11th World Bioenergy Congress and Expo

July 02-04, 2018 | Berlin, Germany

Hydrodeoxygenation of Vanillin as a Model Bio-oil Compound and Kinetic Studies

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for over a decade, the production of renewable liquid biofuels from biomass sources has received significant attention because it shows promising potential to address the anticipated energy crisis and growing concern on environmental implication of fossil fuel consumption. However, raw bio-oil possesses undesirable properties such as thermal and chemical instability, low heating value, storage difficulty due to high corrosivity and incompatibility with existing conventional fuels. This has been linked to the abundant presence of oxygenated molecules in raw bio-oil. To this effect, catalytic processes including hydrodeoxygenation (HDO) and zeolite cracking has shown great potential to achieve significant reduction in oxygen content of raw bio-oils to levels comparable to those of existing conventional fuels. In particular, HDO has emerged as the preferred upgrading route over the last decade on grounds of economic viability and superior quality of the final product. Yet commercialising the HDO process remains at an infant stage due to challenges in the form of rapid catalyst deactivation, exorbitant process cost and unfriendliness, uncertainty around long-term operability as a continuous process and sparse information on kinetics. In this work, optimisation and kinetic studies based on a typical bio-oil model compound, vanillin was carried out in the presence of 1% Pd/Al2O3 catalyst in a 100mL stirred batch reactor. The reaction variables were optimised in the range: reaction time (90 – 450mins), initial H2 pressure (10 - 25bar), temperature (363 – 423K), agitation speed (300 -1000 rpm), catalyst weight (0.04 - 0.25g) and solvent to substrate ratio (40 - 100 mol/mol). The Taguchi method was used to design experimental conditions and establish optimal values for the reaction variables. The optimum values found were reaction time 90mins, reaction temperature 363K, reaction initial pressure 10bar, agitation speed 1000rpm, catalyst weight 0.25g and solvent to substrate ratio 80 mol/mol. It was also found that the most and least influential parameters are catalyst weight and reaction temperature respectively. External mass transfer was overcome from 700rpm as conversion stabilised at 93.3%. Hence, an agitation speed of 1000rpm was used in the kinetic studies to establish the order of reaction with respect to vanillin, which was found to be 1.10 ± 0.1 with an equivalent rate constant of 11.2 ± 1.7 min-1 at 363K.

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