

Pd/C Catalyzed Transfer Hydrogenation of Bio-oil using 2-Propanol as Hydrogen Source

Hoda Shafaghat, Haewon Ryu, Young-Kwon Park*

School of Environmental Engineering, University of Seoul, Seoul 02504, Korea

**Corresponding author: catalica@uos.ac.kr*

Highlights

- Transfer hydrogenation of guaiacol using liquid hydrogen source of 2-propanol.
- Mild operating conditions of temperature and pressure for guaiacol deoxygenation.
- High efficiency of Pd/C in transfer hydrogenation of guaiacol to alkylated cyclohexane.

1. Introduction

Pyrolysis oil (bio-oil) cannot be used directly for transportation fuels due to its undesirable properties of high oxygen content, high water content and low heating value [1]. Catalytic hydrodeoxygenation (HDO) is considered a promising technique for bio-oil upgrading and treats bio-oil at high pressure hydrogen gas provided from an external source. Replacing the hydrogen gas with a chemical of high potential for hydrogen donation in bio-oil HDO can increase the safety of process and its feasibility for large scale industrial application. The mechanism of bio-oil hydrogenation using a hydrogen donor (H-donor) is called transfer hydrogenation [2]. In catalytic transfer hydrogenation, hydrogen released from H-donor is transferred to the acceptor molecule (oxygenates) over active sites of catalyst. Less severe operating conditions (pressure and temperature) are needed for catalytic transfer hydrogenation of bio-oil compared to the catalytic HDO of bio-oil [3].

The aim of this work is to study the transfer hydrogenation of guaiacol (representative model compound for bio-oil) and crude bio-oil using a liquid hydrogen source and Pd/C catalyst. At first, effects of catalyst amount, reaction temperature, H-donor type and reaction time on the selectivity of products obtained from transfer hydrogenation of guaiacol are investigated. Then, transfer hydrogenation of crude bio-oil is carried out at the optimum reaction conditions obtained from guaiacol deoxygenation experiments.

2. Methods

Transfer hydrogenation experiments are conducted in an autoclave batch reactor equipped with a magnetic drive stirrer and water cooling solenoid. Catalyst (10 wt% Pd/C), substrate (guaiacol and bio-oil) and H-donor (methanol, ethanol, 2-propanol and 2-butanol) are loaded into the reactor and the reaction is conducted at 170-230 °C reaction temperature, 8 bar initial nitrogen pressure, 500 rpm and 1-4 h reaction time. Selectivity and yield of product compositions are analyzed using a gas chromatography (7890A Agilent Technologies, Ultra Alloy-5, 30 m × 250 μm × 0.25 μm) coupled with mass spectrometry and flame ionization detectors. Compounds identification is carried out using the NIST (National Institute of Standards and Technology) library.

3. Results and discussion

Transfer hydrogenation of guaiacol (two-oxygen-containing compound) using Pd/C catalyst and 2-propanol H-donor resulted in the formation of 1-methylpropyl cyclohexane, cyclohexanol/methoxycyclohexane/2-cyclohexene-1-ol/2-methylcyclopentanol and 2-methoxycyclohexanone as the oxygen-free, one-oxygen-containing and two-oxygen-containing products, respectively (Figure 1). The two reactions of dehydrogenation of H-donor and hydrogenation of guaiacol are simultaneously occurred on palladium active sites. The precise mechanism of catalytic transfer hydrogenation is not yet clear. Generally, hydrogenation could occur in two mechanisms: (i) decomposition of H-donor to hydrogen molecule which is activated on catalytic active sites for involving in hydrogenation reaction; (ii) transfer of hydrogen atom from H-donor molecule to acceptor on catalytic sites. The exact mechanism of transfer hydrogenation reaction depends on

the type of H-donor and catalyst. An efficient catalyst for transfer hydrogenation reaction should have high potential for adsorption of both hydrogen donor and acceptor molecules. The activated carbon support of Pd/C catalyst facilitates the adsorption of both guaiacol and 2-propanol on the active sites of this catalyst. The product distribution of transfer hydrogenation of guaiacol over Pd/C catalyst using 2-propanol H-donor reveals that the hydrogen provided by H-donor was involved in the guaiacol transformation to 2-methoxycyclohexanone through its benzene ring hydrogenation. Then, methoxycyclohexane and cyclohexanol were produced through hydrogenolysis and demethoxylation of 2-methoxycyclohexanone. 1-Methylpropyl cyclohexane can possibly be formed through alkylation of methoxycyclohexane and cyclohexanol. Meanwhile, 2-cyclohexene-1-ol might be produced from oxidation of cyclohexene (product of guaiacol transfer hydrogenation) by 2-propanol and acetone (product of 2-propanol dehydrogenation). Study of the effects of catalyst content (0.1-0.4 g) on the products selectivity showed that increasing the catalyst amount to 0.3 and 0.4 g led to the formation of 2-methylcyclopentanol which is produced through the ring hydrogenation, ring opening-closing and decarbonylation reactions of catechol (an intermediate of guaiacol transformation).

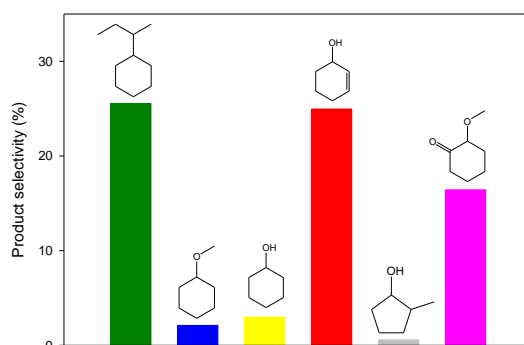


Figure 1. Selectivity of products obtained from transfer hydrogenation of guaiacol (total conversion) using Pd/C catalyst and 2-propanol H-donor. Reaction conditions: guaiacol, 0.5 g; H-donor, 30 g; catalyst, 0.4 g; temperature, 230 °C; reaction time, 4 h and rpm, 500.

4. Conclusions

The substitution of hydrogen gas with a liquid hydrogen source is a new topic in bio-oil upgrading which deserves to be studied in detail. In this work, deoxygenation of guaiacol (model compound of bio-oil) to 1-methylpropyl cyclohexane was successfully carried out through the transfer hydrogenation process using Pd/C as catalyst and 2-propanol as liquid hydrogen source. Since guaiacols are the dominant oxygenated fraction of bio-oils, their conversion to oxygen-free compounds such as 1-methylpropyl cyclohexane is of a great importance in bio-oil upgrading process.

References

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Keywords

Transfer hydrogenation; Guaiacol; 2-Propanol; Pd/C; Alkylated cyclohexane

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