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Liquid phase *in situ* hydrodeoxygenation of biomass-derived phenolic compounds to hydrocarbons over bifunctional catalysts

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ABSTRACT

The objective of this study was to find an effective method for converting renewable biomass-derived phenolic compounds into hydrocarbons bio-fuel via *in situ* catalytic hydrodeoxygenation. The *in situ* hydrodeoxygenation of biomass-derived phenolic compounds was carried out in methanol-water solvent over bifunctional catalysts of Raney Ni and HZSM-5 or H-Beta. In the *in situ* hydrodeoxygenation, the hydrogen was donated by aqueous phase reforming of methanol without external hydrogen gas. This reaction pathway for liquid-phase *in situ* hydrodeoxygenation of phenolic monomers was based on methanol-water as a solvent, stepwise metal-catalyzed hydrogenation, acid-catalyzed dehydration, and metal-catalyzed hydrolysis. The three-step conversion process can be achieved by a one-pot procedure. When HZSM-5 (Si/Al ratio of 25) and Raney Ni were used as the bifunctional catalysts of *in situ* hydrodeoxygenation, more than 90% conversion of phenolic monomers and dimers, approximately 70–90% selectivity of cyclohexanes and hydrocarbons could be obtained at 220 °C with a reaction time of 7 h. The bifunctional catalysts combined Raney Ni with HZSM-5 can achieve the aqueous-phase reforming of methanol, which coupled with the *in situ* hydrodeoxygenation of phenolic compounds. Therefore, this *in situ* hydrodeoxygenation process with bifunctional catalysts provided an efficient route for upgrading bio-oil containing large amounts of phenolic compounds into renewable hydrocarbon products.

1. Introduction

Lignin is an abundant and renewable biopolymer composed of substituted C_6 phenol and C_9 propyl-phenol units, which is casually cross-linked by C—O and C—C bonds [1]. In contrast to hemicellulose and cellulose, from which conversion processing produces high contents of relatively small oxygenates, lignin decomposes the polymer leading to higher concentration of phenolic compounds (such as phenol, anisole, syringol, guaiacol, and their derivatives) [2,3]. Bio-oil is produced by pyrolysis or liquefaction of abundant lignocellulosic biomass and considered as a promising second-generation renewable energy carrier [4]. However, bio-oil with high concentrations of phenolic compounds can not be directly used as liquid transportation fuels, which is limited by its high concentration of oxygen [5]. The phenolic compounds may undergo a self-polymerization reaction and polymerized with aldehydes and ketones, which affects the stability of bio-oil [6]. In this context, refining and upgrading bio-oil into liquid hydrocarbon products or bio-fuels is an important process to accomplish.

Several catalytic refining and upgrading routes that involve hydrogenation and deoxygenation have been widely studied using model monomeric lignin compounds to produce hydrocarbon products [7]. In this context, hydrodeoxygenation has been considered the most effective upgrading method for converting oxygen-rich lignin derived bio-oil into oxygen-free hydrocarbon bio-fuels. Various catalysts as zeolite supported metal catalysts, such as Pt/HBeta [8], Ru/HBeta [9], Ru/HZSM-5 [10], Ni/HZSM-5 [11], and Al/MCM-41 [12] have been widely used in the hydrodeoxygenation with external hydrogen gas for converting model phenolic compounds into cyclohexanes and hydrocarbons. Other dual-functional catalysts, such as Pd/C combine with liquid acid (H_3PO_4) [13] or solid acid (HZSM-5) [14] are also important catalyst components in the presence of external hydrogen gas and water

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solvent for converting lignin-derived model phenolic compounds into hydrocarbons. The study of model phenolic compounds is very important for establishing optimal condition in converting the phenolic-rich bio-oil into high quality fuel. In the real bio-oil system, the highly active oxo-functionalized molecules also readily polymerize, which require further catalytic technology and process to directly hydrodeoxygenate and upgrade the crude bio-oil under suitable condition. Furthermore, there are many previous studies investigated on converting model phenolic compounds into hydrocarbons by common hydrodeoxygenation with external hydrogen gas. There are few reports that have investigated conversion of phenolic compounds derived from biomass into added-value chemicals and hydrocarbons bio-fuel.

In our previous research, we found an effective method for producing phenolic compounds [15] that enabled separated phenolic compounds from liquefied oil. The phenolic compounds fraction that precipitated from aqueous solution was mainly composed of phenolic compounds and their derivatives such as eugenol, vanillin, 4-propyl-2,6-dimethoxyphenol, methoxy-4-propylphenol and 3-methoxy-4-hydroxy-benzoic acid methyl ester. These phenolic derivatives have many advantages with numerous potential applications such as low-molecular weight and good solubility in organic solvents. Compared with natural lignin, these phenolic compounds have higher reactivity for the generation of high added-value chemicals. Following the upgrading process, phenolic compounds derived from biomass could be converted into a high calorific biofuel.

A reactive hydrogen radical intermediate is a necessary requisite to hydrodeoxygenation. As the hydrogen radicals are effectively donated by the catalytic aqueous-phase reforming of methanol in water over the Raney Ni catalyst, some alcohols such as methanol, ethanol, and 2-propanol were chosen and tested as the hydrogen-donating solvents of the *in situ* hydrodeoxygenation. In the common hydrodeoxygenation, the hydrogen was supplied with external input. When the external hydrogen gas was introduced into the reactor, the hydrogen is first cleaved to hydrogen radicals before it reacts with the phenolic compounds and this process requires enough energy and catalyst. In this *in situ* catalytic hydrodeoxygenation investigation, the hydrogen is donated by aqueous phase reforming of methanol without external hydrogen gas. The aqueous phase reforming of methanol to produce a hydrogen-donor (hydrogen radical) could partly avoid the abrasion of reactor and compromise the safety of operation. The effects of different process parameters, including different kinds of catalysts, solvents, hydrodeoxygenation pathways, catalyst amounts, reaction temperature and time are investigated in the designed conditions. The optimal conditions have been investigated for the highest selectively of cyclohexanes in the hydrodeoxygenation of phenols. The mechanisms for *in situ* catalytic hydrodeoxygenation of various lignin-derived phenolic compounds are investigated in this study. The approach for hydrodeoxygenation mainly consists of coupling the hydrogenation and elimination of the methoxy group to cyclohexanol, dehydration of cyclohexanol to cyclohexene, and hydrogenation of cyclohexene to cyclohexane. In the conventional hydrodeoxygenation, the three steps conversion of phenols can also be achieved by a one-pot process with external hydrogen gas [16]. With the aqueous phase reforming of methanol process, the three-step process of various phenols, phenolic dimers, and biomass-derived phenolic compounds were investigated in the presence of Raney Ni and HZSM-5 using methanol as a hydrogen-donating solvent. The process of aqueous-phase reforming of methanol coupled with the *in situ* hydrodeoxygenation of phenolic compounds is also discussed.

2. Experimental

2.1. Chemicals

All chemicals were provided from commercial suppliers: the different phenols (Aladdin Company, 99% GC assay) such as phenol, guaiacol, 4-methyl-2-methoxyl-phenol, and the solvents (Aladdin Company, 99.93% GC assay) such as methanol, ethanol, and 2-propanol. They were of analytical grade and used without further purification. The Raney Ni was supplied by Aladdin Company in Shanghai (425–900 μm), HZSM-5 and H-Beta was obtained from the Catalyst Company of Nankai University. They were used without further treatment.

2.2. Analysis methods

The components of *in situ* catalytic hydrodeoxygenation products were determined by gas chromatography mass spectrometry (GC–MS) (Agilent 5975C VL MSD). The separation was realized on a column of HP-5 (30 m × 0.25 μm × 0.25 nm). Temperature program: 30 °C (hold on 5 min) → 250 °C (5 °C/min, hold on 15 min). The MS detector was operated in the electron ionization mode (70 eV) with an ionization temperature of 220 °C. The mass spectra were recorded in electron ionization mode for *m/z* 50–550. Typically, 0.2 μL of sample was used.

The products of the aqueous phase reforming of methanol and the *in situ* catalytic hydrodeoxygenation of phenolic compounds were analyzed by gas chromatograph (Shimadzu 2010 plus, GC). The contents of products were determined based on GC data using the external standard method. All results were evaluated on the basis of the amount of reactants (including various used phenolic compounds). The conversion of phenolic compounds and the selectivity of main products were calculated as below in Eq. (1), Eq. (2), and Eq. (3). The molecules of H_2 produced from the whole process included two parts: the consumption in the *in situ* hydrodeoxygenation and the moles of H_2 in the gaseous phase after the hydrodeoxygenation process. The chemical reaction formula of the aqueous phase reforming of methanol is shown in Eq. (4).

$$\text{Conversion(wt\%)} = \left(1 - \frac{\text{Weightofrectantinproducts}}{\text{weightofrectantinitially}}\right) \times 100\% \quad (1)$$

$$\text{Slectivityofproduct(wt\%)} = \frac{\text{Weightofproduct}}{\text{Weightofrectantconverted}} \times 100\% \quad (2)$$

$$\text{SelectivityofH}_2\text{(wt\%)} = \frac{\text{Molesofhydrogenconsumptioninhydrodeoxygenation}}{\text{Molesofhydrogenproduced}} \times 100\% \Big/ \frac{\text{Molesofhydrogenconsumptioninhydrodeoxygenation}}{\text{Molesofhydrogen(consumptioninhydrodeoxygenation} + \text{ingaseousphaseafterhydrodeoxygenation)}} \times 100\% \quad (3)$$

$$\text{Aqueous phase reforming of methanol: CH3OH} + \text{H2O} \rightarrow \text{CO}_2 + \text{3H2} \quad (4)$$

2.3. Hydrodeoxygenation reaction

2.3.1. Preparation of phenolic compounds and liquefied oil

The liquefaction of biomass was performed using an autoclave with a 1 L processing capacity. 60 g of moso bamboo powder was introduced into a solution of 420 g methanol and 1.5 g sulfuric acid, and the mixtures were heated in an autoclave at 200 °C for 30 min. The liquid and solid products were separated by filtration. The liquefied filtrate was heated under ambient pressure to remove the methanol, which left a liquefied oil without methanol. The phenolic compounds were obtained by further fractionation of the liquefied filtrate using stepwise precipitation and extraction [15].

2.3.2. In situ hydrodeoxygenation reaction

The *in situ* catalytic hydrodeoxygenation reaction was performed in

the aqueous phase reforming of alcohols for hydrodeoxygenation process over bifunctional catalysts. The bifunctional catalysts included Raney Ni 1.0 g and HZSM-5 or H-Beta 1.5 g, phenolic compounds 0.02 mol (biomass-derived phenolic compounds or liquefied oil 2.0 g from our previous study [15]), solvent 0.1 mol, and distilled water 2.0 mol were placed in a 100 mL autoclave. The autoclave was fitted with a thermocouple, pressure gauge (20 MPa) and stirring device. Using N_2 to evacuate the air in the autoclave, and the initial pressure (p_0) was raised to 0.5 MPa with N_2 before heating. The autoclave was heated at a rate of 5 °C/min until reaching the desired reaction temperatures (200–240 °C) by autogenous pressure (p) and kept for a designed period time (3–11 h) with a stirring rate of 600 r/min. After the reaction, the autoclave was cooled rapidly to room temperature in a water bath. The reaction mixtures were taken out from the autoclave and filtered through a membrane filter (pore size 0.45 μm). Afterwards, the *in situ* hydrodeoxygenation products such as cyclohexanes are readily separated from water after reaction, allowing the produced hydrocarbons can be easily collected.

2.3.3. Common hydrodeoxygenation with external hydrogen gas

The common hydrodeoxygenation of phenols referred to hydrogenation using external hydrogen gas. The equipment, conditions, and reactants were similar as used in section 2.3.2 with purged with 5 MPa H_2 (99.999%) several times. The final reaction mixtures were extracted by extraction, and the solvents and catalysts were separated to get the hydrogenated products.

3. Results and discussion

The *in situ* hydrodeoxygenation process was comprised of aqueous-phase reforming of methanol, the metal-catalyzed hydrogenation and acid-catalyzed hydrolysis/dehydration. A reactive hydrogen radical intermediate is a necessary requisite to hydrodeoxygenation. The hydrogen radicals are effectively donated by the catalytic aqueous-phase reforming of methanol in water. Concurrently, the metal-catalyzed hydrogenation was catalyzed by Raney Ni catalyst. To confirm that *in situ* hydrogenation over Raney Ni catalyst is generally effective for phenolic compounds, different selected model compounds (phenol, guaiacol, vanillin, cresol, and quinol) were investigated as substrates in Fig. S1. In addition, the separated acid-catalyzed hydrolysis/dehydration were catalyzed by HZSM-5 or H-Beta (Table S1).

3.1. In situ hydrodeoxygenation of guaiacol

As shown in Fig. S2 and Fig. S3, the methoxyl (−OCH_3) and hydroxyl (−OH) are the major functional groups of lignin and lignin-derived phenolic compounds. Guaiacol, with adjacent −OCH_3 and −OH functional groups at the aromatic ring, is one of the three basic units of lignin, which is selected as the model phenolic compound to investigate the fundamental chemistry in the liquid-phase *in situ* hydrodeoxygenation. Besides, guaiacol and its derivatives contain three types of C−O bonds for C_{AR}−OH, C_{AR}−OCH_3, and C_{AR}O−R, which are frequently found in the biomass derived bio-oil. In common, hydrodeoxygenation of phenols is mainly used to produce alkanes and their derivatives, which are the key components for hydrocarbon bio-fuel. To achieve optimal results, the process of aqueous-phase reforming of methanol couple with *in situ* hydrodeoxygenation of phenolic compounds was investigated. In our endeavor to design this hydrodeoxygenation, we found that several parameters were key factors for achieving both high conversion of phenolic compounds and high selectivity for products: 1) the type and loading of catalyst, 2) solvent and hydrodeoxygenation pathway, 3) reaction temperature and time. The *in situ* hydrodeoxygenation of guaiacol was carried out at 160–240 °C with the reaction time of 3–11 h over different bifunctional catalysts.

3.1.1. Effect of different catalysts

The *in situ* hydrodeoxygenation process includes the aqueous-phase reforming of methanol coupled with the hydrodeoxygenation of phenolic compound. The specific reaction processes are composed of stepwise aqueous-phase reforming of methanol to produce a hydrogen-donor (over Raney Ni catalyst), metal-catalyzed hydrogenation (over Raney Ni catalyst), acid-catalyzed dehydration (over HZSM-5 or H-Beta catalyst), and metal-catalyzed hydrolysis (over Raney Ni catalyst) cascade reaction. The process of aqueous-phase reforming of methanol may couple with *in situ* hydrodeoxygenation of phenolic compounds.

The different kinds of bifunctional catalysts including Raney Ni with HZSM-5 and Raney Ni with H-Beta were key factors for achieving both high conversion of phenolic compounds and selectivity of hydrodeoxygenation products. The effect of HZSM-5 or H-Beta with different Si/Al ratios was examined in view of selectivity of cyclohexane after *in situ* hydrodeoxygenation. An initial experiment was carried out to investigate the effect of different zeolite catalysts (HZSM-5 and H-Beta) on *in situ* hydrodeoxygenation of guaiacol at 220 °C. In addition, the different zeolite catalysts and Si/Al ratios were shown to be critical factors in determining the acid strength as well as hydrophobicity of the catalyst.

The effect of the Si/Al ratio of H-Beta or HZSM-5 in the *in situ*

Table 1
Effect of different bifunctional catalysts on the *in situ* hydrodeoxygenation.[a]

Catalyst	Si/Al ratio	Conv. (%)	Target products selectivity (%)				Methanol cons. (%)[b]	H_2 selectivity (%)[c]
			Cyclohexane	Cyclohexene	Cyclohexanol	Cyclohexanone		
HZSM-5	25	100	93.4	0.1	0.2	0.3	52.4	47.3
	38	100	92.6	2.7	0.1	0.5	48.6	43.9
	50	99.2	78.6	11.3	4.8	2.9	46.3	40.9
	80	98.2	76.3	5.1	12.3	4.8	43.2	37.7
	200	93.3	64.5	4.3	14.6	9.4	40.5	33.2
H-Beta	25	100	85.6	3.3	5.1	0.7	49.3	46.4
	40	97.2	82.1	2.7	6.8	2.6	45.2	39.2
	60	95.1	74.8	7.9	10.2	0.8	42.2	35.4
	80	92.2	65.3	9.8	14.1	2.1	40.6	36.9
	200	90.0	63.1	6.5	12.4	2.5	37.3	30.3

[a] Reaction condition: guaiacol (0.02 mol), methanol (0.1 mol), water (2.0 mol), HZSM-5 or H-Beta(1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).
[b] Consumption of methanol: Based on the methanol contents in GC–MS results. And the initial amounts of guaiacol and methanol are 0.02 mol and 0.1 mol.
[c] Selectivity of H_2: The calculation method is Eq. (3). The molecules of H_2 produced from the whole process included two parts: the consumption in the *in situ* hydrodeoxygenation and the moles of H_2 in the gaseous phase after the hydrodeoxygenation process.

hydrodeoxygenation of guaiacol is described in Table 1. On average, the conversion of guaiacol varied from 90 to 100% under the investigated conditions. The selectivity of cyclohexane sharply increased with the decreasing Si/Al ratio of HZSM-5, with a significant raised to 93.4% of cyclohexane selectivity for a Si/Al ratio of 25. The dehydration reaction of cyclohexanol was further investigated over HZSM-5 catalyst (Table S1). As expected, the conversion of cyclohexanol to cyclohexene increased with the decreasing Si/Al ratio of HZSM-5 and H-Beta, indicating that HZSM-5 and H-Beta with lowest Si/Al ratio are beneficial for the dehydration of cyclohexanol. In the *in situ* hydrodeoxygenation of guaiacol, the hydrogen radicals were donated by aqueous phase reforming of methanol and water. Moreover, the consumption of methanol and selectivity of H_2 increased with the decreasing Si/Al ratio of HZSM-5 and H-Beta. The above results indicated that the lowest Si/Al ratio of HZSM-5 and H-Beta can achieve the highest selectivity of cyclohexane, which are consistent with more efficient dehydration. Furthermore, from the results regarding the dehydration of cyclohexanol with Si/Al ratio of several times recycled catalysts (Table S2), we know that the zeolite catalyst HZSM-5 is hydrothermally stable and does not deactivate over several numbers of reaction cycles. HZSM-5 showed higher conversions of phenolic compounds compared to H-Beta, which may be due to its relatively high acid concentration (Table S3). Although the conversion of guaiacol on different bifunctional catalysts and reaction temperatures were high (some close to 100%), the distributions of hydrodeoxygenation products were significant different. Our *in situ* hydrodeoxygenation studies were mainly focused on the selectivity of cyclohexane for obtaining high cyclohexane yields. In general, the results of HZSM-5 with Raney Ni catalysts in the *in situ* hydrodeoxygenation of guaiacol were better than that of H-Beta with Raney Ni.

3.1.2. Effect of catalyst (HZSM-5) loading

HZSM-5 with a Si/Al ratio of 25 and 38 were selected to investigate the effect of catalyst concentrations on the *in situ* hydrodeoxygenation of guaiacol due to they produced the highest selectivity of cyclohexane in section 3.1.1. The guaiacol was reacted in methanol-water in the presence of Raney Ni and HZSM-5 (Si/Al ratio of 25 and 38) with loadings from 0.5 g to 2.0 g. The conversion of guaiacol and selectivity of cyclohexanes were improved with the increasing loading of HZSM-5 (Si/Al ratio of 25 and 38), indicating that HZSM-5 with lowest Si/Al ratio is beneficial for the dehydration of cyclohexanol in the *in situ* hydrodeoxygenation. Catalyst HZSM-5 loading determined the availability of acidic reaction sites and influenced the selectivity of desirable products. The selectivity of cyclohexanol obviously decreased from 14.2% to 0.2% (Table 2). However, the selectivity of cyclohexane significantly increased from 55.9% to 93.4%. With adequate HZSM-5 concentrations, cyclohexanol and cyclohexanol derivatives can be quantitatively dehydrated to cyclohexane. Under HZSM-5 (Si/Al ratio of 25) and Raney Ni, the consumption of methanol and selectivity of H_2 changed from 45.3% and 38.3% to 55.5% and 48.2%, respectively. This might because the *in situ* hydrodeoxygenation process was the consecutive reaction with the aqueous phase reforming of methanol and water. As this reaction exhibits a first-order dependence of the substrate concentration, we attribute the high dehydration rates on HZSM-5 loading to a higher concentration of reactants in the zeolite pores. As the aqueous-phase reforming of methanol is coupled with *in situ* hydrodeoxygenation of phenolic compounds, the formation of the final product reduces the concentration of the intermediate product in the reaction system, which is favorable to further increase in the conversion of the reactants and the selectivity of the products. A suitable solid acid should have a high acid-site density in the combination with a sufficient stability under liquid phase at 220 °C.

The results for the conversion of guaiacol indicated that enough solid acid loading is effective for oxygen removing (through dehydration of cyclohexanol). Higher catalyst loading improved the conversion of guaiacol and significantly increased the selectivity of cyclohexane when looking at the change from 0.5 g to 1.0 g. However, a large rise in the loading of HZSM-5 used would greatly increase the production costs. Therefore, there is an optimal loading of HZSM-5 needed to achieve high cyclohexane selectivity at a reasonable economic cost. In this study, the optimum HZSM-5 (Si/Al ratio of 25) loading was 1.5 g and this generated a high cyclohexane selectivity of 93.4%.

3.1.3. Effect of solvent and hydrodeoxygenation pathways

To investigate the effect of hydrodeoxygenation pathways, the *in situ* hydrodeoxygenation and common hydrodeoxygenation were tested at the same condition. In the *in situ* catalytic hydrodeoxygenation investigation, the hydrogen radicals are supplied by aqueous phase reforming of methanol without external hydrogen gas. As the previous reported that the selectivity of hydrogen-donor from catalytic reforming of different alcohols and sugars in water improves in the order of glucose < sorbitol < glycerol < ethylene glycol < methanol [17]. A reactive hydrogen radical intermediate is a necessary requisite to the hydrodeoxygenation. As the hydrogen radicals are effectively donated by the aqueous-phase reforming of hydroxyl-organic solvent with water over the Raney Ni catalyst, some alcohols such as methanol, ethanol, and 2-propanol were chosen and tested as the hydrogen-donating solvents of the *in situ* hydrodeoxygenation. In the common hydrodeoxygenation, the hydrogen was supplied with external hydrogen gas. The methanol, ethanol, 2-propanol, and water were also used as the solvents of hydrodeoxygenation. When the external hydrogen gas was introduced into the reactor, the hydrogen gas was first cleaved to hydrogen radicals before it reacts with the phenolic compounds and this process requires enough energy and catalyst. This maybe the reason that the

Table 2
Effect of HZSM-5 loading with different Si/Al ratios.[a]

HZSM-5 (Si/Al)	Amount (g)	Conv. (%)	Target products selectivity (%)				Methanol cons. (%)[b]	H_2 selectivity (%)[c]
			Cyclohexane	Cyclohexene	Cyclohexanol	Cyclohexanone		
25	0.5	86.0	55.9	3.3	14.2	6.8	45.3	38.3
	1.0	93.2	89.7	1.4	7.2	1.2	47.9	45.9
	1.5	100	93.4	0.1	0.2	0.3	52.4	47.3
	2.0	99.9	94.2	0.2	1.2	0.1	55.5	48.2
38	0.5	82.1	49.0	1.1	17.8	4.2	39.5	40.2
	1.0	97.2	83.2	4.7	3.9	3.3	43.2	42.4
	1.5	100	92.6	2.7	0.1	0.5	48.6	44.0
	2.0	100	93.2	1.2	0.3	0.7	51.8	47.7

[a] Reaction condition: guaiacol (0.02 mol), methanol (0.1 mol),water (2.0 mol), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).
[b] Consumption of methanol: Based on the methanol contents in GC–MS results. And the initial amounts of guaiacol and methanol are 0.02 mol and 0.1 mol.
[c] Selectivity of H_2: The calculation method is Eq. (3). The molecules of H_2 produced from the whole process included two parts: the consumption in the *in situ* hydrodeoxygenation and the moles of H_2 in the gaseous phase after the hydrodeoxygenation process.

Table 3
Effect of different solvent and hydrodeoxygenation pathways.

Hydrodeoxygenation pathways	Solvent	Conv. (%)	Selectivity (%)					Solvent conv. (%)[c]	H_2 pressure (MPa)[d]
									
In situ hydrodeoxygenation[a]	Methanol	100	93.4	0.1	0.2	0.3	–	52.4	2.8
	Ethanol	97.2	88.2	1.3	2.1	2.0	0.3	48.9	3.0
	2-Propanol	93.4	80.2	0.5	1.7	3.2	3.7	50.0	3.2
Common hydrodeoxygenation[b]	Methanol	95.2	89.3	4.2	1.2	3.6	–	–	2.6
	Ethanol	90.9	81.2	5.8	2.4	1.4	–	–	3.2
	2-Propanol	95.7	65.4	3.5	5.8	2.1	–	–	3.5
	Water	94.3	87.2	2.1	0.5	0.3	–	–	2.5

[a] Reaction condition: guaiacol (0.02 mol), solvent (0.1 mol), water (2.0 mol), HZSM-5 (Si/Al = 25) (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).
[b] Reaction condition: guaiacol (0.02 mol), solvent (2.0 mol), HZSM-5 (Si/Al = 25) (1.5 g), Raney Ni (1.0 g), p_0 (H_2, 5.0 MPa), T (220 °C), t (7 h).
[c] Consumption of solvent: Based on the methanol contents in GC–MS results. And the initial amounts of guaiacol and solvent are 0.02 mol and 0.1 mol.
[d] Pressure of H_2: The partial pressure of hydrogen in all the gases after the reaction.

conversion of phenolic compounds and the selectivity of target product in the *in situ* hydrodeoxygenation are higher than that in the common hydrodeoxygenation.

The gas phase products after different hydrodeoxygenation pathways are shown in Table S4, are mainly hydrogen, methane, and carbon dioxide. In this *in situ* hydrodeoxygenation, all the conversion of guaiacol and selectivity of cyclohexane were more than 90% and 80% (Table 3), this may indicate that methanol, ethanol, and 2-propanol as hydrogen-donating solvents were highly productive and effective. Thus, alcohols or polyols are suitable solvents for *in situ* hydrodeoxygenation of phenolic compounds to produce hydrocarbon bio-fuels at 220 °C, and it has been reported that lignin is efficiently converted into added-value products under supercritical methanol [18]. As a surprise, benzene appeared in the product when using 2-propanol as the solvent in the *in situ* hydrodeoxygenation, which maybe because cyclohexene can react with phenol and produce benzene. This ability of cyclohexene to react with phenol to produce benzene was also demonstrated by a previous study at 160 °C for 0.5 h over the Raney Ni catalyst [19]. In the common hydrodeoxygenation, compared with 2-propanol and ethanol, water and methanol were more suitable for converting phenolic compounds into hydrocarbons at 200 °C. Brønsted solid acids such as HZSM-5 were also found effective in the bifunctional catalysts combination for common hydrodeoxygenation of phenols [10]. It is speculated that the micropore size of HZSM-5 only allows the smaller alcohol monomers to reach the Brønsted solid acids sites of the zeolite [19]. Thus, the alcohol monomer-oligomer equilibrium is rapidly shifted towards monomers, which also accelerates the dehydration rate. Besides, the HZSM-5 skeleton in the pore structure maybe suitable for dehydration of cyclohexanol broken chain into cyclohexene.

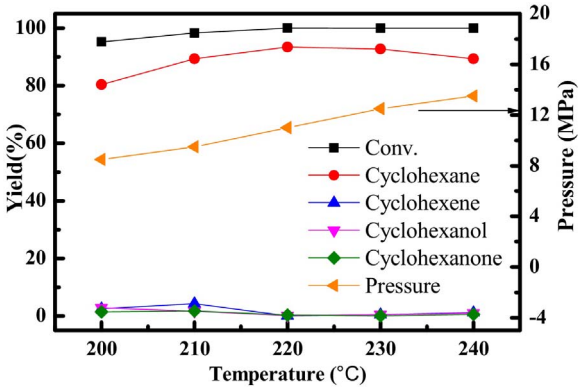


Fig. 1. Effect of different temperatureon the *in situ* hydrodeoxygenation of guaiacol. Reaction condition: guaiacol (0.02 mol), methanol (0.1 mol), water (2.0 mol), HZSM-5 (Si/Al = 25) (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), t (7 h).

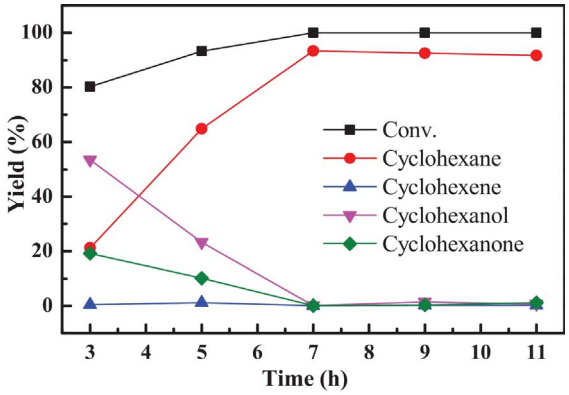


Fig. 2. Effect of different time on the *in situ* hydrodeoxygenation of guaiacol. Reaction condition: guaiacol (0.02 mol), methanol (0.1 mol), water (2.0 mol), HZSM-5 (Si/Al = 25) (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C).

3.1.4. Effect of reaction temperature and time

The effects of reaction temperature and time on the *in situ* hydrodeoxygenation of guaiacol into cyclohexanes with Raney Ni and HZSM-5 as bifunctional catalyst are shown in Fig. 1 and Fig. 2. The effect of reaction temperature on the conversion of reactant and distribution of products was investigated in order to identify the optimum condition for obtaining the highest yield of cyclohexanes from phenolic compounds. It can be seen that reaction temperature played an important role in the *in situ* hydrodeoxygenation (Fig. 1). The experiments were carried out with a reaction time of 7 h, and the conversion of guaiacol exceeded 95% in the temperature range from 200 to 240 °C. As the reaction temperature increased from 200 to 220 °C, the selectivity of cyclohexane increased from 80.4% to 93.2%. When the reaction temperature was further extended to 240 °C, the selectivity of cyclohexane slightly decreased to 89.3%. As the reaction temperature increased, the pressure within the reaction system was gradually increased. It should be noted that higher pressure might harm the equipment. Hydrogenation of the aromatic ring is thermodynamically favorable at high pressure and low temperature, while condensation reactions of aromatic compounds are favored at low pressure and high temperature. Thus, excessively high temperatures are not conducive to industrial application. This result indicated that the optimum reaction temperature was 220 °C during the *in situ* hydrodeoxygenation of guaiacol.

Reaction time also had a pronounced effect on the conversion of guaiacol and selectivity of cyclohexane. In the common hydrodeoxygenation, the ideal reaction was about 0.5–3 h [20–22]. Compared with common hydrodeoxygenation, the reaction time of *in situ* hydrodeoxygenation was longer in this experiment. This is because the *in situ*

hydrodeoxygenation process included the catalytic aqueous-phase reforming of methanol to produce hydrogen-donor and metal-catalyzed hydrogenation of guaiacol, acid-catalyzed dehydration of cyclohexanol, and metal-catalyzed hydrolysis of cyclohexene. Fig. 2 shows the effect of reaction time on *in situ* hydrodeoxygenation of guaiacol at 220 °C ranged from 3 h to 11 h. The process of aqueous-phase reforming of methanol coupled with *in situ* hydrodeoxygenation of phenolic compounds, as the reaction time prolonged from 3 h to 7 h, the conversion of guaiacol significant improved. The contents of hydrodeoxygenation intermediates are shown in Fig. 2. The selectivity of cyclohexanol obviously decreased from 53.51% to 0.2%. However, the selectivity of cyclohexane significantly increased from 21.21% to 93.4%. The cyclohexanol and cyclohexanol derivatives can be quantitatively dehydrated to cyclohexane with longer reaction time. We speculated that dehydration is the rate determining step in the sequence of hydrodeoxygenation reactions. The consumption of hydrogen by the *in situ* hydrodeoxygenation may promote the formation of hydrogen, increase the conversion of guaiacol and the yield of target products. Relatively extending the reaction time is conducive to the aqueous-phase reforming of methanol coupled with *in situ* hydrodeoxygenation of guaiacol. The conversion of guaiacol increased with operating time and full conversion was obtained at 7 h. However, the product distributions were significantly different with reaction time. When the reaction times are extended (> 7 h), there is a slight decrease on the selectivity of cyclohexane, which may due to the deactivation of catalyst and the subsequent polymerization of products. The polymerized product could form macromolecular polymers, which may cover the surface of catalyst, and affect the activity of catalyst. At longer reaction times (> 7 h), competition formed between aromatic hydrogenation and condensation. In order to achieve more hydrocarbons, a moderate reaction time of 7 h proved better for higher selectivity of cyclohexane.

3.2. Hydrodeoxygenation of lignin-derived model phenolic compounds

3.2.1. In situ hydrodeoxygenation of different phenolic monomers

To demonstrate the versatility of this *in situ* hydrodeoxygenation approach, a variety of lignin-derived phenolic monomers used as reactants (–R and/or $-OCH_3$ substituted C_6–C_9 phenolic compounds), such as catechol, 4-methyl-guaiacol, and 6-methoxy-guaiacol were tested under optimized conditions in methanol-water. In an extension to guaiacol, these lignin-monomeric compounds were also efficiently converted into cyclohexane and its derivatives (such as alkyl-cyclohexane, cyclohexene, cyclohexanol, and cyclohexanone) using Raney Ni and HZSM-5 (Si/Al ratio of 25) as bifunctional catalysts under the *in situ* hydrodeoxygenation conditions (at 220 °C with a reaction time of 7 h) (Table 4).

The phenolic monomers showed in Table 4 can be efficiently converted into hydrocarbons, mostly with conversions of reactants were more than 97%, and selectivity of cyclohexanes were approximate 90% obtained after 7 h. In the cases of representative biomass-derived phenolic monomers, such as phenol, guaiacol, catechol, 4-methyl-phenol, 4-*n*-propyl-phenol, and 4-*n*-propyl guaiacol were quantitatively converted into cyclohexanes and hydrocarbons, with the selectivity of cyclohexane and its derivatives ranged from 90.2% to 94.5% under the investigated condition (Table 4, entries 1–3, 5, 8–9). Hydrodeoxygenation of these phenolic monomers leads to a large variety of products including cyclohexanol, cyclohexanone, cyclohexene, cyclohexane, and their alkane derivatives. The three kinds of C_6 phenolic compounds (Table 4, entry 1–3) were transformed to cyclohexanes, led to the selectivity of cyclohexane approximately 90%, and little intermediate byproduct cyclohexene, cyclohexanol or cyclohexanone, emphasizing the importance of this route in terms of energy efficiency and atom economy. The bifunctional catalysts Raney Ni and HZSM-5 (Si/Al ratio of 25) showed moderate activity (85.27% conversion) with syringol (6-methoxy-guaiacol or 2, 6-dimethoxy-phenol) at 220 °C with a reaction time of 7 h (Table 4, entry 4), implied that the two $-OCH_3$ groups may increase the stabilization of the aromatic ring and steric effect, and increased the difficulty of hydrogenation and deoxygenation process. Moreover, other lignin-derived phenolic monomers, containing C_7 to C_9 backbones directly linked with −R or/and $-OCH_3$, were investigated in detail as well. 4-methyl-phenol, 4-methyl-guaiacol, and 4-ethyl-guaiacol were tested under the same conditions. Exceeding 95% conversion was achieved with the selectivities of cyclohexane derivatives more than 92% (Table 4, entry 5–7). Different para-substituted chains on the aromatic ring did not influence the conversions of phenolic reactants and selectivities of products, even in the case of the chains carrying the propenyl group (Table 4, entry 10). Besides, in these reactions the $-OCH_3$ groups were hydrogenolyzed or hydrolyzed to produce methanol.

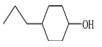
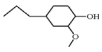
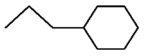
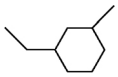
The combination of Raney Ni and HZSM-5 (Si/Al ratio of 25) can quantitatively convert almost mentioned substituted phenolic monomers into their corresponding C_6–C_9 cyclohexanes and hydrocarbons. In most case, the liquid-phase *in situ* hydrodeoxygenation process of different phenolic monomers led to more than 90% selectivities of hydrocarbons. The conversions of phenolic compounds and yields of target product were higher than that by common hydrodeoxygenation using external hydrogen gas [9]. The introduction of methanol as the hydrogen-donating solvent, avoided the high pressure and temperature (5–15 MPa, 200–450 °C) that required for common hydrodeoxygenation using external hydrogen gas and ameliorated reactor clogging. The conversion of methanol in the aqueous-phase reforming reaction can achieve more than 60%. Isomers from cyclohexane were not detected in these experiments, indicated that cyclohexane is more difficult to isomerize than aryl-substituted cyclohexanes [20], which were related to the rule that tertiary carbocation are more stable than the secondary carbocation intermediates during isomerization. These results suggested that the new approach regarding *in situ* hydrodeoxygenation with Raney Ni and HZSM-5 (Si/Al ratio of 25) as bifunctional catalysts could effectively applied for the hydrodeoxygenation of diverse phenolic monomers for upgrading phenolic compounds bio-oil.

3.2.2. Proposed mechanism of in situ hydrodeoxygenation of phenolic monomers

Lignocellulosic biomass (including 20 − 40% lignin) derived bio-oil comprised of a wide variety of C_{aryl}–OH, C_{aryl}–OR, and C_{aryl}–OCH_3 as well as C═O bonds. The three types of C—O single bonds can be directly cracked by a metal-catalyzed hydrolysis process, whereas cleavage of the C═O double bond required a series of stepwise hydrogenation and dehydration [20]. Alternatively, acid sites in HZSM-5 (Si/Al ratio of 25) also catalyzed the cleavage of formed C_{aryl}—$OCH_3$and C_{aryl}—OR bonds via hydrolysis. The formed C_{aryl}—OH single bond can be eliminated through dehydration. Removing oxygen in the C_{aryl}—OH bond, however, involved the cascade reactions of dehydration and hydrogenation. The bond dissociation energies of C_{aryl}—O bonds are 80–100 $kJ \cdot mol^{-1}$ higher than those of C_{aryl}—O bonds, while, the steric constraints of cracking C_{aryl}—O bonds are much higher than that for C_{aryl}—O bonds. Thus, it is highly important to understand the integrated stepwise of hydrolysis, hydrogenolysis, hydrogenation, and dehydration to efficiently cleave the various C—O bonds in phenolic compounds.

To speculate the hydrodeoxygenation mechanism of phenol derivatives, guaiacol, whose aromatic ring have adjacent −OH and $-OCH_3$ functional groups are *in situ* hydrotreated in methanol-water at the temperature of 220 °C with a reaction time of 7 h, in the presence of Raney Ni and HZSM-5 (Si/Al ratio of 25) as bifunctional catalysts (Fig. 3). The main initial product is 2-methoxyl-cyclohexanone, gradually *in situ* hydrogenated to 2-methoxyl-cyclohexanol, suggesting that the fastest step is the metal-catalyzed (Raney Ni) *in situ* hydrogenation of the aromatic-ring but not the hydrolysis or hydrogenolysis of the

Table 4
In situ hydrodeoxygenation of phenolic monomers over bifunctional catalysts.

Entry	Reactants	Conv. (%)	Selectivity (%)				
	C6 backbone						
1		100	93.4	0.3	0.1	–	–
2		99.9	95.2	–	0.1	0.2	–
3		100	94.5	0.3	1.4	0.3	–
4		85.3	65.8	12.1	6.5	12.8	0.2
–							
	C7 backbone						
5		99.6	 93.2	 2.5	 1.3	 1.7	
6		95.3	 90.6	 2.1	 3.7	 1.2	 2.2
–							
	C8 backbone						
7		99.9	 89.2	 5.5	 1.3	 1.4	 2.0
–							
	C9 backbone						
8		99.9	 93.1	 0.5	 1.2	 0.7	
9		98.3	 90.2	 4.3	 1.7	 0.5	 0.3
10		97.2	 86.1	 3.2	5.2	1.2	0.7

Reaction condition: phenolic monomers (0.02 mol), methanol (0.1 mol), water (2.0 mol), HZSM-5 (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).

Fig. 3. Proposed *in situ* catalytic hydrodeoxygenation mechanism of lignin-derived phenolic monomers.

−OCH_3 group. The methoxyl-cyclohexanol were readily dehydrated and hydrolyzed with an acid catalyst (HZSM-5 with hydronium ions) and Raney Ni at 220 °C with a short time to methanol and cyclohexanone. We proposed that the primary reaction pathway for methoxyl-cyclohexanol transition is the metal-catalyzed hydrolysis to cyclohexanol, and 1,2-dihydroxy-cyclohexanol followed by the acid catalyzed dehydration and latter convert into cyclohexanone. Cyclohexanone is gradually hydrogenated and converted into cyclohexanol in turn. Integrated with the results from dehydration of cyclohexanol (Table S1), we speculate the general pathway for the conversion of phenolic monomers with functional groups to cyclohexane and its derivatives. Under the appropriate conditions, phenolic monomers such as guaiacol are first hydrogenated at the aromatic-ring to produce 2-methoxyl-cyclohexanone and subsequently 2-methoxyl-cyclohexanol. The reaction sequence continued with the acid-catalyzed hydrolysis to form specific 1,2-dihydroxy-cyclohexanol, and the dehydration of 1,2-dihydroxy groups to produce cyclohexanone. The sequential hydrogenation of cyclohexanone leads to cyclohexanol. Acid-catalyzed dehydration of cyclohexanol and its derivatives, and metal-catalyzed *in situ* hydrogenation of cyclohexene lead to the final target cyclohexanes products. Besides, zeolite acid catalyst may promote carbon-backbone transformation, also lead to isomerize cyclohexanes, but did not provide the six-carbon-ring opening. This reaction pathway for the stepwise liquid-phase *in situ* hydrodeoxygenation of phenolic monomers is based on methanol-water solvents over bifunctional catalysts, which could couple with the aqueous phase reforming of methanol to provide hydrogen donors (hydrogen radicals), followed by stepwise reactions of metal-catalyzed hydrogenation (over Raney Ni catalyst), acid-catalyzed dehydration (over HZSM-5 catalyst) and metal-catalyzed hydrolysis (over Raney Ni catalyst).

3.2.3. *In situ hydrodeoxygenation of different phenolic dimers*

In addition to studying the conversion of phenolic monomers, we also investigated the *in situ* hydrodeoxygenation of lignin-derived phenolic dimers to cyclohexanes and hydrocarbons with the Raney Ni and HZSM-5 (Si/Al ratio of 25) combination as bifunctional catalysts under designed condition. The lignin-derived phenolic dimers were shown in significant concentrations in bio-oil, because of the incomplete degradation of lignin [21]. Typically, the most representative linkages in phenolic dimers, in natural lignin structure, for example, are α−O−4 (8%), β−O−4 (55%), 4−O−5 (5%), 5−5 (5%), β−5 (10%), β−β (7%), and β−1 (15%) with both C−O−C linkages (2/3) and C−C linkages (1/3) [11]. Therefore, different types of phenolic dimer compounds including both C−O−C and C−C linkages were investigated in the selected liquid-phase *in situ* hydrodeoxygenation at 220 °C with a reaction time of 7 h with bifunctional catalysts Raney Ni and HZSM-5.

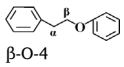
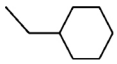
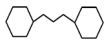
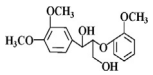
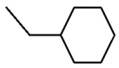
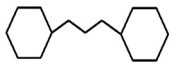
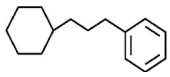
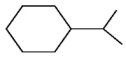
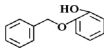
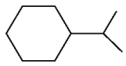
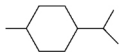
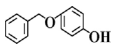
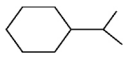
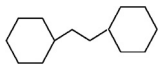
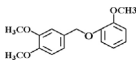
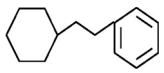
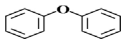
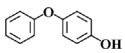
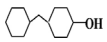
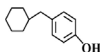
For the C−O−C linkage, the most abundant linkages in lignin (β−O−4, alkyl aryl ether) were selectively converted approximately 73.4% C_6 cyclohexane and 10.7% C_8 ethyl-cyclohexane at 220 °C with a reaction time of 7 h in methanol-water solvents (Table 5, entry 1). The *in situ* hydrodeoxygenation process of β−O−4 linkage dimers with the methoxyl (–OCH_3) and hydroxyl (–OH) was also investigated, and the main products were C_6 cyclohexane, C_8 ethyl-cyclohexane and C_{15} 1, 3-dicyclohexylpropane (Table 5, entry 2). The benzyloxy-benzene (α-O-4) and the *o-/p*-hydroxyl-substituted α-O-4 model compounds were also quantitatively converted with an approximately 50% yield of C_6 cyclohexane and 50% yield of C_7 methyl-cyclohexane under these conditions. The α-O-4 dimers diphenyl ether including four model phenolic dimers were quantitatively converted into C_6–C_9 hydrocarbons approximately 79.6%, 70.8%, 84.8%, and 64.5%, respectively (Table 5, entry 3–6). In previous study [11], thermal conversion of phenol dimers containing β−O−4 and α−O−4 bonds always led to some uncontrolled free-radical reactions and a variety of immediate products with the selectivity of hydrocarbon less than 40% and the conversion of reactants about 10%. Also, by the hydrothermal process, the primary products, such as ethyl-benzene and phenol were at a lower conversion of the β-O-4 dimer, indicating that the C−O−C (alkyl aryl ether) linkage may be opened by pyrolysis or hydrogenolysis with external hydrogen gas [22,23]. Thus, we presumed that the reaction route of α-O-4 and β-O-4 dimers process by Raney Ni that promoted hydrogenolysis to break the C−O bond, followed by removal of the oxygen atoms attached at the aromatic ring by sequential hydrogenation-dehydration-hydrogenation process. In this *in situ* catalytic hydrodeoxygenation, the hydrogen radicals are donated by aqueous phase reforming of methanol. At the same time, the methyl in the −OCH_3 group of phenolic compounds could be converted into the aromatic ring through an acid-catalyzed transalkylation process over the acidic zeolite catalyst HZSM-5 [24]. Therefore, the formation of C_8-C_{10} cyclohexanes in our experiment was speculatively due to the acid catalyzed transalkylation process over HZSM-5 (Si/Al ratio of 25), which was followed by subsequent isomerization of substituted hydrocarbons on the stronger acidic sites of HZSM-5. This result indicated that the phenolic compounds-containing bio-oils can be refined and upgraded by adjusting balance between the metal and acid catalyst.

The diphenyl ether (4-O-5 dimer) including four model phenolic dimers were also quantitatively converted with an approximately 37%, 62%, 56%, and 24% selectively of C6 cyclohexane, and 32%, 13%, 9%, and 24% selectively of C_7 methyl cyclohexane at 220 °C (Table 5, entry 7–10). Hydrolysis of the aryl–aryl ether bond is difficult and required intense conditions and higher reaction temperatures. It should be noted that diphenyl ether (4-O-5 dimer) did not break down when only used HZSM-5 was used as a catalyst under the conditions. However, when Raney Ni and HZSM-5 were applied as bifunctional catalysts, C−O bond cleavage of the aryl–aryl ether bond reacted, which suggested that the combination of Raney Ni and HZSM-5 used as bifunctional catalytic (the acid and metal together) is essential for cleaving the aryl ether bonds.

Through the dehydration and hydrogenation reactions, the C−C linkages in 5-5, β-1, β-β, β-5, and β-5′ were investigated, whereas the substituted −C═O and −OH groups were selectively removed at 220 °C with a reaction time of 7 h, leading to approximately 63–76% yields of C_{12}, C_{14}, and C_{16} bi-cyclohexanes after *in situ* hydrodeoxygenation (Table 5, entry 11−15). The 2–3% isomers of cyclohexanes can be produced by the zeolite acid sites of the H-form of HZSM-5. The β−5 and β−5′ linkage were complex connection with both C−C and C−O−C bonds in aromatic ring containing −OCH_3 groups. Under the reaction conditions, the aromatic ring was selectively broken down at the C−O bonds over bifunctional catalysts. The −OCH_3 groups in this *in situ* hydrodeoxygenation were removed by the subsequent hydrodeoxygenation process.

The *in situ* hydrodeoxygenation of phenolic dimers process contained a hydrogenation–hydrolysis–dehydration–dehydroaromatization cascade, especially in removing oxygen-containing groups (hydroxyl, methoxy, ketone, alkyl−O−aryl, and aryl−O−aryl) in lignin-derived substituted phenolic monomers and dimers. The selectivities of main products were shown in Table 5. In addition, the selectivities of byproducts were not identified and shown. However, it should be mentioned that in some results of *in situ* hydrodeoxygenation, the selectivities of main products did not add up to the conversion of phenolic dimers. A possible explanation is that the reactants did not undergo the whole metal-catalyzed hydrogenation, acid-catalyzed dehydration and metal-catalyzed hydrolysis process, and were not completely hydro-deoxygenated, or the main products were partially polymerized.

Table 5
In situ hydrodeoxygenation of phenolic dimers over bifunctional catalysts.

Entry	Reactants	Conv. (%)	Selectivity of main products (%)			
1	 β-O-4	99.6	 73.4	 10.7	 1.2	 0.3
2	 β-O-4	95.3	 39.2	 20.4	 10.3	 2.4
3	 α-O-4	99.5	 45.7	 31.5	 2.4	 0.5
4	 α-O-4	99.8	 35.5	 33.2	 2.1	 5.4
5	 α-O-4	99.8	 40.8	 37.3	 6.7	 2.1
6	 α-O-4	94.6	 25.3	 39.2	 10.6	 3.6
7	 4-O-5	99.5	 37.6	 32.8	 1.6	 0.5
8	 4-O-5	99.6	 62.3	 13.2	 1.4	 0.8
9	4-O-5	96.3	56.5	9.3	5.4	2.4
10	4-O-5	95.2	23.7	25.8	5.4	2.7
11	5−5	99.6	75.3	2.2	3.2	8.5
12	β−1	99.8	2.1	70.9	3.1	1.7
13	β-β	99.7	1.8	0.4	75.7	10.3
14	β−5	99.6	0.5	2.1	70.3	
15	β−5′	99.6	1.4	1.6	63.1	

Reaction condition: phenolic dimers (0.02 mol), methanol (0.1 mol), water (2.0 mol), HZSM-5 (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).

3.3. *In situ* hydrodeoxygenation of phenolic compounds derived from biomass

According to the above studies, the *in situ* hydrodeoxygenation of phenolic compounds derived from biomass was carried out at 220 °C using bifunctional catalysts of Raney Ni and HZSM-5. The compositions and the relative contents of phenolic compounds before and after *in situ* hydrodeoxygenation reaction changed significantly (Table 6). Both of them contained many organic compounds. Phenolic compounds were mainly converted into alkanes and alcohols, small amounts of intermediates (ketones and esters) and unreacted reactants were also detected. It appears that the conversions of phenolic compounds and the yields of hydro-deoxygenated products were not favorable, which were lower when using a mixture of real biomass liquefied products compared to the model phenolic compounds. The real phenolic compounds containing phenolic monomers, dimers with various functionalities, especially alkyl, methoxy, hydroxyl, carbonyl, and ester groups, were more complex than the model phenolic compounds.

Cyclohexane and cyclohexane derivatives are the principal components of the *in situ* hydrodeoxygenation products (Table 6). It was clearly observed that the content of phenolic compounds significantly decreased from 80.13% to 19.21% after hydrodeoxygenation. Cyclohexane and its derivatives (including alkyl cyclohexanes and methoxy cyclohexanes) produced from the hydrodeoxygenation of phenolic compounds increased about 40.45%. The contents of hydro-deoxygenated intermediates (cyclohexanols, cyclohexanones, and their derivatives) increased approximately 20%. Furfural, β-methoxy-2-furanethanol, and 2-methoxy-2-furyl alcohol identified in the phenolic compounds clearly decreased after *in situ* hydrodeoxygenation. In addition, the compositions of the acids significantly decreased after *in situ* hydrodeoxygenation, resulting in esterification during the upgrading process. There were still parts of phenolic compounds found after the *in*

Table 6
Components of phenolic compounds and hydro-deoxygenated products.[a]

R.T (min)	Ingredient	Relative contents (%)	
		Phenolic compounds	Hydrogenated products
	Aldehydes	**4.78**	**3.03**
6.35	Dihydro-5-methylfuranone	–	2.49
7.24	Furfural	1.39	–
7.76	β-Methoxy-2-furanethanol	2.52	0.54
8.13	2-Methoxy-2-furyl alcohol	0.87	–
–			
	Phenols	**80.13**	**19.21**
10.47	4-Methyl-guaiacol	4.19	1.02
11.59	4-Propyl-guaiacol	1.87	1.59
12.33	Eugenol	8.34	–
13.64	Vanillin	5.67	–
15.78	2,6-Dimethoxy-4-(2-propenyl) phenol	3.24	0.87
17.09	4-Propyl-2,6-dimethoxyphenol	8.52	–
23.56	Methoxy-4-propylphenol	9.57	2.71
25.81	3-Methoxy-4-hydroxy-benzoic acid methyl ester	16.13	5.73
27.02	4-(2-Hydroxyethyl)-2-methoxyphenol	1.98	–
28.46	1-*E*thanone-4-hydroxy-3-methoxyphenyl	1.52	0.34
29.30	1-(1,1-Dimethoxypropan-2-methoxy)benzene	–	1.02
29.87	Methoxy-(3,4-dimethoxyphenyl)methanol	11.35	4.35
30.54	Methyl-2-(4-hydroxy-3-methoxyphenyl)acetate	0.64	0.13
30.80	Methyl-3-(4-hydroxy-3-methoxyphenyl)acrylate	1.42	–
33–35	Phenolic dimers	5.69	1.45
–			
	Alkanes, cycloalkanes	–	**40.45**
4.63	Cyclohexane	–	2.69
4.89	Hexane	–	3.24
5.87	Methyl cyclohexane	–	5.80
6.25	Propyl cyclohexane	–	11.89
7.37	2-Cyclohexane propane	–	5.44
12.38	Benzene-3-cyclohexane propane	–	4.52
15.44	1-(4-Phenol)-4-cyclohexanebutane	–	6.87
–			
	Alcohols, ketones	**3.70**	**23.27**
7.50	Cyclohexanol	–	0.45
7.75	4-Methylcyclohexanol	–	4.41
8.00	1-Hydroxy-2-propanone	1.69	–
8.42	4-Propylcyclohexanol	–	2.87
8.75	1-Hydroxy-2-butanone	2.01	–
8.93	4-Propylcyclohexanone	–	1.02
9.24	4-Methyl-2-methoxycyclohexanol	–	3.91
10.17	4-Propyl-2-methoxycyclohexanol	–	1.54
15.96	4-Propyl-2,6-Dimethoxyclohexanone	–	4.32
18.39	Methyl-2-(4-hydroxy-3-methoxyclohexanol)acetate	–	1.79
24.17	Methyl-2-(4-hydroxy-3-methoxycyclohexane) propionate	–	2.96
–			
	Others	**13.08**	**17.07**
19.36	1,1-Dimethoxy-2-propylbenzene	1.03	–
20.59	2-Phenylcyclohexanone	–	1.23
22.46	3-Methoxybenzoic acid	3.69	–
23.85	2,3-Dihydroxy acid methyl ester	–	5.36
24.761	Hexadecanoic acid methyl ester	1.69	0.76
27.43	3-Methoxybenzoate	–	3.78
	Unknown compounds	6.67	5.94

[a] Reaction condition: phenolic compounds (2.0 g), methanol (0.1 mol), water (2.0 mol), HZSM-5 (1.5 g), Raney Ni (1.0 g), p_0 (N_2, 0.5 MPa), T (220 °C), t (7 h).

situ hydrodeoxygenation process. This may due to the complex structure of phenolic compounds with different side chain groups such as methoxy, alkyl methoxy, alkyl ester, phenyl, and ether linkages are converted into other structure phenolic compounds by decarbonylation or other reaction. Vanillin can be converted into 4-methyl-guaiacol or 2-methylphenol via hydrogenation of the aldehyde group. There were about 6% unknown compounds in the spectrum, which could potentially be phenolic trimers, tetramers, aromatic derivatives, or high-molecular polymers. Absolute structural identification of these complex compounds, however, was not possible since these unknown compounds' authentic standards were not available.

3.4. *In situ* hydrodeoxygenation of liquefied oil

The upgrading of liquefied oil was carried out at 220 °C using bifunctional catalysts by *in situ* hydrodeoxygenation process. Fig. 4 shows that the compositions of bio-oils were relatively complex and contained several kinds of organic compounds. The compositions and relative contents of the liquefied oil before and after *in situ* hydrodeoxygenation reaction has been significantly changed (Fig. 4). The components of biomass liquefied oil before and after *in situ* hydrodeoxygenation are shown in Table S5. There are two platform chemicals in the liquefied oil: furan-like compounds and levulinate compounds were derived from the decomposition of hemicellulose and cellulose, and phenolic compounds were derived from the depolymerization of lignin.

The conversion of phenolic compounds in the liquefied oil was lower than that when used the model phenolic compounds. There were still some phenolic compounds (R.T. 25.5–32.5 min) unreacted after *in situ* hydrodeoxygenation process. The main products of hydrodeoxygenation were not only cyclohexane and alkanes (R.T. 5.0–7.7 min), but also alcohols, ketones, aldehydes, and other substances (R.T. 7.5–10.0 min), and the yields of hydro-deoxygenated products were not favorable. It was speculated that the acids and some unknown compounds (nitrogen- and sulfur-containing compounds) in the phenolic compounds from liquefied oil may affect the activity of the catalyst. In particular, Raney Ni is a highly sulfur sensitive catalyst. Some heat-sensitive compounds in the liquefied oil could form macromolecular polymers, which may cover the surface of the catalyst and affect its activity.

4. Conclusions

The bifunctional catalysts of Raney Ni and HZSM-5 showed a high selectivity in removing oxygen-containing groups (−OH, −C═O, $-OCH_3$, $C_{alkyl}-O-C_{aryl}$, and $C_{aryl}-O-C_{aryl}$) in lignin-derived phenolic monomers and dimers via the *in situ* hydrodeoxygenation process. The process featured a cascade metal- and acid-catalyzed cleavage of C−O bonds in phenolic monomers and dimers, and integrated hydrogenolysis-dehydration-hydrogenation reaction. Under designed conditions, the conversions of phenolic monomers and dimers were more than 90% and the selectivity of hydrocarbons approximately 70–90%. During the *in situ* hydrodeoxygenation process, the hydrogen radicals are donated by aqueous phase reforming of methanol, without external hydrogen gas used. The product cyclohexanes and their derivatives can be easily separated from the solvent because they are immiscible. Hydrogenation and dehydro-aromatization reactions are catalyzed by the Raney Ni particles, while dehydration and hydrolysis are catalyzed by the Brønsted acid sites of HZSM-5. With the *in situ* hydrodeoxygenation over the bifunctional catalysts Raney Ni and HZSM-5, the phenolic compounds can be effectively converted into cyclohexanes and hydrocarbons, with higher conversion of phenols and selectively of cyclohexanes than that with the common hydrodeoxygenation. The bifunctional

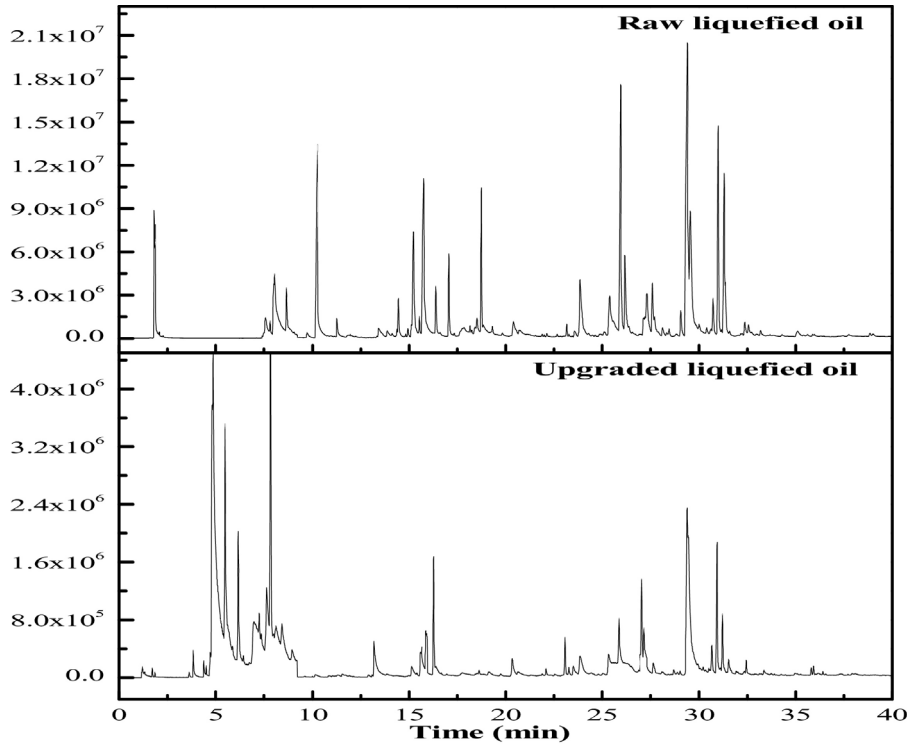


Fig. 4. The GC–MS of biomass liquefied oil before and after *in situ* hydrodeoxygenation.

catalysts combined Raney Ni with HZSM-5 can achieve the aqueous-phase reforming of methanol coupled with the *in situ* hydrodeoxygenation of phenolic compounds. The zeolite catalyst is highly hydrothermally stable and does not deactivate over several times of reaction cycles, showing that the process has great potential to be at the core of new technology for sustainable transportation fuels.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2017.05.022.

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