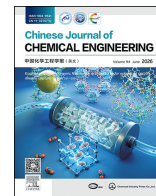




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Full Length Article

Catalytic depolymerization of organic extraction pine lignin over Ni/MLG coupled with NaOH for aromatic monomer production

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ABSTRACT

In order to advance the development of biomass energy chemical field and to increase the utilization efficiency of lignin for valuable chemicals, this study explored the whole process from lignin extraction to depolymerization using pine wood flour as raw material for the production of aromatic monomers. The efficient extraction of lignin from pine wood flour was achieved in 1,4-butanediol solvent at 170 °C, which then was converted to aromatic monomers successfully under the synergistic catalysis of Ni/MLG and NaOH. The usage of 1,4-butanediol extracting pine flour lignin enables to protect the guaiacyl (G) units and prevent the recombination of C—C bonds in the lignin fragments. And the synergistic effect of Ni/MLG and NaOH catalysts can efficiently hydrogenolyze not only lignin feedstock but also lignin oligomer fragments into aromatic monomers, enhancing the yield significantly. As a result, 97.5% lignin conversion and 36.9% yield of aromatic monomers are obtained at 280 °C, with the carbon deposition rate below 6.7%, which is much superior to other Ni-based carbon catalysts and other alkaline catalysts. The major aromatic monomers include guaiacols, syringols, and *p*-hydroxyphenols, and they are promising for subsequent product purification and application as high value chemicals. This study not only proposes an effective way for the utilization of lignin, but also provides valuable reference for the development of biomass energy chemical field.

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1. Introduction

Lignin, as the largest natural source of aromatic compounds on earth [1–3], shows enormous potential in the production of fuels and high-value chemicals [4–9]. Despite its recognized potential, its complex structure and resistance properties hinder its efficient conversion into valuable products [10,11]. As a result, most lignin has long been treated as a kind of low-value energy source for heating or power generation during biomass refining processes, which is a significant waste [11–13]. Lignin consists of three main unit structures of guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl

(H) [14–19]. These units are connected by various chemical bonds (e.g., β -O-4, β - β , 5-5', etc.) [16,20], forming a complex three-dimensional reticulated amorphous structure with structural recalcitrance [21,22].

The complexity and diversity of lignin's structure, combined with its entanglement with cellulose and hemicellulose, creates a natural barrier to degradation, making the separation and extraction difficult. Achieving efficient separation of lignin from cellulose and hemicellulose while maintaining its original structure is a key research focus in the field of biomass refinery. The techniques for lignin extraction mainly include alkali extraction [23], sulfonation extraction [24] and organic solvent extraction [25]. Among them, organic solvent extraction is widely studied because it can selectively dissolve lignin with minimal impact on other components, thus facilitating the extraction of high-purity

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lignin [16]. Zijlstra *et al.* [26] proposed a method to extract lignin from various biomass sources by ethanol, which yielded lignin with a high retention rate of β -O-4 bonds. They also investigated the effect of extraction conditions on lignin yield and β -O-4 retention rate, as well as performed selective depolymerization to obtain high yield of aromatic monomer products. Sun *et al.* [27] studied the effect of 1,4-butanediol on the extraction of lignin from loofah fibers. The optimal extraction conditions for lignin was a reaction temperature of 220 °C, a liquid-to-solid ratio of 1:8, an incubation time of 2.5 h, and a 60% volume fraction of 1,4-butanediol. The lignin extraction rate reached as high as 91.63%. Li *et al.* [28] explored the effects of alkali amount and 1,4-butanediol content on the lignin yield, extraction rate and structure change. They found that the extraction rate of lignin increased with the increase of alkali content, but decreased with the increase of alcohol content. Besides adding different alkalis for extraction, the addition of acids during organic solvent extraction is also a common method to promote the release of extractable lignin fragments while maintaining the integrity of lignin structure [16]. Chen *et al.* [29] found that methanol hydrochloride treatment not only preserved the integrity of the original lignin structure, but also reserved relatively more β -aryl ether bonds and free phenolic hydroxyl groups, which facilitated the downstream depolymerization of lignin into aromatic monomer products. In our previous study, we also compared the effects of various organic solvents on the extraction rate and structure of lignin. The molecular weights of lignin extracted with different organic solvents were less than 2000 g·mol⁻¹. Acetic acid and ethylene glycol enabled to protect the C—O bonds in lignin during the extraction process [30].

The research of lignin extraction is not only to understand the structure of lignin and the protection effect on the structure, but also to obtain more high value chemicals through providing advantage for the lignin depolymerization process [31,32]. Mei *et al.* [33] found that Ni/C catalyst (Ni-NDC-500) derived from a Ni-based metal-organic framework (Ni-MOF) was highly efficient in the hydrogenolysis of β -O-4 ether bonds. In the absence of external hydrogen, the catalyst was able to precisely target the ether bond and break the chemical bond to disintegrate the macromolecular structure of lignin, generating high yield of aromatic monomers with high value. Li *et al.* [22] found that the Ni-0.25%Pd/C-NaOH catalytic system exhibited good performance in catalyzing the hydrogenolysis of lignin model compounds, especially β -O-4 model compound. Under mild conditions (150 °C, 2 MPa H₂, 3h), β -O-4 model compound was completely converted with a monomer yield as high as 95.6%. The Ni/C catalyst had good hydrogenation activity and promoted hydrogenolysis cleavage of C—O and C—C bonds in lignin. The addition of alkali further weakened the chemical bonds in lignin by forming intermediate products such as phenolic salts, reducing bond energy and making bond cleavage easier [34]. Although a series of research progresses have been proposed in the valorization of lignin, there are still some gaps in the acquisition of efficient approach to high yield of aromatic monomers under mild conditions. And the reaction mechanism has not been revealed out clearly.

In this study, 1,4-butanediol as solvent extraction was selected for the lignin extraction from pine wood flour, and the effect of lignin extraction on the lignin structure was explored. Afterwards, the effects of different Ni-based catalytic systems on the depolymerization of lignin were investigated systematically. By using various analytical methods, such as GC-MS, FT-IR, GPC, *etc.*, the lignin depolymerization products were characterized and analyzed in detail. The synergistic catalytic system of Ni/MLG coupled with NaOH successfully realized the efficient conversion of lignin to high yield of aromatic monomers. The reaction mechanism of lignin hydrogenolysis and products distribution was also revealed out.

2. Materials and Methods

2.1. Materials

The pine flour used in the experiment was masson pine, a representative of softwood, which was obtained from the pilot production base of Shanshui in Foshan, Guangdong, China. KOH, NaOH, Na₂CO₃, H₃PO₄, ZnCl₂, MgCl₂ and AlCl₃ were obtained from Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China. Anhydrous ethanol, 1,4-butanediol and Ni(NO₃)₂·6H₂O were purchased from Guanghua Chemical and Drug Factory. Glacial acetic acid, hydrochloric acid (35%) and concentrated sulfuric acid (98%) were purchased from Guangzhou Chemical Reagent Factory. Activated carbon (AC) and SBA-15 were purchased from Hebei Tangshan Huaneng Activated Carbon Co. Deionized water, mesoporous carbon (CMK-3), and multilayer graphite (MLG) were manufactured in the laboratory.

2.2. Lignin extraction

The raw material of pine flour was pre-treated and dried in the oven at 100 °C for 48 h. Then the material was crushed, passed through a 40–60 mesh (0.25–0.42 nm) sieve, and then stored for usage. 30 ml of 75% 1,4-butanediol/water solution, 21 ml of glacial acetic acid, 1.82 g of 98% concentrated sulfuric acid were thoroughly mixed, and then combined with 25.0 g of pretreated pine flour in a 500 ml stainless steel high-pressure reactor. The reaction was carried out at 160 °C for 1 h. At the end of the reaction, the mixture was filtered to collect the filtrate. Excess deionized water was added to the filtrate until no more precipitate formed. Then the mixture was filtered and separated again after washing. Finally, the solid was placed in a refrigerator for 0.5 h and dried in a freeze dryer for 24 h. The obtained solid was the 1,4-butanediol lignin, represented as HSL lignin.

2.3. Catalyst preparation and characterization

The synthesis of catalysts was carried out following the method described in the reported literatures [35–37] and the details were elaborated as below.

Preparation of CMK-3: 3.75 g of sucrose and 0.42 g of concentrated sulfuric acid were added to 15 ml of deionized water and stirred to dissolve. Then, 3 g of SBA-15 was added, stirred and ultrasonic until homogeneous, finally dried at 160 °C for 8 h. Subsequently, the second loading was carried out. 0.24 g of sucrose and 0.27 g of concentrated sulfuric acid were added into 15 ml of deionized water and stirred. SBA-15 was added after the first loading, and the resultant solid was ground and carbonized at 900 °C for 3 h under nitrogen protection. The carbonized solid was refluxed twice in 1 mol·L⁻¹ NaOH solution to remove the template of the molecular sieve. Finally, the sample was filtered and washed to be neutral, and then dried at 100 °C to obtain the ordered mesoporous carbon CMK-3.

Preparation of MLG: 69 ml of 98% concentrated sulfuric acid that has been frozen for about 1 h was added to a 500 ml round-bottomed flask in an ice bath. Then, 2 g of graphite was added and stirred at a constant speed for 30 min. After pre-oxidation, 8 g of potassium permanganate was added as slowly as possible until the solution turned dark green. The solution was transferred to a 35 °C water bath and stirred for 12 h until the solution was brown. Afterwards, 276 ml of deionized water was added to the solution while stirring for 2 h. The reaction was terminated by adding 25 ml of 30% hydrogen peroxide to the solution and stirring for 2 h until the solution turned yellow. The reaction solution was centrifuged in a high-speed centrifuge at 8000 r·min⁻¹ for 10 min and the

solid was collected. The solid was washed with 5% HCl and deionized water for three times, and then centrifuged the washed solution at $10000\text{ r}\cdot\text{min}^{-1}$ for 20 min to obtain the solid. The resulting solid was freeze-dried at $45\text{ }^{\circ}\text{C}$ for 24 h. The final black solid obtained was the multi-layer graphite (MLG).

Different Ni-based catalysts were prepared by impregnation method and the Ni metal loadings were all 10% (mass). Ni/C catalyst was prepared as an example. 0.4953 g of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml of deionized water. 1.0 g of AC powder was added, and the catalyst was impregnated at room for 12 h. The catalyst was heated and stirred with gradient heating until the water evaporated, and then dried at $120\text{ }^{\circ}\text{C}$ for 4 h. Before usage, the catalysts were reduced in the reduction device with hydrogen at $550\text{ }^{\circ}\text{C}$ for 4 h. The flow rate of hydrogen was maintained at $20\text{ ml}\cdot\text{min}^{-1}$ throughout the process. Ni/CMK-3 and Ni/MLG catalysts were also produced by the above method.

N_2 adsorption-desorption isotherms were performed on an Autosorb-iQ-2 (Qudresorb SI, Quantachrome Instruments) instrument to measure specific surface area and pore structure. About 150 mg of dried samples were degassed in a vacuum at $280\text{ }^{\circ}\text{C}$ for 10 h before testing. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size characteristics of the samples were calculated using the Barrett-Joyner-Halenda (BJH) model. X-ray diffraction (XRD) was performed on an X'Pert3 Powder (PANalytical, Netherlands) instrument using $\text{Cu K}\alpha$ rays, $\lambda = 0.15406\text{ nm}$. The operating voltage was 40 kV, and the current was 40 mA. The scanning range for small-angle diffraction was $2\theta = 0^{\circ}$ to 5° , and regular diffraction was $2\theta = 5^{\circ}$ to 90° . The morphology of the catalyst was analyzed by high resolution field emission transmission electron microscopy (TEM). HSQC tests were performed on a Bruker AVANCE III 300WB (7.05T) instrument using $\text{DMSO}-d_6$ deuterium band reagent as solvent. Elemental analysis of feedstock and oligomers were performed on top of a Vario EL III elemental analyzer. The operating conditions were 0.12 MPa He and 0.2 MPa oxygen atmosphere at $1145\text{ }^{\circ}\text{C}$ using a TCD detector.

2.4. Hydrogenolysis reaction of lignin

Hydrogenolysis reaction of extracted lignin were carried out in a 100 ml auto-stirred high pressure batch reactor. 0.5 g of HSL lignin, 0.1 g of Ni-based catalyst, 0.2 g of acid or base catalyst and 30 ml of anhydrous ethanol were added to the reactor and sealed. Hydrogen was introduced into the reaction system, and after displacing the air for three times, the hydrogen pressure was increased to 2.0 MPa. The reactor was heated to the specified temperature for reacting. After finished, the reactor was cooled down to room temperature. The liquid product was analyzed for products identification.

After the hydrogenolysis reaction, the mixture was filtered to separate the filtrate and solid residues. The solid residue was washed with anhydrous ethanol for three times, and the eluent and filtrate were combined to form a liquid product. Finally, excess deionized water was added to the liquid product to ensure complete precipitation of lignin for conversion rate calculation. The product separation process is illustrated in Fig. 1. The volatile components of the liquid products were analyzed by gas chromatography Agilent 5890 Agilent 5975 mass spectrometry. Quantitative analysis was performed by gas chromatography with FID detector, SHIMADZU GC2010, using acetophenone as internal standard. Both GC-MS and GC analysis utilized an HP-INNDWAX column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The programmed temperature was set to $260\text{ }^{\circ}\text{C}$, and the incubation procedure was $60\text{ }^{\circ}\text{C}$ for 2 min, then $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $260\text{ }^{\circ}\text{C}$ for 10 min, with a split ratio of 5:1 and an injection volume of $1\text{ }\mu\text{l}$. The molecular weight

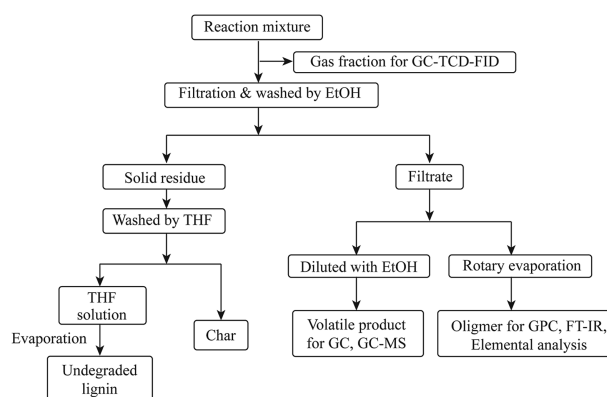


Fig. 1. Product separation procedure and characterization methods.

distribution of the liquid products was determined on an Agilent 1260 gel permeation chromatography (GPC) with a $7.8\text{ mm} \times 300\text{ mm}$ (HR 4E THF) column. Tetrahydrofuran was used as the mobile phase. The liquid product was rotary evaporated and dried to obtain the oligomers, and a certain amount was added to tetrahydrofuran (THF) to be solved. The infrared analysis of the oligomers was performed using a Nicolet 50 infrared spectrometer with the potassium bromide compression method.

The equations for calculating the yield of each component are as following.

$$Y_V = W_V / W_L \times 100\% \quad (1)$$

$$Y_A = W_A / W_L \times 100\% \quad (2)$$

$$Y_P = W_P / W_L \times 100\% \quad (3)$$

$$Y_G = W_G / W_L \times 100\% \quad (4)$$

$$Y_B = W_B / W_L \times 100\% \quad (5)$$

$$Y_{\text{others}} = Y_V - Y_A - Y_P - Y_G - Y_B \quad (6)$$

Wherein, W_L : Mass of lignin. W_V : Mass of aromatic monomer products. W_A : Mass of arene products. W_P : Mass of phenol products. W_G : Mass of guaiacol products. W_B : Mass of benzyl alcohol products. Y_V : Yield of aromatic monomer products. Y_A : Yield of arene products. Y_P : Yield of phenol products. Y_G : Yield of guaiacol products. Y_B : Yield of benzyl alcohol products. Y_{others} : Yield of other aromatic monomer products.

3. Results and Discussion

3.1. Lignin extraction and analysis of HSL lignin

The lignin fractions were analyzed using the NREL method [38] and the results were shown in Table 1. The lignin extraction rate using 1,4-butanediol solvent is above 90%. HSL lignin has a lignin content of 97.37%, with no cellulose or hemicellulose detected. The element analysis results show that the content of C in HSL lignin is 66.7%. Conversely, the O and N contents are relatively low. Moreover, the average molecular weight of HSL lignin was analyzed using GPC measurement. The average molecular weight (M_w) of HSL lignin is $1919\text{ g}\cdot\text{mol}^{-1}$, which indicates that the lignin structure are 5-mers to 10-mers of benzene ring [39]. And the PDI value of 2.05 demonstrates that the molecular weight distribution is relative wide.

Table 1

Basic property analysis of the raw pine and HSL lignin.

Materials	Component analysis/% (mass)				
	Lignin	Cellulose	Hemicellulose	Ash	Moisture
Raw pine	22.93	42.69	22.60	0.59	4.89
HSL lignin	97.34	0	0	2.66	0
Materials	Elemental content/% (mass)				
	C	H	O ^①	N	S
HSL lignin	66.68	6.72	26.40	0.07	0.13
	Experimental molecular formula				
	C ₉ H _{10.88} O _{2.67} N _{0.008} S _{0.007}				
Materials	Average molecular weight/g·mol ⁻¹				
	M _w ^②	M _n ^②	M _z ^②	Polydispersity index (PDI)	
HSL lignin	1919	933.7	3152	2.05	

^① The oxygen content was estimated by the conservation of mass based on the assumption that samples only contain C, H, N, S and O.

^② M_w (g·mol⁻¹): weight average molecular weight; M_n (g·mol⁻¹): number average molecular weight; M_z (g·mol⁻¹): Z-average molecular weight.

HSQC analysis was performed on HSL lignin to reveal out the lignin structure, with the results shown in Fig. 2. It can be observed that lignin primarily contains three aromatic functional groups of G, S, and H units. HSL lignin has a high content of G units and a low content of H units, indicating that HSL lignin preserves the G units greatly. This is because the acetic acid added during 1,4-butanediol extraction process facilitates the dissociation of hydrogen atoms that stabilizes the oxygen-rich free radical lignin fragments. Fang *et al.* [40] modified 1,4-butanediol organosolv pretreatment with different additives for efficient coproduction of fermentable sugars and lignin antioxidants from hardwood poplar and softwood masson pine. They found that the residual lignin content in masson pine was much higher than that of poplar, indicating the poorer delignification capacity on masson pine. This was likely because the lignin structural unit of softwood masson pine was mostly G units. The result in this work is in good line with the above reported literature. The functional groups in the carbon chains of the HSL lignin were also analyzed. The fatty side chain region of lignin exhibits absorption peaks corresponding to β -O-4, β - β , β -5, and *p*-hydroxycinnamyl alcohol. The intensive signals of the characteristic absorption regions of β -O-4, β - β , β -5, *etc.* suggest that 1,4-butanediol with high boiling point is effective in preventing the re-aggregation of C—C bonds in the lignin fragments.

3.2. Hydrogenolysis of HSL lignin for aromatic monomers

The different Ni/C catalysts were prepared using the traditional impregnation method. Table 2 presents the analysis results of surface area and pore size characteristics for different catalysts. It can be observed that the Ni/AC catalyst has a largest specific surface area of 376.20 m²·g⁻¹, while the Ni/MLG catalyst has a smallest specific surface area of 94.24 m²·g⁻¹. Comparing the different Ni-based catalysts with the corresponding single supports, it is evident that Ni-based catalysts exhibits a drop on the specific surface area and pore size, which is probably attributed to the blockage effect of Ni particles on the support pores [41].

XRD characterizations of the different Ni-based catalysts were carried out. The diffraction peaks of Ni particles appears near $2\theta = 45^\circ$, 52° and 76° , as shown in Fig. 3. It can be observed that the Ni metal diffraction signal in Ni/AC sample is the strongest at the characteristic absorption peak of $2\theta = 76^\circ$, which may be due to that the complex pore structure of AC support leads to the agglomeration of large Ni metal particles on the support surface. The Ni metal particles diffraction signal in Ni/CMK-3 is the weakest, which is probably due to the regular mesoporous characteristics of CMK-3 support that forms small Ni metal particles [42].

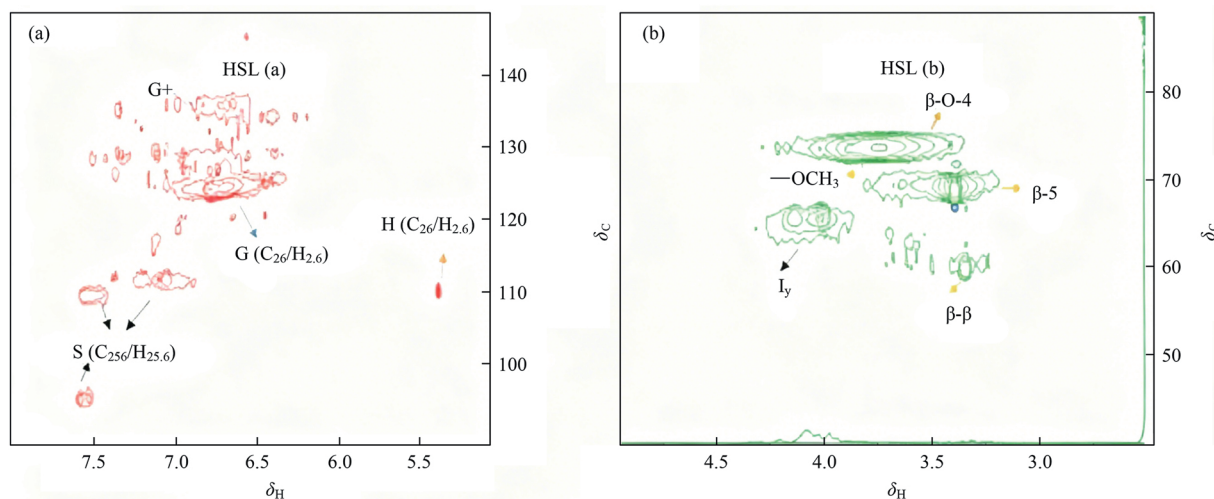


Fig. 2. HSQC analysis of (a) aromatic groups and (b) carbon chain of HSL lignin.

Table 2
Analysis of surface area and pore size characteristics for different catalysts.

Catalyst	Specific surface area/m ² ·g ⁻¹	Pore size/nm	Total pore volume/cm ³ ·g ⁻¹
AC	619.14	2.70	0.42
CMK-3	370.29	3.66	0.34
MLG	138.20	2.13	0.32
Ni/AC	376.20	2.75	0.26
Ni/CMK-3	290.48	3.42	0.25
Ni/MLG	94.24	1.93	0.34

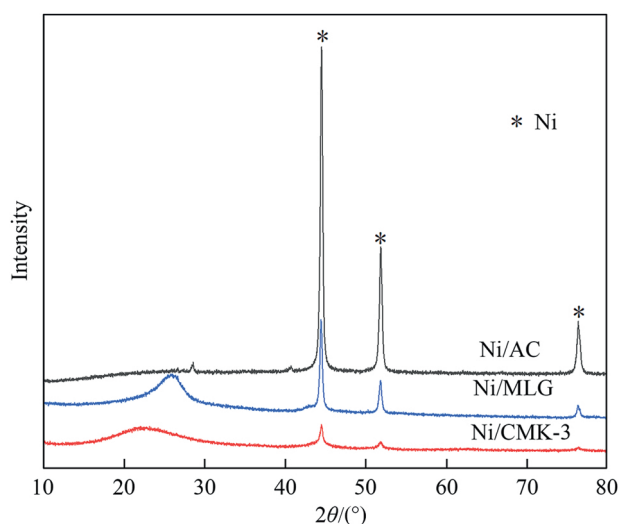


Fig. 3. XRD spectra of different Ni-based catalysts.

The morphology of different Ni-based catalysts was observed by TEM characterization (Fig. 4). The Ni metal particles in the Ni/AC catalyst are large and unevenly distributed. The complex pore structure of AC material is probably the main reason and it is difficult for Ni particles to enter into the inner pores. The Ni metal particles in the Ni/CMK-3 catalyst are the smallest and uniformly distributed in the mesoporous pores, showing a good dispersion. The Ni metal particle size in the Ni/MLG catalyst shows uneven distribution, which may be due to the fact that part of Ni metal particles have entered into the graphite layer to form small Ni particles and part of Ni metal particles haven't entered into the graphite layer and distributed on the graphite surface with large Ni particles.

The hydrogenolysis of HSL lignin was carried out in different catalytic systems (Table 3). Hydrogenolysis of HSL lignin in all catalytic systems can achieve the carbon balance above 80%, guaranteeing the precision of reaction results. The carbon deposition rate is relative high when NaOH is used for hydrogenolysis, but the yield of aromatic monomers is improved significantly. Notably, Ni/MLG catalyst combined with NaOH using for lignin hydrogenolysis presents a relative low carbon deposition rate. Moreover, the conversion rate of HSL lignin is above 80% in all the cases. The conversion rate improves when Ni/MLG coupled with various acid or base catalysts. The highest conversion rate is achieved in the case of Ni/MLG coupled with NaOH. Regarding the yield of aromatic monomers, when a single Ni-based catalyst (Ni/MLG, Ni/AC or Ni/CMK-3) is used, the yield of aromatic monomers reaches approximately 16% to 17% and shows no significant difference. And the yield in the case of Ni/MLG is a little higher than those of Ni/AC and Ni/CMK-3. Single NaOH used as catalyst obtains 29.8% yield of aromatic monomers in the lignin hydrogenolysis. And Ni/MLG coupled with different base catalysts improves the

yield of aromatic monomers significantly. The highest yield of aromatic monomers is 36.9% when Ni/MLG is coupled with NaOH for HSL lignin hydrogenolysis. And when Lewis acid catalysts are used with Ni/MLG for hydrogenolysis, the yield of aromatic monomers is approximately 20% for all cases. Overall, the synergistic catalytic system of Ni/MLG and NaOH demonstrates great potential on the lignin hydrogenolysis.

HSL lignin hydrogenolysis under the catalysis of Ni/MLG coupled with NaOH obtains the yield of aromatic monomers of 36.9%, which presents much superiority to the reported similar results of Ni-based catalysts. García-Rollán *et al.* [43] proposed the dual valorization of lignin by the preparation of carbon-based catalysts for the catalytic hydrogenolysis of lignin to obtain aromatic monomers. The carbon supports for the preparation of Ni, NiMo and CoMo catalysts contained active metal phosphides (Ni₁₂P₅ and MoNiP), and the optimal NiMo catalyst presented a monomer yield of 12.50% at 350 °C. Yu *et al.* [44] obtained M₅Zn₅AlO_x (M = Co, Ni and Cu) catalysts by the co-precipitation method and then used the catalyst in organosolv lignin depolymerization. Among these catalysts, the highest yield of monophenols was 17.18% obtained over the Ni₃Zn₇AlO_x catalyst at the temperature of 270 °C. Yan *et al.* [45] proposed a non-precious carbon based metal-Mo₂C catalytic system for selective production of phenolic monomers from organosolv lignin depolymerization. With the optimized catalyst of Ni-Fe-Mo₂C, 89.56% of liquefaction and 35.53% of phenolic monomers yields were achieved under 260 °C. Kong *et al.* [46] also catalyzed direct hydrogenolysis of lignin over a series of supported Ni or Re catalysts in ethanol solvent. The best results showed that 5Ni-5Re/Nb₂O₅ catalyst achieved the monomer yield of 35.41% under mild condition, and low-molecular-weight aromatic alcohols were the main component in the liquid products. Overall comparatively, our work presents a good lignin depolymerization performance for the production of valuable aromatic monomers.

Based on the above results, the analysis of volatile hydrogenolysis products was conducted (Table 4). The influences of single Ni/C catalysts and Ni/MLG coupled with various acid and base catalysts on the product distribution of HSL lignin hydrogenolysis were further explored. The results show that when Ni/MLG is used, the yield of guaiacol products is relatively high, and no phenol products are detected. And the yield of total aromatic monomers reaches the highest value of 17.2%. However, when Ni/AC is used as catalyst, the yield of phenol products is higher, but the yield of total aromatic monomers is relative lower. Under the single catalysis of NaOH, the yields of arenes and benzyl alcohols are 10.6% and 6.1%, respectively. As for the case of Ni/MLG coupled with different base catalysts, the yield of total aromatic monomers increases, primarily reflecting in arenes and benzyl alcohols product. Notably, when Ni/MLG is coupled with NaOH for the lignin hydrogenolysis, the yields of arenes and benzyl alcohols get to 11.1% and 7.3%, respectively. In the Na₂CO₃ catalyst system, the yield of benzyl alcohols is as high as 5.2%, suggesting that a weakly base environment is favorable for the formation of benzyl alcohols. As for Ni/MLG coupled with various Lewis acid, the distribution of aromatic monomers shows little difference compared to the hydrogenolysis performance using single Ni/MLG catalyst, mainly on the arenes and benzyl alcohols products.

The recycling performance of the Ni/MLG catalyst was also investigated. The homogeneous property of NaOH makes the recovery difficult, and the addition of NaOH catalyst is conducted for every recycle runs. NaOH is a typical strong base and its treatment is necessary to lower down the pollution risk, with acid-base neutralization as the typical choice. With further separation procedures, the aromatic monomer products can be purified and the pollution risk of NaOH catalyst can be eliminated. Thus, the Ni/

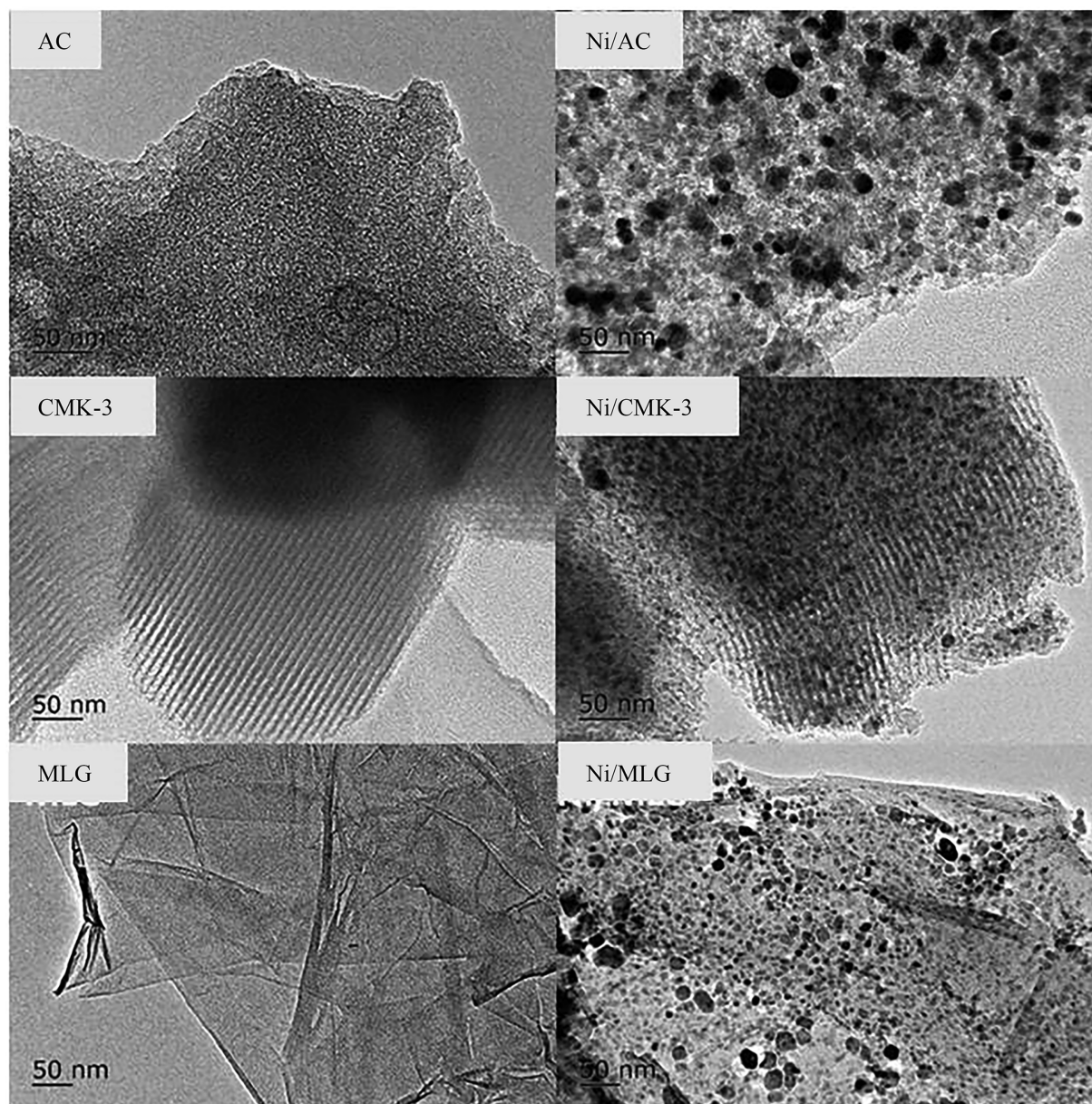


Fig. 4. TEM image of the different supports and different Ni-based catalysts.

MLG catalyst is the key subject for the recycling performance. The results in Fig. 5 show that the conversion keeps high after third run, with the value of 92.5%. While, the yield of aromatic monomer exhibits a slight drop, with the value decreased from 36.9% to 30.2%. According to our previous study [20], carbon deposition coated on the metal site surface that resulted from the repolymerization of lignin-derived products is considered as the reason for the activity loss of Ni/MLG catalyst.

3.3. Analysis of oligomers in different catalytic systems

Element analysis of lignin feedstock and oligomers in different catalytic systems were carried out (Table 5). Hydrogenolysis of HSL lignin increases the content of elemental H in the oligomers, which may be due to that HSL lignin fragments have underwent a hydrogenation reaction [47]. When a single Ni-based catalyst (including Ni/MLG, Ni/AC or Ni/CMK-3) is used for the lignin hydrogenolysis, the oligomers show a higher calorific value. Taking

Ni/MLG as an example, the calorific value of the hydrogenolysis oligomers reaches $30.98 \text{ MJ} \cdot \text{kg}^{-1}$, which is a significant improvement compared to the $27.32 \text{ MJ} \cdot \text{kg}^{-1}$ of the raw HSL lignin. This enhancement is likely due to the ability of Ni/MLG catalyst to effectively promote the breakage and reorganization of chemical bonds in lignin, making more addition of H element. Ni, as the active metal center, can catalyze the cleavage of C—C, C—O, and other bonds in lignin, while the support can help to disperse Ni particles, improving the stability and activity of the catalyst [48]. Analysis of the elemental composition in the oligomers of HSL lignin hydrogenolysis reveals that the oxygen content increases a little in the case of Ni/MLG coupled with KOH system, which is consistent with the trends in the volatile products. In the KOH system, the proportion of oxygen-free arenes is relatively low, while the proportion of oxygen-containing benzyl alcohols is higher. When Ni/MLG is coupled with AlCl_3 to be used for the hydrogenolysis of HSL lignin, a significant increase of oxygen content is also observed. These results indicate that KOH and AlCl_3

Table 3

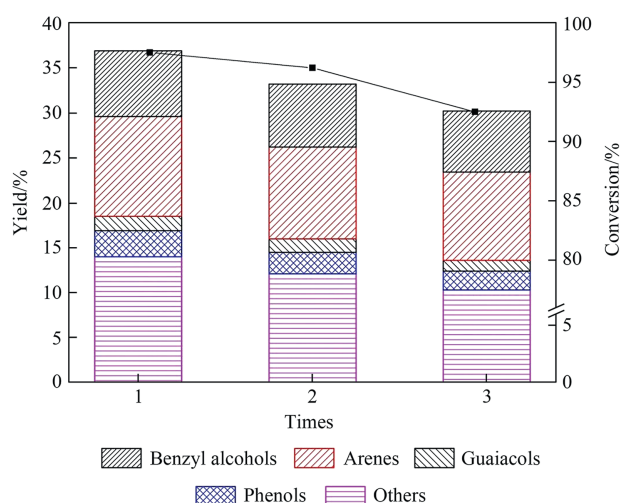
Hydrogenolysis performance and product distribution from different catalytic systems.

Entry	Catalyst	Conversion/%	Y_A /%	Carbon deposits/%	Carbon balance/%
1	Ni/MLG	84.9	17.2	4.2	101
2	Ni/AC	85.1	16.1	8.3	107
3	Ni/CMK-3	82.6	16.7	2.2	101
4	NaOH	96.9	29.8	7.4	81
5	Ni/MLG + NaOH	97.5	36.9	6.7	80
6	Ni/MLG + KOH	95.3	25.6	11.7	82
7	Ni/MLG + Na ₂ CO ₃	90.6	17.9	12.5	108
8	Ni/MLG + ZnCl ₂	90.0	16.2	5.4	100
9	Ni/MLG + MgCl ₂	90.7	20.6	3.3	96
10	Ni/MLG + AlCl ₃	92.4	23.9	6.3	87

Note: Conditions—0.5 g HSL lignin, 0.1 g Ni-based catalyst, 0.2 g base or acid catalyst, 30 ml ethanol, 280 °C, 4 h, 2 MPa H₂.**Table 4**

Volatile products of lignin hydrogenolysis from different catalytic systems.

Catalyst	Yield/%					
	Arenes	Phenols	Guaiacols	Benzyl alcohols	Others	Total yield
Ni/MLG	0.1	2.9	2.9	0	11.2	17.2
Ni/AC	0.3	7.2	1.3	1.1	6.2	16.1
Ni/CMK-3	0.2	4.8	1.0	1.0	9.7	16.7
NaOH	10.6	2.4	1.5	6.1	9.2	29.8
Ni/MLG + NaOH	11.1	2.9	1.6	7.3	14.0	36.9
Ni/MLG + KOH	2.9	2.8	1.8	3.3	14.8	25.6
Ni/MLG + Na ₂ CO ₃	0.1	5.2	1.0	1.8	9.8	17.9
Ni/MLG + ZnCl ₂	3.6	2.5	1.9	1.1	7.1	16.2
Ni/MLG + MgCl ₂	0.9	4.6	1.6	1.2	12.3	20.6
Ni/MLG + AlCl ₃	0.7	2.3	1.3	2.1	17.5	23.9

Note: Conditions—0.5g HSL lignin, 0.1 g Ni-based catalyst, 0.2 g base or acid catalyst, 30 ml ethanol, 280 °C, 4 h, 2 MPa H₂.**Fig. 5.** The recycling performance of the catalyst in the HSL lignin hydrogenolysis. Reaction condition: 0.5 g HSL lignin, 0.1 g Ni/MLG, 0.2 g NaOH, 30 ml ethanol, 280 °C, 4 h, 2 MPa H₂.

catalysts are partial to promote the reservation of oxygen-containing groups.

The molecular weights of oligomers after catalytic hydrogenolysis of lignin in different catalytic systems were analyzed (Table 6). By comparing the GPC results of the HSL lignin feedstock and the oligomers of single Ni-based catalyst, it can be observed that the molecular weight of the HSL lignin feedstock is primarily distributed around 1500 g·mol⁻¹. After hydrogenolysis, the molecular weight of oligomers shifts toward smaller molecular fragments. When Ni/CMK-3 is used as the catalyst, the molecular weight of the oligomers mainly distributes around 300 g·mol⁻¹

and 500 g·mol⁻¹. In contrast, in the case of Ni/MLG catalyst, the oligomers have a molecular weight primarily around 600 g·mol⁻¹. This indicates that the Ni/MLG catalyst can hydrogenolyze lignin oligomer fragments into volatile aromatic monomers effectively. Further analysis of the oligomers from the hydrogenolysis of HSL lignin using Ni/MLG coupled with different acid and base catalysts is also presented. The molecular weight of oligomers shifts toward smaller molecular fragments in all systems, suggesting that lignin has undergone effective depolymerization in all the catalytic systems. Particularly, the Ni/MLG coupled with NaOH system shows the best depolymerization effect, with the polydispersity index closer to 1 (1.42), indicating a more concentrated molecular weight distribution. In contrast, the depolymerized oligomer fragments in the catalytic system of AlCl₃ exhibit a larger molecular weight distribution. This is likely due to the dual acid and base nature of AlCl₃, which can cause the intermediate products to undergo repolymerization reactions at high temperature.

FT-IR characterizations of raw HSL lignin and oligomers from different catalytic systems were carried out to study the changes of lignin structure during the reaction (Fig. 6). The broad absorption peak at 3427 cm⁻¹ is the absorption peak of hydroxyl group in lignin [49]. There are absorption peaks of ethyl group and methylene group at 2931 cm⁻¹ and 2850 cm⁻¹, and the characteristic absorption peaks of carbonyl group at 1701 cm⁻¹. The three absorption peaks at 1617 cm⁻¹, 1517 cm⁻¹ and 1454 cm⁻¹ are characteristic absorption peaks of benzene rings in lignin, and the absorption peaks 1272 cm⁻¹ and 1234 cm⁻¹ are assigned to carbon-carbon and ether bonds on aliphatic branched chains, respectively [50,51]. After hydrogenolysis with Ni/MLG coupled with NaOH catalyst, the characteristic absorption peaks at 1272 cm⁻¹ and 1234 cm⁻¹ disappear in the oligomers, which indicates that the base catalyst enables to promote the breakage of C—C and C—O bonds. The peaks at 1573 cm⁻¹ are characteristic peaks of benzene ring, which indicates that some recombination

Table 5

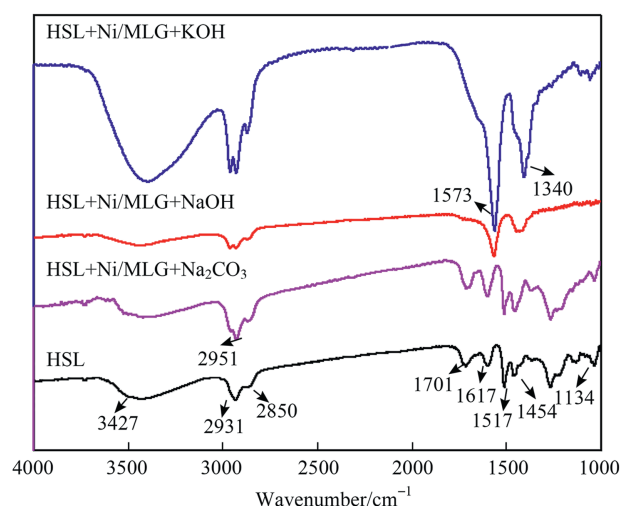
Element analysis of lignin feedstock and oligomers in different catalytic systems.

Catalyst	Elemental content/% (mass)					Experimental molecular formula	Degree of unsaturation [⊗]	HHV [⊗] /MJ·kg ⁻¹
	C	H	O [⊙]	N	S			
Raw HSL lignin	66.59	6.69	26.54	0	0.18	C ₉ H _{10.85} O _{2.69} S _{0.01}	4.57	27.32
Ni/MLG	73.34	6.81	19.79	0.06	0	C ₉ H _{10.03} O _{1.82} N _{0.006}	4.98	30.98
Ni/AC	75.1	7.05	17.85	0	0	C ₉ H _{10.14} O _{1.60}	4.93	32.26
Ni/CMK-3	73.71	6.32	19.97	0	0	C ₉ H _{9.26} O _{1.83}	5.37	30.37
NaOH	61.26	6.93	31.7	0.06	0.05	C ₉ H _{12.22} O _{3.49} N _{0.08} S _{0.03}	3.89	24.94
Ni/MLG + NaOH	64.85	7.06	27.91	0.07	0.11	C ₉ H _{11.76} O _{2.91} N _{0.08} S _{0.005}	4.12	27.02
Ni/MLG + KOH	56.51	5.93	37.56	0	0	C ₉ H _{11.33} O _{4.49}	4.33	20.87
Ni/MLG + Na ₂ CO ₃	74.05	6.68	19.27	0	0	C ₉ H _{9.74} O _{1.76}	5.13	31.12
Ni/MLG + ZnCl ₂	70.92	7.07	22.01	0	0	C ₉ H _{10.77} O _{2.09}	4.62	30.13
Ni/MLG + MgCl ₂	71.73	6.9	21.14	0	0.23	C ₉ H _{10.39} O _{2.91} S _{0.011}	4.81	30.32
Ni/MLG + AlCl ₃	64.03	6.46	29.09	0	0.42	C ₉ H _{10.90} O _{3.07} S _{0.022}	4.55	25.68

Note: Conditions—0.5 g HSL lignin, 0.2 g base or acid catalyst, 30 ml ethanol, 280 °C, 4 h, 2 MPa H₂.[⊙] The oxygen content was estimated by the conservation of mass based on the assumption that the samples only contain C, N, S and O.[⊗] Degree of unsaturation = $(2 \times n_C + 2 - n_H + n_N)/2$.[⊗] Evaluated by Dulong formula: $\text{HHV}(\text{MJ} \cdot \text{kg}^{-1}) = 0.3383 \times C + 1.422 \times (H - O/8)$.**Table 6**

GPC analysis of raw lignin and oligomer from different catalytic systems.

Sample	<i>M_w</i>	<i>M_n</i>	<i>M_p</i>	<i>M_z</i>	<i>P_D</i>
Raw HSL lignin	1253	558	1356	1911	2.25
Ni/MLG	804	687	496	2029	1.75
Ni/AC	809	413	463	1425	1.96
Ni/CMK-3	767	389	443	1421	1.97
Ni/MLG + NaOH	681	480	331	979	1.42
Ni/MLG + KOH	989	326	297	1009	1.81
Ni/MLG + Na ₂ CO ₃	786	406	431	1419	1.94
Ni/MLG + ZnCl ₂	582	261	104	1112	2.23
Ni/MLG + MgCl ₂	719	343	460	1292	2.10
Ni/MLG + AlCl ₃	822	301	102	1474	2.73

Note: Conditions—0.5g HSL lignin, 0.2g base or acid catalyst, 30 ml ethanol, 280 °C, 4 h, 2 MPa H₂.**Fig. 6.** FT-IR analysis of raw HSL lignin and oligomers from different catalytic systems.

reaction occurs during the hydrogenolysis process. The disappearance of the absorption peak of carbonyl group at 1701 cm⁻¹ shows that hydrogenation reaction occurs during the hydrogenolysis process. Moreover, after lignin hydrogenolysis in the case of Ni/MLG coupled with Na₂CO₃ catalyst, there is no significant change in the characteristic absorption peak species in the oligomers compared to the raw HSL lignin. Only a decrease in the absorption intensity is presented, which shows a consistent trend with the result of aromatic monomer yields.

Based on the reaction results, the lignin depolymerization pathway, as well as the relationship between NaOH and Ni/MLG catalyst, is analyzed in detail. During this process, Ni/MLG and NaOH catalysts present a synergetic effect. Wherein, NaOH catalyst acted as a base and lowered down the activation energy of C—O bond by attacking the oxygen atom, which improved the cleavage of C—O bond. At the same time, Ni/MLG catalyst adsorbed and dissociated the hydrogen to produce active hydrogen species, which can provide hydrogen atom for the cleaved C—O bond and enhance the formation of stable hydrogenolysis products. Besides, Ni/MLG also acted as a catalysis site for hydrogenation to trigger the saturation reaction and form stabilized products. Overall, the hydrogenolysis mechanism of HSL lignin is a complicated network, and not only the catalysis sites but also the reaction conditions affect the hydrogenolysis reaction performance. Ni/MLG and NaOH catalysts present a synergetic effect during the hydrogenolysis reaction and inhibiting subsequent derivatization reaction.

4. Conclusions

In this study, the lignin extraction from pine wood flour using 1,4-butanediol solvent and the catalytic hydrogenolysis of extracted HSL lignin under synergistic catalysis of Ni/MLG and NaOH were carried out. The extraction treatment improves the lignin depolymerization performance and the yield of aromatic monomers significantly by reservation the C—O bonds in the lignin. The catalytic hydrogenolysis of HSL lignin over a single Ni-based catalyst reveals little difference in the yields of liquid-phase volatile products but significant differences in the yields of different types of aromatic monomers. Ni/AC catalyst obtains a high yield of phenolics up to 7.2%. The addition of NaOH into the lignin hydrogenolysis results in high lignin conversion and high yields of volatile aromatic monomers. The homogeneous alkalinity has a strong influence on the distribution of liquid-phase volatile products. Although the weak alkaline Na₂CO₃ system promotes the generation of phenolic compounds, the generation of aromatic hydrocarbons is unfavourable, which have higher yields in the strong alkaline NaOH and KOH systems.

CRediT Authorship Contribution Statement

Ying Xu: Writing — original draft, Methodology, Investigation, Funding acquisition, Conceptualization. Meiziya Gong: Visualization, Validation, Methodology, Formal analysis, Data curation. Lie

Zhou: Resources, Methodology, Investigation, Data curation. Yuanbo Huang: Visualization, Validation, Data curation. Xiaodong Zhang: Validation, Supervision, Resources. Riyang Shu: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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