

A Kinetic Experiment of Vapor Phase Hydrodeoxygenation of a Bio-Oil Model Compound over PdFe/Al-MCM-41 Catalyst

Nga T. T. Tran, Thanh H. Trinh, Yoshimitsu Uemura, Anita Ramli

Abstract: *The lignocellulose biomass resource can be used not only as direct energy in combustion, but also as a more valuable fuel after conversion and upgrading process. Fast pyrolysis is an approach that produces bio-oil from biomass. However, it is very difficult to directly utilize the pyrolysis oil because of the presence of oxygenated compounds (e.g., acids, esters, alcohols, ketones, furans and phenols). Hydrodeoxygenation (HDO) is a prominent process to upgrade bio-oil. The HDO experimental and kinetic study were conducted using PdFe/Al-MCM-41 catalyst in a tubular fixed-bed reactor. Kinetic model was proposed and applied to 21 reaction pathways, 13 compounds. The detailed reaction pathways of HDO of guaiacol and their reaction rates were clarified for a PdFe catalyst. The major reaction pathway of HDO of guaiacol is direct production of phenol and then benzene. The detailed kinetic model is an effective tool to estimate the major reaction pathways of HDO process.*

Index Terms: lignocellulose, biomass resource, pyrolysis oil

I. INTRODUCTION

The lignocellulose biomass resource can be used not only as direct energy in combustion, but also as a more valuable fuel after conversion and upgrading process [1]. Thermal conversion of biomass is one of prominent technology to produce bio-char, bio-oil and bio-gas [2]. In comparing with torrefaction or gasification, pyrolysis is conducted at moderate temperature (400–600 °C) and in the absence of oxygen [3]. The pyrolysis oil (bio-oil) product has significant advantages in storage [4], transport and ability to utilize as useful petrochemical and fuel [5]. However, it is very difficult to directly utilize the pyrolysis oil because the presence of oxygenated compounds (e.g. acids, esters, alcohols, ketones, furans, phenols) makes the bio-oil low heating value, low thermal stability. Hence it is required to remove the oxygen from these compounds by hydrodeoxygenation and makes the bio-oil more stable.

Depending on the reaction conditions, reactor type, utilized catalyst, type of bio-oil, the reaction pathway and mechanism will be different. To further understand the HDO mechanism and reaction pathways, it is necessary to

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investigate the HDO kinetics. To ease understanding and investigation of complex reactions occurring during the HDO process, various model compounds were chosen to study the reaction pathways and kinetic of reactions. Sitthisa [6] studied the kinetic and mechanism of HDO using Cu/SiO₂ catalyst with an assumption that the surface reaction was the rate-determining step and the Langmuir–Hinshelwood model fitted the kinetic data of furfural deoxygenation. He et al. [7] came from another direction in which they estimate the overall reaction mechanism for HDO of phenol based on activation energies of individual reaction steps. This is a prominent way in catalyst optimization which involved the cascade reactions comprised hydrogenation and dehydration steps by balancing metal and acid sites ratio. For the kinetic in vapor phase, Gao et al. [8] studied the reaction of guaiacol in a fixed bed reactor under ambient pressure using Pt/C catalyst. There were two pathways exist for phenol production, i.e., direct demethoxylation of guaiacol and dehydrolysis of catechol. They found that the guaiacol conversion was followed a second reaction order in their research [8] while the 4-methyl anisole conversion was followed the first order reaction in Runnebaum [9] research. Reaction rate constants were estimated for five individual reactions at three temperatures (275, 300, and 325 °C). Lu et al. [10] investigated the reaction mechanism of guaiacol HDO over Pt(111) catalyst from quantum theoretical approach using density functional theory (DFT) and microkinetic modeling. Their results suggest that catechol was the preferable product comparing to other deoxygenation product, such as phenol or benzene.

In the authors research [11], a details GC analysis of products were obtained during the HDO process with the total carbon balance ranging between 91–97 mol.%. In addition to the main compounds such as phenol, cresol, etc., there were a lot of side products that can be counted as trimethyl phenol, xylenol, trimethyl benzene, etc. Lack of taken into account the present of those side products in kinetic model may reduce the accuracy of the kinetic model and also the whole process mechanism. In order to have a deep understanding in the kinetic and reaction pathway of the vapor phase HDO reaction, this manuscript investigate the HDO of guaiacol under vapor phase condition over PdFe/Al-MCM41 support and establish a detail kinetic model that taken into account of those side products.



II. METHODOLOGY

A. Catalyst preparation

Aluminosilicate Al-MCM-41 support (3–4% Al₂O₃) supplied by ACS Material was activated in air at 500°C for 14h. The bimetallic catalyst containing of 10 wt% Fe metal and 2 wt% Pd metal was prepared by the incipient wetness co-impregnation method. Aqueous solutions containing metal precursor were first impregnated on the support overnight at 33°C, and then dried at 105°C for 8 h, followed by calcinations at 500°C for 4 h in air. The calcined catalysts were sieved to give the particles in the size range of 35–60 mesh.

B. Experimental Set up

Catalytic reaction was conducted in a tubular fixed-bed reactor under ambient pressure. Before the reaction, the catalyst bed was reduced with hydrogen (90 mL/min) at 450 °C for 120 min. Guaiacol was fed at flow rate of 1.08 mL/h using a syringe pump, and H₂/guaiacol molar ratio was kept at 25 for all runs. The W/F which is defined as the ratio of catalyst mass (g) to organic feed flow rate (g/h) was adjusted by varying the amount of catalyst. The experiments were conducted for five catalyst weight (W), i.e., 0.25, 0.5, 1, 2, and the products were collected at the outlet and for 30 minutes. Liquid and gas products were analyzed by GC-FID (Shimadzu GC-2014) and GC-TCD (Shimadzu GC-8A), respectively. More details on experimental set up is presented elsewhere [11].

C. Kinetic Modelling

From the details analysis of products obtained during the experiments, the possible pathway was proposed as seen in Fig. 1. Based on the design equation for a fixed-bed reactor and all the possible reaction pathways for each individual compound, the consumption/formation rates of reactant (guaiacol) and products *i* are as below:

$$\frac{dF_{GUA}}{dW} = -r_1 - r_{10} - r_{12} - r_{14} - r_{15} - r_{17} \quad (1)$$

$$\frac{dF_i}{dW} = \sum_j v_j r_j \quad (2)$$

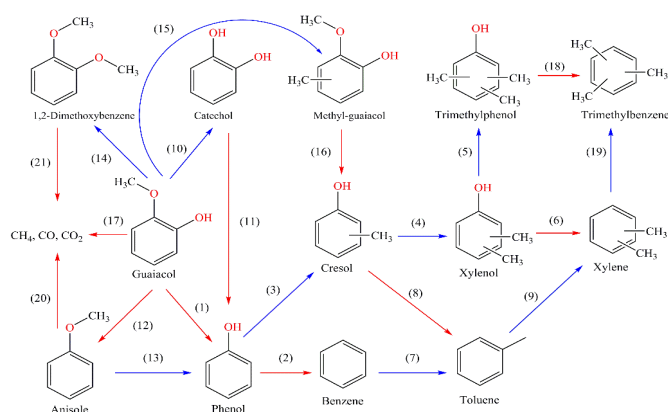


Fig. 1. Possible reaction pathway for vapor phase HDO reaction for PdFe based on the analysed products.

where v_j is the sign represented the formation or

consumption of F_i . It is positive for the product and negative for the reactant in each individual reaction. j subscript is the individual reaction j in Fig. 1.

Assumed that one mole of reactant produces only one mole of product, we obtained the balance as below:

$$F_{GUA} + \sum_i F_i = F_0 \quad (3)$$

If all product follow the ideal gas law, $PV = nRT$, the partial pressure p_i can be express as

$$p_i = F_i \times \frac{P_0}{F_0} \quad (4)$$

where p_0 is the initial inlet pressure.

For each reaction steps, the reaction rate r_j for the intermediate i will be

$$r_j = k_j p_i \quad (5)$$

Replace the p_i in (5) by (4):

$$r_j = k_j p_0 \times \frac{F_i}{F_0} \quad (6)$$

Combine k_j and p_0 , we have

$$r_j = k'_j \times \frac{F_i}{F_0} \quad (7)$$

In this case, F_i/F_0 is the mole fraction of product i in the outlet, n_i , the equation becomes

$$r_j = k'_j \times n_i \quad (8)$$

Divide (2) to F_0 , we can obtain the consumption/formation rate of the reactant or products as below:

$$\frac{dn_i}{dW} = \sum_{i,j} \left(v_j k'_j \times \frac{n_i}{F_0} \right) \quad (9)$$

The reduced reaction rate equation for each individual compound is

$$\frac{dn_i}{dW} = \sum_{i,j} \left(v_j k''_j \times n_i \right) \quad (10)$$

where k''_j is the reduced reaction rate constant, $\text{gc}at^{-1}$; n_i is the mole fraction of product i over the mol of feeding guaiacol, dimensionless.

Equation (10) was applied for all compounds identified as mentioned in Fig. 1, and the set of ODE equation were solved using ode45. Nonlinear least square method was used to fit the experimental data and obtained the reaction rate constant k''_j for each individual reaction with an assumption that all the individual reactions are followed 1st order reaction. The kinetic model was established for PdFe to estimate the individual reaction in the reaction pathway.

III. RESULTS AND DISCUSSION

A. Catalysts characterization

Table 1 demonstrates the textural properties of metal-modified catalysts and support. After calcination, the metal-modified catalysts showed a slight decrease in surface area and pore volume as expected. It caused by the partial blockage of pores



during the metal impregnation. Moreover, the bimetallic catalysts had lower surface area and pore volume than monometallic due to their higher metal concentration. However, the mesoporosity of catalysts did not change significantly. Of interesting here is the particle sizes of metals are larger than the pore size of the support (Table 1). It means that the deposit of metal was mainly on the external surface of the support rather than inside the pore surface of the support.

Table 1: Textural properties of Al-MCM-41 supported bi-metallic catalysts.

Samples	S _{BET} (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Particle size (nm)
Al-MCM-41	742	3.21	0.56	–
Pd-Fe/Al-MCM-41	507	3.69	0.42	17.21

B. Hydrodeoxygenation of Guaiacol Experiment over Bimetallic Catalyst

Fig. 2 compares the conversion of guaiacol and product yields over the supported bi-metallic catalysts at the same conditions. Even though these two catalysts had high conversion of guaiacol, the products distribution were very different. Phenol yield in PdFe is about 1.5 time than that of PdCo. In addition, PdFe has higher mono-oxygenated products and lower gas phase (which mainly content methane) yields than PdCo. The total HDO yields of PdFe and PdCo were around 52 and 44%, respectively. In other words, PdFe shows higher HDO activity than PdCo catalyst.

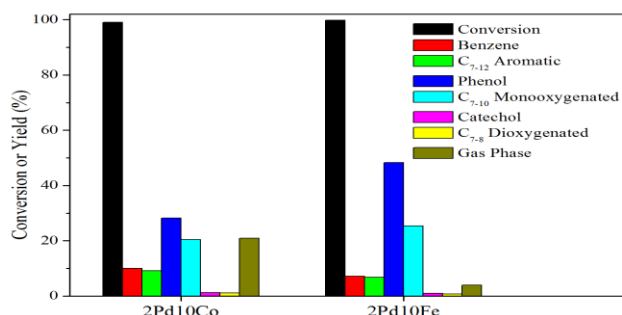


Fig. 2. HDO of guaiacol over PdFe catalyst in comparison with PdCo catalyst. Reaction conditions: T = 400°C, P = 1 bar, W/F = 0.83 h, H₂/Gua = 25, TOS = 30 min.

C. Kinetic Study of HDO of Guaiacol over PdFe Catalyst

Kinetic model is as a tool to justify the direction of individual reactions during the HDO process. From the experimental data for PdFe catalyst, the kinetic model was established for 21 reactions and 13 compounds. Reaction constants were described in Table 2 and the root means square of deviation (RMSD) = 0.7932 mol. %, NRMSD = 0.1115. Fig. 3a shows the experimental and kinetic model profile of some representative compounds during the HDO process over PdFe catalyst.

Table 2: Reactions and reaction constants of each individual step over PdFe/Al-MCM41 catalyst.

No.	Reaction	k'' (g _{cat} ⁻¹)	Average formation/
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			consumption (mol.% g _{cat} ⁻¹)
1	GUI --k1--> Phenol	3.75E+00	99.9848
2	Phenol --k2--> Benzene	2.08E-01	8.9201
3	Phenol --k3--> Cresol	6.37E-02	2.7344
4	Cresol --k4--> Xylenol	1.48E-01	2.0155
5	Xylenol --k5--> TriMePhenol	2.21E-01	0.4362
6	Xylenol --k6--> Xylene	1.00E-06	0.0000
7	Benzene --k7--> Toluene	6.99E-01	3.9127
8	Cresol --k8--> Toluene	1.00E-06	0.0000
9	Toluene --k9--> Xylene	7.26E-01	1.6113
10	GUI --k10--> CAT	0.097425	2.5999
11	CAT --k11--> Phenol	4.06E-01	0.2404
12	GUI --k12--> Anisole	2.48E-01	6.6148
13	Anisole --k13--> Phenol	1.147486	1.3428
14	GUI --k14--> 12DiMeBenzene	1.05E-01	2.8060
15	GUI --k15--> MeGUI	9.99E-01	26.6560
16	MeGUI --k16--> Cresol	23.11009	11.3286
17	GUI --k17--> 7Methane	1.52E-01	4.0564
18	TriMePhenol --k18--> TriMeBenzene	1.00E-06	0.0000
19	Xylene --k19--> TriMeBenzene	8.67E-01	0.5399
20	Anisole --k20--> 7Methane	1.00E-06	0.0000
21	12DiMeBenzene --k21--> 7Methane	1.058643	0.4658

The direct reaction from guaiacol (GUI) formed phenol, methyl guaiacol, anisole, and catechol with k'' of 3.75, 0.9988, 0.2478, and 0.0974 g_{cat}⁻¹, respectively (see Table 2). The reaction constant to produce anisole and catechol are rather smaller than phenol and methyl guaiacol. It means that the reaction from guaiacol is following the order phenol > methyl guaiacol > anisole > catechol. From the bond dissociation energy (BDE) point of view Song [12], the BDE of the C-O bonds are following the order C_{sp3}-OAr < C_{sp2}-OMe < C_{sp2}-OH, which means that GUI is easily produced catechol > phenol > anisole. The formation of anisole is following this BDE rule and is the most difficult reaction from guaiacol. However, the formation of phenol is higher than that of catechol from our kinetic results, and the similar results were also observed in the research of Luo [13] and Song [12]. Instead of directly break the C-O bond, in the present of catalyst, the mechanism of direct demethoxylation of guaiacol can be explained by the rapid hydrogenation of the double bond (HO-C_{sp2}=C_{sp2}-OCH₃) of the aromatic ring or the hydrogenation of the C=O keto form of the methoxy group [14]. These mechanisms may require lower barrier energy as comparing with the required energy to produce catechol through breaking the C_(sp3)-OAr. In addition, the present of methanol in the product is an evidence of the direct demethoxylation of guaiacol to phenol [15].



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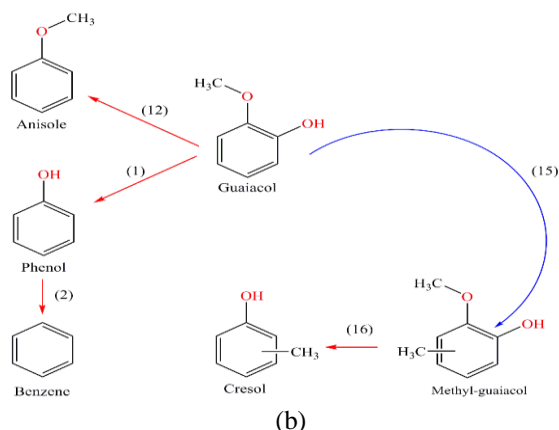
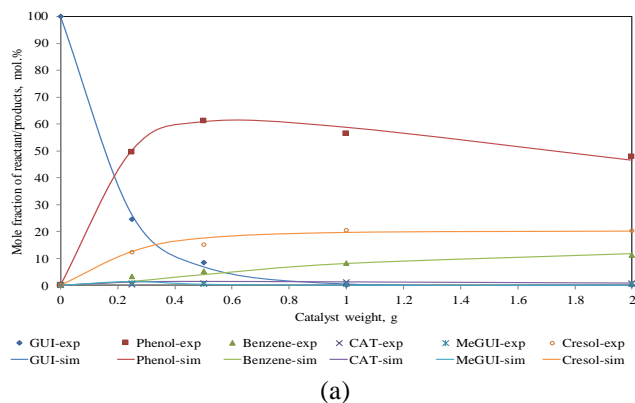


Fig. 3. (a) Experimental and kinetic model profiles of reactant and some representative products versus catalytic weight. Reaction conditions: $T = 400\text{ }^{\circ}\text{C}$, $P = 1\text{ bar}$, $\text{H}_2/\text{GUI} = 25$, $\text{TOS} = 30\text{ min}$. (b) Major reaction route for PdFe based on kinetic results (average reaction formation/consumption $> 5\text{ mol.}\%$ g^{-1}).

The reaction from methyl guaiacol to cresol takes place very fast, therefore most of the methyl guaiacol produced from reaction (15) immediately converted to cresol while the reaction forming cresol from phenol is slow, $k'' = 0.06367466\text{ g}_{\text{cat}}^{-1}$. In contrast, the reaction from cresol to toluene is very slow, or, in other words, there may be no reaction forming toluene from cresol. Over PdFe catalyst, the HDO process mainly produced phenol, the further reaction to eliminate the remaining oxygen and forming benzene, toluene. Another route to eliminate oxygen is through producing cresol. However, from the kinetic model, the average consumption of cresol to produce toluene and xylene were about 0 and 2 $\text{mol}/\text{g}_{\text{cat}}^{-1}$. It seems that cresol is a stable compound hence it is difficult to eliminate or transform to other compound such as toluene or xylene and then to tri-methyl-benzene. Based on the average formation/consumption of individual reaction, it seems that PdFe has a high selectivity toward HDO than that of PdCo (data is not presented). To classify the major reaction route, the route which had average formation/consumption less than 5 $\text{mol.}\%$ $\text{g}_{\text{cat}}^{-1}$ was eliminated from the proposed reaction pathway, and the major HDO reaction route of guaiacol over PdFe catalyst is illustrated in Fig. 3b.

IV. CONCLUSIONS

The detailed reaction pathways of HDO of guaiacol and

their reaction rates were clarified for a PdFe catalyst. The major pathway of HDO is direct production of phenol and then benzene. The detailed kinetic model is an effective tool to estimate the major reaction pathways of HDO process.

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