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Conversion of Pyrolytic Lignin to Arenes and Cycloalkanes in Consecutive Ethanol and Hydrocarbon Solvents

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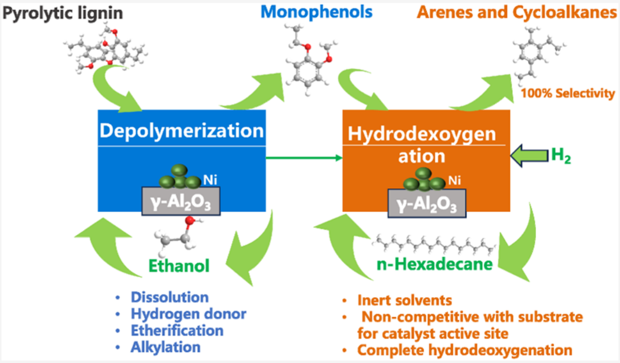

ABSTRACT: Pyrolytic lignin was first depolymerized in ethanol to produce low-molecular-weight phenolic compounds, followed by complete hydrodeoxygenation in hydrocarbon solvents, achieving a total yield of 21 wt % of arenes and cycloalkanes (arenes/cycloalkanes molar ratio = 1:5) using a 15% Ni/γ-Al$_2$O$_3$ catalyst. Ethanol efficiently dissolves and depolymerizes pyrolytic lignin with or without an external hydrogen source. Through etherification and alkylation, ethanol molecules are added to the side chains of the benzene rings, increasing the carbon length of the final products. However, under harsher conditions, ethanol can produce unwanted side products. It can also compete with phenolic intermediates for catalytically active sites, thereby hindering effective hydrodeoxygenation. In contrast, inert hydrocarbon solvents, which lack oxygen-containing functional groups and thus do not adsorb onto the catalyst active sites, were found to be ideal for promoting complete hydrodeoxygenation. Notably, n-hexadecane provided a higher carbon yield compared to hexane and dodecane due to its liquid state at 300 °C and 2 MPa pressure. Catalysts supported on acidic materials, such as Ni/γ-Al$_2$O$_3$, demonstrated higher efficacy in promoting depolymerization and suppressing undesirable condensation reactions compared to basic supports like Pt−Ni/MgO. This two-step approach successfully produced oxygen-free products, which significantly reduces separation costs compared to conventional single-step methods. Future research could focus on optimizing mixed solvent systems that combine the beneficial properties of both ethanol and hydrocarbon solvents to balance solubility and selectivity, thereby improving overall process efficiency, reducing catalyst deactivation, and enhancing product selectivity.

1. INTRODUCTION

Biomass-derived liquid fuels play an important role in reducing carbon emissions in the transportation sector.[1−3] Fast pyrolysis technology, due to its broad feedstock adaptability, low cost, and high energy conversion efficiency, has become one of the key technologies for biomass conversion.[4,5] The main product obtained from biomass fast pyrolysis is bio-oil, which is composed of a large amount of water (15−30 wt %) and various oxygenated monomers or oligomers, including phenols, dehydrated sugars, acids, aldehydes, ketones, and furans. The bio-oil has a low heating value, poor thermal stability, and insufficient stability for direct use as fuel or as a chemical feedstock. Therefore, further upgrading is required.[6,7]

Currently, upgrading bio-oil to fuel mainly focuses on catalytic hydrotreatment to reduce the oxygen content and improve the heating value. Bio-oil is essentially a mixture of lignin fragments emulsified in a carbohydrate-rich aqueous phase.[8] Direct upgrading of bio-oil is challenging, as the water-soluble sugar derivatives in the aqueous phase tend to form char, which deactivates the catalyst and reduces overall conversion efficiency.[9,10] To overcome these challenges, bio-oil is typically demulsified by adding water and vigorous stirring, resulting in a phase separation: a lignin-rich heavy phase, known as pyrolytic lignin, and a carbohydrate-rich aqueous phase, each treated according to its distinct properties.[11]

Pyrolytic lignin is composed of phenolic oligomers formed through depolymerization of native lignin, followed by the repolymerization of the resulting fragments.[12] Compared with milled wood lignin or solvent-extracted lignin, which retain a relatively intact chemical structure, pyrolytic lignin contains more recalcitrant C−C linkages, making it more challenging to convert. Despite the structural diversity of lignin derived from various biomass sources and isolation methods, the primary challenges in converting lignin to aromatic compounds lie in achieving efficient cleavage of C−O and C−C bonds while preventing the recondensation of lignin fragments. Such recondensation can lead to the formation of more stable

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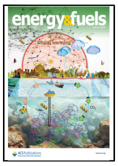

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chemical bonds or multimers, thereby reducing selectivity and monomer yield.[13] Various processes have been investigated for lignin conversion, including oxidation, base- or acid-catalyzed depolymerization, hydroprocessing, pyrolysis, and gasification, each yielding distinct end products depending on the additives and process conditions.[14] In the context of fuel applications, where this study is focused, hydrodeoxygenation (HDO) has emerged as a primary strategy for producing oxygen-free aromatic and cyclic hydrocarbons. This approach can be broadly classified into two main categories.[8] One category involves upgrading lignin under external hydrogen conditions, either in a solvent-free environment[15−17] or in an inert solvent.[18] The other involves using organic polar solvents, such as alcohols[19,20] or tetrahydrofuran,[21] to carry out conversion without external hydrogen. The interaction among the substrate, solvent, and catalyst plays a critical role in determining product distribution and conversion efficiency under different reaction conditions.[22−25] Catalyst design and optimization of reaction conditions are the primary research methods for enhancing process efficiency, controlling product selectivity, and prolonging the catalyst lifespan. The reaction conditions significantly influence the reaction pathways. For instance, in the hydrodeoxygenation of phenol, high-pressure and low-temperature conditions tend to favor hydrogenation of the benzene ring, leading to an increased production of cyclohexanol.[26] Furthermore, the design of hydrodeoxygenation catalysts has long been a research focus. Among various strategies, bimetallic and bifunctional catalysts are more attractive than traditional monometallic catalysts. The addition of another metal can improve the catalyst's activity, selectivity, and stability through modified geometric, electronic, and synergistic effects. For example, Wu et al. demonstrated that a Pt−Co bimetallic catalyst can selectively cleave the C−O(H) bond of guaiacol while retaining the methoxy group.[27] Talebkeikhah et al. found that coating a nickel metal core with a layer of aluminum effectively prevents catalyst sintering and deactivation.[28] Valizadeh et al. incorporated molybdena clusters into Ni/CeO catalysts to enhance the conversion rate of guaiacol through improved Ni dispersion and increased catalyst oxygen vacancies.[29] Bifunctional catalysts typically involve loading an active metal onto an acidic support to enhance activity, where the C−O bond adsorbs at acidic sites and reacts with active hydrogen species generated at nearby metal sites, leading to bond cleavage. For instance, loading Ru onto acid-etched Halloysite nanotubes significantly improved the hydrodeoxygenation activity of guaiacol compared to its neutral counterparts.[30] Among non-noble-metal catalysts, nickel-based bimetallic and bifunctional catalysts are widely used for both depolymerization and hydrodeoxygenation, offering a favorable balance of activity, selectivity, and cost compared to noble metals. Nickel's abundance and low cost make it a practical choice for large-scale applications, while its robust hydrogenation and C−O bond cleavage abilities enhance biomass upgrading.[31] In depolymerization, nickel promotes the cleavage of C−O bonds in the lignin structure by providing active hydrogen, resulting in smaller aromatic fragments. During hydrodeoxygenation, nickel aids in C−O bond scission through metal−support interactions, facilitating the removal of oxygenated functional groups. Unlike platinum or palladium, nickel favors C−O bond hydrogenolysis over benzene ring hydrogenation due to its higher oxophilicity, which leads to increased aromaticity in the upgrading products.[22,26] Furthermore, when supported on metal oxides, nickel benefits from improved metal dispersion and resistance to deactivation, with enhanced stability and reduced coke formation.[32,33] This synergy between nickel and the support often results in higher conversion rates and greater catalytic longevity. Instead of exploring the diverse range of available catalysts in detail, this study focuses on the widely used nickel-based catalyst supported on metal oxides[34−38] to systematically examine the solvent effects on both the depolymerization and hydrodeoxygenation of pyrolytic lignin.

Polar solvents (e.g., alcohols) perform well in dissolving lignin and can promote mass and heat transfer during the reaction. Additionally, due to their ability to participate in reactions, polar solvents can act as protecting groups and external hydrogen source, thereby reducing the degree of repolymerization.[39,40] Compared with other polar solvents, ethanol can be sustainably derived from biomass, resulting in lower carbon emissions.[41] Besides, ethanol serves dual roles as both a hydrogen donor and a capping agent for lignin intermediate fragments during depolymerization.[40,42,43] By donating hydrogen through dehydration with acidic catalysts, ethanol helps to reduce repolymerization and facilitates the selective cleavage of C−O bonds. Additionally, ethanol stabilizes lignin intermediates, preventing recondensation and minimizing the formation of unwanted products. These properties make ethanol an ideal choice for controlling the product selectivity and improving the reaction efficiency. However, since polar solvents contain oxygen atoms, complete deoxygenation is difficult to achieve due to competitive solvent binding to the active sites,[25] and a significant amount of phenolic compounds remains in the products, complicating downstream separation. Furthermore, excessive reaction and consumption of alcohol solvents can diminish the economic and environmental performance of biomass-derived fuel processes, and may even increase carbon emissions, thereby undermining the intended environmental benefits.[44] On the other hand, hydrocarbon-based inert solvents, while exhibiting limited solubility for lignin, demonstrate potential as effective reaction media for hydrodeoxygenation processes due to their nonparticipatory nature in chemical reactions.[45,46]

Based on the respective advantages and disadvantages of polar and inert solvents and considering the distinct chemical processes involved in converting pyrolytic lignin to hydrocarbons, this work proposes an innovative two-step approach. The first step involves depolymerization of pyrolytic lignin in an ethanol system under relatively mild conditions without external hydrogen, followed by comprehensive hydrodeoxygenation of the depolymerized product in a hydrocarbon solvent under harsher condition. Furthermore, this study investigates the impact of different solvents including ethanol, H_2O, hexane, dodecane, and n-hexadecane on the reaction process, contributing insights into optimizing solvent usage and regulating product selectivity. The proposed method reduces ethanol and hydrogen consumption, with the final product consisting solely of aromatic and cyclic hydrocarbons that can be easily separated from the solvent. This minimizes energy usage and carbon emissions, enhancing the process's sustainability. Furthermore, by generating these aromatic and cyclic hydrocarbons, which are essential for sustainable aviation fuels (SAF) due to their material compatibility and specific fuel dielectric constants,[26] this approach supports the development of 100% drop-in SAF, offering substantial potential for scaling up biomass-derived fuel production for industrial applications.

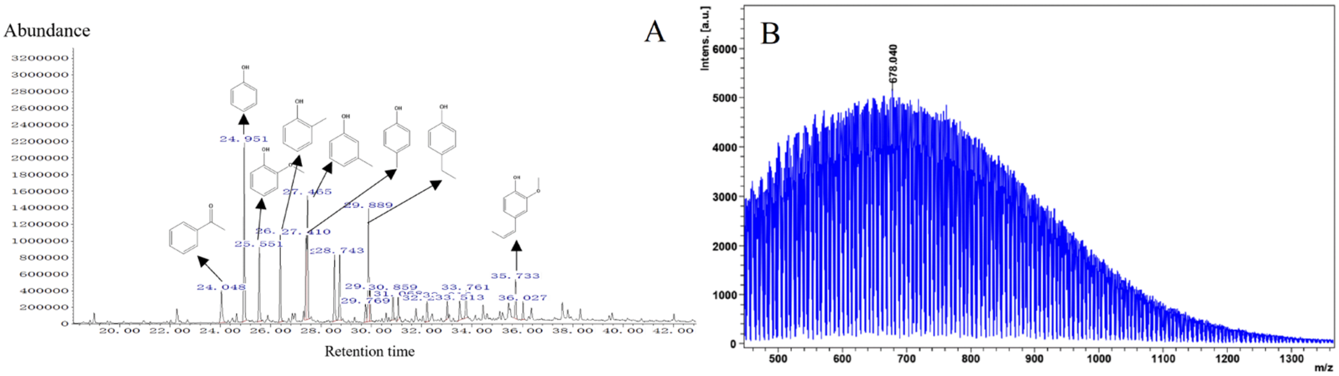

Figure 1. Chromatogram of the volatile fraction of pyrolytic lignin (A) and MALDI-TOF-MS spectrum of the nonvolatile fraction (B).

2. EXPERIMENTAL METHODS

2.1. Material and Catalysts. Pyrolytic lignin used in this study was extracted from the pyrolysis oil of corn stover. The extraction followed a method similar to that described in the literature:[47] the pyrolysis oil was mixed with deionized water at a mass ratio of 1:2 and subjected to vigorous stirring, followed by centrifugation to induce phase separation. The aqueous phase was discarded, and the heavy organic phase was dried to obtain pyrolytic lignin, representing approximately 12 wt % of the total bio-oil yield.

The catalysts used in this study were prepared by the incipient wetness impregnation method using $Ni(NO_3)_2{\cdot}6H_2O$ and $H_2PtCl_6{\cdot}6H_2O$ as precursors for nickel and platinum, respectively. A bimetallic Pt−Ni/MgO catalyst was prepared by sequential loading of Ni onto MgO followed by Pt loading. The prepared catalyst's pore structure characterization can be found in the Supporting Information.

2.2. Depolymerization Experiment. Ethanol was selected as the solvent for depolymerization due to its excellent solubility for lignin and its additional roles as a hydrogen donor and stabilizer for lignin intermediates, as discussed in the Introduction. The 15% Ni/γ-Al_2O_3 catalyst was chosen for its strong hydrogenation activity, which facilitates effective C−O bond cleavage. Additionally, the 2% Pt-10% Ni/MgO catalyst was included based on its proven effectiveness in our previous work,[48] where it was used for upgrading the heavy fraction of bio-oil, primarily composed of pyrolytic lignin. In that study, the Pt−Ni/MgO catalyst demonstrated a high yield of refined oxygenated components, such as esters, alcohols, ketones, and phenols, which are suitable as diesel additives due to the basic properties of MgO. The incorporation of Ni into the Pt/MgO catalyst was found to enhance its hydrogenation, cracking, and reforming abilities, thereby improving the overall catalyst performance. The use of these two catalysts allows for the investigation of both the metal composition and support material in the context of lignin depolymerization. Depolymerization of pyrolytic lignin was carried out by placing 1.2 g of pyrolytic lignin, 15 mL of ethanol, and 0.3 g of catalyst (either 15% Ni/γ-Al2O3 or 2% Pt-10% Ni/MgO) into a batch reactor. After being purged with nitrogen or hydrogen gas and pressurized, the reactor was heated to the desired temperature and maintained for a specific period. The reactor was then cooled to room temperature and depressurized, and the reaction mixture was collected and filtered for analysis.

2.3. Hydrodeoxygenation Experiment. To determine suitable conditions for hydrodeoxygenation (HDO), guaiacol was used as a model compound in the initial experiments. Guaiacol, which consists of a methoxy group ($-OCH_3$) attached to a phenolic ring, is abundant in the products of lignin depolymerization and possesses typical chemical structures found in lignin-derived bio-oil, making it representative of the reactivity of lignin phenolics.[22,49] While real lignin depolymerization products contain a wider variety of phenolic compounds, guaiacol's simpler structure allows for easier detection of interactions with solvents and catalytic systems, helping to isolate key reaction mechanisms. Although guaiacol may differ in reactivity from more complex lignin-derived compounds, its use enables a clearer understanding of the fundamental HDO processes, which can later be applied to more complex bio-oil mixtures. Typically, 1 mL of guaiacol, 0.1 g of catalyst, and 15 mL of a designated solvent, comprising ethanol, H_2O, n-hexane, n-dodecane, and n-hexadecane, were added to the reactor, followed by hydrogen pressurization to the target pressure. The heating procedure for the reactor and the collection of reaction products were similar to those used in the depolymerization experiments. After determining the appropriate HDO conditions using the model compound, the depolymerized product of pyrolytic lignin was subjected to rotary evaporation to remove ethanol, yielding lignin depolymerization oil. This product was then used as the feedstock for the HDO process to convert pyrolytic lignin into hydrocarbon products.

2.4. Products Analysis. Qualitative and quantitative analysis of the liquid products was performed using a gas chromatography−mass spectrometry system (GC-MS, Agilent 8860-5977B GC/MSD). The column used was a DB-1701 capillary column (60 μm × 320 μm × 0.25 μm). The column temperature program started at an initial temperature of 40 °C, increasing at a rate of 5 °C/min to a final temperature of 250 °C, which was then maintained for 15 min. High-purity helium was used as the carrier gas with a split ratio of 20:1. The mass spectrometer's scanning range was set between m/z 10 and 500. Product yields were quantified by using the external standard method. For pyrolytic lignin as the reactant, the yield of product i (Yield_i) is calculated using eq 1. When guaiacol is used as the feedstock, the yield is represented by the carbon yield, calculated using eq 2. The selectivity of product (Selectivity_j) is determined by eq 3:

$$\text{Yield}_i = \frac{S_i \times V}{F_i \times m_L} \tag{1}$$

$$\text{Yield}_j = \frac{S_j \times V \times M_G \times C_j}{F_j \times m_G \times M_j \times C_G} \tag{2}$$

$$\text{Selectivity}_j = \frac{\text{Yield}_j}{\sum_j \text{Yield}_j} \tag{3}$$

where S_i represents the peak area of compound i, F_i is the absolute calibration factor for compound i determined using the external standard method, V is the total volume of the liquid product, m_L is the mass of pyrolytic lignin used in the experiment, and m_G is the mass of guaiacol used. M_i and M_G are the molecular weights of compound i and guaiacol, respectively, and C_i and C_G are the number of carbon atoms in compound i and guaiacol, respectively.

For determining the molecular weight distribution of pyrolytic lignin and its depolymerization products, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS, Bruker) was used. MALDI-TOF-MS is a soft ionization technique that uses a laser to strike a small-molecule matrix, causing the analyte molecules to enter the gas phase without fragmentation or decomposition. The technique measures the mass-to-charge ratio (m/z) of the ionized molecules, allowing for the determination of the molecular weight distribution of the products. The matrix used was 2,5-dihydroxybenzoic acid (DHB) (SIGMA), dissolved in an ACN-H2O-TFA solution (666:333:1) at a concentration of 25.0 mg/mL. After filtration, 0.50 mL of the reaction liquid was dropped onto the MALDI target plate and air-dried at room temperature for analysis. Additionally, 2D HSQC nuclear magnetic resonance spectroscopy (500 MHz Bruker DMX-500) was employed to monitor structural changes before and after lignin depolymerization. Specific parameters for the HSQC analysis were as follows: the spectral width for the F2 (^{1}H) dimension was 12 ppm with 1024 data points, and for the F1 (^{13}C) dimension was 220 ppm with 256 data points. The depolymerized liquid product was concentrated using rotary evaporation to remove ethanol and then dissolved in a DMSO-d_6 solution at a concentration of 100 mg/mL for analysis. Chemical shift calibration was performed using the central peak of DMSO-d6 solvent ($\delta C/\delta H$ = 39.52/2.50 ppm). The characteristic peaks in the HSQC spectra were processed using Bruker Topspin 3.6.5 software.

3. RESULTS AND DISCUSSION

3.1. Pyrolytic Lignin Depolymerization in Ethanol.

The pyrolytic lignin extracted using the aforementioned method was viscous and tar-like, easily forming an emulsion with ethanol but incompatible with water and hydrocarbon solvents. The volatile fraction of the lignin was analyzed using GC-MS, and the results are shown in Figure 1A. The volatiles primarily consisted of low-molecular-weight phenolic compounds, with phenol and cresol being the most abundant, followed by ethyl phenol, guaiacol, and 4-allylguaiacol. The total content of monomeric phenols accounted for 3.9 wt % of the total lignin mass that was analyzed.

To better understand the composition of the nonvolatile fraction, the lignin was further analyzed using MALDI-TOF-MS and HSQC NMR techniques. As shown in Figure 1B, the nonvolatile fraction mainly consisted of macromolecules with molecular weights ranging from 500 to 1300, with a peak at 678. The two-dimensional NMR spectrum, depicted in Figure 2, exhibited strong signals in the aromatic region. Based on the molecular weight distribution, it was inferred that the nonvolatile fraction of pyrolytic lignin was primarily composed of phenolic oligomers. Literature-based[50,51] analysis was used to correlate NMR signals with their corresponding chemical structures, as shown in Table 1. The phenolic oligomers were found to be rich in methoxy groups. The relative abundance of monomer units within the oligomers was calculated based on the NMR signal intensities of coumaryl alcohol (H-unit), coniferyl alcohol (G-unit), and sinapyl alcohol (S-unit) carbon atoms. The ratio of G/H/S was determined to be 1:0.76:0.14, which aligns with the GC-MS analysis of the volatiles. In the native lignin of corn stover, the H-unit content is minimal, indicating that extensive demethoxylation occurs during the formation of phenolic oligomers, leading to an increase in the H-unit content.

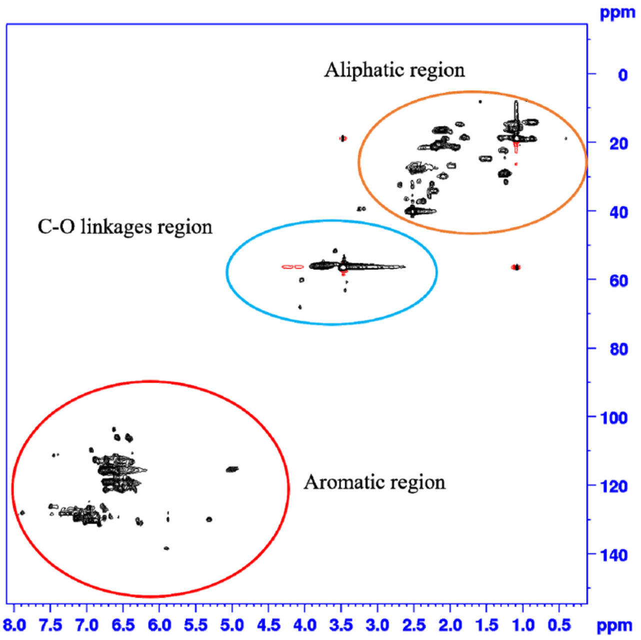

Figure 2. 2D $^{1}H-^{13}C$ HSQC spectrum of pyrolytic lignin.

Table 1. Signal Assignments of the 2D $^{1}H-^{13}C$ HSQC Spectrum

peak	ν(F2) (ppm)	ν(F1) (ppm)	signal attribution
1	7.0062	130.6385	C2,6-H2,6 in PB
2	6.8304	130.3943	CαHα in p-Coumaryl alcohol
3	6.9183	129.6618	C3/H3 in G units
4	7.1233	129.4176	C3,5/H3,5 in H units
5	6.9915	129.1734	C3,5/H3,5 in H units
6	6.9476	128.9293	C3/H3 in G units
7	6.9329	126.7317	(Cα/β–Hα/β) stilbene
8	6.4058	119.6506	C5/H5 in G units
9	6.7279	119.1622	C5/H5 in G units
10	6.7719	115.4996	C6/H6 in G units
11	6.6694	115.2554	C2,6/H2,6 in H units
12	6.5459	105.7784	C2,6/H2,6 in S unit
13	4.0335	60.0716	CβHβ in p-Coumaryl alcohol
14	3.5064	56.6531	CH2 in ethanol
15	3.7407	55.6764	OMe
16	2.5104	39.6736	DMSO-d_6
17	2.4222	37.4759	β-1 linkage
18	2.166	20.2995	aryl methylene aryl
19	1.0881	18.4289	CH3 in ethanol

Pyrolytic lignin requires further depolymerization and hydrodeoxygenation to be converted into hydrocarbon fuels. Given the good compatibility between pyrolytic lignin and ethanol, ethanol was used as the solvent for upgrading the lignin. Previous research by our group demonstrated that supercritical ethanol can improve the physicochemical properties of bio-oil and phenolic oligomers.[52] However, at elevated temperatures, ethanol tends to undergo increased side reactions under catalytic conditions, leading to higher consumption. Therefore, we set the temperature to 250 °C, and under these reaction conditions, the internal pressure of the reactor was monitored to reach 6.8 MPa, ensuring that the ethanol reached a supercritical state.

Figure 3A shows the molecular weight distribution of pyrolytic lignin under different reaction times during the supercritical ethanol upgrading process. After 90 min, numerous low-molecular-weight compounds with molecular weights below 300 were observed. When the reaction time was extended to 180 min, the intensity of the high-molecular-weight peaks decreased, and the quantity of phenolic trimers and tetramers was reduced, with the product primarily containing phenolic dimers. Upon further extension of the reaction time to 450 min, the concentration of oligomers with molecular weights between 300 and 600 increased significantly, indicating the reformation of a large number of phenolic

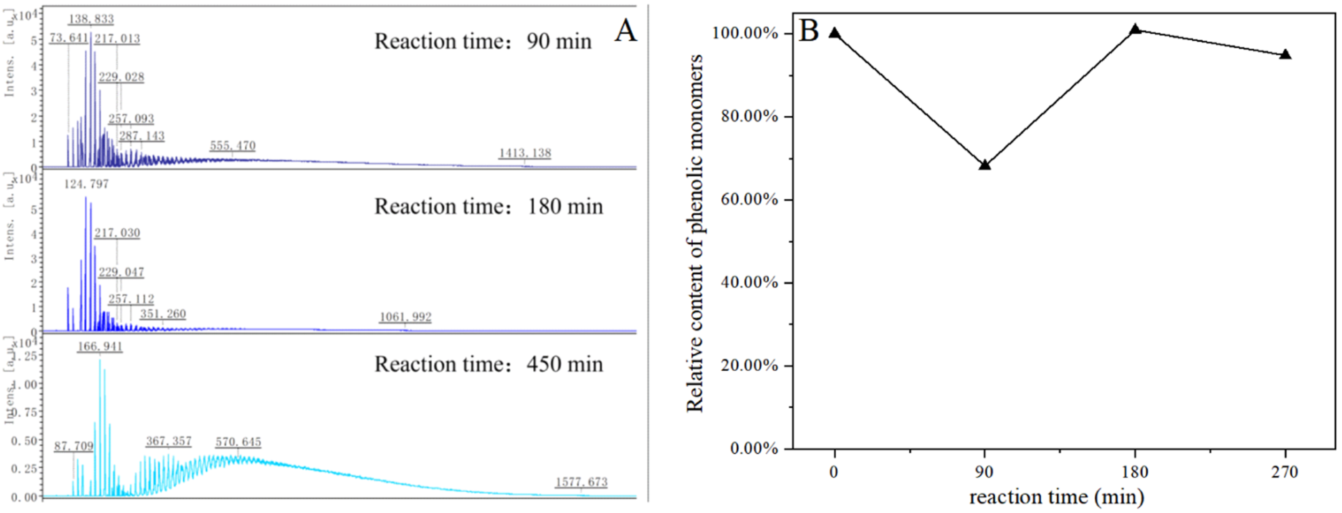

Figure 3. Molecular weight distribution of pyrolytic lignin under different reaction times during supercritical ethanol upgrading (A) and relative content changes of monomeric phenols detected by GC-MS (B). Reaction temperature: 250 °C, catalyst: 2% Pt-10% Ni/MgO 0.3 g, atmosphere: nitrogen, initial pressure: 1 bar.

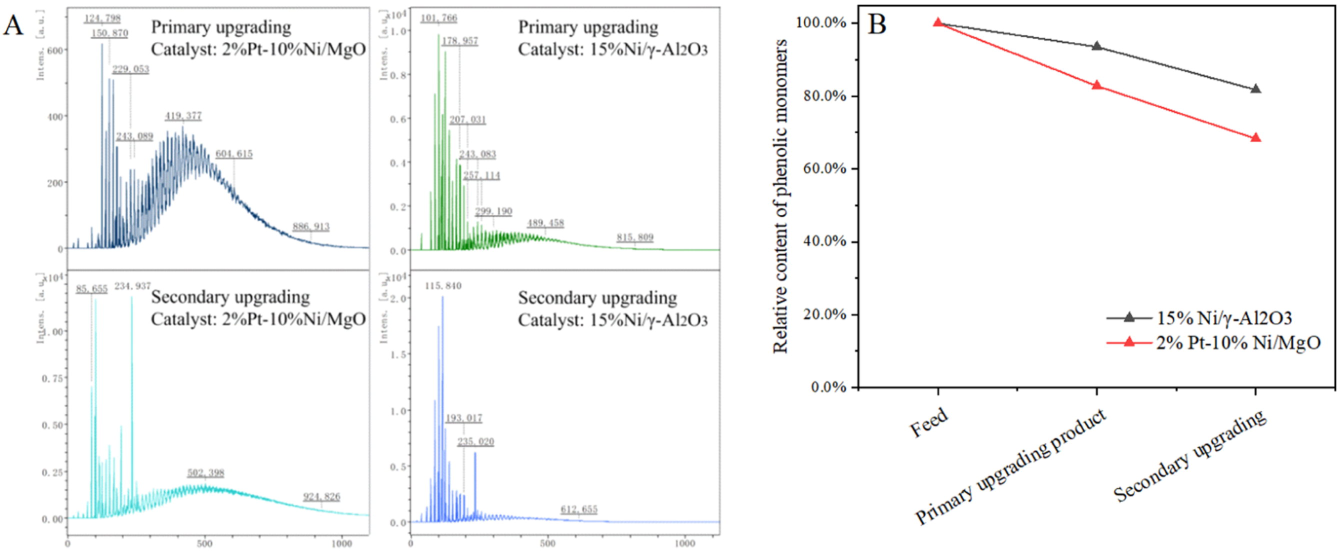

Figure 4. Changes in molecular weight distribution of pyrolytic lignin during two-stage ethanol-based hydrogen upgrading (A) and changes in the monomeric phenol concentration (B). Reaction temperature: 250 °C, reaction time for each stage: 60 min, initial hydrogen pressure: 4 MPa, catalyst amount: 0.3 g.

oligomers. These results suggest that phenolic oligomers are depolymerized into smaller molecules during the upgrading process, but prolonged reaction times lead to the dominance of condensation reactions among the phenolics.

Despite significant changes in the molecular weight distribution of pyrolytic lignin, the content of monomeric phenols remained largely unchanged, as shown in Figure 3B. Based on the molecular weight analysis, it was inferred that after the depolymerization of oligomers, the products were primarily dimers, without further breakdown into monomeric phenols.

In the upgrading experiments described above, no fully deoxygenated products were detected, and about 34 wt % coke was formed based on the weight of the lignin feedstock, indicating a certain degree of condensation. To investigate whether the conversion of lignin to hydrocarbons can be achieved in ethanol, a two-stage upgrading experiment was conducted using 2% Pt-10% Ni/MgO and 15% Ni/γ-Al_2O_3 as catalysts under an external hydrogen pressure of 4 MPa. Specifically, after the first upgrading reaction, the solid residue was separated, and fresh catalyst was added, followed by the reintroduction of hydrogen for a second upgrading. Each stage of upgrading lasted for 60 min, with other reaction conditions unchanged.

Figure 4A shows the molecular weight distribution of the two-stage upgrading products under the stringent conditions of an initial hydrogen pressure of 4 MPa. In the experiment using Pt–Ni/MgO as the catalyst, after the first upgrading stage, the molecular weight peak for nonvolatile products was observed at m/z 419. After the second upgrading stage, the higher-molecular-weight compounds in the nonvolatile fraction decreased, with most compounds having a molecular weight under 250. However, oligomers with a molecular weight around 500 remained. Additionally, the content of monophenols decreased by 30% (Figure 4B), which mirrors the trend observed when hydrogen was not used. We hypothesize

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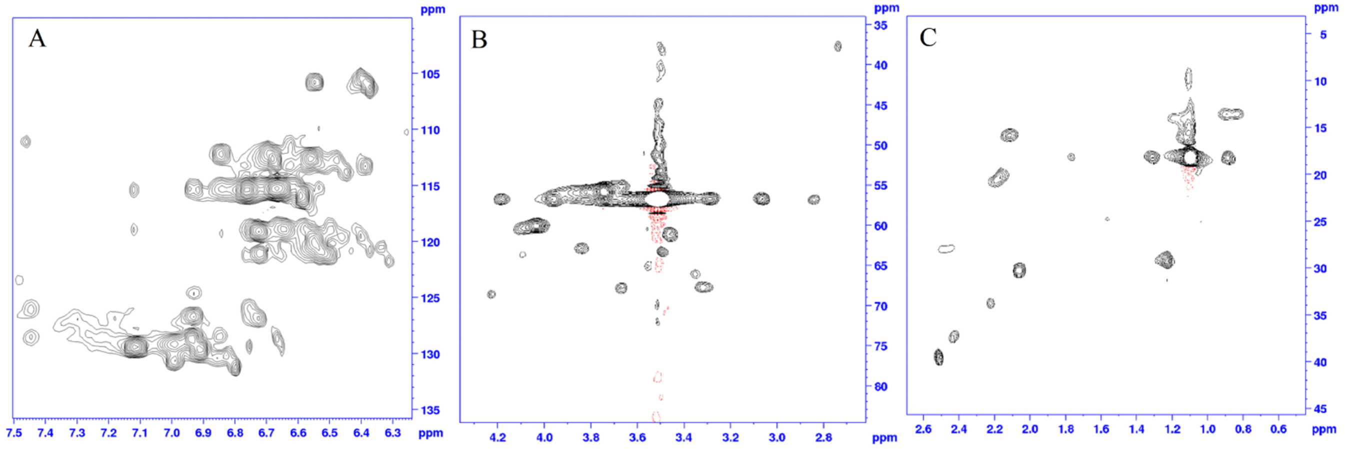

Figure 5. 2D HSQC NMR spectrum of products from two-stage ethanol upgrading of pyrolytic lignin. (A) Aromatic region, (B) lignin C−O bond region, and (C) aliphatic side-chain region. Reaction temperature: 250 °C, reaction time for each stage: 60 min, initial hydrogen pressure: 4 MPa, catalyst: 15% Ni/γ-Al_2O_3, 0.3 g.

that while hydrogen does facilitate some depolymerization of pyrolytic lignin, it does not promote further cleavage of dimers into monomers, limiting the increase in monomeric phenols. The observed limited effect of gas-phase hydrogen aligns with the findings of Ma et al.,[42] who indicated that the presence of gas-phase hydrogen can inhibit the depolymerization of kraft lignin by suppressing the chemisorption of ethanol on the catalyst surface. In this system, the lack of a clear hydrogen effect is likely because the depolymerization and hydrodeoxygenation of lignin require active hydrogen species such as hydrogen radicals. Ethanol itself can undergo dehydrogenation on the catalyst to produce hydrogen and, via a hydrogen spillover effect, provide active hydrogen species to the substrate. As a result, external hydrogen is not necessary for the process. Second, for external hydrogen to participate in the reaction, it must first dissociate on the catalyst surface. However, ethanol competes with hydrogen for adsorption on the catalyst, inhibiting hydrogen's participation in the reaction and further hindering the process. In addition, the catalytic activity was analyzed based on the product distribution. As shown in Figure 4A, after 1 h of upgrading, the use of 15% Ni/γ-Al_2O_3 as the catalyst resulted in most products having m/z values of less than 300, indicating the formation of lower-molecular-weight compounds. In contrast, the MgO-supported catalyst showed a significant proportion of compounds with m/z values in the range of 300−600 and a lower content of monomeric phenols, and the content of monomeric phenols was also lower compared to the Al_2O_3-supported catalyst (Figure 4B). This suggests that acidic supports such as γ-Al_2O_3 are more effective in promoting hydrogenolysis of pyrolytic lignin. 2D HSQC NMR analysis of the products from the two-stage upgrading revealed strong signals for oxidized G-type monomers in the $\delta C/\delta H$ range of 130/7.0−7.4. In the aliphatic C−O bond region and the C−C bond region, common lignin C−O bond signals such as β−O−4 and α−O−4 disappeared, while signals from β-1, 5−5, stilbene, and other C−C bonds directly connected to aromatic carbon atoms were prominent (Figure 5). This indicates that the residual dimers in the upgraded product were primarily linked through persistent $C-C_{Ar}$ bonds.

3.2. Solvent Effects on the Hydrodeoxygenation of Phenolics. The above study shows that ethanol as a solvent can facilitate the depolymerization of pyrolytic lignin, but even with external hydrogen, it is challenging to achieve the hydrodeoxygenation of monomeric phenolic compounds. Considering the significant effect of the solvent on reaction selectivity, experiments were conducted using ethanol, water, n-hexane, n-dodecane, and n-hexadecane as solvents, with 15% Ni/γ-Al_2O_3 as the catalyst for hydrodeoxygenation of guaiacol.

Figure 6A presents the product distribution when ethanol is used as the solvent. The major products can be categorized into several groups: aliphatic compounds, primarily n-butanol and n-hexanol; ethers, including 1-methoxyethane, 1,1-diethoxyethane, and 1-(1-ethoxyethoxy)butane; esters, such as ethyl acetate and butanoic acid ethyl ester; and aromatics, consisting of C6−C15 arenes, phenols, and benzyl ethers. Under both hydrogen and nitrogen atmospheres, the carbon yields of the liquid-phase products were 205 and 140%, respectively, both exceeding the carbon content of the guaiacol input. This suggests that ethanol underwent etherification with the hydroxyl or methoxy groups of guaiacol or substitution reactions with the aromatic ring, resulting in multiple aromatic derivatives. Furthermore, n-butanol and n-hexanol are generated through the Guebert reaction,[53] wherein ethanol molecules undergo a series of transformations, including dehydrogenation, aldol condensation, dehydration, and hydrogenation, ultimately forming heavier alcohols. Ethers and esters were also observed in the products of lignin depolymerization with ethanol as the solvent in previous studies.[40,42] These compounds are believed to arise from the esterification or etherification of ethanol with lignin-derived intermediates. In this study, since the substrate was exclusively guaiacol, we hypothesize that these products may be derived from active intermediates originating from guaiacol, such as methoxy and ethoxy groups, through a series of reactions. The chemical process is summarized in Figure 6B. While these products hold potential value for chemical applications, their separation remains an area requiring further investigation. With the presence of hydrogen gas, hydrocarbons such as benzene, ethylbenzene, cyclohexane, and ethylcyclohexane were formed, with a total yield of 8%. However, hydrogen also enhanced other reactions, and the selectivity for the hydrocarbon products was only 4%. Similar observations were made by Hellinger et al.,[54] who proposed that oxygenated solvents might strongly adsorb onto active catalytic sites, blocking them

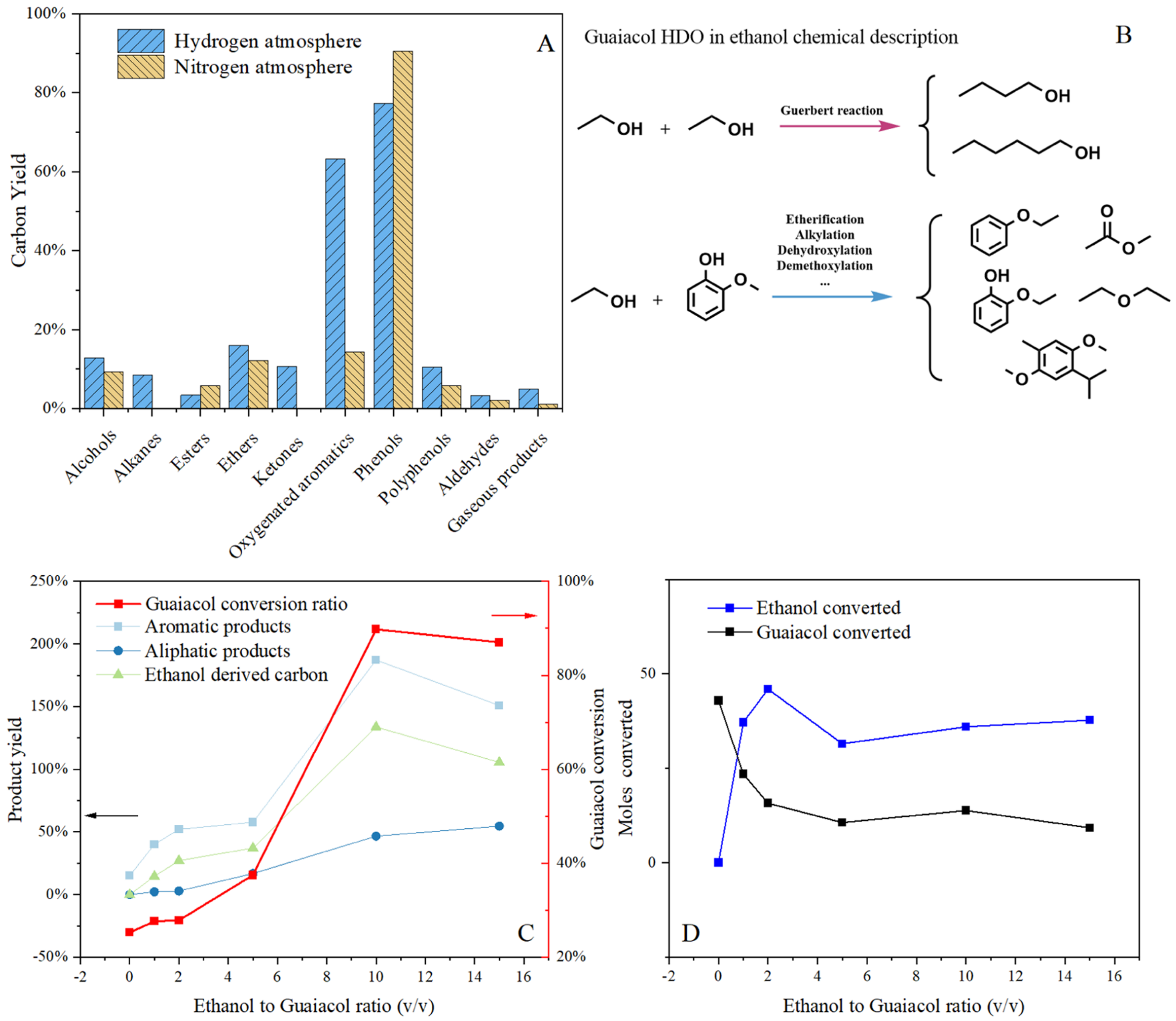

Figure 6. Product distribution of guaiacol reactions in ethanol (A) under the following reaction conditions: 300 °C, 6 h, 1 mL of guaiacol, 15 mL of ethanol, 0.1 g of the 15% Ni/γ-Al_2O_3 catalyst, and hydrogen or nitrogen gas at 1 MPa. Proposed chemical process of guaiacol HDO in ethanol (B). Guaiacol conversion rate and product yield under different ethanol-to-guaiacol ratios (C) and moles of carbon converted in ethanol and guaiacol (D). Reaction conditions: 300 °C, 6 h, initial hydrogen pressure of 1 MPa, and 0.1 g of 15% Ni/Al_2O_3 catalyst, with the total volume of guaiacol and ethanol maintained at 16 mL.

and rendering them unavailable for the deoxygenation of guaiacol.

However, ethanol has good solubility for pyrolytic lignin, and the long-chain alcohols and esters formed as byproducts have the potential for further upgrading to fuel. Therefore, in ethanol systems, it is necessary to control the conversion ratio between ethanol and phenolic compounds to improve the selectivity toward the target reaction. This study investigated the relative conversion rates of ethanol and guaiacol under varying ratios while keeping the number of catalytic active sites constant. Figure 6C shows that as the ethanol-to-guaiacol v/v ratio increased, the proportion of carbon derived from ethanol in the liquid product also increased. When the ethanol-to-guaiacol ratio exceeded 10, the amount of carbon derived from ethanol equaled that from guaiacol. Although the input of guaiacol decreased, the overall carbon content of aromatic products continued to increase, indicating that ethanol had been extensively attached to the side chains of aromatic rings. When the ethanol-to-guaiacol ratio exceeded 10, the conversion rate of guaiacol approached 90%. At this point, the carbon content of aromatic products ceased to grow, whereas the carbon content of aliphatic products continued to rise, indicating that these aliphatic products were primarily derived from ethanol. This can be explained as follows: with a fixed number of active sites on the catalyst, an increasing ethanol concentration increases the likelihood of ethanol molecules interacting with one another. When the ethanol-to-guaiacol ratio surpasses a certain threshold, the adsorption of guaiacol onto the catalyst becomes more challenging, limiting its further conversion. Moreover, as shown in Figure 6D, the number of moles of converted ethanol and guaiacol approached a constant value as the ethanol-to-guaiacol ratio increased, stabilizing at approximately 3 when the ratio was above 5. The coconversion of ethanol and phenolic substrates

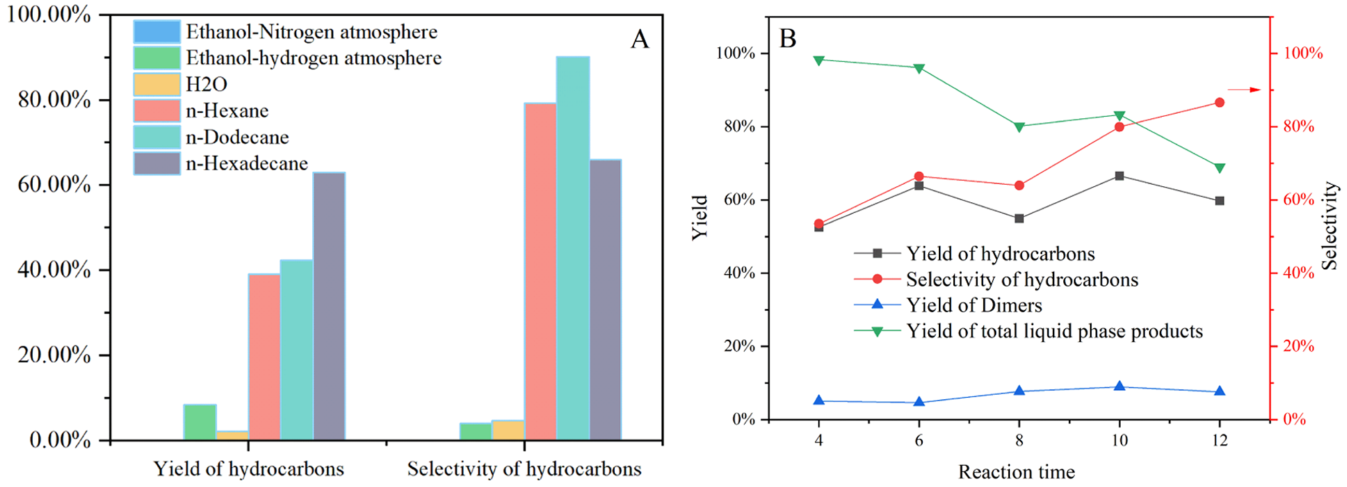

Figure 7. Yield and selectivity of hydrocarbon products from hydrodeoxygenation of guaiacol in different solvents (A) and changes in product yield and selectivity over time when n-hexadecane is used as the solvent (B). Reaction conditions: 300 °C, 6 h, 1 mL of guaiacol, 0.1 g of 15% Ni/γ-Al_2O_3 catalyst, 15 mL of solvent, with an initial hydrogen pressure of 1 MPa unless otherwise specified.

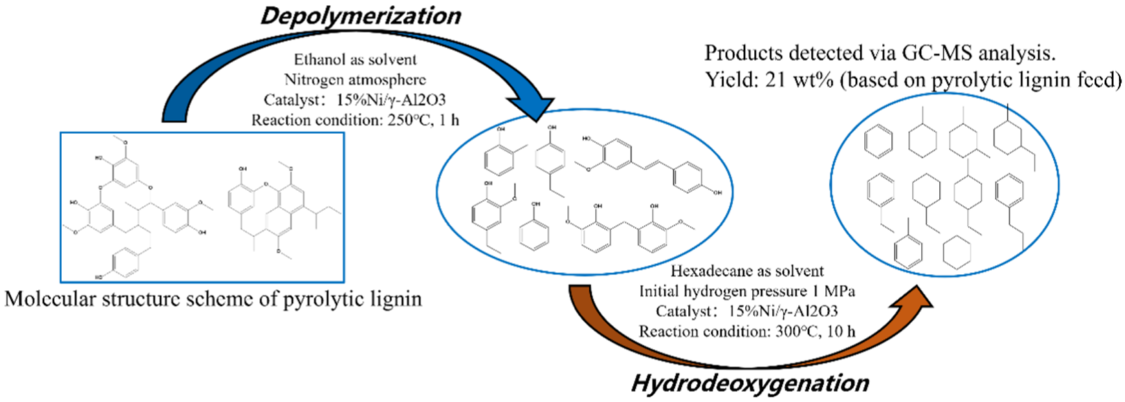

Figure 8. Two-step process for producing hydrocarbon fuels from pyrolytic lignin: experimental procedure and results.

can introduce carbon-containing groups onto the side chains of aromatic rings, increasing the carbon number of phenolic products, which is beneficial for upgrading them to aromatic hydrocarbons that meet jet fuel carbon specifications. However, excessive ethanol leads to an increase in aliphatic byproducts and adds extra costs for solvent separation. Based on the findings of this study, an ethanol-to-oil ratio below 5 can effectively balance the selectivity for target products and the generation of byproducts, optimizing the economic feasibility of the reaction.

Compared to the complexity of the products obtained when ethanol was used as the solvent, the products derived from using water or hydrocarbons as solvents were exclusively derived from guaiacol. These products mainly included partially deoxygenated compounds such as phenol, 2-methylphenol, cyclohexanone, and cyclohexanol, as well as hydrocarbons like benzene, cyclohexane, and a small amount of bicyclic compounds such as dicyclohexane and cyclohexylbenzene. Figure 7A summarizes the yield and selectivity of hydrocarbon products formed after the reaction of guaiacol with different solvents.

When water was used as the solvent, the hydrodeoxygenation activity was minimal, with a guaiacol conversion rate of 60%, but a hydrocarbon yield of only 2%. Phenol was the main component of the products. In contrast, hydrocarbon solvents exhibited excellent hydrodeoxygenation activity with a guaiacol conversion rate of 100%. The yield of hydrocarbon products exceeded 40% in n-hexane and n-dodecane, whereas in n-hexadecane, the yield unexpectedly increased to 60%. However, the selectivity for hydrocarbons in n-hexadecane was lower than that in n-hexane and n-dodecane, with the former at 66%, while the latter two were close to 80%.

Further analysis showed that when n-hexane and n-dodecane were used as solvents, the carbon yield of the liquid-phase products was 46 and 49%, respectively, whereas n-hexadecane as the solvent resulted in a carbon yield of 83%. This suggests that oxygenated products were retained more in n-hexadecane compared to n-hexane and n-dodecane. A possible explanation for this phenomenon is that under the reaction conditions, n-hexadecane remained in the liquid phase, whereas n-hexane and n-dodecane were in the gas phase. Given that the metal catalyst was located at the bottom of the reactor, reactants adsorbed onto the catalyst surface are more readily desorbed in the liquid phase, whereas in the gas phase, they stay on the catalyst surface for a longer duration, leading to over-reaction and eventually forming oligomers and coke.

To verify this hypothesis, the reaction time in the n-hexadecane system was extended. It was found that the selectivity of hydrocarbon products continued to increase, while the carbon yield of the liquid-phase products gradually decreased. Additionally, the detected content of dimers also showed an increasing trend, as illustrated in Figure 7B. These

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Table 2. Comparison of Lignin Alcoholysis Methods and Efficiency in This Study with Previous Research

refs	substrate	catalyst	solvent	product distribution
19	pyrolytic lignin	$CuAlMgO_x$	methanol	alcohols and alkylated phenols with 50% carbon yield, no alkanes observed
55	organosolv lignin	Ni/Al_2O_3	ethanol	29.7 wt % phenolic monomers, no alkanes observed
56	technical lignin	RuZnAc	1,4-dioxane/methanol, 5:1 v/v	5−23 wt % phenolic monomers, no alkanes observed
57	organosolv birch lignin	Ni/Nb_2O_5	Isopropanol	dimers and trimers comprising 24.7% and 60.5% of the lignin-oil
this study	pyrolytic lignin	Ni/Al_2O_3	ethanol, n-hexadecane	21 wt % cycloalkanes and aromatic hydrocarbons with 100% selectivity

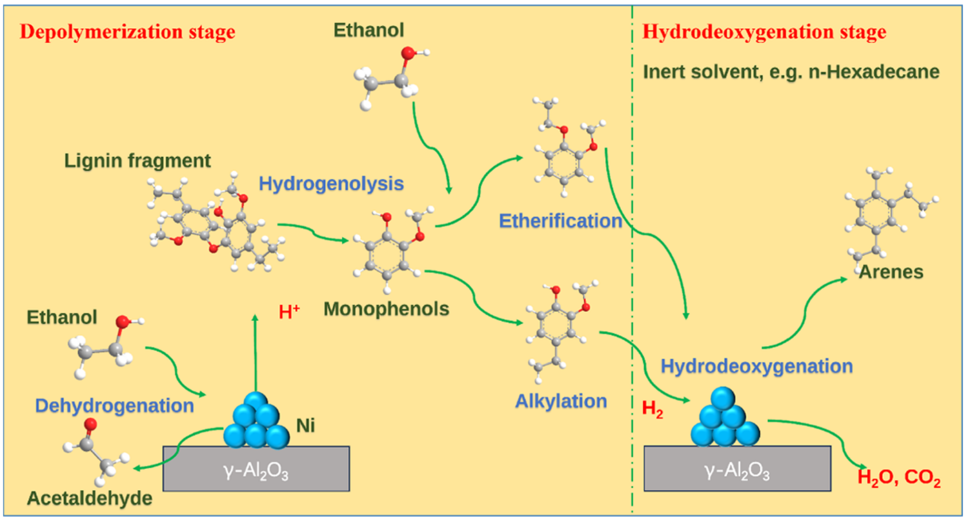

Figure 9. Proposed reaction scheme for the two-stage lignin conversion process.

experimental results indicate that over-reaction leads to carbon loss, and controlling the residence time of guaiacol and other reactants on the catalyst is crucial to improving the yield and selectivity of deoxygenated products.

3.3. Two-Step Conversion of Pyrolytic Lignin. Based on the above research results and considering the specific characteristics of the lignin depolymerization and hydrodeoxygenation processes, an optimized two-step process for converting pyrolytic lignin into hydrocarbon fuels has been proposed. The first step involves the depolymerization of lignin in ethanol using an acidic 15% $Ni/\gamma\text{-}Al_2O_3$ as the catalyst to facilitate phenolic oligomer fragmentation. Given that molecular hydrogen had little impact on the observed molecule weight distribution of lignin depolymerization products, an inert nitrogen atmosphere was applied. The reaction time was set to 60 min under 250 °C to avoid reoligomerization. The resulting liquid product was then subjected to rotary evaporation to remove ethanol and subsequently transferred to an n-hexadecane solvent for hydrodeoxygenation. In the second step, hydrodeoxygenation was again carried out using 15% $Ni/\gamma\text{-}Al_2O_3$ as the catalyst. At the beginning of the reaction, 1 MPa of hydrogen was introduced into the reactor. The reaction time was set to 10 h at 300 °C to deliver an exhaust hydrodeoxygenation. The process flow and the final products are illustrated in Figure 8. After the two-step conversion, the GC-MS detectable products consisted solely of aromatic hydrocarbons and cycloalkanes, accounting for 21 wt % of the input pyrolytic lignin. These were present in a 1:5 ratio with carbon numbers ranging from C6 to C11. This method operates under mild reaction conditions, effectively reducing ethanol consumption and requiring a lower hydrogen pressure. The resulting product contains only hydrocarbons, which simplifies subsequent separation and purification. Compared with single processes using alcohols or mixed solvents that yield phenolic monomers and oligomers as major products, this approach produces more handleable non-oxygen-containing products suitable for fuel applications, with competitive yield and selectivity, as shown in Table 2.

3.4. Discussion. Lignin is notorious for its recalcitrant and complex structure composed of phenolic monomers linked by various C−C and C−O bonds. This nature of lignin results in both a low catalytic reactivity and a wide spectrum of product distributions, which impedes the overall conversion efficiency of biomass refining processes. As pyrolytic lignin undergoes fragmentation and repolymerization during pyrolysis, it has fewer functional groups and more C−C linkages compared with protolignin. To avoid further polymerization to coke under high temperature in the gas phase, hydrothermal/solvolysis methods have been employed in the conversion of pyrolytic lignin. Alcohols have demonstrated good solubility to pyrolytic lignin and act as hydrogen donors and free radical scavenging agents, thereby promoting the breakdown of phenolic oligomers into monomers. However, hydrodeoxygenation of the produced monomers for fuel application is actually blocked by alcohol molecules due to competitive adsorption on catalysts' active sites. To address this issue, this study transfers the phenolic monomers into an inert solvent, e.g., n-hexadecane, to facilitate complete hydrodeoxygenation and achieve higher alkane selectivity compared with previous studies that use a single alcohol solvent, as demonstrated in Table 2.

This strategy divides the multistep lignin conversion process into two distinct stages that can be treated separately under appropriate reaction conditions, such as different solvents, catalysts, and temperatures. Chemical reactions can be regulated via solvents and process conditions to enhance product selectivity, as illustrated in Figure 9. In the ethanol system, in situ hydrogen is generated through ethanol dehydrogenation, promoting hydrogenolysis of lignin on the surface of Ni/γ-Al_2O_3. Additionally, ethanol molecules are added to the side chains of benzene rings through alkylation and etherification, which can benefit the carbon length of the final products. Meanwhile, hydrodeoxygenation is more efficient in a non-oxygen-containing environment and requires harsher conditions; thus, inert solvents and molecular hydrogen can be adopted. Based on this scheme, a mixed solvent system may be developed to integrate depolymerization and hydrodeoxygenation reactions into a single step. Existing studies have explored dual-solvent systems, such as alcohol/water[58] and dioxane/alcohol,[56] for lignin conversion. Although enhanced depolymerization efficiency has been observed, the resulting products still contain mainly phenols and oligomers, which are difficult to separate and purify. Instead, introducing an inert solvent to a functional solvent and optimizing their ratio may have the potential to facilitate lignin depolymerization while achieving high selectivity toward alkanes simultaneously.

4. CONCLUSIONS

In this study, we developed an innovative two-step process to convert pyrolytic lignin to hydrocarbon fuels under relatively mild conditions. The process involves initial depolymerization in an ethanol system followed by comprehensive hydrodeoxygenation in an n-hexadecane system, achieving a yield of 21 wt % of hydrocarbon products, mainly composed of aromatic and alicyclic hydrocarbons. This method demonstrates high selectivity toward desired products while minimizing byproduct formation and solvent consumption, even at moderate temperatures and pressures.

Ethanol, as a solvent, not only effectively dissolves lignin and facilitates depolymerization but also reacts with aromatic structures to increase the carbon content of the resulting fuel molecules, making them more suitable for aviation applications. However, excessive ethanol leads to increased side reactions and higher solvent consumption, which must be carefully controlled. Notably, the addition of hydrogen in the ethanol system showed no significant improvement in depolymerization, indicating that external hydrogen is unnecessary in this stage. In terms of catalyst performance, 15% Ni/γ-Al_2O_3 was found to be more effective than Pt−Ni/MgO in promoting hydrogenolysis of pyrolytic lignin, resulting in lower-molecular-weight products. During the hydrodeoxygenation process, the use of an inert solvent, such as n-hexadecane, that does not compete with the substrate for catalytically active sites proved to be advantageous. The solvent's phase state under reaction conditions also played a critical role in the efficiency of the HDO step. By carefully selecting solvents that align with the specific demands of both the depolymerization and HDO processes, this study optimized reaction conditions to maximize overall efficiency and minimize resource consumption.

Despite the promising results, the two-step process faces several practical challenges. Separating ethanol from the depolymerized products requires substantial energy, and the high viscosity of the lignin-derived oil complicates its transfer to the hydrocarbon solvent. Additionally, some oligomers are insoluble in hydrocarbon solvents, leading to losses during the transfer process. Future research should focus on simplifying the process by designing a unified system that can handle both depolymerization and hydrodeoxygenation. One potential solution is to design an ethanol−hydrocarbon mixed solvent system that balances both the solubility of lignin and the selectivity of the hydrogenation process, reducing energy consumption and minimizing material loss.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c06287.

Surface area and pore texture characterization results for 15%Ni/Al_2O_3 and 2%Pt-10%Ni/MgO (PDF)

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Notes

The authors declare no competing financial interest.

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