Chapter 4

Experimental and modeling studies on the Ru/C catalyzed levulinic acid hydrogenation to γ-valerolactone in packed bed microreactors

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Abstract

The hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) was performed in perfluoroalkoxy alkane capillary microreactors packed with a carbon-supported ruthenium (Ru/C) catalyst with an average particle diameter of 0.3 or 0.45 mm. The reaction was executed under an upstream gas–liquid slug flow with 1,4-dioxane as the solvent and H₂ as the hydrogen donor in the gas phase. Operating conditions (i.e., flow rate and gas to liquid flow ratio, pressure, temperature and catalyst particle size) were varied in the microreactor to determine the influence of mass transfer and kinetic characteristics on the reaction performance. At 130 °C, 12 bar H₂ and a weight hourly space velocity of the liquid feed (WHSV) of 3.0 g\text{feed}/(g\text{cat}·h), 100% LA conversion and 84% GVL yield were obtained. Under the conditions tested (70–130 °C and 9–15 bar) the reaction rate was affected by mass transfer, given the notable effect of the mixture flow rate and catalyst particle size on the LA conversion and GVL yield at a certain WHSV. A microreactor model was developed by considering gas–liquid–solid mass transfer therein and the reaction kinetics estimated from the literature correlations and data. This model well describes the measured LA conversion for varying operating conditions, provided that the internal diffusion and kinetic rates were not considered rate limiting. Liquid–solid mass transfer of hydrogen towards the external catalyst surface was thus found dominant in most experiments. The developed model can aid in the further optimization of the Ru/C catalyzed levulinic acid hydrogenation in packed bed microreactors.

4.1. Introduction

Biomass is an abundantly available and renewable source of carbon with potential to replace fossil (petroleum) sources in the production of chemicals and fuels.¹ One of the most promising biobased platform chemicals is levulinic acid (LA),²,³ which is typically produced by the acid-catalyzed rehydration of furans (i.e., 5-hydroxymethylfurfural (HMF) or furfuryl alcohol) derived from C₅- and C₆-sugars obtained from (hemi-)cellulosic biomass.⁴ LA can be converted into a large variety of chemicals. Its catalytic hydrogenation/dehydration results in γ-valerolactone (GVL), with potential uses as food or fuel additive.⁵-⁷ GVL is also a non-toxic solvent,⁵,⁸ with reported applications in e.g., the homogeneous acid catalyzed production of LA from cellulose,⁹ the
heterogeneously catalyzed synthesis of HMF from glucose\(^\text{10}\) and microwave-assisted peptide synthesis.\(^\text{11}\) Furthermore, GVL can be converted into a variety of value-added products including solvents (e.g., alkyl 4-alkoxyvalerates),\(^\text{12}\) polymer precursors (e.g., dimethyl adipate for producing nylons and \(\alpha\)-methylene-\(\gamma\)-valerolactone (MeMBL; an acrylic monomer)\(^\text{13}\)), biofuels (e.g., 2-methyltetrahydrofuran (MTHF), valeric esters and alkane fuels) and specialty chemicals (e.g., adipic acid, caprolactone and 5-nonanone).\(^\text{7}\) Depending on the catalyst and reaction conditions, the synthesis of GVL from LA is typically performed via \(\alpha\)-angelicalactone (\(\alpha\)-AL; by the dehydration of LA) or 4-hydroxypentanoic acid (HPA; by the hydrogenation of LA) as the intermediate (Scheme 4.1). GVL can be further over-hydrogenated towards MTHF.

\begin{center}
\includegraphics[width=\textwidth]{Scheme_4.1.png}
\end{center}

\textbf{Scheme 4.1.} Hydrogenation of LA to GVL with HPA and/or \(\alpha\)-AL as the possible intermediate and MTHF as the over-hydrogenation product.

Molecular \(\text{H}_2\) is commonly utilized as the reduction agent, although the use of other (liquid phase) hydrogen donors like formic acid has also been reported.\(^\text{14}\) The hydrogenation of LA is commonly performed over heterogeneous catalysts.\(^\text{15-18}\) Noble metal catalysts, with Ru in particular, have received much research attention due to the high selectivity towards GVL (i.e., in several cases up to 100%) and good catalyst stability.\(^\text{19-22}\) A variety of catalyst supports have been used for the immobilization of Ru (e.g., carbon, alumina, titania, zirconia).\(^\text{23}\) Ru supported on carbon (Ru/C) has the advantage of high specific catalyst surface area and is thus used extensively in the hydrogenation of LA to GVL,\(^\text{20,23-27}\) and many other hydrogenation reactions.\(^\text{28-32}\) The Ru/C catalyzed hydrogenation of LA to GVL is often conducted with water as the solvent, although organic solvents have also been used (e.g., GVL,\(^\text{9}\) methanol,\(^\text{20}\) 1,4-dioxane,\(^\text{13,21,23-25}\)
tetrahydrofuran (THF). GVL was used as the solvent for its own synthesis by the hydrogenation of LA (extracted from a water phase) over a Ru-Sn/C catalyst. This organic phase was further hydrogenated in order to convert the extracted LA therein to GVL over Ru-Sn/C. 1,4-Dioxane has similar properties to GVL and is thus often used as a mimic solvent for research purposes to facilitate GVL product quantification. However, the toxicity of 1,4-dioxane makes it a less attractive solvent for industrial applications. The use of organic solvents with low boiling points (like THF, methanol) instead of water for LA hydrogenation can facilitate the product retrieval (e.g., due to energy saving in the downstream distillation) without wastewater generation.

The Ru/C catalyzed hydrogenation of LA to GVL has been performed in continuous flow reactors (e.g., packed bed milli-reactors) for catalyst stability testing, along with several studies in batch reactors to obtain mechanistic or kinetic insights. The Ru/C catalyzed LA hydrogenation is generally considered 0.5 order in H\(_2\) and zero order in the LA substrate. This was also observed in the hydrogenation of glucose to sorbitol and of alkyl levulinates to GVL. In the latter case, a 1st order dependency in the substrate was observed at relatively low initial substrate concentrations (0.03 – 0.15 M) in methanol. Piskun et al. found that in batch reactors (operated at 30 – 60 bar and 343 – 403 K) with water as the solvent, the 5 wt% Ru/C catalyzed hydrogenation of LA to GVL was partly limited by intraparticle mass transfer. The Weisz-Prater numbers, calculated as the ratio between the experimentally observed reaction rate and the rate of internal diffusion, indicated that diffusion limitations occurred within the catalyst pores. These (intraparticle) mass transfer limitations of both hydrogen and LA were also observed in a packed bed milli-reactor, especially due to the larger catalyst particles used therein.

Dedicated studies focusing on reactor engineering aspects (e.g., in terms of the effect of reactor type and operating conditions on gas-liquid-solid mass transfer characteristics) for the optimization of reactor performance in the (Ru/C catalyzed) hydrogenation of LA are not widely performed to this date. The use of conventional gas-liquid-solid (e.g., batch, packed bed, slurry) reactors may not be promising in optimization primarily due to a limited control over the three-phase contact and heat or mass transfer thereof. In this respect, process intensification methods for gas-liquid-solid reactions have been developed. Particularly continuous flow microreactors have received much research interest. Microreactors allow multiphase
operation under well-defined flow patterns (e.g., gas-liquid or liquid-liquid slug flow) that facilitate to investigate reaction kinetics and mass transfer characteristics thereof.\textsuperscript{37} Due to their small internal channel sizes (i.e., diameter on the order of ca. 1 mm or below), microreactors offer several fundamental advantages (e.g., enhanced heat/mass transfer and reduced safety risks).\textsuperscript{37,38} The enhanced mass transfer in microreactors makes them interesting for multiphase reactions that tend to be limited by the species transport in (either of) the multiple phases, which is the case particularly when the intrinsic kinetic rate is relatively fast.\textsuperscript{39} Furthermore, the superior heat transfer capability in microreactors, as well as the small lateral channel dimensions, allows safer operation by the precise temperature control and reduced explosion risk (e.g., in the case of strongly exothermic reactions or operation in the explosive regime).\textsuperscript{40,41} These merits are advantageous for hydrogenation reactions that often require high pressure operation to improve mass transfer (e.g., given low hydrogen solubility in the reaction solvent) and fine temperature control to avoid the hotspot formation in the reactor leading to runaway. Solid catalysts for such reactions can be also well handled in microreactors and are usually incorporated as wall-coatings or as small particles in a packed bed configuration.\textsuperscript{42–44} To the best of the authors’ knowledge, only one report dealt with the LA hydrogenation to GVL in microreactors.\textsuperscript{45} Herein the reaction was performed with formic acid as the hydrogen donor in water/methanol. A stainless steel capillary microreactor was wall-coated with silver/palladium nanoparticles supported on graphited carbon nitride (AgPd/g-C\textsubscript{3}N\textsubscript{4}). In 50 min residence time at 70 °C, 100% GVL yield was obtained. The immobilization of solid catalysts onto a microreactor wall often requires tedious coating procedures and the catalyst replacement (i.e., in the case of irreversible catalyst deactivation or reactor malfunctioning) may require energy intensive procedures.\textsuperscript{38,46,47} An alternative and more convenient way is by loading small catalyst particles to an empty microchannel (e.g., by gravitational or vacuum filling). Catalyst particles can then be held in place by filters or small inert particles (e.g., glass beads) to form a packed bed configuration.\textsuperscript{48–50} This allows the direct use of commercial or laboratory-prepared catalysts (sometimes particle sieving or shaping is needed for compatibility with the microchannel dimension).

Although gas-liquid flow characteristics have been widely examined in conventional macroscale packed bed reactors,\textsuperscript{51} hydrodynamics in packed bed microreactors are not widely reported yet.\textsuperscript{49,50,52–59} The dominance of
surface forces over gravitational forces on the micrometer scale results in new gas-liquid flow features in packed bed microreactors. A hydrodynamic study during the benzyl alcohol oxidation in a packed bed microreactor (containing 1 wt% Au-Pd/TiO$_2$ catalyst) revealed two major gas-liquid flow patterns including the liquid-dominated slug flow and gas-continuous flow. The liquid-dominated slug flow is similar to the induced pulsing flow in conventional large-scale packed bed reactors, and the gas-continuous flow to the trickle flow. A transitional segregated flow pattern exists in between the two major flow patterns mentioned above, where the catalyst bed is alternatingly wetted by the gas and liquid phases. The transition from the liquid-dominated slug flow to gas-continuous flow was found to take place at a much smaller liquid to gas flow ratio than that observed in conventional packed bed reactors, due to the dominance of surface forces in packed bed microreactors. This transition further depends on several other factors such as the upstream gas–liquid flow pattern before entering the bed, particle size, shape and configuration, and the channel to particle diameter ratio.

Packed bed microreactors offer a better radial heat transfer than conventional (milli-scale or larger) packed beds, thus suppressing effectively the formation of hot spots and/or the explosion risks. Higher gas-liquid-solid mass transfer rate is also attainable in packed bed microreactors due to smaller particles accommodated. Thus, gas-liquid hydrogenation reactions in packed bed microreactors have gained increased research attention over the past decade. In some cases, mass transfer limitations were (almost) eliminated and the reactions were under kinetic control, making packed bed microreactors a promising tool for kinetic investigations.

In this work, the hydrogenation of LA was performed in capillary microreactors made of perfluoroalkoxy alkane (PFA) packed with 0.5 wt% Ru/C as the solid catalyst. Molecular H$_2$ was used as the gas phase and 1,4-dioxane as the organic solvent. The effect of various operating parameters in the packed bed microreactor (e.g., flow rate and ratio, temperature, pressure, catalyst particle size and concentration) on the reaction performance (in terms of the LA conversion and GVL yield) was investigated. A microreactor model was subsequently developed to describe the experimental results and to further identify the rate limiting steps (i.e., gas-liquid mass transfer, external or internal liquid-solid mass transfer, or kinetics). Finally, with the developed model, directions for further reaction optimization in the microreactor could be established.
4.2. Experimental

4.2.1. Materials and chemicals

Levulinic acid (> 98%) and γ-valerolactone (> 98%) were obtained from Acros Organics, 1,4-dioxane (> 99%) and dodecane (> 99.5%) from TCI Europe N.V., 2-methyltetrahydrofuran (> 99%), α-angelicalactone (98 %), D2O (99.9 %) and SiC particles (with an average diameter of 0.48 mm) from Sigma-Aldrich and 0.5 wt% Ru/C catalyst particles (surface area of ca. 1000 m²/g) from Strem Chemicals. The catalyst particles were ground and sieved into different size fractions before use (with an average particle diameter (dₚ) being ca. 0.3 or 0.45 mm, respectively). H₂ and N₂ gases were obtained from Linde Gas (99.9%).

4.2.2. Setup and procedure

Reactions were performed in a Microactivity Effi reactor from PID Eng&Tech (Figure 4.1). The liquid solution, consisting of 5 – 10 wt% LA and 1 wt% dodecane (in situ internal standard) in the 1,4-dioxane solvent, was fed at an inlet flow rate (Qₗ₀) of 0.05 – 0.17 mL/min by a Williams piston pump (model P250 V225) to a stainless steel T-junction (0.75 mm bore size). H₂ or N₂ gas (supplied from a gas cylinder) was regulated by a mass flow controller (MFC) from Bronkhorst (EL-FLOW Select F-211CV) at an inlet gas flow rate (Q₉₀; i.e., at room temperature and reactor pressure) ranging from 0.16 to 0.33 mL/min. The gas and liquid feeds were guided through separate polytetrafluoroethylene (PTFE) capillaries (inner diameter: 0.8 mm; length: ca. 50 cm) that were preheated in an oven operated at a temperature of 70 – 130 °C. An upstream gas-liquid slug flow was then generated by mixing both feeds in a transparent PTFE capillary (inner diameter: 0.8 mm) for flow visualization. This was then connected to capillary microreactors (with inner diameter of dₑ = 1.6 mm) made of PFA, packed with 0.5 wt% Ru/C catalyst particles (weight (wₑ) of 0.45 – 0.9 g) by gravitational filling. During the filling procedure, the PFA capillary was frequently tapped to ensure a dense and reproducible packing state. Packed beds with lengths (Lₑ) of 0.4 – 0.8 m were used in a vertical configuration where the gas-liquid mixture was introduced at the top to realize a downward flow. Polyether ether ketone (PEEK) connectors containing filters (75 μm mesh) made of PTFE and chlorotrifluoroethylene (CTFE) were incorporated at the in- and outlet of the bed to keep the packing in place. In some experiments, an additional PFA capillary, packed with inert SiC
particles, was placed in front of the packed bed microreactor to generate an upstream slug flow with shorter gas bubbles and liquid slugs. The outlet of the microreactor was connected to a PTFE capillary (inner diameter: 0.8 mm) and directed towards a liquid level indicator/controller (LIC) where the gas and liquid phases were separated. The separator consisted of a capacitive level sensor with a very low dead volume.\(^{67}\) This separation was regulated by a needle valve (i.e., controlled by the Effi operating system; Figure 4.1) in the liquid outlet. The pressure \((p)\) of the outlet gas stream was maintained at 9 – 15 bar with a pressure control valve located after the gas-liquid separator, after which it was exhausted to the fume hood. This valve was operated by the Effi, based on the measured pressure at the gas outlet by a pressure transducer from Sensor-Technik Wiedemann GmbH (model A09). The gas-liquid flows at the inlet (after the T-junction) and outlet (before the gas-liquid separator) of the packed bed microreactor were passed through a six-way valve. This pneumatic valve (controlled by an electrovalve) could be operated in two different positions: i) passing the gas-liquid stream through the packed bed and ii) directing the gas-liquid inlet flow immediately towards the gas-liquid separator and thus bypassing the microreactor (Figure 4.1). Photos of the packed bed microreactor and slug flow profiles (both upstream and downstream; at room temperature and using \(\text{N}_2\) as the inert gas instead of \(\text{H}_2\)) are also shown in Figure 4.1, which were taken by a Nikon D3300 digital camera equipped with a Nikon lens (AF-S Micro Nikkor 60mm f/2.8 G ED). Note that an isothermal microreactor operation is assumed in this work, given the preheating of the feeds, the insignificant reaction heat released (e.g., the estimated adiabatic temperature rise being around 7 °C for 5 wt% LA concentration at inlet; calculation details not shown for brevity) and the fast heat transfer of the microreactor.

Liquid samples were collected every 20 min time on stream and prepared for gas chromatography and/or \(^1\)H-NMR analysis. The experimental data presented in this work are based on the measured sample concentrations under steady state conditions. Steady state was achieved once the measured concentration at the microreactor outlet did not alter for a given time on stream, which was usually after ca. 60 min (cf. Section S4.1 in the Supporting Information). This relatively long time required is mainly due to the large empty volume (i.e., between the microreactor and the gas-liquid separator) of the system and the low flow rates used.
4.2.3. Analysis

The LA and GVL concentrations in the liquid samples were analyzed by gas chromatography with a Restek Stabilwax-DA column (30 m × 0.32 mm × 1 µm) equipped with a flame ionization detector (GC-FID). GC-samples were prepared by diluting 0.2 mL of the reaction mixture (i.e., collected from the liquid sample vessel; cf. Figure 4.1) or the liquid feed with ca. 1.8 mL 1,4-dioxane. The temperature of the column was increased from 60 °C to 250 °C at 20 °C/min and held at 250 °C for 2 min. Helium was used as the carrier gas at 2.5 mL/min. For all experiments the relative error in the measured LA and GVL concentrations was found below 10%.

The molar ratios of LA, HPA and GVL in the above prepared analytic sample mixture were determined by $^1$H-NMR (300 MHz operated at 25 °C). One drop of such sample mixture was mixed with approximately 1 mL D$_2$O. The molar ratio of each species in the mixture was the determined from the ratio of the respective NMR peak heights (2.1 ppm for LA, 1.03 ppm for HPA, and 1.3 ppm for GVL; cf. Supporting Information, Section S4.1).
4.2.4. Definitions

The LA conversion \( (X_{LA}) \), GVL yield \( (Y_{GVL}) \) and selectivity \( (\sigma_{GVL}) \) are determined as follows

\[
X_{LA} = \left(1 - \frac{C_{LA,1}}{C_{LA,0}}\right) \times 100\% \quad (4.1)
\]

\[
Y_{GVL} = \frac{C_{GVL}}{C_{LA,0}} \times 100\% \quad (4.2)
\]

\[
\sigma_{GVL} = \frac{Y_{GVL}}{X_{LA}} \times 100\% \quad (4.3)
\]

where \( C_{LA,0} \) and \( C_{LA,1} \) are the LA concentrations at the microreactor inlet and outlet, respectively. \( C_{GVL} \) is the concentration of GVL at the microreactor outlet.

The weight hourly space velocity of the liquid phase \( (WHSV; \text{ in } \text{g feed}/(\text{g cat} \cdot \text{h})) \) is defined as

\[
WHSV = \frac{m_L}{W_c} \quad (4.4)
\]

where \( m_L \) is the liquid mass flow rate.

The void fraction in the packed bed microreactor \( (\varepsilon) \) is determined by

\[
\varepsilon = 1 - \frac{W_c}{V_{bed} \rho_S} \quad (4.5)
\]

where \( \rho_S \) is the average density of the solid (catalyst) particles and \( V_{bed} \) is the bed volume.

4.3. Results and discussion

4.3.1. Mass balance and reaction profile

A typical reaction profile for the hydrogenation of LA to GVL is depicted in Figure 4.2. The reaction was performed in the packed bed microreactor with a fixed length \( (L_{bed} = 0.8 \text{ m}) \), where the weight hourly space velocity \( (WHSV; \text{ Eq. 4.4}) \) was varied by adjusting the total flow rate \( (Q_{tot} = Q_G + Q_L) \), where \( Q_G \) and \( Q_L \) are the respective gas and liquid flow rates under the reaction temperature and pressure without consideration of the flow rate change due to reaction consumption) while the gas to liquid volumetric flow ratio \( (Q_{G,0} / Q_{L,0}) \) was kept equal. Note that the pressure drop in the packed
bed microreactor estimated according to the literature\textsuperscript{59} was found insignificant compared to the total pressure applied. The results at $\text{WHSV} = 6.0 \text{ g}_{\text{feed}}/(\text{g}_{\text{cat}} \cdot \text{h})$ are used as the benchmark conditions throughout this work ($C_{\text{LA,0}} = 5 \text{ wt\%}, Q_{\text{G,0}} / Q_{\text{L,0}} = 4.5$, 12 bar $\text{H}_2$, 130 $^\circ\text{C}$, $L_{\text{bed}} = 0.8 \text{ m}$, $w_c = 0.9 \text{ g}$, $d_p = 0.45 \text{ mm}$). Only the LA and GVL concentrations at the microreactor outlet could be determined quantitatively by GC-FID. The GVL yield (Eq. 4.2) was consistently lower than the LA conversion (Eq. 4.1), indicating that the reaction was not fully selective towards GVL and a closed mass balance could not be obtained by GC-FID analysis alone (Figure 4.2).

![Figure 4.2](imageURL)

**Figure 4.2.** Influence of the inverse weight hourly space velocity ($1/\text{WHSV}$) on the LA conversion, GVL and HPA yields at the bed outlet. The values at $1/\text{WHSV} = 0$ correspond with the microreactor inlet. Conditions: $C_{\text{LA,0}} = 5 \text{ wt\%}, Q_{\text{G,0}} / Q_{\text{L,0}} = 4.5$, 12 bar $\text{H}_2$, 130 $^\circ\text{C}$, $L_{\text{bed}} = 0.8 \text{ m}$, $w_c = 0.9 \text{ g}$, $d_p = 0.45 \text{ mm}$. Lines are solely for illustrative purposes. Error bars above and hereafter represent the standard deviation based on at least three measurements at different times on stream under steady state conditions.

The gap in the mass balance was attributed to the HPA intermediate that could not be measured quantitatively by GC-FID. HPA could be detected by $^1\text{H}$-NMR, from which the molar ratios of LA, GVL and HPA in the reaction mixture were determined. These ratios, combined with the measured LA and GVL concentrations, resulted in nearly closed mass balances (cf. Section S4.1 in the Supporting Information for more detailed explanation). As such, the HPA yield was determined from the LA conversion and GVL yield, assuming a 100% total selectivity towards HPA and GVL. This was further proven by the fact that alternative hydrogen products (i.e., MTHF and $\alpha$-AL; cf. Scheme 4.1) were neither detected by GC nor $^1\text{H}$-NMR. For
the over-hydrogenation of GVL towards MTHF, it is expected that much higher temperature/pressure and longer residence times are required. For instance, it has been reported that no GVL conversion was found after 4 h at 130 °C and 100 bar H\textsubscript{2} for the solvent-free conversion of GVL over 5 wt% Ru/C.\textsuperscript{68} Also by using GVL (with an initial concentration of \(C_{GVL,0}\) at 5 wt%) instead of LA as the substrate under otherwise the same benchmark conditions shown above, no appreciable decrease (< 5%) in the GVL concentration and no MTHF formation was observed at the microreactor outlet, implying that the further hydrogenation of GVL did not occur (at a noteworthy rate) under the reaction conditions tested.

As Figure 4.2 reveals, the measured LA conversion and GVL yield increase with increasing 1/WHSV (i.e., decreasing WHSV; translated into the prolonged residence time in the bed of a fixed length). Significant amounts of HPA (ca. 20 – 45% yield) were formed at a relatively low WHSV (i.e., up to 2.5 g\textsubscript{feed}/(g\textsubscript{cat}·h)) under the reaction conditions used. This shows that the formation of HPA from LA is faster than the subsequent formation of GVL from HPA (Scheme 4.1). Only when the majority of LA was converted, the HPA yield started to decline because of its further conversion towards GVL. The abundant formation of HPA is probably because the lactonization of HPA to GVL under such relatively low temperature level is the rate limiting step (Scheme 4.1).\textsuperscript{25} This was also observed under similar reaction conditions in batch experiments performed at 373 K using 1,4-dioxane as the solvent and Ru/ZrO\textsubscript{2} as the catalyst,\textsuperscript{25} where the HPA intermediate was formed abundantly due to its relatively slow transformation towards GVL under the not strongly acidic conditions.

The LA conversion and GVL yield were almost identical when performing the reaction in several microreactors with separate packings under the same operating conditions. This confirms that the packing methodology and experimental procedure were highly reproducible (cf. Supporting Information, Section S4.2).

4.3.2. Influence of operating variables on the reaction performance

Several operation conditions were varied in the packed bed microreactor to investigate their influence on the mass transfer characteristics and reaction rate during LA hydrogenation over Ru/C. An initial LA concentration of 5 wt% was used in the majority of experiments. A few additional experiments were conducted with 10 wt% LA, which resulted in a lower LA
conversion and GVL yield implying that the apparent LA consumption rate in the microreactor is below first order in LA (cf. Section S4.3 in the Supporting Information for a more detailed explanation). The influence of gas-liquid flow behavior (i.e., total flow rate and gas to liquid flow ratio), H₂ pressure, reaction temperature and catalyst particle size on the measured LA conversion and GVL yield at the outlet of the packed bed microreactor is presented in Figure 4.3. The selectivity towards GVL is on the order of ca. 40 – 60% for most experiments depicted (i.e., in the case of not all LA being consumed).

*Influence of flow rate.* The total mixture flow rate was altered \( Q_{\text{tot}} = 0.27 \text{–} 0.55 \text{ mL/min} \) at a fixed inlet gas to liquid volumetric flow ratio \( Q_{G,0} / Q_{L,0} = 4.5 \). The WHSV was kept equal by varying the total mixture flow rate proportionally with the bed length \( L_{\text{bed}} = 0.4 \text{–} 0.8 \) or alternatively the total catalyst weight in the bed \( w_c = 0.45 \text{ –} 0.9 \text{ g}；\text{particle size being ca. 0.45 mm} \). For a given WHSV, both the LA conversion and GVL yield increased with the increasing flow rate (Figure 4.3a). Since parameters that could affect the intrinsic kinetic rate (i.e., temperature, concentrations of reactants, WHSV and gas-liquid flow ratio) were not changed, the observed difference in the reaction performance strongly indicates mass transfer limitations at lower flow rates. In other words, operation at higher flow rates would positively affect the gas-liquid\(^{50,69,70}\) and liquid-solid\(^{71,72}\) mass transfer coefficients in packed bed microreactors, therewith improving the overall reaction rate (in terms of the increased conversion and yield) if the intrinsic kinetic rate is relatively fast.

*Influence of gas to liquid flow ratio.* The inlet gas to liquid volumetric flow ratio was varied \( Q_{G,0} / Q_{L,0} = 2.24 \text{–} 6.71 \) by keeping the total mixture flow rate equal \( Q_{\text{tot}} = 0.55 \text{ mL/min} \), the bed length being unchanged at 0.8 m (with a catalyst weight of 0.9 g). The LA conversion and GVL yield increased with the increasing gas to liquid flow ratio (Figure 4.3b). Although the gas-liquid and external liquid-solid mass transfer coefficients in packed bed (micro)reactors are (slightly) affected by \( Q_{G,0} / Q_{L,0} \) under otherwise the same reaction conditions,\(^{50,69–72}\) the main reason is probably that this ratio increase negatively affected the weight hourly space velocity of the liquid phase \( WHSV = 3 \text{ or } 9 \text{ g}_{\text{feed}}/(\text{g}_{\text{cat}} \cdot \text{h}) \) for \( Q_{G,0} / Q_{L,0} \) of 6.71 or 2.24, respectively). In other words, there was more catalyst available for the conversion of LA at an increased \( Q_{G,0} / Q_{L,0} \), resulting in a higher LA conversion and subsequently the GVL yield at the reactor outlet under such conditions.
Figure 4.3. Influence of reaction parameters on the measured LA conversion and GVL yield. (a) Influence of total mixture flow rate ($Q_{\text{tot}}$) under equal WHSV by varying the bed length ($L_{\text{bed}} = 0.4 – 0.8 \text{ m}$) and thus the catalyst weight ($w_c = 0.45 – 0.9 \text{ g}$), (b) influence of the inlet gas to liquid volumetric flow ratio ($\text{WHSV} = 3 – 9 \text{ gfeed}/(\text{gcat} \cdot \text{h})$), (c) influence of pressure, (d) influence of temperature and (e) influence of catalyst particle size ($L_{\text{bed}} = 0.75 \text{ mm for } 0.3 \text{ mm diameter particles}$). Conditions (unless stated otherwise): $C_{\text{LA,0}} = 5 \text{ wt\%}$, $Q_{G,0} / Q_{L,0} = 4.5$, $130 \text{ °C}$, $12 \text{ bar H}_2$, $L_{\text{bed}} = 0.8 \text{ m}$, $w_c = 0.9 \text{ g}$, $\text{WHSV} = 6.0 \text{ gfeed}/(\text{gcat} \cdot \text{h})$, Ru/C catalyst particle size ($d_p$) at 0.45 mm. The modeled LA conversions are shown for comparison, according to Eqs. 4.28 (assuming the reaction rate was fully determined by the gas-liquid and external liquid-solid mass transfer of H$_2$) and 4.20 (based on a zero order in LA and 0.5$^{th}$ order in H$_2$; with the effectiveness factor calculated with Eq. 4.16 and the overall reaction rate constant ($k$) assumed equal to the estimated one ($k_{\text{est}}$) from the data of Ftouni et al.$^{24}$).
Influence of \( H_2 \) pressure. The \( H_2 \) pressure was varied while keeping other reaction conditions unchanged (Figure 4.3c). A higher \( H_2 \) pressure resulted in a somewhat linear increase in the LA conversion and GVL yield (Figure 4.3c). The increased \( H_2 \) pressure enhanced the liquid phase \( H_2 \) concentration which in turn positively affected the transfer rate of \( H_2 \) to the catalyst, or more specifically, increased the hydrogenation concentration over the catalyst external surface and thus the kinetic reaction rate (when the reaction is above zero order in \( H_2 \)). As a result, the apparent reaction rate would increase with increased \( H_2 \) pressure.

Influence of reaction temperature. An increase in the reaction temperature, under otherwise unchanged conditions, resulted in a remarkable increase in the LA conversion and GVL yield (Figure 4.3d). The temperature increase not only enhanced the intrinsic kinetic rate significantly according to the Arrhenius equation, but also improved to some extent the mass transfer rate of \( H_2 \) given the increased diffusion coefficient and solubility of \( H_2 \) in the liquid phase (i.e., 1,4-dioxane).\(^{73}\) The latter mass transfer rate enhancement also contributed to the observed LA conversion or GVL yield increase as is better explained in the modeling section (cf. Section 4.3.5).

Influence of catalyst particle size. Reactions were performed in packed bed microreactors with two different catalyst particle sizes (diameter of ca. 0.45 and 0.3 mm) (Figure 4.3e). The same catalyst weight was used and the resulted length of the packed bed microreactor was almost equal (\( L_{\text{bed}} = 0.8 \) m and 0.75 m for \( d_p = 0.45 \) and 0.3 mm, respectively) given no order-of-magnitude difference in the particle diameter, so that the void fraction (\( \varepsilon \)) was nearly equal (Eq. 4.5). The LA conversion and GVL yield were significantly higher for a certain \( WHSV \) when using smaller catalyst particles (Figure 4.3e), where 100% LA conversion and 84% GVL yield were obtained at 130 °C, 12 bar \( H_2 \) and a \( WHSV \) of 3.0 \( g_{\text{feed}}/(g_{\text{cat}} \cdot h) \). It is commonly known that the use of smaller particles significantly enhances the specific catalytic area, therewith increasing the external liquid-solid \( H_2 \) transfer rate.\(^{22,27}\) Furthermore, the internal diffusion of both \( H_2 \) and LA within smaller particles tends to be improved.\(^{24}\) Thus, the increase in the overall reaction rate observed here with smaller particle sizes is an additional indication of the presence of liquid-solid mass transfer limitations.
4.3.3. Comparison with literature results

The measured microreactor performance is further compared with the literature results, where a weight hourly space velocity of the LA itself \( \text{WHSV}_{(\text{LA})} \) (in \( \text{g}_{\text{LA}}/(\text{g}_{\text{cat}} \cdot \text{h}) \)) was recalculated in order to account for the LA concentration difference in all works (Table 4.1). The value of \( \text{WHSV}_{(\text{LA})} \) was estimated for packed bed reactors or microreactors from the division of the inlet mass flow rate of LA by the packed catalyst weight, and for batch slurry reactors from the initial mass of LA divided by the product of the suspended catalyst weight and the batch reaction time.

Table 4.1. Comparison of Ru/C catalyzed hydrogenation of LA to GVL in different reactor configurations.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Ru/C (wt%)</th>
<th>( d_p ) (mm)</th>
<th>Solvent</th>
<th>( \text{WHSV}<em>{(\text{LA})} ) (g</em>{\text{LA}}/(g_{\text{cat}} \cdot \text{h}))</th>
<th>( T ) (°C)</th>
<th>( P_{\text{H}_2} ) (bar)</th>
<th>( X_{\text{LA}} ) (%)</th>
<th>( Y_{\text{GVL}} ) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR</td>
<td>0.5</td>
<td>0.3</td>
<td>dioxane</td>
<td>0.15</td>
<td>130</td>
<td>12</td>
<td>100</td>
<td>84</td>
<td>This work</td>
</tr>
<tr>
<td>Batch</td>
<td>5</td>
<td>-</td>
<td>dioxane</td>
<td>2.1</td>
<td>100</td>
<td>30</td>
<td>-</td>
<td>97</td>
<td>24</td>
</tr>
<tr>
<td>Batch</td>
<td>5</td>
<td>-</td>
<td>dioxane</td>
<td>16.7</td>
<td>150</td>
<td>30</td>
<td>-</td>
<td>99</td>
<td>24</td>
</tr>
<tr>
<td>Batch</td>
<td>3</td>
<td>0.06</td>
<td>water</td>
<td>50</td>
<td>130</td>
<td>45</td>
<td>97</td>
<td>88</td>
<td>27</td>
</tr>
<tr>
<td>PBR</td>
<td>0.5</td>
<td>1.88</td>
<td>water</td>
<td>4.15</td>
<td>130</td>
<td>45</td>
<td>99</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>

\(^{a}\) Microreactor \((d_c = 1.6 \text{ mm})\). \(^{b}\) Packed bed reactor \((6 \text{ mm inner diameter})\). \(^{c}\) Reaction temperature. \(^{d}\) \( \text{H}_2 \) pressure.

In the current microreactor \((d_c = 1.6 \text{ mm} \text{ and } L_{\text{bed}} = 0.8 \text{ m})\) with 1,4-dioxane as the solvent, a best GVL yield of 84% was obtained at 100% LA conversion over the 0.3 mm diameter particles of Ru/C catalyst under a weight hourly space velocity of the liquid phase \( \text{WHSV} \) of 3.0 \( \text{g}_{\text{feed}}/(\text{g}_{\text{cat}} \cdot \text{h}) \) (corresponding to \( \text{WHSV}_{(\text{LA})} = 0.15 \text{ g}_{\text{LA}}/(\text{g}_{\text{cat}} \cdot \text{h}) \)), 130 °C and 12 bar \( \text{H}_2 \). As Table 4.1 reveals, under similar reaction conditions (i.e., 100 or 150 °C, 30 bar \( \text{H}_2 \) and 1,4-dioxane as the solvent), nearly 100% GVL yield was obtained over 5 wt% Ru/C catalyst at a \( \text{WHSV}_{(\text{LA})} \) of 2.1 or 16.7 \( \text{g}_{\text{LA}}/(\text{g}_{\text{cat}} \cdot \text{h}) \) in a batch autoclave.\(^{24}\) Performing the reaction with water as the solvent and otherwise similar reaction conditions in a batch setup \((130 \text{ °C and } 45 \text{ bar } \text{H}_2)\) resulted in 97% LA conversion and 88% GVL yield over 3 wt% Ru/C catalyst at a \( \text{WHSV}_{(\text{LA})} \) of 50 \( \text{g}_{\text{LA}}/(\text{g}_{\text{cat}} \cdot \text{h}) \),\(^{27}\) whereas a \( \text{WHSV}_{(\text{LA})} \) of 4.15 \( \text{g}_{\text{LA}}/(\text{g}_{\text{cat}} \cdot \text{h}) \) was required to achieve similar results in the milli-reactor packed with 0.5 wt% Ru/C at the same temperature and pressure.\(^{22}\) The lesser performance in the latter case, in terms of a lower \( \text{WHSV}_{(\text{LA})} \) value required for a similar LA conversion or GVL yield level, was probably due to the lower Ru loading and the much larger catalyst particles used \((d_p = 1.88 \text{ mm vs. } 60 \mu\text{m} \text{ in the batch autoclave})\), which has caused liquid-solid mass transfer limitations that resulted in a slower reaction rate. In
other words, batch reactors allow the use of finer catalyst particles than in packed bed reactors (i.e., due to otherwise the excessive pressure drop generated in the latter). As such, external and internal liquid-solid mass transfer limitations can be significantly improved or even overcome in batch reactors by the increased specific catalyst area and shorter diffusion distance within catalyst pores, therewith accelerating the reaction rate towards obtaining the intrinsic one. These would also largely explain the observed less satisfactory performance in the current packed bed microreactor compared with its batch counterparts. Despite the larger catalyst particles used in the milli-packed bed reactor,\textsuperscript{22} a better performance was found than the microreactor studied here. This may be attributed to the use of higher H\textsubscript{2} pressure and water as the solvent in the former case. The better reaction performance of water than 1,4-dioxane as the solvent was also seen in batch reactor studies,\textsuperscript{24,27} likely due to the solvent effect on the kinetic parameters. Besides that, H\textsubscript{2} has a higher solubility and diffusivity in water than in 1,4-dioxane,\textsuperscript{73–75} which positively affected both the H\textsubscript{2} mass transfer rate towards the catalyst internal surface and the kinetics (i.e., in the case the rate is above zero order in H\textsubscript{2}).

4.3.4. Development of the microreactor model

To explain the observed reaction performance in the packed bed microreactor, the gas-liquid-solid contact behavior and the associated mass transfer characteristics, the intrinsic kinetics and their roles in determining the overall reaction rate need to be well understood. This eventually would lead to the establishment of a microreactor model that describes the LA hydrogenation results (especially in terms of the LA conversion) under steady state conditions and indicate the direction of improvement in the microreactor design and operation.

Gas-liquid flow pattern in the packed bed microreactor. From the respective gas and liquid superficial velocities (i.e., $j_G$ and $j_L$) of experiments in this work, the gas-liquid flow pattern in the packed bed microreactor was predicted to be liquid-dominated slug flow based on the flow map proposed by Al-Rifai \textit{et al.}\textsuperscript{58} (Figure 4.4). This flow map was derived based on their experiments with a square microreactor (width $\times$ height $\times$ length = 300 $\mu$m $\times$ 600 $\mu$m $\times$ 190 mm), packed with 1 wt% Au-Pd/TiO\textsubscript{2} catalyst ($d_p = 65$ $\mu$m) operated under an upstream slug or (wavy-)annular flow profile at 120 °C and 1 bar.\textsuperscript{58} Thus, such flow map is expected applicable to a large extent in the current work, given similar inlet mixing conditions (i.e.,...
an upstream gas-liquid slug flow profile) and value range of the microchannel diameter to particle ratio.

![Figure 4.4. Influence of the superficial gas and liquid velocities on the gas-liquid flow pattern in the packed bed microreactor. Lines depict the transition boundary between each flow pattern according to the experimental work of Al-Rifai et al.](image)

In most experiments the upstream slug flow profile had relatively long gas bubbles and liquid slugs (Figure 4.1). To test if this negatively affected the reaction performance, the upstream gas-liquid slug flow profile was further altered by placing a PFA capillary (inner diameter: 1.6 mm) packed with an inert bed of SiC particles (particle diameter: 0.48 mm; bed length: 10 cm) right after the stainless steel T-junction, by which significantly shorter bubbles/slugs were generated in the connected short PTFE capillary and subsequently fed to the packed bed microreactor. The change of the upstream slug flow profile did not have a considerable effect on the LA conversion and GVL yield for given reaction conditions (cf. Section S4.4 in the Supporting Information for more details). Thus, it is concluded that even in the case of the relatively long bubbles/slugs in the upstream flow, the gas-liquid-solid contact pattern and the associated mass transfer in the packed bed microreactor are not much negatively affected. From this it is safely assumed that all experiments in this work were performed in the liquid-dominated slug flow regime, indicating a high liquid-solid interaction. It thus seems that channeling is not appreciable in the packed bed microreactor, despite the moderate particle to channel ratio therein.

*Mass transfer and reaction analyses in the packed bed microreactor.* In the heterogeneously catalyzed hydrogenation of LA, H₂ is first transferred
from the gas to the liquid phase, and then both LA and the dissolved H$_2$ travel towards the solid catalyst active sites. The microreactor model was therefore based on the mass transfer and reaction steps of H$_2$ and LA, consisting of (1) transfer of H$_2$ from the gas bulk to the gas-liquid interface and the subsequent H$_2$ absorption at the interface, (2) H$_2$ transfer from the liquid interface to the liquid bulk, (3) H$_2$/LA transfer from the liquid bulk to the external catalyst surface (3a and b) and finally (4) the internal diffusion of H$_2$/LA into the catalyst pores, with the reaction occurring on the catalytic surface of the pores (Figure 4.5). The transfer rate for each individual step is estimated based on the literature (empirical) mass transfer or kinetic correlations. The physical fluid properties relevant to such estimation are given in Section S4.5 in the Supporting Information.

**Figure 4.5.** Schematic overview of mass transfer and reaction steps for the heterogeneously catalyzed LA hydrogenation. (1) Transfer of H$_2$ from the gas bulk ($C_{H_2,G}$) to the gas-side interface ($C_{H_2,G}$) and its subsequent absorption at the interface. (2) H$_2$ transfer from the liquid-side interface ($C_{H_2,L}$) to the liquid bulk ($C_{H_2,L}$). (3a) H$_2$ diffusion from the liquid bulk to the catalyst external surface ($C_{H_2,S}$). (3b) LA diffusion from the liquid bulk ($C_{LA}$) to the catalyst external surface ($C_{LA,S}$). (4) Internal diffusion of H$_2$/LA into the catalyst particle surface, adsorption and reaction on the active site. The term in the above brackets designates the concentration of H$_2$ or LA at the respective location.

The simplified mass transfer and reaction steps shown in Figure 4.5 were applied to the microreactor cross-section at one axial location. This, combined with the estimated transfer rate of each step and the overall mass
balance in the microreactor, finally resulted in a one-dimensional model (vide infra).

Gas-liquid mass transfer. Since pure H$_2$ gas was used, there were no gas phase mass transfer limitations and the H$_2$ concentration in the gas bulk ($C_{H_2,g}$) is equal to the gaseous H$_2$ concentration at the interface ($C_{H_2,i,g}$). The liquid phase H$_2$ concentration at the interface ($C_{H_2,i,l}$) is thus derived as

$$C_{H_2,i,l} = \frac{C_{H_2,g}}{H}$$

(4.6)

where $H$ is the Henry constant, determined from the solubility of H$_2$ in the 1,4-dioxane solvent (cf. Supporting Information, Section S4.5.1).$^{73}$

The transport rate of H$_2$ from the liquid interface to the liquid bulk ($r_{H_2,g-l}$) is described by

$$r_{H_2,g-l} = V_{bed}k_ia_i(C_{H_2,i,l} - C_{H_2,b,l})$$

(4.7)

where $k_i$ is the liquid phase mass transfer coefficient, $a_i$ is the specific gas-liquid interfacial area (based on the total reactor/bed volume $V_{bed}$) and $C_{H_2,b,l}$ denotes the H$_2$ concentration in the liquid bulk.

The volumetric liquid phase mass transfer coefficient ($k_ia_i$) for packed bed microreactors is estimated by the empirical correlation proposed by Zhang et al.$^{69}$

$$k_ia_i = \frac{3.41 \times 10^{-5} \chi_G^{0.08}Re_L^{3.1}We_L^{-1.33}D_{H_2}}{d_p^{3}}$$

(4.8)

where $\chi_G$ is the Lockhart-Martinelli ratio, $Re_L$ and $We_L$ are the Reynolds and Weber numbers of the liquid phase, respectively, and $D_{H_2}$ is the mass diffusivity of H$_2$ in 1,4-dioxane (estimated by the Wilke-Chang correlation,$^{75}$ see Section S4.5.2 in the Supporting Information for calculation details). Eq. 4.8 was developed based on experiments with chemical absorption of CO$_2$ into the aqueous methyl diethanolamine solution under liquid-dominated slug flow through microreactors (inner diameter: 3.05 – 4.57 mm) packed with inert glass beads (particle size: 75 – 355 μm; bed length: 10 cm),$^{69}$ and is considered roughly applicable to describe $k_ia_i$ in the current microreactor system given more or less similar process parameters (e.g., gas-liquid flow regime, microreactor diameter and particle size range).
External liquid-solid mass transfer. The rates of H₂ and LA transfer from the liquid bulk to the external catalyst surface ($r_{H₂,L-S}$ and $r_{LA,L-S}$, respectively) are described by

$$r_{H₂,L-S} = \alpha \omega \cdot k_s \cdot a_c \cdot (C_{H₂,L} - C_{H₂,S})$$  \hspace{1cm} (4.9)$$

$$r_{LA,L-S} = \alpha \omega \cdot k_s \cdot a_c \cdot (C_{LA} - C_{LA,S})$$  \hspace{1cm} (4.10)$$

where $k_s$ is the liquid-solid mass transfer coefficient and $a_c$ the specific external surface area of the solid catalyst (based on the catalyst weight). $C_{H₂,S}$ and $C_{LA,S}$ are the H₂ and LA concentrations on the catalyst external surface, respectively. $C_{LA}$ is the bulk liquid concentration of LA. $\alpha$ is the wetted fraction of the catalyst external surface. In the current work, $\alpha$ is taken as 1 given the presence of a good catalyst wetting in the involved liquid-dominated slug flow regime.\(^{58}\)

For spherical catalyst particles $a_c$ is derived from

$$a_c = \frac{A_c}{V_c \rho_S} = \frac{\pi d_p^2}{\frac{6}{\pi} d_p^3 \rho_S} = \frac{6}{d_p \rho_S}$$  \hspace{1cm} (4.11)$$

where $A_c$ and $V_c$ are the surface area and volume of the catalyst particles, respectively.

$k_s$ can be obtained from the literature correlations for the Sherwood number ($Sh$) defined for packed bed (micro)reactors as

$$Sh = \frac{k_s d_p}{D_L}$$  \hspace{1cm} (4.12)$$

Correlations for estimating $Sh$ as a function of the conventional large packed bed reactor geometry and flow conditions are extensively reported, however, these are limited for packed bed microreactor configurations where the inner channel to particle diameter ratio ($d_c / d_p$) is generally low (e.g., being $3.55 - 5.33$ in this work).\(^{71,72}\) According to Tidona et al.\(^{71}\), $Sh$ for (capillary) reactors with low values of $d_c / d_p$ ($< 6.6$) is best described by the correlation of Wakao and Funakasri\(^{76}\):

$$Sh = 2 + 1.1 \cdot Re_L^{0.6} \cdot Sc_L^{1/3}$$  \hspace{1cm} (4.13)$$

where $Sc_L$ is the liquid phase Schmidt number.

According to Eq. 4.13, the liquid-solid mass transfer coefficient of H₂ ($k_s = 2.05 \times 10^{-5} \text{ m/s}$) is significantly lower than that of LA in 1,4-dioxane ($k_s = 7.13 \times 10^{-5} \text{ m/s}$) under the benchmark conditions in this work, mainly due to their different mass diffusivities in 1,4-dioxane (cf. Table S4.1 and
Section S4.5.2 in the Supporting Information for calculation details). Above that, the initial LA concentration \( (C_{LA,0} = 0.44 \text{ mol/L}) \) in the liquid phase is far higher than that of \( \text{H}_2 \) (i.e., being \( 5.38 \times 10^{-3} \text{ mol/L} \) under the benchmark conditions; Eq. 4.6). As such, the transfer rate of LA from the liquid bulk to the external catalyst surface is considered not limiting compared with that of \( \text{H}_2 \) (Eqs. 4.9 and 4.10).

**Internal liquid-solid mass transfer and kinetics.** The \( \text{H}_2 \) internal diffusion within the catalyst particle pores is combined with surface reaction by using the concept of the effectiveness factor of the catalyst \( (\eta) \). The obtained actual rate of reaction \( (r_{H_2,R}) \) is described by

\[
r_{H_2,R} = w_c \eta r_{H_2,S}^{'}
\]

where \( r_{H_2,S}^{'} \) is the surface kinetic reaction rate per unit mass of catalyst (in \( \text{mol/}(g_{\text{cat}} \cdot \text{s}) \)).

The kinetics of the Ru/C catalyzed hydrogenation of LA has been described by a Langmuir-Hinshelwood mechanism\(^{26,27} \), according to which the conversion of LA to HPA takes place on the catalyst surface by two subsequent half-hydrogenations (cf. the reaction equations S4.9-S4.12 in the Supporting Information). Computational studies have suggested that the successive half-hydrogenation of the previously half-hydrogenated LA intermediate on the catalyst surface \( (\text{LA-H}^\circ) \) is the rate limiting step.\(^{77} \)

When considering that the catalyst’s active sites are far from being fully covered by \( \text{H}_2 \) with almost zero coverage of LA,\(^{26} \) the kinetic rate can be simply described as 0.5\(^{th} \) order in \( \text{H}_2 \) and zero order in LA (cf. Supporting Information, Section S4.6 for a more detailed explanation).\(^{26,27} \) Under such assumptions, Eq. 4.14 is rewritten as

\[
r_{H_2,R} = w_c \eta k C_{H_2,S}^{1/2}
\]

This 0.5\(^{th} \) order in \( \text{H}_2 \) and zero order in the liquid substrate (LA in this case) are often observed for gas-liquid-solid (Ru/C-catalyzed) hydrogenation reactions (e.g., glucose to sorbitol,\(^{32} \) cyclohexene to cyclohexane\(^{78} \)). So far, the detailed information of the overall reaction rate constant \( (k) \) related to LA or \( \text{H}_2 \) consumption is still not available for the current reaction system. Thus, it was roughly estimated from the reported batch studies by Ftouni \textit{et al.}\(^{24} \) on the 5 wt% Ru/C catalyzed hydrogenation of LA in 1,4-dioxane. Herein, their measured GVL yields at different reaction times and temperatures were used to obtain an estimated \( k \) value (referred to as \( k_{\text{est}} \)), based on the assumptions of a 100% selectivity to GVL as well
as a 0.5th order in H₂ and a zero order in LA.⁶⁶,⁶⁷ (cf. Supporting Information, Section S4.7). This approach underestimates the actual k values since the LA conversion (not reported in their work) should be higher than the GVL yield to a certain extent because of the presence of HPA as the intermediate (e.g., at short reaction times). However, k_{est} is still expected to be around the same order of magnitude as the actual k value, which is sufficient to reveal the dominant role of mass transfer in the present microreactor experiments (vide infra). The k_{est} values at different reaction temperatures (323 – 423 K) were then used to derive the activation energy (E_a = 58 kJ/mol) and the pre-exponential factor (A = 1770 (mol·L)^0.5/(g_{cat}·h)), so that k_{est} could be estimated as a function of temperature with the Arrhenius equation. Albeit the rather approximate nature of this estimation, the obtained E_a value is close to that obtained in the cases of the hydrogenation of LA to HPA in water (E_a = 48 kJ/mol)⁶⁶ and hydrogenation of alkyl (i.e., methyl, ethyl and butyl) levulinates to their corresponding alkyl-3-hydroxyvalerates (i.e., the ethers of HPA; Scheme 4.1) in methanol (E_a = 41, 45 or 58 kJ/mol, respectively), both over 5 wt% Ru/C.³¹

Effectiveness factors were estimated with the Thiele modulus (ϕ), that represents the ratio between the surface reaction rate (according to the kinetics) and the diffusion rate through the catalyst pores (cf. Section S4.8 in the Supporting Information for calculation details). For low values of the Thiele modulus (e.g., ϕ < 0.2), η approaches 1 and the internal diffusion is not rate-limiting. For larger values (e.g., ϕ > 15), η is much smaller than 1 with the surface reaction being not rate limiting and its value for an n-th-order reaction over spherical catalyst particles is roughly estimated as

\[
\eta = \left(\frac{2}{n+1}\right)^{1/2} \frac{3}{\phi}
\]  

(4.16)

When assuming no concentration gradient of the other reacting component within the catalyst pores, the Thiele moduli were estimated as 31.0 for H₂ and 1.48 for LA under the benchmark conditions, corresponding to effectiveness factors of η_{H₂} = 0.11 (i.e., based on Eq. 4.16 with n = 0.5) and η_{LA} can be assumed as 1, respectively (cf. Section S4.8 in the Supporting Information for elaboration).⁷⁹

**Overall reaction rate and LA conversion.** At steady state conditions, 
\[ r_{H₂,G-L} = r_{H₂,L,S} = r_{H₂,R}. \]  
Thus, the overall rate of H₂ consumption (\( r_{H₂} \)) is expressed by combining Eqs. 4.6, 4.7, 4.9 and 4.15 as
\[ r_{H_2} = \frac{C_{H_2,G} / H}{V_{\text{bed}} k_L a_i + \frac{1}{\alpha w_c k_S a_c} + \frac{r_{H_2}}{(w_c \eta k)^2}} \]  

(4.17)

It is finally obtained that

\[ r_{H_2} = \frac{-\left( \frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{\alpha w_c k_S a_c} \right) + \sqrt{\left( \frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{\alpha w_c k_S a_c} \right)^2 + \frac{4C_{H_2,G}}{H(w_c \eta k)^2}}}{2\left(\frac{r_{H_2}}{(w_c \eta k)^2}\right)} \]  

(4.18)

Given no occurrence of other hydrogenation reactions (e.g., the formation of \( \alpha \)-AL and MTHF), the rate of LA consumption \( r_{LA} \) is assumed equal to \( r_{H_2} \). Since the reaction is zero order in LA, \( r_{H_2,i} \) is not affected by the change in \( C_{LA} \) along the microreactor (Eq. 4.15). Also, \( C_{H_2,G} \) is constant as the gas phase consisted of pure \( H_2 \) and the pressure drop over the bed is not significant compared with the pressure applied (i.e., the partial \( H_2 \) pressure is approximately equal at the bed in- and outlet).\(^{59}\) Thus, \( r_{LA} \) is constant throughout the microreactor. The LA concentration at the outlet of the packed bed microreactor \( (C_{LA,1}) \) is then derived from the overall mass balance as

\[ C_{LA,1} = C_{LA,0} - \frac{r_{LA}}{Q_{L,0}} = C_{LA,0} - \frac{r_{H_2}}{Q_{L,0}} \]  

(4.19)

under the condition that \( C_{LA,1} = 0 \) when \( C_{LA,0} \leq r_{LA} / Q_L \).

The modeled LA conversion is obtained by combining Eqs. 4.1, 4.18 and 4.19 as

\[ \chi_{LA} = \frac{r_{LA}}{Q_{L,0} C_{LA,0}} = \frac{-\left( \frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{\alpha w_c k_S a_c} \right) + \sqrt{\left( \frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{\alpha w_c k_S a_c} \right)^2 + \frac{4C_{H_2,G}}{H(w_c \eta k)^2}}}{2Q_{L,0} C_{LA,0} \left(\frac{r_{H_2}}{(w_c \eta k)^2}\right) + \left(\frac{r_{H_2}}{(w_c \eta k)^2}\right)} \]  

(4.20)

**GVL formation rate and yield.** Conversion of HPA to GVL is considered via an equilibrium intramolecular esterification reaction (Scheme 4.1), catalyzed by a Brønsted acid (e.g., from the dissociation of LA and HPA).\(^{26,27}\) Thus, the reaction is expected to occur in the liquid bulk rather than at the catalyst surface. The GVL formation rate \( r_{GVL} \) is considered first order in both HPA and the acid (i.e., based on kinetic studies in water).\(^{26,27}\) That is,
\[ r_{\text{GVL}} = k_2 C_{\text{HPA}} C_{H^+} - k_{-2} C_{\text{GVL}} C_{H^+} \]  
\( (4.21) \)

where \( k_2 \) and \( k_{-2} \) are the reaction rate constants for the forward and backward conversions of HPA to GVL, respectively. \( C_{\text{HPA}} \) and \( C_{H^+} \) are the respective HPA and acid concentrations in the liquid bulk. The value of \( C_{H^+} \) can be estimated from the dissociation constants of LA and HPA in 1,4-dioxane (i.e., in the case of no other acid presence).\(^{27}\)

In the current microreactor setup (Figure 4.1), this HPA to GVL conversion presumably did not solely occur in the liquid contained in the catalyst bed, but also in the liquid segment present in the subsequent heated tubing sections between the microreactor outlet and the gas-liquid separator. For an accurate estimation of the GVL yield, the total liquid volume heated at the reaction temperature \( (V_{L,\text{tot}}) \) should thus be taken into consideration. The relation of the GVL formation and thus its yield as a function of \( V_{L,\text{tot}} \) is then described as

\[ Q_{L,0} \frac{dC_{\text{GVL}}}{dV_{L,\text{tot}}} = Q_{L,0} C_{\text{LA},0} \frac{dY_{\text{GVL}}}{dV_{L,\text{tot}}} = r_{\text{GVL}} \]  
\( (4.22) \)

Eqs. 4.21 and 4.22 do not consider the influence of mass transfer effects (e.g., HPA diffusion from the catalyst surface to the liquid bulk). Moreover, the kinetic parameters of the HPA lactonization to GVL in the 1,4-dioxane solvent are not available yet. Thus, the GVL yield is not dealt with in the current model.

4.3.5. Model discussion

The experimental LA conversion under the operating conditions was compared with the model prediction (Eq. 4.20; Figure 4.3). The effectiveness factor was determined by Eq. 4.16 (for the case of zero order in LA and 0.5\(^{\text{th}}\) order in \( H_2 \)) and the kinetic constant was assumed equal to that estimated in Section S4.7 of the Supporting Information \( (k = k_{\text{est}}) \). For each experimental condition the measured LA conversion was largely underestimated by Eq. 4.20 (Figure 4.3). This is probably because \( k_{\text{est}} \) underestimates the actual \( k \) value, as already mentioned before. Despite this, the general trend could be followed by the model. An analysis over the different mass transfer and reaction steps was performed to unravel the reason for this underestimation. To investigate the individual contribution of reaction parameters to the different steps of \( H_2 \) transfer involved in the process (cf. Figure 4.5), the respective resistances (in \( \text{s/m}^3 \)) for the gas-
liquid mass transfer of $H_2 (\Omega_{H_2,G-L})$, the external liquid-solid mass transfer of $H_2 (\Omega_{H_2,L-S})$, and the combined resistance for internal diffusion of $H_2$ and surface reaction ($\Omega_{H_2,R}$) were estimated according to the following relation:\textsuperscript{80}

$$r_{H_2} = \frac{C_{H_2,G} / H}{\Omega_{H_2,G-L} + \Omega_{H_2,L-S} + \Omega_{H_2,R}}$$  

(4.23)

These resistances are defined as

$$\Omega_{H_2,G-L} = \frac{1}{V_{bed} k_L a_l}$$  

(4.24)

$$\Omega_{H_2,L-S} = \frac{1}{\alpha w_c k_g a_c}$$  

(4.25)

$$\Omega_{H_2,R} = \frac{r_{H_2}}{(w_c \eta k)^2}$$  

(4.26)

A comparison of these resistances can give valuable insights in finding the rate limiting step under the tested reaction conditions and beyond, as shown in Figure 4.6. Since $k_{est}$ likely underestimates the actual kinetic constant, two $k$ values were used in the comparison of $\Omega_{H_2,R}$. That is, the estimated kinetic constant ($k = k_{est}$) and a tripled value ($k = 3k_{est}$).
Figure 4.6. Influence of reaction parameters on the different resistances (Ω; Eqs. 4.24-4.26). Conditions (unless stated otherwise): $C_{LA,0} = 5$ wt%, $Q_{tot} = 0.55$ mL/min, $Q_{G,0} / Q_{L,0} = 4.5$, 130 °C, 12 bar $H_2$, $L_{bed} = 0.8$ m, $w_c = 0.9$ g, WHSV = 6.0 g$_{feed}$(g$_{cat}$·h), Ru/C catalyst particle size ($d_p$) at 0.45 mm. (a) Influence of the total volumetric flow rate ($Q_{tot} = 0.007 – 1.0$ mL/min) with equal WHSV and $Q_{G,0} / Q_{L,0}$ and varying bed length ($L_{bed} = 0.01 – 2$ m) and catalyst weight ($w_c = 0.011 – 2.25$ g), (b) Influence of gas to liquid volumetric flow ratio ($Q_{G,0} / Q_{L,0} = 0.4 – 10$) corresponding to a WHSV between 2.71 – 21 g$_{feed}$(g$_{cat}$·h)), (c) influence of pressure (5 – 25 bar), (d) influence of temperature (300 – 450 K) and (e) influence of catalyst particle size ($d_p = 1 \mu m – 1$ mm). In the calculation of $\Omega_{R_2,L}$ (Eq. 4.26), the estimated $k$ value ($k = k_{est}$) or a tripled value ($k = 3k_{est}$) was used.
According to the modeled resistances, the reaction rate was predominantly limited by the liquid-solid mass transfer of \( \text{H}_2 \) towards the external catalyst surface and/or the internal diffusion of \( \text{H}_2 \) combined with kinetics (i.e., when \( k = k_{\text{est}} \)), given the dominant contributions of \( \Omega_{\text{H}_2, L-S} \) and/or \( \Omega_{\text{H}_2, R} \) (Figure 4.6). This does not necessarily represent the real-case scenario since \( \Omega_{\text{H}_2, R} \) is very likely overestimated, primarily because of an underestimation of the overall reaction rate constant \( k \) (cf. Supporting Information, Section S4.7). Since this estimation is just an order of magnitude analysis and the actual \( k \) value should be higher, the influence of \( \Omega_{\text{H}_2, R} \) was also evaluated with a higher and more realistic \( k \) value for a better illustration (e.g., \( k = 3k_{\text{est}} \) as shown in this figure). In the latter case, \( \Omega_{\text{H}_2, R} \) becomes much less significant under our experimental conditions. For such \( k \) value the external liquid-solid transfer of \( \text{H}_2 \) is dominant under nearly all tested reaction conditions as indicated by the much higher value of \( \Omega_{\text{H}_2, L-S} \) over the other resistance values. Hence, it is possible that the overall reaction rate is mainly limited by the external liquid-solid mass transfer of \( \text{H}_2 \) over most reaction conditions. This high \( \Omega_{\text{H}_2, L-S} \) is mainly because of the relatively large catalyst particles (0.3 or 0.45 mm) used, resulting in a relatively low specific catalyst area (Eq. 4.11) and therewith reducing the external liquid-solid mass transfer rate of \( \text{H}_2 \) (Eq. 4.9).

To confirm that the actual kinetic parameter (\( k \)) is underestimated by \( k_{\text{est}} \) such that the actual \( \Omega_{\text{H}_2, R} \) should be unimportant in the resistance under our experimental conditions, the above model is further simplified by considering very fast kinetics. Although faster kinetics results in a (slightly) lower effectiveness factor by the increased Thiele modulus (cf. Section S4.6 in the Supporting Information), the combined rate of internal diffusion and surface reaction will increase so that \( \Omega_{\text{H}_2, R} \) becomes significantly smaller (Eq. 4.26). Then, the overall reaction rate is fully determined by the combined gas-liquid and external liquid-solid mass transfer. Accordingly, the \( \text{H}_2 \) consumption rate is rewritten as

\[
r_{\text{H}_2} = \frac{C_{\text{H}_2, G} / H}{1 + \frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{\alpha \omega_i k_S a_c}}
\]  

(4.27)

From Eqs. 4.1, 4.19 and 4.27, the modeled LA conversion is simplified as
The experimental LA conversion is generally well described by Eq. 4.28 with an acceptable accuracy under all reaction conditions tested (Figure 4.3). This simplified model also corresponds roughly with experiments conducted at a higher initial LA concentration of 10 wt% (cf. Supporting Information, Section S4.3 for more details). Thus, the actual $k$ value should be indeed higher than $k_{est}$ (cf. Supporting Information, Section S4.7) and the reaction under the present experiments is predominantly limited by the combined gas-liquid and liquid-solid mass transfer of $H_2$ from the gas-liquid interface towards the external catalyst surface (and especially by latter under the majority of conditions). For a more accurate kinetic description towards obtaining the fully informative model, dedicated kinetic studies on the hydrogenation of LA to HPA and GVL in 1,4-dioxane are required.

By comparing the resistance trends, the contribution of individual reaction parameter to each $H_2$ transfer or reaction step and further on to the overall reaction rate could be made clear over a wide range of conditions (Figure 4.6). Here, the influence of the combined internal diffusion/kinetic resistance ($\Omega_{H_2,r}$) is roughly evaluated with the illustrative case of $k = 3k_{est}$ (since the exact $k$ value is unknown).

Each resistance decreases upon increasing the mixture flow rate (with a fixed gas-liquid flow ratio and $WHSV$ being kept equal by varying the bed length; Figure 4.6a). This is because the bed length is proportional to the catalyst weight (or bed volume), and an increase of this negatively contributes to all resistances (Eqs. 4.24-4.26). This also explains the observed LA conversion increase with the flow rate increase (Figure 4.3a). It should be noted that at lower flow rates (corresponding to a shorter bed), the measured LA conversion was underestimated by the model (Figure 4.3a). Under such low flow rates, it might take (much) longer time for the upstream slug flow to develop into liquid-dominated slug flow in the catalyst bed. This would lead to a lower mass transfer rate in the bed (at least near the inlet section) and thus the overall reaction performance turned out to be somewhat significantly lower than predicted by the model.

The measured LA conversion gradually increased with the increasing gas to liquid flow ratio for a given mixture flow rate as approximately predicted by the simplified model (Figure 4.3b). However, the external liquid-solid
mass transfer resistance of \( \text{H}_2 \) (i.e., the most dominant one) is actually (slightly) increased with the gas to liquid flow ratio (Figure 4.6b). The increase in the LA conversion at higher flow ratios is thus mainly attributed to the reduced liquid flow rate \( (Q_{L,0}; \text{cf. Eq. 4.28}) \). The gas-liquid mass transfer resistance is also slightly increased by the higher gas to liquid flow ratio (Figure 4.6b), whereas the combined internal diffusion/kinetic resistance seems not (significantly) affected by this.

The \( \text{H}_2 \) pressure does not significantly affect the mass transfer coefficients \((k_{La_i} \text{ and } k_{Sa_c}; \text{Eqs. 4.8 and 4.13})\), but does affect the \( \text{H}_2 \) concentration in the liquid phase. The \( \text{H}_2 \) pressure is linearly proportional to \( C_{\text{H}_2,L_L} \) (Eq. 4.6) and thus significantly increases \( X_{LA} \) under otherwise unchanged reaction conditions (Eq. 4.28; Figure 4.3c). The pressure does not affect the gas-liquid and external liquid-solid mass transfer resistances (Eqs. 4.7 and 4.9).

An increase in pressure does positively affect the internal diffusion/kinetic resistance, mainly due to the half-order dependency of \( \text{H}_2 \) on the kinetic rate (Figure 4.6c).

The reaction temperature, under otherwise unchanged conditions, resulted in a significantly higher LA conversion (Figure 4.3d). This is mainly due to its positive effect on the gas-liquid and (external) liquid-solid mass transfer rates of \( \text{H}_2 \) (e.g., by decreasing the value of Henry coefficient (Eqs. 4.6 and 4.7) and increasing the mass diffusivity (Eqs. 4.8 and 4.12)). For the temperature tested in this work (i.e., between 70 – 130 °C), the overall reaction rate is preliminary determined by the external liquid-solid mass transfer rate. However, at lower temperatures the intrinsic kinetic rate would become sufficiently small, and the liquid phase mass transfer coefficient \((k_{La_i}; \text{Eq. 4.8})\) is lowered more than the external liquid-solid mass transfer coefficient \((k_{Sa_c}; \text{Eq. 4.12})\). Thus, a temperature reduction results in a more appreciable increase in \( \Omega_{H_2,G-L} \text{ and } \Omega_{H_2,R} \) as compared to \( \Omega_{H_2,L-S} \), making the former two resistances to play a more dominant role at relatively low temperatures (Figure 4.6d).

The change in the relative importance of each resistance is further seen from the modeled influence of catalyst particle size as depicted in Figure 4.6e. Both the gas-liquid and external liquid-solid mass transfer resistances decrease with a reduction of the particle size, due to the improved mass transfer coefficients (Eqs. 4.8 and 4.12) and the specific catalyst surface area. This corresponds with the measured LA conversion increase in experiments using smaller catalyst particles \((d_p = 0.3 \text{ mm}; \text{Figure 4.3e})\).
Under the involved conditions, the model suggests that $\Omega_{H_2,L-S}$ is lower than $\Omega_{H_2,R}$ when $d_p$ is below ca. 0.03 mm (i.e., for $k = 3k_{\text{est}}$; Figure 4.6e). Furthermore, for $d_p$ below ca. 0.14 mm $\Omega_{H_2,G-L}$ exceeds $\Omega_{H_2,L-S}$ and as such should also be significantly lowered (e.g., by increasing the temperature; cf. Figure 4.6d). The use of smaller catalyst particles in the current experiments may have resulted in a slightly higher pressure drop over the packed bed microreactor, so that for a given outlet pressure the average pressure over the reactor may have been even higher. This would increase the $H_2$ concentration in the liquid phase, which in turn attributes to a further increase in the (gas-liquid and liquid-solid) mass transfer rate of $H_2$ (Eqs. 4.7 and 4.9). However, the estimated pressure drop (i.e., calculated by the empirical correlation proposed by Zhang et al.) was too insignificant to have a noteworthy contribution.

In the model, the mass transfer resistance of LA is not considered since it has been shown above (under the benchmarking conditions) that the liquid-solid mass transfer coefficient of LA and its initial concentration are much higher than those of $H_2$, and the internal diffusion of LA within the catalyst pores is faster than that of $H_2$ (i.e., $\eta_{L_A} > \eta_{H_2}$) under most reaction conditions. Only when the bulk LA in the liquid is almost depleted (i.e., at a close to full conversion occurred near the end of the packed bed), the external and internal liquid-solid mass transfer resistances of LA start to have a more significant influence on the reaction rate. However, throughout the entire packed bed this influence on the overall reaction rate is expected negligible.

A first attempt to apply this model in alternative packed bed configurations (i.e., by the immersion of inert SiC particles in the catalyst bed) has been made for the same reaction (cf. Section S4.9 in the Supporting Information). The measured microreactor performance appeared much lower than the prediction of the simplified model (i.e., even when considering the lower catalyst weight used), which is probably caused by the incomplete catalyst wetting by 1,4-dioxane as a result of the dilution of catalyst bed with SiC. Other packed bed microreactor characteristics (e.g., particle shape, microreactor inner diameter and geometry) need to be tested for a further validation of this model, which is part of our ongoing work.

In the current model, the reaction is simply considered as 0.5th order in $H_2$ and zero order in LA. This reaction order dependency is in line with
literature observations on the Ru/C-catalyzed hydrogenation of LA (in water)\textsuperscript{26,27} as well as hydrogenation of other liquid substrates (e.g., glucose to sorbitol,\textsuperscript{32} cyclohexene to cyclohexane\textsuperscript{78}). The overall reaction rate constant ($k$) was roughly estimated from the data of Ftouni \textit{et al.}\textsuperscript{24}, which seems to also suggest that the reaction order might have changed to 1\textsuperscript{st} order at high LA conversions (i.e., when the GVL selectivity is assumed 100\% and the LA concentration is typically low). Although this has to be further checked in future dedicated kinetic studies, $k$ values were also approximately estimated for the hypothetical case of a (0.5, 1)-th order reaction in LA hydrogenation (note that also in this case the actual $k$ value should be higher; cf. Section S4.7 in the Supporting Information). Under such circumstances, the current model (Eq. 4.20) can be further extended to estimate the LA conversion (cf. Section S4.10 in the Supporting Information). Given the additional facts that the initial LA concentration used in this study is relatively high (5 – 10 wt\%), the measured LA conversion in microreactors is mostly below ca. 80\% and generally in a good agreement with the current model prediction, the assumption of a (0.5, 0)-th order reaction is expected very reasonable.

4.4. Microreactor optimization strategy

A relatively low selectivity towards GVL was obtained (i.e., in the case that LA was not fully converted yet; Figure 4.3) in our experiments. This is mainly because the transformation of the HPA intermediate towards GVL was slower than the formation of HPA from LA under the conditions tested. The formation of GVL from HPA is accelerated by the acidity of the liquid phase and, as such adding small amounts of sulfuric acid can significantly improve the GVL yield in the Ru/C catalyzed hydrogenation of LA in 1,4-dioxane.\textsuperscript{25} Despite this, the LA consumption rate was highly limited by the external liquid-solid mass transfer of $H_2$. Given the acceptable accuracy of the developed microreactor model under mass transfer limited conditions (i.e., Eq. 4.28, or Eq. 4.20 provided that the accurate kinetic parameters are available), this allows to predict favorable design parameters for further reaction optimization. To increase the LA consumption rate (and therewith the GVL production rate) per catalyst weight, external liquid-solid mass transfer limitations should be overcome. This can be done by increasing the flow velocity (i.e., the bed length should be increased as well to remain the same WHSV), as inferred from Eq. 4.13. Furthermore, temperature and $H_2$
pressure accelerate both the reaction kinetics and physical mass transfer rates. Especially because of the relatively low solubility of H\textsubscript{2} in 1,4-dioxane,\textsuperscript{73} elevated H\textsubscript{2} pressures are essential to promote the (external liquid-solid) H\textsubscript{2} mass transfer.\textsuperscript{48} In the current setup much higher temperatures and pressures were not attainable, due to the limited resistance of the PFA capillary and PEEK connectors used. Alternative (capillary) microreactor/connector materials (e.g., stainless steel) may benefit the reaction performance from operation under elevated conditions, although the use of such non-transparent materials makes the packed bed filling procedure and the analysis of gas-liquid hydrodynamics more difficult. Furthermore, the influence of liquid to solid particle wettability on the liquid-solid mass transfer characteristics should be studied in packed bed microreactors (e.g., in the case of bed dilution) to prevent wall-channeling and improve the reaction performance (cf. Section S4.9 in the Supporting Information).

The reaction rate may also be enhanced under relatively mild reaction conditions. For instance, the use of smaller diameter catalyst particles significantly increases the specific catalytic surface area and accelerates the (external) liquid-solid mass transfer (Eqs. 4.13 and 4.25). However, a downside is the higher pressure drop possibly generated over the microchannel.\textsuperscript{59,81} Thus, a compromise between the maximum allowable pressure drop in the microreactor and the acceptable performance improvement needs to be considered. In this regard, the immersion of very fine solid catalyst powders in a packed bed configuration may become less appealing for practical applications. Alternative methods for the incorporation of solid catalysts in microreactors with a high specific catalyst area, but without excessive pressure drop penalty, are by wall-coating or the use of hollow spheres or catalytic foams.\textsuperscript{82,83} In such foams, relatively high mass transfer performance could be obtained.\textsuperscript{84} However, the development of these may require cumbersome catalyst incorporation and/or production techniques.\textsuperscript{38} Another less reported method is to disperse the catalyst as nano- or microparticles in a continuous liquid flow (i.e., forming a gas-liquid slurry). In such configuration, relatively small catalyst particles can be used while still benefitting from the enhanced heat and (gas-liquid) mass transfer in microreactors, at the possible cost of channel fouling or local blockage leading to the device malfunction.\textsuperscript{85}
4.5. Conclusions

The Ru/C catalyzed hydrogenation of LA to GVL was performed in packed bed microreactors made of PFA with H$_2$ gas as the hydrogen donor and 1,4-dioxane as the solvent. The influence of operating conditions (i.e., flow rate, gas to liquid flow ratio, temperature, pressure and catalyst particle size) on the reaction performance was investigated. HPA was identified as an abundantly formed intermediate, which was only further converted to GVL once the majority of LA was consumed. At 130 °C and 12 bar H$_2$, an LA conversion of 100% and a GVL yield of 84% were obtained at a weight hourly space velocity of the liquid phase (WHSV) of 3.0 g$_{\text{feed}}$/ (g$_{\text{cat}}$·h). A microreactor model was developed by considering the respective rates of gas-liquid and external liquid-solid mass transfer, internal diffusion combined with surface reaction based on the literature correlations and data. The model was able to describe the LA conversion as a function of the different reaction conditions, provided that the internal diffusion and kinetic rates were not considered rate limiting. Under the majority of operating conditions (70 – 130 °C and 9 – 15 bar), the reaction was found limited by external liquid-solid mass transfer of H$_2$, primarily due to the relatively low flow rates used and relatively large catalyst particles (diameter of 0.3 or 0.45 mm) in the bed. The developed model allows to propose a further optimization strategy for reaction improvement of the Ru/C catalyzed hydrogenation of LA to GVL in packed bed microreactors.

The modeling approach of this work may guide industrial applications (e.g., numbered-up packed bed microreactors for hydrogenations in fine chemical/pharmaceutical synthesis), under the preconditions that gas-liquid-solid hydrodynamics and mass transfer characteristics (i.e., $k_La_i$ and $k_S$) as well as reaction kinetics are well described. Gas-liquid hydrogenation reactions are often limited by external or internal liquid-solid mass transfer limitations. Under such circumstances, (the often expensive) heterogeneous catalyst is not optimally utilized. With the aid of such modelling, operating conditions where mass transfer limitations are avoided may be identified for an optimal catalyst usage (e.g., in the kinetic regime).

**Notation**

$a_c$ Specific catalyst surface area (m$^2$/g$_{\text{cat}}$)

$a_i$ Specific gas-liquid interfacial area (m$^2$/m$^3$)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Pre-exponential factor for $(0.5, 0)$-order $((\text{mol} \cdot \text{L})^{0.5}/(\text{g}<em>{\text{cat}} \cdot \text{s}))$ or for $(0.5, 1)$-order reaction $((\text{L}^3/\text{mol})^{0.5}/(\text{g}</em>{\text{cat}} \cdot \text{s}))$</td>
</tr>
<tr>
<td>$A_c$</td>
<td>Surface area of catalyst particles (m$^2$)</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration (mol/m$^3$)</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter (m)</td>
</tr>
<tr>
<td>$D$</td>
<td>Mass diffusivity (m$^2$/s)</td>
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<tr>
<td>$D_{\text{eff}}$</td>
<td>Effective diffusivity (m$^2$/s)</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy (J/mol)</td>
</tr>
<tr>
<td>$H$</td>
<td>Henry coefficient (-)</td>
</tr>
<tr>
<td>$j$</td>
<td>Superficial velocity ($= 4Q / \pi d_c^2$) (m/s)</td>
</tr>
<tr>
<td>$k$</td>
<td>Overall reaction rate constant for $(0.5, 0)$-order $((\text{mol} \cdot \text{L})^{0.5}/(\text{g}<em>{\text{cat}} \cdot \text{s}))$ or for $(0.5, 1)$-order reaction $((\text{L}^3/\text{mol})^{0.5}/(\text{g}</em>{\text{cat}} \cdot \text{s}))$</td>
</tr>
<tr>
<td>$k_L$</td>
<td>Liquid phase mass transfer coefficient (m/s)</td>
</tr>
<tr>
<td>$k_S$</td>
<td>Liquid-solid mass transfer coefficient (m/s)</td>
</tr>
<tr>
<td>$L$</td>
<td>Length (m)</td>
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<tr>
<td>$m$</td>
<td>Mass flow rate (kg/s)</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure (Pa)</td>
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<tr>
<td>$Q$</td>
<td>Volumetric flow rate (m$^3$/s)</td>
</tr>
<tr>
<td>$r$</td>
<td>Rate of transfer (mol/s)</td>
</tr>
<tr>
<td>$r'$</td>
<td>Rate of transfer per unit mass of catalyst (mol/(g$_{\text{cat}}$·s))</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature (°C or K)</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume (m$^3$)</td>
</tr>
<tr>
<td>$w_c$</td>
<td>Catalyst weight (g)</td>
</tr>
<tr>
<td>$\text{WHSV}$</td>
<td>Weight hourly space velocity $(g_{\text{feed}}/(g_{\text{cat}} \cdot \text{h})$ or $g_{\text{LA}}/(g_{\text{cat}} \cdot \text{h}))$</td>
</tr>
<tr>
<td>$X$</td>
<td>Conversion (%)</td>
</tr>
<tr>
<td>$Y$</td>
<td>Yield (%)</td>
</tr>
</tbody>
</table>

**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$\alpha$</td>
<td>Wetted catalyst fraction (-)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension (N/m)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Bed porosity (-)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Effectiveness factor (-)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity (Pa·s)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density (g/m$^3$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Selectivity (%)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Thiele modulus (-)</td>
</tr>
</tbody>
</table>
$\chi_G$ \hspace{1cm} Lockhart-Martinelli ratio \( (= \frac{j_G\sqrt{\rho_G}}{(j_L\sqrt{\rho_L})}) \) (-)

**Subscripts**
- 0 \hspace{1cm} At the packed bed microreactor inlet
- 1 \hspace{1cm} At the packed bed microreactor outlet
- B \hspace{1cm} In the bulk
- c \hspace{1cm} Catalyst
- C \hspace{1cm} Capillary microreactor
- HPA \hspace{1cm} 4-Hydroxypentanoic acid
- G \hspace{1cm} Gas
- GVL \hspace{1cm} γ-Valerolactone
- I \hspace{1cm} At the interface
- L \hspace{1cm} Liquid
- LA \hspace{1cm} Levulinic acid
- p \hspace{1cm} Particle
- S \hspace{1cm} Surface reaction

**Dimensionless numbers**
- $Re$ \hspace{1cm} Reynolds number \( (= \frac{\rho j d_p}{\mu} ) \)
- $Sc$ \hspace{1cm} Schmidt number \( (= \frac{\mu}{\rho D} ) \)
- $Sh$ \hspace{1cm} Sherwood number \( (= \frac{k_s d_p}{D} ) \)
- $We$ \hspace{1cm} Weber number \( (= \frac{\rho j^2 d_p}{\gamma} ) \)

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Supporting Information – Chapter 4

S4.1. Data analysis and mass balance

The LA conversion and GVL yield versus the time on stream ($t$) under the benchmark conditions in the packed bed microreactor are depicted in Figure S4.1. The experimental data points reported (as depicted in Figures 4.2 and 4.3) are based on the average concentration of at least three samples collected at different times under steady state conditions (i.e., after ca. $t = 60$ min). For most experiments, the relative experimental error in the measured LA and GVL concentrations was found below 10%.

![Figure S4.1](image)

**Figure S4.1.** Influence of time on stream on the LA conversion ($X_{LA}$) and GVL yield ($Y_{GVL}$) at the benchmark conditions in the packed bed microreactor ($C_{LA,0} = 5$ wt%, $Q_{G,0} / Q_{L,0} = 4.5$, $T = 130$ °C, $p_{H_2} = 12$ bar, $L_{bed} = 0.8$ m, $w_c = 0.9$ g, $d_p = 0.45$ mm, $WHSV = 6.0$ g$_{feed}$(g$_{cat}$·h$)^{-1}$).

Only LA and GVL could be (quantitatively) measured by GC-FID. However, there was no closed mass balance for most experimental conditions (i.e., the GVL yield was usually lower than the LA conversion). To exclude the formation of undetected side products one experiment was performed using $N_2$ as the inert gas phase under otherwise the same benchmark conditions ($C_{LA,0} = 5$ wt%, $Q_{G,0} / Q_{L,0} = 4.5$, $T = 130$ °C, $p = 12$ bar, $L_{bed} = 0.8$ m, $w_c = 0.9$ g, $d_p = 0.45$ mm, $WHSV = 6.0$ g$_{feed}$(g$_{cat}$·h$)^{-1}$)). The LA concentration at the bed outlet was found practically the same as the inlet concentration, showing no accumulation or (thermal) decomposition of LA in the setup under reactive conditions. Furthermore, under the same benchmarking conditions using $H_2$ as the gas phase, but in
the absence of Ru/C catalyst, the measured LA concentration in the collected liquid sample at the setup outlet (Figure 4.1) was measured to be the same as that in the feed. This proves no reaction occurrence with LA outside the packed bed and the observed LA conversion as well is purely due to the catalytic effect. Similarly, to exclude the further conversion of GVL towards side products (e.g., MTHF; cf. Scheme 4.1), additional experiments were performed with GVL as the substrate and H$_2$ as the gas phase under otherwise the same benchmark conditions. Given no considerable difference (i.e., < 5%) found between GVL concentrations at the in- and outlet of the microreactor, it can be concluded that GVL was not further converted under the reaction conditions tested. This is further confirmed by no MTHF observed in the GC-FID chromatograms. Also α-angelicalactone (α-AL), a commonly formed intermediate in the hydrogenation of LA to GVL (Scheme 4.1), was not observed in the GC-FID chromatograms. Another intermediate, 4-hydroxypentanoic acid (HPA), is known to be formed abundantly in 1,4-dioxane under non-acidic conditions.$^{1}$ HPA could not be detected with GC-FID chromatography (i.e., due to its acidity and the polar column used), but was observed in $^1$H-NMR analysis.

Assuming only LA, HPA and GVL are present in the reaction mixture, the concentrations of these components could be estimated based on the relative proton content determined by $^1$H-NMR spectra. Thus, the derived LA conversion (Eq. 4.1) and GVL yield (Eq. 4.2) were very similar to those measured by GC-FID (Figure S4.2), indicating that the gap in the mass balance from the GC-FID measurements could be attributed to the HPA intermediate. Since $^1$H-NMR is generally considered less suitable for quantitative analysis, the LA conversion and GVL yield presented in this work are based on the GC-FID analysis.
Figure S4.2. Comparison of the LA conversion and yields of GVL and HPA (if detected) from the (relative) concentration measurements by $^1$H-NMR (assuming no formation of other components) and GC-FID under (a) $p_{H_2} = 9$ bar and (b) $p_{H_2} = 12$ bar. Other conditions are the same as shown in Figure S4.1.

S4.2. Experimental reproducibility

The experimental reproducibility was tested by comparing the reaction performance in two identical microreactors with separate catalyst packing ($L_{bed} = 0.8$ m) under the same operating conditions. There was no significant difference in the LA conversion and GVL yield for both beds (Figure S4.3), showing a good reproducibility of the experimental results as well as the packing methodology (cf. Section 4.2.2).

Figure S4.3. Reproducibility of the LA conversion and GVL yield measured over two identical packed bed microreactors under the same conditions as shown in Figure S4.1.
S4.3. Influence of the initial LA concentration

Experiments were performed with an initial LA concentration at the microreactor inlet \( C_{LA,0} \) of 5 or 10 wt%. At \( C_{LA,0} = 10 \) wt%, the LA conversion and GVL yield were significantly lower at a certain WHSV than at 5 wt% LA (Figure S4.4). Since WHSV is inversely proportional to the mean residence time (i.e., at a certain gas to liquid flow ratio) in the packed bed microreactor, it appears that the overall LA consumption and GVL formation rates in the microreactor are below first order in LA under such conditions. This is in line with an apparent zero order dependency in LA as previously observed in the Ru/C catalyzed hydrogenation of LA (of ca. 10 wt% initial concentration) with water as the solvent in batch reactor studies.\(^2\)\(^3\)

The lower LA conversion for \( C_{LA,0} = 10 \) wt% was also predicted by the model (Eq. 4.28 in Section 4.3.5; Fig S4.4a). This is because of mass transfer limitations identified in the model for the current microreactor operation. In other words, the intrinsic kinetic rate was assumed much faster than the gas-liquid-solid mass transfer rate. The model prediction is somewhat above the measured LA conversion for this concentration level, but is still in a similar value range. This overprediction might be due to the catalyst active sites being more occupied by LA, inhibiting \( \text{H}_2 \) adsorption and thus slowing the intrinsic kinetic rate to some extent (cf. Section S4.6).

At relatively high initial LA concentrations, the Microactivity Effi reactor operation was complicated by a poor gas-liquid separation in the LIC (Figure 4.1). This is likely due to the probe coating in the separator being slightly worn out, which led to its malfunction in the effective measurement of the dielectric potential due to interference of slightly polar solvents (i.e., it was unable to achieve a proper separation of gas and liquid with water as the solvent). The increasing polarity of the reaction mixture at higher LA concentrations may have caused a disturbance in the probe measurement. For lower LA concentrations this was not the case and as such, other experiments in this work were performed with 5 wt% LA inlet feed.
Figure S4.4. Influence of the initial LA concentration on (a) the LA conversion and (b) GVL yield at different values of weight hourly space velocity (WHSV) in the microreactor. Other conditions are the same as shown in Figure S4.1. In (a) the modeled LA conversions (according to Eq. 4.28) for both initial LA concentrations are included for comparison.

S4.4. Influence of the upstream gas-liquid slug flow profile

Under most operating conditions in this work, an upstream slug flow profile with relatively long gas bubbles and liquid slugs was generated (Figure 4.1). To investigate if this negatively affected mass transfer characteristics in the packed bed microreactor (e.g., by causing a relatively low gas-liquid interfacial area or a somewhat poor liquid coverage of the solid catalyst particles), the reaction performance thereof was compared to those found from additional experiments where an upstream gas-liquid slug flow profile with shorter bubbles/slugs was generated under otherwise the same conditions. Such shorter bubbles/slugs upstream were realized by inserting a short PFA capillary of 1.6 mm inner diameter packed with an inert bed of SiC particles (particle diameter: 0.48 mm; bed length: 10 cm) after the inlet T-junction for two-phase mixing (Figure 4.1). The inert bed was followed by another empty PTFE capillary (inner diameter: 0.8 mm; length: 20 cm) that was connected to the packed bed microreactor. In the inert bed, the generated slug flow with long bubbles/slugs seemed to be further fractured, which eventually resulted in shorter bubbles/slugs that appeared in the following empty PTFE capillary and were fed into the packed bed microreactor containing catalyst particles (Figure S4.5).
The difference in the gas-liquid upstream slug flow profile (i.e., relatively long or short bubbles and slugs) did not cause a significant change in the measured LA conversion and GVL yield (Figure S4.6). The slightly inferior reaction performance in the case of long bubbles/slugs upstream is possibly due to the somewhat lower mass transfer rate in the inlet section of the catalyst bed where breakup of bubbles/slugs into smaller ones could have occurred. It is expected that in the major part of the packed bed, a liquid-dominated slug flow with a good gas-liquid dispersion was generated in both slug flow profile cases and thus led to similar mass transfer characteristics, as supported by the very close LA conversion or GVL yield observed in each case. In other words, the reaction performance is not much affected by the upstream slug flow profile under the current reaction conditions.

Figure S4.6. Influence of the bubble(slug length in the upstream gas-liquid slug flow profile on the LA conversion ($X_{LA}$) and GVL yield ($Y_{GVL}$) measured in the downstream packed bed microreactor. Other conditions are the same as shown in Figure S4.1. The short bubble/slugs lengths were realized by placing an additional inert bed of SiC particles before the microreactor.

Figure S4.5. Upstream gas-liquid slug flow profile to the packed bed microreactor (a) without and (b) with the presence of the additional inert bed placed before the microreactor.
S4.5. Determination of physical fluid properties

In the model, several physical fluid properties are used to estimate the gas-liquid and liquid-solid mass transfer coefficients. In this section the values of these properties as a function of the reaction conditions (e.g., temperature and pressure) are estimated. The parameter values under the benchmark conditions are shown in Table S4.1. It is assumed that the relatively low LA (5 wt%) and dodecane (1 wt%) concentrations in use did not considerably affect the physical properties for the reaction mixture which are thus approximately equal to those of 1,4-dioxane (i.e., when it comes to the calculation of the diffusivities of H$_2$ ($D_{H_2}$) and LA ($D_{LA}$), Henry coefficient ($H$) and surface tension ($\gamma$)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{H_2}$</td>
<td>$8.90 \times 10^{-10}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{LA}$</td>
<td>$4.71 \times 10^{-9}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$H$</td>
<td>67.4</td>
<td>-</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$1.88 \times 10^{-2}$</td>
<td>N/m</td>
</tr>
<tr>
<td>$\rho_G$</td>
<td>0.73</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_L$</td>
<td>$1.01 \times 10^3$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_S$</td>
<td>$2.27 \times 10^3$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\mu_G$</td>
<td>$1.09 \times 10^{-5}$</td>
<td>Pa·s</td>
</tr>
<tr>
<td>$\mu_L$</td>
<td>$3.71 \times 10^{-4}$</td>
<td>Pa·s</td>
</tr>
</tbody>
</table>

$^a$ $D_{H_2}$, $D_{LA}$, $H$, and $\gamma$ are based on pure 1,4-dioxane as the liquid phase. $^b$ G, L and S subscripts for the density ($\rho$) and viscosity ($\mu$) indicate the (H$_2$) gas phase, liquid mixture and (catalyst) solid particles, respectively.

### S4.5.1. Henry coefficient

The Henry coefficient ($H$) of H$_2$ in 1,4-dioxane as a function of temperature is determined by

$$H = \frac{C_{H_2,G}}{C_{H_2,I,L}} = \frac{C_{H_2,G}M_{W,L}}{x_0 \rho_L}$$  \hspace{1cm} (S4.1)

Here $x_0$ is the molar fraction of H$_2$ in 1,4-dioxane and $M_{W,L}$ is the molar mass of the 1,4-dioxane solvent (88.11 g/mol). $\rho_L$ is the liquid density. The influence of temperature ($T$) on $x_0$ (at 1 bar partial pressure of H$_2$) is estimated by a linear regression of the experimental data in the literature (Figure S4.7).
Figure S4.7. Influence of temperature on the molar fraction of $H_2$ in 1,4-dioxane at 1 bar partial pressure of $H_2$.\textsuperscript{4}

S4.5.2. Mass diffusivity

The mass diffusivities ($D_i$; $i$ being $H_2$ or LA) in 1,4-dioxane as a function of temperature ($T$ in K) are estimated by the Wilke-Chang correlation\textsuperscript{5}

$$D_i = \frac{1.173 \times 10^{-16} (\psi M_{W,L})^{0.5} T}{\mu_L \psi^{0.6}}$$  \hspace{1cm} (S4.2)

where $\psi$ is the association constant (equal to 1 for 1,4-dioxane) and $\nu$ is the molar volume at normal boiling point (being $1.64 \times 10^{-3}$ m$^3$/mol for $H_2$ and $1.02 \times 10^{-4}$ m$^3$/mol for LA). $\mu_L$ is the liquid viscosity.

S4.5.3. Viscosity

The mixture viscosity of 1,4-dioxane containing 5 wt% LA and 1 wt% dodecane ($\mu_L$) and the gas hydrogen viscosity ($\mu_G$) for different temperatures were determined by a pure component property analysis using Aspen Plus software (version 8) from AspenTech (Figure S4.8). Based on the simulated data, these viscosities at a given temperature can then be fitted by

$$\mu_L = C_1 \times T^{C_2}$$  \hspace{1cm} (S4.3)

$$\mu_G = C_3 \times T + C_4$$  \hspace{1cm} (S4.4)

where the fitting parameters are $C_1 = 2 \times 10^7$, $C_2 = -4.119$ for the 1,4-dioxane case and $C_3 = 1.7 \times 10^{-8}$, $C_4 = 4.043 \times 10^{-4}$ for $H_2$ gas, and $T$ is in K.
S4.5.4. Density

The density of H₂ gas (ρ₆) under reaction conditions is determined by the ideal gas law using its density at standard pressure and temperature (i.e., pₚₑᵣᵣ = 1 bar and Tₚₑᵣᵣ = 273.15 K, respectively) as the reference value (ρ₆,ᵣₑᵣᵣ = 89.89 g/m³). That is,

$$\rho_G = \rho_{G,ref} \frac{p}{p_{ref}} \frac{T_{ref}}{T} \quad \text{(S4.5)}$$

The liquid density of 1,4-dioxane containing 5 wt% LA and 1 wt% dodecane (ρ₇) as a function of temperature was calculated by a pure component analysis in Aspen Plus (Figure S4.9). ρ₇ can then be described by a linear regression of the simulated values.

$$\rho_L = C_5 \times T + C_6 \quad \text{(S4.6)}$$

where the fitting parameters are C₅ = -0.4195 and C₆ = 1174.7, and T is in K.

In the case of the packed bed consisting of Ru/C catalyst diluted with inert SiC particles, the averaged solid particle density (ρₛ) is defined as

$$\rho_s = \frac{w_{Ru/C} + w_{SiC}}{w_{Ru/C} \rho_{Ru/C} + w_{SiC} \rho_{SiC}} \quad \text{(S4.7)}$$

where w₁₆₆ and w₁₈₆ are the respective weights of the 0.5 wt% Ru/C catalyst particles and the inert SiC particles. ρ₁₆₆ is the density of the 0.5 wt% Ru/C catalyst particles (approximated as the density of graphite; 2260 kg/m³)⁶ and ρ₁₈₆ is the density of SiC (3210 kg/m³).⁷
S4.5.5. Surface tension

The gas-liquid surface tension ($\gamma$) at different temperatures was estimated by a pure component property analysis in Aspen Plus (Figure S4.10). Herein, it is assumed that the surface tension of H$_2$ with the liquid reaction feed mixture is equal to that of H$_2$ with pure 1,4-dioxane. By a linear regression of the estimated values the following relationship is obtained:

$$\gamma = C_7 \times T + C_8$$  \hspace{1cm} (S4.8)

where the fitting parameters for the H$_2$-1,4-dioxane system are $C_7 = -1.37 \times 10^{-4}$, $C_8 = 0.074$, and $T$ is in K.
S4.6. Derivation of the kinetic rate equation

The Ru/C catalyzed hydrogenation of LA can be interpreted by a Horiuti-Polanyi interpretation with the simplified reaction schemes shown in Eqs. S4.9-S4.12.2

\[
\text{LA} + K_1 \leftrightarrow \text{LA}^* \quad \text{(S4.9)}
\]

\[
\text{H}_2 + 2K_2 \leftrightarrow 2\text{H}^* \quad \text{(S4.10)}
\]

\[
\text{LA}^* + \text{H}^* \leftrightarrow \text{LA-H}^* + \text{H}^* \quad \text{(S4.11)}
\]

\[
\text{LA-H^* + H}^* \rightarrow \text{HPA} + 2^* \quad \text{(S4.12)}
\]

where \( K_1, K_2, K_3 \) are the equilibrium constants and \( k_4 \) the kinetic constant for reaction steps S4.9-S4.12, respectively.

According to this interpretation, LA undergoes a molecular adsorption (Eq. S4.9) and \( \text{H}_2 \) a dissociative one (Eq. S4.10) on the Ru active sites (denoted as *).2 The adsorbed LA (i.e., \( \text{LA}^* \)) is then reduced in two subsequent hydrogen atom addition steps to form HPA (Eqs. S4.11 and S4.12). The second hydrogen atom addition (i.e., of the half-hydrogenated intermediate \( \text{LA-H}^* \); Eq. S4.12), resulting in the desorption of HPA, is often considered the rate limiting step due to the strong bonding of the \( \text{LA-H}^* \) intermediate to the Ru catalyst.2,3

Then, in the case of non-competitive adsorption of LA and \( \text{H}_2 \) (i.e., they bind on different sites), the overall kinetic rate expression is derived by a Langmuir-Hinshelwood analysis as2

\[
\dot{r}_{\text{H}_2,S} = \frac{k_4K_1K_2K_3C_{\text{LA},S}C_{\text{H}_2,S}}{\left(1 + K_1C_{\text{LA},S} + K_1^{1/2}K_2^{1/2}K_3C_{\text{LA},S}C_{\text{H}_2,S}^{1/2}\right)\left(1 + K_2^{1/2}C_{\text{H}_2,S}^{1/2}\right)} \quad \text{(S4.13)}
\]

where \( C_{\text{H}_2,S} \) and \( C_{\text{LA},S} \) represent the concentrations of \( \text{H}_2 \) and LA on the catalyst internal surface, respectively.

Considering that the active catalyst sites are far from being fully adsorbed by \( \text{H}_2 \) with an almost zero coverage of LA and the LA-H intermediate is strongly bound to the catalyst active sites (i.e., assumed to approach saturation on the available sites for its adsorption), the following conditions apply:2

\[
1 >> K_2^{1/2}C_{\text{H}_2,S}^{1/2} \quad \text{(S4.14)}
\]

\[
1 >> K_1C_{\text{LA},S} \quad \text{(S4.15)}
\]

\[
1 << K_1K_2^{1/2}K_3C_{\text{LA},S}C_{\text{H}_2,S}^{1/2} \quad \text{(S4.16)}
\]
As a result, Eq. S4.13 is simplified to

$$r'_{H_2,S} = \frac{k_4 K_1 K_2}{K_0 K_2} \frac{C_{LA,S} C_{H_2,S}}{C_{LA,S} C_{H_2,S}} = k_4 K_2^{1/2} C_{H_2,S}^{1/2} = k C_{H_2,S}^{1/2}$$

(S4.17)

with the overall reaction rate constant being \(k = k_4 K_2^{1/2}\).

**S4.7. Estimation of kinetic parameters**

A rough estimation of kinetic parameters was obtained from the reported experimental results on the 5 wt% Ru/C catalyzed hydrogenation of LA in a stirred batch reactor using 1,4-dioxane as the solvent in the work of Ftouni *et al.*, based on the assumption that (external and internal) mass transfer limitations were not present. It is further assumed that the reaction is 0.5th order in \(H_2\) and zero order in LA as indicated in the aqueous phase hydrogenation of LA over Ru/C catalysts, and that the reaction is fully selective towards GVL so that the initial rate of GVL formation is equal to the observed \(H_2\) (and thus LA) consumption rate \(r_{H_2,obs}\). Thus, a Ru weight-based reaction rate constant \(k_{Ru}\) is estimated from

$$r_{H_2,obs} = V_L \frac{dC_{GVL}}{dt} = w_{Ru} k_{Ru} C_{H_2,S}^{1/2} = w_{Ru} k_{Ru} C_{H_2,L}^{1/2}$$

(S4.18)

where \(w_{Ru}\) is the Ru weight in the catalyst and \(V_L\) the liquid volume in the used batch reactor. \(C_{H_2,S}\) and \(C_{H_2,L}\) are the \(H_2\) concentrations on the catalyst internal surface and in the liquid, respectively, and \(C_{GVL}\) is the GVL concentration in the liquid. Thus, \(k_{Ru}\) is approximated as

$$k_{Ru} = \frac{V_L}{w_{Ru} C_{H_2,L}^{1/2}} \frac{dC_{GVL}}{dt} = \frac{V_L C_{LA,0}}{w_{Ru} C_{H_2,L}^{1/2}} \frac{dY_{GVL}}{dt}$$

(S4.19)

The initial GVL formation rate was estimated for different reaction temperatures via a linear line regression of the reported GVL yields at the first two reaction times in the work of Ftouni *et al.*, as shown in Figure S4.11a. The corresponding \(k_{Ru}\) values were then determined by Eq. S4.19, from which the estimated overall reaction rate constant \(k_{est}\) for 0.5 wt% Ru/C was found as

$$k_{est} = \frac{k_{Ru} w_{Ru}}{w_c}$$

(S4.20)

and is shown in Table S4.2.
Figure S4.11. (a) Derivation of the initial GVL formation rate for the 5 wt% Ru/C catalyzed hydrogenation of LA in a batch reactor with 1,4-dioxane as the solvent. (b) Comparison of the estimated GVL yield profile based on a first order rate dependency in LA ($A = 1995 \text{ (L/mol)}^{0.5}/(\text{g}_{\text{cat}} \cdot \text{s})$ and $E_a = 58 \text{ kJ/mol}$). Conditions: 10 wt% LA, 30 bar $H_2$, the weight ratio of the initial LA to Ru in the reactor at 1000 g/g. Experimental data are taken from the work of Ftouni et al.\textsuperscript{8}

Table S4.2. Estimated overall reaction rate constants for LA hydrogenation over 0.5 wt% Ru/C catalyst at different temperatures based on the data of Ftouni et al.\textsuperscript{8}

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k_{est}$ $^a$ (mol·L)$^{0.5}$/(g$_{cat}$·s)</th>
<th>$k_{est}$ $^b$ (L$^3$/mol)$^{0.5}$/(g$_{cat}$·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>$6.50 \times 10^{-7}$</td>
<td>$2.23 \times 10^{-6}$</td>
</tr>
<tr>
<td>373</td>
<td>$1.87 \times 10^{-5}$</td>
<td>$7.25 \times 10^{-5}$</td>
</tr>
<tr>
<td>423</td>
<td>$1.02 \times 10^{-4}$</td>
<td>$6.47 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

$^a$In the case of a 0.5$^{th}$ order in $H_2$ and zero order in LA. $^b$In the case of a 0.5$^{th}$ order in $H_2$ and first order in LA.

From the $k_{est}$ values obtained at different temperatures, the activation energy ($E_a = 58 \text{ kJ/mol}$) and the pre-exponential factor ($A = 1770 \text{ (mol·L)}^{0.5}/(\text{g}_{cat} \cdot \text{s})$) for the case of zero order dependency in LA and 0.5$^{th}$ order in $H_2$ were derived with the Arrhenius equation (i.e., via a linear fitting by plotting $\ln(k_{est})$ versus $1/T$):

$$k_{est} = Ae^{-\frac{E_a}{RT}}$$  \hspace{1cm} (S4.21)

Note that the values for $A$ and $E_a$ are merely a rough estimation since an underestimation of the actual $k$ values is expected with this approach. First of all, this underestimation is caused by the simple assumption of a 100% selectivity to GVL. In the work of Ftouni et al.,\textsuperscript{8} the LA conversion was not reported and should be in principle higher than the GVL yield due to the presence of HPA as the intermediate (e.g., at short reaction times). Moreover, no proof of the absence of mass transfer limitations was provided in their work. However, an order of magnitude analysis of $k$ values is still
expected, which is sufficient to reveal the dominant role of mass transfer in the present microreactor experiments. Despite this approximated kinetic parameter analysis, the estimated \( E_a \) value is on the same order of magnitude as that in the cases of the 5 wt% Ru/C catalyzed hydrogenation of LA using water as the solvent (\( E_a = 48 \) kJ/mol)\(^2\) and of alkyl (i.e., methyl, ethyl and butyl) levulinates to their corresponding alkyl-3-hydroxyvalerates with methanol as the solvent (\( E_a = 41, 45 \) or 58 kJ/mol, respectively).\(^9\)

The data of Ftouni et al.\(^8\) also seem to suggest that the reaction order in LA might not be always zero (if we assume a full selectivity towards GVL), especially at long reaction times or alternatively low LA concentrations (Figure S4.11a). Although the zero-order dependency in LA and other liquid substrates is often considered for the (Ru/C-catalyzed) hydrogenation reactions,\(^2,3,10,11\) a first-order dependency in the substrate was observed during the hydrogenation of alkyl levulinates to GVL over Ru/C catalyst at a relatively low initial substrate concentrations (0.03 – 0.15 M) in methanol.\(^9\) For hydrogenation of LA in 1,4-dioxane over the same catalyst, whether there is a presence of such first-order dependency still has to be thoroughly checked in future kinetic studies. However, in order not to exclude this possibility, an additional attempt was made to interpret the data of Ftouni et al.\(^8\) based on a (0.5, 1)-th-order reaction using otherwise the same approach as stated above. That is

\[
V_L \frac{dC_{GVL}}{dt} = w_{Ru} k_{Ru} C_{H_2,L}^{1/2} C_{LA}
\] (S4.22)

This equation is further reduced to

\[
V_L \frac{dY_{GVL}}{dt} = w_{Ru} k_{Ru} C_{H_2,L}^{1/2} (1 - Y_{GVL})
\] (S4.23)

Finally, after integration between the start and final reaction time, it is obtained that

\[
k_{Ru} = \frac{-V_L \ln(1 - Y_{GVL})}{w_{Ru} C_{H_2,L}^{1/2} t}
\] (S4.24)

And thus, the values of \( k_{est} \) are derived according to Eq. S4.20 as

\[
k_{est} = \frac{-V_L \ln(1 - Y_{GVL})}{w_c C_{H_2,L}^{1/2} t}
\] (S4.25)

The data of Ftouni et al.\(^8\) was fitted with Eq. S4.25, as shown in Figure S4.11b. The obtained \( k_{est} \) values at different temperatures are shown in Table S4.2 as well, from which \( A = 6.97 \times 10^4 \) (L\(^3\)/mol\(^{0.5}\))/(g\(_{cat}\)·s) and \( E_a = 64.7 \) kJ/mol were estimated with the Arrhenius equation (Eq. S4.21).
As discussed above, an underestimation of the actual $k$ values to a certain extent is expected as well in this case.

**S4.8. Estimation of Thiele modulus and the effectiveness factor**

The effectiveness factor ($\eta$) of the spherical catalyst particles is a function of the Thiele modulus ($\phi$). The Thiele moduli of $\text{H}_2$ ($\phi_{\text{H}_2}$) and $\text{LA}$ ($\phi_{\text{LA}}$) for an $(m, n)$-th-order reaction in $\text{H}_2$ and $\text{LA}$, respectively, are defined as

\[
\phi_{\text{H}_2} = \frac{d_p}{2} \sqrt{\frac{k \rho_S C_{\text{H}_2,S}^{m-1} C_{\text{LA},S}^{n}}{D_{\text{H}_2,\text{eff}}}} \quad (S4.26)
\]

\[
\phi_{\text{LA}} = \frac{d_p}{2} \sqrt{\frac{k \rho_S C_{\text{H}_2,S}^{m} C_{\text{LA},S}^{n-1}}{D_{\text{LA},\text{eff}}}} \quad (S4.27)
\]

The above definition of Thiele modulus for each reactive species is based on the limiting condition that there is no concentration gradient of the other species within the catalyst pores, viz. the reaction is treated as pseudo $m$th or $n$th order (in $\text{H}_2$ or $\text{LA}$).

The kinetic constant ($k$) for the case of a 0.5$^{\text{th}}$ order in $\text{H}_2$ and zero or first order in $\text{LA}$ has been roughly estimated in Section S4.7. The effective diffusivity of the species $i$ ($D_{i,\text{eff}}$; $i$ being $\text{H}_2$ or $\text{LA}$) is described by

\[
D_{i,\text{eff}} = \frac{D_i \epsilon_t \delta}{\tau} \quad (S4.28)
\]

where $\epsilon_t$ is the catalyst porosity available for transport, $\delta$ is the constrictivity and $\tau$ the tortuosity in the catalyst.$^{12}$ Since such values are not precisely known, it is roughly assumed that for Ru/C catalysts $D_{i,\text{eff}} = 0.1 D_i$. $^{3,10}$ This is in line with the literature report that the effective diffusivity is approximately 0.1 – 0.2 times the diffusivity in the liquid bulk.$^{13}$

Typical values of $\phi_{\text{H}_2}$ and $\phi_{\text{LA}}$ were evaluated under the benchmark reaction conditions ($130 \degree \text{C}$ and 12 bar $\text{H}_2$ with an average catalyst particle diameter of 0.3 or 0.45 mm), based on the interfacial concentration of $\text{H}_2$ in the liquid and inlet LA concentration (i.e., assuming $C_{\text{H}_2,S} = C_{\text{H}_2,I,L}$ and $C_{\text{LA},S} = C_{\text{LA},I}$ in Eqs. S4.26 and S4.27). The estimated values for a (0.5,0)-th or (0.5,1)-th-order reaction in $\text{H}_2$ and $\text{LA}$, are shown in Table S4.3.
Table S4.3. Estimated Thiele moduli for $\text{H}_2$ and LA internal diffusion and reaction within the Ru/C catalyst pores.

<table>
<thead>
<tr>
<th>$d_p$ (mm)</th>
<th>(0.5, 0)-th-order reaction</th>
<th>(0.5, 1)-th-order reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\phi_{\text{H}_2}$</td>
<td>$\phi_{\text{LA}}$</td>
</tr>
<tr>
<td>0.45</td>
<td>31.0</td>
<td>1.48</td>
</tr>
<tr>
<td>0.3</td>
<td>20.7</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Other conditions: 130 °C, 12 bar $\text{H}_2$, $C_{\text{H}_2,S} = C_{\text{H}_2,0}$, $C_{\text{LA},S} = C_{\text{LA},0}$ (5 wt%).

For relatively low values of the Thiele modulus (e.g., $\phi < 0.2$), internal diffusion is not rate-limiting and the effectiveness factor approaches 1. For larger values of the Thiele modulus (e.g., $\phi > 15$), the effectiveness factor of an $n$-th order reaction is roughly estimated as\textsuperscript{12}

$$\eta = \left( \frac{2}{n+1} \right)^{1/2} \left( \frac{2}{\phi} \right)$$  \hspace{1cm} (S4.29)

Given the relatively high Thiele moduli in all cases depicted in Table S4.3, the internal diffusion of both components appears to be slower than the kinetic rate. Under the benchmark conditions in the case of a (0.5, 0)-th-order reaction, the respective effectiveness factors for $\text{H}_2$ and LA are estimated as $\eta_{\text{H}_2} = 0.11$ (i.e., for $\phi_{\text{H}_2} = 31.0$; based on Eq. S4.29 with $n = 0.5$) and $\eta_{\text{LA}}$ can be assumed as 1 (i.e., for $\phi_{\text{LA}} = 1.48$; based on a zero order reaction and Figure 12-5a in the book of Fogler.\textsuperscript{12} When the reaction is considered zero order in LA, $\eta_{\text{LA}}$ is consistently higher than $\eta_{\text{H}_2}$ for all experimental conditions, thus it is assumed that the internal LA diffusion is (much) faster than that of $\text{H}_2$ and not limiting the overall reaction rate. For a first order dependency in LA, $\phi_{\text{LA}}$ is still much lower than $\phi_{\text{H}_2}$ (Table S4.3), thus $\eta_{\text{LA}}$ is still much higher than $\eta_{\text{H}_2}$. However, these calculations are based on the inlet LA concentration ($C_{\text{LA},S} = C_{\text{LA},0}$), whereas in reality $C_{\text{LA},S}$ logically decreases over the course of the reaction. At high LA conversions (or low LA concentrations), $\phi_{\text{H}_2}$ typically decreases for the (0.5, 1)-th-order reaction case (Eq. S4.26), whereas $\phi_{\text{LA}}$ is not affected by the LA concentration (Eq. S4.27). Thus, when the LA concentration decreases such that $\phi_{\text{H}_2}$ becomes lower than $\phi_{\text{LA}}$, the intrinsic mass transfer of LA might become limiting. Since such high LA conversions were generally not obtained in this work, it is safe to assume that the intrinsic LA mass transfer is consistently faster than that of $\text{H}_2$.\textsuperscript{12}
It must be admitted that there are some uncertainties in these
effectiveness factor calculations as the actual Thiele modulus values may
deviate much from the predictions of Eqs. 4.26 and 4.27. The determination
of both $D_{i,\text{eff}}$ and $k$ are based on rough and error-prone estimations. In the
case of mass transfer limitations, also it cannot be simply assumed that
there is an absence of the ($H_2$ or LA) concentration gradient within the liquid
bulk and catalyst pores. In other words, the concentration of component $i$
at the catalyst external surface ($C_{i,S}$) and that in the pores tend to be lower
than that in the liquid bulk.

S4.9. Influence of the catalyst weight fraction in SiC-diluted
packings

To further check the model applicability, experiments were performed
using a packing mixture of the Ru/C catalyst ($d_p = 0.45$ mm) with inert SiC
particles (of average diameter at 0.48 mm) (Figure S4.12). Inert solid
particles are typically added to dilute catalyst packings for the prevention
of thermal hotspots in the bed (e.g., by the local temperature excursion
from an exothermic reaction), thus improving heat distribution over the
catalytic reactor. Multiple packed bed microreactors of the same length
($L_{\text{bed}} = 0.8$ m) were prepared with mixtures of 0.5 wt% Ru/C and inert SiC
particles (Ru/C weight fractions of 0.5, 0.61 and 0.75). Both the measured
LA conversion and GVL yield increased for given reaction conditions with
less diluted packing (Figure S4.12a), due to more catalyst available.
Although the simplified model according to Eq. 4.28 predicts the LA
conversion well for microreactors packed with pure Ru/C (Figure 4.3), the
experimental results using a packing diluted with SiC is over-predicted by
the model (Figure S4.12a). According to the model, the external liquid-solid
mass transfer limitations are dominant for all packing mixtures (i.e., in the
case $k = 3k_{\text{est}}$ or higher; Figure S4.12b). The reason for this over-predicted
reaction performance may be better explained by the packing formation and
the influence of particle properties (e.g., wettability) on its interaction with
gas-liquid flow pattern in the bed. Mixtures of SiC and 0.5 wt% Ru/C
resulted in some segregation that may be caused by the difference in
affinity between SiC and Ru/C. Contrary to Ru/C, SiC is slightly
hydrophilic $^{14,15}$ and could be repulsed from the hydrophobic PFA
microreactor wall. This may have caused the relatively large voids along the
microchannel wall leading to flow bypass. Furthermore, 1,4-dioxane has a
better wettability on Ru/C and the PFA wall than on SiC (i.e., due to the
difference in hydrophilicity).\textsuperscript{14,15} This may additionally cause the liquid to be more attracted to the PFA wall than the bed of mixed SiC and Ru/C solid particles as a whole, further promoting liquid bypassing.\textsuperscript{16} Liquid bypassing reduces the liquid-solid interaction and may result in not all solid particles being wetted by the liquid (i.e., $\alpha < 1$). Thus, particularly under the external liquid-solid mass transfer limitations, this could have significantly reduced the reaction rate, which may explain the over-prediction of the model.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s4.12.png}
\caption{(a) Influence of the Ru/C catalyst ($d_p = 0.45$ mm) weight fraction on the experimental and modeled LA conversions and (b) on the individual resistances (Eqs. 4.24-4.26). The remainder of the weight was attributed to inert SiC particles of a similar size (with an average diameter of 0.48 mm). Other conditions: $C_{LA,0} = 5$ wt\%, $Q_{G,0} / Q_{L,0} = 4.5$, 130 °C, 12 bar H$_2$, $L_{\text{bed}} = 0.8$ m, WHSV = 6.0 g\textsubscript{feed}/(g\textsubscript{cat}\cdot\text{h}).}
\end{figure}

**S4.10. Model extension to the case of (0.5, 1)-th order reaction**

In the case of the LA hydrogenation reaction being considered as 0.5\textsuperscript{th} order in H$_2$ and 1\textsuperscript{st} order in LA, the current model can be adapted by incorporating the corresponding kinetic rate:

$$r_{H_2,R} = w_c \eta k_{H_2,S}^{1/2} C_{LA,S}$$  \hfill (S4.30)

This equation combined with Eqs. 4.6, 4.7, 4.9, is then used to obtain the overall rate of H$_2$ consumption ($r_{H_2}$) as

$$r_{H_2} = \frac{C_{H_2,G} / H}{\frac{1}{V_{\text{bed}} k_L a_i} + \frac{1}{aw_c k_c a_c} + \frac{r_{H_2}}{w_c \eta k_{C_{LA,S}}^2}}$$  \hfill (S4.31)

Then, it can be further derived that
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The differential mass balance equation for LA in the packed bed microreactor is written as

\[ r_{H_2} = \left( \frac{1}{V_{\text{bed}} k_{L,i}} + \frac{1}{\alpha w \varepsilon k_{s,i} a_c} \right) \left( \frac{1}{V_{\text{bed}} k_{L,i}} + \frac{1}{\alpha w \varepsilon k_{s,i} a_c} \right)^2 + \frac{4C_{H_2,G}}{H \left( w \eta k C_{LA,S} \right)^2} \]  

(S4.32)

An integration of Eq. S4.33 (combined with Eq. 4.32) between the microreactor inlet and outlet can then be used to find the LA concentration at the outlet and thus the modeled LA conversion (according to Eq. 4.1). It is obvious that in this case the analytic solution is not straightforward to obtain, and a numerical integration approach might be used.

References


