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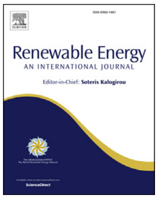

# BTX from the gas-phase hydrodeoxygenation and transmethylation of guaiacol at room pressure

Xiwei Xu [a], Enchen Jiang [a, *], Yanhong Du [a], Bosong Li [b, c]

[a] College of Materials and Energy in South China Agricultural University, Guangzhou 510640, PR China
[b] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, PR China
[c] Guangzhou Experimental Station, Chinese Academy of Tropical Agricultural Sciences, Guangzhou 510140, PR China

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## ABSTRACT

Biosourced aromatics (benzene–toluene–xylene (BTX) and phenols) could be obtained by catalytic hydrodeoxygenation (HDO) coupled with transmethylation at atmospheric pressure in a fixed-bed reactor. We choose guaiacol as a model compound to investigate the catalytic HDO over Fe/Ni/HBeta catalyst. The active amount (5%–15%), temperature (250–400 °C), and 1/WHSV (1.5–4.0) significantly influenced the hydrogenolysis of the $C_{aromatic}$–O bond and transmethylation. The mechanism showed that feed and intermediate products formed the “surface pool” on the catalyst surface, which enabled the HDO reaction by the reduced intermediate species (Z-$FeH^{2+}$ and Z-$NiH^{+}$). Fe/Ni/HBeta exhibited good activity for both methyl transfer and HDO. Moreover, the aromatic ring did not undergo catalytic hydrogenation, and most methyl or methoxyl molecules transferred onto the phenolic or benzene ring and remained after deoxygenation. Consequently, carbon loss was minimized, and hydrogen consumption was reduced.

## 1. Introduction

Upgrading pyrolysis bio-oil from lignin degeneration is challenging. Aromatic hydrocarbons are the building blocks and key products from lignin pyrolysis bio-oil [1,2]. In particular, BTX, which comprises conventional fuel additives and solvents, are starting blocks for plastics, rubber, and fiber, among others [3,4]. Traditionally, BTX products originate from catalytic-reforming processes of naphtha or paraffins refined from petroleum, including naphtha reforming with Pt/$Al_2O_3$ catalyst and paraffin conversion with Ga/ZSM-5 catalyst). Lignin valorization for aromatic hydrocarbons such as BTX is expected to significantly impact lignin biorefinery and mitigate the fossil-energy crisis [3–5].

Hydrodeoxygenation (HDO) is important in bio-oil conversion to obtain chemicals that are used as the fuel or fuel additives. Pyrolysis and liquid-phase hydrogenation are intensively studied [3]. Currently, liquid-phase hydrogenation involves treatment with high pressure (50–100 bar) at temperature (250–500 °C) in a solvent [6–8] with $H_2$ or an H donor (e.g., alcohol). However, the main products are difficult to separate from catalyst mixtures, byproducts, unreacted lignin, and solvent [9]. The cost of solvent and requirement of high-pressure equipment are also important problems in liquid-phase hydrogenation. For these reasons, the gas-phase HDO of pyrolysis bio-oil is deemed a good alternative because of the separation convenience and non-requirement of solvent.

In the present research, we aimed to convert bio-oil refined from lignin by gas-phase HDO at room pressure and low temperature. Guaiacol (with one phenyl ring, –OH, and –$OCH_3$), which is the representative of phenol derivatives and lignin-derived oligomers [10], was used as a model compound. The HDO of compounds from biomass at room or low pressures have been previously studied (Table 1). We know that most of them use noble metals as active materials, and the conversion of lignin-based materials is around 0%–100%. In our research, we use the transition metals Fe and Ni as active components and achieve >80% guaiacol conversion. The content of BTX and other aromatic hydrocarbon exceeds 20%, and the hydrocarbon content is much lower at room than at high pressure. The support also plays an important role in the conversion. During the process of bio-oil hydrotreating, the oxygen content of phenolics significantly declines over sulfided catalysts [18–22]; however, this process results in a significant loss of carbon number, a reduction in liquid products, and a high consumption of

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* Corresponding author.
*E-mail address:* jiangenchen200801@hotmail.com (E. Jiang).

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**Table 1**
The research of Lignin-Based Compounds HDO.

| Entry | Active phase | Support | *T*(K) | *P* (atm) | Feed composition (%) | X (%)[a] | $Y_{aromatics}{}^{b}$ (%) | Ref |
|---|---|---|---|---|---|---|---|---|
| 1 | Pt | HBeta and $SiO_2$ | 673 | 1 | 2% anisole with 98% $H_2$ as the carrier | 0–100 | 5–85 | [11] |
| 2 | Pt–Sn | Carbon nanotubes coated monolith | 673 | 1 | 0.6% guaiacol or anisole with 16.9% $H_2/N_2$ as the carrier gas | 0–100 | 0–70 | [12] |
| 3 | Pd and CoMo | $Al_2O_3$ | 573 | 1 | 0.024% guaiacol with 80% $H_2/N_2$ as the carrier gas | 1–70 | 0 | [13] |
| 4 | Pd–$Nb_2O_5$ | $SiO_2$ | 170 | 2.5 | – | – | (94–95%) | [14] |
| 5 | Pt | $Al_2O_3$ | 300–500 | 1 | 2% cresol with $H_2$ | – | – | [15] |
| 6 | Mo2 | C | 423 | 1 | $H_2$/anisole molar ratio similar to 110 | – | – | [16] |
| 7 | Pt | Mesoporous Y and mesoporous MFI | 523 | 40 | – | 0–90 | 0–90 | [17] |
| 8 | Fe–Ni | H-Beta | 523–673 | 1 | 8% guaiacol with 92% $H_2$/Ar as the carrier gas | 80–100 | 0–20 | This paper |

[a] Conversion of lignin-based material.
[b] Carbon content of aromatic products.

hydrogen. Currently, zeolite is widely used in bio-oil upgrading to reduce the carbon loss and the cost of $H_2$. For example, Lin et al. [23–25] improved hydrogen efficiency during the process of hydrogenation of aromatic hydrocarbons over supported Pt catalysts at room pressure and high temperature with low $H_2$ consumption). Although a considerable number of researchers have examined guaiacol HDO, studies on the effects of carbon loss combined with HDO are few. In the present study, we focus on the HDO and transmethylation of guaiacol with bimetal and zeolites.

## 2. Experimental

### 2.1. Catalyst preparation

HBeta (grounded and sieved <0.45 mm) was impregnated in iron nitrate nonahydrate and nickel nitrate nonahydrate (Sigma) solution in deionized water. The mixture was ultrasonicated at room temperature for 30 min and dried at 100 °C for 24 h. Afterwards, they were calcined at 500 °C for 3 h in air, ground, and sieved (0.177–0.43 mm). The amount of iron and nickel was controlled at 5 wt%, 10 wt%, and 15 wt% Fe, Ni-based on the mass of support.

### 2.2. Characterization

Specific surface areas and pore volumes were determined through $N_2$ adsorption/desorption isotherms at 77 K collected on a Gemini VII 2390 gas-adsorption analyzer.

Temperature-programmed ammonia desorption ($NH_3$-TPD) was analyzed using a Chembet Pulsar TPR/TPD. Every sample had initially been heated at 300 °C for 2 h and cooled down to 50 °C. Then, 0.1 g samples were saturated with dried ammonia by replacing the $N_2$-flow with $NH_3$ for 2 h and treated with 50 ml/min $N_2$ flow for 1 h to remove remaining $NH_3$. The temperature was slowly heated up to 800 °*C* at a rate of 10 °C/min, and ammonia was flushed out with 50 ml/min $N_2$.

The amount of carbon deposition on spent catalysts were tested using a STA449CJupiter® thermogravimetric analyzer. Scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) analyses of the surface morphology of fresh catalysts and the carbon deposited onto these spent catalysts were performed as in our previous research [26,27].

The crystallographic phases of the samples were confirmed by XRD measurements (D8 VENTURE Bruker, CuKα radiation). The powder patterns were collected within a 2 theta range from 5° to 80° with a step of 0.02° and 30 s counting time per angle.

The extractive from $CCl_4$ solution of carbon deposition was analyzed by a GC-MS system (SHIMADZU QP2010 Ultra) equipped with an Rtx-Wax column and an FID detector. The spent catalyst was dipped in the $CCl_4$ solution and shook with ultrasonic for 0.5 h at room temperature and stayed at room temperature for 20 h before it was analyzed by GC-Mass. The GC-MS conditions were as follows. The capillary column was 19091IV-136INNOWAX. The initial temperature was set at 70 °C, held for 3 min before increasing to 170 °C at a heating rate of 10 °C/min. Finally, temperature was increased to 220 °C at a heating rate of 5 °C/min. The temperature at the entrance was 250 °C, and the ratio of diversion was 30:1. The MS: EI condition was chosen as the ion source, the energy of the electron was 70 eV, and the scanning range was 35–350 m/z.

### 2.3. Catalytic runs

The experimental setup is shown in Fig. 1. $H_2$ was introduced with a mass flow controller. Guaiacol was injected with a syringe pump. A fixed bed made of a 30 mm i. d. quartz tube was used as the catalytic reactor. The conditions for all runs were P = 1–1.1 bar. The molar ratio of $H_2$ and guaiacol was 40:1. All runs lasted for 60 min. The catalysts used in the reaction were held by the quartz wool. Before the reaction, guaiacol was pumped into the tube, vaporized, and then mixed with $H_2$. The part of quartz tube reached out of the oven was kept at 220 °C to avoid condensation. The products were cooled and collected, and the liquid products were analyzed with a GC system (Agilent 19091N-133) equipped with an HP-INNOWax column (30 m × 250 μm × 0.25 μm) and an FID detector. Acetophenone served as the internal standard.

### 2.4. Definition

$$Conversion = \frac{M_{(reactant)in} - M_{(reactant)out}}{M_{(reactant)in}} \times 100\% \qquad (1)$$

The conversion percentage of products was calculated using Eq. (1). $M_{(reactant)in}$ is the initial molar amount of reactant, and $M_{(reactant)out}$ is the molar amount of reactant remaining after reaction.

$$C_i\% = \frac{M_{ci}}{\sum M_{cn}} \times 100\% \qquad (2)$$

$C_i$%, which was the content of i product, was calculated using Eq. (2), where $M_{ci}$ is the molar amount of product i, and $\sum M_{cn}$ is the total molar amount of all liquid products.

$$W_{CH_4}\% = \frac{V_{CH_4}}{V_{H_2} + V_{CH_4} + V_{CO_2}} \times 100\% \qquad (3)$$