, phosphotungstic acid-catalyzed neutral deep eutectic solvent was used to pretreat corn stover at lower temperatures for efficient removal of lignin and hemicellulose, high cellulose retention, enhanced enzymatic yield, and obtaining high-purity, low-molecular-weight lignin nanoparticles [11]. Hu et al. showed that with different γ-pentolactone concentration pretreatments, the elevated concentration prompted an increase in the molecular weight of the lignin and a decrease in the β-O-4 bond; γ-pentolactone lignin produced significantly more phenolics than cellulose enzyme lignin in hydrolytic deoxygenation due to higher purity and lower polymerization [12].

Solvent-driven lignin separation, on the other hand, can be affected by the type and nature of the solvent, as well as by adjusting the extraction parameters to affect the lignin structure. The results of Biswas et al. showed that aqueous solvents had the highest bio-oil yield (38.0 wt.%) at 280 °C, and the phenolic compounds content of the oils produced amounted to 60%; alcohol solvents liquefied the products with more ester functionalities, and the different solvents significantly altered the distribution of the components of the bio-oils and the residue The different solvents significantly changed the distribution of bio-oil components and residue decomposition [13]. Yang et al. used a high boiling point solvent method to isolate lignin, and structural characterization showed that lignin solubilization was positively correlated with tight structure and hydrogen bonding content [14]. By comparing four methods: organic solvents, ionic liquids, deep eutectic solvents and acid-alcohol, Yan et al. found that toluene sulfonic acid and deep eutectic solvents can efficiently separate lignin, and that low consistency lignin is more conducive to phenolic monomers production, but that the formation of C-C condensation bonds in the separation inhibits depolymerization [15]. Li et al. revealed changes in the structure and distribution of lignin in corn stover during organic solvent pretreatment, noting that lignin removal began in the secondary wall and gradually expanded to the middle layer of the complex [16]. In addition, this study pointed out that early lysed lignin contained more cedrol-type units, and the proportion of guaiacol-type units increased in the later stages, confirming that the structural differences stemmed from its regional distribution in the cell wall. Cronin et al. used lactic acid/choline chloride deep eutectic solvent treatment of corn stover hydrolysate to extract lignin efficiently with a yield as high as 75% and a purity as high as 94.7%; the molecular weight of the lignin and the content of the functional groups could be regulated by optimizing the parameters such as the temperature, time, and solvent ratios [17]. By analyzing a large dataset, Bergrath et al. revealed the correlation between the variation of process parameters, such as temperature and time, and the distribution of degradation/ condensation reactions in the acidic ethanol-organic solvent method, which provided a theoretical basis for the customized isolation of lignin with specific structures (e.g., molecular weight, hydroxyl ratio) according to the needs of downstream applications [18].

Pyrolysis is not only one of the main ways of efficient biomass conversion and utilization, but also the basis of thermochemical conversion technologies such as biomass combustion and gasification [19, 20]. And the oleophenolic compounds produced by lignin pyrolysis not only enable lignin to be utilized efficiently, but also reduce the use of fossil fuels after modification, and the selection of such compounds is affected by the structure of lignin. Khongchamnan et al. proposed an acid-catalyzed one-step solvothermal method using ethyl acetate/ethanol/water solvent mixture (30:25:45) for the efficient isolation of lignin from maize stover; the lignin removal reached 75.0% and the recovery was 72.9% at 180°C, 49.1 min and 0.08 M sulfuric acid, and the resulting lignin was enriched in β-O-4 structure and no new C-C bonds were formed [21]. Jia et al. pretreated corn stover using an organic solvent/ethylenediamine system at 200°C to achieve efficient lignin removal (96.05%); and nitrogen-rich regenerated lignin and hemicellulose exhibited excellent fluorescence properties that can be used for information encryption and Fe^{3+}selective detection [22]. Sahayaraj et al. used a flow reactor for methanol/ethanol solvent decomposition of industrial corn stover lignin, whereas rapid pyrolysis of the pretreated product increased the phenolic monomer yield to 23.86% and enhanced the aromatic yield in catalytic pyrolysis [23]. Lu et al. used acidic (lactic acid, etc.) and alkaline (glycerol, etc.) deep eutectic solvents to mildly extract lignin from corn cobs, whereas lignin obtained from acidic solvents had higher monophenol yields from pyrolysis, with a predominance of low-methoxylphenols, which are more suitable for conversion to high-calorie biofuels [24]. Yang et al. catalyzed the hydrodeoxygenation of corn stover lignin under hydrothermal conditions using flower-like nickel-cobalt alloy catalysts; the optimized catalysts increased the lignin oil and phenolic monomer yields to 63.37% versus 46.63% at 240 °C [25].

Several studies have found that the solvent and parameters can affect the structure of lignin and the selectivity of phenolic products from pyrolysis oils. Haverly et al. investigated the liquefaction process of technical lignin in o-cresol/tetralin mixtures, and the optimization of the conditions showed that when the content of tetralin was lower than 30%, it was able to effectively enhance the liquid yield and the phenolic monomer selectivity, and at the same time reduce the generation of solids [26]. Liu et al. focused on the structure and pyrolysis properties of corn stover lignin from bioethanol waste residue; the analysis showed that the bioethanol production process mainly breaks the β-O-4 ether bond, leading to an increase in the carboxyl group and the G'/S'-type unit; and that the pyrolysis products have a high selectivity for vinylphenols (e.g., 4-vinylguaiacol) [27]. Ye et al. results showed a 4.98% yield of 4-vinylphenol (4-VP) when the elongated stem bark was pyrolyzed at 300°C; the study revealed that high-value phenolic and furan compounds can be produced by selective targeted pyrolysis by modulating the growth stage and site of the feedstock [28]. Zhao et al. obtained a bio-oil yield of 46.7% with the help of direct microwave pyrolysis of corn stover; the selectivity of phenolic compounds in bio-oil could be significantly regulated by adjusting the temperature and power, with an optimum value of 49.4% (area ratio) [29]. Tong et al. combined surfactant and hydrothermal pretreatment of corn stover, and this combined pretreatment altered the lignin structure, improved the thermal stability, and contributed to the enrichment of phenols and other compounds in the pyrolysis products, revealing the pathway by which cetyltrimethylammonium bromide, a surfactant, synergizes with medium- and high-temperature pyrolysis to promote the directed generation of high-value phenols [30].

The above studies confirmed that the solvent type and extraction parameters could modulate the lignin structure of corn stover and the phenolic product selectivity of pyrolysis oil. However, the correlation analysis regarding the correlation between lignin structure and its pyrolysis oil phenolic product selectivity is insufficient, and the economic and production scale considerations under lignin separation and pyrolysis by different solvent use and extraction parameter adjustments have to be optimized. Therefore, by revealing the changing rules of solvent type and extraction parameter adjustments of solvent pretreatment on the effects of corn stover lignin structure and selectivity to pyrolysis oil phenolic products, it helps to optimize and develop solvents and process parameters with more economic value and large-scale production benefits.

In this paper, five CO_2 switching solvents, DMCHA, TEA, TNA, DMOA, and DCEMA, were selected to investigate the extraction rate of oleophenolic products under different solvents, and the effects of extraction parameters, such as extraction time, extraction temperature, particle size of lignin, material-liquid ratio, and ultrasonicating time, on the extraction rate were analyzed. On this basis, the structure of lignin and its influence on the choice of switching solvent in the pyrolysis process were analyzed. Finally, the effects of switching solvents on the selectivity of the phenolic products of lignin pyrolysis oil from corn stover and the mechanism of solvent action were further investigated.

2 Performance study of lignin extraction from corn stover by CO_2 switch solvent

In this chapter, CO_2 switching solvent and corn stover lignin were selected as experimental raw materials, and the effects of switching solvent type and parameters on the extraction rate of the phenolic products of corn stover lignin pyrolysis oil were investigated.

2.1 CO_2 stimulus-responsive switching solvents

The mechanism of switching solvents is that as the external trigger conditions change, the nature of the solvent also changes, and this transformation is controllable and reversible. According to the different triggering conditions, the switching solvents are divided into the following categories: temperature switch, pH switch, electrochemical switch, optical switch, ionic switch and CO_2 switch. In this paper, CO_2 stimulation-responsive switching solvents are selected for experimental study, which are mainly divided into two categories: switching solvents and switching surfactants.

2.1.1 CO_2 switching solvents

CO_2-switching solvents can change the solvent solubility state in water by artificially controlling the state of CO_2 inflow and outflow, so that the solvent can be dissolved in water or separated from water, and this process is reversible, and the separated solvent can be utilized repeatedly for many times. CO_2-switching solvents mainly include alcohol + amidine/alcohol + guanidine mixed systems, amine systems, amine + amidine/amine + guanidine mixed systems, and amidine derivatives.

(1) Alcohol + amidine/alcohol + guanidine mixed system

The system in which alcohol and amidine/guanidine are mixed in a 1:1 ratio by volume has the characteristic of a switching solvent with controllable polarity. As the amidine or guanidine group contained in the mixed system is protonated by CO_2, the polarity of the solvent is increased and it becomes an ionic liquid with high viscosity. When N_2 is introduced or CO_2 is discharged by heating, the protonated amidine or guanidine group is deprotonated and returns to its original state, becoming a low-viscosity liquid in molecular form.

(2) Amine system

Amines are common liquid compounds that are weakly basic and are widely available, inexpensive and easy to obtain. Amines generate an amine carbonate-like compound by combining with CO_2, with a significant change in polarity.

(3) Amine + amidine/guanidine hybrid system

For the CO_2 switching solvent of the amine + amidine/guanidine mixed system, the switching mechanism is similar to that of the alcohol + amidine/alcohol + guanidine mixed system.

In the tertiary amine and amidine mixed system, since the tertiary amine has stronger acidity than the alcohol, it is more likely to lose its proton and combine with the amidine or guanidine group.

In the mixed system of primary amines and amidinamidine groups, primary amines are induced by CO_2 to lose protons and combine with CO_2 to form a bicarbonate, and the amidinamidine group is ionized by obtaining hydrogen protons on primary amines.

(4) Amidine derivatives

When CO_2 is introduced into a solution containing amidine derivatives, a large number of hydrogen ions are generated when CO_2 is dissolved in water, and an ionic compound is generated when hydrogen ions are combined with the amidine group, and the solution containing the ionic compound has strong water solubility compared with the original solution. As long as CO_2 is removed, the solution can regain weak water solubility, and it has a strong switching property.

2.1.2 CO_2-switching surfactants

The switching performance of CO_2-switching surfactants lies in the fact that their surface activity can be transformed as CO_2 is passed in and out, and there are three major systems of CO_2-switching surfactants: amidinium system, guanidinium system, and amine system.

(1) Amidine-based system

CO_2-switching surfactants in the amidine system are hydrophobic and do not have surface activity under normal conditions. However, when CO_2 is introduced into an aqueous solution, the generated hydrogen ions combine with their amidine groups, and the amidine groups are protonated into the hydrophilic ionic state, resulting in the compound becoming a hydrophilic compound. When CO_2 is discharged from the solution by the addition of N_2, the ionic equilibrium of the solution is broken, the concentration of hydrogen ions in the solution decreases, and the amidine group that has been protonated is deprotonated, and the hydrophilic state is restored to the hydrophobic state.

(2) Guanidine system

The structure of guanidine is similar to that of amidine, and the reaction mechanism is also similar, but the structure of guanidine is more stable than that of amidine, and the ability to bind protons is stronger, so the deprotonation reaction process needs to consume more energy, and the reaction conditions are also more demanding, so there are fewer researches on it at present.

(3) Amine-based system

ODPTA is a polyamine surfactant, which is able to realize the transition between low viscosity emulsion and transparent viscoelastic colloidal solution before and after the passage and discharge of CO_2. With the passage of CO_2 into the aqueous ODPTA solution, the low-viscosity emulsion of ODPTA at room temperature reacted to produce a protonation product, which transformed the solution viscosity into a viscoelastic colloidal solution with a large increase in viscosity, and the solution returned to a low-viscosity emulsion when N_2 was passed into the colloidal solution at 75 °C to remove CO_2. In addition, UC22AMPM is a tertiary amine CO_2-switching surfactant, which also possesses a CO_2-switching reaction mechanism.

2.2 Experimental materials and methods

2.2.1 Experimental raw materials

The purity of corn stover lignin was greater than 90%.N,N-dimethylcyclohexylamine

(DMCHA), triethylamine (TEA), tri-n-propylamine (TNA), N,N-dimethyloctylamine (DMOA), N,N-dicyclohexylmethylamine (DCEMA) were analytically pure. The experimental water was deionized water.

2.2.2 Experimental apparatus

OPUS7.5 Fourier Transform Infrared Spectrometer. T6 UV-Vis Spectrophotometer. D204 Differential Scanning Calorimeter. TG209F3 Potentiometric Titrator. ZD2 Thermogravimetric Analyzer. FA-D Analytical Balance. JJ-6S Constant-speed, six-unit water-bath electric stirrer. TDL-5A Low-speed, large-capacity centrifuge. KM1-98-I-B electronic thermoregulation heating jacket. DZ-3BCII electric vacuum drying oven. OIL480 infrared spectrophotometer. S-F-Al-T Halogen Moisture Tester. JY-PH8.0 On-line pH Tester. SIN-TDS210 Conductivity Meter. 40L CO_2 Gas Cylinder. 40L N_2 Gas Cylinder. KH-300 Ultrasonic Cleaner.

2.2.3 Experimental methods

(1) Demethylation modification of lignin

Corn stover lignin was weighed and dissolved in aqueous sodium hydroxide solution under strong stirring, sodium sulfite was added proportionally, and the reaction solution was adjusted to a suitable pH with 1 mol/L sodium hydroxide solution, and then cooled down to room temperature after reacting for a certain period of time at a set temperature. The reaction product was precipitated out using 0.1 mol/L dilute hydrochloric acid solution, and then washed with distilled water to neutral. Filtered, dried and sealed for storage.

(2) Complex modification of lignin

Weigh the appropriate amount of corn stover lignin, dissolve it in aqueous sodium hydroxide solution under strong stirring, add sodium sulfite proportionally, adjust the solution with 1 mol/L sodium hydroxide solution to a suitable pH value, and then take it out and cool it down to room temperature after reacting for a certain period of time under the set temperature conditions. Then add an appropriate amount of glyoxal solution, adjust the system to a suitable pH value, and continue the reaction at a set temperature for a certain time, the modified lignin was precipitated using 0.1 mol/L dilute hydrochloric acid solution, and then washed with distilled water to neutral. Filtering, drying, and then sealed and stored for spare.

(3) Curing of lignin

The compound modified lignin was precipitated from the solution, dried and ground into powder, a quantitative amount of lignin was taken and added into the made container, suitable curing agent was added according to the ratio, curing was carried out for 3 hours under the heating condition of 120℃, let it to room temperature and then grinded to powder for testing and spare.

(4) Extraction of lignin pyrolysis oil phenolic products using CO_2 switching solvent

The technology of CO_2-stimulated switching solvent treatment of lignin is based on the reversibility of the switching solvent, through a one-time addition of switching solvent, the conventional operating conditions can be realized in the three-phase separation of the oil phase, aqueous phase, and solid phase, to obtain a relatively cleaner oil, water, residue and recyclable switching solvent. The whole process is simple, mild conditions, the specific operating procedures are:

1) The composite modified corn stover lignin, switch solvent and water in a certain proportion and order to join the extraction reaction device, heating and stirring to make it fully mixed. At this time, the switch solvent and the oil obtained from lignin pyrolysis are miscible to form the oil phase, and there is a three-phase state of oil phase, water phase and solid phase in the device.

2) Separate the solid phase by centrifugal separation device, and the remaining liquid phase

into the reaction kettle 1, at this time to the reaction kettle 1 access to CO_2 aeration device, the switching solvent to produce protonation reaction, from hydrophobic to hydrophilic transformation and dissolved in the aqueous phase, the oleophenol products from the switching solvent is separated.

3) The separated oil phenolic products are recovered, and the remaining aqueous phase enters the reactor 2, at which time the N_2 aeration device is connected to the reactor 2 to remove CO_2 from the system, the deprotonation reaction is completed, the switching solvent recovers hydrophobicity, and the switching solvent is separated from the water.

4) The separated switch solvent is recovered and can be recycled.

2.3 Lignin analytical tests

2.3.1 Determination of total hydroxyl content

In this experiment, the total hydroxyl content of lignin was determined using the acetylation titration method, and the principle of lignin acetylation is shown in Figure 1.

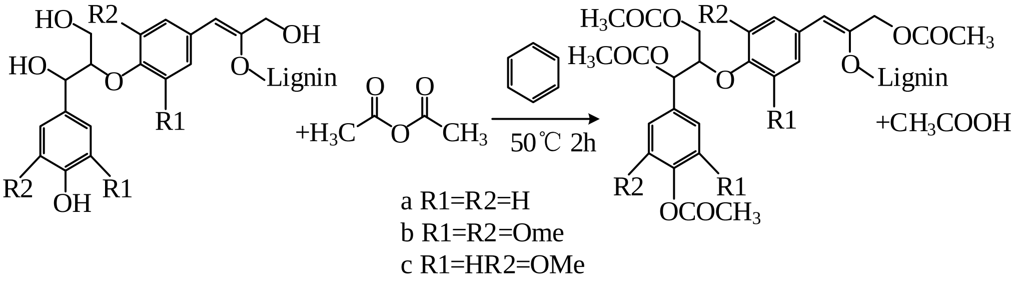


Figure 1: Reaction equation for lignin acetylation

The acetylation reagent was prepared by accurately measuring pyridine, acetic anhydride and dioxane in the volume ratio of 4:4.7:4.4, mixing well and setting aside.

The total hydroxyl content of lignin was calculated as shown in equation (1):

$$\left[\mathrm{OH}\right]=\frac{(b_0-b))\,f\times1.7\times5\times100}{A} \tag{1}$$

where b_0 denotes the volume of NaOH solution consumed by the blank sample (mL), b denotes the volume of NaOH solution consumed by the test sample (mL), f denotes the correction factor of 0.1 mol/L NaOH standard solution, and A denotes the mass of corn stover lignin (g).

2.3.2 Determination of phenolic hydroxyl groups of lignin

Weigh about 18 mg of the sample in 12 mL of dioxane and dissolve it, then take 2 portions of 3 mL of the solution, respectively, with $pH=6$ buffer solution of $\mathrm{NaH_2PO_4}$ and NaOH and 0.2 mol/L of NaOH solution to 60 mL, and analyze the samples by using UV-visible spectrophotometer, and use $pH=6$ lignin sample solution as a reference sample to determine the absorbance of 0.2 mol/L NaOH lignin sample solution at wavelengths of 320 nm and 380 nm as D' and D'', respectively.

The differential extinction coefficient was calculated by equation (2):

$$\Delta\varepsilon = \frac{D}{c \cdot l} \tag{2}$$

where c denotes the concentration of lignin solution (g/L) and l denotes the thickness of the cuvette (cm).

The phenolic hydroxyl content was calculated by Eqs. (3) to (5):

$$\mathrm{OH_{I+III}} = \frac{(\Delta\varepsilon' + 0.238\Delta\varepsilon'') \cdot 1700}{4000} = 0.425\Delta\varepsilon' + 0.101\Delta\varepsilon'' \tag{3}$$

$$\mathrm{OH_{II+IV}} = \frac{\Delta\varepsilon'' \cdot 1700}{21000} = 0.081\Delta\varepsilon'' \tag{4}$$

$$\mathrm{OH_{I+II+III+IV}} = 0.425\Delta\varepsilon' + 0.182\Delta\varepsilon'' \tag{5}$$

2.3.3 Infrared spectral analysis

Lignin was analyzed by attenuated total reflection infrared spectroscopy using an OPUS 7.5 infrared spectrometer with a scanning range of 400-4000 cm^{-1} and a resolution of 4 cm^{-1}.

2.3.4 Differential scanning calorimetric analysis (DSC)

A D204 heat flow type differential scanning calorimeter was selected to analyze and test the lignin samples. The scanning temperature range was from room temperature to 600°C, the heating rate was 12 K/min, the purge gas and protective gas was nitrogen, the gas flow rate was 36 mL/min, and the sampling volume was about 6 mg.

2.3.5 Thermogravimetric analysis (TGA)

The TG209F3 thermogravimetric analyzer was selected to analyze the sample thermogravimetrically. The scanning temperature range was from room temperature to 600°C, the heating rate was 12K/min, the atmosphere was nitrogen, the gas flow rate was 60mL/min, and the sample sampling was about 6mg.

3 Experimental results and analysis

3.1 Effect of solvent type and extraction parameters on oil phenolic products

In this section, the effect of different CO_2-switching solvents and extraction parameters on the extraction rate of the oleophenolic products obtained from the pyrolysis of corn stover lignin was investigated.

3.1.1 Effect of different switching solvents on extraction rate

The switching hydrophilic solvents differ in their lipophilicity, i.e., the $\mathrm{Log}K_{OW}$ of tertiary amines, their mutual solubility with oil phenolic products, and their ability to penetrate lignin cells. In this regard, five tertiary amines of the same type with different $\mathrm{Log}K_{OW}$ were selected as the switching hydrophilic solvents in this experiment to study the effect of the lipophilicity of the solvents on the extraction rate of oleophenolic products. Since the maximum value of $\mathrm{Log}K_{OW}$ of the tertiary amines constituting the switching hydrophilic solvent is below 4, the

$\mathrm{Log}K_{OW}$ of the tertiary amines selected in this experiment basically covers the range of Log Kow of the switching hydrophilic solvent with a certain broad spectrum. The effect of different switching hydrophilic solvents on the extraction rate is shown in Fig. 2.

It can be seen that with the increase of the value of tertiary amine $\mathrm{Log}K_{OW}$, the extraction rate of the oleophenolic products is first a small increase and then a relatively large decrease, which may be due to the fact that with the increase of the lipophilicity of the solvent, the solvent enters into the lignin cells with greater difficulty gradually. Therefore, a switching hydrophilic solvent for the extraction of oleophenolic products needs to have a moderate lipophilicity. The solvent extracts the oleophenolic products best when the lipophilicity of the solvent, i.e., the value of $\mathrm{Log}K_{OW}$, is in the range of 1.4-3.6. DMCHA, which has the best switching properties, was chosen as the switching hydrophilic solvent to study the effect of other factors on the extraction rate of the oleophenolic products.

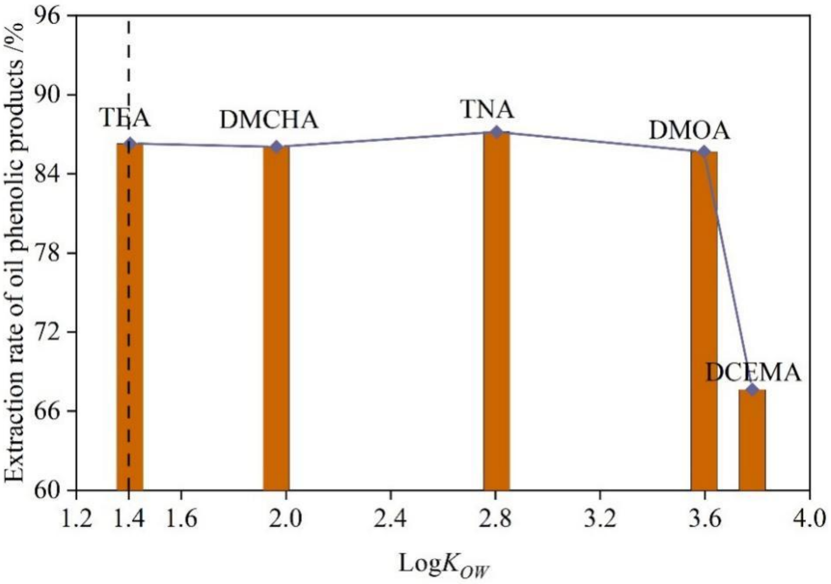


Figure 2: The influence of different switch hydrophilic solvents on the extraction rate

3.1.2 Effect of extraction parameters on extraction rate

(1) Effect of extraction time on extraction rate

The results of the effect of different extraction times on the extraction rate of the oleophenolic products under the conditions of 240 r/min, 24°C, and material-liquid ratio of 1:4 are shown in Fig. 3. It was observed that the extraction rate of the oleophenolic products increased with the extension of the extraction time and reached 95.42% at 80 min, after which there was little change in the extraction rate. Therefore, the extraction time of 80 min was selected.

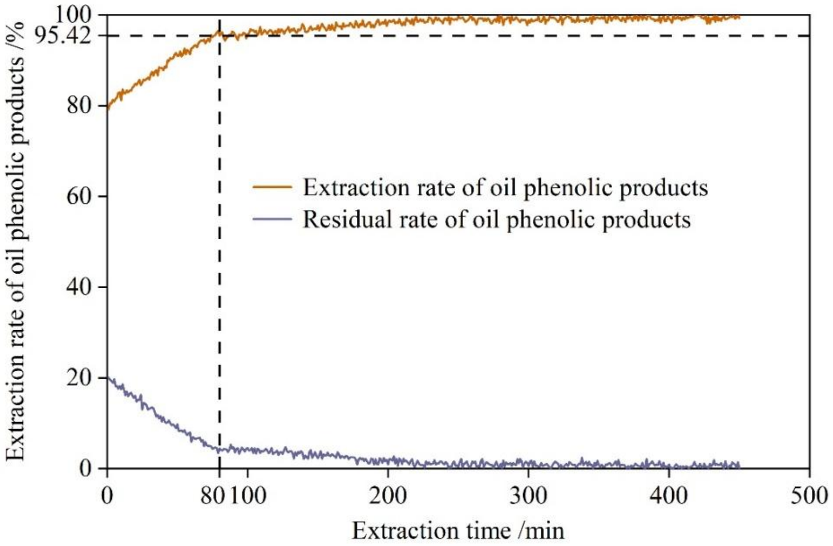


Figure 3: The influence of extraction time on the extraction rate

(2) Effect of material-liquid ratio on extraction rate

The temperature was 24°C, stirring 240 r/min, and the extraction time was 80 min. The effect of the feed-liquid ratio on the extraction rate of the oleophenolic products is shown in Fig. 4. The scales 1:1, 1:2, 1:3, 1:4, 1:5, 1:6 in the figure indicate the material-liquid ratio.

It can be seen that with the increase of the material-liquid ratio, the extraction rate of the oleophenolic products increased, the residual rate decreased, the material-liquid ratio of 1:4, the ratio of the switch hydrophilic solvent and the oleophenolic products has been sufficient, and then increase the amount of solvent, there is no longer a major impact on the extraction rate, it will only be a waste of solvent. Therefore, the material-liquid ratio of 1:4 was used.

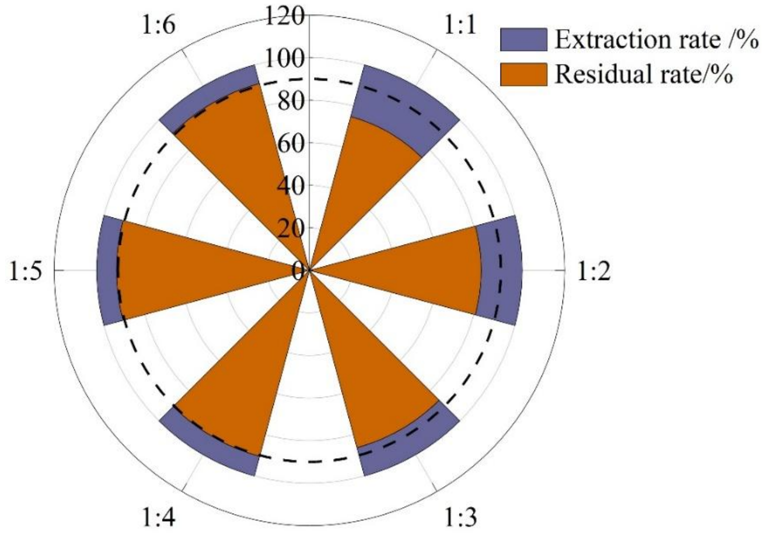


Figure 4: The influence of solid-liquid ratio on the extraction rate

(3) Effect of ultrasound time on extraction rate

Ultrasound will increase the disturbance between the lignin cells of corn stover, which can make the solvent enter the lignin cells better and increase the extraction rate of lignin pyrolysis oil phenolic products. The experimental results of ultrasound-assisted extraction on the extraction rate of oil phenolic products are shown in Fig. 5, with an ultrasound power of 400W.

It was observed that the extraction rate of oil phenolic products increased and the residual rate decreased with the increase of ultrasound time. This indicates that ultrasound has a promoting effect on the extraction of oil phenolic products. However, when the ultrasonication time is greater than 25 min, its effect on the extraction rate of oil phenolic products has become very small.

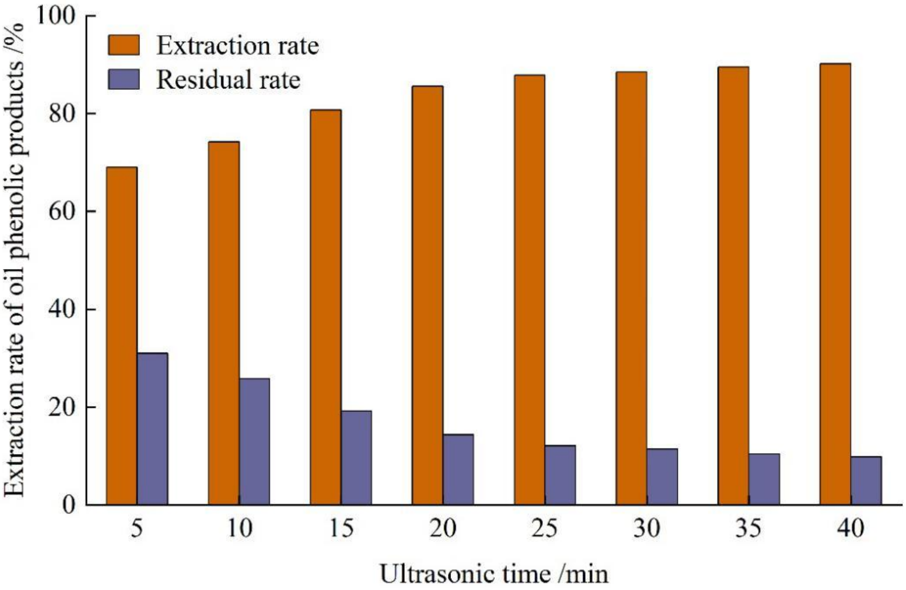


Figure 5: The influence of ultrasonic time on the extraction rate

(4) Effect of extraction temperature on extraction rate

The effect of temperature on the extraction rate of oil phenolic products is shown in Figure 6. The scale 20~60 in the figure indicates the extraction temperature in °C. With the increase of temperature, the extraction rate of oil phenolic products had a small increase, but the increase was small. Therefore, it can be inferred that the switching solvent extraction of oil phenolic products is not sensitive to temperature, and the temperature has basically no effect on the extraction rate of oil phenolic products.

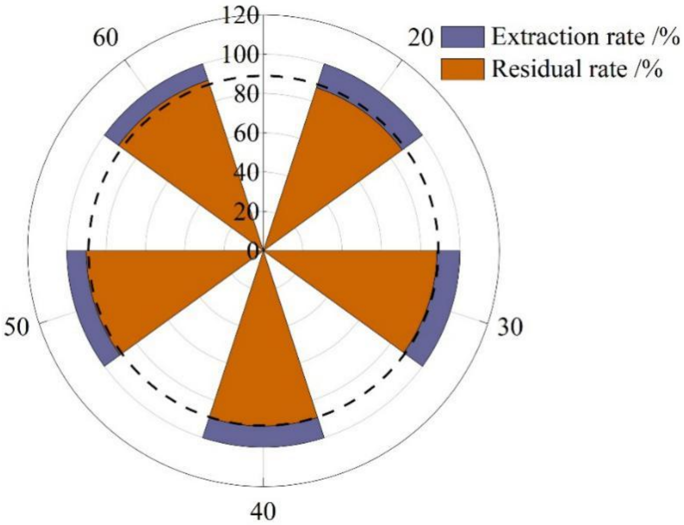


Figure 6: The influence of extraction temperature on the extraction rate

(5) Effect of particle size of lignin on extraction rate

The effect of particle size of corn stover lignin on the extraction rate of oil phenolic products is shown in Fig. 7. It can be seen that as the particle size of lignin decreases, the extraction rate of oil phenolic products increases and the residual rate decreases. Since the particle size of lignin and the specific surface area of lignin are directly proportional to each other, when the particle size of lignin is larger, its total surface area is smaller, and the contact area with the switch hydrophilic solvent per unit of time is smaller, and the extraction rate of the oleophenolic products is smaller. On the contrary, when the particle size of lignin is small its total surface area is larger, the area in contact with the solvent per unit time is larger, and the extraction rate of oil phenolic products is larger. Therefore, the smaller the particle size of lignin, the better its extraction rate.

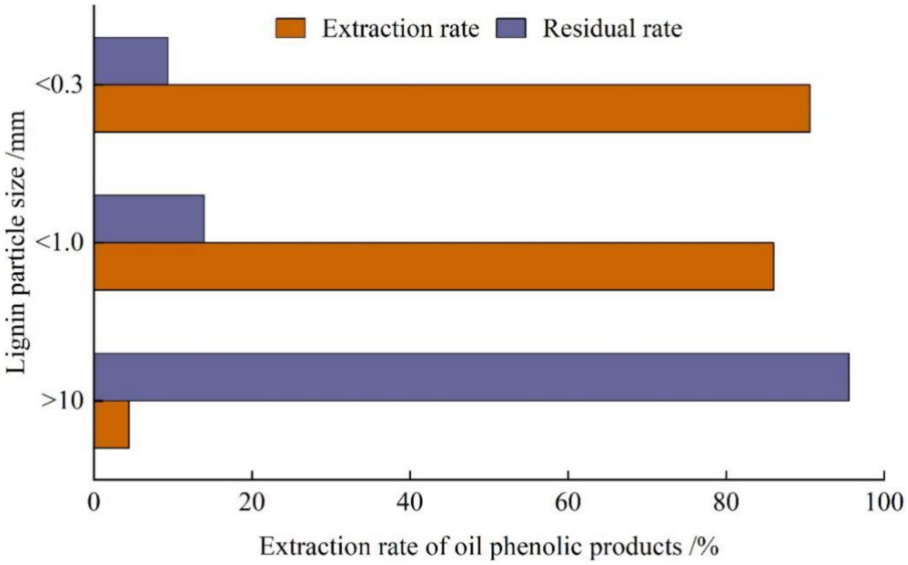


Figure 7: The influence of lignin particle size on the extraction rate

3.2 Effect of lignin structure on solvent selection for pyrolytic switching

In this chapter, corn stover lignin (CSL), pine organic solvent lignin (POSL), and birch organic solvent lignin (BOSL) were structurally characterized by two-dimensional hydrocarbon correlation spectroscopy (2D HSQC NMR) to investigate the effect of structural differences in lignin on the choice of solvent for CO_2 switching during pyrolysis.

3.2.1 Structural analysis of lignin

2D-HSQC NMR is a commonly used tool to analyze the structure of lignin. 2D-HSQC NMR analysis of CSL, POSL and BOSL can obtain information about the structural units and connecting bonds of lignin. It was found that there were large differences in the unit linkage bonds of CSL, POSL and BOSL, which greatly affected the pyrolysis of lignin in CO_2-switching solvents.

The specific relevant peaks attributed in the 2D-HSQC NMR spectra of different lignins were compared with literature data, and the corresponding lignin substructures are shown in Fig. 8. Among them, A denotes the β-O-4 ether-bonded structure, A' denotes the Cγ-OH acetylated β-O-4 ether-bonded structure, B denotes the resinoid alcohol structure consisting of β-β, α-O-γ, and γ-O-α linkages, C denotes the phenylcoumarin structure consisting of β-5 and α-O-4 linkages, D denotes the spirocyclo-dienone structure, I denotes the p-hydroxycinnamic acid end-group structure, and I' denotes the Cγ-OH acetylated p-hydroxycinnamyl alcohol end-group structure, J denotes hydroxycinnamaldehyde end-group structure, pCA denotes pcoumarate structure, FA denotes ferulic acid ester, BE denotes benzyl ether structure, T denotes trichothecene structure, S denotes S-type structure, S' denotes S-type structure oxidized by Cα-OH to C=O, G denotes G-type structure, G' denotes G-type structure oxidized by Cα-OH to C=O, H denotes H-type structure.

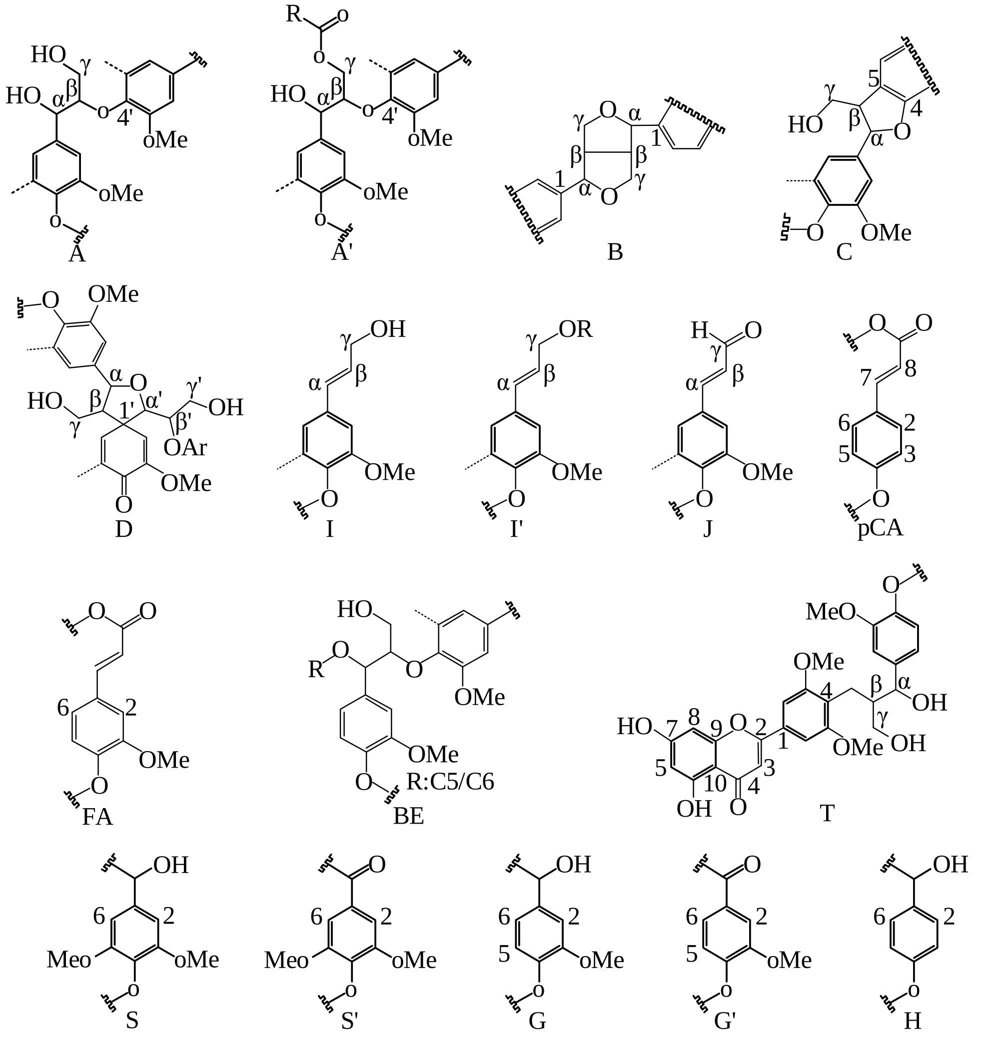


Figure 8: The main structure in the 2D HSQC NMR of lignin

The unit linkage bonds of CSL, POSL and BOSL were quantitatively analyzed by MestReNova software, respectively, and their structural unit ratios were integrated and calculated, and the results of the two-dimensional NMR quantitative analysis of lignin structure were obtained as shown in Table 1.

It can be seen that CSL is a lignin with a high degree of condensation, and the contents of its unit linkage bonds β-O-4, β-β, β-5, and B-1 in CSL are 27.84/100Ar, 12.37/100Ar, 7.46/100Ar, and 1.16/100Ar, respectively, which can be seen that CSL has a relatively dense and stubborn structure. 4bonds and high C-C bonds make it difficult to depolymerize to obtain more monophenolic compounds, so it is more effective to extract the products to the organic phase by organic switching solvents to inhibit the recombination of the products to improve the yield of monophenolic compounds, and the extraction ability of solvents is especially important in this process.

The contents of β-O-4 unit linkage bonds in POSL and BOSL were 53.86/100Ar and 53.51/100Ar, respectively. The higher content of β-0-4 bonds made these two lignans have more reactive sites relative to CSL, and the promotion of β-O-4 bond breaking was the key to improve the yield of monophenolic products. Alcohols play the role of in situ hydrogen donor in the lignin pyrolysis process, which can promote the breaking of lignin-cellulose intermolecular as well as lignin intramolecular connecting bonds, which is conducive to the conversion of lignin. The hydrolysis products of ester switch solvents can stabilize the reaction intermediates by alkylation and esterification reactions with reactive groups such as -OH. As a result, POSL as well as BOSL were able to achieve high monophenol yields in alcohol/water as well as ester/water biphasic solvent systems. From this, it can be inferred that in two-phase systems for lignin depolymerization containing a high content of β-O-4 bonds, those that can provide a hydrogen supplying solvent have a better depolymerization effect.

However, the amount of C-C structural unit connecting bonds β-β and β-5 is higher in POSL with 11.58/100Ar and 19.35/100Ar, respectively, and the amount of C-C structural unit connecting bonds Β-Β, Β-5, and Β-1 in BOSL is 13.64/100Ar, 1.24/100Ar, and 0.94/100Ar, respectively, which is obvious that The ratio of S/G/H of POSL is 13/85/6, which is a typical G-type lignin, while the ratio of S/G/H of BOSL is 74/27/4, which is an S-type lignin. The Β-0-4 bond connecting the G-type structure has higher dissociation energy than that of S-type structure, therefore, it is relatively more difficult for POSL to depolymerize. The n-butanol/water system is more advantageous for the depolymerization of POSL.

Table 1: Structural characteristics of lignin from integration of 2D-HSQC NMR spectra

Lignin interunit linkages	CSL (per 100Ar)	POSL (per 100Ar)	BOSL (per 100Ar)
β-O-4	27.84	53.86	53.51
β-β	12.37	11.58	13.64
β-5	7.46	19.35	1.24
β-1	1.16	-	0.94
S/G/H	12/82/8	13/85/6	74/27/4

3.2.2 Characterization of switching solvents in lignin depolymerization

The interaction of the ester switch solvent with the pyrolysis products was further verified by analyzing the depolymerization products obtained from BOSL in different solvent systems, and the gas chromatography mass spectrometry (GC-MS) spectra are shown in Figure 9.

The ester products 3-(4-hydroxy-3-methoxyphenyl)propyl acetate (23.59 min) and 3-(4-hydroxy-3,5-dimethoxyphenyl)propyl acetate (27.12 min) were observed in the depolymerization products obtained from different ester/water biphasic solvent systems, whereas the pyrolysis products obtained from BOSL in the pure aqueous system as well as in the n-butanol/water system showed almost no ester production, indicating that the formation of esterification products is closely related to the ester switching solvent. In the pyrolysis products of the ethanol/water and acetic acid/water systems, ester products were also observed, but in smaller amounts, attributed to the homogeneous system which makes the products susceptible to rehydrolysis after esterification. BOSL is more likely to produce side-chain -OH-containing products and less likely to produce side-chain COOH-containing products under pyrolysis conditions with both n-butanol/water and methyl acetate/water as the solvent system, which is also responsible for the low number of ester products in the ethanol/water system. In addition, the GC-MS spectra clearly showed the changing pattern of the content of esterification products: methyl acetate > ethyl acetate > butyl acetate. With the increase of the difficulty of hydrolysis of ester solvents, the esterification products gradually decreased, while the yields of monophenolic compounds also gradually decreased. It can be concluded that the appearance of esterified products in the depolymerization products is due to the ester medium hydrolyzed under the pyrolysis conditions produced by acetic acid, alcohols and side chain containing -OH,

-COOH pyrolysis products esterification reaction, mainly acetic acid and the side chain of the esterification of -OH, this esterification makes the product in the reaction conditions are more stable, and improves the product selectivity, and at the same time, biphasic system will be extracted into the organic phase to further prevented the recombination and promoted the depolymerization of lignin to obtain higher yields of monophenolic products.

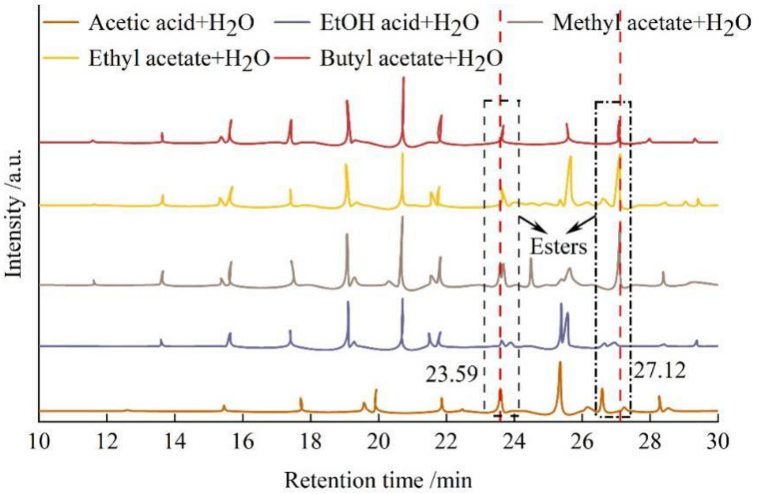


Figure 9: GC-MS spectra of BOSL depolymerization products in different solvent systems

In addition, it was found that MIBK has good extraction ability for different phenols.The highest monophenolics yield of 17.83 wt% was obtained by pyrolysis of CSL in MIBK/H_2O system, which indicates that the extraction ability of the solvent is beneficial for the obtaining and stabilization of monophenolics in CSLs with a low content of B-0-4 bonds. When the content of B-O-4 bonds is high, other characteristics of the solvent will affect the depolymerization of lignin and the selectivity of the products. The hydrolysis products of n-butanol and methyl acetate have hydrogen donor properties and can promote the depolymerization of lignin. POSL and BOSL obtained relatively high yields of monophenolic compounds through thermal decomposition in the n-butanol/water system, with yields of 26.41wt% and 33.05wt% respectively. In the methyl acetate/water system, they obtained yields of 25.24wt% and 36.08wt% of monophenolic compounds respectively through thermal decomposition. The esterification of the ester hydrolysis product acetic acid with -OH can make the active end of the product passivated and easy to be extracted into the organic phase, which is more conducive to the stabilization and generation of such products, thus affecting the selectivity of phenolic monomers and promoting the further conversion of lignin to pyrolysis.The BOSL structure has a higher content of B-O-4 bonds and has a lower dissociation energy, whereas the content of the C-C bond is low, which makes it more likely to generate products containing the side chain -OH. OH, the stabilization of the product at this time will contribute to the increase of the yield of monophenolic compounds.

3.3 Selectivity and mechanism analysis of lignin pyrolysis oil phenolic products

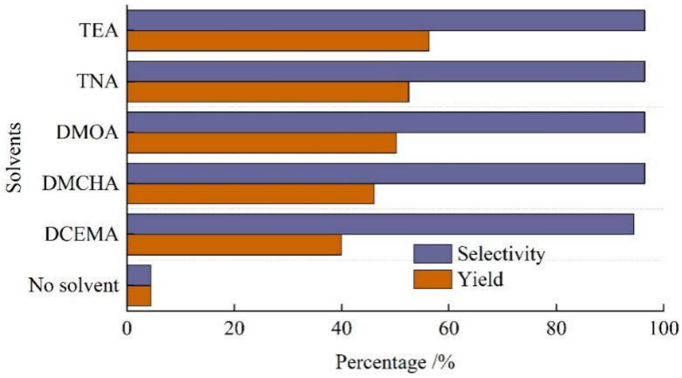
In this section, the effects of switching solvents with different polarities on the yields and selectivity of the oleophenolic products obtained from the pyrolysis of corn stover lignin were investigated to finalize the targeted modulation of the oleophenolic products from the pyrolysis of corn stover lignin, as well as the role played by the switching solvents in the reaction process was characterized and analyzed.

3.3.1 Effect of solvent on yield and selectivity of oil phenolic products

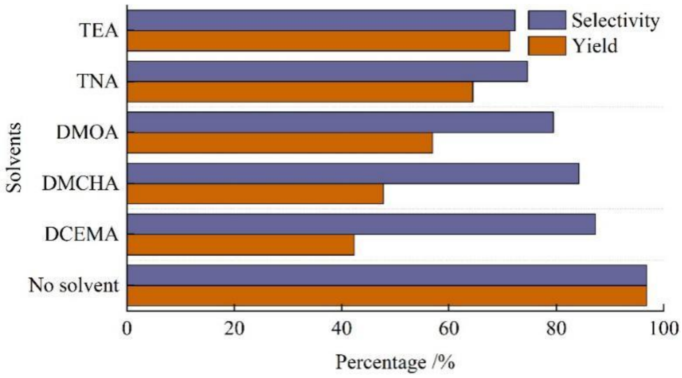
In this section, 4-methylphenol and 2,6-dimethoxyphenol were selected as the target oleophenolic products after the pyrolysis of corn stover lignin to investigate the effects of different switching solvents on the yields and selectivity of the two oleophenolic products as shown in Fig. 10, in which (a)~(b) denote 4-methylphenol and 2,6-dimethoxyphenol, respectively, and the solvents were none, N,N-dicyclohexylmethylamine (DCEMA), N. N-dimethylcyclohexylamine (DMCHA), N,N-dimethyloctylamine (DMOA), tri-n-propylamine (TNA), and triethylamine (TEA) with increasing polarity.

The pyrolysis products of meso-lignin after the addition of switch solvent were basically concentrated on the lignin pyrolysis product 4-methylphenol, and the yield of 4-methylphenol gradually increased with the increasing polarity of the added switch solvent. The selectivity of another oil phenolic product 2,6-dimethoxyphenol could reach 96.77% without the addition of the switching solvent, and its selectivity appeared to decrease after the addition of the switching solvent and decreased with the increase of the polarity of the added switching solvent. 2,6-dimethoxyphenol yield appeared to decrease significantly after the addition of the switching solvent, and the lowest yield of 2,6-dimethoxyphenol was 71.25% with the addition of TEA. 71.25%. As the polarity of the added switching solvent increased the yield showed a gradual increase, and when TNA was added, the yield of 2,6-dimethoxyphenol was the highest at 64.43%.

Considering the lignin conversion rate and the yields and selectivity of the oleophenolic products 4-methylphenol and 2,6-dimethoxyphenol, TNA was determined to be the optimal solvent for the lignin pyrolysis reaction.



(a) 4-methylphenol



(b) 2,6-dimethoxyphenol

Figure 10: The influence of different solvents on the yield and selectivity of the product

3.3.2 Analysis of solvent action mechanism

(1) UV absorption curves of four phenolic compounds

The UV absorption spectra of m/p-cresol and 4-methylphenol and 2,6-dimethoxyphenol, the pyrolysis products of corn stover lignin, in the wavelength range of 200-400 nm are shown in Figure 11. The wave numbers corresponding to the E2 absorption bands (around 210 nm) of the four phenolic compounds, m-cresol, p-cresol, 4-methylphenol and 2,6-dimethoxyphenol, are about 209 nm, 212 nm, 213 nm and 214 nm, respectively, and the wave numbers corresponding to the B absorption bands (around 270 nm) are about 269 nm, 270 nm, 276 nm and 277 nm, respectively.

According to the wave numbers corresponding to the E2 and B absorption bands of phenolic compounds, it can be seen that the wave numbers corresponding to the absorption peaks of 4-methylphenol and 2,6-dimethoxyphenol in the UV spectra are larger than those of m-cresol and p-cresol. This is due to the different positions of methyl groups on different phenolic molecules during the UV test, which affects the II→II* transition of electrons.

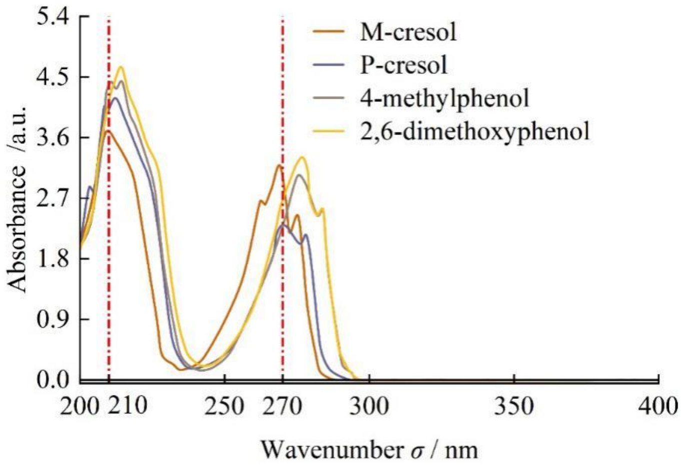
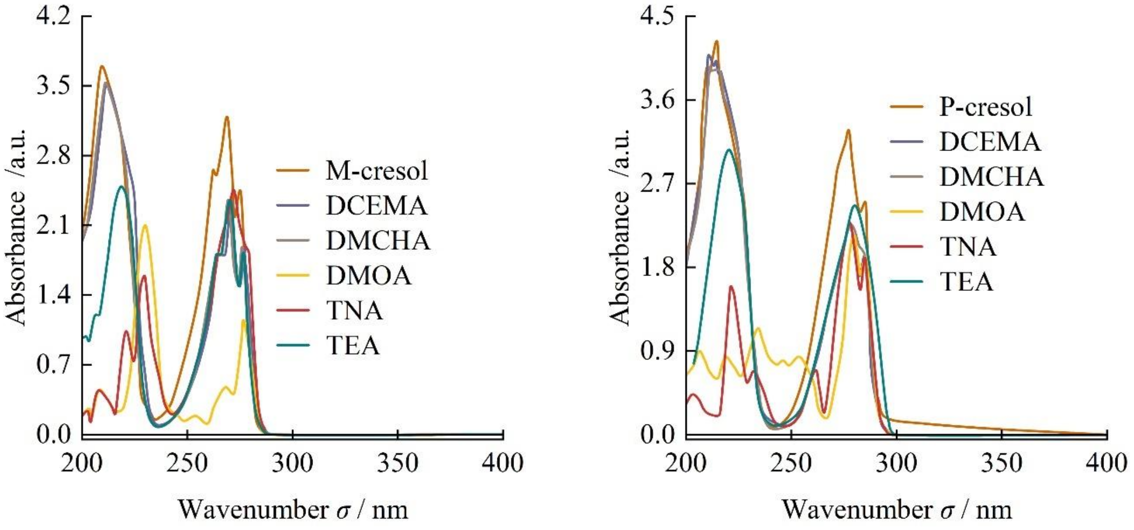


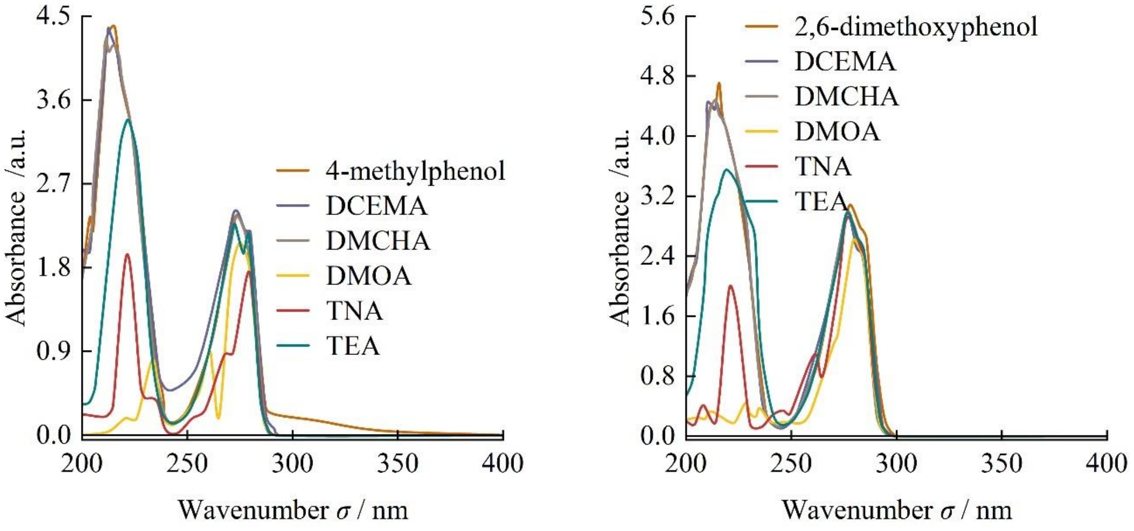
Figure 11: Ultraviolet absorption curves of four phenolic standard substances

(2) Solvent effect between solvent-phenolic compounds

The UV absorption curves of m/p-cresol and 4-methylphenol and 2,6-dimethoxyphenol, the pyrolysis products of corn stover lignin, after the addition of different switching solvents are shown in Fig. 12 from (a) to (d). As the polarity of the added switching solvent increases, the fine structures appearing in the E2 and B absorption bands of the four phenols obviously disappear. This is because the four phenols are polar molecules, and as the polarity of the added switching solvent continues to increase, the interactions between phenol molecules and the switching solvent molecules gradually increase, and the free rotation of phenol molecules and their own vibrations are restricted by such solute-solvent interactions, resulting in the disappearance of the fine structure that originally appeared in the UV spectra, the absorption peaks became smoother, and the absorption intensity decreased to different degrees. In addition, after the addition of the switching solvent, the wave numbers corresponding to the E2 absorption bands of the phenolics were significantly red-shifted compared with those without the switching solvent. The reason for this phenomenon is that the increase of the dielectric constant of the added switching solvent affects the π→π* electron jump on the benzene ring of the phenolic molecules, which shifts the peak position of the E2 absorption band to the long-wave direction compared with that without the addition of the switching solvent. The results of UV spectra indicate the existence of a solvent effect between the switching solvent and the phenolic compounds.



(a) M-cresol (b) P-cresol



(c) 4-methylphenol (d) 2,6-dimethoxyphenol

Figure 12: Ultraviolet absorption curves of phenolic compounds in different solvents

4 Conclusion

In this paper, the structure of corn stover lignin and the yield and selectivity of its pyrolyzed oleophenolic products have been deeply investigated by using the type of CO_2 switching solvent as well as the extraction parameters as control variables. The main conclusions from the study are as follows:

(1) The optimal LogK_{OW} of solvent lipophilicity for the extraction of corn stover lignin pyrolyzed oleophenolic products using CO_2-switching hydrophilic solvents ranges from 1.4 to 3.6, and when the solvent's lipophilicity exceeds this range, the extraction yields of oleophenolics products produce a relatively large decrease.

(2) The optimum conditions for the extraction of the oleophenolic products using CO_2 switch hydrophilic solvent were as follows: DMCHA as solvent, ambient temperature, the size of soybean powder particles is less than 0.30 mm, the material-liquid ratio is 1:4, and the extraction time is 80 min. the extraction rate of soybean oil was 95.42% under these conditions.

The effect of temperature on the extraction rate was negligible.

(3) The contents of β-O-4 bonds in corn stover lignin (CSL), pine organic solvent lignin (POSL), and birch organic solvent lignin (BOSL) were 27.84/100Ar, 53.86/100Ar, and 53.51/100Ar, respectively, and the different β-O-4 bond contents of lignin and the difficulty of breaking the bonds influenced the choice of switching solvent.

(4) The existence of solvent effects between the switching solvents and different phenolic compounds was stronger between 4-methylphenol as well as 2,6-dimethoxyphenol and the solvents than m-cresol and p-cresol.

The results of this paper help to promote lignin pyrolysis and increase the yield of monophenolic compounds. However, the structure of lignin is complex and the influencing factors of its pyrolysis process are very many, so the next study can provide a deeper understanding of the interactions among lignin, catalysts, products, and solvents, which can guide the regular solvent selection for the efficient pyrolysis of lignin.

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