

HYDROTREATMENT OF HEAVY LIGNIN PYROLYSIS BIO-OILS AND CO-PROCESSING WITH PETROLEUM FRACTIONS

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ABSTRACT

Lignin is one of the main components of lignocellulosic biomass and can be converted to phenolic/aromatic bio-oils via pyrolysis and hydrogenolysis which can be upgraded to naphtha, marine and jet-type cyclo-alkane sustainable biofuels. Within this context, two approaches were followed: in the first approach, lignin bio-oils were mildly hydrotreated aiming to marine fuels while in the second approach deep hydrodeoxygenation led to drop-in aviation/road biofuels.

Regarding the first approach, the heavy fraction of lignin pyrolysis bio-oils was hydrotreated in alcohols under mild conditions to increase the hydrogenolysis of oligomers to monomers and decrease their viscosity. The bio-oils were treated in methanol/ethanol at 250°C, 1 h, 30-50 bar H₂ using traditional hydrogenolysis catalysts (3% Ru/AC) as well novel bifunctional nickel zeolite catalysts. During the hydrotreatment, the composition of the bio-oils was maintained with alkoxyated (50-60%) and alkylated phenols (15-25%) being the most abundant compounds. Based on the elemental analysis, the hydrotreated samples exhibit high carbon content 63-73%, hydrogen 6.8-8% and are nitrogen/sulfur free, resulted in HHV=27.2-33.5 MJ/kg, slightly lower than the petroleum derived marine fuels. Furthermore, the hydrotreated bio-oils exhibit lower viscosity (525-8273 mPa/s, at 50°C) compared to the initial lignin pyrolysis bio-oil (298147 mPa/s, at 50°C).

In the second approach, the heavy pyrolysis bio-oils were hydrodeoxygenated under more severe conditions towards drop-in aviation biofuels. The experiments were performed at 220-400°C, for 3-8 h, using 50-80 bar H₂ while hexadecane was used as model substrate. Under mild conditions (220°C, 1 h, 50 bar H₂), low hydrodeoxygenation was achieved (<10%). Under more severe conditions (320°C, 3h and 50 bars H₂), the HDO was increased to 18% while further improvement to 94% was observed at 400°C. The main compounds were cycloalkanes and aromatics, derived via the hydrodeoxygenation of lignin compounds as well as hydrocarbons derived via the controlled hydrocracking of hexadecane. Under the optimized conditions, lignin pyrolysis bio-oils were also co-processed with vacuum gas oil. The co-processed product exhibits 82% non-oxygenated compounds, in the range of C₁₀-C₃₀.

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KEYWORDS: lignin, pyrolysis bio-oil, hydrodeoxygenation, co-processing, hydrocarbons