**Kinetic modelling for hydrogenation of levulinic acid and its esters.**

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**Highlights**

* Mass transfer study
* Kinetic modelling for hydrogenation of levulinic acid and its esters.
* Relationships between reactivity and structure.

**1. Introduction**

Nowadays, biomass valorization has attracted great interests as its products have shown potential to substitute the fossil-oriented products. Conversion of biomass to biofuels and chemicals is one of the hot topic in chemical engineering. Levulinic acid (LA) is regarded as one of the top 12 building-block molecules from biomass. Besides, hydrogenation of levulinic acid and its esters leads to γ-valerolactone (GVL) [1], which is also another important platform molecule for biofuel production and industrial applications. GVL can also be used as industrial solvent, fuel additives, food and pharmaceutical industries.

From our previous research, the safe operation conditions for hydrogenation of levulinic acid to γ-valerolactone were determined from thermal risk assessment, which could provide an operational guide for further study of this process [2]. However, as LA is corrosive to the reactor system, a comparison of kinetic for hydrogenation of LA and its esters, such as methyl levulinate (ML), ethyle levulinate (EL) and butyl levulinate (BL) which could be obtained by alcoholysis of cellulose, is important for a better optimization of GVL synthesis.

The hydrogenation process of LA and its esters in GVL has two steps: the first step is the hydrogenation of the ketone group to the intermediates and the second step is the intra-molecule cyclization to get the final product GVL and its corresponding water or alcohol. The objective of this study is to study the kinetic modelling for hydrogenation of levulinic acid and its esters. Then, we will determine a relationship between the structure of the different substrates and their kinetics.

**2. Methods**

Experiments were performed in a Parr reactor equipped with efficient gas entrainment impeller, hydrogen reservoir, pressure and temperature recording system. GC-MS and GC were used to identify and quantify the compositions of the sample.

**3. Results and discussion**

Due to space limitation, we did not include the mass transfer study. Based on this study, we were able to determine the value of the mass transfer coefficient and Henry’s constants at different temperature.

For the kinetic study, different parameters such as substrate concentration, catalyst loading, pressure and temperature were studied for hydrogenation of levulinic acid and its esters to GVL. Figure 1 shows the good fit of simulated data to the experimental data.

**Figures 1.** The fit of simulated data to experimental data for Ethyl levulinate hydrogenation. Reaction conditions: EL 2mol/L, Ru/C catalyst 1.4g, Hydrogen pressure 20bar, Temperature 413K, stirring speed 1000rpm.

**4. Conclusion**

Figure 1 shows that the simulated data from kinetic model could fit the experimental data. The continuation of this work is to compare the kinetic between the different substrates to find a more efficient hydrogenation process and look for a possible relationship between the reactivity and structure.

**References**

1. Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. Green Chem 2013;15:584.

[2] Wang, Y., Vernières-Hassimi, L., Casson-Moreno, V., Hébert, J. P., & Leveneur, S. (2018). Thermal risk assessment of levulinic acid hydrogenation to γ-valerolactone. Organic Process Research & Development, 22(9), 1092-1100.