



# Noble metal catalyzed aqueous phase hydrogenation and hydrodeoxygenation of lignin-derived pyrolysis oil and related model compounds



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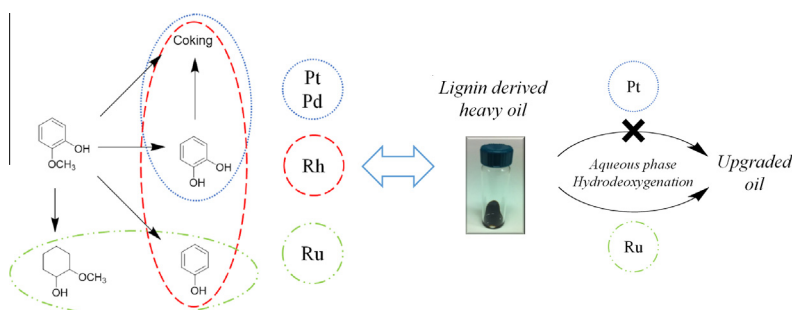
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## HIGHLIGHTS

- Three model compounds were used to study the lignin derived heavy oil upgrading.
- Four noble metal catalysts were evaluated and the reaction mechanism was deduced.
- The coking induced catalyst deactivation was systematically studied and characterized.
- Two catalysts (Pt and Ru) were picked for lignin heavy oil upgrading.
- Tentative reaction path of oil upgrading matches mechanism from model compound study.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Aqueous phase hydrodeoxygenation of lignin pyrolysis oil and related model compounds were investigated using four noble metals supported on activated carbon. The hydrodeoxygenation of guaiacol has three major reaction pathways and the demethylation reaction, mainly catalyzed by Pd, Pt and Rh, produces catechol as the products. The presence of catechol and guaiacol in the reaction is responsible for the coke formation and the catalysts deactivation. As expected, there was a significant decrease in the specific surface area of Pd, Pt and Rh catalysts during the catalytic reaction because of the coke deposition. In contrast, no catechol was produced from guaiacol when Ru was used so a completely hydrogenation was accomplished. The lignin pyrolysis oil upgrading with Pt and Ru catalysts further validated the reaction mechanism deduced from model compounds. Fully hydrogenated bio-oil was produced with Ru catalyst.

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## 1. Introduction

The growth of global energy consumption makes biofuel an attractive alternative fuel source. Lignin, the second most abundant nature-made polymer, receives little attention because of its

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complex structure and poor thermal stability. The US paper industry produces over 50 million tons of lignin per year. Over 98% of it is burned directly (Calvo-Flores and Dobado, 2010). Another major source of lignin is bioethanol plant. Regardless of the technology employed, almost all bioprocessing approaches result in the formation of a waste lignin process stream (Wyman, 2007). Different from other biomass wastes, lignin is energy-rich. Therefore it is pragmatic and desirable to find an efficient approach to convert lignin into fuel and useful chemicals.

Pyrolysis is an economical and feasible approach for lignin conversion (Maschio et al., 1992). Slow pyrolysis produces heavy oil and light oil (Mohan et al., 2006). Heavy oil consists of compounds that are water-insoluble. The molecular structures in heavy oil are mainly dimers and trimers. Light oil is mostly composed of water-soluble monomers. Both oil products possess several poor properties, such as thermal instability, corrosiveness, low volatility, high coking tendency, low heating value, and immiscible with petroleum fuels (Mu et al., 2013). Further upgrading of pyrolysis oil provides insight into the conversion from biomass to fuels.

Hydrodeoxygenation (HDO) has been widely used for pyrolysis bio-oil upgrading (Furimsky, 2000). Noble metal catalysts are very reactive in HDO reactions. The performance of the commonly used noble metal catalysts for HDO reaction was reviewed in our previous publication (Mu et al., 2013). The sulfur-induced noble metal catalyst deactivation does not pose a problem in this study because biomass contains a small amount of sulfur. Most of the studies reported in the review paper were done under various conditions with different supporting materials, making the evaluation of catalytic performance very difficult.

The purpose of this study is to compare the performance of commonly used noble metal catalysts at similar condition to understand the mechanism differences between noble metal catalysts in HDO reaction. Four noble metal catalysts (Pd, Pt, Rh, Ru) were used with activated carbon being the support material. Compared to oxidic supports, activated carbon is suitable to study the catalytic behavior of active metal without interference due to its neutral surface and little interaction with metals (Furimsky, 2008). DI water with pH 7 was used as dispersant in the reaction. The neutral aqueous phase can reveal the genuine catalytic behavior of the noble metals. By understanding the detailed reaction mechanism from model compound study, two catalysts with low and high robustness were picked and applied to real lignin derived pyrolysis oil.

## 2. Methods

### 2.1. Lignin purification and process of pyrolysis

The milled pinewood was ethanol-organosolv pretreated as previously described in literature (Hallac et al., 2010). Pyrolysis experiments were conducted in a quartz tube heated with a split-tube furnace. The experiment condition can be found in previous publication (Ben and Ragauskas, 2011a).

### 2.2. Hydrogenation reaction for model compounds and EOL heavy oil

All catalysts used in this study were purchased from Sigma-Aldrich. The catalysts were used directly without any pretreatment. HDO of both model compounds and EOL heavy oil were carried out in a 75 mL Parr 4590 Micro Stirred Reactor. One step HDO was used in model compounds study. In a typical run, 25 mmol model compound and 20 mL DI water were loaded in a glass liner with 50.0 mg of 5 wt% noble metal catalyst. The reactor was purged 5 times with nitrogen gas and then 5 times with hydrogen gas consecutively. When the target temperature was

reached, the reactor is pressurized with hydrogen gas to 4.0 MPa. The reaction was conducted under 250 °C for 2 h.

For EOL heavy oil, HDO reaction was performed in two steps. In the first step, 150.0 mg of heavy oil and 20.00 mL of DI water were loaded in a glass liner with 15.0 mg of noble metal catalyst. The reactor was purged 5 times with nitrogen gas and then 5 times with hydrogen gas consecutively. The reactor was heated at 300 °C for 4 h and the pressure was stable at ~14 MPa. The aqueous solution of the products was filtered through a 0.45 µm PTFE syringe filter to remove the spent catalyst. The filtrate was further upgraded by the second step of HDO, which was conducted at 250 °C for 2 h with the initial hydrogen pressure of 10 MPa and 10.0 mg fresh catalyst.

### 2.3. Characterization of catalysts and oil products

BET surface area measurements of the catalysts were carried out in a Quadrasorb system from Quantachrome instruments. Metal dispersions were measured in a AutoChem II 2920. TEM images were taken with a JEOL 100CX II 100 kV. The carbon contents of the upgraded bio-oil were determined by total organic carbon (TOC) analyzer (Ionics Inc 1555B). All products were characterized by a Bruker Avance/DMX 400 MHz NMR spectrometer. The detailed parameters were reported in previous publications. (Ben and Ragauskas, 2011a,b)

## 3. Results and discussion

### 3.1. Reactivity with model compounds

Phenol, catechol and guaiacol are commonly used as model compounds to study the reaction mechanism of lignin pyrolysis oil upgrading. The conversions of these model compounds for all four catalysts are summarized in Fig. 1(a). As shown in Fig. S1 (see Supplementary Information), three major reaction pathways are observed in the HDO of guaiacol: (1) direct hydrogenation of aromatic ring, (2) demethylation reaction and (3) demethoxylation reaction. No transalkylation reaction is observed due to the use of a carbon support. For phenol and catechol, all four catalysts show similar reactivity. However, both Pt and Pd catalysts could not catalyze the HDO reaction of guaiacol.

The experimental result with different guaiacol/catalyst weight ratios is shown in Fig. 1(b). Ru was the best catalyst at all ratios. When the weight ratio was 20, the conversion of Ru catalyzed guaiacol HDO was almost 100%. Rh was the second best catalyst. When the weight ratio of guaiacol to the catalyst was decreased, the difference in the conversion of guaiacol with Ru and Rh catalysts was also decreased. Pt and Pd catalysts had approximately zero guaiacol conversion at a weight ratio of 20 and 60. When the weight ratio was decreased to 2, the conversions were over 80%.

#### 3.1.1. Platinum and palladium catalyzed guaiacol HDO

Runnebaum et al. reported that demethylation was a fast reaction step in the HDO of guaiacol using Pt catalyst, which yielded catechol (Runnebaum et al., 2012). Another paper demonstrated that coke was formed with the presence of both guaiacol and catechol (Furimsky, 2000). It is reasonable to propose that the presence of guaiacol and catechol deactivates both Pt and Pd catalysts. To validate this hypothesis, three groups of control experiments were performed and summarized in Table S1 (see Supplementary Information).

In group 1, Ru catalyst was used in the HDO reaction of both guaiacol and catechol because Ru exhibits excellent reactivity with guaiacol or catechol individually. The low guaiacol conversion

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