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Wenel Naudy Vásquez Salcedo, Mélanie Mignot, Bruno Renou, Sébastien Leveneur. Assessment of kinetic models for the production of γ -valerolactone developed in isothermal, adiabatic and isoperibolic conditions. *Fuel*, 2023, 350, pp.128792. 10.1016/j.fuel.2023.128792 . hal-04115376

HAL Id: hal-04115376

<https://normandie-univ.hal.science/hal-04115376>

Submitted on 2 Jun 2023

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

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9

10

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

26

27 **Greek letters**

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

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29

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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

36 1. Introduction

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

39 The use of lignocellulosic biomass (LCB) for biofuel production is seen as a better alternative to fossil
40 fuel because of its global availability, lower environmental impact, and cost [2–6]. Besides, such raw
41 materials are not in competition with the alimentary sector, avoiding the dilemma of food versus fuel
42 [7,8]. The sugar parts of LCB, i.e., cellulose and hemicellulose, are mainly used to produce chemicals,
43 materials or fuels. The valorization of these polymers of sugar can lead to several platform molecules
44 and their derivatives, such as succinic acid, furfural, 5-HMF, levulinic acid, glycerol, etc. [9–12].

45 The chemical γ -valerolactone (GVL), produced from the hydrogenation of levulinic acid or ester
46 levulinate, is also considered as a platform molecule [13,14]. Hydrogenation of bio-based carboxylic
47 acids, esters or related compounds is considered a step toward a sustainable and carbon-neutral process
48 [15]. In fine chemistry, GVL is considered an excellent aprotic solvent [16–21] because of its low vapor
49 pressure, high flash point, and potential to increase acid activity [22–26]. In polymer science, GVL is a
50 promising starting material for producing greener monomers [27–30].

51 In the energy field, GVL cannot be used directly as a fuel [31], but it can be used as an additive fuel
52 [32–35]. GVL is a promising feedstock for producing hydrocarbon fuels [31,36–42] or pentanoic
53 biofuels [43].

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

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

60 -*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

90 2. Experimental section

91 2.1. Chemicals

92 Chemicals used during this research for analytical and experimental purposes were purchased from
93 different providers and used without further purification: n-Butyl levulinate (n-BL), acquired from Alfa
94 Aesar with a purity $\geq 98\%$, CAS: 2052-15-5. Hydrogen gas (H_2), acquired from Linde group with a
95 purity $\geq 99.99\%$, CAS: 1333-74-0. γ -Valerolactone (GVL), acquired from Sigma Aldrich with a purity
96 $\geq 99\%$, CAS: 108-29-2. 1-Butanol (BuOH), acquired from LabLine with a purity $\geq 99\%$, CAS: 71-36-
97 3. Ruthenium on activated carbon (Ru/C), acquired from Alfa Aesar, 5% of ruthenium powder, reduced,
98 50% nominally wet, CAS: 7440-18-8. Acetone, acquired from Fischer Scientific with a purity $\geq 99\%$,
99 CAS: 67-64-1.

100

101 2.2. Analytical system

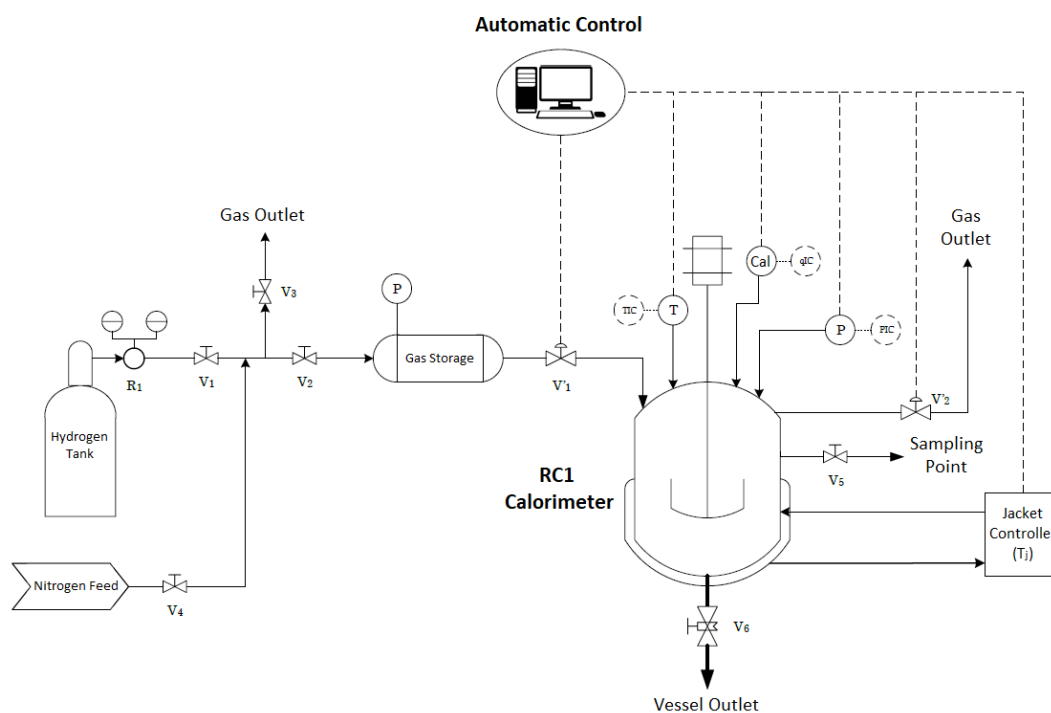
102 Gas chromatography coupled with a flame ionization detector (GC-FID) technique was applied to
103 quantify the amount of chemicals in samples. GC-FID equipment is from Scion Instruments supplier.
104 GC-FID was equipped with a low polarity column (Phenomenex, ZB-5) composed of 95% dimethyl
105 siloxane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

107 Helium (99.99%) was used as carrier gas at a constant flow rate of 1.2 mL/min. The temperature of the
108 injector and the detector were set at 250 °C. The oven temperature ramp was set to 50 °C (1 min) – 20
109 °C /min – 200 °C (1 min). Samples were diluted in acetone to be analyzed, the injection volume was 1
110 μL and the split ratio was 20:1.

111 2.3. RC1 reactor

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

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



121

122 Fig. 1. RC1mx Calorimeter installation.

123

124 2.4. Determination of the global heat transfer

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

130 2.5. Gas-liquid mass transfer measurement

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

135 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

136

137

138

139 2.6. Kinetic modeling

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

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

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

152 GREGPLUS uses successive quadratic programming starting from our initial guess values to minimize
153 $OF(\xi)$ [100].

$$154 \quad OF(\xi) = (a + b + 1) \cdot \ln|v(\xi)| \quad (1)$$

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

157 Each element of the covariance matrix of the responses is

$$158 \quad v_{ij}(\xi) = \sum_{u=1}^n \omega_u \cdot [Y_{iu} - f_{iu}(\xi)] \cdot [Y_{ju} - f_{ju}(\xi)] \quad (2)$$

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

162

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

$$165 \quad k(T) = \exp \left[\ln \left(k(T_{ref}) \right) + \frac{E_a}{R \cdot T_{ref}} \cdot \left(1 - \frac{T_{ref}}{T} \right) \right] \quad (3)$$

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

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

169 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} (Jkg ⁻¹ K ⁻¹)	UA ₀ (WK ⁻¹)	[BL] ₀ (molm ⁻³)	[BHP] ₀ (molm ⁻³)	[GVL] ₀ (molm ⁻³)	[BuOH] ₀ (molm ⁻³)	Tr ₀ (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

170

171

172

173

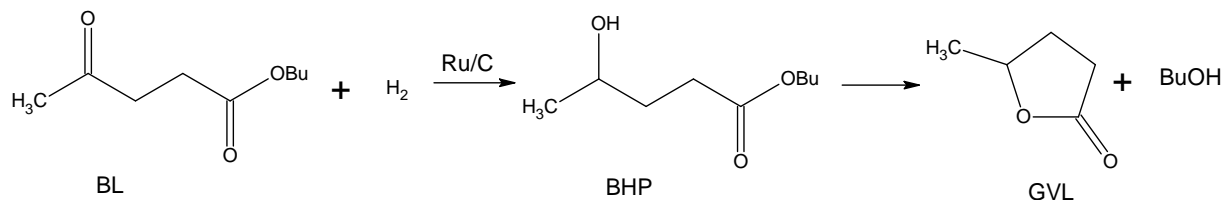
Table 3. Experimental matrix with initial conditions for validation

Run	P (bar)	m_{0BL} (kg)	m_{0GVL} (kg)	m_{0Ru} (kg)	C_{p0} (Jkg ⁻¹ K ⁻¹)	UA_0 (WK ⁻¹)	$[BL]_0$ (molm ⁻³)	$[BHP]_0$ (molm ⁻³)	$[GVL]_0$ (molm ⁻³)	$[BuOH]_0$ (molm ⁻³)	T_{r0} (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

176 3. Results and discussion

177 3.1. Kinetics

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



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

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

- 184
- 185 • Eley-Rideal (ER1): This kinetic model considers that only BL is adsorbed into active sites of the
186 catalyst, and then molecular hydrogen collides directly to the adsorbed BL.
 - 187 • Langmuir Hinshelwood with molecular adsorption of H₂ (LH1): This kinetic model considers that
188 all reactants, BL and molecular hydrogen, are adsorbed into the active sites of the catalyst without
189 dissociation, then the chemical reaction takes place between adsorbed molecules.
 - 190 • Langmuir Hinshelwood with hydrogen dissociation (LH2): As LH1 this kinetic model considers
191 that all reactants, BL and molecular hydrogen, are adsorbed into the active sites of the catalyst.
192 However, in this case, molecular hydrogen is dissociated into atomic hydrogen; then the chemical
193 reaction takes place between adsorbed BL and adsorbed atomic hydrogen.
 - 194 • Non-competitive Langmuir Hinshelwood with molecular adsorption of H₂ (NCLH1): This kinetic
195 model considers that there is no competition between the reactants for the active sites of the catalyst,
196 so that it is considered that BL and molecular hydrogen are adsorbed in different active sites.
197 Chemical reaction occurs between adsorbed BL and adsorbed molecular hydrogen without
198 dissociation.
 - 199 • Non-competitive Langmuir Hinshelwood with hydrogen dissociation (NCLH2): As NCLH1 this
kinetic model consider that there is no competition between the reactants. BL and molecular

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

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

204

205 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)	$\frac{k_1 \cdot K_H \cdot K_C \cdot K_{BL} \cdot [H_2]}{\sqrt{K_H \cdot [H_2]} + 1} \cdot \frac{[BL] \cdot \omega_{Cat.}}{K_{BL} \cdot [BL] + K_C \cdot \sqrt{K_H \cdot [H_2]} \cdot K_{BL} \cdot [BL] + K_{BHP} \cdot [BHP] + 1}$

206

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

$$208 \quad R_{Cyclization} = k_2 \cdot [BHP] \quad (4)$$

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

210

211

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 $\frac{E_{a1}}{R \cdot T_{ref}}$

214 3.2. Material and energy balances

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

$$217 \frac{dC_{BL}}{dt} = -R_{Hydrogenation} \quad (5)$$

$$218 \frac{d[H_2]_{liq}}{dt} = k_L \cdot a \cdot ([H_2]_{liq}^* - [H_2]_{liq}) - R_{Hydrogenation} \quad (6)$$

$$219 \frac{dC_{BHP}}{dt} = R_{Hydrogenation} - R_{Cyclization} \quad (7)$$

$$220 \frac{dC_{BuOH}}{dt} = R_{Cyclization} \quad (8)$$

$$221 \frac{dC_{GVL}}{dt} = R_{Cyclization} \quad (9)$$

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

230 The heat balance equation for the liquid phase leads to

$$231 \frac{dT_R}{dt} = \frac{(-R_{Hydrogenation} \cdot \Delta H_{R,Hydrogenation} \cdot V - R_{Cyclization} \cdot \Delta H_{R,Cyclization} \cdot V) + UA \cdot (T_j - T_R) + \alpha \cdot (T_{amb} - T_R)}{m_R \cdot C_{PR} + m_{insert} \cdot C_{pinsert} + m_{catalyst} \cdot C_{p catalyst}} \quad (10)$$

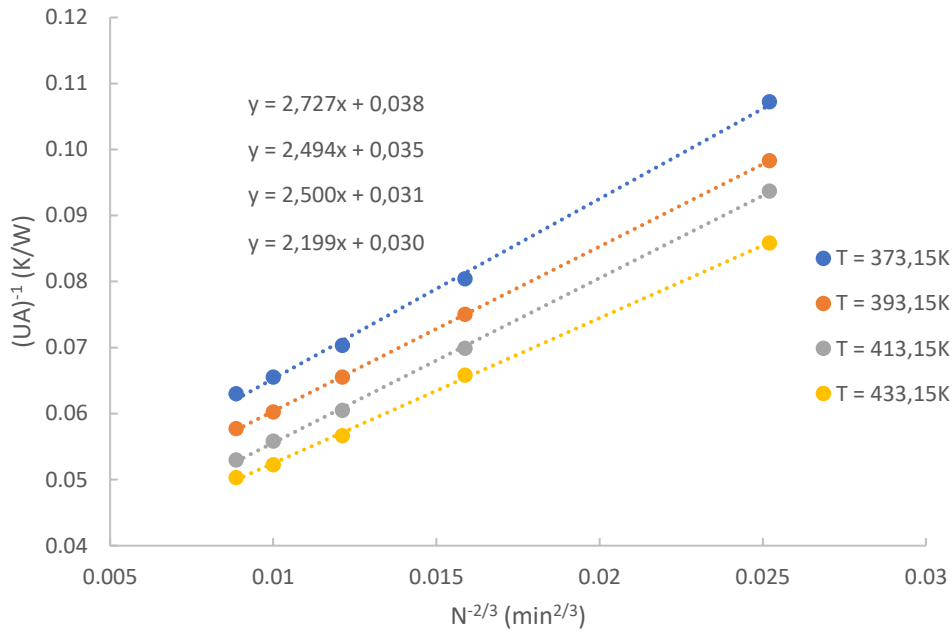
232 The term $\alpha \cdot (T_{amb} - T_R)$ represents the heat loss with the surroundings. The term $UA \cdot (T_j - T_R)$ is the
 233 heat flow rate exchanged with the heat carrier, and UA is the global heat transfer, T_j and T_R are the jacket
 234 and reaction temperatures. The term $m_R \cdot C_{PR}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

240 3.3. Calibration results (Wilson plot)

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



245
 246 Fig. 3. Wilson plot.

247 3.4. Gas-liquid mass transfer results

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

$$250 \quad k_L a = (k_L a)_{modified} \cdot \left(\frac{T_{liq}}{\mu_{liq}}\right)^{0.5} \cdot \left(\frac{\rho_{liq}}{\mu_{liq}}\right)^{0.25} \quad (11)$$

251 The constant $(k_L a)_{modified}$ was calculated from experiments shown in Table 1 as described in
 252 Supplementary Material (S1). From Table S1.1, one can notice that the calculated value of
 253 $(k_L a)_{modified}$ for each run is very similar. The average value of $(k_L a)_{modified}$ was found to be $2.25 \cdot 10^{-6}$
 254 $(\text{Pa}\cdot\text{s}\cdot\text{K}^{-1})^{0.5}(\text{Pa}\cdot\text{s}\cdot\text{kg}^{-1}\cdot\text{m}^{-3})^{0.25}\cdot\text{s}^{-1}$ and the standard deviation was equal to $0.14 (\text{Pa}\cdot\text{s}\cdot\text{K}^{-1})^{0.5}(\text{Pa}\cdot\text{s}\cdot\text{kg}^{-1}\cdot\text{m}^{-3})^{0.25}$
 255 $\cdot\text{s}^{-1}$. This value was found to be similar than the one of Wang et al. [57].

256 3.5. Kinetic modeling

257 3.5.1. Regression

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

260
$$AIC: \text{number of independant event} \cdot \ln \left(\frac{[Y_{ju} - f_{ju}(\xi)]^2}{\text{number of independant event}} \right) +$$

261
$$2 \cdot \text{Number of estimated parameters} \tag{12}$$

262

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

265 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

266

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

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

275

276

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	-	

277

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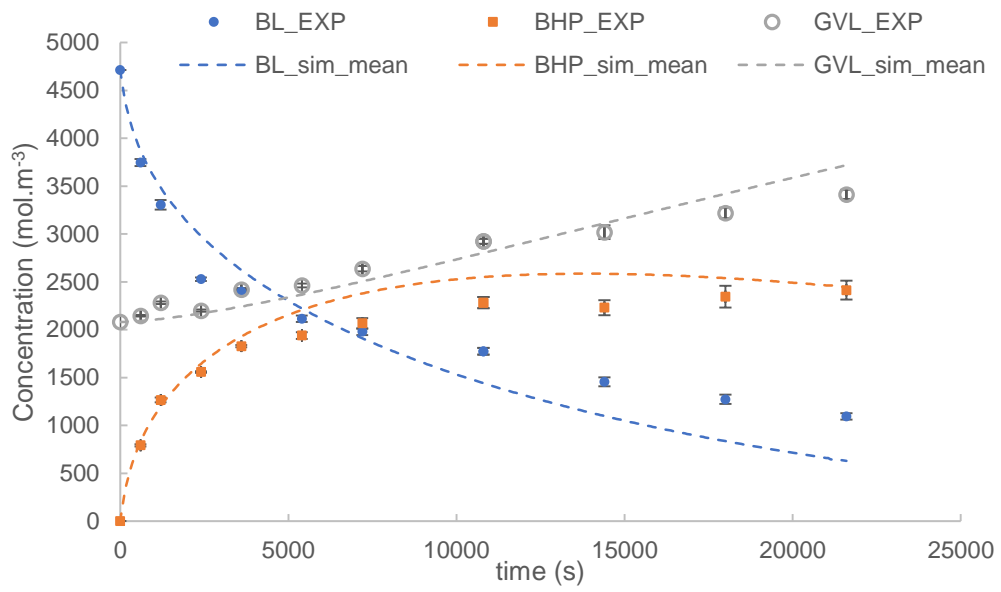
Table 8. Normalized parameter covariance matrix for NCLH1.

	$\ln(k_1(T_{ref}))$	$\ln(k_2(T_{ref}))$	$\frac{E_{a1}}{R \cdot T_{ref}}$	$\frac{E_{a2}}{R \cdot T_{ref}}$	$\ln(K_H)$
$\ln(k_1(T_{ref}))$	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

279

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.



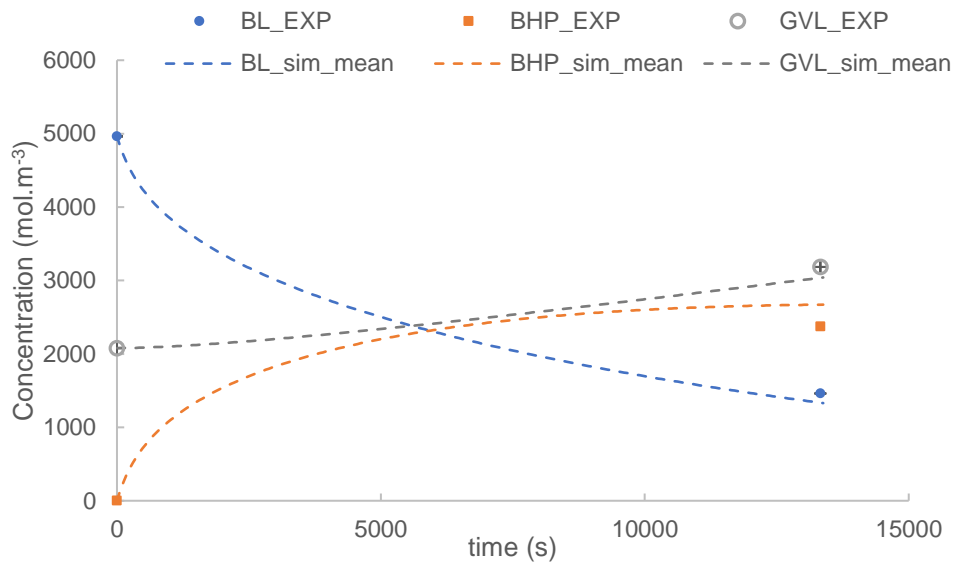
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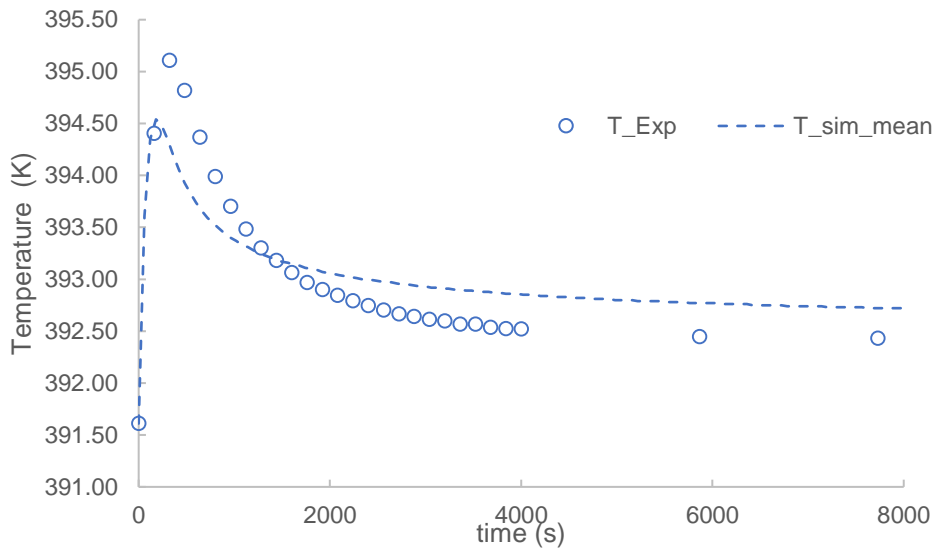
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Fig. 4. Fit of the NCLH1 model to isothermal experimental data for Run 1.

292



293



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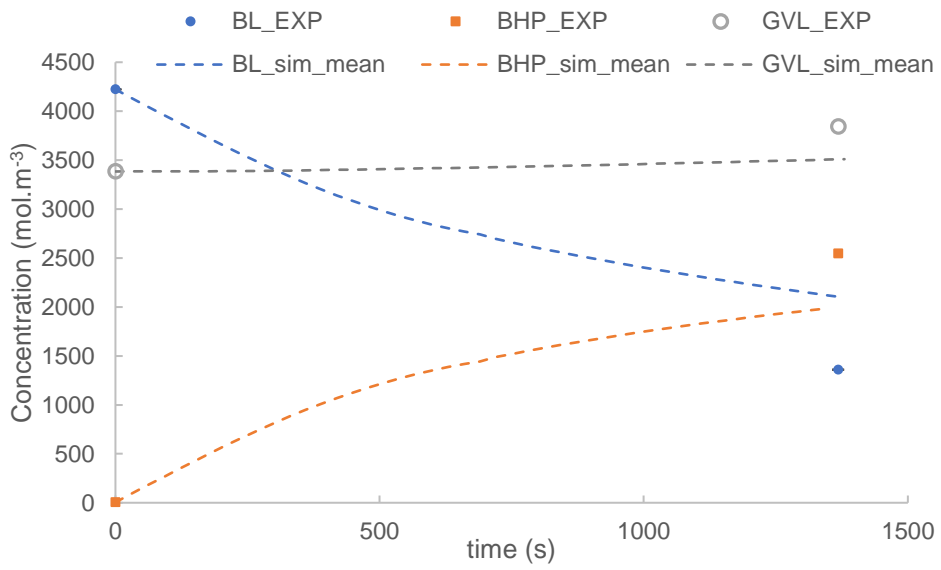
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Fig. 5. Fit of the NCLH1 model to isoperibolic experimental data for Run 2.

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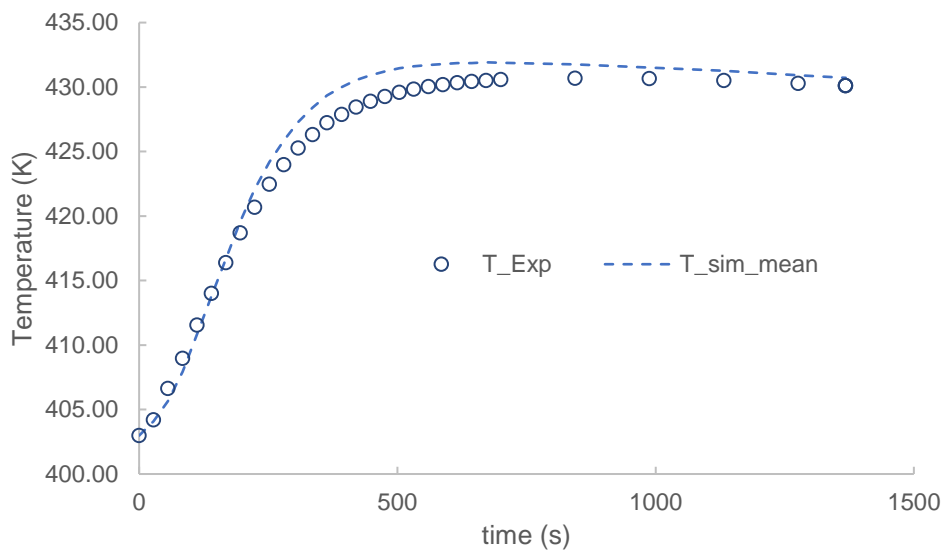
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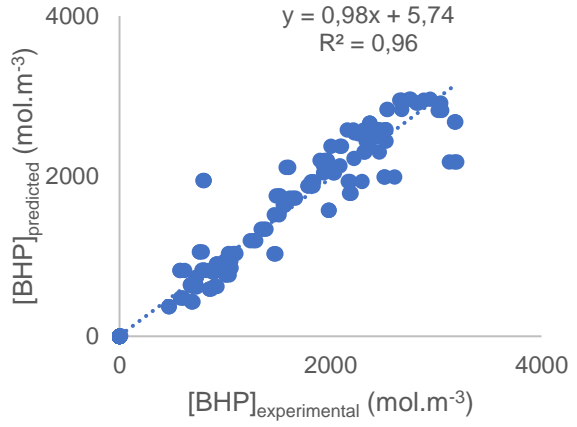
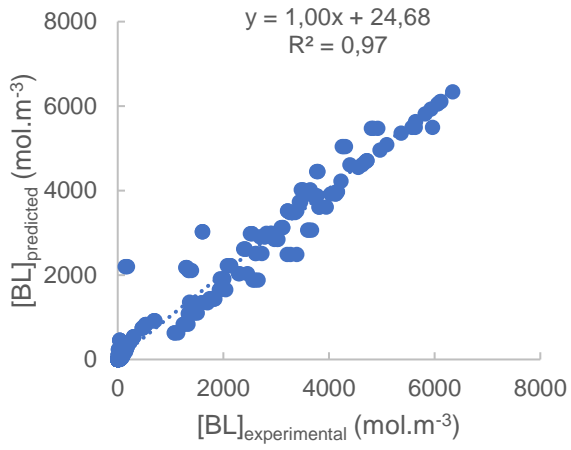
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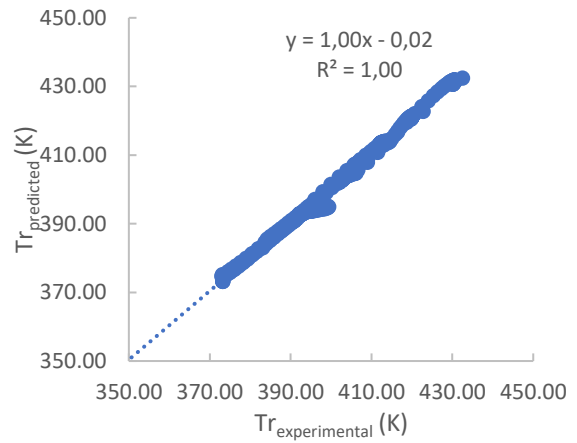
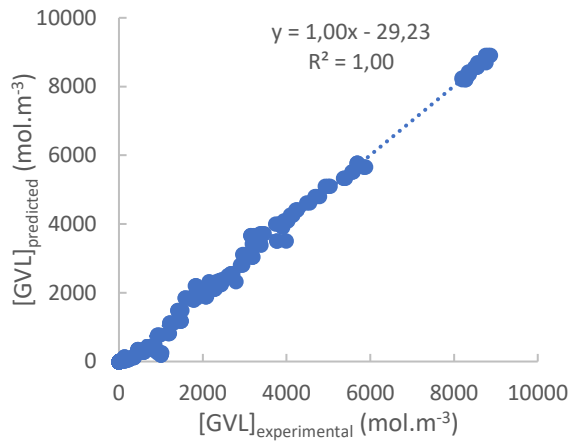
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Fig. 6. Fit of the NCLH2 model to adiabatic experimental data for Run 6.



307



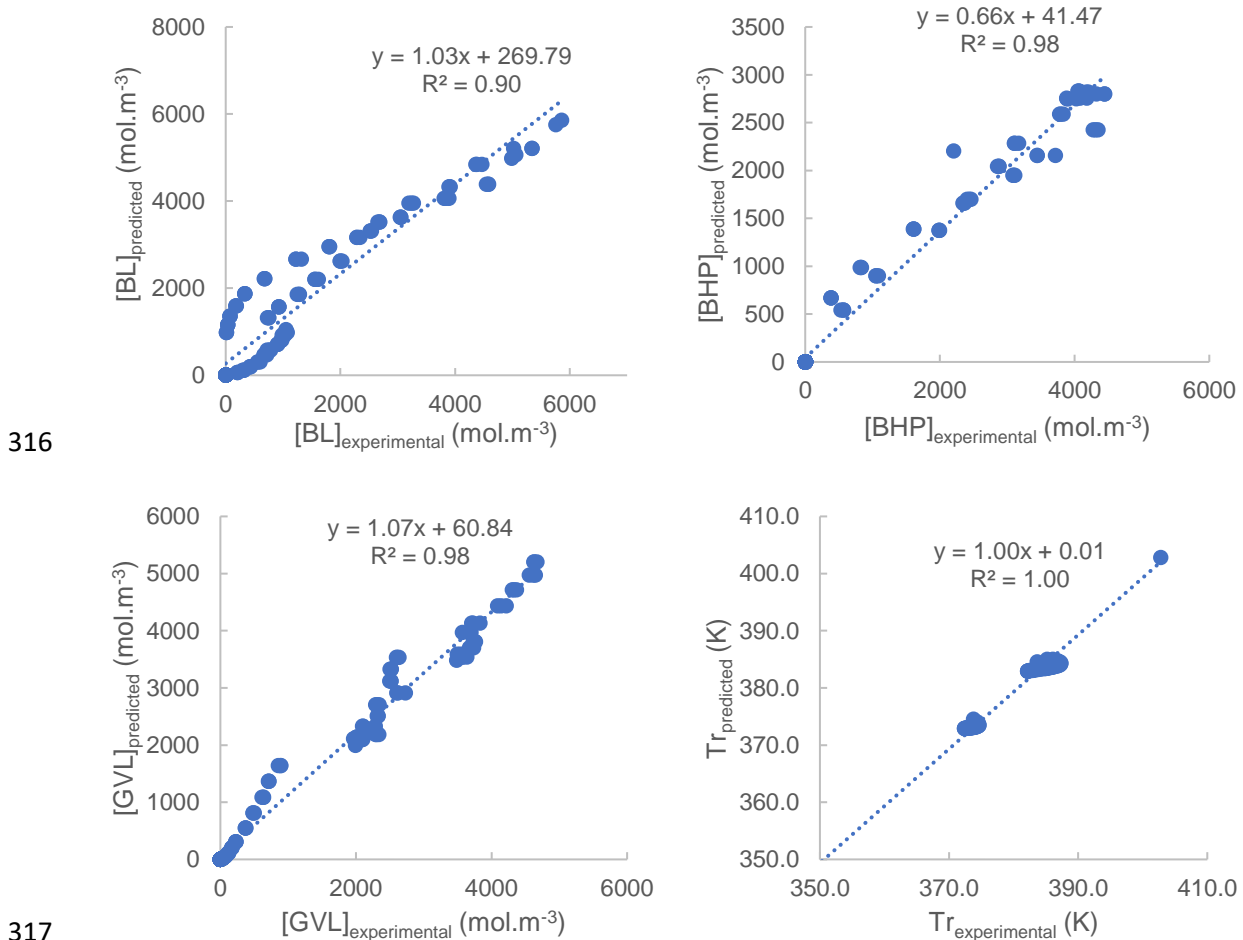
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Fig. 7. Parity plots from regression stage (model NCLH1)

310 3.5.2. Validation stage

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



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

319

320 4. Conclusions

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

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

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

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

342

343 **Acknowledgments**

344 This investigation was carried out in the framework of the ARBRE project (Risk Analysis to processes
345 valorizing 2nd generation biomass and using Renewable energies). ARBRE is cofounded by European
346 Union through the European Regional Development Fund (agreement n° 00130305) and by Normandy
347 Region (agreement n° 21E05304), via the support of "pôle CTM (Continuum Terre-Mer) and EP2M
348 (Énergies, Propulsion, Matière, Matériaux) de Normandie université". The authors thank the Ministry
349 of High Education, Science and Technology of Dominican Republic (MESCYT).

350 For the analytical part, this work has been partially supported by University of Rouen Normandy, INSA
351 Rouen Normandy, the Centre National de la Recherche Scientifique (CNRS), European Regional
352 Development Fund (ERDF) N° HN0001343, Labex SynOrg (ANR-11-LABX-0029), Carnot Institute
353 I2C, the graduate school for reasearch XL-Chem (ANR-18-EURE-0020 XL CHEM) and by Region
354 Normandie. GC was financed by FEDER RIN Green Chem 2019NU01FOBC08 Number: 17P04374.

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