

Effect of Fe, Ni, and Co on the hydrothermal liquefaction of Chinese herb residue for bio-oil production

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Abstract. This study investigated the effects of reaction temperature (300–360 °C), reaction time (0–60 min), and the ratio of raw materials to solvent (1:5–1:15; g/mL) on the HydroThermal Liquefaction (HTL) of Chinese Herb Residues (CHR) for Bio-Oil (BO) production. Optimal HTL conditions for CHR were determined. To enhance both the yield and quality of BO, metal-modified catalysts including Fe/MCM-41, Co/MCM-41, and Ni/MCM-41 were prepared. These catalysts, after hydrogen reduction, loaded metal elements in their elemental state onto the carrier. Subsequently, CHR catalytic HTL experiments were conducted at 330 °C for 15 min with a ratio of 1:10 (g/mL). BO analysis was performed using EA, GC-MS, and FT-IR. Under the optimal HTL conditions (330 °C/15 min/1:10), the BO yield reached 24.57 wt.%, with a Higher Heating Value (HHV) of 25.96 MJ/kg. The major components of the BO included phenols, ketones, acids, and esters. In the catalytic HTL, Fe/MCM-41 (26.15 wt.%), Ni/MCM-41 (26.2 wt.%), and Co/MCM-41 (27.05 wt.%) catalysts each achieved higher BO yields. When using Ni/MCM-41 catalyst, the highest HHV of BO reached 32.01 MJ/kg, representing an 81% improvement over CHR HHV of 17.66 MJ/kg. Additionally, with Fe/MCM-41 catalyst, the lowest oxygen content in BO was 9.68%, and the selectivity for phenols and ketones was the highest, showing increases of 15.22% and 33.15%, respectively, reaching 44.13% and 24.5%. The results indicate that HTL can effectively convert high-moisture CHR into valuable products. Hydrogen-reduced metal-modified catalysts contribute significantly to increasing BO yield, promoting deoxygenation and hydrogenation reactions, and markedly improving HHV and the selectivity of chemical components, thereby effectively enhancing both the yield and quality of BO.

Keywords: Chinese herb residue, Hydrothermal liquefaction, Bio-oil, Metal catalyst, Conversion.

1 Introduction

Chinese Herb Residues (CHR) contains a high level of moisture and residual nutrients, making it prone to decay and emitting foul odors, posing a potential threat to environmental safety [1, 2]. Annually, China's CHR emissions exceed 60 million tons, with over 70% of the total attributed to pharmaceutical residue generated from proprietary Chinese medicine production [3]. At present, the primary disposal methods for CHR include regional stacking, landfilling, and incineration, leading to exacerbated resource depletion and environmental pollution [4]. CHR characterized by its concentrated emissions, shares a similar

chemical constitution with common lignocellulosic biomass [5, 6]. Compared to pyrolysis and gasification, HydroThermal Liquefaction (HTL) offers lower reaction temperatures and higher energy efficiency. It can directly handle high-moisture substances, eliminating the need for drying-related time and costs [7, 8]. Therefore, HTL is better suited for the conversion of high-moisture CHR into biofuels.

HTL depolymerizes biomass under sub-critical or near-critical conditions, showcasing a notable advantage in its exceptional versatility concerning biomass feedstock [9]. Typically conducted at temperatures ranging from 250 °C to 374 °C and pressures between 2 and 25 MPa, utilizes water as a solvent for the depolymerization, converting high-moisture content biomass into smaller molecules while reducing its oxygen content. This process facilitates the production of Bio-Oil (BO) fuel or valuable chemicals. The

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resulting liquid phase products include organic acids such as formic acid and acetic acid, furans like furfural and 5-hydroxymethylfurfural, as well as phenols such as phenol and guaiacol. However, the yield and quality of BO remain unsatisfactory, primarily due to its elevated oxygen content, resulting in reduced calorific value, increased viscosity, heightened instability, and complex organic components. These factors limit its industrial applicability. The process is primarily influenced by variations in raw materials, temperature, catalysts, solvents, reaction time, and the solid-liquid ratio [10]. Increased reaction temperature promotes BO, but exceeding the limit value reduces BO yield due to increased gas formation during carbon formation in repolymerization reactions or when surpassing the water critical [11, 12]. Extending the reaction time can enhance BO yield, but excessively long reaction times lead to the repolymerization of BO molecules, yielding opposite results [13]. A small ratio of raw material to solvent hampers rapid HTL reactions, while a large ratio results in excessive waste resources [14]. Hence, according to the different kinds of raw materials, it is necessary to select the optimal reaction temperature, time, and solid-liquid ratio conditions for the production of BO. Although organic solvents exhibit excellent depolymerization effects, their high cost restricts widespread application [15–18]. Therefore, using water as the reaction solvent, characterized by its low cost and easy accessibility, enables the acquisition of essential data. This characteristic facilitates enhanced solubility for numerous components in BO under high-temperature and high-pressure conditions near the critical point [19]. Currently, a variety of catalysts have been employed to enhance the properties and yield of BO in the biomass HTL process. Molecular sieve catalysts, particularly, exhibit high activity and facilitate easy separation and recycling from liquid products, reducing costs associated with the entire production chain of BO [20]. Incorporation of precious metals, transition metals, and oxides onto molecular sieves offers significant advantages, enhancing BO yield, reducing oxygen content, increasing hydrogen content, and improving component distribution [21–23]. In previous studies, algae, lignin, and untreated biomass have been commonly chosen as subjects for HTL. These materials possess richer and relatively concentrated components, favoring the performance of catalysts. In contrast, there has been less exploration of organic waste emitted naturally by factories. CHR waste materials have lost a significant portion of intrinsic components during the extraction of valuable products, resulting in more complex remaining components. Using pharmaceutical companies naturally emitted Chinese medicine residues allows a more comprehensive assessment of the overall performance of previous catalysts. In contrast to the typical use of metal catalysts in their oxidized state in past experiments, the catalyst employed in this study has undergone hydrogen reduction.

Currently, there is a limited exploration of the catalytic performance of CHR in HTL and the composition of liquid phase products. The objective of this study is to recycle CHR and produce renewable fuel. Firstly, the chemical composition of CHR was analyzed to study the influence of reaction conditions on the distribution of liquefaction

products and product yield. The feasibility of HTL as a disposal method for CHR resources was verified. Secondly, Fe/MCM-41, Ni/MCM-41, and Co/MCM-41 catalysts were prepared to catalyze HTL under specific conditions (330 °C/15 min/solid-liquid ratio 1:10). Detailed characterization was conducted on both catalysts and BO, allowing us to investigate how these catalysts affect product distribution and quality.

2 Materials and methods

2.1 Materials

CHR is derived from the Wood-Mixed Residue (WHR) of a traditional Chinese medicine produced by a pharmaceutical company in Shandong Province. Firstly, the wet samples are pre-dried at 105 °C in a forced-air drying oven for 12 h. Subsequently, the samples are crushed and sieved to obtain particles with a size range of 40–100 mesh. Finally, the remaining moisture in the samples is further dried and stored in drying dishes for later use. The Vario EIII elemental analyzer is employed to determine the content of C, H, N, S, and O in WHR. The Higher Heating Value (HHV) of WHR is calculated using the Dulong formula. The thermal analysis of WHR is analyzed using the TGA5500 thermogravimetric analyzer under an N₂ atmosphere, with a heating rate of 10 °C/min, ramping from 50 °C to 1000 °C.

The MCM-41 (M) molecular sieve catalyst was purchased from *Zhengzhou Feynman Biotechnology Co., Ltd.* Other chemical reagents, all AR pure, were obtained from *Simopharm Chemical Reagents Co., Ltd.* Deionized water is produced by the laboratory-grade water purifier with the model TANKPE030 model.

2.2 Preparation of catalyst

The MCM-41 was calcined at 550 °C in a muffle furnace for 4 h and sieved through a 100-mesh sieve. A metallic catalyst with 10 wt.% loading was synthesized via the impregnation method. (Fe(NO₃)₃·9H₂O), (Ni(NO₃)₂·6H₂O), and (Co(NO₃)₂·6H₂O) were dissolved in deionized water to form a nitrate metal precursor solution. Subsequently, the solution and molecular sieve were mixed, ultrasonicated for 30 min, stirred at 50 °C for 24 h, and dried at 105 °C for 12 h. Finally, the dried catalyst material was sieved through a 100-mesh sieve, calcined at 550 °C for 4 h, and pressed and screened to obtain particles sized between 50 and 60 mesh. Based on H₂-TPR characterization, the catalyst material was reduced to 10% H₂ for 2 h at a specific temperature in a tubular furnace.

2.3 HTL experimental procedures

HTL experiment utilized a 100 mL batch reactor with a magnetic coupling agitator (HT-100FJ, *Shanghai Huotong Instrument Co., Ltd.*), featuring a design temperature of 400 °C and a pressure capability of 20 MPa. In the reactor, 7 g of WHR, 0.14 g of catalyst, and 70 mL of deionized water were sealed (Fig. 1). N₂ purging (4–5 times) eliminates internal air. The reactor temperature was set at

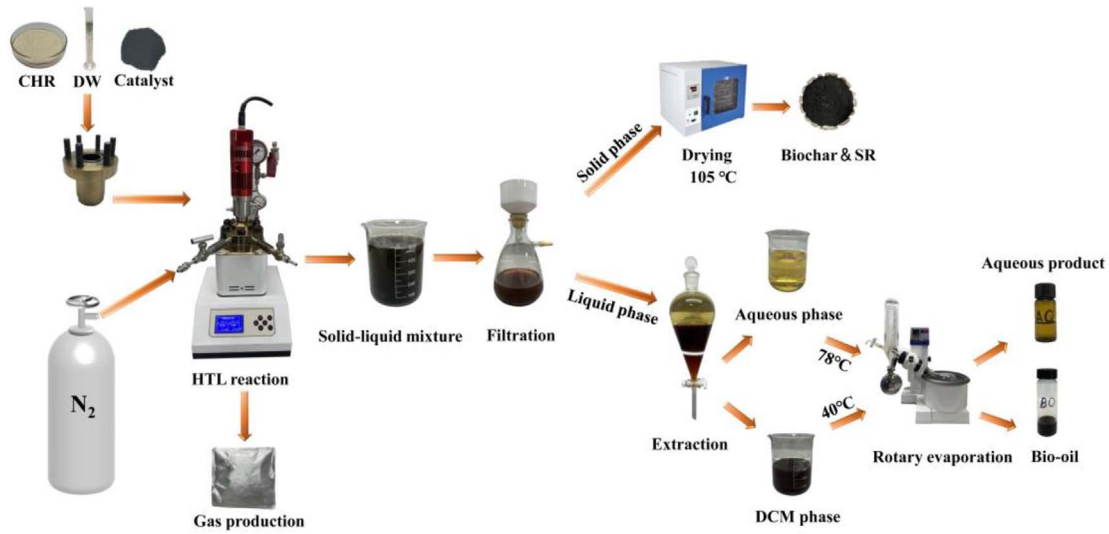


Fig. 1. Flow chart of preparation of bio-oil by WHR catalytic hydrothermal liquefaction.

330 °C with a magnetic stirrer speed of 800 rpm. The desired temperature was reached at a rate of approximately 10 °C/min and maintained for minutes. Gas products were collected using airbags when the reactor was cooled below 40 °C. The solid-liquid mixture was collected using deionized water and DiChloroMethane (DCM), followed by 30 min of ultrasonication DCM was used as the extraction solvent for BO, and solid separation was performed using quantitative filter paper and a Brinell funnel. The resulting Solid Residue (SR) was dried overnight at 105 °C. The DCM phase and Aqueous Phase (AP) were separated using a separation funnel, and the solvent was removed at 40 °C and 78 °C, respectively, in a rotary evaporator to obtain BO and the AP product, which were then weighed. The experiments were conducted in triplicate, and the formula for calculating the yield of HTL products is as follows:

$$\text{Yield}_{\text{BO}\backslash\text{SR}\backslash\text{AP}} = \frac{w2\backslash w3\backslash w4}{w1} \times 100\% \quad (1)$$

$$\text{Yield}_{\text{Gas}} = \frac{w1 - w2 - w3 - w4}{w1} \times 100\% \quad (2)$$

$$\text{Conversion} = 1 - \text{Yield}_{\text{SR}} \quad (3)$$

The HHV of BO is calculated through the Dulong formula:

$$\text{HHV (MJ/kg)} = 0.3383C + 1.428\left(H - \frac{O}{8}\right) + 0.095S \quad (4)$$

$w1$: weight of WHR; $w2$: weight of BO; $w3$: weight of SR; $w4$: weight of AP product.

2.3 Analysis method

2.3.1 Characterization analysis of catalysts

A Temperature Programmed Reduction test (H_2 -TPR) was conducted using a Builder Electronic PCA-1200 chemisorption analyzer to determine the reduction characteristics of transition metal-modified molecular sieves. Initially, the sample was purged with Ar at 200 °C for 30 min, then gas

(10% H_2) was used, and the temperature was heated to 800 °C for 20 min. The surface morphology of the catalyst was observed using a Hitachi S-4800 FE-SEM field emission scanning electron microscope. X-Ray Diffraction (XRD) analysis of the catalyst's ground form was performed on a Rigaku Ultima IV X-ray diffractometer with a Cu target, scanning at 2 °/min in the range of (2 θ) 5°–90° to observe its crystal characteristics. The specific surface area and pore structure of the catalyst were determined using a Builder Electronic Kubo-X1000 BET instrument. Prior to testing, the sample underwent degassing at a vacuum degassing station at 260 °C for 8 h.

2.3.2 Analysis of products

The C, H, N, S, and O content of BO was analyzed using the Thermo Scientific Flash 2000 Element Analyzer (EA). EA was performed twice to obtain average values. Compounds distribution in BO was determined by Gas Chromatography-Mass Spectrometry (GC-MS) on an Anyep 7700 A instrument with an HP-5 MS column (30 mm $\times$ 0.25 mm $\times$ 0.25 μ m). He was used as the carrier gas at a flow rate of 1 mL/min. The inlet temperature was set at 280 °C, and the ion source temperature at 230 °C, with a 1 μ L injection and a 30:1 splitter ratio. Maintain at an initial temperature of 40 °C for 5 min, then ramp up to 300 °C at a rate of 5 °C/min, and hold for 10 min. Matching test results using the NIST database. The functional groups in WHR, BO, and SR were characterized using the Bruker INVENIO S Fourier Transform Infrared Spectrometer (FT-IR).

3 Results and discussions

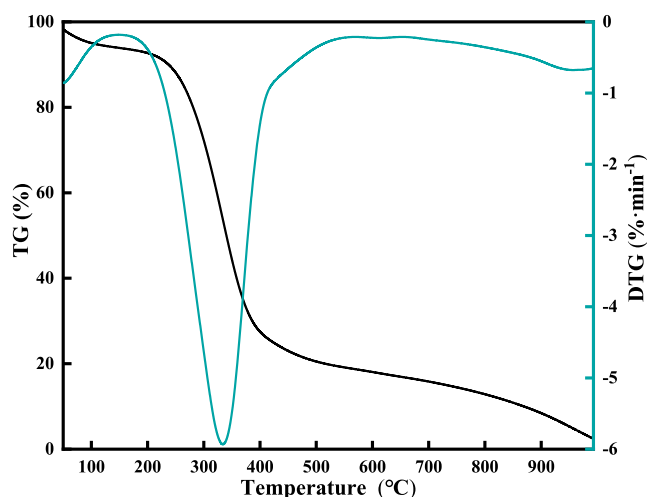
3.1 WHR characterization

Based on the comprehensive analysis of WHR, as presented in Table 1, it is evident that WHR shares a composition distribution similar to conventional biomass. However, owing to the extraction of medicinal properties or specific

Table 1. WHR characterization.

Ultimate analysis (%)		Other analysis (%)		Proximate analysis (%)	
C	46.6	Cellulose	37.66	Moisture	0.97
H	6.35	Hemicellulose	23.21	Volatile	4.01
N	1.42	Lignin	20.11	Ash	88.52
S	0.29	Protein	4.4	Fixed carbon	6.51
O	40.36	Lipid	1		
HHV (MJ/kg)	17.655	Carbohydrate	89.7		

The content of O is determined utilizing the difference method: $O = 100 - C - H - N - S - M - V$. M: moisture; V: volatile.

**Fig. 2.** TG/DTG of WHR.

types of WHR, its protein and lipid content are lower, while the carbohydrate content is higher. Despite this, the lignin-cellulose composition in WHR surpasses that of other urban wastes, with a carbon content reaching 46.6%, while sulfur and nitrogen contents remain relatively low. These attributes make it a suitable raw material for HTL [13]. Through TG/DTG curves, the weight loss rate of WHR during temperature variations can be elucidated. As depicted in Figure 2, the primary pyrolysis phase of WHR occurs between 200 °C and 500 °C, primarily attributed to the thermal decomposition of hemicellulose, cellulose, and lignin in WHR. The maximum weight loss rate is achieved at 337 °C. Notably, the peak weight loss rate of WHR occurs within the range of 300–360 °C, indicating enhanced combustibility of the sample in this interval, with the majority of volatiles being released. This suggests optimal pyrolysis efficacy within this temperature range, making it the chosen investigation range for liquefaction temperature to obtain the most favorable liquefaction reaction temperature.

3.2 Catalyst characterization

The redox performance of transition metal oxide catalysts was assessed through H_2 -TPR testing, depicted in Figure 3a. Temperature variations resulting from the interaction between the loaded metal and the molecular sieve carrier

lead to distinct reduction temperatures, depending on the quality of the metal being loaded [24]. Fe/MCM-41 catalyst exhibits two prominent reduction peaks, with the first peak at 385 °C corresponding to the reduction of Fe_2O_3 to Fe_3O_4 . Subsequently, a subsequent reduction occurs at 627 °C, forming FeO [25]. Ni/MCM-41 catalyst shows a strong peak at 565 °C, indicating the reduction of NiO to elemental Ni, albeit delayed due to the influence of MCM-41. Co/MCM-41 displays two distinct reduction peaks: the reduction of Co_3O_4 to CoO at 355 °C, followed by the reduction of CoO to metallic Co at 658 °C. When Fe and Co are co-loaded, their interaction broadens the reduction peak. Increasing the number of supported metals shifts the reduction temperature towards lower temperatures. Simultaneously support of two metals results in an even lower reduction temperature compared to a single metal, indicating weakened active metal-carrier interaction and enhanced REDOX ability of the catalyst. Therefore, we designated the final main peak temperature observed during H_2 -TPR characterization as the designated H_2 reduction temperature for all catalysts. The metal elements in the reduced catalyst are loaded onto the MCM-41 support in the form of metal monomers and subsequently participate in the catalytic liquefaction process.

The wide-angle XRD patterns of catalyst samples are shown in Figure 3b. A distinctive diffraction peak pattern at a low angle, typically around $2\theta = 23^\circ$, was detected for both MCM-41 and all metal-supported catalyst samples. Additional peaks emerged in the XRD patterns of Fe/MCM-41, Ni/MCM-41, and Co/MCM-41 catalysts post-impregnation. The diffraction peaks of Fe/MCM-41 appeared at $2\theta = 44.67^\circ$, 65.02° and 82.33° , for Ni/MCM-41 at 44.49° , 51.84° , and 76.38° , and for Co/MCM-41 at 44.21° , 54.52° , and 75.85° , respectively [26–28]. These strong diffraction peaks indicate the presence of well-dispersed metallic Fe, Ni, and Co species on the surface of the MCM-41 support after reduction from their respective metal oxide states. The pattern is nearly equivalent to that of MCM-41, signifying the incorporation of metallic elements into the molecular sieve carrier. Importantly, the metal modification process has lesser influence on the structural integrity and fundamental framework of MCM-41. Consequently, the structure of MCM-41 remains unchanged throughout the impregnation process [29].

To investigate morphological changes and metal loading of the metal-modified molecular sieve catalyst, SEM

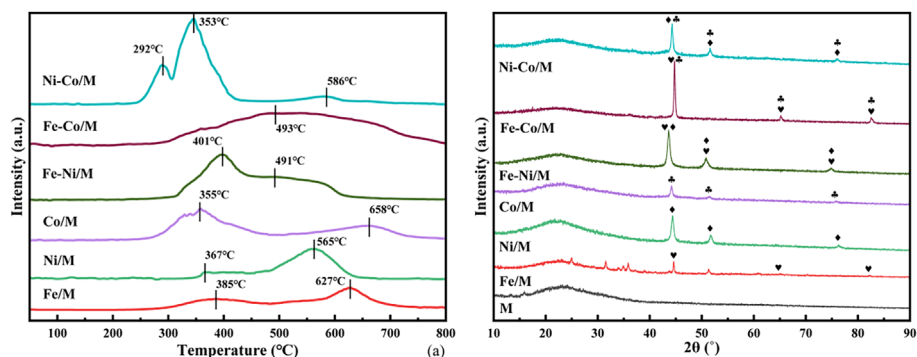


Fig. 3. H₂-TPR (a) and XRD (b) patterns of all as-prepared catalysts (♠: Fe; ◆: Ni; ♣: Co).

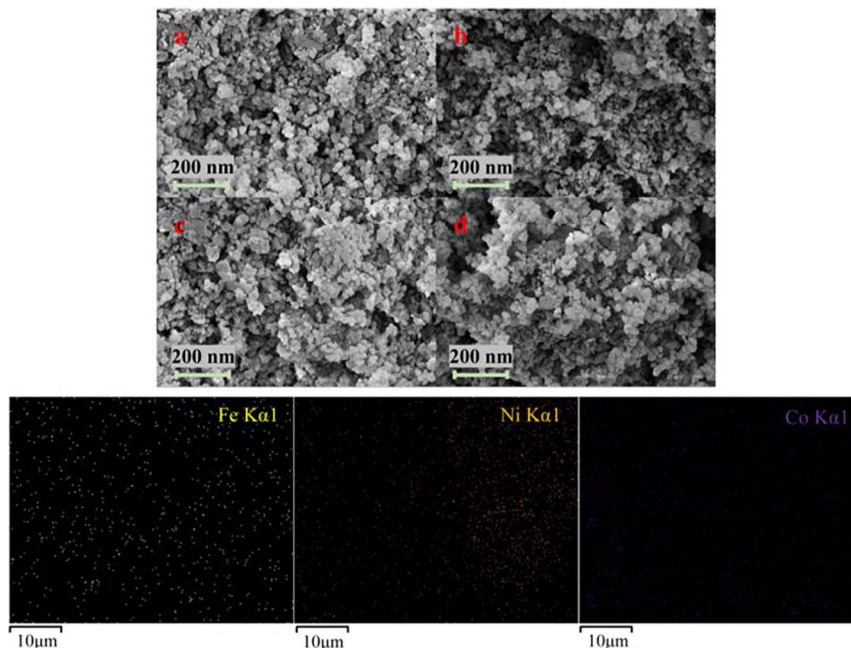


Fig. 4. SEM and mapping images of MCM-41 and single metal supported catalysts. (a) MCM-41; (b) Fe/MCM-41; (c) Ni/MCM-41; (d) Co/MCM-41.

analysis and mapping characterization were conducted on the single metal-supported catalyst, as shown in Figure 4. The MCM-41 exhibits a predominantly uniform and spherical shape. The introduction of transition metals did not significantly impact the morphology and aggregation state of the support material (MCM-41), thus preserving its original properties. In the mapping analysis, three color points represent the distribution of corresponding metal elements, indicating uniform dispersion of Fe, Ni, and Co metals on the surface of MCM-41 in a particulate state.

Table 2 presents the BET surface area, pore volume, and pore size distribution results of the catalyst samples. MCM-41 exhibits a significantly high specific surface area (711.2 m²/g) and pore volume (0.978 cm³/g). Modification with metal causes a substantial decrease in both specific surface area and pore volume, accompanied by an increase in pore size. This is attributed to the high content of added metal, resulting in surface coverage by metal particles and

blockage of carrier pores [30]. In contrast, the specific surface area reduction in Fe load is more pronounced compared to Ni and Co catalysts, owing to higher metal content insertion into the MCM-41 framework. The results demonstrated that the incorporation of metal had a negligible impact on the pore structure of the MCM-41 mesoporous molecular sieve, as indicated by the alteration in catalyst pore volume.

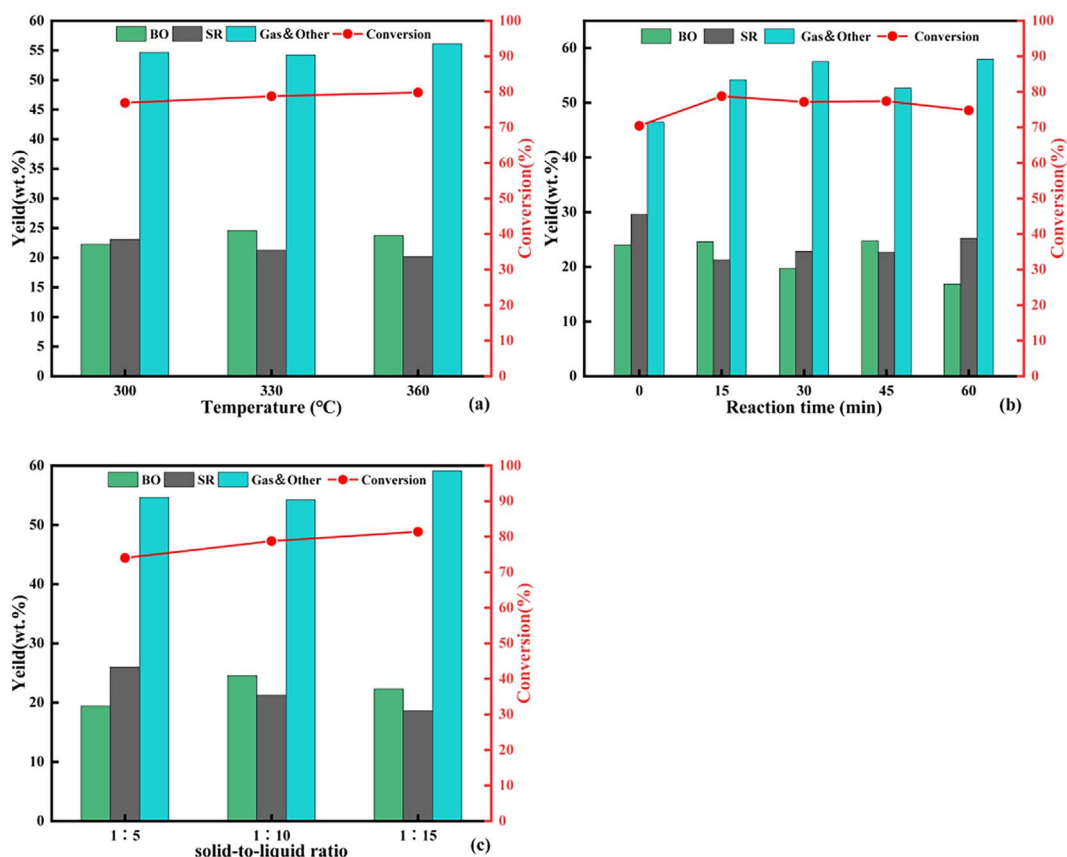
3.3 HTL product yield

3.3.1 Temperature, time, and solid–liquid ratio on product yield

Figure 5 illustrates the influence of various reaction conditions on HTL product distribution without a catalyst. To assess the impact of reaction temperature on product distribution, liquefaction of WHR was conducted at various

Table 2. Catalysts surface area, pore size, and pore volume analysis.

Catalyst	Surface area (m ² /g)	pore volume (cm ³ /g)	Average pore sizes (nm)
M	711.2	0.978	2.75
Fe/M	359.2	0.649	3.62
Ni/M	435.7	0.858	3.94
Co/M	435.6	0.699	3.21
Fe-Ni/M	231.5	0.494	4.27
Fe-Co/M	258.6	0.539	4.17
Ni-Co/M	351.1	0.776	4.42

**Fig. 5.** Effects of different reaction conditions on product yield. (a) Temperature; (b) reaction time; (c) solid-to-liquid ratio.

temperatures (300\330\360 °C) with a reaction time of 15 min and a solid-liquid ratio of 1:10. Results show (Fig. 5a) a substantial increase in BO yield with the temperature rise, and SR yield decreased from 24.1 wt.% to 19.19 wt.%. Under the conditions of 330 °C, the maximum BO yield is 24.57 wt.%; whereas at 360 °C, the conversion rate reaches a peak of 80.81%. These indicate that higher temperatures effectively enhance WHR macromolecule degradation, facilitating the breakdown of cellular compounds like proteins, lipids, and carbohydrates, leading to increased BO yield [31]. However, excessively high liquefaction temperatures can cause non-condensable gas cracking, resulting in reduced BO yield. In order to maximize bio-oil yield,

minimize product gasification, and reduce unnecessary energy consumption, a reaction temperature of 330 °C is selected for the subsequent catalytic liquefaction.

At a reaction temperature of 330 °C and a solid-liquid ratio of 1:10, the liquefaction of WHR was investigated at various time points within the range of 0–60 min. In Figure 5b, the reaction time has an impact on the BO yield. With an increase in reaction time, the BO yield exhibits a trend of initially increasing and then decreasing, reaching its peak at 15 min. where the SR yield is at its minimum, measuring 21.24 wt.%. However, further extending the reaction time to 30 min and 60 min results in a decrease in BO yield and an increase in SR yield. This is attributed

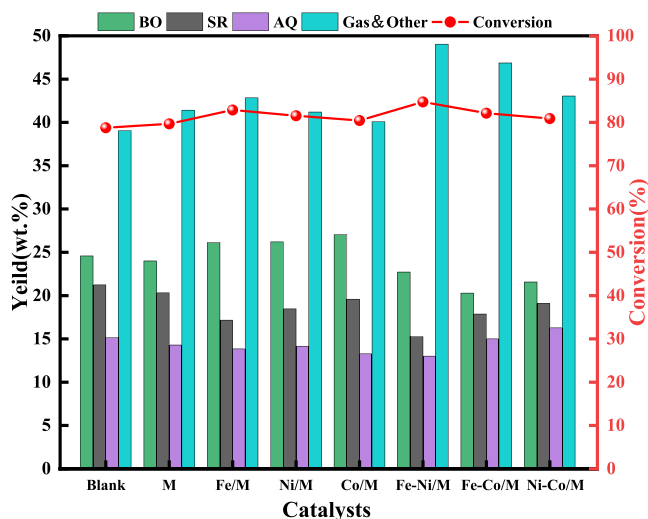


Fig. 6. Effect of different catalysts on product distribution.

to the continuous reaction time causing the aggregation of BO into solids, simultaneously prompting the continuous secondary cracking of BO molecules, leading to gas formation. The research findings suggest that extending the reaction time promotes the conversion of WHR to BO, generating more BO. However, beyond a certain point, the increase in BO yield is marginal, and unstable secondary reactions of BO may result in the formation of solids or gases. Therefore, selecting the initial 15 min, where the BO yield reaches its maximum, as the reaction time for subsequent catalytic experiments is deemed appropriate.

In Figure 5c, it can be observed that with an increase in the solid-to-liquid ratio, the conversion rate gradually rises. The BO yield follows a trend of initial increases, peak at 24.57 wt.%, and subsequent decline to 22.31 wt.%. This phenomenon is attributed to the uneven heating of WHR at high solid concentrations, hindering its thermal decomposition. As the solid concentration decreases, the interaction between the solvent and the raw material intensifies, enhancing the solubility of components. At this point, the sample reacts more thoroughly, thereby promoting its conversion to BO. Therefore, to maintain a higher BO yield while conserving water resources, it is advisable to choose a lower solid-to-liquid ratio. In the subsequent catalytic reaction, a solid-to-liquid ratio of 1:10 is selected.

The results reveal that higher temperatures favor the depolymerization of CHR, and reducing reaction time can prevent the secondary reactions leading to the formation of solid and gaseous by-products in bio-oil. Moreover, a higher solid-to-liquid ratio enhances BO yield and conserves water resources. The optimal liquefaction conditions for CHR were ultimately determined to be 330 °C/15 min/1:10, resulting in the highest BO yield of 24.57 wt.%.

3.3.2 Effect of catalyst on product yield

Under these conditions, the impact of MCM-41, mono-metallic, and polymetallic MCM-41 catalysts on liquefaction product distribution was investigated. As shown in

Figure 6, the influence of MCM-41 on the BO yield is negligible. However, there is a slight reduction in SR and AP yields, accompanied by a small increase in gas. This can be attributed to the higher reaction temperature saturating the SR conversion rate during the HTL process. Consequently, a small amount of MCM-41 has limited effects on WHR fragmentation and disintegration, failing to provide an enhanced depolymerization effect. The incorporation of metals becomes necessary to enhance the catalyst's depolymerization capability toward WHR during the HTL reaction.

Utilizing a supported metal catalyst enhances BO yield and conversion rate while reducing SR and AP yields. Fe/MCM-41, Ni/MCM-41, and Co/MCM-41 supported catalysts yield 26.15 wt.%, 26.2 wt.%, and 27.05 wt.% of BO, respectively. Fe/MCM-41 shows the highest conversion rate (82.85%) and gas yield (42.85 wt.%). Co/MCM-41 catalyst achieving a minimum AP yield of 13.28 wt.%. Ni/MCM-41 exhibited the highest AP yield (14.14 wt.%), but it also facilitated bioseparation in the aqueous phase, reducing AP yield compared to the blank group and MCM-41. The results demonstrate that MCM-41 itself possesses a mesoporous molecular sieve structure with a small number of acid sites, while the incorporation of metal ions enhances the catalyst's acidity and activity, thereby accelerating the reaction rate. This promotes WHR depolymerization and further decomposition based on MCM-41. The single metal-supported catalyst exhibits favorable surface activity and acidity, enhancing BO yield while reducing SR and AP yields, thus facilitating WHR depolymerization. In this context, Fe metal generates a significant amount of gas, while Ni metal enhances the water solubility of certain components in BO, allowing them to enter the aqueous phase. Conversely, Co facilitates the reduction of water-soluble components, converting them into BO.

The impact of a bimetal-supported catalyst on product distribution in HTL was further investigated. In this study, the use of bimetallic catalysts did not enhance the BO yield. Figure 6 shows a decrease in BO yields to 22.71 wt.%, 20.28 wt.%, and 21.57 wt.% with Fe-Ni/MCM-41, Fe-Co/MCM-41, and Ni-Co/MCM-41 bimetallic catalysts compared to mono-metal catalysts. However, the conversion rate (80.89–84.73%) and gas yield (43.04–49.02 wt.%) are higher than those achieved by mono-metal catalysts, indicating a positive impact on further enhancing WHR depolymerization. Nevertheless, the high acidity of the bimetallic catalyst surface accelerates WHR cracking, promoting gas production. On the one hand, Fe and Ni exhibit excellent catalytic capabilities in hydrogenation and methane reforming reactions, with Fe showing outstanding performance, particularly in hydrogen production. On the other hand, excessive catalyst loading and high reaction temperatures contribute to intensified gasification reactions of BO [32]. This phenomenon was further confirmed by an increase in conversion efficiency and gas yield. Bimetal-supported catalysts lead to increased AP, with Ni-Co/MCM-41 achieving a remarkable 16.28 wt.%. This may be attributed to the promotion of intermediate decomposition and the generation of water-soluble small organic molecules after loading bimetallic catalysts. Consequently, it restricts the conversion

Table 3. EA of bio-oil obtained by different catalysts.

Catalyst	Ultimate analysis (%)					
	C	H	N	S	O	HHV
Blank	57.26	6.14	0.62	0.07	12.22	25.964
M	60.27	6.32	1.07	0.12	13.25	27.06
Fe/M	68.46	6.73	1.03	0.09	9.68	31.051
Ni/M	70.99	6.89	0.43	0.06	10.35	32.013
Co/M	68.87	6.51	0.15	0.08	10.29	30.766
Fe-Ni/M	69.46	6.27	0.12	0.06	14.55	29.861
Fe-Co/M	70.97	6.19	0.12	0.06	14.82	30.209
Ni-Co/M	67.89	5.97	0.14	0.07	14.45	28.72

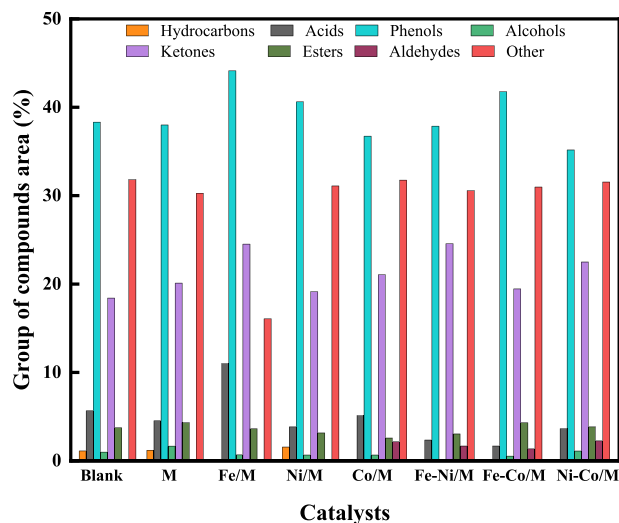
of intermediates to BO, leading to an increase in acetic acid AP yield and a decrease in BO yield.

3.4 Bio-oil characterization

3.4.1 Element analysis

Table S1 in the [Supplementary materials](#) provides the distribution of BO element content and HHV value under various reaction conditions. Reaction temperature and duration notably affect the HHV and element distribution. C and H content increase with liquefaction temperature and duration, while reduced O content contributes to a higher HHV for BO. At 360 °C, C content of 59.01% is achieved, yielding the highest HHV of 27.032 MJ/kg. The maximum C content of 60.09% is attained at 330 °C and 60 min. Prolonged reaction time facilitates further dehydration and depolymerization of hemicellulose and cellulose in WHR, leading to a significant transfer of capacity elements to BO and AP. Elevated temperature and extended duration enhance the distribution of BO elements and increase HHV. Decreasing the solid-liquid ratio from 1:5 to 1:10 increases the C content of BO from 55.43% to 57.26%. A further reduction to 1:15 decreases the C recovery rate of BO to 54.74%. Reducing the solid-liquid ratio enhances carbon retention in the liquid phase, inhibiting its conversion into SR through an aromatization reaction. It also allows for a higher input of liquid water, mitigating carbonization effects [33]. Therefore, a 1:10 solid-liquid ratio is deemed appropriate. In comparison to WHR, HTL significantly reduces the O content of BO while simultaneously increasing both C and HHV values, highlighting HTL's effectiveness in converting CHR.

Table 3 presents the EA results of BO obtained from HTL using various catalysts, highlighting improved BO quality compared to non-catalyst reactions. MCM-41 incorporation significantly enhanced BO C, H, and O contents to 60.27%, 6.32%, and 13.25%, respectively, elevating the HHV to 27.06 MJ/kg. BO with individual metal catalysts, exhibited an enhanced C content (approximately 70%). Specifically, the C content of BO was measured at 68.46%, 70.99%, and 68.87% when Fe/MCM-41, Ni/MCM-41, and Co/MCM-41 were employed, separately. The maintained C contents of BO is 69.46%, 70.97%, and

**Fig. 7.** Compound distribution from HTL under different catalysts of WHR at optimum conditions.

67.89% using bimetallic catalysts (Fe-Ni/MCM41, Fe-Co/MCM41, Ni-Co/MCM41), indicating improved surface recarbonization [34]. The H content of BO, modified by three different metal catalysts, exhibited an increase. Ni-MCM-41, especially, increased H content to 6.89% in BO, contributing to the highest HHV of 32.013%. Fe/MCM-41 demonstrated superior deoxidation performance as a catalyst and exhibited an O content of 9.68%. However, a bimetal-supported catalyst impedes the reduction of O content in BO. The findings suggest that the O content in the WHR decreases via decarboxylation, a single-metal reforming catalyst showcasing the exceptional performance of deoxidation and hydrogenation. Among the tested catalysts, Fe/MCM-41 demonstrates superior deoxidation performance in BO production owing to its moderate acidity, while Ni metal significantly influenced BO carbon and H content. Notably, all catalyst-assisted reactions reduced the N content of BO to a minimum of 0.12%, attributed to acidic catalysts promoting protein hydrolysis, leading to the water solubility of nitrogen-containing compounds being enhanced, and the N content of BO being reduced [35].

3.4.2 GC-MS analysis

Figure 7 illustrates the composition of BO, which consists mainly of acids, phenols, alcohols, ketones, esters, and aldehydes. Compounds with a relative area < 0.5%, including nitrogen-containing compounds and methoxys, are classified as other. Compounds with multiple functional groups are placed in a single class. Table S2 ([Supplementary materials](#)) details the contents of compounds in BO with a relative area ≥ 1%.

BO is abundant in phenols and ketones, as indicated in Table S2. The primary compounds include 2,6-dimethoxyphenol, 2-methoxyphenol, 3-methoxy-1,2-benzenediol, and 4-ethyl-2-methoxyphenol. Ketones are predominantly composed of 2-methyl-2-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one, and 2,3-dimethyl-2-cyclopenten-1-one.

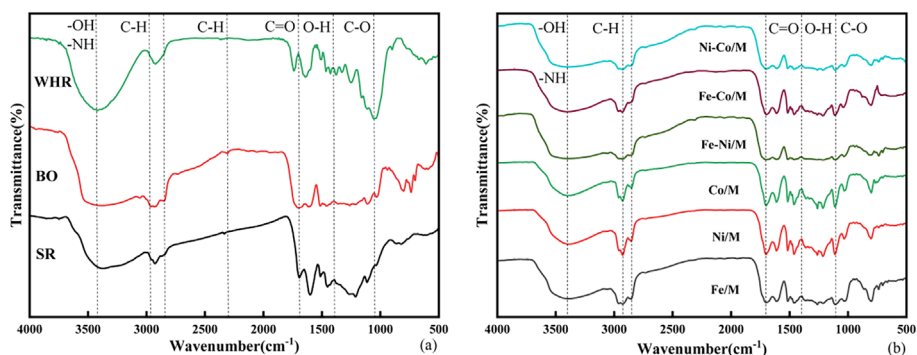


Fig. 8. FI-TR spectra without catalyst (a) and with catalyst (b) under optimal conditions.

The catalyst used affects the chemical composition distribution of BO (Fig. 7). In the absence of a catalyst, BO organic component ranks highest to lowest as phenols (38.3%), ketones (18.4%), acids (5.66%), esters (3.74%), hydrocarbons (1.1%), and alcohols (0.96%). Phenolic compound formation in WHR is linked to lignin cleavage, a three-dimensional macromolecule consisting of various phenolic units (e.g., guaiac-based and syringyl) interconnected by different types of C-O-C (β -O-4, α -O-4) and C-C (β - β , α -4) bonds [36]. The utilization of transition metal-supported molecular sieves significantly improves bond fracture efficiency when compared to MCM-41, leading to an increased abundance of BO. The Fe/MCM-41 catalyst exhibited remarkable selectivity towards phenols and ketones, with 44.13% and 24.5%, respectively. This was followed by the Fe-Co/MCM-41 catalyst, which showed 41.79% for phenols and 19.44% for ketones, while the Ni/MCM-41 catalyst demonstrated slightly lower selectivity with 40.63% for phenols and 19.13% for ketones. The introduction of metal catalysts accelerates the cleavage of β -O-4 and C-C bonds, significantly enhancing the yield of phenolic compounds. Therefore, it can be stated that metal-modified catalysts demonstrate excellent performance in selectively promoting the cleavage of β -O-4 and C-C bonds [37].

The higher area percentage of phenolic compounds in the WHR catalytic-polymerization process can be attributed to the pore size, specific surface area, and increased surface acidity of both Brønsted and Lewis of the employed catalysts [38]. It is likely that the use of MCM-41 mesoporous molecular sieve as a carrier contributes to this. The rise in the relative ketone content suggests that the catalyst's organic acids facilitate WHR hydrolysis, while the acidic environment hampers the direct polymerization of ketones into aromatic compounds [33]. This trend is observed with Co/MCM-41, Fe-Ni/MCM-41, and Ni-Co/MCM-41 supported catalysts. Additionally, the catalyst reduces the ester content in BO, potentially attributed to the catalyst's facilitation of acid or alcohol conversion into ketone and subsequent indirect inhibition of the esterification reaction [39]. The Fe-Co/MCM-41 catalyst shows the highest concentration of phenol, 2,6-dimethoxy, likely inducing ether bond cleavage or other ingredient conversion to phenol. Except for Fe/MCM-41, which increases the acid content of BO (11.01%), other catalysts lead to a reduction

in BO acidity. Therefore, the metal catalyst used in this study helps improve the high acidity and corrosion of BO.

3.4.3 FT-IR analysis

The FT-IR spectra of the WHR raw materials, as well as the BO and SR samples obtained under optimized conditions, are illustrated in Figure 8a. A spectral band around 3420 cm^{-1} signifies the presence of -NH and -OH functional groups, where -NH bonds represent indole and imidazole, and -OH bonds signify unstable phenols and alcohols. GC-MS analysis validates these findings. Due to the destruction of the densely packed WHR structure, both the intensity of WHR and SR bands is lower than that of BO bands. Peaks indicating C-H functional groups are observed in the range of $2962\text{--}2849\text{ cm}^{-1}$, suggesting the presence of alkanes. The absence of the C-H functional group is noted on SR, but methyl C-H stretching at a wavenumber of 2358 cm^{-1} is detected throughout the material's surface. Methyl C-H stretches are identified in BO samples around 2305 cm^{-1} but not in WHR and SR samples. The fracture of hydrocarbons indicates the formation of carbonyl functional groups, while a strong C-O absorption band at approximately 1736 cm^{-1} suggests the presence of ketones and aldehydes in BO. The presence of phenol is indicated by an O-H bend at 1398 cm^{-1} , while the C-H functional group representing alcohol or ether was observed in WHR near 1047 cm^{-1} ; however, the C-O expansion was absent in BO and SR. The oxygen-containing compounds present in BO suggest a possible reduction in the number of oxygen atoms, which may impact BO performance after modification.

The functional groups of BO after catalytic HTL, as depicted in Figure 8b FI-TR, exhibit similar characteristics with the modified intensity and slight peak shifts upon catalyst utilization. The broad absorption band at $3600\text{--}3030\text{ cm}^{-1}$ corresponds to the stretching vibration of the -OH bond, indicating the presence of alcohol, phenol, and carboxylic acid functional groups in the BO. The band observed at $1705\text{--}1690\text{ cm}^{-1}$ corresponds to the vibrational stretching of the carbonyl group (C=O) in BO. Ni/MCM-41 and Co-MCM-41 catalysts increased the carbonyl peaks of BO, consistent with other studies on liquefied BO [36, 40]. Additionally, using single metal catalysts more

peaks of BO, suggesting different catalysts promoted the formation of specific functional groups in BO.

4 Conclusions

This study investigated the impact of different reaction temperatures, reaction times, and solid-liquid ratios on the HTL of CHR for BO production. Under the conditions of 330 °C/15 min/1:10, the maximum BO yield reached 24.57 wt.%, with an HHV of 25.96 MJ/kg. The utilization of transition metal-modified molecular sieve catalysts significantly enhanced both the yield and quality of BO. Specifically, using Co/MCM-41 resulted in the highest BO yield of 27.05 wt.%, while employing Ni/MCM-41 yielded the highest HHV of 32.01 MJ/kg. Furthermore, when utilizing the Fe/MCM-41 catalyst, the BO exhibited the lowest oxygen content, with the highest selectivity for phenols (44.13%) and ketones (24.5%). This study confirms the potential and feasibility of HTL in converting high-moisture CHR into valuable products. The metal-modified catalysts, after reduction, displayed uniformly distributed surface metal particles and outstanding overall performance, exerting a positive influence on enhancing both the yield and quality of BO.

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Conflict of Interest

The authors declared that there is no conflict of interest.

Data availability statement

Data will be made available on request.

Supplementary material

Supplementary materials are available at <https://doi.org/10.2516/stet/2024018/olm>.

- Table S1. EA of bio-oil obtained from reaction conditions.
- Table S2. The chemical composition of WHR bio-oils obtained from GC-MS at optimum conditions.

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