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In situ catalytic hydrogenation of model compounds and biomass-derived phenolic compounds for bio-oil upgrading

Junfeng Feng [a, b], Zhongzhi Yang [a], Chung-yun Hse [b], Qiuli Su [a], Kui Wang [a], Jianchun Jiang [a, c, *], Junming Xu [d, **]

[a] Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, National Engineering Lab. for Biomass Chemical Utilization, Key Lab. of Biomass Energy and Material of Jiangsu Province, Nanjing 210042, China
[b] United States Department of Agriculture Forest Service, Southern Research Station, Pineville, LA 71360, USA
[c] Jiangsu Qianglin Biomass Energy Co., Ltd., Liyang 213364, China
[d] Research Institute of Forestry New Technology, Chinese Academy of Forestry, Beijing 100091, China

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ABSTRACT

The renewable phenolic compounds produced by directional liquefaction of biomass are a mixture of complete fragments decomposed from native lignin. These compounds are unstable and difficult to use directly as biofuel. Here, we report an efficient *in situ* catalytic hydrogenation method that can convert phenolic compounds into saturated cyclohexanes. The process has high potential for production of hydrocarbon transportation fuels. In the *in situ* catalytic hydrogenation system, phenolic compounds were converted into cyclohexanol derivatives (that can be efficiently converted into cyclohexane-hydrocarbon fuels by acid-catalyzed dehydration) with a conversion yield 98.22 wt% under mild conditions (220 °C for 7 h with Raney Ni). The *in situ* catalytic hydrogenation of phenolic compounds, using methanol as a liquid hydrogen donor, was found to be superior to traditional hydrogenation using external hydrogen gas. The *in situ* hydrogenation of phenolic compounds was coupled with aqueous-phase reforming of methanol. The conversion of guaiacol and target product yields were significantly higher than by traditional hydrogenation.

1. Introduction

The dwindling reserves of fossil feedstock as a source of chemicals and fuels have driven attention to biomass as a renewable resource [1]. Lignocellulosic biomass is one of the most inexpensive and abundant sources of biomass, and can be used as feedstock for the production of renewable biofuels and chemicals [2–4]. Thermochemical conversion of lignocellulosic biomass into high added-value chemicals and biofuels has attracted increased attention due to the growing demand for sustainable bio-products [5,6]. Bio-oil or liquefied oil, usually produced by thermochemical conversion (pyrolysis/liquefaction) of biomass, has been identified as a renewable chemical source and fuel that can be produced from lignocellulosic biomass [7]. However, the complex composition and high oxygen content of bio-oil prevents its direct use as high quality biofuel because of its low heating value, instability and corrosiveness [8]. Bio-oil therefore needs to be refined and upgraded. Among the upgrading approaches, hydrotreatment of bio-oil has been widely investigated and shown to significantly increase its storage stability and heating value [9,10]. However, the traditional hydrogenation process conditions using external hydrogen gas are rather severe (350–450 °C, 5–15 MPa), leading to reactor clogging and catalyst deactivation, which limit its industrial application [11].

On the other hand, directional upgrading of bio-oil is difficult since it is a complex mixture of more than 200 chemicals. A reasonable method has been proposed to obtain biofuels or chemicals by separation of bio-oil into different platform compounds according to their original molecular structure [12]. Many separation methods have been used to extract phenolic compounds from bio-oil, including ionic exchange resins [13], membrane processes [14] and liquid-liquid extraction [15,16]. However, there need to be improvements in the use of ionic exchange resins and

* Corresponding author. Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, National Engineering Lab. for Biomass Chemical Utilization, Nanjing 210042, China.
** Corresponding author.
E-mail addresses: jiangjc@icifp.cn (J. Jiang), lang811023@163.com (J. Xu).

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membrane processes, since the extraction methods are difficult. For liquid-liquid extraction, many different organic solvents [17] have been introduced to separate bio-oil. However, residual solvent hampers upgrading and refining of phenolic compounds. Additionally, there are few reports that describe conversion of phenolic compounds derived from bio-oil into added-value chemicals.

In previous research, our group found a simple method for production of phenolic compounds [18] that enabled separation of the liquefied materials into two platform products. The phenolic compounds that precipitated from aqueous solution were mainly composed of phenolic derivatives such as guaiacol and 2-methoxy-4-propyl-phenol. These phenolic derivatives have many advantages with numerous potential applications, such as low-molecular weight and good solubility in organic solvents. Further, compared to macromolecular lignin, the phenolic compounds have higher reactivity for generation of added-value products. Phenolic compounds are the preferred substrates for chemical conversion to many other useful products (alkanes and resins) via various hydrogenation and polymerization reactions [19]. Following the upgrading process, phenolic compounds derived from bio-oil could be converted into a highly calorific biofuel.

In situ hydrogenation is a novel method to upgrade complex chemicals in bio-oil [20]. This study investigated this *in situ* process using aqueous-phase reforming of methanol to produce hydrogen rather than using external hydrogen gas for hydrogenation of bio-oil. The effect of different parameters on the reaction process for *in situ* hydrogenation of different phenolic model compounds was also investigated. The process coupling *in situ* hydrogenation of phenolic compounds with aqueous-phase reforming of methanol was studied in detail. The phenolic compounds were converted into cyclohexanol and its derivatives under mild conditions by the *in situ* catalytic hydrogenation process. The cyclohexanol and cyclohexanol derivatives can be quantitatively dehydrated to cyclohexenes using common mineral acids within a short time at low temperature [21–23]. Herein, for the preparation of high quality hydrocarbon biofuel from lignocellulosic biomass, the important technology is hydrotreatment of depolymerized native lignin (phenolic compounds) to produce cyclohexanol derivatives. Furthermore, introduction of methanol as the hydrogen donor, avoiding the high pressure required for traditional hydrogenation, ameliorated reactor clogging. The aqueous phase reforming of methanol and *in situ* hydrogenation of phenolic compounds in the liquid phase was also studied using recycled and regenerated Raney Ni catalysts. The possible reactions occurring during the *in situ* hydrogenation process were explored, and the typical compositions of raw and upgraded phenolic compounds were investigated in detail.

2. Experimental

2.1. Materials

Bamboo was collected from a local farm (Jiangsu, China) as industrial waste material, pulverized to pass through a 50 mesh sieve, oven dried at 105 °C for 24 h and then stored in a sealed bag until needed. Analysis of the composition of bamboo, including ash, extraction by 1% NaOH, acid-insoluble lignin, holocellulose and pentosan, was conducted using standard test methods according to ASTM 2007. The elemental analysis for the bamboo was C (48.46%), H (4.22%), O (46.95%), N (0.08%), and S (0.29%). The quantity of benzene-ethanol soluble matter in the bamboo was 3.69 wt%, determined using ASTM D 1107-1996 (ASTM 2007). The amount of lignin in the bamboo was 23.45%, determined using ASTM D 1106-1996 (ASTM 2007). The amount extracted by 1% NaOH from the raw bamboo was 27.71 wt% (ASTM D 1109-1984, ASTM 2007). Ash in the raw material was 1.18 wt% (ASTM D 1102-1984, ASTM 2007). Catalysts, including Raney Ni, Pt/Al_2O_3, Pd/C and Pd/Al_2O_3, were obtained from Aladdin Company, Shanghai, China. All other chemicals in the study were of analytical grade, commercially available and used without further purification.

Directional liquefaction is focused on the integrated utilization of three major components (cellulose, hemicellulose and lignin) in lignocellulosic biomass. In that regard, we first demonstrated the possibility to prevent side reactions in the production of two fractionated platform products (phenolic compounds and glycoside compounds) according to their original molecular structure [18]. The phenolic compounds were obtained as a yellowish powder by stepwise precipitation from liquefied bamboo oil (Fig. S1 in the Supporting Information). The bio-oil was prepared by heating 60 g powdered moso bamboo in a solution of 420 g methanol containing 1.5 g sulfuric acid in an autoclave at 200 °C for 30 min. Liquefied products (bio-oil) were separated by the addition of a sufficient amount of water-ethyl acetate.

According to GC-MS analysis (Table S1 and Fig. S2 in the Supporting Information), the phenolic compounds were largely separated from bio-oil by water-ethyl acetate assisted extraction using a stepwise method. The phenolic compounds mainly consisted of phenols and their derivatives, including phenol, guaiacol, vanillin, 4-methyl-2-methoxyphenol, 2-methylphenol, eugenol, 3,4-dimethoxyphenol and 3-methoxy-4-hydroxyphenylacetic acid. The FT-IR and GPC analysis of phenolic compounds fraction and bio-oil were showed in Table S2, Figs. S3 and 4 (Supporting Information).

2.2. Analytical methods

Phenolic compounds and hydrogenated products were determined by gas chromatography-mass spectrometry (GC-MS) (Agilent, USA, 5975C VL MSD). The separation was realized on a HP-5 (30 m × 0.25 μm × 0.25 nm) column. The temperature program was as follows: 45 °C (held for 5 min) → 250 °C (5 °C min^{-1}, held for 20 min). The MS detector was operated in electron ionization mode (70 eV) with an ionization temperature of 220 °C, scanning m/z 50–550. Typically, 0.2 μL of sample was used.

The components of the hydrogenation gas products were determined by gas chromatography (GC) (Shimadzu, Japan, GC-2014) on an Al_2O_3 column. The detectors included a thermal conductivity detector (TCD) (mainly to identify H_2, CO and CO_2) and a hydrogen flame ionization detector (mainly to identify CH_4, C_2H_6, C_2H_4 and C_2H_2).

Functional groups present in phenolic compounds and bio-oil were identified using a Nicolet iS10 FT-IR spectrometer (Thermo-Fisher Scientific, USA). The scanned ranged was 4600 to 500 cm^{-1}, with resolution greater than 0.4 cm^{-1} and ASTM standard linearity better than 0.1% T.

Molecular weights of the phenols were measured by gel permeation chromatography (GPC) using a Waters-1515 system (USA) equipped with a manually packed column. The injection volume was 25 μL, analysis time was 25 min, sample solvent was tetrahydrofuran and polystyrene was used as reference.

The $^1H-^{13}C$ correlation heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectra were recorded using a Bruker (Germany) DRX 500 NMR spectrometer operating at 500 MHz. The spectral widths were 120.0 and 8.5 ppm for the ^{13}C and ^1H dimensions, respectively. Measurements were conducted in dimethyl sulfoxide at 30 °C, and tetramethylsilane was used as an internal standard.

Analyses were conducted in triplicate and used to calculate the standard deviation to indicate the experimental error range. The conversion of phenolic compounds was calculated by Eq. (1) and

the conversion of guaiacol calculated by Eq. (2).

$$\text{Phenolic compounds conversion (wt\%)} = \left(1 - \frac{\text{phenolic compounds weight in product}}{\text{phenolic compounds weight in material}}\right) \times 100\% \quad (1)$$

$$\text{Guaiacol conversion } (wt\%) = \left(1 - \frac{\text{guaiacol weight in product}}{\text{guaiacol weight in material}}\right) \times 100\% \quad (2)$$

2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku (Japan) D/MAX-RC X-ray diffractometer set at 40 kV and 40 mA using Cu Kα radiation. Data were collected at steps of 0.02° in the 2θ range of 10°–80°. A SEM S-3400N (5–10 kV accelerated voltage) scanning electron microscope (SEM) was used to check the morphology of the Raney-Ni. Specimens for SEM inspection were gold-plated prior to analysis. The Brunauer-Emmett-Teller (BET) surface area analysis of catalysts was measured by N_2 adsorption-desorption at liquid nitrogen temperature using a Beishide (China) instrument (3H-2000PS1).

2.4. Hydrogenation reactions

2.4.1. In situ hydrogenation

The *in situ* catalytic hydrogenation process was carried out using aqueous phase reforming of methanol for hydrogenation of phenols. Raney Ni catalyst (0.5 g), phenols or phenolic compounds (2 g), methanol (10 g) and distilled water (40 g) were placed in a 100 mL autoclave fitted with a thermocouple, a pressure gauge (40 MPa), and a stirring device. The initial pressure (p_0) in the autoclave was raised to 0.1–4 MPa with N_2 before heating. The autoclave was heated at a rate of 3 °C min^{-1} and a stirring rate of 500 rpm until the desired reaction temperature was reached (160–240 °C) under autogenous pressure and kept for a set time period (1–9 h). After reaction, the autoclave was cooled rapidly in a water bath to room temperature. The reaction mixtures were removed from the autoclave and filtered through a membrane filter (pore size 8 μm). The hydrogenation products were then obtained in high purity by distillation of the filtrate under vacuum at 60 °C to recover the methanol and water. The recovered methanol and water were used in subsequent hydrogenation reactions.

2.4.2. Traditional hydrogenation using external hydrogen gas

Traditional hydrogenation of phenols refers to hydrogenation using external hydrogen gas. The equipment, conditions and reactants were similar to those used in Section 2.4.1 (without distilled water). The vessel was purged with 5 MPa H_2 (99.999%) several times. The final reaction mixtures were subjected to rotary evaporation, and then the methanol and catalysts were separated to obtain the hydrogenated products.

3. Results and discussion

3.1. Model reactions using different hydrogenation methods

Phenolic compounds in bio-oil mainly consisted of phenol, eugenol, vanillin, guaiacol and their derivatives (Supporting Information Table S1). Besides, the HSQC spectrum technique is a powerful tool for detailed understanding of phenolic compounds separated from bio-oil. The phenolic compounds 2D HSQC spectra are summarized in Figs. S5(a) and (b), illustrating the aliphatic side chain and aromatic $^{13}C-^{1}H$ correlations. The main cross peaks were presented in Table S3. The signals for methoxyl and β-O-4 substructures were the most prominent ones in the HSQC spectrum. Guaiacol, containing adjacent hydroxyl and methoxy functional groups on the aromatic ring, is one of the three basic units of lignin and was selected as a model compound to investigate the hydrogenation of phenolic compounds. According to relevant studies on lignin degradation [24], guaiacol contains three types of C–O bonds (C_{AR}–OH, C_{AR}–OCH_3, and $C_{AR}O$–CH_3) that are frequently found in phenolic compounds derived from thermochemical conversion of renewable lignocellulosic biomass.

Active hydrogen could be produced by catalytic reforming of biomass-derived hydroxylic compounds in liquid water under certain condition. The selectivity for H_2 production by catalytic reforming of biomass-derived hydrocarbons in water solvent improves in the order of glucose < sorbitol < glycerol < ethylene glycol < methanol [25]. In this experiment, the aqueous-phase reforming of methanol was coupled with the *in situ* hydrogenation of phenolic compounds.

Initially, the effect of different catalysts on traditional hydrogenation was studied in methanol. The main products of guaiacol hydrogenation were cyclohexanol, cyclohexanone, 3-methoxy-cyclohexanol and 3-methyoxy-cyclohexanone. These cyclohexane derivatives can easily be converted into aromatics and cycloalkanes by deoxygenation [23,26,27]. The aromatics and cycloalkanes can be used as high quality transportation fuel. It is apparent from Table 1 that the performance of the catalysts on guaiacol conversion followed an overall trend of: Raney Ni > Pt/Al_2O_3>Pt-SBA-15 > Pd/Al_2O_3>Pd/C.

Methanol can produce hydrogen over many kinds of catalysts during aqueous phase reforming. The influence of different catalysts on *in situ* hydrogenation of guaiacol was also investigated in detail (Table 2). The performance of non-precious metal catalysts compared favorably to the three platinum-based catalysts for hydrogenation of guaiacol. The performance of Raney Ni was superior to the other catalysts. Raney Ni has a large surface area, which may increase the reaction surface and improve reactivity during aqueous phase reforming of methanol and hydrogenation of phenols. In addition, nickel has greater potential for use in many industrial fields [28] compared to noble metal catalysts such as Pd or Pt. In general, Raney Ni has good catalytic properties for both aqueous phase reforming of methanol and hydrogenation of phenols. Phenols can therefore be effectively transformed into cyclohexanol by hydrogenation over Raney Ni. Raney Ni may also decrease the rate of methane formation by C=O bond breakdown, while maintaining the high rate of C=C bond breakdown required for H_2 formation during aqueous phase reforming of methanol [29].

Comparing the data in Tables 1 and 2, guaiacol conversion and the yields of target products (T.P., including cyclohexanol,

Table 1
Effect of different catalysts on traditional hydrogenation of guaiacol.

Yield (wt%)	Catalysts				
	Raney Ni	Pt/Al_2O_3	Pd/C	Pd/Al_2O_3	Pt-SBA-15
Guaiacol conversion	82.45	80.30	67.03	73.11	78.42
Cyclohexanol	27.81	22.40	18.30	13.02	10.68
Cyclohexanone	12.17	7.31	16.04	3.28	10.21
2-Methyl cyclohexanol	32.73	13.87	8.91	24.21	30.15
2-Methoxy cyclohexanol	6.21	20.33	12.06	18.36	19.83
Cyclohexane	0.57	1.38	2.03	0.42	5.42
Target products	79.49	65.19	55.34	56.29	76.29

Reaction condition: $m(H_2O)$:m(guaiacol) = 20:1, T = 220 °C, p_0 = 3 MPa(N_2), t = 5 h.

Table 2
Effect of different catalysts on *in situ* hydrogenation of guaiacol.

Yield (wt%)	Catalysts				
	Raney Ni	Pt/Al_2O_3	Pd/C	Pd/Al_2O_3	Pt-SBA-15
Guaiacol conversion	97.35	85.47	75.09	85.32	90.32
Cyclohexanol	65.01	23.60	19.61	17.01	40.10
Cyclohexanone	26.62	10.89	7.82	12.39	24.59
2-Methyl cyclohexanol	2.16	24.07	22.15	27.13	16.77
2-Methoxy cyclohexanol	1.12	15.44	11.65	14.22	2.21
Cyclohexane	0.54	1.87	1.30	0.85	4.51
Target products	96.32	75.87	68.53	71.60	88.18

Reaction condition: $m(H_2O)$:m(guaiacol):$m(CH_3OH)$ = 20: 1: 5, T = 220 °C, p_0 = 3 MPa (N_2), t = 5 h.

cyclohexanone, 2-methyl-cyclohexanol, 2-methoxy-cyclohexanol and cyclohexane) were higher using *in situ* hydrogenation than traditional hydrogenation, exceed about 15 wt% and 17 wt%. The results demonstrate that *in situ* catalytic hydrogenation using methanol as the liquid hydrogen donor was superior to traditional hydrogenation using external hydrogen gas. The active hydrogen generated from the aqueous-phase reforming of methanol can be quickly removed from the active sites of catalyst through *in situ* hydrogenation of phenols, improving the selectivity of the reaction. Furthermore, high selectivity for the target products (96 wt% of the total conversion to cyclohexanol and its derivatives) was achieved by *in situ* hydrogenation over Raney Ni catalyst, which was superior to traditional hydrogenation with external hydrogen gas. The aqueous phase reforming of methanol can therefore be used in the hydrogenation process instead of external hydrogen gas.

The gas phase products formed during guaiacol hydrogenation, which are mainly hydrogen, methane and carbon dioxide, are shown in Table 3. The overall reaction is aqueous phase reforming of methanol (Eq. (3)). The gas phase products suggest that reactions may take place via the formation of CO as an intermediate byproduct (Eq. (4)) that is subsequently converted into CO_2 by water-gas-shift reaction (Eq. (5)). Aqueous phase reforming of methanol may also be accompanied by Fischer–Tropsch or methanation reactions, which produce methane (Eq. (6)) and other alkanes and reduce the selectivity for H_2.

$$\text{Aqueous phase reforming}: CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad (3)$$

$$\text{Reforming}: CH_3OH \rightarrow CO + 2H_2 \quad (4)$$

$$\text{Water} - \text{gas} - \text{shift reaction}: CO + H_2O \rightarrow CO_2 + H_2 \quad (5)$$

$$\text{Side Reaction}: CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (6)$$

Based on the reaction products, a mechanism for *in situ* hydrogenation of guaiacol is proposed in Fig. 1. *In situ* hydrogenation of the most representative phenolic monomer, guaiacol, which contains phenolic hydroxyl and methoxy groups, led to a variety of products including cyclohexanol, cyclohexanone, 2-methyl-cyclohexanol and 2-methoxy-cyclohexanol at 220 °C (Table 2). The intermediate, 2-methoxy-cyclohexanone, can be converted into either 2-hydroxy-cyclohexanone via isomerization or 2-methoxy-cyclohexanol via further hydrogenation. The 2-hydroxy-cyclohexanone can then be converted into cyclohexanone or cyclohexanol by continued hydrogenation. On the other hand, 2-hydroxy-cyclohexanone can be converted into 1,2-dihydroxy-cyclohexane by *in situ* hydrogenation over Raney Ni. Although 2-methoxy-cyclohexanone is relatively stable, some may also be transformed into 1,2-dihydroxy-cyclohexane. Like 2-hydroxy-cyclohexanone, 1,2-dihydroxy-cyclohexane can also be converted to cyclohexanone or cyclohexanol by continued hydrogenation.

3.2. Parameters affecting the in situ hydrogenation of guaiacol

In our endeavors to design this *in situ* hydrogenation reaction, we found that three parameters were key factors to achieve both high conversion of phenols and high selectivity for the target products (cyclohexanol and its derivatives): 1) initial pressure (p_0), 2) reaction time (t), 3) reaction temperature (T) in the autoclave. Pure N_2 was introduced into the autoclave to provide different initial pressures. The initial pressure affected not only the aqueous phase reforming of methanol for hydrogen generation, but also the hydrogenation of phenolic compounds.

The *in situ* hydrogenation of phenolic compounds is coupled to the aqueous-phase reforming of methanol. As shown in Table 4a, the conversion of guaiacol and selectivity for the target products were changed when different initial pressures were used at 220 °C for 5 h. Nitrogen gas was used to provide the initial pressure and to keep all reactants in the liquid phase during the aqueous phase reforming reaction and *in situ* hydrogenation process. The liquid reactants can be desorbed from the catalyst active site. The rate of aqueous phase reforming of methanol for H_2 generation was increased at higher initial pressure. At 220 °C, when the initial pressure was increased from 0.1 MPa to 4 MPa, the conversion of guaiacol first fell slightly and then increased significantly as the pressure continued to rise. In contrast, the initial pressure had a negative effect on the selectivity for H_2 production. The selectivity for H_2 production slightly decreased as the initial pressure was increased from 0.1 MPa to 4 MPa. As the initial pressure was increased, so did the selectivity for the target products. The change in the selectivity for the target products may be associated with the activity of the catalyst, which is in agreement with results in the literature [29] that suggest that the reaction pressure can influence the activity of Raney Ni. This may be because the *in situ* hydrogenation process is consecutive to the aqueous phase reforming of methanol. The consumption of H_2 during catalytic hydrogenation can promote methanol conversion to H_2 and target product production. Further, as the initial reaction pressure continues to rise, the partial pressure of H_2 is increased in the gas products. Thus, the reaction equilibrium is disturbed and the rate of reaction decreases in consequence. Further increases of pressure result in a reduced rate of H_2 production and desorption from the catalytic site. It is likely that the side reaction (Eq. (6)) leads to the decrease of H_2 production. To prevent the side reaction, a moderate initial pressure of 3 MPa was effective, and the conversion of guaiacol

Table 3
Gas phase compositions of guaiacol under different hydrogenation pathway.

Gas compositions	Traditional hydrogenation (wt%)	*In situ* hydrogenation (wt%)
Hydrogen	70.32	34.86
Methane	21.67	39.33
Carbon dioxide	4.89	17.50
Ethane	0.52	1.28
Others	2.60	6.03

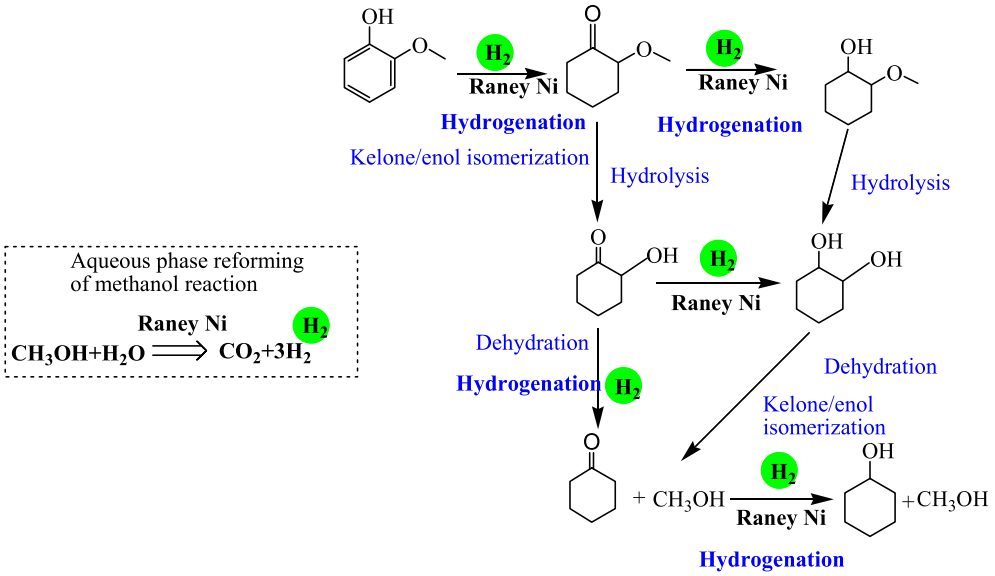

Fig. 1. Proposed mechanism on *in situ* hydrogenation of guaiacol.

Table 4a
Effect of initial pressure (p_0) on the *in situ* hydrogenation of guaiacol.

p_0 (MPa)	Guaiacol		Methanol	
	C(wt%)	S(wt%)(T.P)	C(wt%)	S(wt%)(H_2)
0.1	84.87	96.17	38.57	50.27
1	75.44	94.57	50.62	47.62
2	87.01	97.08	57.21	45.87
3	97.35	98.94	63.19	43.93
4	95.29	98.92	65.05	38.16

Reaction condition: $m(H_2O)$:m(guaiacol):$m(CH_3OH)$ = 20: 1: 5, T = 220 °C, t = 5 h.
C: Conversion, S: Selectivity, T.P: Target products.

Table 4b
Effect of reaction time (t) on the *in situ* hydrogenation of guaiacol.

t (h)	Guaiacol		Methanol	
	C(wt%)	S(wt%)(T.P)	C(wt%)	S(wt%)(H_2)
1	76.81	91.68	27.33	56.22
3	89.39	93.48	34.09	53.91
5	97.35	98.94	63.19	43.93
7	98.22	99.48	68.42	42.18
9	98.30	97.09	70.09	41.09

Reaction condition: $m(H_2O)$:m(guaiacol):$m(CH_3OH)$ = 20: 1: 5, T = 220 °C, p_0 = 3 MPa (N_2).
C: Conversion, S: Selectivity, T.P: Target products.

Table 4c
Effect of reaction temperature (T) on the *in situ* hydrogenation of guaiacol.

T (°C)	Guaiacol		Methanol	
	C(wt%)	S(wt%)(T.P)	C(wt%)	S(wt%)(H_2)
160	65.33	82.30	23.65	52.19
180	88.72	96.16	27.54	46.87
200	93.09	96.98	40.27	45.58
220	98.22	99.48	68.42	42.18
240	98.03	97.23	70.13	40.22

Reaction condition: $m(H_2O)$:m(guaiacol):$m(CH_3OH)$ = 20: 1: 5, p_0 = 3 MPa (N_2), t = 7 h.
C: Conversion, S: Selectivity, T.P: Target products.

(97.35 wt%) and selectivity for the target products (98.94 wt%) reached their highest levels.

At 220 °C and 3 MPa, the reaction time was investigated over 1–7 h. As can be seen in Table 4b, there were significant increases in the conversion of guaiacol and selectivity for the target products as the reaction time was increased. In the aqueous phase reforming of methanol, as the reaction time was increased from 1 h to 7 h the conversion of methanol increased from 27.33 wt% to 70.09 wt% (Table 4b). The selectivity for H_2 production varied from 56.22 wt% to 41.09 wt%, but there were only modest changes when the reaction time was less than 3 h. The consumption of hydrogen by *in situ* hydrogenation may promote hydrogen production and improve the conversion of guaiacol and the yield of target products. At longer reaction times (>7 h) the selectivity of target products decreased because of a consequence of product polymerization.

The effect of reaction temperature on the *in situ* hydrogenation of guaiacol was investigated at an initial pressure of 3 MPa and a reaction time of 7 h. The results are shown in Table 4c. Reaction temperature had a significant effect on the aqueous phase reforming of methanol and the *in situ* hydrogenation of guaiacol. In the aqueous phase reforming of methanol reaction, there was a substantial rise in the in the conversion of methanol and selectivity for H_2 production. As the temperature was increased, the conversion of guaiacol also increased remarkably. At 220 °C the conversion of guaiacol (98.22 wt%) and selectivity for the target products (99.48 wt%) reached their peak and then began to fall as the temperature was increased above 220 °C. It appeared that side reactions occurred during the reaction. To prevent side reactions, a moderate reaction temperature of 220 °C therefore proved better for hydrogenation of phenols and aqueous phase reforming of methanol.

3.3. Recyclability of the catalyst after in situ hydrogenation

To study the recyclability of the catalyst, a series of Raney Ni catalysts was used repeatedly for *in situ* catalytic hydrogenation of guaiacol at 220 °C for 7 h. The products (identified by GC-MS) from *in situ* hydrogenation of guaiacol using several times recycled

Table 5
The GC-MS products with recycled catalysts on *in situ* hydrogenation of guaiacol.

Yield (wt%)	Recycled time of Raney Ni				Regenerated Raney Ni[a]
	Fresh	One-times	Two-times	Three-times	
Guaiacol conversion	98.22	95.27	85.47	75.09	92.89
Target products	97.71	93.22	75.87	68.53	90.17
Cyclohexanol	64.38	64.42	43.60	45.61	57.21
Cyclohexanone	27.56	24.19	20.89	17.82	23.82
2-Methyl cyclohexanol	1.77	3.11	4.07	2.15	3.57
2-Methoxy-cyclohexanol	3.85	1.43	5.44	1.65	4.32
Cyclohexane	0.15	0.07	1.87	1.30	1.21

Reaction condition: $m(H_2O):m(guaiacol):m(CH_3OH) = 20: 1: 5$, T = 220 °C, $p_0 = 3$ MPa(N_2), t = 7 h.
[a] Regeneration process: The recycled catalyst was washed away the surface adsorbed substance with hot water, then the catalyst was soaked and corroded with 20% NaOH at 80–100 °C for several hours, and finally the catalyst was washed with distilled water or ethanol until PH = 9–10.

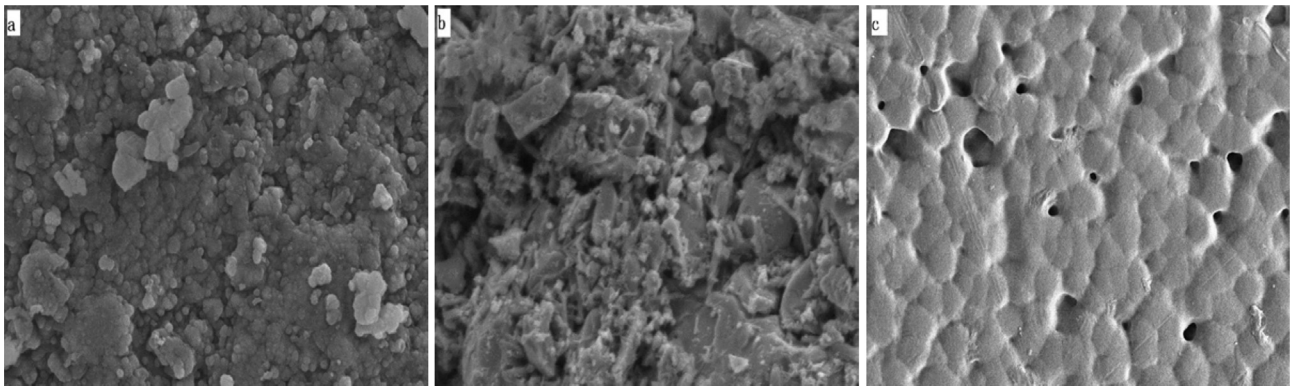

Fig. 2. SEM analysis of fresh Raney Ni (a), three-times recycled Raney Ni (b) and regenerated Raney Ni (c).

catalysts are shown in Table 5. The product distribution demonstrated that guaiacol was mostly converted into cyclohexanol and cyclohexanol derivatives. The conversion of guaiacol was approximately 75% in three subsequent experiments with three-time recycled catalyst. Fresh catalyst gave almost 100% guaiacol conversion and a target product yield of 98% after 7 h. On the other hand, guaiacol conversion was 75% and target product yield 68% using three-time recycled catalyst. The conversion dropped from 98.22% to 75.09%. The product distribution indicated that the catalyst was significantly deactivated during the *in situ* catalytic hydrogenation of phenolic compounds.

The XRD and SEM analyses (Figs. 2 and 3) demonstrated differences between fresh and three-times recycled Raney Ni. The physical properties of fresh and three-times recycled Raney Ni catalyst were also analyzed, as shown in Table 6. From the results, we can speculate that the reason for the catalyst deactivation may be oxidation of the catalyst surface, and/or the porous surface is covered by reactants during the hydrogenation. Accumulation of organic species in the catalyst pores may also contribute to the deactivation process.

To reduce costs, the catalyst should be activated and regenerated for subsequent use in the *in situ* catalytic hydrogenation of phenolic compounds. Catalyst was regenerated after three uses by the previously reported method [30], treating the deactivated Raney Ni with a basic solution. As can be seen in Table 5, regeneration enables recovery of high catalytic activity. The XRD and SEM analyses (Figs. 2 and 3) confirmed that regenerated Raney Ni catalyst was similar to the fresh catalyst. Using the regenerated catalyst, guaiacol conversion reached 92.89 wt% with a target product yield of about 90 wt% after 7 h.

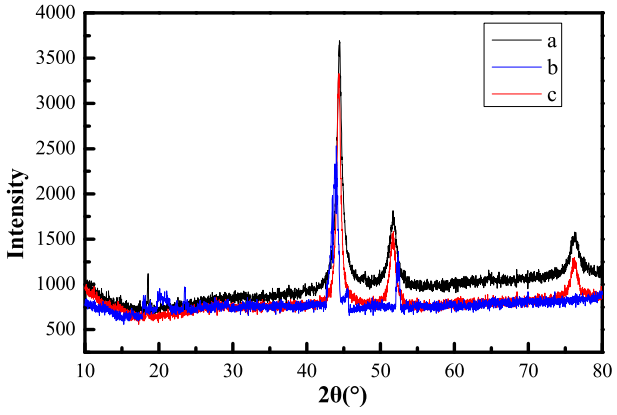

Fig. 3. XRD analysis of fresh Raney Ni (a), three-times recycled Raney Ni (b) and regenerated Raney Ni (c).

3.4. *In situ* hydrogenation of selected model compounds from bio-oil

Pyrolysis of lignin produces oxygen-containing compounds including guaiacol (typically 39%), syringyl (16%), hydroxyphenyl

Table 6
Physical properties[a] of fresh, third recycled and regenerated Raney Ni.

Raney Ni	A_{BET} (m^2 g^{-1})	V_p (m^2 g^{-1})	D_p (nm)
Fresh	15.37	0.013	4.20
Three-times recycled	10.26	0.016	3.90
Regenerated	13.42	0.015	4.10

[a] Evaluated from N_2 adsorption-desorption isotherms.

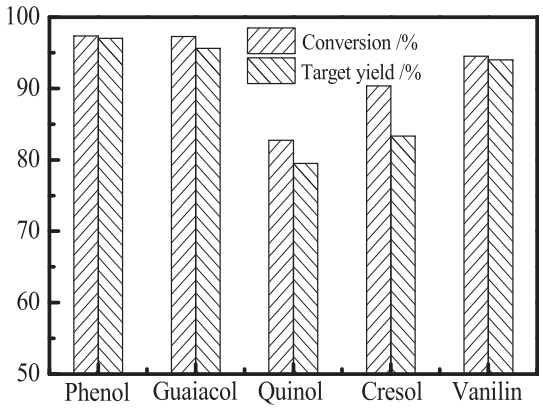

Fig. 4. Results on *in situ* hydrogenation of different phenolic compounds.

derivatives (45%) and other phenolic monomers containing various functional groups, especially methyl, methoxy, and vinyl [31]. 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. Fig. 4 shows the results from *in situ* hydrogenation of different phenols. Most target product yields were more than 83%, except from quinol. The conversions of phenol and guaiacol were about 97%, which were higher than for other phenols. Raney Ni is not only able to catalyze the aqueous phase reforming of methanol but is also general for hydrogenation of different phenols [32]. Accordingly, the *in situ* hydrogenation approach using Raney Ni catalyst can convert most benzene ring structures into cyclohexanes.

3.5. *In situ hydrogenation of phenolic compounds separated from bio-oil*

According to the aforementioned studies, the *in situ* hydrogenation of phenolic compounds from bio-oil was investigated. The GC-MS chromatograms of phenolic compounds before and after *in situ* hydrogenation and their relative compositions are shown in Fig. 5 and Table 7, respectively. It can be seen that in the *in situ* hydrogenation, phenolic compounds were partly converted into alcohols, ketones and esters, and small amounts of unreacted phenolic compounds were detected. It appears that the conversion to hydrogenated products is lower when using a mixture of real lignin pyrolysis products compared to the single model compounds. The real system contained many different compounds, including acids, alcohols, esters and others, which is more complex than the model phenols. It is speculated that the acids in the phenolic compounds from bio-oil can affect catalytic activity.

In addition, the compositions of the acids were significantly altered after *in situ* hydrogenation, resulting in esterification during the upgrading process. Furfural, 2-furancarboxaldehyde and 2-methoxy-2-furyl alcohol identified in the phenolic compounds completely disappeared after hydrogenation. Interestingly, many methyl-cyclopentanones were observed in the hydrogenated products. This is in agreement with a previous report [33] that found 2-methylcyclopentanone in the hydrogenated bio-oil obtained over hydrogenation catalyst. These cyclopentanones were reported to be produced from furfurals via hydrogenation [34]. Cyclohexanol and cyclohexanol derivatives are the principal components of the hydrogenated products. It was clearly observed that the phenol content was drastically decreased from 83.27% to 19.75% after hydrotreatment. Cyclohexanol and its derivatives (including alcohols and ketones) produced from the hydrogenation of phenolic compounds increased to 54.32%.

There were still part of phenolic compounds found in the hydrogenated products. This may be because complex structure phenolic compound with different side chain groups such as methoxy, alkyl ester, alkyl methoxy and ether linkages, are converted into simple structure phenolic compounds by decarbonylation or other reaction because of its active α-hydrogen through hydrogenation [35]. The different phenolic compounds and corresponding hydrogenated products in our study are shown in Table S4. Vanillin may be converted into 4-methyl-2-methoxyphenol or 2-methylphenol via hydrogenation of the aldehyde group. 3-methoxy-4-hydroxyphenylacetic acid is a representative component found at high levels in bio-oil, which could theoretically be converted into Methoxy-4-ethylphenol by esterification with methanol. In addition, small quantities of hydrocarbons, such as propylcyclohexane, were also found. This might result from trace amounts of acid present in the separated phenolic compound fraction, which can act as Brønsted acids and catalyze hydrodeoxygenation of phenolic compounds during the hydrogenation process. Only a small increase in the content of 4-methyl-cyclohexanone was observed in the hydrogenated products. The levels of esters in the products of *in situ* hydrogenation increased dramatically from 2.89% to 20.89%. This may because both esterification and hydrogenation occurred during the upgrading of phenolic compounds.

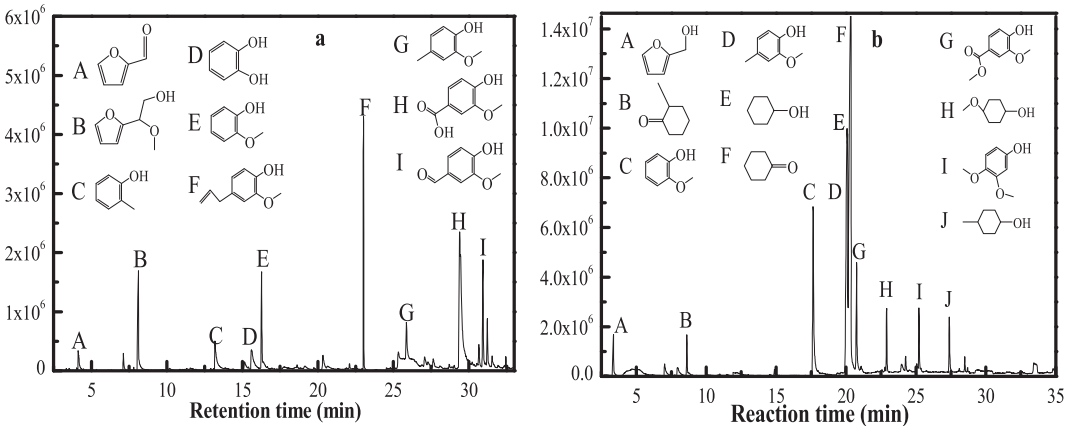

Fig. 5. GC-MS analysis of phenolic compounds before (a) and after (b) *in situ* hydrogenation.

Table 7
The components of phenolic compounds and hydrogenated phenolic compounds.[a]

Retention time	Ingredient	Relative contents (%)	
		Phenolic compounds	Hydrogenated products
	Acids	**3.37**	–
4.412	2,3-dihydroxy acid	2.61	–
29.575	4-hydroxy-3-methoxy benzeneacetic acid	0.67	–
	Alcohols	–	**23.95**
5.350	cyclohexanol	–	11.96
6.816	2-methyl cyclohexanol	–	4.86
10.175	4-methoxy cyclohexanol	–	7.13
	Aldehydes	**6.14**	**4.47**
6.322	dihydro-5-methylfuranone	–	1.78
7.120	furfural	1.96	–
7.569	furfural alcohol	–	2.69
7.757	β-methoxy-2-furanethanol	3.04	–
8.134	2-methoxy-2-furyl alcohol	1.14	–
	Ketones	**2.41**	**30.37**
5.432	cyclohexanone	–	16.07
6.935	4-methyl-cyclohexanone	–	11.62
9.873	1-(2-furanyl)-ethanone	2.24	–
11.217	2-methoxy-cyclohexanone	–	1.51
19.880	1-(2,4,6-trihydroxy-3-methylphenyl)-butanone	0.17	–
	Phenols	**83.27**	**19.75**
16.300	guaiacol	5.19	2.02
17.095	2-methylphenol	5.57	2.71
17.632	4-methyl-2-methoxyphenol	16.13	7.73
18.511	phenol	1.98	0.14
20.350	2-isopropyl-4-methoxyphenol	1.52	–
21.177	4-propyl-2-methylphenol	–	1.02
22.713	vanillin	11.35	5.35
23.013	2-methoxy-4-propylphenol	0.64	0.13
24.106	2,5-dimethoxy-3-phenol aldehyde	1.42	–
26.331	catechol	2.50	–
29.057	eugenol	16.67	0.65
29.714	3,4-dimethoxyphenol	2.56	–
31.373	3-methoxy-4-hydroxyphenylacetic acid	17.74	–
	Esters	**1.69**	**20.69**
23.851	2,3-dihydroxy acid methyl ester	–	1.36
24.761	hexadecanoic acid methyl ester	1.69	0.76
27.546	3-methoxy-4-hydroxybenzoate	–	17.07
28.091	*p*-hydroxybenzoic acid methyl ester	–	1.50
	Others	**3.12**	**0.77**
19.268	1,1-dimethoxy-2-propylbenzene	3.12	–
20.950	2-phenylcyclohexanone	–	0.23
32.012	propylcyclohexane	–	0.54

[a] Reaction condition: $m(H_2O)$:m(phenols):$m(CH_3OH) = 20: 1: 5$, T = 220 °C, $p_0 = 3$ MPa (N_2), $t = 7$ h.

4. Conclusion

Hydrogenation of phenolic compounds separated from bio-oil has been investigated. The *in situ* hydrogenation of guaiacol was conducted at 220 °C for 7 h; the guaiacol was mostly (98.22 wt%) converted into cyclohexanol and cyclohexanol derivatives. The cyclohexanol and cyclohexanol derivatives can be quantitatively dehydrated to cyclohexane-hydrocarbon fuels using common mineral acids within a short time under mild conditions. Using guaiacol as a model compound and Raney Ni catalyst, aqueous phase reforming of methanol combined with *in situ* hydrogenation was superior to traditional hydrogenation. The drawbacks associated with prior bio-oil hydrogenation processes are overcome by operating at moderate temperatures (≤220 °C), with no catalyst coking observed. Recycled catalyst can be regenerated using a simple procedure. The regenerated catalyst is able to achieve guaiacol conversion of 92.89 wt% and a target product yield of 90.17 wt% via *in situ* catalytic hydrogenation.

The *in situ* hydrogenation of phenolic compounds from bio-oil was carried out at 220 °C for 7 h. After upgrading, the compositions of phenolic compounds were improved significantly. After *in situ* hydrogenation, the quantities of phenolic compounds drastically decreased from 83.27% to 19.75%. The contents of cyclohexanol and its derivatives (including alcohols and ketones), produced by hydrogenation of phenolic compounds, increased to 54.32%. In addition, the ester content increased from 2.89% to 20.89%. During the *in situ* process, hydrogenation and esterification were the main reactions of the phenolic compounds from bio-oil. In conclusion, the *in situ* hydrogenation process could be an efficient method to convert renewable phenolic compounds or other real bio-oil systems into hydrocarbon transportation biofuel.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.renene.2016.12.054.

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