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Kinetic modeling of levulinic acid hydrogenation to γ -valerolactone in water using a carbon supported Ru catalyst

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ABSTRACT

γ -Valerolactone (GVL) is considered a very interesting green, bio-based platform chemical with high application potential for the production of both biofuels and biobased chemicals. In this contribution, we report a kinetic study on the hydrogenation of levulinic acid (LA) to 4-hydroxypentanoic acid (4-HPA) and the subsequent intramolecular esterification to GVL in water using Ru/C (3 wt.% Ru) as the catalyst in a batch set-up. A large number of experiments was performed in a temperature range of 343–403 K, a hydrogen pressure range from 30 to 60 bar and initial LA concentrations between 300 and 2500 mol m⁻³. Experimental data, supported by calculation, indicate that intra-particle diffusion of LA and hydrogen affect the overall reaction rate and as such a heterogeneous model with both reaction and diffusion was used to model the data. The hydrogenation reaction of LA to 4-HPA was modelled using a Langmuir-Hinshelwood type expression whereas the reaction of 4-HPA to GVL was modelled as an equilibrium reaction occurring in the bulk of the liquid, catalyzed by a Brønsted acid, in this case LA and 4-HPA. A good fit between experiments and model was observed. The results were compared to a kinetic model without considering mass transfer and diffusion limitations.

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1. Introduction

A substantial amount of research activities is currently undertaken worldwide to identify attractive routes to produce biofuels and biobased chemicals from lignocellulosic biomass [1–3]. A very promising and versatile option is the conversion of the carbohydrate fractions in lignocellulosic biomass to levulinic acid (LA, 4-oxo-pentanoic acid) [4–6]. LA is an interesting building block that can be converted to a variety of useful compounds with high application potential such as, 1,4-pentanediol, 2-methyltetrahydrofuran (2-MTHF) [4,5], mixtures of alkanes, butenes, 5-nonanone, adipic acid and γ -valerolactone (GVL) [7–9]. Among the derivatives of LA, GVL is identified as a promising platform chemical for the synthesis of biofuels and biobased chemicals. Examples are the use as an oxygenate in transportation fuels, as a co-monomer for the preparation of polymers like polyhydroxyalkanoates [7], as a precursor for long chain alkanes, to be used as a hydrocarbon fuels

[8,9], and as a starting material for the synthesis of adipic acid and derivatives.

GVL can be obtained by the hydrogenation of LA using either heterogeneous or homogeneous catalysts in the liquid or gas phase. Palkovits and co-workers recently published a detailed review on LA hydrogenations using heterogeneous catalysts [10]. A wide range of catalysts has been used, the most common being supported noble metals. Particularly Ru based catalysts have shown to be very efficient and close to quantitative GVL yields have been reported at high LA conversions. A number of studies have been reported on bimetallic Ru catalysts and the use of co-catalysts. Bimetallic catalysts like RuSn/C are in general less active but lead to enhanced catalyst stability [11]. Co-catalysts and particularly heterogeneous acids have been reported to significantly increase the reaction rate [12–14]. For instance, the LA conversion for hydrogenations with Ru/C and Ru/Al₂O₃ as catalysts in the presence of Amberlyst A70 was twice as high as a reaction in the absence of the solid acid co-catalyst at otherwise similar conditions.

Solvent effects have been investigated in detail and have shown to play an important role. It appears that supported Ru catalysts are particularly active in water. For instance Al-Shaal et al. investigated the hydrogenation of LA and alkyl-levulinates using

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Nomenclature

Symbols

a	Interfacial area, m^{-2}
C	Concentration, mol m^{-3}
$D_{i,\text{eff}}$	Effective diffusivity of component i in the catalyst particles, $\text{m}^2 \text{s}^{-1}$
d_p	Particle diameter, m
GVL	γ -Valerolactone
HPA	4-Hydroxy pentanoic acid
J	Molar mass transfer flux, $\text{mol m}^{-2} \text{s}^{-1}$
$K_{LA}, K_{H_2}, K_{HPA}, K_{GVL}$	Adsorption equilibrium constant
$k_{l,i}$	Liquid solid mass transfer coefficient of component i , m s^{-1}
k_r	Reaction rate constant
k_2, k_{-2}	Reaction rate constants in the reversible conversion of HPA to GVL, Eq. (23)
LA	Levulinic acid
LAH	Intermediate reaction product, half hydrogenated levulinic acid
N_{WP}	Weisz-Prater number, $N_{WP,i} = (R^2 R_{1(S),r=R}) / (D_{i,\text{eff}} C_{i(S),r=R})$
R	Catalyst particle diameter, m
R_1	Rate of the reaction of HPA to GVL, $\text{mol m}^{-3} \text{s}^{-1}$
R_2	Rate of the hydrogenation reaction of LA, $\text{mol m}^{-3} \text{s}^{-1}$
r	Radial coordinate in catalyst particle modeling, m
s	Active site in the catalyst particles
t	Time, s
w	Weight factor, see Eq. (27)

Greek symbols

χ^2	Objective function in the parameter optimization, see Eq. (27)
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Subscripts

GVL	γ -Valerolactone
HPA	4-Hydroxy pentanoic acid
H_2	Hydrogen
i	Component i
LA	Levulinic acid
(LS)	Liquid solid
(L)	Liquid phase
(S)	Solid phase

ruthenium-based catalysts (Ru/C, Ru/Al₂O₃ and Ru/SiO₂) in alcohol and alcohol/water mixtures [15]. A significant increase in the LA conversion and GVL selectivity was observed when part of the alcohol was replaced by water. Similar positive effects of water on catalyst activity and selectivity were reported by Sautet et al. using Ru-supported catalysts in water and THF. DFT calculations [16] revealed that the increase in activity of Ru catalysts in water compared to organic solvents lies in a hydrogen bonding effect of a chemisorbed water molecule on the surface with a ketone group. Thus, the use of water as a solvent is not only cheap and environmental friendly, but also results in higher catalytic activity for Ru-based catalysts for ketone hydrogenations.

Two possible pathways have been proposed for the liquid phase hydrogenation of LA to GVL. The first involves dehydration of LA to α -angelicalactone (α -AL) [17] followed by a subsequent hydrogenation of the C=C double bond to form GVL (Scheme 1). The alternative route involves hydrogenation of the carbonyl group of LA to form 4-hydroxypentanoic acid (4-HPA). In the next step, an intramolecular esterification leads to the formation of GVL. Experi-

mental studies reveal that the second route is dominant when using Ru catalysts, though the first cannot be excluded a priori.

Hydrogenation of LA at elevated temperatures can lead to over-hydrogenation and the formation of 1,4-pentanediol (1,4-PDO) [18,19], 2-methyltetrahydrofuran (2-MTHF) [18,19], pentanoic acid (PA) [20,21] and 5-nonanone [22] (Scheme 1). Though not desired when targeting GVL, some of these products have also potential for commercialization.

Despite high academic and industrial interest on the catalytic hydrogenation of LA to GVL, a very limited number of kinetic studies on the reaction have been reported yet. These studies are of pivotal importance i) to gain insights in the reaction pathways and catalytic steps and ii) for scale up purposes and the development of optimum reactor configurations for the hydrogenation of LA to GVL. In 2012, we reported a detailed experimental study on LA hydrogenation to GVL in water using Ru/C as the catalyst (5 wt.% Ru) [23]. In this research, the effect of reaction temperature and catalyst intake on LA conversion and product selectivity was determined. This research was the first step to obtain a kinetic model for the hydrogenation of LA to GVL. While performing this research, Bond et al. published a kinetic model for the hydrogenation of aqueous LA solution to GVL over Ru/C catalyst (5 wt.% Ru) in a packed bed reactor [24]. It was assumed that the reaction proceeds via the 4-HPA route (Scheme 1). The hydrogenation reaction was modelled using a simplified Langmuir-Hinshelwood expression (Eq. (1)). As such, the reaction was proposed to be zero order in LA and half order in hydrogen. The apparent activation energy the hydrogenation reaction was calculated to be $48 \pm 5 \text{ kJ mol}^{-1}$.

$$r_1 = k_4 \cdot K_2^{1/2} \cdot p_{H_2}^{1/2} \quad (1)$$

The esterification of 4-HPA to GVL was modelled as homogeneous acid-catalyzed reaction which occurs in the liquid phase. Reversibility was not taken into account in the model. The activation energy for the esterification reaction was calculated to be $70 \pm 4 \text{ kJ mol}^{-1}$.

Another relevant kinetic study is from Zhang et al. [25]. They studied the hydrogenation of LA to GVL using Pd/C as the catalyst in a batch set-up. The experimental data were successfully modelled using a Langmuir type equation with dissociative adsorption of hydrogen. The activation energy for the hydrogenation reaction was calculated to be 33 kJ mol^{-1} .

We here report a detailed kinetic study on the conversion of LA to GVL using a Ru/C catalyst. The hydrogenation reaction was carried out in water, an environmentally benign solvent, and in a batch set-up. Reaction conditions like temperature (343–403 K), hydrogen pressure (30–60 bar) and initial LA concentration ($300\text{--}2500 \text{ mol m}^{-3}$) were varied in a systematic manner. The experimental data for the hydrogenation of LA to 4-HPA were modelled using a Langmuir-Hinshelwood model, the ring-closure of 4-HPA to GVL as an acid catalyzed equilibrium reaction.

2. Experimental section

2.1. Materials

The Ru/C catalyst (3 wt.% Ru) was obtained from Evonik. The d_{10} was $5 \times 10^{-6} \text{ m}$, d_{50} $25 \times 10^{-6} \text{ m}$ and d_{90} $75 \times 10^{-6} \text{ m}$ and an average of $60 \times 10^{-6} \text{ m}$ was taken for calculations. Ruthenium is well dispersed on the catalyst support and the average Ru particle size is between 1 and 3 nm (TEM, Supplementary information, Fig. S5). Levulinic acid (purity > 98%); γ -valerolactone (purity 98%); deuterium oxide, D₂O (purity > 99%); 1,4-dioxane (purity 99.5%) were purchased from Acros Organics. Hydrogen (purity > 99.999 vol.%) and nitrogen gas (purity > 99.9 vol.%) were from Linde. Milli-Q

Scheme 1. Catalytic hydrogenation of LA to GVL and subsequent products.

Table 1
Reactor and catalyst properties.

Reactor volume (L-phase)	1×10^{-4}	m ³
Catalyst intake	1.47×10^{-4}	kg
Average catalyst particle radius	30×10^{-6}	m
Catalyst particle density	7.50×10^2	kg/m ³
Catalyst hold-up	1.97×10^{-3}	m ³ _{cat} /m ³ _L
Liquid-solid area	1.97×10^2	m ² /m ³

water was used for all experiments. All chemicals were used without purification.

2.2. Experimental procedure for hydrogenation of levulinic acid

The hydrogenation reactions were performed in a 300 mL stainless steel batch autoclave (Buchi GmbH). The mantle of the autoclave was equipped with (electrically operated) heating rods and a cooling coil (using water) to allow for good temperature control. The reactor content was well mixed using a magnetically induced overhead stirrer equipped with a Rushton type impeller. The temperature and pressure were measured online. The reactor was equipped with a dip-tube to allow for liquid sampling during reaction. An overview of relevant reactor and catalyst properties is given in Table 1.

Water (100 mL) with the appropriate amount of LA and catalyst was introduced into the autoclave. At a stirring rate of 2000 rpm, the system was flushed with nitrogen for 5 min. The mixture was heated to the desired temperature and subsequently hydrogen was admitted until the target pressure was reached. This moment is set as $t = 0$ min. During the reaction, the pressure was maintained constant by the supply of hydrogen. Samples were collected at different time intervals and analysed for their composition by ¹H NMR.

2.3. Concentration calculations from ¹H NMR analysis

The composition of a reaction mixture (LA, HPA and GVL) was determined quantitatively by ¹H NMR. A sample (approximately

200 μL) was weighed, dissolved in D₂O and 1,4-dioxane (internal standard, IS, 10 μL) was added. All spectra were integrated using MestReNova software. The number of moles of A in a sample was calculated using Eq. (2).

$$N_A = N_{IS} \cdot \frac{I_A}{I_{IS}} \cdot \frac{H_{IS}}{H_A} \quad (2)$$

where N_A is the number of moles of A in the sample, N_{IS} the known amount of moles of the internal standard in the sample, I_A is the peak area of the methyl group of component A δ 2.1 ppm for LA, δ 1.03 ppm for 4-HPA and δ 1.3 ppm for GVL, I_{IS} the peak area of the CH₂ groups in 1,4-dioxane at δ 3.6 ppm and H_{IS} and H_A are the number of H atoms corresponding with the relevant NMR peak (3 for H_A and 8 for H_{IS}). The concentrations of LA, GVL and 4-HPA in the samples were calculated using Eq. (3).

$$C_A = \frac{N_A}{V_t} \cdot D_f \quad (3)$$

where V_t is the liquid volume in the NMR tube and D_f the dilution factor, which was calculated using Eq. (4).

$$D_f = \frac{\text{mass of the sample} + \text{mass of D}_2\text{O} + \text{mass of internal standard}}{\text{mass of the sample}} \quad (4)$$

2.4. Definitions

The conversion of LA, the yield and the selectivity of 4-HPA and GVL were calculated according to Eqs. (5)–(8).

$$X_{LA} = \frac{C_{LA,0} - C_{LA}}{C_{LA,0}} \cdot 100\% \quad (5)$$

$$Y_{GVL} = \frac{C_{LA,0} - C_{LA} - C_{4-HPA}}{C_{LA,0}} \cdot 100\% \quad (6)$$

$$Y_{4-HPA} = \frac{C_{LA,0} - C_{LA} - C_{GVL}}{C_{LA,0}} \cdot 100\% \quad (7)$$

Table 2
Range of conditions of the hydrogenation runs.

property	range
T(K)	343–403
P _{H2} (bar)	30–60
(C _{LA}) _{initial} (mol/m ³)	300–2500

Fig. 1. Experimental and model data for two selected experiments (top: run 7, 363 K, 45 bar; bottom: run 11, 363 K, 45 bar).

$$S_i = \frac{Y_i}{X_{LA}} \cdot 100\% \quad (8)$$

Where X_{LA} is the conversion of LA (mol.%); $C_{LA,0}$ the initial concentration of LA (mol m⁻³); C_{LA} the concentration of LA at a certain time t (mol m⁻³); Y_{GVL} the yield of GVL (mol.%); Y_{4-HPA} the yield of 4-HPA (mol.%) and S_i the selectivity to GVL or 4-HPA (mol.%).

3. Results and discussion

3.1. Screening experiments

All experiments were carried out in a batch reactor with Ru/C (3 wt.% Ru) as the catalyst (powder). A total of 29 experiments was performed within the experimental window of operation (Table 2, see Table S6 in the Supplementary information for the conditions for the individual experiments).

An experimental set of data was obtained, consisting of the concentration profiles of LA, HPA and GVL. Two typical concentration versus time profiles are given in Fig. 1.

Fig. 2. Effect of the agitation rate on the LA conversion (initial LA concentration: 600 mol/m³, 45 bar, 363 K, Ru/C, 40 min batch time).

Only 4-HPA was observed as an intermediate in all experiments. Even at higher temperatures, neither α -angelicalactone nor subsequent hydrogenation products of GVL like 1,4-pentandiol or 2-MTHF were observed at the prevailing reaction conditions (HPLC, supported by ¹H NMR). In some of the cases, particularly at low temperatures and low initial LA concentrations, the amount of 4-HPA shows a clear optimum, see Fig. 1 (bottom) for details. The selectivity to 4-HPA can be as high as 40–50%. These observations indicate that the conversion of LA to GVL involves two consecutive reactions: the hydrogenation of LA to 4-HPA followed by intramolecular esterification of 4-HPA to GVL. All reaction mixtures contained significant amounts of 4-HPA after reaction, even after prolonged reaction times, indicating that the conversion of 4-HPA to GVL is an equilibrium reaction in water (Scheme 2). Extended equilibrium studies for the 4-HPA/GVL equilibrium reaction, supplemented by DFT calculations, have been carried and will be published in due course [26].

Based on the concentration time profiles in the batch reactor set-up, a reaction network for the hydrogenation of LA in water using Ru/C catalysts is proposed and given in Scheme 2.

3.2. Mass transfer limitations

The catalytic hydrogenation of LA in water using a Ru/C catalyst is an example of a three phase gas-liquid-solid reaction. As such, the conversion rate and product selectivity may be affected by mass-transfer limitations of the reactants. To gain insights in possible mass transfer effects of hydrogen from the gas to the liquid phase, the effect of the stirring rate on the LA conversion was determined and the results are presented in Fig. 2. It shows that the LA conversion does not depend on the stirring rate provided that the stirring rate exceeds 1200 rpm. Thus, to avoid gas-liquid transfer limitation, all reactions for the kinetic modeling were performed at a stirring rate of 2000 rpm.

To further assess intra-particle mass transfer limitation of hydrogen and LA, the Weisz-Prater criterion [27] was determined for a number of experiments; see Supplementary information for calculation details. The values of Weisz-Prater criterion for the selected experiments are between 0.2 and 6.1 for LA and 0.7 and 6.9 for H₂. This implies that the reaction does not solely take place in the kinetic regime and that at least intra-particle pore diffusion limitations of hydrogen and LA play a role in these experiments,

Table 3Mechanism A with molecular H₂ adsorption.

A1	$LA + s \rightleftharpoons LA \cdot s$
A2	$H_2 + s \rightleftharpoons H_2 \cdot s$
A3	$LA \cdot s + H_2 \cdot s \rightleftharpoons HPA \cdot s$
A4	$HPA \cdot s \rightleftharpoons HPA + s$

Table 4Mechanism B with dissociative H₂ adsorption.

B1	$LA + s \rightleftharpoons LA \cdot s$
B2	$H_2 + 2s \rightleftharpoons 2H \cdot s$
B3	$LA \cdot s + H \cdot s \rightleftharpoons LAH \cdot s$
B4	$LAH \cdot s + H \cdot s \rightleftharpoons HPA \cdot s$
B5	$HPA \cdot s \rightleftharpoons HPA + s$

3.4. Model development for the catalytic hydrogenation reaction

Kinetic studies on the hydrogenation of ketone and aldehyde groups using support Ru/C catalysts have been reported in the literature. Examples include the hydrogenation of 2-butanone [28], cinnamaldehyde [29], D-glucose [30] and D-lactose [31]. Typically, Langmuir–Hinshelwood type of mechanisms are proposed. The exact form is depending on whether adsorption, reaction or desorption is assumed to be rate determining and on competitive or non-competitive adsorption of the reactants. In the literature on Ru/C catalyzed hydrogenations of carbonyl groups ample arguments can be found for both competitive and non-competitive adsorption. For simplicity, but also in the absence of any contradicting indications, we have applied a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model with competitive adsorption of hydrogen and organic molecules on the metal sites (s). Depending on the type of hydrogen adsorption, two mechanisms are considered here. In mechanism A molecular hydrogen adsorption is assumed, while in mechanism B adsorption of hydrogen is dissociative, see Tables 3 and 4.

The adsorption and desorption steps are assumed to be rapid. Therefore the hydrogenation rate is determined by the rate of a surface reaction, step A3 in mechanism A, and steps B3 or B4 in mechanism B. Reaction rate equations can be derived, following the LHHW methodology, as

$$R_{1,A3} = \frac{k_{r,A3} C_{LA} C_{H_2}}{(1 + K_{LA} C_{LA} + K_{H_2} C_{H_2} + K_{HPA} C_{HPA} + K_{GVL} C_{GVL})^2} \quad (19)$$

$$R_{1,B3} = \frac{k_{r,B3} C_{LA} \sqrt{C_{H_2}}}{(1 + K_{LA} C_{LA} + \sqrt{K_{H_2} C_{H_2}} + K_{HPA} C_{HPA} + K_{GVL} C_{GVL})^2} \quad (20)$$

$$R_{1,B4} = \frac{k_{r,B4} C_{LA} C_{H_2}}{(1 + K_{LA} C_{LA} + \sqrt{K_{H_2} C_{H_2}} + K_{HPA} C_{HPA} + K_{GVL} C_{GVL})^2} \quad (21)$$

The production rates of the components, as mentioned in Eq. (16) can be identified as

$$R_{LA(S)} = R_{H_2(S)} = -R_{HPA(S)} = -R_{1(S)} \quad (22)$$

where $R_{1(S)}$ is given by Eqs. (19), (20) or (21).

The possible involvement of GVL in the denominator term was also assessed experimentally by performing a hydrogenation reaction at standard conditions in the presence of GVL. The results are given in Fig. 4. Clearly, the presence of GVL retards the reaction rate and suggests that GVL adsorption to active catalysts sites affects the reaction rate and justifies the introduction of an additional GVL denominator term.

Hydrogenation reactions with pure 4-HPA could not be performed as it is well known that the intramolecular esterification of 4-HPA to GVL is a relatively fast reaction at 90 °C (*vide infra*) and as such GVL formation interferes with the rate data analysis.

Fig. 4. Effect of the presence of GVL on the LA conversion. □: only LA (0.6 M), ■: LA + GVL (LA 0.6 M, GVL 0.6 M, 45 bar, 90 °C, Ru/C intake: 2 wt.% on LA).

The possibility of considerable catalyst deactivation of the Ru/C on the timescale of the experiments (typically less the 3 h) is not likely on the basis of extensive studies in a continuous set-up for runtimes of over 100 h with this particular catalyst [32]. As such, it was not considered in this kinetic study.

3.5. Modeling of the intermolecular esterification of 4-HPA to GVL

Regarding the intramolecular esterification reaction of 4-HPA to GVL, it is assumed that the reaction is an equilibrium reaction which occurs in the bulk water phase and is catalyzed by a Brønsted acid [24,27]. The latter assumption is justified by individual studies using Brønsted acids and is in line with recent data from Bond [24].

$$R_2 = k_2 C_{H^+(L)} C_{HPA(L)} - k_{-2} C_{H^+(L)} C_{GVL(L)} \quad (23)$$

Two acids, LA and 4-HPA, are present in the reaction mixture and it is assumed that both catalyse the esterification reaction. The proton concentration for a mixture of two acids in different concentrations can be approximated by:

$$C_{H^+} = \sqrt{C_{LA} K_{a,LA} + C_{HPA} K_{a,HPA}} \quad (24)$$

Where $K_{a,LA}$ and $K_{a,HPA}$ are dissociation constants of levulinic acid ($10^{-4.6}$) and 4-hydroxypentanoic acid ($10^{-5.7}$), respectively [33]. A more detailed explanation regarding the derivation and validity of Eq. (24) is given in the Supplementary information.

3.6. Modeling of the mass transfer coefficients

In stirred slurry and gas slurry reactors the mass transfer coefficient for transport from the liquid to the solid phase is usually correlated via dimensionless numbers with an equation of the form

$$Sh = 2 + f(Re, Sc) \quad (25)$$

where the Sherwood number is obtained as a function of the Reynolds and Schmidt numbers [27]. With the small particle diameters used here, the second part of the relation for Sherwood is negligible, and the liquid solid mass transfer coefficients, $k_{l,i}$, can be calculated from

$$Sh = \frac{k_{l,i} d_p}{D_{i,eff}} = 2 \quad (26)$$

3.7. Model solution and parameter optimization

The mathematical model for calculating the liquid phase concentration profiles over time was programmed in MATLAB. The set

of ordinary differential equations (ODE's) for the concentrations, Eqs. (9)–(15), was solved numerically using the ode23s routine. The right-hand-sides of the ODE's needed for the integration were obtained from solving the catalyst particle problem Eqs. (16)–(18) with the bvp4c routine.

The solution algorithm of the mathematical model is incorporated as a subroutine of the parameter optimization process. For a specific kinetic model as given by Eqs. (19), (20) and (21) the unknown parameters comprise reaction rate constants and adsorption equilibrium constants. The optimization was achieved by minimization of the differences between the calculated and measured concentration data:

$$\chi^2 = \sum_i \sum_j \sum_k \left(\frac{\hat{C}_{i,j,k} - C_{i,j,k}}{w_i} \right)^2 \quad (27)$$

For each experiment the weight factor, w_i , was taken as the initial LA concentration. This way, all concentrations are scaled between 0 and 1, and the experiments each contribute with approximately the same weight to the solution. The parameters were optimised using the fminsearch function where initial values were generated from a limited number of iterations with the lsqnonlin function.

3.8. Model results

An experimental set of data was obtained, consisting of the concentration profiles of LA, HPA and GVL, as described in the experimental section. The challenge of finding optimum parameters of LHHW type of kinetic models is notorious due to local minima of the objective function and strong correlations among the parameters. This is especially true if the temperature dependency is taken into account via an Arrhenius type of dependency for the reaction rate constants or a Van't Hoff dependency for the adsorption equilibrium constants.

Therefore we applied a two-step strategy where each model was first optimized taking into account only the experiments performed at 363 K. This temperature is the intermediate of the experimental range of temperatures applied here. An initial optimization revealed that for each model the adsorption equilibrium constants of hydrogen and HPA were statistically not significant; their 95% confidence intervals encompassed zero. Apparently, the surface coverages of hydrogen and HPA were very small as compared to the other components. Consequently, the terms pertaining to the adsorption equilibria of hydrogen and HPA in the denominator of the LHHW reaction rate models were dropped, and the model equations reduce to

$$R_{1,A3} = \frac{k_{r,A3} C_{LA} C_{H_2}}{(1 + K_{LA} C_{LA} + K_{GVL} C_{GVL})^2} \quad (28)$$

$$R_{1,B3} = \frac{k_{r,B3} C_{LA} \sqrt{C_{H_2}}}{(1 + K_{LA} C_{LA} + K_{GVL} C_{GVL})^2} \quad (29)$$

$$R_{1,B4} = \frac{k_{r,B4} C_{LA} C_{H_2}}{(1 + K_{LA} C_{LA} + K_{GVL} C_{GVL})^2} \quad (30)$$

The models A3 and B4 are not distinguishable any more, compare Eqs. (28) and (30), due to the low hydrogen coverage. The optimized parameters for the models of Eqs. (28)–(30) are shown in Table 5.

The confidence intervals are calculated from comparing χ^2 -values where one of the parameters is varied until the χ^2 -value has increased to the value given by

$$(\chi^2)_{95\%} = (\chi^2)_{min} \left[1 + \frac{m}{N-m} F(m, N-m, 0.95) \right] \quad (31)$$

Table 5

Optimized parameters at 363 K with 95% confidence intervals.

model	A3,B4	B3
$k_r \left(\frac{m^3}{mol \cdot s} \text{ or } \frac{m^{1.5}}{mol^{0.5} \cdot s} \right)$	$(63.3 \pm 2.9) \times 10^{-3}$	$(343 \pm 15) \times 10^{-3}$
$K_{LA} \left(\frac{m^3}{mol} \right)$	$(1.32 \pm 0.06) \times 10^{-3}$	$(1.61 \pm 0.07) \times 10^{-3}$
$K_{GVL} \left(\frac{m^3}{mol} \right)$	$(0.84 \pm 0.12) \times 10^{-3}$	$(0.89 \pm 0.13) \times 10^{-3}$
$k_2 \left(\frac{m^3}{mol \cdot s} \right)$	$(0.41 \pm 0.03) \times 10^{-3}$	$(0.40 \pm 0.03) \times 10^{-3}$
$k_{-2} \left(\frac{m^3}{mol \cdot s} \right)$	$(0.042 \pm 0.013) \times 10^{-3}$	$(0.039 \pm 0.01) \times 10^{-3}$
error sum	0.988	1.170

Table 6

Activation energies and 95% confidence intervals.

parameter	E_A (J/mol)
k_r	$(54.9 \pm 2.7) \times 10^3$
k_2	$(66.9 \pm 3.3) \times 10^3$
k_{-2}	$(70.6 \pm 5.6) \times 10^3$

where $F(m, N-m, 0.95)$ denotes the 95% value of the Fisher distribution with $(m, N-m)$ degrees of freedom. Because model A3,B4 results in a smaller sum of errors, as compared to model B3, it is selected as the preferred model henceforth. Some typical results are shown in Fig. 1.

In the second step of the optimization strategy, the temperature dependency of the preferred model A3,B4 was optimized. The kinetic parameters were expressed as

$$k_r = (k_r)_{363K} \exp \left[\frac{-E_{A,k_r}}{R} \left(\frac{1}{T} - \frac{1}{363} \right) \right] \quad (32)$$

$$k_2 = (k_2)_{363K} \exp \left[\frac{-E_{A,k_2}}{R} \left(\frac{1}{T} - \frac{1}{363} \right) \right] \quad (33)$$

$$k_{-2} = (k_{-2})_{363K} \exp \left[\frac{-E_{A,k_{-2}}}{R} \left(\frac{1}{T} - \frac{1}{363} \right) \right] \quad (34)$$

For simplicity, the variation of the adsorption equilibrium constants with the temperature was not taken into account here. Using the data from kinetic experiments at temperatures of 343–403 K the optimized activation energy data were obtained as shown in Table 6. Some typical results are shown in Fig. 5.

Agreement between experimental and modeled data for the dataset is good, see the parity plot in Fig. 6 for details.

4. Discussion

The modeling activities indicate that the hydrogenation of LA is best described by a LHMW mechanism with a dual site surface reaction as the rate determining step. The mechanism is characterized by dissociative hydrogen adsorption and competitive adsorption of LA and GVL at the active sites of the catalyst surface. The competitive adsorption of the GVL is rationalized by the observed reduction in initial reaction rate when performing a hydrogenation reaction in the presence of GVL (Fig. 4). The values for the adsorption constants (K_x with $x = \text{LA}$ and GVL) are 1.32×10^{-3} and $0.84 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, respectively.

The apparent activation energy for the hydrogenation reaction is $54.9 \pm 2.7 \text{ kJ mol}^{-1}$, which is slightly higher than reported by Bond et al. ($48 \pm 5 \text{ kJ mol}^{-1}$) [24]. The small differences may be related to the experimental set-ups used for the experiments (batch here versus a continuous packed bed reactor) and differences in catalyst supplier. It is well known that the activity of Ru/C catalysts is a function of, among others, the preparation method and the type of carbon support used and major activity differences have been reported [34]. In addition, our studies were performed with a dif-

Fig. 5. Experimental and model data for two selected experiments (top: run 26, 403 K, 45 bar; bottom: run 30, 343 K, 45 bar).

Fig. 6. Modeled versus experimental LA, HPA and GVL concentrations.

ferent Ru loading (3%) than Bond (5%). The activation energy for Ru/C as found in our study is much higher than for Pd/C by Zhang et al. (33 kJ mol^{-1}) [25]. Whether this relatively low value is indeed an intrinsic feature of the Pd/C catalyst or that the kinetic analysis did not include proper attention to diffusional issues, is not clear.

Table 7

Comparison of kinetic data for the homogeneous and heterogeneous model.

model	Heterogeneous (A3, B4)	Homogeneous
$k_r \left(\frac{\text{m}^3}{\text{mol}} \cdot \text{s} \right)$	$(63.3 \pm 2.9) \times 10^{-3}$	$(53.3 \pm 5.4) \times 10^{-3}$
$K_{LA} \left(\frac{\text{m}^3}{\text{mol}} \right)$	$(1.32 \pm 0.06) \times 10^{-3}$	$(1.51 \pm 0.4) \times 10^{-3}$
$K_{HPA} \left(\frac{\text{m}^3}{\text{mol}} \right)$	–	$(0.45 \pm 0.06) \times 10^{-3}$
$K_{GVL} \left(\frac{\text{m}^3}{\text{mol}} \right)$	$(0.84 \pm 0.12) \times 10^{-3}$	$(0.79 \pm 0.08) \times 10^{-3}$
$k_2 \left(\frac{\text{m}^3}{\text{mol}} \cdot \text{s} \right)$	$(0.41 \pm 0.03) \times 10^{-3}$	$(0.4 \pm 0.02) \times 10^{-3}$
$k_{-2} \left(\frac{\text{m}^3}{\text{mol}} \cdot \text{s} \right)$	$(0.042 \pm 0.013) \times 10^{-3}$	$(0.04 \pm 0.01) \times 10^{-3}$
$E_A \text{ (J/mol) for } k_r$	$(54.9 \pm 2.7) \times 10^3$	$(34.1 \pm 0.1) \times 10^3$
$E_A \text{ (J/mol) for } k_2$	$(66.9 \pm 3.3) \times 10^3$	$(62.5 \pm 3.6) \times 10^3$
$E_A \text{ (J/mol) for } k_{-2}$	$(70.6 \pm 5.6) \times 10^3$	$(65.7 \pm 6.8) \times 10^3$

The intramolecular esterification reaction was modeled as an acid catalyzed equilibrium reaction with a first order dependency in reactants and products. The kinetic constants for the forward reaction (k_2) was $0.41 \pm 0.03 \times 10^{-3} \text{ (m}^3 \text{ mol}^{-1} \text{ s}^{-1})$ at the reference temperature (363 K), versus $0.042 \pm 0.013 \times 10^{-3} \text{ (m}^3 \text{ mol}^{-1} \text{ s}^{-1})$ for the backward reaction (k_{-2}). As such the forward reaction is much faster and the equilibrium is far on the side of the product GVL. These findings are in line with the experimental observations (see e.g. Fig. 1). The value for the equilibrium constant (k_2/k_{-2}) is about 10 at 363 K. This value is lower than that observed for the independently experimentally determined equilibrium constant for the reaction at 293 K (16.5), due to the temperature dependence of the equilibrium constant. The activation energy for the forward reaction was $66.9 \pm 3.3 \text{ kJ mol}^{-1}$, which is very close to the 70 kJ mol^{-1} reported by Bond et al. [24].

The activation energy for the intramolecular esterification reaction is larger than for the hydrogenation reaction. As such, the esterification reaction is favored at higher temperatures and the amounts of GVL and 4-HPA are expected to be at equilibrium values when performing the reaction at the high end of the temperature range (403 K). This is indeed experimentally observed, see Fig. 1 for details. Thus, when aiming for high amounts of 4-HPA, the reaction should be carried out at low temperatures whereas GVL formation is favored at higher temperatures. However, it should be stressed that 100% selectivity to GVL is not possible in water in the temperature range studies (333–403 K) due to equilibrium considerations. As such, reported literature studies with quantitative GVL selectivity in water are highly doubtful and likely related to analytical issues.

In the development of this study, the experimental data were first fitted to a homogeneous model, i.e. without taking any mass transfer or diffusion limitations into account, see Supplementary information for details. With the homogeneous model also a good fit was obtained. However, calculation of the Weisz-Prater numbers from experimentally observed rates indicated that diffusion limitation in the catalyst particles occurred. A comparison of the kinetic parameters for both the homogeneous and heterogeneous model is given in Table 7.

The majority of the kinetic parameters are about similar, particularly when considering the confidence intervals. The two main exceptions are the values for k_r and the corresponding activation energy for this reaction. The activation energy for the homogeneous model is much lower than for the heterogeneous model. This is in line with the known fact that the apparent activation energies for mass transfer limited reactions are always lower than that of the intrinsic kinetics of the reaction, and in the limit approaches a value of half of the intrinsic one [27].

A comparison of the experimental data and the heterogeneous model with and without any mass transfer limitation is given in Fig. 7. Indeed clear differences are observed. For instance, the model without diffusional components predicts that the drop in

Fig. 7. Comparison of the experimental data and the heterogeneous model with and without any mass transfer limitation. Symbols: measured concentrations run 7, 363 K, 45 bar; solid lines: calculated with the final kinetic model; dotted lines: calculated with the same kinetic model but without any mass transfer or diffusion limitation.

Fig. 8. Calculated relative hydrogen concentration profiles in the catalyst (top) and the relative LA concentration profiles in the catalyst (bottom, run 11, 363 K, 45 bar).

LA concentration *versus* time is much more profound than for the heterogeneous model with diffusional limitations, as expected.

To further illustrate that the full heterogeneous model needs to be employed at the conditions used here, the concentration profiles inside the catalyst particles were extracted from the software. Some typical results are shown in Fig. 8.

The figures nicely illustrate a pattern that is generally observed with the experiments; significant concentration variations occur within the catalyst particles. Initially, at $t=0$, it is especially the hydrogen concentration that decreases at the interior of the particle. At the center however the concentration is still more than 40%

Fig. 9. Weisz-Prater numbers, and catalyst efficiency (Run 11, 363 K, 45 bar).

of the liquid bulk value. Therefore, even initially, all catalyst volume does participate in catalyzing the reaction and there is no inactive part of the catalyst as would have been the case with more severe diffusion limitation. As time progresses the hydrogen concentration inside the particle increases until near the end when most of the LA is converted the concentration is equal to the liquid bulk value throughout the particles.

An opposite trend is seen with the LA concentration profiles, see Fig. 8 (bottom). Initially the LA concentration decreases in the catalyst particle, but at the center the value still is some 75% of the liquid bulk value. But now, with increasing time, the concentration in the catalyst decreases. The observations are reflected in the catalyst effectiveness, see Fig. 9. At the start of the experiment the effectiveness is close to 75%, mainly due to the decreased availability of hydrogen. Hydrogen is limiting here, despite its much higher diffusion coefficient, because of its low concentration. During the experiment, gradually the limitation is shifted from the hydrogen availability towards the LA availability. This is also illustrated by the Weisz-Prater numbers, N_{WP} , for hydrogen and LA that are also shown in Fig. 9. The initially high N_{WP} of hydrogen gradually drops to very low values and on itself would lead to the erroneous conclusion that after $t=2000$ the situation is free of diffusion limitation. Here the high N_{WP} of LA is determining the system behavior and still causes some diffusion limitation. For all experiments the catalyst effectiveness factors were found to be in the range of 70–95%, varying from initially lower values to higher values near the end at high conversion.

Both external mass transfer limitations, due to the finite values of the mass transfer coefficients $k_{l,i}$, and the intra-particle diffusion limitations, due to the finite values of the effective diffusion coefficients $D_{i,eff}$, determine the overall reaction rate (Fig. 3). By applying the principle of resistances in series, the relative contribution of the external liquid–solid mass transfer, as compared to the amount due to the intra-particle diffusion limitation, to the overall transport limitation can be calculated. With the experimental runs obtained here, intra-particle diffusion limitations is by far more important than external liquid–solid mass transfer and accounts for 70–90% of the total mass transfer resistance.

5. Conclusions

Ru/C is an active catalyst for the hydrogenation of LA to GVL in water at relatively low temperatures ($<100^\circ\text{C}$). 4-HPA is a clear intermediate and relatively high amounts of 4-HPA may be obtained when performing the reaction at relatively low temperatures and low initial LA concentrations. Kinetic modelling activities

reveal that particularly intra-particle diffusion limitation of both LA and hydrogen affect the overall reaction rates. As such, a heterogeneous model was developed incorporating both diffusion and reaction rates. The intrinsic kinetics of the hydrogenation reaction of LA to 4-HPA was successfully modelled using a Langmuir-Hinshelwood type expressions with competitive adsorption of LA and GVL on the surface of catalyst. The subsequent intramolecular esterification of the hydrogenation product 4-HPA to GVL was modelled as a homogeneous acid catalyzed equilibrium reaction. Good agreement between experimental concentration *versus* time profiles and the model was obtained. The kinetic parameters extracted from the heterogeneous model were compared with that of a homogeneous model, which assumes the absence of diffusion limitations. The main difference between both models is the activation energy for the hydrogenation reaction, which was by far lower for the homogeneous model.

The modelling activities indicate that the hydrogenation of LA with hydrogen in water using Ru/C is a fast reaction, for which diffusion limitations and particularly intra-particle limitations of both LA and hydrogen play a significant role, even with the relatively small catalyst particle sizes ($d_p = 60 \times 10^{-6}$ m) and the low catalyst hold-up used in this study. As such, experimental data on LA hydrogenations in water using supported Ru catalysts should be considered carefully as the reported conversion rates may have been affected by intra-particle diffusion limitation. The kinetic model developed here will be used for further reactor engineering studies and particularly for selection of the most suitable reactor configuration (e.g. packed bed *versus* slurry reactors) and reactor sizing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2016.06.033>.

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