

Hydrothermal liquefaction of alkaline lignin with *in situ* hydrogen supply from formic acid

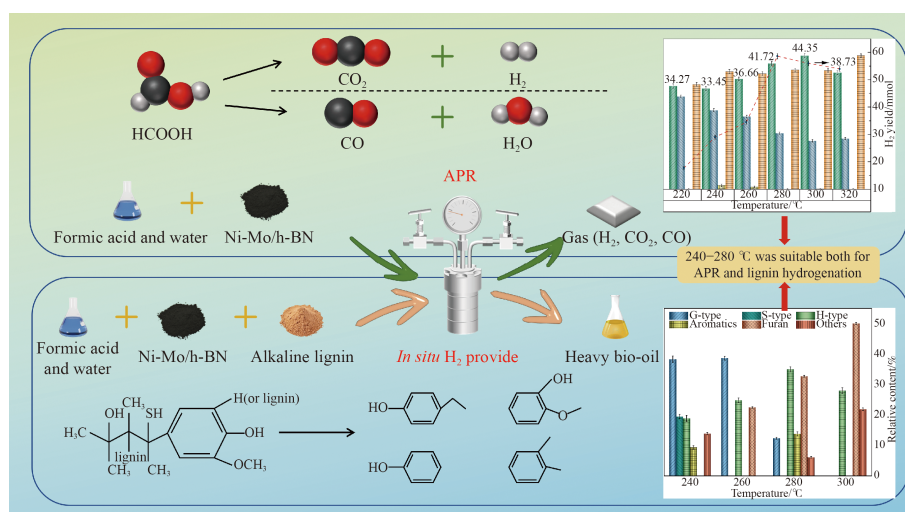
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Abstract: Alkali lignin, a high-volume byproduct generated from pulp and paper manufacturing as well as biomass refining, represents a promising natural feedstock for aromatic hydrocarbon production in liquid fuels owing to its high energy density and abundant aromatic moieties. However, its highly cross-linked polymeric structure hinders its efficient valorization and

high-value conversion. In this work, alkali lignin was used as the feedstock to investigate the catalytic conversion into bio-oil under *in situ* H₂ supply from formic acid. A series of Ni-Mo/h-BN bimetallic catalysts with varied metal ratios were synthesized by the impregnation method, and their physicochemical properties were systematically characterized by XPS, XRD and other techniques. The effects of reaction parameters on H₂ production via aqueous-phase reforming of formic acid were first evaluated. The optimal H₂ yield was achieved at a formic acid-to-water molar ratio of 1:10 and a Ni/Mo atomic ratio of 3:1. The H₂ yield increased monotonically with temperature in the range of 220–280 °C, reaching a maximum of 38.48 mmol. Subsequently, the influences of reaction temperature and residence time on bio-oil production from alkali lignin were examined. The highest heavy bio-oil yield (18.93%) and the maximum relative content of aromatic hydrocarbons (13.81%) were both achieved at 280 °C. Prolonged reaction time reduced the heavy bio-oil yield and the relative abundance of aromatic hydrocarbons, while favoring the formation of furan derivatives. This work demonstrates good synergy and consistency between *in situ* hydrogen generation from formic acid and lignin hydrogenation in the temperature range of 240–280 °C.

Key words: formic acid; alkali lignin; hydrothermal liquefaction; *in situ* hydrogen; bio-oil



Rapid global economic development and industrialization have led to a continuously growing demand for energy. The excessive exploitation and consumption of fossil fuels have given rise to pressing issues including energy scarcity, environmental pollution and the greenhouse effect. Consequently, the exploration of clean, renewable energy alternatives to fossil fuels has become an urgent and

imperative task^[1]. As a widely available, abundant, renewable, and carbon-neutral energy source, biomass exhibits great potential to replace fossil energy^[2–3].

Liquid biofuels constitute one of the most viable pathways for fossil fuel displacement. Currently, the primary technologies for converting biomass into liquid fuels include biochemical and thermochemical conversion

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routes. Compared with biochemical conversion, thermochemical technologies feature shorter reaction residence times and superior conversion efficiencies^[4–5]. Thermochemical conversion mainly includes pyrolysis and hydrothermal liquefaction (HTL). Specifically, HTL is a process that converts macromolecular organic polymers in biomass into bio-crude oil through a series of reactions including hydrolysis, rearrangement, and condensation under moderate temperature (250–370 °C) and high pressure (5–20 MPa), taking advantage of the unique physicochemical properties of subcritical and supercritical water^[6–8]. Due to its broad feedstock adaptability and high conversion efficiency, HTL has become a research hotspot worldwide in recent years.

Hydrodeoxygenation (HDO) is a key technology for bio-crude upgrading, as it can effectively reduce the high oxygen content of bio-crude while maintaining superior carbon atom economy^[9]. Studies have shown that the overall rate of HDO reactions is generally governed or influenced by mass transfer^[10]. Therefore, reducing mass transfer resistance is an effective strategy to enhance reaction rates. *In situ* hydrogen supply has become a research focus in the field of HDO due to its remarkable ability to reduce mass transfer resistance^[11]. *In situ* hydrogen supply couples hydrogen generation from hydrogen donors with biomass hydrogenation, enabling direct utilization of hydrogen or active hydrogen species produced *in situ* from hydrogen-donor solvents for bio-oil hydrogenation without external H₂ input^[12]. This strategy simplifies the process flow and improves the selectivity of hydrogen generation from hydrogen donors. Moreover, *in situ* generated hydrogen exhibits higher reactivity than externally supplied hydrogen, thus promoting more efficient catalytic hydrogenation. Based on different hydrogen donors, *in situ* hydrogen supply technologies can be classified into combined reforming and hydrodeoxygenation (RHDO), combined metal hydrolysis and hydrodeoxygenation process (HHDO), self-supported hydrogenolysis (SSH), and catalytic transfer hydrogenation (CTH)^[13].

CTH employs organic molecules (e.g., methanol, formic acid, ethanol, isopropanol, hydrazine, tetralin) as both reaction media and hydrogen-donor solvents. Under catalytic conditions, hydrogen is generated *in situ* and transferred to reaction substrates, enabling efficient upgrading^[14–15]. Among various hydrogen donors, formic acid has attracted extensive attention due to its high hydrogen storage capacity^[16], facile decomposition, and easy separation of by-products, making it a highly promising hydrogen-donor solvent for CTH^[17]. Zhang et al.^[18] investigated the liquid-phase hydrogenation of phenol over Pd catalysts supported on different carriers including activated carbon (AC) and TiO₂ with formic acid as the hydrogen donor. They demonstrated that unstable components in bio-oil (e.g., phenol) could be upgraded into more stable products (e.g., cyclohexanone) *via in situ* hydrogenation over Pd/AC under mild conditions, thereby improving bio-oil quality. Tan et al.^[19] conducted *in situ*

hydrogenation of phenol and furfural over Pd/C and RZ409 (Ni-based) catalysts using formic acid and acetic acid as hydrogen donors, respectively. They found that H₂ production was mainly determined by the catalyst and substrate types, and both phenol and furfural could be hydrogenated by *in situ* generated H₂ into various products. Patil et al.^[20] achieved selective, efficient, and sustainable conversion of phenol to cyclohexanone over supported Pd catalysts using potassium formate as the hydrogen source under atmospheric pressure and mild conditions. They identified reaction temperature, catalyst type (Pd/C), solvent volume (water), and hydrogen-donor type as key factors governing conversion efficiency. In addition, potassium formate played a dual role: acting as a hydrogen donor for phenol hydrogenation and as an additive to enhance cyclohexanone selectivity. These studies confirm the excellent hydrogen-donating performance of formic acid. However, most CTH investigations for high-grade bio-oil production have been limited to biomass model compounds and noble-metal catalysts, which restricts their practical applicability.

A variety of catalysts have been investigated for CTH, including nickel-based, sulfur-based and noble-metal catalysts. However, sulfur-based catalysts require the addition of sulfur-containing compounds to maintain catalytic activity, and these externally introduced sulfur species can contaminate bio-oil during HDO. Noble metals such as Pd, Pt and Ru exhibit superior catalytic activity and selectivity toward alkanes in HDO, but their scarcity and high cost significantly hinder large-scale industrial application. In recent years, Ni-based catalysts have attracted considerable attention due to their favorable hydrogenation performance and low cost. Nevertheless, monometallic Ni catalysts tend to induce excessive condensation and dehydrogenation of reaction intermediates during the high-temperature HDO of biomass, which leads to coke formation that covers active sites and thus causes catalyst deactivation. Moreover, their poisoning resistance and thermal stability are unsatisfactory. Li et al.^[21] prepared a Ni-Mo bimetallic catalyst supported on ZIF-8, in which the interaction between Ni and Mo promoted the reduction of Mo and increased the proportion of low-valence Mo species. The catalyst also possessed abundant acidic sites at low and medium temperatures, enhancing catalytic activity. As a result, the HDO performance was significantly improved compared with monometallic Ni catalyst after Mo incorporation. Besides active metal components, catalyst supports also play a crucial role in regulating CTH performance. Weber et al.^[22] explored hexagonal boron nitride (h-BN) as a catalyst support by loading Pd nanoparticles, highlighting its great potential as an innovative catalyst support for selective catalysis due to its excellent thermal stability, ultrahigh thermal conductivity, acid and alkali corrosion resistance, and low dielectric constant.

In this study, alkali lignin was selected as the feedstock, and a series of Ni-Mo/h-BN catalysts with different bimetallic loading ratios were prepared. The effects of

catalyst composition, reaction temperature, and formic acid concentration on hydrogen production *via* aqueous-phase reforming (APR) of formic acid were systematically investigated. Furthermore, the influence of reaction conditions on bio-oil production from alkali lignin under *in situ* hydrogen supply from formic acid were explored, and the coupling mechanism between *in situ* hydrogen generation from formic acid and HTL of alkali lignin was elucidated.

1 Experimental

1.1 Materials and reagents

Alkali lignin was purchased from Nanjing Duly Biotechnology Co., Ltd. Formic acid (HCOOH) and nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was supplied by Shanghai Macklin Biochemical Co., Ltd. Hexagonal boron nitride (h-BN, pore size: 15–20 nm) was provided by the Key Laboratory of Boron Nitride, Hebei University of Technology.

1.2 Catalyst preparation

The Ni-Mo/h-BN catalyst was prepared by the impregnation method. Specifically, 2.00 g of h-BN support, 0.55 g of nickel nitrate hexahydrate, and 0.20 g of ammonium molybdate tetrahydrate were mixed in a 100 mL beaker, followed by the addition of 30 mL of deionized water. The mixture was stirred at 75 °C and 300 r/min until surface-dry, then dried in a constant-temperature blast drying oven at 105 °C for 12 h. After drying and grinding, the sample was calcined in a muffle furnace at 550 °C for 2 h. Before catalytic tests, the catalyst was reduced in a tubular furnace under a hydrogen atmosphere at 600 °C for 2 h. To prepare catalysts with different metal loading ratios while maintaining a constant total metal loading, the masses of nickel nitrate hexahydrate and ammonium molybdate tetrahydrate were adjusted accordingly. Catalysts denoted as 10%Ni-Mo/h-BN (Ni:Mo=1:1, 2:1 and 3:1) were prepared following the same procedure.

1.3 APR of formic acid for hydrogen production

APR experiments for hydrogen production from formic acid were conducted in a 100 mL stainless-steel high-pressure autoclave. Predetermined amounts of formic acid and deionized water were introduced into the autoclave at molar ratios of 1:10, 1:15 and 1:20. After sealing, the reactor was purged with high-purity argon (0.3 MPa each time) for five cycles to ensure complete removal of air. Argon served as both a protective gas and an internal standard. Circulation cooling water and mechanical stirring were turned on, with a stirring rate of 300 r/min. 0.50 g of

catalyst was loaded into the autoclave, which was then heated to the target reaction temperature and held for 60 min under the determined solvent ratio and temperature for APR tests. After completion of the reaction, the autoclave was naturally cooled to ambient temperature. Gaseous products were collected using a gas sampling bag. Solid and liquid products were separated by filtration and stored in sealed containers for further analysis.

1.4 HTL of alkali lignin for bio-oil production

HTL experiments of alkali lignin were carried out in the same 100 mL stainless-steel autoclave. A certain amount of alkali lignin and 0.50 g of catalyst were added into the autoclave, followed by a mixed solution of formic acid and deionized water as the solvent. The solvent ratio and catalyst type were selected based on the results of formic acid APR experiments. After sealing, the autoclave was purged with high-purity argon for 2 min to remove residual air. Circulation cooling water and mechanical stirring were initiated at a stirring rate of 300 r/min. The autoclave was then heated to the desired reaction temperature and held for the predetermined reaction time. After completion of the reaction, the reactor was cooled to ambient temperature, and gaseous products were released through the exhaust valve. Liquid products were directly collected and subjected to vacuum filtration. The filtrate was extracted with 20 mL of dichloromethane to obtain the liquid-phase products. The filter membrane and inner wall of the reactor were rinsed with acetone until colorless to collect the acetone-soluble fraction. After filtration, the solid residue on the membrane was dried in an oven at 105 °C to constant weight. The acetone-soluble fraction was subjected to rotary evaporation at 58 °C to remove acetone, yielding heavy bio-oil.

The heavy bio-oil yield and lignin conversion were calculated using the following equations:

$$Y_{\text{heavy bio-oil}} (\%) = \frac{W_{\text{heavy bio-oil}}}{W_{\text{lignin}}} \times 100\% \quad (1)$$

$$Y_{\text{solid residue}} (\%) = \frac{W_{\text{solid residue}}}{W_{\text{lignin}}} \times 100\% \quad (2)$$

$$Y_{\text{gas+aqueous}} (\%) = 100\% - Y_{\text{heavy bio-oil}} \% - Y_{\text{solid residue}} \% \quad (3)$$

$$Y_{\text{conversion}} (\%) = 100\% - Y_{\text{solid residue}} \% \quad (4)$$

where $Y_{\text{heavy bio-oil}}$, $Y_{\text{solid residue}}$, $Y_{\text{gas+aqueous}}$ and $Y_{\text{conversion}}$ represent the heavy bio-oil yield (%), solid residue yield (%), gas and aqueous phase yield (%), and lignin conversion (%), respectively. $W_{\text{heavy bio-oil}}$ represents the mass of heavy bio-oil, $W_{\text{solid residue}}$ represents the mass of solid residue and W_{lignin} represents the mass of alkali lignin.

1.5 Product analysis methods

1.5.1 Catalyst characterization

X-ray photoelectron spectroscopy (XPS) analysis was

performed on an ESCALAB 250Xi spectrometer equipped with an Al $K\alpha$ X radiation source to determine the chemical states of the elements on the catalyst surface.

X-ray diffraction (XRD) patterns of the supports and catalysts were recorded on an Ultima IV diffractometer using Cu $K\alpha$ radiation. Powdered samples were scanned over a 2θ range of 10° – 90° at a scanning rate of $1^\circ/\text{min}$.

Hydrogen temperature-programmed reduction (H_2 -TPR) was carried out on a PCA-1200 chemisorption analyzer. The samples were first pretreated in 100% Ar to remove moisture and other impurities by heating to 230°C at $10^\circ\text{C}/\text{min}$ and holding for 60 min. After cooling to 50°C , a 10% H_2 /90%Ar mixture was used as the reducing gas. The temperature was increased to 800°C at $10^\circ\text{C}/\text{min}$ and maintained for 10 min. Hydrogen consumption at different temperatures was monitored using a thermal conductivity detector (TCD).

The acidity and acid type of the catalysts were characterized by pyridine adsorption infrared spectroscopy (Py-FTIR) using a Bruker Tensor 27 Fourier transform infrared spectrometer. The samples were pretreated at 350°C under vacuum for 1 h and then cooled to 150°C . A background spectrum was collected at 150°C prior to pyridine adsorption. Pyridine vapor was then introduced into the sample cell at the same temperature until saturation adsorption was achieved. Subsequently, physically adsorbed pyridine molecules were removed by evacuation or purging with an inert gas. Spectra were recorded at 150°C and subsequently at 250 and 350°C after equilibration and evacuation at each temperature. The spectra were collected in the wavenumber range of 1700 – 4000 cm^{-1} .

Ammonia temperature-programmed desorption (NH_3 -TPD) experiments were conducted on a XianQuan 5080 temperature-programmed chemisorption analyzer. The samples were placed in a quartz reactor and heated from room temperature to 300°C at $10^\circ\text{C}/\text{min}$ for drying pretreatment. After cooling to 50°C under He flow (purged for 1 h), a 10% NH_3 /He mixture was introduced for 1 h to achieve saturation adsorption. The system was then switched back to He and purged for 1 h to remove weakly physically adsorbed NH_3 . Finally, desorption was carried out under He by heating to 800°C at $10^\circ\text{C}/\text{min}$, and the desorbed gases were detected by TCD.

The actual loadings of Ni and Mo in the catalysts were determined by inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) using an Agilent 5110 instrument.

Thermogravimetric (TG) analysis was performed on a Netzsch STA 449 F3 thermal analyzer. The samples were purged with N_2 at room temperature for 30 min, then switched to a 10% O_2/N_2 mixture. The temperature was increased from room temperature to 800°C at $10^\circ\text{C}/\text{min}$ and held isothermally for 30 min before cooling to room temperature. The sample mass (mg) and mass percentage (%) as a function of temperature were continuously recorded throughout the experiment.

1.5.2 Gaseous product analysis

Gaseous products were analyzed using a gas chromatograph (GC, GC9790Plus). The oven temperature program was as follows: the column was initially preheated to 50°C and held for 5 min, then ramped to 130°C at $10^\circ\text{C}/\text{min}$ and maintained for 30 min. The instrument was calibrated using standard gas samples. Components were identified by retention times, and semi-quantitative analysis was performed using the peak-area normalization method.

1.5.3 Bio-oil analysis

Organic compounds in bio-oil were analyzed using a gas chromatography-mass spectrometry system (GC-MS, Agilent 7697A). A certain amount of bio-oil was diluted with acetone, mixed thoroughly, and filtered through a $0.22\text{ }\mu\text{m}$ organic syringe filter. The filtrate was withdrawn using a disposable sterile syringe and transferred into a glass vial. The sample ($1.5\text{ }\mu\text{L}$) was injected into the GC-MS system. High-purity helium was used as the carrier gas at a flow rate of $1.0\text{ mL}/\text{min}$ with a split ratio of 1:10. Separation was performed on an HP-5MS capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The oven temperature program was: initially held at 40°C for 5 min, then increased to 130°C at $10^\circ\text{C}/\text{min}$, further increased to 280°C at $5^\circ\text{C}/\text{min}$ and maintained for 10 min.

The mass spectrometer was operated in electron ionization (EI) mode with an electron energy of 70 eV , and the mass scan range was 20 – 550 amu . Compounds were identified by matching with the NIST mass spectral library; only compounds with a matching degree $> 70\%$ were used for qualitative analysis. The relative contents of individual components were calculated semi-quantitatively by the peak-area normalization method.

2 Results and discussion

2.1 Catalyst characterization

XPS was employed to investigate the surface elemental composition and valence states of Ni-Mo/h-BN catalysts with different bimetallic ratios. Survey spectra confirmed the presence of Ni, Mo, B, N and O. All binding energies were calibrated using the $\text{C}1\text{s}$ peak at 284.8 eV .

For Mo $3d$ spectra (Figure 1(a)–(c)), two main peaks at approximately 229.1 and 232.3 eV were attributed to Mo^{2+} (Mo $3d_{3/2}$ and Mo $3d_{5/2}$). Two minor peaks at around 227.9 and 231.2 eV corresponded to Mo^0 (Mo $3d_{5/2}$). Additional weak peaks at approximately 230.5 and 233.7 eV assigned to Mo^{4+} (Mo $3d_{3/2}$) were observed in the 1:1 and 3:1 catalysts. These results indicate that Mo existed mainly as Mo^{2+} , with small amounts of Mo^0 and Mo^{4+} .

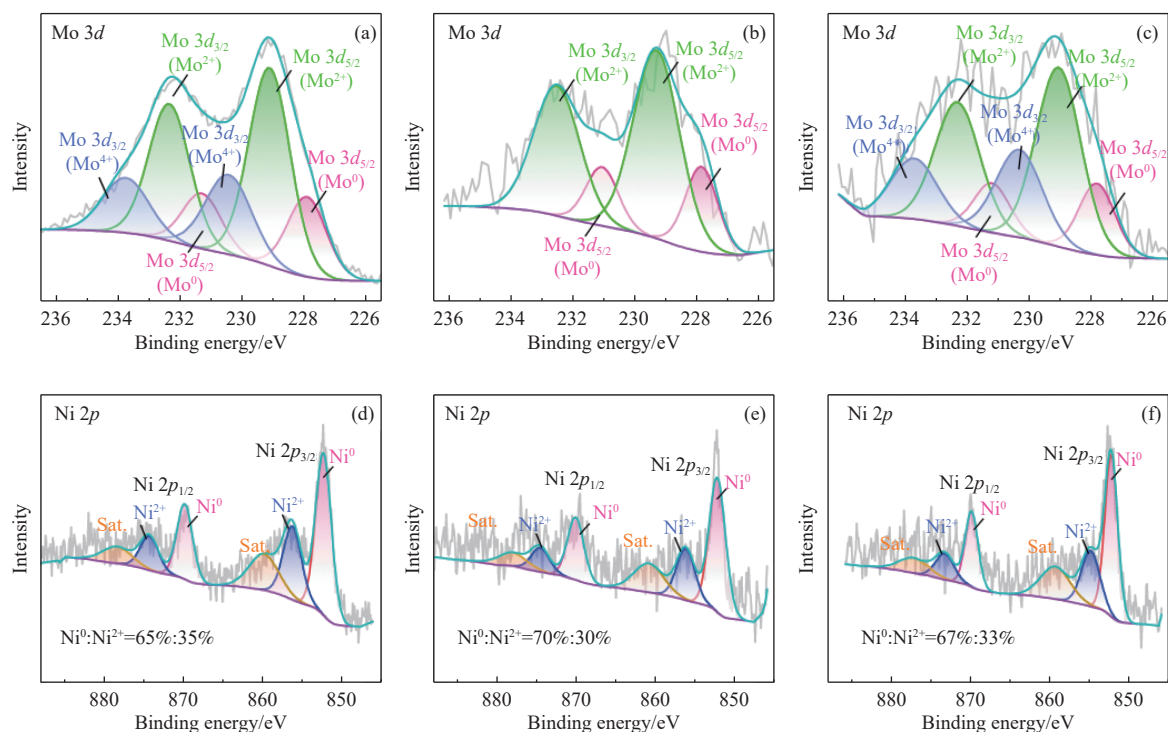


Fig. 1 XPS spectra of Ni-Mo/h-BN catalyst in the Mo 3d (Ni:Mo = 1:1 (a), 2:1 (b), 3:1 (c)) and Ni 2p (Ni:Mo = 1:1 (d), 2:1 (e), 3:1 (f))

For Ni 2p spectra (Figure 1(d)–(f)), two dominant peaks at approximately 852.4 and 870.1 eV were assigned to metallic Ni⁰, and two minor peaks at around 856.2 and 874.5 eV correspond to Ni²⁺ (Ni 2p_{3/2} and Ni 2p_{1/2})^[23]. The peak-area ratio of Ni⁰ to Ni²⁺ was close to 7:3 for all catalysts, indicating that Ni existed predominantly in the metallic state. The satellite (Sat) features at higher binding energies confirmed the successful loading and effective reduction of Ni species^[24].

XRD patterns (Figure 2) showed a distinct diffraction peak at $2\theta = 26.8^\circ$, indexed to the BN (002) plane. A strong peak at approximately 43.3° was assigned to the Ni(200) plane, corresponding to NiO. In addition, a peak at around 51° confirmed the existence of metallic Ni⁰(311)^[25]. A low-angle peak at 14.4° may be indexed to the (110) plane of nickel molybdate (NiMoO₄), indicating the possible formation of this phase. These results indicate that Ni mainly exists in the forms of Ni⁰ and Ni²⁺ in the catalysts, which is consistent with the XPS analysis. The diffraction peak at near 28.1° corresponded to the (110) plane of MoO₂^[26] and two weak peaks at $\sim 41^\circ$ and 73.6° were attributed to the (110) and (211) planes of Mo⁰, indicating the presence of metallic Mo. Slight peak shifts toward lower angles were ascribed to the lattice variation and strong metal-support interactions.

H₂-TPR profiles (Figure 3) showed reduction peak at 593.3 °C (1:1), 524.2 and 629.2 °C (2:1) and 634.2 °C (3:1). The reduction temperature shifted toward higher temperatures with increasing Ni loading due to enlarged particle size^[27]. Most Ni species were reduced to metallic Ni⁰, while only a small fraction of Mo was reduced to metallic state, consistent with XPS results. This single reduction peak for 1:1 and 3:1 catalysts indicated the

formation of strongly interacting Ni-Mo bimetallic structures similar to NiMoO₄, which were reduced continuously^[28]. In contrast, the 2:1 catalyst contained relatively independent Ni and Mo species, leading to two separate reduction peaks.

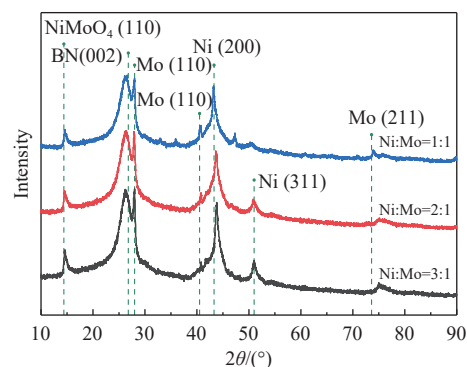


Fig. 2 XRD patterns of Ni-Mo/h-BN catalysts

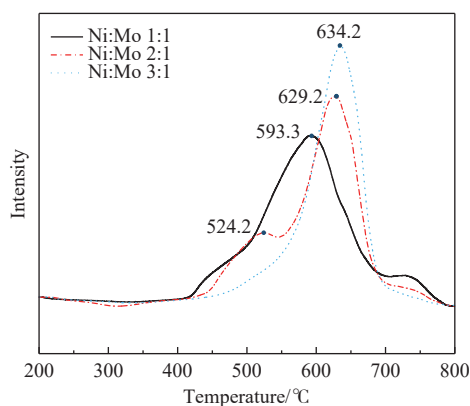


Fig. 3 H₂-TPR curves of Ni-Mo/h-BN catalysts

Py-FTIR spectra (Figure 4) revealed the presence of Lewis acid sites (LAS, $\sim 1450\text{ cm}^{-1}$) and Brønsted acid sites (BAS, 1540 cm^{-1}), with LAS dominant. The band centered at about 1490 cm^{-1} is attributed to pyridine interacting with both Lewis and Brønsted acid sites simultaneously^[29]. The peak areas of both acid sites decrease gradually as the Ni:Mo ratio increased from 1:1 to 3:1.

NH_3 -TPD profiles (Figure 5) exhibited three desorption peaks corresponding to weak ($100\text{--}300\text{ }^\circ\text{C}$), medium ($300\text{--}500\text{ }^\circ\text{C}$), and strong ($600\text{--}700\text{ }^\circ\text{C}$) acid sites^[30]. Weak acid sites were dominant for all samples. The 1:1 catalyst showed a noticeable shift of the weak and medium acid peaks toward lower temperatures, and the highest total acidity (1.17 mmol/g). These results suggest that Mo fraction significantly enhanced the strength of weak and medium acid sites.

ICP-OES results (Table 1) confirmed that Ni and Mo were successfully loaded onto h-BN *via* impregnation, with actual loadings close to nominal values.

2.2 Gaseous product analysis of formic acid APR

2.2.1 Effects of reaction conditions on formic acid APR

High formic acid concentrations cause severe corrosion to the autoclave alloy liner; thus, a formic acid-to-water molar ratio of 1:10 was established as the upper operational limit. As shown in Figure 6, increasing the molar ratio from 1:20 to 1:10 increased H_2 yield but decreased H_2 fraction. CH_4 was negligible, and CO_2 was the main byproduct.

Formic acid decomposes *via* two competing pathways: dehydrogenation ($\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$) and dehydration ($\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$)^[31]. Dilute formic acid favored dehydrogenation, while concentrated conditions promoted dehydration and reverse water-gas shift reactions, reducing H_2 selectivity^[32]. At the same liquid volume, higher initial formic acid concentration (1:10) led to a faster reaction rate and higher H_2 yield within 1 h despite lower selectivity.

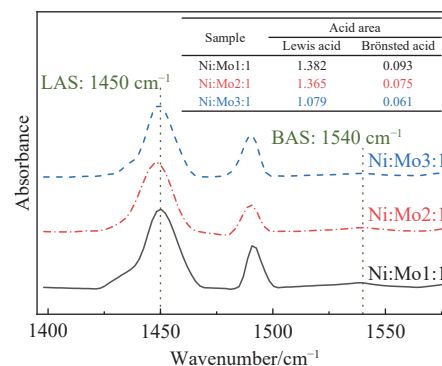


Fig. 4 Py-FTIR spectra of Ni-Mo/h-BN catalysts

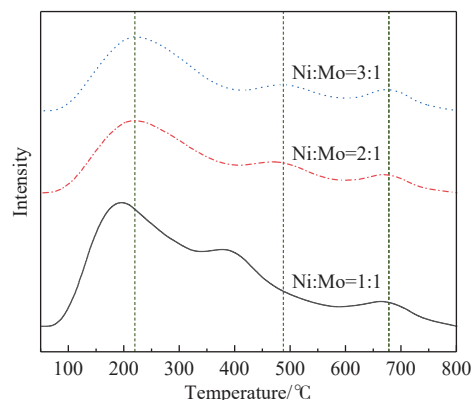


Fig. 5 NH_3 -TPD spectra of Ni-Mo/h-BN catalysts

Table 1 Acid amount and actual metal loading of Ni-Mo/h-BN catalyst

Sample	Acid amount ($\text{mmol} \cdot \text{g}^{-1}$)	Actual content/%	
		Ni	Mo
10%Ni-Mo/h-BN (1:1)	1.18	4.91	4.88
10%Ni-Mo/h-BN (2:1)	0.68	6.88	3.49
10%Ni-Mo/h-BN (3:1)	0.66	7.53	2.54

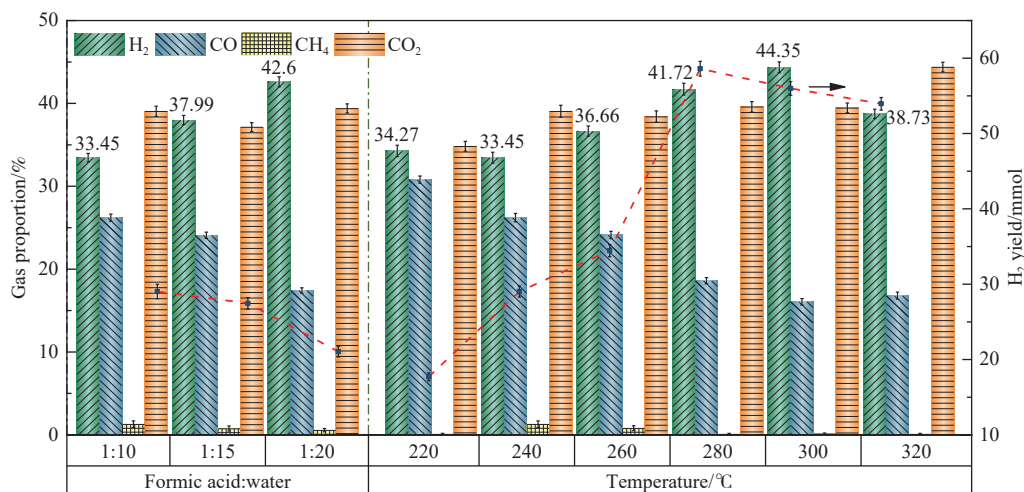


Fig. 6 Composition and H_2 yield of gas products under different reaction conditions

Temperature had little effect on H₂ fraction between 220–260 °C. Within 280–320 °C, H₂ fraction first increased (max 44.35% at 300 °C) then decreased, while CO fraction declined gradually. H₂ yield increased with temperature up to 280 °C (max 58.61 mmol) then decreased. The slightly higher H₂ yield than CO₂ indicated that water participated in APR and contributed to extra H₂ formation.

2.2.2 Effects of catalysts on formic acid APR

APR gas products were mainly H₂, CO₂ and CO (Figure 7). For 10%Ni-Mo/h-BN catalysts, H₂ fraction and yield first increased then decreased, reaching maxima of 32.61% and 38.48 mmol at Ni:Mo = 3:1. Carbon conversion was approximately 40% for bimetallic and Mo monometallic catalysts, lower (32.79%) for Ni monometallic catalyst.

Based on the characterization results of the three bimetallic catalysts with varying Ni:Mo ratios, XPS analysis confirmed the presence of Mo⁴⁺ species in the samples with Ni:Mo= 1:1 and 3:1. Meanwhile, H₂-TPR profiles showed a single reduction peak for these two catalysts, which indicated the formation of Ni-Mo bimetallic structures with strong metal-metal interactions. Notably, the catalyst with a Ni:Mo atomic ratio of 3:1 exhibited the highest reduction temperature, suggesting the strongest metal-metal interaction. Such strong interactions can effectively anchor Ni species, suppressed particle sintering, and generate highly dense and stable active sites^[33], thereby promoting efficient H₂ production from formic acid decomposition. NH₃-TPD and Py-FTIR results demonstrated that all three catalysts were dominated by Lewis acid sites, with only a small fraction of Brönsted acid sites. Additionally, the total acidity of the catalysts gradually decreased with increasing Ni and Mo loading. The decomposition pathway of formic acid was closely related to the nature of acid sites: Lewis acid centers facilitated the cleavage of O–H bond and promoted the dehydrogenation pathway for H₂ production, whereas Brönsted acid sites tend to catalyze the dehydration pathway, leading to the formation of CO and H₂O^[34]. The relatively higher total acidity of the 1:1 and 2:1 catalysts

may induce excessive adsorption of reactants or carbon deposition, thereby reducing the H₂ content and yield. In contrast, the 3:1 catalyst possessed fewer acid sites, which not only mitigated excessive adsorption and coke formation but also maintained favorable synergistic interactions between Ni and Mo. Moreover, this catalyst contained the lowest proportion of Brönsted acid sites, resulting in the effective suppression of side reactions. These combined advantages are consistent with the superior H₂ fraction and yield observed for the Ni:Mo= 3:1 catalyst in the APR experiments.

Although monometallic Ni and Mo catalysts exhibited slightly higher H₂ fractions compared to their bimetallic counterparts, their H₂ yields were significantly lower than that of the bimetallic catalyst with a Ni:Mo atomic ratio of 3:1. Ni-based catalysts can effectively cleave the C–H bond in formic acid, accelerating hydrogen dissociation from the formic acid molecule and promoting the dehydrogenation pathway, which results in a relatively high H₂ concentration. However, pure Ni catalysts are prone to aggregation and severe sintering, leading to a reduction in the density and stability of active sites, thereby limiting the H₂ yield of the Ni/h-BN catalyst^[35]. In contrast, although the Mo/h-BN catalyst showed high selectivity toward dehydrogenation, its intrinsic activity remained relatively low, resulting in a slow overall reaction rate and limited H₂ production. As discussed above, the introduction of Mo into the bimetallic system provided highly dense and stable active sites. The synergistic effect, in which Ni served as the primary active component for H₂ generation, while Mo enhanced the activity and stability of Ni, thereby effectively accelerating the reaction rate and improving H₂ production.

Based on the above results, a formic acid-to-water molar ratio of 1:10 and a Ni:Mo atomic ratio of 3:1 were identified as optimal for achieving the highest H₂ production performance. These solvent conditions and catalyst were therefore selected for subsequent HTL of alkali lignin, where formic acid served as an *in situ* hydrogen donor. The experiments were conducted to investigate whether the effect of temperature on hydrogen production from the hydrogen donor aligned with its effect on substrate hydrogenation.

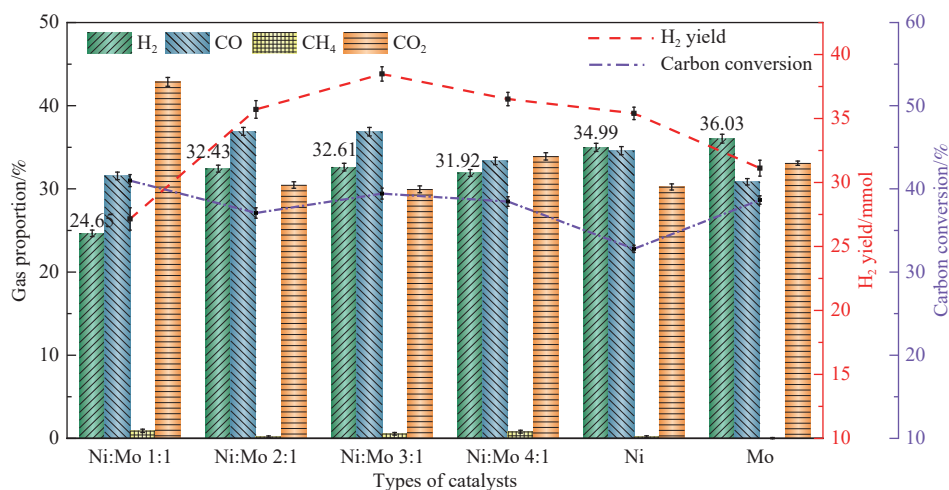


Fig. 7 Gas composition, H₂ yield and conversion of gas products under different catalysts (240 °C, 1 h, formic acid:water=1:10)

2.2.3 Catalyst recycling in formic acid APR

To assess the stability and recyclability of the 10%Ni-Mo/h-BN (Ni:Mo = 3:1) catalyst, four consecutive recycling tests were conducted at 240 °C, 1 h, and formic acid-to-water molar ratio = 1:10 to evaluate catalyst stability. The H₂ yield after each cycle was used as the evaluation metric for catalyst stability. The H₂ yields were 39.73, 36.85, 35.38 and 31.64 mmol, retaining 79.64% of the initial yield after four cycles, indicating good stability. To further investigate metal leaching and carbon deposition, the fresh catalyst and the catalyst after four cycles were characterized by ICP-OES and TG analyses. ICP results showed that the total metal loading decreased from 10.07% before reaction to 8.14% after four cycles, corresponding to a loss of 1.93%, suggesting a certain degree of metal leaching. As shown in Figure 8, TG analysis revealed slight weight loss for both fresh and used catalysts in the temperature range of room temperature to 200 °C, which was mainly attributed to the removal of physically adsorbed water acquired during preparation and storage. For the fresh catalyst, the TG curve remained relatively stable and gradually increased in the range of 200–800 °C, which was ascribed to the slow surface oxidation of the h-BN support. In contrast, the used catalyst exhibited a pronounced weight loss between 200 and 500 °C, followed by a relatively stable curve from 500 to 800 °C. These results indicated that the deposited carbon species mainly consisted of highly reactive, structurally disordered amorphous carbon and filamentous carbon. Carbon deposits formed in the low- to medium-temperature range can cover the active sites of Ni and Mo or block the pores of the h-BN support, which were considered the primary causes of catalyst deactivation. After four cycles, the total weight loss reached 14.7%.

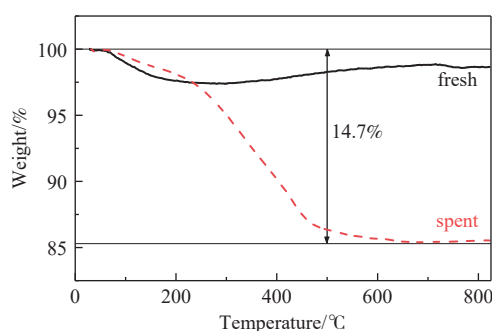


Fig. 8 TG curves of the spent and fresh catalysts

2.3 Characterization of bio-oil

2.3.1 Effects of reaction conditions on bio-oil yield

Table 2 summarized the mass balance results, including bio-oil yield and alkali lignin conversion, under different reaction temperatures and times. At a reaction time of 1 h, the heavy bio-oil yield initially increased and then decreased with rising temperature, rising from 11.30% at

240 °C to a maximum of 18.93% at 280 °C, followed by a decrease to 17.83% at 300 °C. In contrast, the solid residue yield exhibited an opposite trend, decreasing from 7.75% at 240 °C to 6.05% at 260 °C and then increasing to 8.65% at 300 °C. These results suggested that effective depolymerization, driven by hydrogen donation from formic acid, dominated within the temperature range of 240–260 °C. As temperature increased, the reaction rate accelerated, thereby enhancing bio-oil yield and suppressing solid residue formation. However, when the reaction temperature exceeded 280 °C, condensation reactions prevailed over depolymerization, leading to the formation of dimers or larger insoluble polymers that ultimately converted into solid residues. At 280 °C, extending the reaction time from 1 to 3 h resulted in a gradual decrease in both heavy bio-oil and solid residue yields. This behavior may be attributed to the secondary overcracking and thermal decomposition of bio-oil and solid residues under prolonged high-temperature conditions, which converted these products into gaseous and aqueous-phase fractions.

Table 2 Mass balance of reactions under different conditions

Sample	Heavy bio-oil yield/%	Solid residue yield/%	Gas + aqueous yield/%	Conversion /%
240 °C-1 h	11.30	7.75	80.95	92.25
260 °C-1 h	13.73	6.05	80.22	93.95
280 °C-1 h	18.93	8.10	72.97	91.90
280 °C-2 h	16.50	4.75	78.75	95.25
280 °C-3 h	17.25	4.60	78.15	95.40
300 °C-1 h	17.83	8.65	73.52	91.35

2.3.2 Bio-oil component analysis

The chemical composition of bio-oils derived under varied reaction conditions was analyzed by GC-MS. Compounds were classified based on aromatic ring substituents: G-type phenolics (one methoxy group), S-type phenolics (two methoxy groups), H-type phenolics (no methoxy group)^[36], aromatic hydrocarbons, furans, and other compounds (ketones, aldehydes, ethers, etc.). Figure 9 illustrates the effect of reaction temperature on bio-oil component distribution, while Figure 10 presents a representative GC-MS chromatogram at 300 °C. Phenolic compounds remained the predominant fraction across all temperatures, despite significant variations in relative proportions of individual components. The relative content of H-type phenolics increased initially and then decreased with temperature, formed primarily *via* the removal of oxygen-containing functional groups (e.g., methoxy substituents) from phenolic precursors. Aromatic hydrocarbons, generated *via* HDO of phenolic compounds, reached a maximum proportion of 13.81% at 280 °C. In contrast, the contents of G-type and S-type phenolics

decreased significantly with increasing temperature, attributed to enhanced hydrogen participation under high-temperature conditions that facilitated the demethoxylation of G-type and S-type phenolics to form H-type phenolics and dehydroxylation to yield aromatic hydrocarbons. These trends align with formic acid APR results, where H_2 production followed a similar increasing-then-decreasing pattern with temperature. Moreover, the proportion of furan compounds increased markedly with rising temperature, reaching 50.03% at 300 °C, as high temperatures and the acidic environment from formic acid facilitated dehydration of lignin-derived sugar fragments and reaction intermediates^[37].

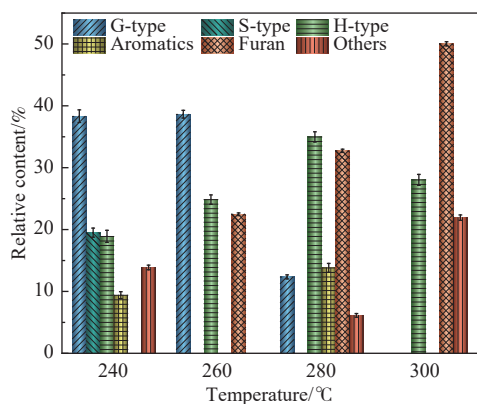


Fig. 9 Distribution of bio-oil under different reaction temperatures (1 h, formic acid: water=1:10, Ni:Mo=3:1)

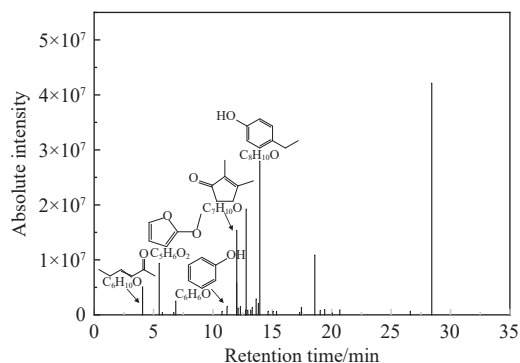


Fig. 10 Typical GC-MS spectrum at a reaction temperature of 300 °C

The effect of reaction time on bio-oil composition was investigated at 280 °C (Figure 11). With prolonged reaction time, the relative content of G-type phenolics and aromatic hydrocarbons decreased gradually: aromatic hydrocarbons declined from 13.81% to 1.03% at 2 h and were undetectable at 3 h. Conversely, furan compound content increased, reaching its maximum at 40.72% at 2 h. At 1 h, alkali lignin macromolecules underwent hydrolysis to form abundant phenolic monomers; sufficient H_2 from formic acid APR at 280 °C enabled demethoxylation and dehydroxylation, generating a certain amount of aromatic hydrocarbons. However, extended reaction time induced

further transformation and ring-opening of aromatic hydrocarbons into low-molecular-weight esters. Furan formation, which arises from the dehydration and cyclization of lignin-derived sugar fragments, requires longer reaction times and proceeds more completely at 3 h. Additionally, some small-molecular aldehyde-ketone intermediates (with carbonyl and double bonds) from lignin depolymerization may undergo condensation in the acidic hydrothermal environment to form furan structures.

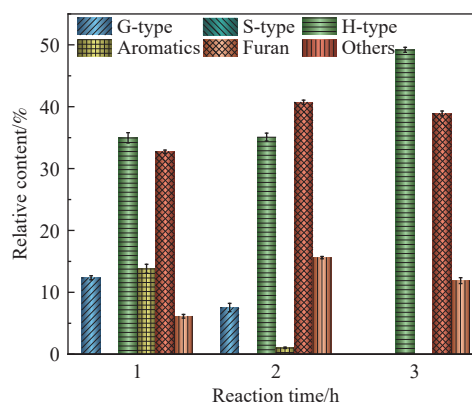


Fig. 11 Distribution of bio-oil components under different reaction times

3 Conclusions

In this study, a series of Ni-Mo/h-BN catalysts with different metal ratios were synthesized for the HTL of alkali lignin using formic acid as an *in situ* hydrogen donor. The influences of reaction parameters and catalyst composition on formic acid APR and bio-oil production were systematically investigated. The 10%Ni-Mo/h-BN (Ni:Mo=3:1) catalyst demonstrated the best catalytic performance for formic acid APR, achieving a maximum H_2 yield of 38.48 mmol at 280 °C with a formic acid-to-water molar ratio of 1:10. For bio-oil production, a higher reaction temperature favors the heavy bio-oil yield, while a prolonged reaction time leads to a slight decrease in its yield. The maximum bio-oil yield (18.93%) was obtained at 280 °C for 1 h. The relative contents of H-type phenolics and aromatic hydrocarbons peaked at 280 °C (34.98% and 13.81%, respectively). Extending reaction time reduced aromatic hydrocarbon content and increased furan compound proportion. This study demonstrates that *in situ* hydrogen generation from formic acid and lignin hydrogenation exhibit good consistency in response to temperature changes in the range of 240–280 °C, providing a feasible and efficient strategy for the valorization of alkali lignin into high-quality bio-oil.

Declaration of Competing Interest

The authors declare no conflict of interest.

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甲酸原位供氢下碱木质素水热液化实验研究

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摘要: 碱木质素作为造纸工业和生物质精炼的副产物, 产量高、来源广泛, 然而复杂的聚合结构限制了其高值转化与有效利用。由于其能量密度高且富含芳环结构, 被认为是生产液体燃料中芳香烃组分的天然原料。本研究以碱木质素为原料, 考察甲酸原位供氢下不同反应条件对碱木质素催化转化制生物油的影响。采用浸渍法制备了 Ni-Mo/h-BN 双金属催化剂, 并通过 XPS、XRD 等表征分析了不同金属比例催化剂的结构和物化特征。研究了不同反应条件对甲酸水相重整制氢的影响。结果表明, 甲酸和水摩尔比 1:10、催化剂 Ni:Mo=3:1 时产氢效果最佳, 在 220–280 °C 下 H₂ 产量随温度升高而增加, 最大为 38.48 mmol。探究了甲酸原位供氢下反应温度、时间对碱木质素制生物油的影响, 实验结果表明, 反应温度 280 °C 时生物油重油收率达到最大值 18.93%, 生物油组分中芳香烃类化合物相对含量达到最大值 13.81%, 反应时间的延长会降低重油收率以及芳香烃类化合物的相对含量, 提升呋喃类化合物在生物油组分中的占比。研究表明, 240–280 °C, 甲酸原位供氢与木质素加氢表现出较好的一致性。

关键词: 甲酸; 碱木质素; 水热液化; 原位供氢; 生物油

中图分类号: TK6

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