ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering

20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Intrinsic kinetic constants versus safety parameters: hydrogenation of levulinic acid to γ-valerolactone.

Yanjun Wang[1], Lamiae Vernières-Hassimi[1], Valeria Casson-moreno[3], Sébastien Leveneur[1,2]*

[1]*Normandie Université LSPC-Laboratoire de Sécurité des Procédés Chimiques, EA4704, INSA/Université Rouen, BP08, Avenue de l'Université, 76801 Saint-Etienne-du-Rouvray, France.*
[2]*Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland.*
[3]*Dipartimento di Ingegneria Chimica, Civile, Ambientale e dei Materiali, Alma Mater Studiorum—Università di Bologna, via Terracini 28, 40131 Bologna, Italy*

Corresponding author: sebastien.leveneur@insa-rouen.fr

Highlights
- Thermal risk assessment for the production of γ-valerolactone.
- Simplified kinetic model under adiabatic conditions for the determination of $TMR_{ad}(T_p)$.
- Intrinsic kinetic model under isothermal conditions.

1. Introduction

The development of processes using lignocellulosic biomass is increasing because of its non-competition with food. From one hand, processes using biomass raw materials are usually perceived as thermally and/or toxicology safer or even completely harmless with respect to other conventional chemical processes. On the other hand, hazardous materials and severe process conditions are required to valorize biomass. In the last decade, there have been several accidents involving bioenergy production and feedstock supply chain that raised concern on the safety of such technologies [1-2]. Thus, risk assessment for these processes should be done to preserve this positive image. Levulinic acid (LA), product of lignocellulosic biomass hydrolysis, is of particular interest and has been identified as a promising building block by the US department of energy. The platform molecule levulinic acid can be transformed in different chemicals. LA can be hydrogenated to become γ-valerolactone (GVL), which is also platform molecule. One of the most used way of production for GVL is the hydrogenation of aqueous LA with H_2 over heterogeneous catalyst (Ru/C) [3].

The goal of this study is to propose a thermal risk assessment for the hydrogenation of levulinic acid. For that, it is compulsory to determine the severity of the thermal risk characterized by the adiabatic temperature rise ΔT_{ad}, and the probability of the thermal risk characterized by the time-to-maximum rate under adiabatic conditions at a process temperature $TMR_{ad}(T_p)$. Then, an intrinsic kinetic model will be developed by using the RC1 Mettler Toledo calorimeter.

2. Methods

To build a simplified kinetic model, different experiments were performed in the calorimeter ARSST, standing for Advanced Reactive System Screening Tool. This calorimeter works under near-adiabatic conditions [4]. A background heating rate βel is used. The benefits of this calorimeter are the use of small amount of chemicals, used of high pressure to neglect evaporation and fast screening of exothermic reactions. The intrinsic kinetic model was built by using the RC1 Mettler Toledo calorimeter.

3. Results and discussion

According to Abdelrahman et al. [5], the mechanism of hydrogenation of LA can be decomposed into 2 steps. The first step is the hydrogenation of the ketone group bore by LA leading to the formation of 4-hydroxypentanoic acid (HPA). Then, there is the ring closure reaction leading to GVL.

For the simplified kinetic model, quasi-steady state approximation was applied on HPA, and the second reaction was assumed to be the rate determining step.

Energy balance in the liquid phase was expressed as

$$\frac{dT}{dt} = \frac{q_{rx}}{m_{LA} \cdot C_{P_{LA}} + m_W \cdot C_{P_W} + m_{GVL} \cdot C_{P_{GVL}} + m_{cat} \cdot C_{P_{cat}} + m_{insert} \cdot C_{P_{insert}}} + \beta_{el} \text{ with } q_{rx} = -R_{Reaction} \cdot V_{liq} \cdot \Delta H_{R,Reaction}.$$

The goal of this simplified kinetic model was to estimate the kinetic constants to estimate the TMR$_{ad}$(T$_p$) at different operating conditions. For that, reaction temperature was used as the observable and the objective function was defined as $\omega = \sum(y_e - \hat{y}_e)^2$, where y_e is the experimental data temperature and $\hat{y}_e$ is the simulated one. Ordinary differential equations were solved out by using ODESSA algorithm. The objective function was minimized by the simplex algorithm, when the knowledge of the initial guess values was not known. After that, the objective function was minimized with the Levenberg-Marquardt algorithm. Figure 1 shows the fitting of the model to the experimental data.
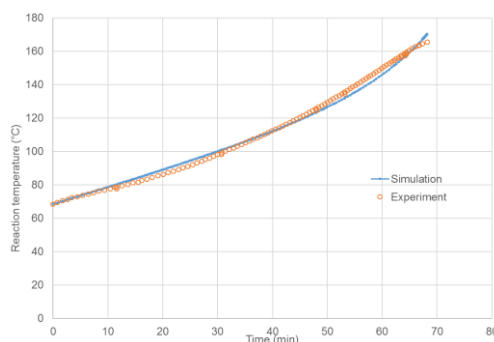

Figure 1. Fit of the model to the experimental data with an initial concentration of LA equal to 5.43 mol/L; catalyst loading of 0.027 kg/L and βel of 0.43°C/min.

Based on this model, we have found that the catalyst loading affects the values of safety parameters (Table 1).

Table 1. Effect of catalyst with the following initial conditions: T$_P$=130°C; [LA]$_0$=4.72 mol/L; [LA]$_0$=22.83 mol/L and P$_{H2}$=35 bar.

Catalyst loading (kg/L)	TMR$_{ad}$ (hrs)	ΔT$_{ad}$ (°C)
0.154	0.08	143.68
0.046	0.25	148.49
0.008	1.48	150.29

4. Conclusions

Prior work has studied the kinetics of hydrogenation of LA to GVL by using Ru/C. However, none of them has discussed the thermal aspect of this reaction. A simplified kinetic model was built to determine the safety parameters. In the second step of this work, an intrinsic kinetic model will be developed by using RC1 reactor. A comparison between both kinetic models will be carried out.

References

[1]   V. Casson Moreno, V. Cozzani, J. Loss Prev. Process Ind. 35 (2015) 135–144.
[2]   V. Casson Moreno, S. Papasidero, G.E. Scarponi, D. Guglielmi, V. Cozzani, Renew. Energy 96 (2016) 1127-1134.
[3]   B.T. Huang, S. Leveneur, T. Zamar, J.-P. Mikkola, B. Taouk, Int. J. Chem. Reactor Eng. 13 (2015) 119–127.
[4]   E. Marco, S. Cuartielles, J.A. Peña, J. Santamaria, Thermochim. Acta 362 (2000) 49–58.
[5]   O.A. Abdelrahman, A. Heyden, J.Q. Bond, ACS Catal. 4 (2014) 1171–1181.