

## Upgrading of Bio-Oil by Bio-Pd Catalyst

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**Abstract :** This paper reports the application of a bacteria-supported palladium catalyst to the hydrodeoxygenation (HDO) of pyrolysis bio-oil, towards producing an upgraded transport fuel. Biofuels are key to the timely replacement of fossil fuels in order to mitigate the emissions of greenhouse gases and depletion of non-renewable resources. The process is an essential step in the upgrading of bio-oils derived from industrial by-products such as agricultural and forestry wastes, the crude oil from pyrolysis containing a large amount of oxygen that requires to be removed in order to create a fuel resembling fossil-derived hydrocarbons. The bacteria supported catalyst manufacture is a means of utilizing recycled metals and second life bacteria, and the metal can also be easily recovered from the spent catalysts after use. Comparisons are made between bio-Pd, and a conventional activated carbon supported Pd/C catalyst. Bio-oil was produced by fast pyrolysis of beechwood at 500 °C at a residence time below 2 seconds, provided by Aston University. 5 wt % BioPd/C was prepared under reducing conditions, exposing cells of *E. coli* MC4100 to a solution of sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>), followed by rinsing, drying and grinding to form a powder. Pd/C was procured from Sigma-Aldrich. The HDO experiments were carried out in a 100 mL Parr batch autoclave using ~20g bio-crude oil and 0.6 g bio-Pd/C catalyst. Experimental variables investigated for optimization included temperature (160-350°C) and reaction times (up to 5 h) at a hydrogen pressure of 100 bar. Most of the experiments resulted in an aqueous phase (~40%) and an organic phase (~50-60%) as well as gas phase (<5%) and coke (<2%). Study of the temperature and time upon the process showed that the degree of deoxygenation increased (from ~20 % up to 60 %) at higher temperatures in the region of 350 °C and longer residence times up to 5 h. However minimum viscosity (~0.035 Pa.s) occurred at 250 °C and 3 h residence time, indicating that some polymerization of the oil product occurs at the higher temperatures. Bio-Pd showed a similar degree of deoxygenation (~20 %) to Pd/C at lower temperatures of 160 °C, but did not rise as steeply with temperature. More coke was formed over bio-Pd/C than Pd/C at temperatures above 250 °C, suggesting that bio-Pd/C may be more susceptible to coke formation than Pd/C. Reactions occurring during bio-oil upgrading include catalytic cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation and hydrogenation. In conclusion, it was shown that bio-Pd/C displays an acceptable rate of HDO, which increases with residence time and temperature. However some undesirable reactions also occur, leading to a deleterious increase in viscosity at higher temperatures. Comparisons are also drawn with earlier work on the HDO of *Chlorella* derived bio-oil manufactured from micro-algae via hydrothermal liquefaction. Future work will analyze the kinetics of the reaction and investigate the effect of bi-metallic catalysts.

**Keywords :** bio-oil, catalyst, palladium, upgrading

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