



Article Thermal Stability for the Continuous Production of γ -Valerolactone from the Hydrogenation of N-Butyl Levulinate in a CSTR

Wenel Naudy Vásquez Salcedo ^{1,2}, Bruno Renou ² and Sébastien Leveneur ^{1,*}

- ¹ INSA Rouen Normandie, University Rouen Normandie, Normandie Université, LSPC, UR 4704, F-76000 Rouen, France
- ² INSA Rouen-Normandie, UNIROUEN, CNRS, CORIA, Normandie University, F-76000 Rouen, France
- * Correspondence: sebastien.leveneur@insa-rouen.fr

Abstract: γ -valerolactone can be a game-changer in the chemical industry because it could substitute fossil feedstocks in different fields. Its production is from the hydrogenation of levulinic acid or alkyl levulinates and can present some risk of thermal runaway. To the best of our knowledge, no studies evaluate the thermal stability of this production in a continuous reactor. We simulated the thermal behavior of the hydrogenation of butyl levulinate over *Ru/C* in a continuous stirred-tank reactor and performed a sensitivity analysis. The kinetic and thermodynamic constants from Wang et al.'s articles were used. We found that the risk of thermal stability is low for this chemical system.

Keywords: simulation; GVL; thermal stability; hydrogenation

1. Introduction

The shift from fossil raw materials to renewable raw materials in the chemical industry is mandatory to make this industry sustainable and decrease its negative environmental impact. Among renewable raw materials, lignocellulosic biomass (LCB), that is not in competition with the food sector, is an excellent candidate because it could avoid the dilemma of food versus fuel that led to the alimentary crisis in the late 2000s. Even if there is divergence on the role of biofuel production in explaining the food shortage [1,2], non-food-use raw materials for chemical, biofuel, or material production should be favored [3].

LCB is available worldwide and can be obtained from agricultural wastes, such as maize stover, straw, wheat straw, sugarcane bagasse, rice husk, etc.; forestry residues including remaining wood harvestings, such as roots, branches, and leaves; dedicated crops on marginal land that is not suitable for food growth (e.g., miscanthus, switchgrass, eucalyptus, etc.); and the paper industry [4,5].

LCB consists of three main elements: cellulose and hemicellulose, which are polymers of sugars, and lignin, a polymer of aromatic compounds. The percentage of these three elements varies with species, location, and seasons, making it challenging to develop the same pretreatment or valorization process for all LCB raw materials. Nevertheless, these raw materials can lead to the production of fuels, materials, and chemicals.

The sugar fraction valorization can produce valuable platform molecules or building blocks such as levulinic acid/levulinate, furfural, GVL, HMF, etc. [3,6,7]. The potential use of GVL in fuels, materials, and chemicals is enormous [8–13]. GVL was found to be a suitable solvent for the dissolution of lignin, hemicellulose, cellulose, or fructose [14–19]. GVL can reduce CO exhaust, unburned fuel, and smoke [20]. GVL updated to hydrocarbons can be a temporary solution for jet fuels [21]. The valorization of GVL into alpha methylene can lead to an excellent substitute for acrylate [22,23].

GVL is produced from the hydrogenation of levulinic acid or alkyl levulinates. There are three main approaches: molecular hydrogen, catalytic transfer hydrogenation via the use of alcohol, or the in situ decomposition of formic acid [24–26]. The most common approach is using molecular hydrogen over Ru on activated carbon.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). There are two types of catalytic systems in GVL production: homogeneous and heterogeneous. The advantage of homogeneous systems is their high catalytic performance [27,28]. However, separation processes need to be implemented to separate the catalyst from the final products, while heterogeneous catalysts are easy to remove and can be recycled [29,30].

In heterogeneous systems, the most common catalysts for GVL production from levulinic acid and alkyl levulinates are ruthenium (Ru), rhodium (Rh), palladium (Pd), platinum (Pt), gold (Au), and rhenium (Re) in which the noble metal Ru exhibits a high selectivity [8]. Manzer studied the hydrogenation of levulinic acid over a series of metal catalysts (Ir, Rh, Pd, Ru, Pt, Re, and Ni) supported on carbon (metal loading was equal to 5%) wherein a 5 wt.% *Ru/C* catalyst had the highest performance in terms of conversion and selectivity [23]. The catalytic activity of *Ru/C* and some other solid catalysts show promising results for the hydrogenation of butyl levulinate [31–34].

We have demonstrated that the hydrogenation of levulinic acid or alkyl levulinates presents some risk of thermal runaway when the thermal mode is adiabatic and in batch conditions [35,36]. One way to decrease the thermal risk is to work in continuous mode in a steady-state regime [37]. Nevertheless, one needs to assess the thermal stability of such continuous reactor [38,39]. In the literature we can find studies about thermal stability, dynamic stability, and sensitivity assessments in continuous reactors for reactions such as the hydrolysis of acetic anhydride, polystyrene production in CSTRs, and light-cycle oil hydrotreatment [40–43]. To the best of our knowledge, such a study has not been conducted for the continuous production of GVL.

In this paper, we focused on evaluating the thermal stability of GVL production from butyl levulinate over *Ru/C* and included a sensitivity approach. We modeled the thermal behavior of an ideal continuous stirred-tank reactor (CSTR) and used the kinetic and thermodynamic constants from Wang et al. [35,44]. A CSTR was chosen because its mixing is more efficient than other continuous reactors, which is vital for a gas–liquid–solid system.

2. Materials and Methods

2.1. Kinetics

Wang et al. showed that the hydrogenation of BL over Ru/C is a two-step reaction (Figure 1). BHP stands for butyl 4-hydroxypentanoate, and it is an intermediate. They performed this study by using GVL as a solvent.



Figure 1. Reaction scheme for BL hydrogenation.

The rate expression for the hydrogenation step is derived as follows:

$$R_1 = k_1 \cdot [BL]_{Liq} \cdot [H_2]_{Liq} \cdot \omega_{Ru/C} \tag{1}$$

The rate expression for the cyclization is:

$$R_2 = k_2 \cdot [BHP]_{Lia} \tag{2}$$

where $\omega_{Ru/C}$ is the catalyst loading in kg/L.

The kinetic and thermodynamic constants from the articles of Wang et al. [35,44] were used (Table 1).

	Values	Units
k ₁ (T = 403.15 K)	$3.09 \cdot 10^{-6}$	$m^6 \cdot mol^{-1} \cdot kg^{-1} \cdot s^{-1}$
Ea ₁	9.68	kJ·mol ^{−1}
ΔH_{R1}	-38.66	kJ·mol ^{−1}
$k_2 (T = 403.15 \text{ K})$	$1.88 \cdot 10^{-4}$	s^{-1}
Ea ₂	10.25	kJ·mol ^{−1}
ΔH_{R2}	6.50	kJ·mol ^{−1}

Table 1. Kinetic and thermodynamic constants.

2.2. Mass and Energy Balances

In this study, the flow distribution was assumed to be ideal. Thus, the material balance for a compound *j* can be written:

$$\frac{dC_j}{dt} = \frac{C_{j_{in}} - C_{j_{out}}}{\tau} + \sum_i v_{j,i} R_i$$
(3)

where *i* represents the reaction index, τ is the space-time, $v_{j,i}$ represents the stoichiometry coefficient of compound *j* in reaction *i*, and *Ri* is the reaction rate.

In a previous study by our group [44], we showed that the kinetics of hydrogen mass transfer from the gas to the liquid phase can be considered fast when GVL is the solvent. Thus, the hydrogen concentration in the liquid phase (reaction mixture) can be assumed to be constant. The solubility of hydrogen in GVL solvent was calculated from the following relationships:

$$C_{H2} = P_{H_2} \cdot He\left(T_{Ref} = 373.15\mathrm{K}\right) \cdot exp\left(\frac{-\Delta H_{Sol.}}{R} \cdot \left(\frac{1}{T_R} - \frac{1}{373.15}\right)\right)$$
(4)

where P_{H_2} is the hydrogen pressure in the reactor, $He(T_{Ref} = 373.15K) = 1.86 \text{ mol} \cdot \text{m}^{-3} \cdot \text{bar}^{-1}$ is Henry's constant at 373.15 K, and $\Delta H_{Sol.} = 5936.8 \text{ J} \cdot \text{mol}^{-1}$ is the enthalpy of solubilization [44].

For an ideal CSTR, the energy balance of the reactionary phase can be written as:

$$\left[\left(\rho\hat{C}_{P}\right)_{liq}+\left(\rho\hat{C}_{P}\right)_{ins}\right]\frac{dT_{r}}{dt}=\frac{\sum C_{j_{in}}C_{P_{j}}}{\tau}(T_{in}-T_{r})+Ua(T_{c}-T_{r})-\sum_{i}R_{i}\Delta H_{i}$$
(5)

where ρ is the volumic mass, \hat{C}_P is the specific heat capacity, T_r is the reactionary media temperature, T_C is the temperature of the heat carrier in the jacket, Ua is the global heat transfer coefficient, *ins* represents the reactor insert, and ΔH_i is the enthalpy of reaction *i*. Data for heat capacities and volumetric mass were found in the literature [45,46].

The flow distribution of the heat carrier fluid is ideal; thus, the energy balance is:

$$\rho_c \hat{C}_{P_c} \frac{dT_c}{dt} = \frac{\rho_c \hat{C}_{P_c}}{\tau_c} (T_{c_0} - T_c) + Ua(T_r - T_c)$$
(6)

where ρ_c and \hat{C}_{P_c} are the volumic mass and heat capacity of the heat carrier, and T_{c_0} is the heat carrier temperature at the inlet.

Figure 2 is a schematic representation of the reactor setup.

In this study, we will consider the steady-state regime; thus, Equations (3), (5), and (6) become:

$$\frac{dT_c}{dt} = \frac{dT_R}{dt} = 0 \operatorname{K} \cdot \operatorname{s}^{-1} and \ \frac{dC_j}{dt} = 0 \operatorname{mol} \cdot \operatorname{L}^{-1} \cdot \operatorname{s}^{-1}$$
(7)



Figure 2. Reactor setup.

2.3. Operating Conditions

The simulation was performed under isobaric conditions within a reaction temperature range of 300–600 K. Table 2 shows the operating conditions used during the simulation. The inlet concentrations, catalyst loading, and temperature were in the same ranges as the ones from Wang et al. [44].

Table 2. Operating conditions used in this study.

Inlet Parameters	Values	Units
C_{BL_0}	4840	mol·m ⁻³
C_{BHP_0}	0	$mol \cdot m^{-3}$
C_{GVL_0}	2080	$mol \cdot m^{-3}$
C_{BuOH_0}	0	$mol \cdot m^{-3}$
ω_{Cat}	10	$kg \cdot m^{-3}$
T_r	300 to 600	K
T_{in}	333.15	Κ
P_{H_2}	25	bar
τ	2000	S
Ua	17,000	$W \cdot m^{-3} \cdot K^{-1}$

2.4. Thermal Stability Criterion

To assess the stationary thermal stability, the van Heerden criterion was calculated during the course of the reaction. The van Heerden criterion is a stability-based criterion defined as [47–49]:

$$\frac{dQ_{Removal}}{dt} > \frac{dQ_{Generated}}{dt}$$
(8)

where $Q_{Removal}$ is the amount of energy exchange between the reactionary media and the heat carrier fluid, and $Q_{Generated}$ is the amount of energy released during the reaction.

The van Heerden criterion is necessary to satisfy stationary stability and states that the energy removed from a reactionary system must be higher than the energy generated by the system.

 $\frac{dQ_{Removal}}{dt}$ and $\frac{dQ_{Generated}}{dt}$ were calculated from the material and energy balances.

2.5. Simulation and Parametric Sensitivity

MATLAB R2021b software was used to make the simulation and to solve the mathematical equations presented during thermal analysis. The ODE15s routine was used to solve stiff differential equations. The FSOLVE routine was used to solve the system of nonlinear equations and the energy and mass balance in the steady-state regime. The EIG routine was used to calculate the eigenvalues and eigenvectors of the Jacobian matrix.

Parametric sensitivity analysis studies the relationship between the system behavior according to changes in the inlet parameters. As mentioned by Varma et al. [50], if a slight variation in the input parameter values can lead to a significant change, then the chemical system is qualified as sensitive.

The parametric sensitivity is defined as follows:

$$S\left(\overrightarrow{y},\phi\right) = \frac{d\,\overrightarrow{y}}{d\phi}\tag{9}$$

For a dynamic system, we have that:

$$\frac{dS\left(\vec{y},\phi\right)}{dt} = J \cdot S\left(\vec{y},\phi\right) + \frac{d\vec{f}}{d\phi}$$
(10)

Solving the expression above for $S(\vec{y}, \phi)$ in the steady state, we obtain:

$$\frac{dS\left(\overrightarrow{y},\phi\right)}{dt} = 0 \tag{11}$$

$$S\left(\vec{y},\phi\right) = -J^{-1} \cdot \frac{d\vec{f}}{d\phi} \text{ with } \frac{d\vec{f}}{d\phi} = \begin{pmatrix} \frac{df_1}{d\phi} \\ \vdots \\ \frac{df_n}{d\phi} \end{pmatrix}$$
(12)

To compare the sensitivity of one output variable according to different parameters, we can define the normalized parametric sensitivity as follows:

$$S_n(y,\phi_j) = \frac{\phi_j}{y} \frac{dy}{d\phi_j}$$
(13)

3. Results and Discussion

3.1. Effect of Space-Time on Conversion

Figure 3 shows the effect of temperature on BL conversion at different space-times. As the reaction temperature and space-time increase, the BL conversion increases. A space-time value of 2000 s was found to be a good compromise between time and conversion since the space-time increase does not significantly improve the conversion. We can realize from Figure 3, comparing the space-times equal to 2000 s and 10,000 s, that the difference in the BL conversion is less than 15%, while space-time is multiplied by a factor of 5.

3.2. Comparison of Heat Flow Rate Exchange Due to Chemical Reactions

By solving the energy balance in the reactionary medium, one obtains:

$$T_c = T_r + \frac{1}{Ua} \sum_i R_i \Delta H_i - \frac{\sum C_{j_{in}} \overline{C}_{P_j}}{\tau \cdot Ua} (T_{in} - T_r)$$
(14)

Figure 4 shows the heat flow rates due to chemical reactions in the temperature range of 300–600 K. We plotted the heat flow rate generated in watts per cubic meters for different space-times from 100 s to 10,000 s. Based on the results presented in Figure 4, we can



conclude that the energy release per unit of time per unit of volume decreases if we increase the space-time. Such results are expected for an ideal CSTR.

Figure 3. BL conversion as a function of T_r for different space-times.



Figure 4. Heat flow as a function of T_r for different space-times.

Figure 5 represents the application of the van Heerden criterion to determine if the reactionary system is stable from the thermal point of view operating at a steady-state regime. This criterion solves the energy balance and determines if T_r is related to T_c by a one-to-one function (injective function). When the one-to-one function relates T_r and T_c , there is no multiplicity of steady states; consequently, the system is stable.



Figure 5. Reactor temperature vs. jacket temperature.

From Figure 5, we can realize that T_r and T_c are related by a one-to-one function in the range 300 K < T_r < 600 K. Thus, we can conclude that there is no multiplicity of steady-states and also that the reactionary system can stably operate in a steady-state regime.

3.3. Parametric Sensitivity

In this part, we evaluate the parametric sensitivity of the BL concentration in the outlet flow, the GVL concentration in the outlet flow, and the reactor temperature. We decided to focus on these three variables since they represent the main reagent, the main product, and the variable linked to thermal stability.

The parameters considered for this evaluation were C_{BL_0} , k_{hyd} , k_{cyc} , Ua, τ , ω_{Cat} , and T_{in} . Figure 6 shows the normalized parametric sensitivity of the BL concentration in the outlet flow as a function of the reaction temperature. From Figure 6, we can notice that the final BL concentration is more sensitive to the inlet BL concentration, space-time, and catalyst loading. This means that variations in these parameters significantly change the final BL concentration.



Figure 6. Parametric sensitivity for the outlet BL concentration.

Figure 7 represents the normalized parametric sensitivity of the GVL concentration in the outlet flow as a function of the reaction temperature. Based on the results, we found

that the GVL concentration is more sensitive to variations in the inlet BL concentration, the space-time, and the cyclization rate constant. If any of these parameters increase, then the GVL production also increases. From Figure 7, we can also realize that GVL's sensitivity to these parameters gains importance as we increase the reaction temperature.







Figure 8 represents the normalized parametric sensitivity of the reaction temperature in the range of temperatures from 300 K to 600 K. Figure 8 shows how sensitive the reaction temperature is to the operating parameters. We found that reaction temperature is more sensitive to variations in the inlet temperature, the inlet BL concentration, space-time, and the heat transfer coefficient. Based on these results, we can conclude that the inlet BL concentration, the hydrogenation and cyclization rate constants, the heat transfer *Ua*, the space-time τ , the catalyst loading $\omega_{Ru/C}$, and the inlet temperature T_{in} have a low impact on the reaction temperature within the temperature range of 300–600 K. This low influence explains the low risk of thermal instability for this reaction in a CSTR.



Figure 8. Results: Parametric sensitivity for the reactor temperature (T_r) .

3.4. Dynamic Thermal Stability

In this part, we seek to evaluate the dynamic response of the system to perturbations near stationary conditions. For this purpose, we applied the linear dynamic model of perturbation.

Considering our dynamical model:

$$\frac{dy_i}{dt} = f_i(y_1, y_2, \dots, y_n, \phi, t)$$
(15)

where y_i represents the variables of the system, and ϕ represents the other parameters.

$$y_i = C_{BL}, C_{BHP}, C_{GVL}, C_{BuOH}, T_r, T_c$$
(16)

Let us define a small perturbation (x_i) on the whole set of variables as follows:

$$x_i = y_i - y_{i,s} \tag{17}$$

Therefore:

$$y_i = y_{i,s} + x_i \tag{18}$$

Now we can define the perturbed dynamical model as follows:

$$\frac{d(y_{i,s}+x_i)}{dt} = f_i(y_{1,s}+x_1, y_{2,s}+x_2, \dots, y_{n,s}+x_n, \phi, t)$$
(19)

As we have an interest in making a linear analysis, we used the 1st-order Taylor expansion of the perturbed dynamical model to obtain:

$$\frac{d(y_{i,s}+x_i)}{dt} = f_i(y_{1,s}, y_{2,s}, \dots, y_{n,s}+x_n, \phi, t) + \left(\frac{\partial f_i}{\partial y_1}\right) \cdot x_1 + \left(\frac{\partial f_i}{\partial y_2}\right) \cdot x_2 + \dots + \left(\frac{\partial f_i}{\partial y_n}\right) \cdot x_n \tag{20}$$

Under stationary conditions:

$$\frac{d(y_{i,s}+x_i)}{dt} = 0 \tag{21}$$

$$f_i(y_{1,s}, y_{2,s}, \dots, y_{n,s} + x_n, \phi, t) = 0$$
(22)

Therefore, the linear model of perturbation under stationary conditions is:

$$\frac{dx_i}{dt} = \left(\frac{\partial f_i}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_i}{\partial y_2}\right)_s \cdot x_2 + \dots + \left(\frac{\partial f_i}{\partial y_n}\right)_s \cdot x_n \tag{23}$$

Developing the linear model of perturbation under stationary conditions for a system with *n* variables, we have:

$$\begin{cases} \frac{dx_1}{dt} = \left(\frac{\partial f_1}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_1}{\partial y_2}\right)_s \cdot x_2 + \dots + \left(\frac{\partial f_1}{\partial y_n}\right)_s \cdot x_n \\ \vdots \\ \frac{dx_i}{dt} = \left(\frac{\partial f_i}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_i}{\partial y_2}\right)_s \cdot x_2 + \dots + \left(\frac{\partial f_i}{\partial y_n}\right)_s \cdot x_n \\ \vdots \\ \frac{dx_n}{dt} = \left(\frac{\partial f_n}{\partial y_1}\right)_s \cdot x_1 + \left(\frac{\partial f_n}{\partial y_2}\right)_s \cdot x_2 + \dots + \left(\frac{\partial f_n}{\partial y_n}\right)_s \cdot x_n \end{cases}$$
(24)

In a matrix formalism, we can define the linear dynamical model of perturbation as follows:

$$X = J \cdot X$$

where

$$X = \begin{pmatrix} x_1 \\ \vdots \\ x_n \end{pmatrix}; \quad \dot{X} = \begin{pmatrix} \frac{dx_1}{dt} \\ \vdots \\ \frac{dx_n}{dt} \end{pmatrix}; \quad J = \begin{pmatrix} \frac{df_1}{dy_1} & \cdots & \frac{df_1}{dy_n} \\ \vdots & \ddots & \vdots \\ \frac{df_n}{dy_1} & \cdots & \frac{df_n}{dy_n} \end{pmatrix}$$
(25)

Solving the linear system leads to these solutions for all the perturbations around the stationary point:

$$\begin{cases} x_1 = \sum_{m=1}^n a_m \cdot U_{1,m} \cdot e^{\lambda_m t} \\ \vdots \\ x_i = \sum_{m=1}^n a_m \cdot U_{i,m} \cdot e^{\lambda_m t} \\ \vdots \\ x_n = \sum_{m=1}^n a_m \cdot U_{n,m} \cdot e^{\lambda_m t} \end{cases}$$
(26)

where U_i is the *i*th eigenvector of *J* associated to the eigenvalue λ_i . The condition of asymptotic stability is:

$$/k \lim_{t \to \infty} x_k = 0 \tag{27}$$

This leads to the following:

$$\lambda_i \in \mathbb{C} \cdot \Re e(\lambda_i) < 0 \tag{28}$$

To evaluate the dynamic thermal stability, we defined the Jacobian matrix of the dynamic model in the range of temperature of 300 K to 600 K and calculated the eigenvalues of the Jacobian matrix for each temperature value. The eigenvalues are plotted in Figure 9.



Figure 9. Dynamic Stability—Eigenvalues.

Figure 9 shows the eigenvalues obtained from the Jacobian matrix of the reactionary system in the range of temperature from 300 K to 600 K. This Jacobian matrix was generated from the material and energy balances. It is considered that there are dynamic thermal instabilities in the system when there are eigenvalues whose real parts are positive ($\text{Re}(\lambda) > 0$). From Figure 9, we can conclude that the CSTR reactor is dynamically stable in the temperature range of 300 K to 600 K since the real parts of all eigenvalues are negative. Visualizing the eigenvalues also helps to identify which variable is responsible for instabilities when the system is not dynamically stable.

4. Conclusions

This article deals with the safety production of GVL from the hydrogenation of butyl levulinate over Ru/C in a continuous stirred-tank reactor (CSTR) in a steady-state regime. The kinetic and thermodynamic constants determined from Wang et al.'s articles were used to simulate the thermal behavior in a CSTR. The van Heerden criterion showed that the risk of thermal instability is low for this reaction system with the operating conditions used in this study.

The sensitivity analysis demonstrated that the kinetic constants, global heat transfer, inlet concentrations, space-time, inlet temperature, and catalyst loading have a low impact on the reaction temperature. Nevertheless, the inlet concentration of BL, space-time, and cyclization rate constant have a non-negligible impact on the outlet concentration of GVL.

A continuation of this study could be the study of thermal stability during the transient phase and for non-ideal flow in continuous reactors.

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