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**Assessment of kinetic models for the production of γ -valerolactone developed in
isothermal, adiabatic and isoperibolic conditions**

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11 **Abstract**

12 The use of lignocellulosic biomass as raw materials for the production of biofuels is increasing. There
13 are several potential processes valorizing these raw materials, but the shift from lab-scale to industrial
14 scale requires the development of reliable and robust kinetic models. Usually, these models are
15 developed in isothermal mode, limiting their use for thermal risk assessment or pinch analysis. We
16 developed and assessed several kinetic models for the hydrogenation of butyl levulinate to γ -
17 valerolactone over Ru/C in different thermal modes, i.e., isothermal, isoperibolic and adiabatic modes.
18 The reaction calorimeter Mettler-Toledo RC1 was used to perform kinetic experiments. Bayesian
19 inference was used during the regression stage to calculate the credible intervals. The validation stage
20 was done by a holdout method. From the regression and validation stage, we found that the non-
21 competitive Langmuir Hinshelwood with hydrogen non-dissociation and dissociation were the most
22 reliable models. These models can predict the kinetics of this reaction system in different thermal modes.

23 **Keywords:** kinetic modeling, gamma valerolactone, levulinate, calorimetry, adiabatic

24

25 Abbreviations

C_p	Specific heat capacity [$\text{J.kg}^{-1}.\text{K}^{-1}$]
E_a	Activation energy [J.mol^{-1}]
$f_{iu}(\xi)$	Estimated concentration or temperature
H_e	Henry's coefficient [$\text{mol.m}^{-3}.\text{bar}^{-1}$]
k	Rate constant
K_i	Adsorption rate of specie i [$\text{m}^3.\text{mol}^{-1}$]
$k_{L,a}$	Volumetric mass transfer coefficient [s^{-1}]
$(k_{L,a})_{\text{modified}}$	Modified volumetric mass transfer coefficient [$(\text{Pa.s.K}^{-1})^{0.5}(\text{Pa.s.kg}^{-1}.\text{m}^{-3})^{0.25}.\text{s}^{-1}$]
m	Mass [kg]
P	Pressure [bar]
R_i	Reaction rate i [$\text{mol.m}^{-3}.\text{s}^{-1}$]
R	Gas constant [$\text{J.mol}^{-1}.\text{K}^{-1}$]
T	Temperature [K]
UA	Global heat transfer coefficient [W.K^{-1}]
$ \nu(\xi) $	Determinant of the covariance matrix of responses
Y_i	Experimental concentration of specie i or temperature

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27 Greek letters

$\omega_{Cat.}$	Catalyst loading [kg.m^{-3}]
μ_{liq}	Liquid viscosity [Pa.s]
ρ_{liq}	Mass density [kg.m^{-3}]

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32 Subscripts and superscripts

Liq	Liquid phase
Ref	Reference
o	Initial
*	Interfacial value

33

34 Abbreviations

AIC	Akaike information criterion
BL	Butyl levulinate
BHP	Butyl 4-hydroxypentanoate
BuOH	Butanol
ER	Eley-Rideal kinetic model with no adsorption of hydrogen
GC	Gas chromatography
GVL	γ -valerolactone
HPD	Highest Posterior Density
LH1	Langmuir-Hinshelwood kinetic model with molecular adsorption of hydrogen
LH2	Langmuir-Hinshelwood kinetic model with hydrogen dissociation
NCLH1	Non-competitive Langmuir-Hinshelwood kinetic model with no dissociation of hydrogen
NCLH2	Non-competitive Langmuir-Hinshelwood kinetic model with hydrogen dissociation
ODEs	Ordinary differential equation system
OF(ξ)	Objective function
RKMC	Redlich-Kwong-Mathias-Copeman equation of state
Ru/C	Ruthenium on activated carbon

35

1. Introduction

Our dependency on fossil raw materials is very high in the modern society. Over 80% of the world's primary energy consumption in the energy sector was from fossil raw materials in 2020 [1].

The use of lignocellulosic biomass (LCB) for biofuel production is seen as a better alternative to fossil fuel because of its global availability, lower environmental impact, and cost [2–6]. Besides, such raw materials are not in competition with the alimentary sector, avoiding the dilemma of food versus fuel [7,8]. The sugar parts of LCB, i.e., cellulose and hemicellulose, are mainly used to produce chemicals, materials or fuels. The valorization of these polymers of sugar can lead to several platform molecules and their derivatives, such as succinic acid, furfural, 5-HMF, levulinic acid, glycerol, etc. [9–12].

The chemical γ -valerolactone (GVL), produced from the hydrogenation of levulinic acid or ester levulinate, is also considered as a platform molecule [13,14]. Hydrogenation of bio-based carboxylic acids, esters or related compounds is considered a step toward a sustainable and carbon-neutral process [15]. In fine chemistry, GVL is considered an excellent aprotic solvent [16–21] because of its low vapor pressure, high flash point, and potential to increase acid activity [22–26]. In polymer science, GVL is a promising starting material for producing greener monomers [27–30].

In the energy field, GVL cannot be used directly as a fuel [31], but it can be used as an additive fuel [32–35]. GVL is a promising feedstock for producing hydrocarbon fuels [31,36–42] or pentanoic biofuels [43].

From a safety, cost and environmental standpoint, determining the best operating conditions for the production of GVL is vital [44–46]. The literature proposes several routes for producing GVL by hydrogenating raw lignocellulosic biomass, cellulose, glucose or fructose [47]. These different routes require the hydrogenation of levulinic acid or alkyl levulinates, and there are three different hydrogenation options:

- use of molecular hydrogen [34,48–65]

- in situ* FA decomposition producing hydrogen [66–74]

61 -Meerwein-Ponndorf-Verley reaction involving the use of alcohol for hydrogen transfer [75–82]

62 The use of molecular hydrogen and ruthenium-based catalyst is the most efficient system to produce
63 GVL. Developing such a process at an industrial scale requires reliable and robust kinetic models. Such
64 models are essential to optimize the operating cost to get the highest GVL yield. There are several
65 models for the hydrogenation of levulinates or levulinic acid [52,53,57,64,83–87]. These models were
66 developed using experiments performed in isothermal mode, and could limit their application to pinch
67 analysis or process safety.

68 Generally speaking, the development of kinetic models in different thermal modes, e.g., isothermal,
69 adiabatic, isoperibolic, or dynamic modes, is quite seldom in the literature.

70 In adiabatic mode, one can only use the reaction temperature as an observable [88–90] allowing to obtain
71 reliable models for thermal risk assessment [91]. It is impossible to withdraw samples during the
72 reaction; otherwise, the reaction temperature signal is perturbed. Hence, kinetic models only developed
73 in adiabatic mode are limited for thermal risk assessment.

74 In isoperibolic mode, for some chemical systems, it is possible to track the reaction temperature and
75 withdraw some samples to track the concentration in the liquid phase [92–94], allowing the development
76 of reliable kinetic models considering concentration and temperature as observables.

77 There is a need to have kinetic models developed in different thermal modes to improve their reliability
78 and robustness and to be used universally for process safety, process intensification, and cost evaluation.
79 To do that, one must carry out different experiments in isothermal conditions to track the species
80 concentration and in non-isothermal conditions (isoperibolic and adiabatic modes) to track the reaction
81 temperature.

82 To the best of the authors' knowledge, such an approach is highly seldom in the literature [94]. In this
83 study, we developed kinetic models for the hydrogenation of butyl levulinate into GVL over Ru/C in
84 three thermal modes: isothermal, isoperibolic and adiabatic. A high concentrated solution of BL was
85 used to perform experiments. The state-of-the-art reaction calorimeter Mettler-Toledo RC1 was used to
86 perform experiments in different thermal modes. The developed models were validated to assess their

87 reliability and select the most reliable ones. Butyl levulinate was chosen because it is gaining a lot of
88 interest as a platform molecule and can be used in different areas [16,95].

89

2. Experimental section

2.1. Chemicals

Chemicals used during this research for analytical and experimental purposes were purchased from different providers and used without further purification: n-Butyl levulinate (n-BL), acquired from Alfa Aesar with a purity $\geq 98\%$, CAS: 2052-15-5. Hydrogen gas (H_2), acquired from Linde group with a purity $\geq 99.99\%$, CAS: 1333-74-0. γ -Valerolactone (GVL), acquired from Sigma Aldrich with a purity $\geq 99\%$, CAS: 108-29-2. 1-Butanol (BuOH), acquired from LabLine with a purity $\geq 99\%$, CAS: 71-36-3. Ruthenium on activated carbon (Ru/C), acquired from Alfa Aesar, 5% of ruthenium powder, reduced, 50% nominally wet, CAS: 7440-18-8. Acetone, acquired from Fischer Scientific with a purity $\geq 99\%$, CAS: 67-64-1.

2.2. Analytical system

Gas chromatography coupled with a flame ionization detector (GC-FID) technique was applied to quantify the amount of chemicals in samples. GC-FID equipment is from Scion Instruments supplier. GC-FID was equipped with a low polarity column (Phenomenex, ZB-5) composed of 95% dimethyl siloxane and 5% of phenyl groups. Column dimensions: length: 30 m, internal diameter: 0.32 mm, coating width: 0.25 μ m.

Helium (99.99%) was used as carrier gas at a constant flow rate of 1.2 mL/min. The temperature of the injector and the detector were set at 250 °C. The oven temperature ramp was set to 50 °C (1 min) – 20 °C /min – 200 °C (1 min). Samples were diluted in acetone to be analyzed, the injection volume was 1 μ L and the split ratio was 20:1.

2.3. RC1 reactor

To develop a robust kinetic model for GVL production from n-BL, different experiments were performed in the Mettler-Toledo RC1mx calorimeter, considering isothermal and non-isothermal conditions.

The RC1mx is a high-performance calorimeter with a heating and cooling loop system, allowing us to have a very accurate temperature control of the reaction media. The RC1mx vessel is made of Hastelloy C22 metal one, with a 1.8 L capacity and 100 bar of tolerance. A gas inlet and outlet system are connected to the vessel to control the pressure. A PID automatically controls this system. The RC1mx is also equipped with a calibration heater that evaluates the heat capacity (C_p) and the reaction media's global heat transfer coefficient (UA). Fig. 1 represents the RC1mx installation.

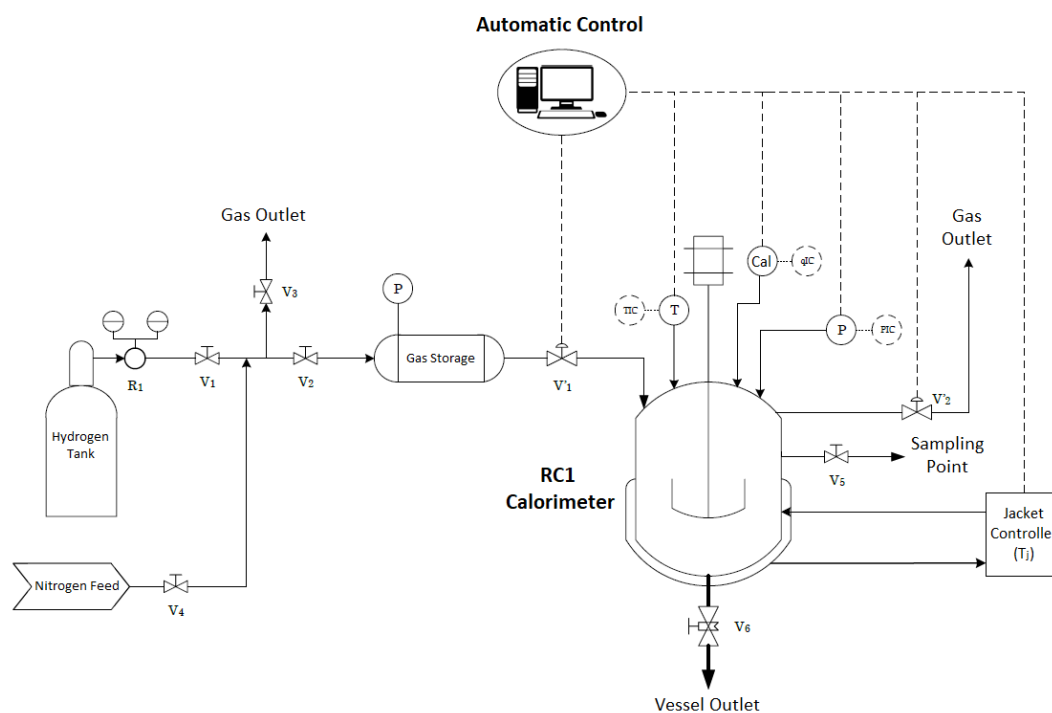


Fig. 1. RC1mx Calorimeter installation.

2.4. Determination of the global heat transfer

The global heat transfer UA plays a fundamental role in the energy balance to characterize the transfer between the heat carrier and reaction temperature. Thus, it is vital to measure it correctly. This value was determined by electrical calibration [96–98]. Calibration experiments were performed without catalysts, and a highly concentrated solution of BL, i.e., weight percentage higher than 98%, was used initially. We varied the temperature and rotating speed to be able to draw the Wilson plot.

2.5. Gas-liquid mass transfer measurement

Table 1 shows the experimental matrix for mass transfer study. These experiments were performed in the absence of catalyst to avoid chemical reactions. The Redlich–Kwong–Mathias–Copeman (RKMC) equation of state was used to quantify the number of moles of hydrogen into the gas phase. According to Nasrifar, the RKMC equation is more accurate and robust [99].

Table 1. Experimental matrix for gas-liquid mass transfer measurement.

Run	m₀BL (kg)	Tr₀ (K)	P (bar)
1_MT	0.520	373.15	25
2_MT	0.520	373.15	25
3_MT	0.520	413.15	25
4_MT	0.520	433.15	25

2.6. Kinetic modeling

Parameter estimation, simulation and curve fitting were performed using the commercial software Athena Visual Studio V.14.2 [100]. Athena Visual Studio uses a Bayesian framework more suitable for multi-response parameter estimation than the classical nonlinear least squares method [101,102]. Indeed, Bayesian inference requires calculating the determinant criterion [103].

The following observables were used for the parameter estimation stage: BL, BHP, GVL and reaction temperatures. Only two samples were withdrawn for experiments performed in isoperibolic or adiabatic conditions: at the beginning and the end of the reaction. Several samples were withdrawn for isothermal kinetic experiments, and the reaction temperature was constant.

The ODEs, obtained from material and energy balances, were integrated by the DDAPLUS solver, a modified Newton algorithm [104]. The GREGPLUS subroutine package was used to minimize the objective function $OF(\xi)$ and to calculate the highest probability density HPD, i.e., credible intervals, of the estimated parameters and the normalized covariance matrix.

GREGPLUS uses successive quadratic programming starting from our initial guess values to minimize $OF(\xi)$ [100].

$$OF(\xi) = (a + b + 1) \cdot \ln|v(\xi)| \quad (1)$$

where a is the number of events in response, b is the number of responses and $|v(\xi)|$ is the determinant of the covariance matrix of the responses.

Each element of the covariance matrix of the responses is

$$v_{ij}(\xi) = \sum_{u=1}^n \omega_u \cdot [Y_{iu} - f_{iu}(\xi)] \cdot [Y_{ju} - f_{ju}(\xi)] \quad (2)$$

where, ω_u is the weight factor, Y_{iu} the experimental concentration or temperature and $f_{iu}(\xi)$ the estimated value for response i and event u ; Y_{ju} the experimental concentration and $f_{ju}(\xi)$ the estimated value for response j and event u .

A modified Arrhenius equation was used to decrease the correlation between the pre-exponential factor and the activation energy by linearizing the original Arrhenius equation as

$$k(T) = \exp \left[\ln \left(k(T_{ref}) \right) + \frac{E_a}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T} \right) \right] \quad (3)$$

where, T_{ref} is the reference temperature chosen in the considered experimental temperature range.

Table 2 shows the experimental matrix for the regression and Table 3 shows the experimental matrix for the validation stage.

Table 2. Experimental matrix for regression with initial conditions.

Run	P (bar)	m ₀ BL (kg)	m ₀ GVL (kg)	m ₀ Ru (kg)	C _{p0} (J kg ⁻¹ K ⁻¹)	UA ₀ (W K ⁻¹)	[BL] ₀ (mol m ⁻³)	[BHP] ₀ (mol m ⁻³)	[GVL] ₀ (mol m ⁻³)	[BuOH] ₀ (mol m ⁻³)	T _{r0} (K)	Thermal mode
1	35	0.415	0.105	0.005	2736	17	4712	0	2082	29	393	isothermal
2	35	0.500	0.000	0.007	2736	19	5929	0	28	65	423	isothermal
3	35	0.500	0.000	0.007	2736	19	9	2222	3909	2883	432	isothermal
4	15	0.117	0.402	0.004	2736	17	1359	2	8198	8	403	isothermal
5	20	0.520	0.000	0.006	3131	17	6105	0	4	3	394	isothermal
1	22	0.500	0.000	0.005	2755	18	6114	0	0	0	412	isoperibolic
2	30	0.400	0.100	0.005	2773	17	4963	0	2079	0	392	isoperibolic
3	30	0.420	0.100	0.005	2646	17	4713	1	1853	31	403	isoperibolic
4	35	0.420	0.100	0.008	3131	17	5090	1	2040	3	393	isoperibolic
1	36	0.520	0.000	0.006	2751	17	5816	0	0	0	393	adiabatic
2	35	0.520	0.000	0.006	2789	15	6056	0	3	53	373	adiabatic
3	25	0.520	0.000	0.005	2704	15	5360	0	0	0	373	adiabatic
4	35	0.420	0.100	0.007	2624	15	4553	0	1786	31	373	adiabatic
5	25	0.520	0.000	0.006	2705	16	5635	0	20	37	383	adiabatic
6	30	0.350	0.170	0.008	2705	17	4223	4	3384	25	403	adiabatic
7	25	0.400	0.120	0.005	3131	18	4681	10	2337	30	413	adiabatic
8	20	0.520	0.000	0.004	3131	17	6339	0	8	62	403	adiabatic

Table 3. Experimental matrix with initial conditions for validation

Run	P (bar)	m ₀ BL (kg)	m ₀ GVL (kg)	m ₀ Ru (kg)	C _{p0} (J kg ⁻¹ K ⁻¹)	UA ₀ (W K ⁻¹)	[BL] ₀ (mol m ⁻³)	[BHP] ₀ (mol m ⁻³)	[GVL] ₀ (mol m ⁻³)	[BuOH] ₀ (mol m ⁻³)	Tr ₀ (K)	Thermal mode
6	38	0.415	0.105	0.005	2736	17	1050	2202	3482	1356	403	isothermal
7	35	0.415	0.105	0.005	2736	15	5059	0	2092	0	373	isothermal
8	20	0.520	0.000	0.006	2736	16	5756	0	4	34	384	isothermal
5	35	0.520	0.000	0.007	2788	15	5857	0	0	0	373	isoperibolic
6	35	0.420	0.100	0.008	2728	16	4984	1	1993	33	383	isoperibolic

3. Results and discussion

3.1. Kinetics

The global kinetics for the hydrogenation of BL is a two-step reaction (Fig. 2).

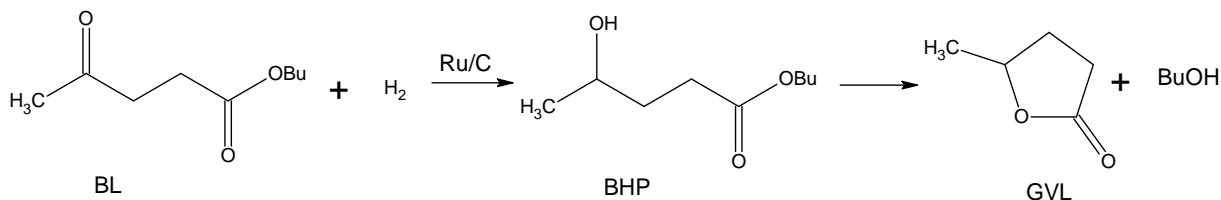


Fig. 2. Reaction pathway for the hydrogenation of BL over Ru/C.

The hydrogenation of the carbonyl group can take different routes, as illustrated in a previous article of our group [105]. In this work we considered five kinetic models to determine the most reliable, these kinetic models are described below:

- Eley-Rideal (ER1): This kinetic model considers that only BL is adsorbed into active sites of the catalyst, and then molecular hydrogen collides directly to the adsorbed BL.
- Langmuir Hinshelwood with molecular adsorption of H_2 (LH1): This kinetic model considers that all reactants, BL and molecular hydrogen, are adsorbed into the active sites of the catalyst without dissociation, then the chemical reaction takes place between adsorbed molecules.
- Langmuir Hinshelwood with hydrogen dissociation (LH2): As LH1 this kinetic model considers that all reactants, BL and molecular hydrogen, are adsorbed into the active sites of the catalyst. However, in this case, molecular hydrogen is dissociated into atomic hydrogen; then the chemical reaction takes place between adsorbed BL and adsorbed atomic hydrogen.
- Non-competitive Langmuir Hinshelwood with molecular adsorption of H_2 (NCLH1): This kinetic model considers that there is no competition between the reactants for the active sites of the catalyst, so that it is considered that BL and molecular hydrogen are adsorbed in different active sites. Chemical reaction occurs between adsorbed BL and adsorbed molecular hydrogen without dissociation.
- Non-competitive Langmuir Hinshelwood with hydrogen dissociation (NCLH2): As NCLH1 this kinetic model considers that there is no competition between the reactants. BL and molecular

hydrogen are adsorbed into different actives sites, then the adsorbed molecular hydrogen is dissociated into atomic hydrogen. The chemical reaction occurs between adsorbed BL and adsorbed atomic hydrogen.

Table 4 shows the rate expression for the different possible reaction mechanisms.

Table 4. Kinetic expression for the different mechanisms for the hydrogenation step.

Kinetic model	Rate expression
Eley-Rideal with no adsorption of hydrogen (ER1)	$\frac{k_1 \cdot [H_2] \cdot K_{BL} \cdot [BL] \cdot \omega_{Cat.}}{(K_{BL} \cdot [BL] + K_{BHP} \cdot [BHP] + 1)}$
Langmuir Hinshelwood with molecular adsorption of H ₂ (LH1)	$\frac{k_1 \cdot K_{H_2} \cdot [H_2] \cdot K_{BL} \cdot [BL] \cdot \omega_{Cat.}}{(K_{H_2} \cdot [H_2] + K_{BL} \cdot [BL] + K_{BHP} \cdot [BHP] + 1)^2}$
Langmuir Hinshelwood with hydrogen dissociation (LH2)	$\frac{k_1 \cdot K_H \cdot [H_2] \cdot K_i \cdot K_{BL} \cdot [BL] \cdot \omega_{Cat.}}{(\sqrt{K_H \cdot [H_2]} + K_{BL} \cdot [BL] + K_{BHP} \cdot [BHP] + K_i \cdot K_{BL} \cdot [BL] \cdot \sqrt{K_H \cdot [H_2]} + 1)^2}$
Non-competitive Langmuir Hinshelwood with no dissociation of hydrogen (NCLH1)	$\frac{k_1 \cdot K_{H_2} \cdot [H_2]}{(1 + K_{H_2} \cdot [H_2])} \cdot \frac{K_{BL^*} \cdot [BL]}{(1 + K_{BHP^*} \cdot [BHP] + K_{BL^*} \cdot [BL])} \cdot \omega_{Cat.}$
Non-competitive Langmuir Hinshelwood with hydrogen dissociation (NCLH2)	$\frac{k_1 \cdot K_H \cdot K_C \cdot K_{BL^*} \cdot [H_2]}{\sqrt{K_H \cdot [H_2]} + 1} \cdot \frac{[BL] \cdot \omega_{Cat.}}{K_{BL^*} \cdot [BL] + K_C \cdot \sqrt{K_H \cdot [H_2]} \cdot K_{BL^*} \cdot [BL] + K_{BHP^*} \cdot [BHP] + 1}$

The kinetic expression for the second reaction step, i.e., the cyclization step, was expressed as

$$R_{Cyclization} = k_2 \cdot [BHP] \quad (4)$$

We applied linearization on the rate constant, and kinetic factors are displayed in Table 5.

Table 5. Kinetic factors and estimated parameters.

Models	Kinetic factors	Estimated parameters
ER1	$\exp\left(\ln(K_{BL}) + \ln(k_1(T_{ref})) + \frac{E_{a1}}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$	$\ln(K_{BL}),$ $\ln(k_1(T_{ref})), \frac{E_{a1}}{R \cdot T_{ref}}$ and $\ln(K_{BHP})$
LH1	$\exp\left(\ln(K_{H2}) + \ln(K_{BL}) + \ln(k_1(T_{ref})) + \frac{E_{a1}}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$	$\ln(K_{H2}), \ln(K_{BL}),$ $\ln(k_1(T_{ref})), \frac{E_{a1}}{R \cdot T_{ref}}$ and $\ln(K_{BHP})$
LH2	$\exp\left(\ln(K_H) + \ln(K_{BL}) + \ln(K_i) + \ln(k_1(T_{ref})) + \frac{E_{a1}}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$	$\ln(K_H), \ln(K_{BL}), \ln(K_i),$ $\ln(k_1(T_{ref})), \frac{E_{a1}}{R \cdot T_{ref}}$ and $\ln(K_{BHP})$
NCLH1	$\exp\left(\ln(K_{H2}) + \ln(K_{BL}^{\wedge}) + \ln(k_1(T_{ref})) + \frac{E_{a1}}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$	$\ln(K_{H2}), \ln(K_{BL}^{\wedge}), \ln(K_{BHP}^{\wedge}),$ $\ln(k_1(T_{ref}))$ and $\frac{E_{a1}}{R \cdot T_{ref}}$
NCLH2	$\exp\left(\ln(K_H) + \ln(K_{BL}^{\wedge}) + \ln(K_c) + \ln(k_1(T_{ref})) + \frac{E_{a1}}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T}\right)\right)$	$\ln(K_H), \ln(K_{BL}^{\wedge}), \ln(K_{BHP}^{\wedge}),$ $\ln(K_c),$ $\ln(k_1(T_{ref}))$ and $\frac{E_{a1}}{R \cdot T_{ref}}$

3.2. Material and energy balances

Due to the vigorous stirring, ideal hydrodynamics was assumed in the RC1 reactor. Material balances for different compounds in the liquid phase leads to:

$$\frac{dC_{BL}}{dt} = -R_{Hydrogenation} \quad (5)$$

$$\frac{d[H_2]_{liq}}{dt} = k_L \cdot a \cdot ([H_2]_{liq}^* - [H_2]_{liq}) - R_{Hydrogenation} \quad (6)$$

$$\frac{dC_{BHP}}{dt} = R_{Hydrogenation} - R_{Cyclization} \quad (7)$$

$$\frac{dC_{BuOH}}{dt} = R_{Cyclization} \quad (8)$$

$$\frac{dC_{GVL}}{dt} = R_{Cyclization} \quad (9)$$

The term $[H_2]_{liq}^*$ is hydrogen concentration at the gas-liquid interface. This value depends on temperature and was determined through Henry's constant: $He(T) = \frac{[H_2]_{liq}^*}{P_{H_2,Reactor}}$ [54]. A separate mass transfer coefficient study was carried out to estimate the volumetric gas-to-liquid mass transfer coefficient for hydrogen. A similar methodology applied in a previous study of our group was used [57] to estimate this mass transfer coefficient by taking into account density and viscosity of the reaction mixture [106]. For the sake of clarity, this information was added in Supplementary Material (S1). The value of $He(T)$ can change with temperature and chemical composition, the results from Capecci et al. were used [54].

The heat balance equation for the liquid phase leads to

$$\frac{dT_R}{dt} = \frac{(-R_{Hydrogenation} \cdot \Delta H_{R,Hydrogenation} \cdot V - R_{Cyclization} \cdot \Delta H_{R,Cyclization} \cdot V) + UA \cdot (T_j - T_R) + \alpha \cdot (T_{amb} - T_R)}{m_R \cdot C_{PR} + m_{insert} \cdot C_{pinsert} + m_{catalyst} \cdot C_{p_{catalyst}}} \quad (10)$$

The term $\alpha \cdot (T_{amb} - T_R)$ represents the heat loss with the surroundings. The term $UA \cdot (T_j - T_R)$ is the heat flow rate exchanged with the heat carrier, and UA is the global heat transfer, T_j and T_R are the jacket and reaction temperatures. The term $m_R \cdot C_{PR} + m_{insert} \cdot C_{pinsert} + m_{catalyst} \cdot C_{p_{catalyst}}$ represents the

235 thermal inertia, where $m_{insert} \cdot Cp_{insert}$ is equal to $52 \text{ J}\cdot\text{K}^{-1}$, according to the manufacturer, C_{PR} was
236 evaluated based on the evolution of chemical composition and temperature [24] and $Cp_{catalyst}$ was
237 found based on the article of Lu et al. [107]. Reaction enthalpies for hydrogenation $\Delta H_{R,Hydrogenation}$
238 and cyclization $\Delta H_{R,Cyclization}$ were the ones calculated by Wang et al. [46].

239

3.3. Calibration results (Wilson plot)

In order to verify the thin wall approximation between the heat carrier and reaction mixture and to predict the UA values with reaction temperature, UA value was calculated at different temperatures and rotating speeds in the absence of reaction, i.e., Wilson plot [98]. Fig. 3 shows the linearity between $1/UA$ and $N^{-2/3}$, confirming the thin wall approximation.

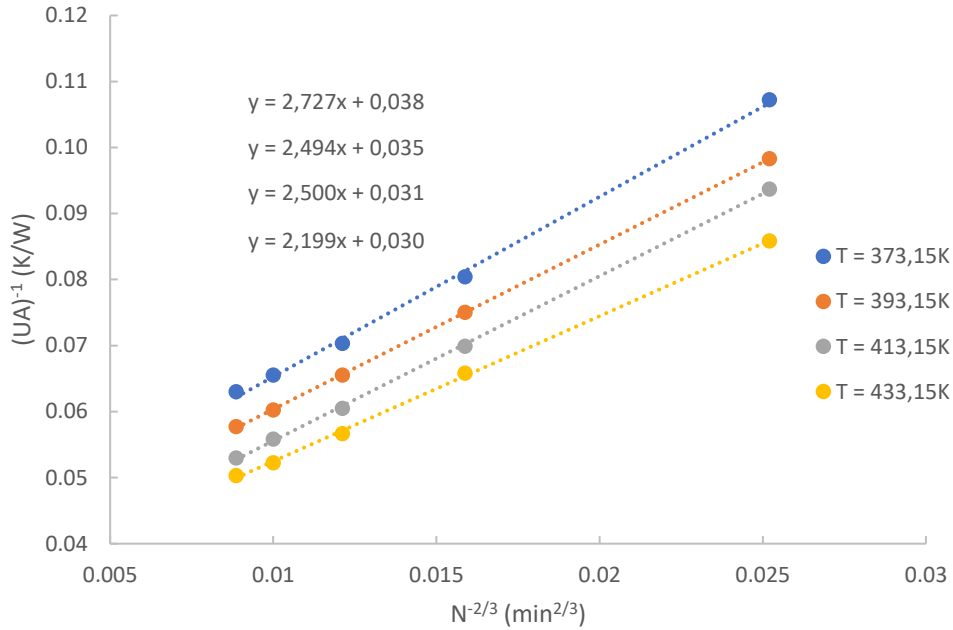


Fig. 3. Wilson plot.

3.4. Gas-liquid mass transfer results

In these experiments, rates of hydrogenation and cyclization are equal to zero, thus one should integrate Eq. (6) to estimate the $k_L a$ value. The volumetric mass transfer coefficient was expressed as [57]:

$$k_L a = (k_L a)_{modified} \cdot \left(\frac{T_{liq}}{\mu_{liq}} \right)^{0.5} \cdot \left(\frac{\rho_{liq}}{\mu_{liq}} \right)^{0.25} \quad (11)$$

The constant $(k_L a)_{modified}$ was calculated from experiments shown in Table 1 as described in Supplementary Material (S1). From Table S1.1, one can notice that the calculated value of $(k_L a)_{modified}$ for each run is very similar. The average value of $(k_L a)_{modified}$ was found to be $2.25 \cdot 10^{-6} \text{ (Pa} \cdot \text{s} \cdot \text{K}^{-1})^{0.5} \text{ (Pa} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \text{m}^{-3})^{0.25} \cdot \text{s}^{-1}$ and the standard deviation was equal to $0.14 \text{ (Pa} \cdot \text{s} \cdot \text{K}^{-1})^{0.5} \text{ (Pa} \cdot \text{s} \cdot \text{kg}^{-1} \cdot \text{m}^{-3})^{0.25} \cdot \text{s}^{-1}$. This value was found to be similar than the one of Wang et al. [57].

3.5. Kinetic modeling

3.5.1. Regression

The five models were tested during the regression (ER1, LH1, LH2, NCLH1 and NCLH2). The Akaike information criterion (AIC) was used to evaluate the most reliable models, and it was calculated as

$$AIC: \text{number of independant event} \cdot \ln \left(\frac{[Y_{ju} - f_{ju}(\xi)]^2}{\text{number of independant event}} \right) + 2 \cdot \text{Number of estimated parameters} \quad (12)$$

This criterion penalizes models with numerous parameters to estimate. Table 6 shows the values for each observable.

Table 6. AIC values for each observable and model.

	AIC				Number of parameters to estimate
	BL	BHP	GVL	Tr	
ER1	2529	2010	2151	36	6
LH1	2498	2008	2131	117	7
LH2	2500	2010	2133	118	8
NCLH1	2520	1993	2139	54	7
NCLH2	2508	2056	2161	38	8

Table 6 shows that NCLH1 and NCLH2 are the most reliable model by considering the AIC for all observables. Indeed, NCLH1 and NCLH2 models present a good compromise between the lowest AIC values for Tr and medium AIC values for BL, BHP and GVL.

For the sake of clarity, modeling results using NCLH1 model are displayed, and the others are in Supplementary Material (S2). Table 7 shows the value of the estimated parameters and the statistical values. The model can estimate the kinetic constants with low credible intervals. However, the estimation of adsorption constants is more challenging due to the difficulty to estimate such thermodynamic constants.

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Table 7. Estimated values at $T_{ref} = 398.15$ K and statistical data for NCLH1.

	Units	Estimate	HPD	HPD%
$\ln(k_1(T_{ref}))$	mol. kg_dry basis $\text{RuC}^{-1} \cdot \text{s}^{-1}$	5.34	0.12	2.17
$\ln(k_2(T_{ref}))$	s^{-1}	-10.19	0.03	0.28
$\frac{E_{a1}}{R \cdot T_{ref}}$	-	9.25	0.73	7.92
$\frac{E_{a2}}{R \cdot T_{ref}}$	-	8.09	0.59	7.27
$\ln(K_H)$	$\text{m}^3 \cdot \text{mol}^{-1}$	-2.91	0.26	8.93
$\ln(K_{BL}^{\wedge})$	$\text{m}^3 \cdot \text{mol}^{-1}$	0.011	-	
$\ln(K_{BHP}^{\wedge})$	$\text{m}^3 \cdot \text{mol}^{-1}$	7.961	-	

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Table 8. Normalized parameter covariance matrix for NCLH1.

	$\ln(k_1(T_{ref}))$	$\ln(k_2(T_{ref}))$	$\frac{E_{a1}}{R \cdot T_{ref}}$	$\frac{E_{a2}}{R \cdot T_{ref}}$	$\ln(K_H)$
$\ln(k_1(T_{ref}))$	1				
$\ln(k_2(T_{ref}))$	0.07	1			
$\frac{E_{a1}}{R \cdot T_{ref}}$	-0.163	-0.047	1		
$\frac{E_{a2}}{R \cdot T_{ref}}$	-0.086	-0.671	-0.059	1	
$\ln(K_H)$	-0.981	-0.071	0.123	0.081	1

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280 Correlation between the majority of estimated parameters are lower than 0.90 in absolute value, thus
 281 one can consider that the estimated parameters are not correlated [108]. This absence of correlation
 282 shows that the parameters are well identified. The parameter $\ln(k_1(T_{ref}))$ and $\ln(K_H)$ are strongly
 283 correlated, due to the difficulty to correctly track the hydrogenation rate.

284 Figs 4-6 show the fit of the model to experimental data in different thermal modes for NCLH1 model.
 285 Generally, the model fits well the experimental data in these modes as it is confirmed with the parity
 286 plot (Fig. 7). In isothermal mode, experimental temperatures were not considered in the objective
 287 function, because the reaction temperature is stable along the reaction course. For adiabatic and
 288 isoperibolic experiments, we measured concentrations at the beginning and at the end of the reaction.

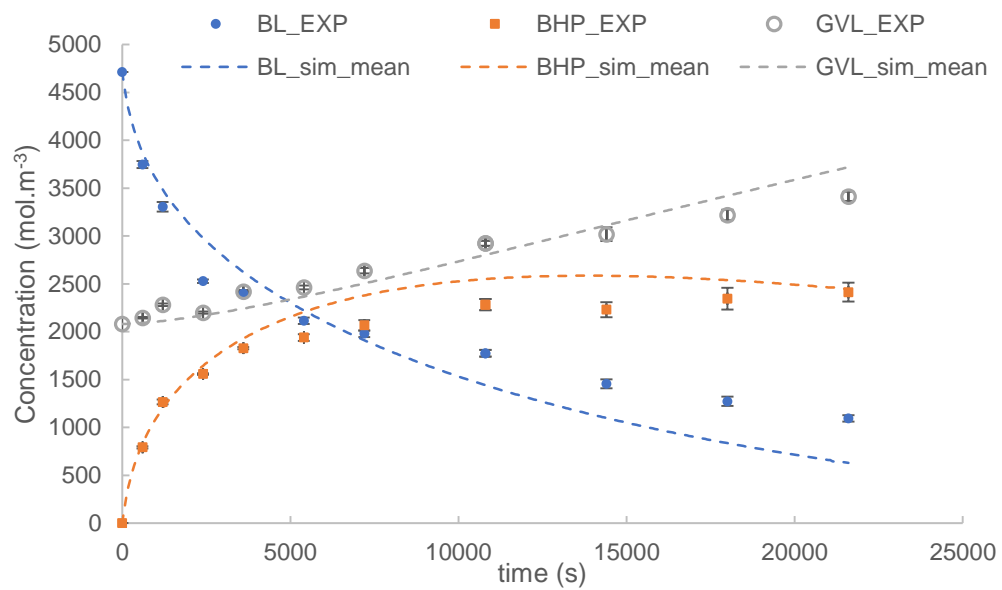
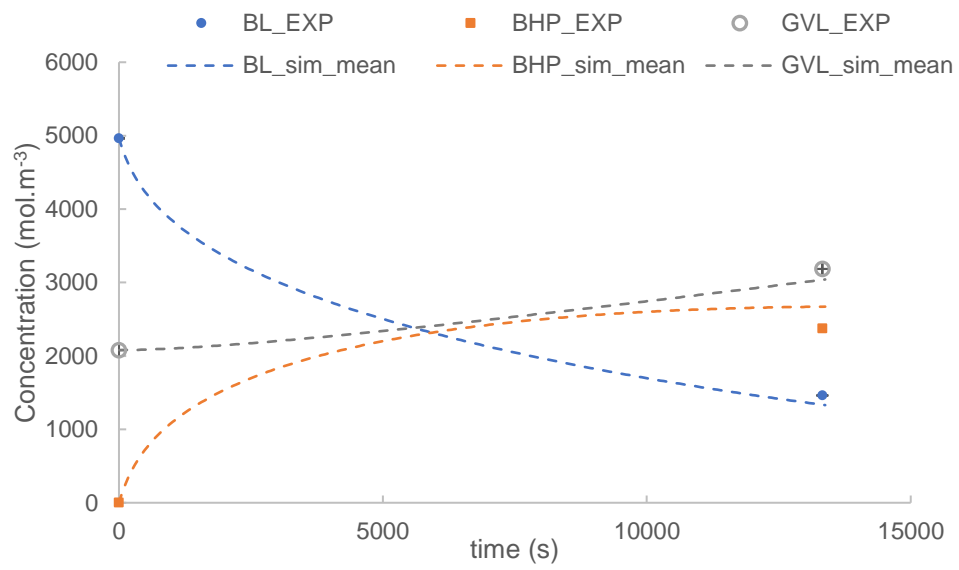
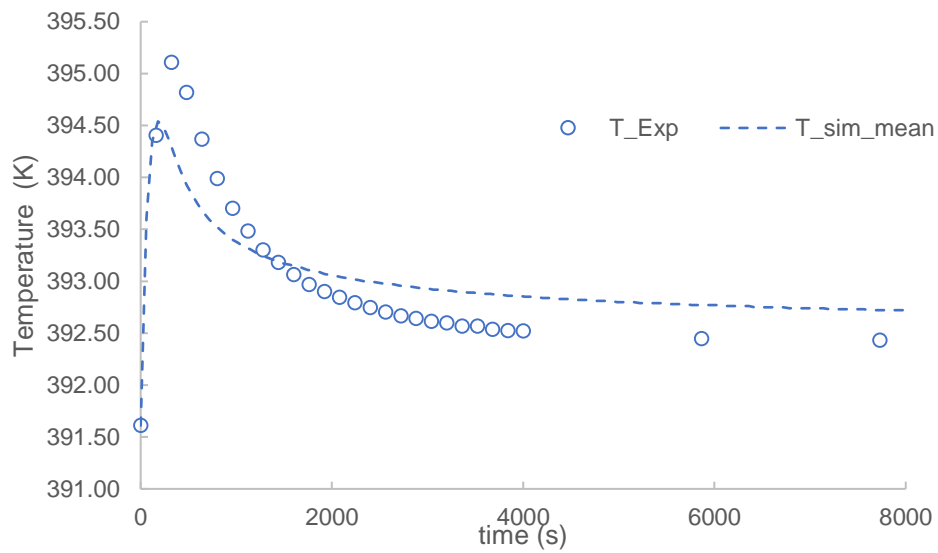


Fig. 4. Fit of the NCLH1 model to isothermal experimental data for Run 1.

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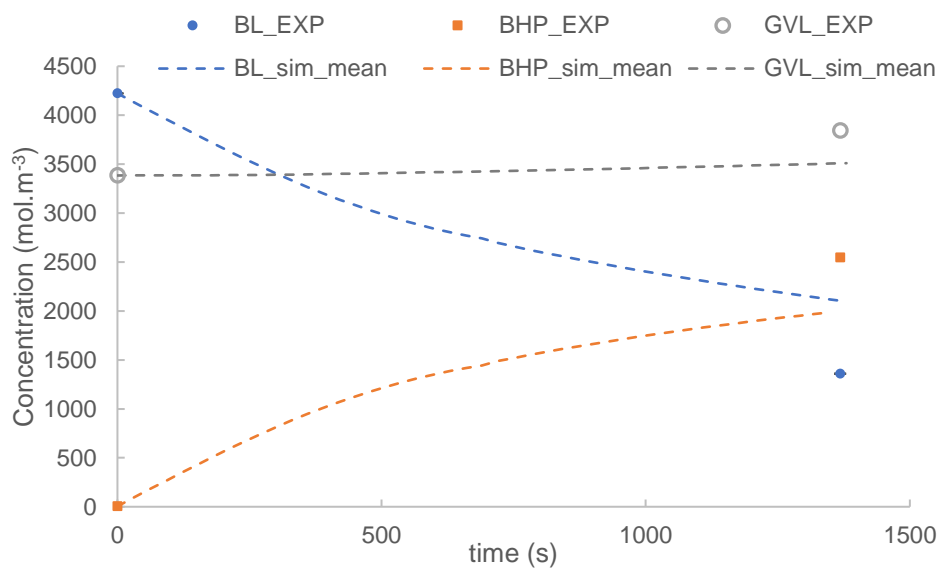
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Fig. 5. Fit of the NCLH1 model to isoperibolic experimental data for Run 2.

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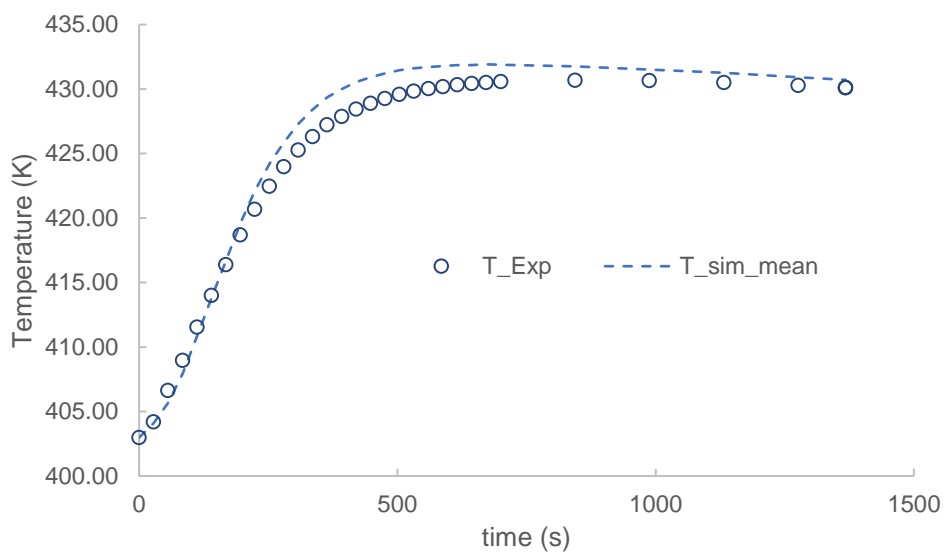
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Fig. 6. Fit of the NCLH2 model to adiabatic experimental data for Run 6.

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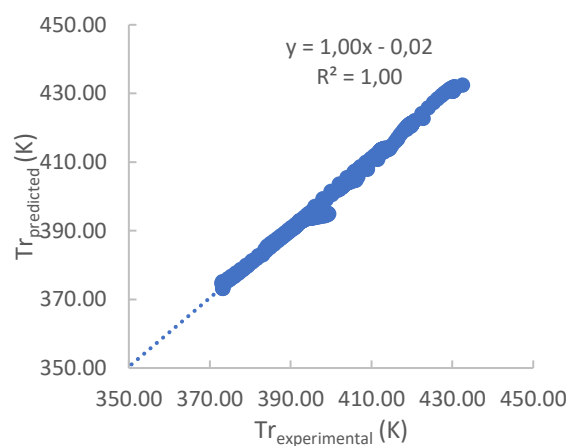
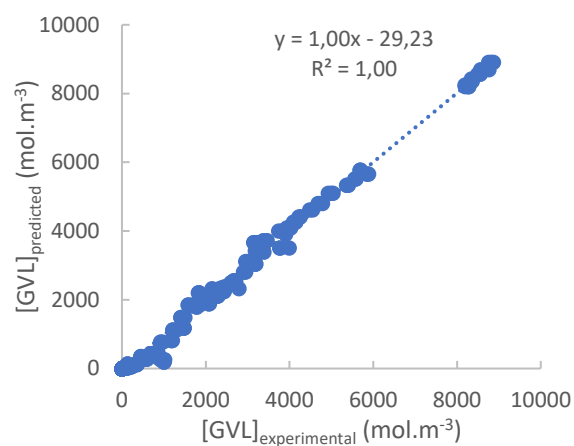
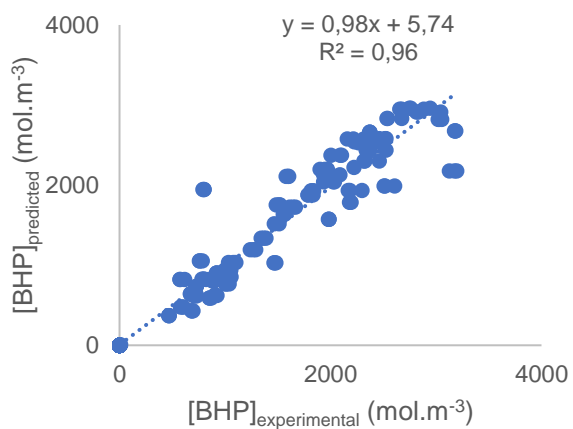
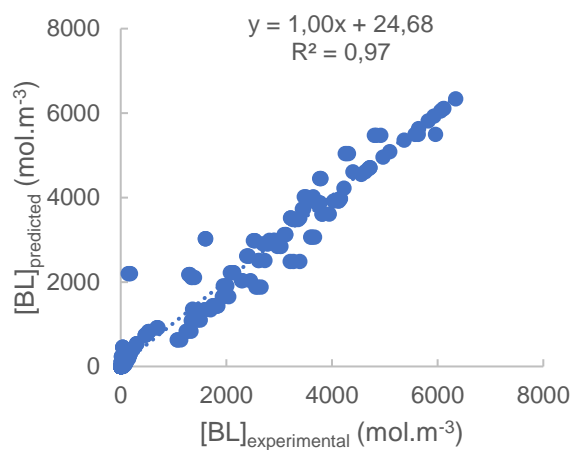


Fig. 7. Parity plots from regression stage (model NCLH1)

3.5.2. Validation stage

A holdout validation method was used. The estimated kinetic and thermodynamic constants obtained from the regression stage were used to predict the kinetic profile by using initial experimental conditions from Table 3. Fig. 8 show parity plots for the validation experiments for NCLH1, showing the good prediction capacity of NCLH1. NCLH1 can correctly predict BL and GVL concentrations, as well as reaction temperature. This model is less accurate for BHP concentration.

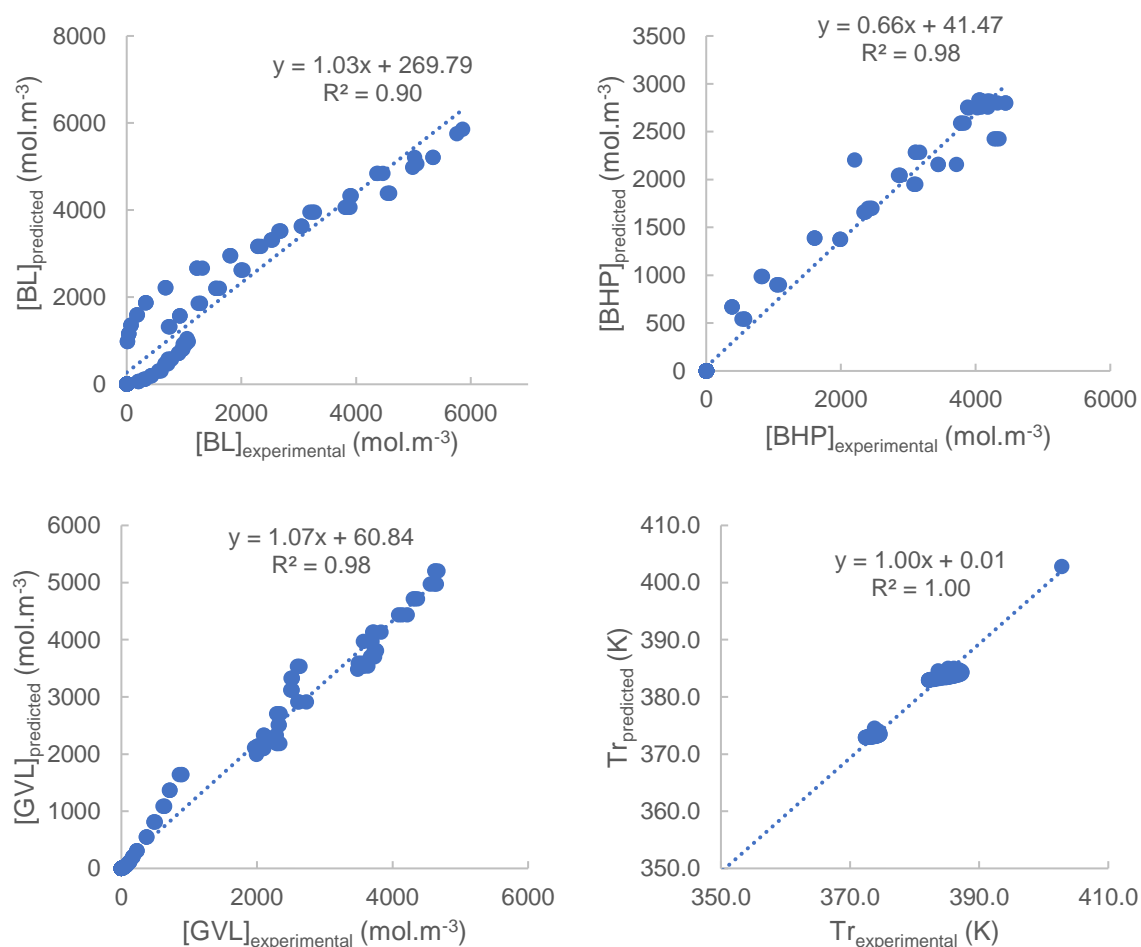


Fig. 8. Parity plots from validation stage (model NCLH1)

4. Conclusions

There is a need to develop reliable and robust kinetic models to scaleup, optimize process production, energy consumption and production, cost production and for thermal risk assessment. Traditionally, these types of kinetic models are developed in isothermal conditions without considering the energy balance. Thus, such models are limited for energy optimization or thermal risk assessment.

In this work, we developed and assessed 5 kinetic models in different thermal modes, i.e., isothermal, adiabatic and isoperibolic one. We applied this approach for the production of γ -valerolactone from the hydrogenation of butyl levulinate. To the best of the authors' knowledge, it is the first time that kinetic model are done in different thermal modes. Such models can provide crucial information in process optimization, scaleup, energy recovery for pinch analysis and thermal risk assessment.

Kinetic experiments were performed by using high concentrated solution of BL in the RC1 calorimeter using three thermal modes (isothermal, isoperibolic and adiabatic). For the regression stage, we varied the initial temperature from 383 to 430 K, catalyst loading from 6.5 to 13.5 kg/m³ and hydrogen pressure from 15 to 35 bar. We were able to estimate kinetic constants for 5 kinetic models: Eley-Rideal with no adsorption of hydrogen (ER1), Langmuir Hinshelwood with molecular adsorption of H₂ (LH1), Langmuir Hinshelwood with hydrogen dissociation (LH2), Non-competitive Langmuir Hinshelwood with no dissociation of hydrogen (NCLH1) and Non-competitive Langmuir Hinshelwood with hydrogen dissociation (NCLH2). From the AIC criterion, we found that NCLH1 and NCLH2 models were the most reliable model. A validation stage was done using a holdout method, and confirmed the reliability of NCLH1 model.

A continuation of this work could be the determination of these constants from quantum mechanics method.

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References

- [1] Rapier R. Highlights From The BP Statistical Review Of World Energy 2021 2021.
<https://sourcezon.com/articles/highlights-from-the-bp-statistical-review-of-world-energy-2021?slug=highlights-from-the-bp-statistical-review-of-world-energy-2021&q=> (accessed February 5, 2023).
- [2] Manikandan S, Vickram S, Sirohi R, Subbaiya R, Krishnan RY, Karmegam N, et al. Critical review of biochemical pathways to transformation of waste and biomass into bioenergy. *Bioresour Technol* 2023;372:128679. <https://doi.org/10.1016/j.biortech.2023.128679>.
- [3] Amerit B, Ntayi JM, Ngoma M, Bashir H, Echegu S, Nantongo M. Commercialization of biofuel products: A systematic literature review. *Renew Energy Focus* 2023;44:223–36. <https://doi.org/10.1016/j.ref.2022.12.008>.
- [4] Jiang Y, Li Z, Li Y, Chen L, Zhang H, Li H, et al. Recent advances in sustainable catalytic production of 5-methyl-2-pyrrolidones from bio-derived levulinate. *Fuel* 2023;334:126629. <https://doi.org/10.1016/j.fuel.2022.126629>.
- [5] Ashokkumar V, Venkatkarthick R, Jayashree S, Chuetor S, Dharmaraj S, Kumar G, et al. Recent advances in lignocellulosic biomass for biofuels and value-added bioproducts - A critical review. *Bioresour Technol* 2022;344:960–8524. <https://doi.org/10.1016/j.biortech.2021.126195>.
- [6] Liu WJ, Yu HQ. Thermochemical Conversion of Lignocellulosic Biomass into Mass-Produced Fuels: Emerging Technology Progress and Environmental Sustainability Evaluation. *ACS Environ Au* 2022;2:98–114. <https://doi.org/10.1021/acsenvironau.1c00025>.
- [7] Jamil F, Saleem M, Ali Qamar O, Khurram MS, Al-Muhtaseb AH, Inayat A, et al. State-of-the-art catalysts for clean fuel (methyl esters) production—a comprehensive review. *JPhys Energy* 2023;5:014005. <https://doi.org/10.1088/2515-7655/aca5b3>.
- [8] Tomei J, Helliwell R. Food versus fuel? Going beyond biofuels. *Land Use Policy*

- 2016;56:320–6. <https://doi.org/10.1016/j.landusepol.2015.11.015>.
- [9] Alonso DM, Wettstein SG, Mellmer MA, Gurbuz EI, Dumesic JA. Integrated conversion of hemicellulose and cellulose from lignocellulosic biomass. *Energy Environ Sci* 2013;6:76–80. <https://doi.org/10.1039/c2ee23617f>.
- [10] Li G, Liu W, Ye C, Li X, Si CL. Chemocatalytic Conversion of Cellulose into Key Platform Chemicals. *Int J Polym Sci* 2018;2018. <https://doi.org/10.1155/2018/4723573>.
- [11] Guo K, Guan Q, Xu J, Tan W. Mechanism of Preparation of Platform Compounds from Lignocellulosic Biomass Liquefaction Catalyzed by Bronsted Acid: A Review. *J Bioresour Bioprod* 2019;4:202–13. <https://doi.org/10.12162/jbb.v4i4.009>.
- [12] Di Menno Di Bucchianico D, Wang Y, Buvat JC, Pan Y, Casson Moreno V, Leveneur S. Production of levulinic acid and alkyl levulinates: A process insight. *Green Chem* 2022;24:614–46. <https://doi.org/10.1039/d1gc02457d>.
- [13] Yan K, Yang Y, Chai J, Lu Y. Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals. *Appl Catal B Environ* 2015;179:292–304. <https://doi.org/10.1016/J.APCATB.2015.04.030>.
- [14] Kerkel F, Markiewicz M, Stolte S, Müller E, Kunz W. The green platform molecule gamma-valerolactone - ecotoxicity, biodegradability, solvent properties, and potential applications. *Green Chem* 2021;23:2962–76. <https://doi.org/10.1039/d0gc04353b>.
- [15] Qu R, Junge K, Beller M. Hydrogenation of Carboxylic Acids, Esters, and Related Compounds over Heterogeneous Catalysts: A Step toward Sustainable and Carbon-Neutral Processes. *Chem Rev* 2022. <https://doi.org/10.1021/acs.chemrev.2c00550>.
- [16] Di Menno Di Bucchianico D, Buvat JC, Mignot M, Casson Moreno V, Leveneur S. Role of solvent the production of butyl levulinate from fructose. *Fuel* 2022;318:123703. <https://doi.org/10.1016/j.fuel.2022.123703>.
- [17] Liu C, Wei M, Wang J, Xu J, Jiang J, Wang K. Facile Directional Conversion of Cellulose and

Bamboo Meal Wastes over Low-Cost Sulfate and Polar Aprotic Solvent. ACS Sustain Chem Eng 2020;8:5776–86. <https://doi.org/10.1021/acssuschemeng.0c01280>.

[18] Wang S, Zhao Y, Lin H, Chen J, Zhu L, Luo Z. Conversion of C5 carbohydrates into furfural catalyzed by a Lewis acidic ionic liquid in renewable γ -valerolactone. Green Chem 2017;19:3869–79. <https://doi.org/10.1039/c7gc01298e>.

[19] Chew AK, Walker TW, Shen Z, Demir B, Witteman L, Euclide J, et al. Effect of Mixed-Solvent Environments on the Selectivity of Acid-Catalyzed Dehydration Reactions. ACS Catal 2020;10:1679–91. <https://doi.org/10.1021/acscatal.9b03460>.

[20] Kang D, Choi M, Kim D, Han J. Environmental Analysis of Catalytic Adipic Acid Production Strategies from Two Different Lignocellulosic Biomasses. ACS Sustain Chem Eng 2022. <https://doi.org/10.1021/acssuschemeng.2c00070>.

[21] Motagamwala AH, Won W, Maravelias CT, Dumesic JA. An engineered solvent system for sugar production from lignocellulosic biomass using biomass derived γ -valerolactone. Green Chem 2016;18:5756–63. <https://doi.org/10.1039/c6gc02297a>.

[22] Baco S, Klinksiek M, Ismail Bedawi Zakaria R, Antonia Garcia-Hernandez E, Mignot M, Legros J, et al. Solvent effect investigation on the acid-catalyzed esterification of levulinic acid by ethanol aided by a Linear Solvation Energy Relationship. Chem Eng Sci 2022;260:117928. <https://doi.org/10.1016/j.ces.2022.117928>.

[23] Pokorný V, Štejfá V, Fulem M, Červinka C, Růžička K. Vapor Pressures and Thermophysical Properties of Ethylene Carbonate, Propylene Carbonate, γ -Valerolactone, and γ -Butyrolactone. J Chem Eng Data 2017;62:4174–86. <https://doi.org/10.1021/acs.jced.7b00578>.

[24] Ariba H, Wang Y, Devouge-Boyer C, Stateva RP, Leveneur S. Physicochemical Properties for the Reaction Systems: Levulinic Acid, Its Esters, and γ -Valerolactone. J Chem Eng Data 2020;65:3008–20. <https://doi.org/10.1021/acs.jced.9b00965>.

[25] Horváth IT, Mehdi H, Fábos V, Boda L, Mika LT. γ -Valerolactone—a sustainable liquid for

energy and carbon-based chemicals. *Green Chem* 2008;10:238–24.
<https://doi.org/10.1039/b712863k>.

[26] Raj T, Chandrasekhar K, Banu R, Yoon JJ, Kumar G, Kim SH. Synthesis of γ -valerolactone (GVL) and their applications for lignocellulosic deconstruction for sustainable green biorefineries. *Fuel* 2021;303:121333. <https://doi.org/10.1016/j.fuel.2021.121333>.

[27] Al-Naji M, Puértolas B, Kumru B, Cruz D, Bäuml M, Schmidt BVKJ, et al. Sustainable Continuous Flow Valorization of γ -Valerolactone with Trioxane to α -Methylene- γ -Valerolactone over Basic Beta Zeolites. *ChemSusChem* 2019;12:2628–36.
<https://doi.org/10.1002/cssc.201900418>.

[28] Manzer LE. Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer. *Appl Catal A Gen* 2004;272:249–56.
<https://doi.org/10.1016/J.APCATA.2004.05.048>.

[29] Choi M, Byun J, Park H, Jeong K, Kim SM, Han J. Economically-feasible “greener” transformation of gamma-valerolactone to nylon 6,6. *Biomass and Bioenergy* 2022;162:106503. <https://doi.org/10.1016/J.BIOMBIOE.2022.106503>.

[30] Hayes G, Laurel M, MacKinnon D, Zhao T, Houck HA, Becer CR. Polymers without Petrochemicals: Sustainable Routes to Conventional Monomers. *Chem Rev* 2022.
<https://doi.org/10.1021/acs.chemrev.2c00354>.

[31] Alonso DM, Bond JQ, Dumesic JA. Catalytic conversion of biomass to biofuels. *Green Chem* 2010;12:1493–513. <https://doi.org/10.1039/c004654j>.

[32] Dutta S, Yu IKM, Tsang DCW, Ng YH, Ok YS, Sherwood J, et al. Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: A critical review. *Chem Eng J* 2019;372:992–1006.
<https://doi.org/10.1016/j.cej.2019.04.199>.

[33] Making alternative fuels cheaper | MIT News | Massachusetts Institute of Technology n.d.

<https://news.mit.edu/2013/making-alternative-fuels-cheaper-0617> (accessed February 5, 2023).

- [34] Anagnostopoulou E, Lilas P, Diamantopoulou P, Fakas C, Krithinakis I, Patatsi E, et al. Hydrogenation of the pivotal biorefinery platform molecule levulinic acid into renewable fuel γ -valerolactone catalyzed by unprecedented highly active and stable ruthenium nanoparticles in aqueous media. *Renew Energy* 2022;192:35–45. <https://doi.org/10.1016/j.renene.2022.04.081>.
- [35] Kasar GB, Date NS, Bhosale PN, Rode C V. Steering the Ester and γ -Valerolactone Selectivities in Levulinic Acid Hydrogenation. *Energy and Fuels* 2018;32:6887–900. <https://doi.org/10.1021/acs.energyfuels.8b01263>.
- [36] Alonso DM, Wettstein SG, Dumesic JA. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green Chem* 2013;15:584–95. <https://doi.org/10.1039/c3gc37065h>.
- [37] Yan K, Lafleur T, Wu X, Chai J, Wu G, Xie X. Cascade upgrading of γ -valerolactone to biofuels. *Chem Commun* 2015;51:6984–7. <https://doi.org/10.1039/c5cc01463h>.
- [38] Ayodele OO, Dawodu FA, Yan D, Dong H, Xin J, Zhang S. Production of Bio-Based Gasoline by Noble-Metal-Catalyzed Hydrodeoxygenation of α -Angelica Lactone Derived Di/Trimers. *ChemistrySelect* 2017;2:4219–25. <https://doi.org/10.1002/slct.201700451>.
- [39] Wang H, Wu Y, Guo S, Dong C, Ding M. γ -Valerolactone converting to butene via ring-opening and decarboxylation steps over amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst. *Mol Catal* 2020;497:111218. <https://doi.org/10.1016/j.mcat.2020.111218>.
- [40] Wang H, Wu Y, Li Y, Peng J, Gu XK, Ding M. One-step synthesis of pentane fuel from γ -valerolactone with high selectivity over a Co/HZSM-5 bifunctional catalyst. *Green Chem* 2021;23:4780–9. <https://doi.org/10.1039/d1gc01062j>.
- [41] Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA. Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels. *Science* (80-) 2010;327:1110–4. <https://doi.org/10.1126/science.1184362>.

- 480 [42] Han J. Integrated process for simultaneous production of jet fuel range alkenes and N-
481 methylformanilide using biomass-derived gamma-valerolactone. *J Ind Eng Chem*
482 2017;48:173–9. <https://doi.org/10.1016/j.jiec.2016.12.036>.
- 483 [43] He J, Lin L, Liu M, Miao C, Wu Z, Chen R, et al. A durable Ni/La-Y catalyst for efficient
484 hydrogenation of γ -valerolactone into pentanoic biofuels. *J Energy Chem* 2022;70:347–55.
485 <https://doi.org/10.1016/j.jechem.2022.02.011>.
- 486 [44] Casson Moreno V, Garbetti AL, Leveneur S, Antonioni G. A consequences-based approach for
487 the selection of relevant accident scenarios in emerging technologies. *Saf Sci* 2019;112:142–
488 51. <https://doi.org/10.1016/j.ssci.2018.10.024>.
- 489 [45] Wang Y, Vernières-Hassimi L, Casson-Moreno V, Hébert JP, Leveneur S. Thermal Risk
490 Assessment of Levulinic Acid Hydrogenation to γ -Valerolactone. *Org Process Res Dev*
491 2018;22:1092–100. <https://doi.org/10.1021/acs.oprd.8b00122>.
- 492 [46] Wang Y, Plazl I, Vernières-Hassimi L, Leveneur S. From calorimetry to thermal risk
493 assessment: γ -Valerolactone production from the hydrogenation of alkyl levulinates. *Process*
494 *Saf Environ Prot* 2020;144:32–41. <https://doi.org/10.1016/j.psep.2020.07.017>.
- 495 [47] Karanwal N, Kurniawan RG, Park J, Verma D, Oh S, Kim SM, et al. One-pot, cascade
496 conversion of cellulose to γ -valerolactone over a multifunctional Ru–Cu/zeolite-Y catalyst in
497 supercritical methanol. *Appl Catal B Environ* 2022;314:121466.
498 <https://doi.org/10.1016/j.apcatb.2022.121466>.
- 499 [48] Siddiqui N, Pendem C, Goyal R, Khatun R, Khan TS, Samanta C, et al. Study of γ -
500 valerolactone production from hydrogenation of levulinic acid over nanostructured Pt-
501 hydrotalcite catalysts at low temperature. *Fuel* 2022;323:124272.
502 <https://doi.org/10.1016/j.fuel.2022.124272>.
- 503 [49] Mehdi H, Fábos V, Tuba R, Bodor A, Mika LT, Horváth IT. Integration of homogeneous and
504 heterogeneous catalytic processes for a multi-step conversion of biomass: From sucrose to

levulinic acid, γ -valerolactone, 1,4-pentanediol, 2-methyl-tetrahydrofuran, and alkanes. Top. Catal., vol. 48, Springer; 2008, p. 49–54. <https://doi.org/10.1007/s11244-008-9047-6>.

[50] Luo W, Deka U, Beale AM, Van Eck ERH, Bruijninx PCA, Weckhuysen BM. Ruthenium-catalyzed hydrogenation of levulinic acid: Influence of the support and solvent on catalyst selectivity and stability. J Catal 2013;301:175–86. <https://doi.org/10.1016/j.jcat.2013.02.003>.

[51] Hengne AM, Rode C V. Cu–ZrO₂ nanocomposite catalyst for selective hydrogenation of levulinic acid and its ester to γ -valerolactone. Green Chem 2012;14:1064–72. <https://doi.org/10.1039/c2gc16558a>.

[52] Piskun AS, van de Bovenkamp HH, Rasrendra CB, Winkelman JGM, Heeres HJ. Kinetic modeling of levulinic acid hydrogenation to γ -valerolactone in water using a carbon supported Ru catalyst. Appl Catal A Gen 2016;525:158–67. <https://doi.org/10.1016/j.apcata.2016.06.033>.

[53] Capecchi S, Wang Y, Delgado J, Casson Moreno V, Mignot M, Grénman H, et al. Bayesian Statistics to Elucidate the Kinetics of γ -Valerolactone from n-Butyl Levulinate Hydrogenation over Ru/C. Ind Eng Chem Res 2021;60:11725–36. <https://doi.org/10.1021/acs.iecr.1c02107>.

[54] Capecchi S, Wang Y, Casson Moreno V, Held C, Leveneur S. Solvent effect on the kinetics of the hydrogenation of n-butyl levulinate to γ -valerolactone. Chem Eng Sci 2021;231:116315. <https://doi.org/10.1016/j.ces.2020.116315>.

[55] Xu H, Hu D, Zhang M, Wang Y, Zhao Z, Jiang Z, et al. Bimetallic NiCu Alloy Catalysts for Hydrogenation of Levulinic Acid. ACS Appl Nano Mater 2021;4:3989–97. <https://doi.org/10.1021/acsanm.1c00339>.

[56] Al-Shaal MG, Wright WRH, Palkovits R. Exploring the ruthenium catalysed synthesis of γ -valerolactone in alcohols and utilisation of mild solvent-free reaction conditions. Green Chem 2012;14:1260–3. <https://doi.org/10.1039/c2gc16631c>.

[57] Wang Y, Cipolletta M, Vernières-Hassimi L, Casson-Moreno V, Leveneur S. Application of the concept of Linear Free Energy Relationships to the hydrogenation of levulinic acid and its

530 corresponding esters. Chem Eng J 2019;374:822–31. <https://doi.org/10.1016/j.cej.2019.05.218>.

531 [58] Li C, Xu G, Zhai Y, Liu X, Ma Y, Zhang Y. Hydrogenation of biomass-derived ethyl
532 levulinate into Γ -valerolactone by activated carbon supported bimetallic Ni and Fe catalysts.
533 Fuel 2017;203:23–31. <https://doi.org/10.1016/j.fuel.2017.04.082>.

534 [59] Yan K, Chen A. Selective hydrogenation of furfural and levulinic acid to biofuels on the
535 ecofriendly Cu–Fe catalyst. Fuel 2014;115:101–8.
536 <https://doi.org/10.1016/J.FUEL.2013.06.042>.

537 [60] Li Z, Hao H, Lu J, Wu C, Gao R, Li J, et al. Role of the Cu–ZrO₂ interface in the
538 hydrogenation of levulinic acid to γ -valerolactone. J Energy Chem 2021;61:446–58.
539 <https://doi.org/10.1016/j.jechem.2021.01.046>.

540 [61] Fang S, Cui Z, Zhu Y, Wang C, Bai J, Zhang X, et al. In situ synthesis of biomass-derived
541 Ni/C catalyst by self-reduction for the hydrogenation of levulinic acid to Γ -valerolactone. J
542 Energy Chem 2019;37:204–14. <https://doi.org/10.1016/j.jechem.2019.03.021>.

543 [62] Orlowski I, Douthwaite M, Iqbal S, Hayward JS, Davies TE, Bartley JK, et al. The
544 hydrogenation of levulinic acid to Γ -valerolactone over Cu–ZrO₂ catalysts prepared by a pH-
545 gradient methodology. J Energy Chem 2019;36:15–24.
546 <https://doi.org/10.1016/j.jechem.2019.01.015>.

547 [63] Shen Q, Zhang Y, Zhang Y, Tan S, Chen J. Transformations of biomass-based levulinate ester
548 into Γ -valerolactone and pyrrolidones using carbon nanotubes-grafted N-heterocyclic carbene
549 ruthenium complexes. J Energy Chem 2019;39:29–38.
550 <https://doi.org/10.1016/j.jechem.2019.01.007>.

551 [64] Delgado J, Vasquez Salcedo WN, Bronzetti G, Casson Moreno V, Mignot M, Legros J, et al.
552 Kinetic model assessment for the synthesis of γ -valerolactone from n-butyl levulinate and
553 levulinic acid hydrogenation over the synergy effect of dual catalysts Ru/C and Amberlite IR-
554 120. Chem Eng J 2022;430:133053. <https://doi.org/10.1016/j.cej.2021.133053>.

- 555 [65] Shimizu KI, Kanno S, Kon K. Hydrogenation of levulinic acid to γ -valerolactone by Ni and
556 MoO_x co-loaded carbon catalysts. *Green Chem* 2014;16:3899–903.
557 <https://doi.org/10.1039/c4gc00735b>.
- 558 [66] Hengne AM, Malawadkar A V., Biradar NS, Rode C V. Surface synergism of an Ag-Ni/ZrO₂
559 nanocomposite for the catalytic transfer hydrogenation of bio-derived platform molecules. *RSC*
560 *Adv* 2014;4:9730–6. <https://doi.org/10.1039/c3ra46495d>.
- 561 [67] Heeres H, Handana R, Chunai D, Borromeus Rasrendra C, Girisuta B, Jan Heeres H.
562 Combined dehydration/(transfer)-hydrogenation of C₆-sugars (D-glucose and D-fructose) to γ -
563 valerolactone using ruthenium catalysts. *Green Chem* 2009;11:1247–55.
564 <https://doi.org/10.1039/b904693c>.
- 565 [68] Fellay C, Dyson PJ, Laurenczy G. A viable hydrogen-storage system based on selective formic
566 acid decomposition with a ruthenium catalyst. *Angew Chemie - Int Ed* 2008;47:3966–8.
567 <https://doi.org/10.1002/anie.200800320>.
- 568 [69] Fábos V, Mika LT, Horváth IT. Selective conversion of levulinic and formic acids to γ -
569 valerolactone with the shvo catalyst. *Organometallics* 2014;33:181–7.
570 <https://doi.org/10.1021/om400938h>.
- 571 [70] Deng L, Zhao Y, Li J, Fu Y, Liao B, Guo QX. Conversion of levulinic acid and formic acid
572 into γ -valerolactone over heterogeneous catalysts. *ChemSusChem* 2010;3:1172–5.
573 <https://doi.org/10.1002/cssc.201000163>.
- 574 [71] Deng L, Li J, Lai DM, Fu Y, Guo QX. Catalytic conversion of biomass-derived carbohydrates
575 into γ -valerolactone without using an external H₂ supply. *Angew Chemie - Int Ed*
576 2009;48:6529–32. <https://doi.org/10.1002/anie.200902281>.
- 577 [72] Ruppert AM, Jędrzejczyk M, Słonek-O, Keller N, Dumon AS, Michel C, et al. Ru
578 catalysts for levulinic acid hydrogenation with formic acid as a hydrogen source. *Green Chem*
579 2016;18:2014–28. <https://doi.org/10.1039/c5gc02200b>.

- 580 [73] Yuan J, Li SS, Yu L, Liu YM, Cao Y, He HY, et al. Copper-based catalysts for the efficient
581 conversion of carbohydrate biomass into γ -valerolactone in the absence of externally added
582 hydrogen. *Energy Environ Sci* 2013;6:3308–13. <https://doi.org/10.1039/c3ee40857d>.
- 583 [74] Son PA, Nishimura S, Ebitani K. Production of γ -valerolactone from biomass-derived
584 compounds using formic acid as a hydrogen source over supported metal catalysts in water
585 solvent. *RSC Adv* 2014;4:10525–30. <https://doi.org/10.1039/c3ra47580h>.
- 586 [75] Li H, Fang Z, Yang S. Direct catalytic transformation of biomass derivatives into biofuel
587 component γ -valerolactone with magnetic nickel-zirconium nanoparticles. *Chempluschem*
588 2016;81:135–42. <https://doi.org/10.1002/cplu.201500492>.
- 589 [76] Chia M, Dumesic JA. Liquid-phase catalytic transfer hydrogenation and cyclization of
590 levulinic acid and its esters to γ -valerolactone over metal oxide catalysts. *Chem Commun*
591 2011;47:12233–5. <https://doi.org/10.1039/c1cc14748j>.
- 592 [77] Li H, Fang Z, Yang S. Direct Conversion of Sugars and Ethyl Levulinate into γ -Valerolactone
593 with Superparamagnetic Acid-Base Bifunctional ZrFeOx Nanocatalysts. *ACS Sustain Chem*
594 *Eng* 2016;4:236–46. <https://doi.org/10.1021/acssuschemeng.5b01480>.
- 595 [78] Ju Z, Feng S, Ren L, Lei T, Cheng H, Yu M, et al. Probing the mechanism of the conversion of
596 methyl levulinate into γ -valerolactone catalyzed by Al(OiPr)₃ in an alcohol solvent: A DFT
597 study. *RSC Adv* 2022;12:2788–97. <https://doi.org/10.1039/d1ra08429a>.
- 598 [79] Ortuño MA, Rellán-Piñeiro M, Luque R. Computational Mechanism of Methyl Levulinate
599 Conversion to γ -Valerolactone on UiO-66 Metal Organic Frameworks. *ACS Sustain Chem Eng*
600 2022;10:3567–73. <https://doi.org/10.1021/acssuschemeng.1c08021>.
- 601 [80] Chen X, Zhao T, Zhang X, Zhang Y, Yu H, Lyu Q, et al. Synthesis of ternary magnetic
602 nanoparticles for enhanced catalytic conversion of biomass-derived methyl levulinate into γ -
603 valerolactone. *J Energy Chem* 2021;63:430–41. <https://doi.org/10.1016/j.jechem.2021.07.013>.
- 604 [81] Zhang C, Huo Z, Ren D, Song Z, Liu Y, Jin F, et al. Catalytic transfer hydrogenation of

605 levulinate ester into γ -valerolactone over ternary Cu/ZnO/Al₂O₃ catalyst. J Energy Chem
606 2019;32:189–97. <https://doi.org/10.1016/j.jechem.2018.08.001>.

607 [82] Wu J, Zhu Y, Liao P, Xu T, Lu L, Zhang X, et al. Sustainable metal-lignosulfonate catalyst for
608 efficient catalytic transfer hydrogenation of levulinic acid to γ -valerolactone. Appl Catal A Gen
609 2022;635:118556. <https://doi.org/10.1016/j.apcata.2022.118556>.

610 [83] Protsenko II, Nikoshvili LZ, Matveeva VG, Sulman EM. Kinetic Modelling of Levulinic Acid
611 Hydrogenation Over Ru-Containing Polymeric Catalyst. Top Catal 2020;63:243–53.
612 <https://doi.org/10.1007/s11244-020-01223-0>.

613 [84] Huang X, Liu K, Vrijburg WL, Ouyang X, Iulian Dugulan A, Liu Y, et al. Hydrogenation of
614 levulinic acid to γ -valerolactone over Fe-Re/TiO₂ catalysts. Appl Catal B Environ
615 2020;278:119314. <https://doi.org/10.1016/j.apcatb.2020.119314>.

616 [85] Chalid M, Broekhuis AA, Heeres HJ. Experimental and kinetic modeling studies on the
617 biphasic hydrogenation of levulinic acid to γ -valerolactone using a homogeneous water-soluble
618 Ru-(TPPTS) catalyst. J Mol Catal A Chem 2011;341:14–21.
619 <https://doi.org/10.1016/j.molcata.2011.04.004>.

620 [86] Abdelrahman OA, Heyden A, Bond JQ. Analysis of kinetics and reaction pathways in the
621 aqueous-phase hydrogenation of levulinic acid to form γ -Valerolactone over Ru/C. ACS Catal
622 2014;4:1171–81. <https://doi.org/10.1021/cs401177p>.

623 [87] Molleti J, Tiwari MS, Yadav GD. Novel synthesis of Ru/OMS catalyst by solvent-free method:
624 Selective hydrogenation of levulinic acid to γ -valerolactone in aqueous medium and kinetic
625 modelling. Chem Eng J 2018;334:2488–99. <https://doi.org/10.1016/j.cej.2017.11.125>.

626 [88] Leveneur S, Pinchard M, Rimbault A, Safdari Shadloo M, Meyer T. Parameters affecting
627 thermal risk through a kinetic model under adiabatic condition: Application to liquid-liquid
628 reaction system. Thermochim Acta 2018;666:10–7. <https://doi.org/10.1016/j.tca.2018.05.024>.

629 [89] Cao CR, Liu SH. Thermal hazard characteristic evaluation of two low-temperature-reactive azo

630 compounds under adiabatic process conditions. *Process Saf Environ Prot* 2019;130:231–7.
631 <https://doi.org/10.1016/j.psep.2019.08.020>.

632 [90] Bhattacharya A. A general kinetic model framework for the interpretation of adiabatic
633 calorimeter rate data. *Chem Eng J* 2005;110:67–78. <https://doi.org/10.1016/j.cej.2005.05.003>.

634 [91] Stoessel F. *Thermal Safety of Chemical Processes: Risk Assessment and Process Design*.
635 Wiley-VCH; 2008. <https://doi.org/10.1002/9783527621606>.

636 [92] Zheng JL, Wärnå J, Salmi T, Burel F, Taouk B, Leveneur S. Kinetic modeling strategy for an
637 exothermic multiphase reactor system: Application to vegetable oils epoxidation using
638 Prileschajew method. *AIChE J* 2016;62:726–41. <https://doi.org/10.1002/aic.15037>.

639 [93] Xie Q, Zhang Z, Zhang L, Xie Y, Liu W, Chen H. Thermal decomposition behavior and
640 kinetics for nitrolysis solution from the nitration of hexamethylenetetramine. *React Kinet Mech*
641 *Catal* 2019;128:645–62. <https://doi.org/10.1007/s11144-019-01658-x>.

642 [94] Andreozzi R, Canterino M, Caprio V, Di Somma I, Sanchirico R. Batch salicylic acid nitration
643 by nitric acid/acetic acid mixture under isothermal, isoperibolic and adiabatic conditions. *J*
644 *Hazard Mater* 2006;138:452–8. <https://doi.org/10.1016/j.jhazmat.2006.05.104>.

645 [95] Alamgir Ahmad K, Haider Siddiqui M, Pant KK, Nigam KDP, Shetti NP, Aminabhavi TM, et
646 al. A critical review on suitability and catalytic production of butyl levulinate as a blending
647 molecule for green diesel. *Chem Eng J* 2022;447:137550.
648 <https://doi.org/10.1016/j.cej.2022.137550>.

649 [96] Delgado J, Vásquez Salcedo WN, Devouge-Boyer C, Hebert JP, Legros J, Renou B, et al.
650 Reaction enthalpies for the hydrogenation of alkyl levulinates and levulinic acid on Ru/C–
651 influence of experimental conditions and alkyl chain length. *Process Saf Environ Prot*
652 2023;171:289–98. <https://doi.org/10.1016/j.psep.2023.01.025>.

653 [97] Zheng JL, Wärnå J, Salmi T, Burel F, Taouk B, Leveneur S. Kinetic modeling strategy for an
654 exothermic multiphase reactor system: Application to vegetable oils epoxidation using

655 Prileschajew method. *AIChE J* 2016;62:726–41. <https://doi.org/10.1002/aic.15037>.

656 [98] Lavanchy F. Development of reaction calorimetry... - Google Scholar. n.d.

657 [99] Nasrifar K. Comparative study of eleven equations of state in predicting the thermodynamic
658 properties of hydrogen. *Int J Hydrogen Energy* 2010;35:3802–11.
659 <https://doi.org/10.1016/j.ijhydene.2010.01.032>.

660 [100] Stewart WE, Caracotsios M. *Computer-Aided Modeling of Reactive Systems*. First. New
661 Jersey: 2008. <https://doi.org/10.1002/9780470282038>.

662 [101] Stewart WE, Caracotsios M, Sørensen JP. Parameter estimation from multiresponse data.
663 *AIChE J* 1992. <https://doi.org/10.1002/aic.690380502>.

664 [102] Kopyscinski J, Choi J, Hill JM. Comprehensive kinetic study for pyridine
665 hydrodenitrogenation on (Ni)WP/SiO₂ catalysts. *Appl Catal A Gen* 2012;445–446:50–60.
666 <https://doi.org/10.1016/j.apcata.2012.08.027>.

667 [103] Van Boekel MAJS. Statistical aspects of kinetic modeling for food science problems. *J Food*
668 *Sci* 1996;61:477–86. <https://doi.org/10.1111/j.1365-2621.1996.tb13138.x>.

669 [104] Caracotsios M, Stewart WE. Sensitivity analysis of initial value problems with mixed odes and
670 algebraic equations. *Comput Chem Eng* 1985;9:359–65. [https://doi.org/10.1016/0098-](https://doi.org/10.1016/0098-1354(85)85014-6)
671 [1354\(85\)85014-6](https://doi.org/10.1016/0098-1354(85)85014-6).

672 [105] Capecci S, Wang Y, Delgado J, Casson Moreno V, Mignot M, Grénman H, et al. Bayesian
673 Statistics to Elucidate the Kinetics of γ -Valerolactone from n-Butyl Levulinate Hydrogenation
674 over Ru/C. *Ind Eng Chem Res* 2021;60:11725–36.
675 https://doi.org/10.1021/ACS.IECR.1C02107/ASSET/IMAGES/LARGE/IE1C02107_0008.JPEG
676 G.

677 [106] Ariba H, Wang Y, Devouge-Boyer C, Stateva RP, Leveneur S. Physicochemical Properties for
678 the Reaction Systems: Levulinic Acid, Its Esters, and γ -Valerolactone. *J Chem Eng Data*
679 2020;65:3008–20. <https://doi.org/10.1021/acs.jced.9b00965>.

680 [107] Lu X, Wang Y, Estel L, Kumar N, Grénman H, Leveneur S. Evolution of specific heat capacity
681 with temperature for typical supports used for heterogeneous catalysts. *Processes* 2020;8:911.
682 <https://doi.org/10.3390/PR8080911>.

683 [108] Toch K, Thybaut JW, Marin GB. A systematic methodology for kinetic modeling of chemical
684 reactions applied to n-hexane hydroisomerization. *AIChE J* 2015;61:880–92.
685 <https://doi.org/10.1002/aic.14680>.

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687