





## Supplementary Materials

### Kinetic modeling for the gas-phase hydrogenation of the LOHC $\gamma$ -Butyrolactone – 1,4-Butanediol on a copper-zinc catalyst

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#### Section S1: Comparison of different LOHC systems.

**Table S1.** Comparison of different LOHC systems.

Characteristics	GBL/BDO*	H0-BT/H12-BT	H0-DBT/ H18-DBT	H0-NEC/ H12-NEC	TOL/MCH*
Mass H <sub>2</sub> capacity (wt%)	4.5	6.2	6.2	5.8	6.1
Volume H <sub>2</sub> capacity (L <sub>H2</sub> .L <sup>-1</sup> LOHC)	613	788	829	856	680
Reaction enthalpy (kJ.mol <sup>-1</sup> )	31*/42(Liquid)	63.5	65	52	68*
Melting point (°C at 1atm)	-45/20	-30/**	-39/-50	69/84	-95/-127
Boiling point (°C at 1atm)	206/230	280/270	390/370	378/281	101/111
Viscosity (mPa.s at 25°C)	1.90(20°C)/71.5	3.98(20°C)/5.62	37.5/219.7	Solid	6.98·10 <sup>-3</sup> */0.73*
Catalyst	CuZnO supported or bulk	Noble metal	Noble metal	Noble metal	Noble metal
GHS pictograms					

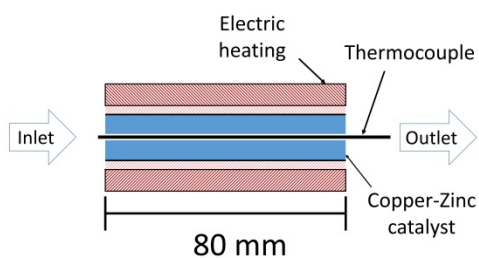
\*Gas-phase [1,16,19-22]. \*\* Data unknown.

#### Section S2: Experimental data extracted from the PhD thesis of J.H. Schlender [25,26]

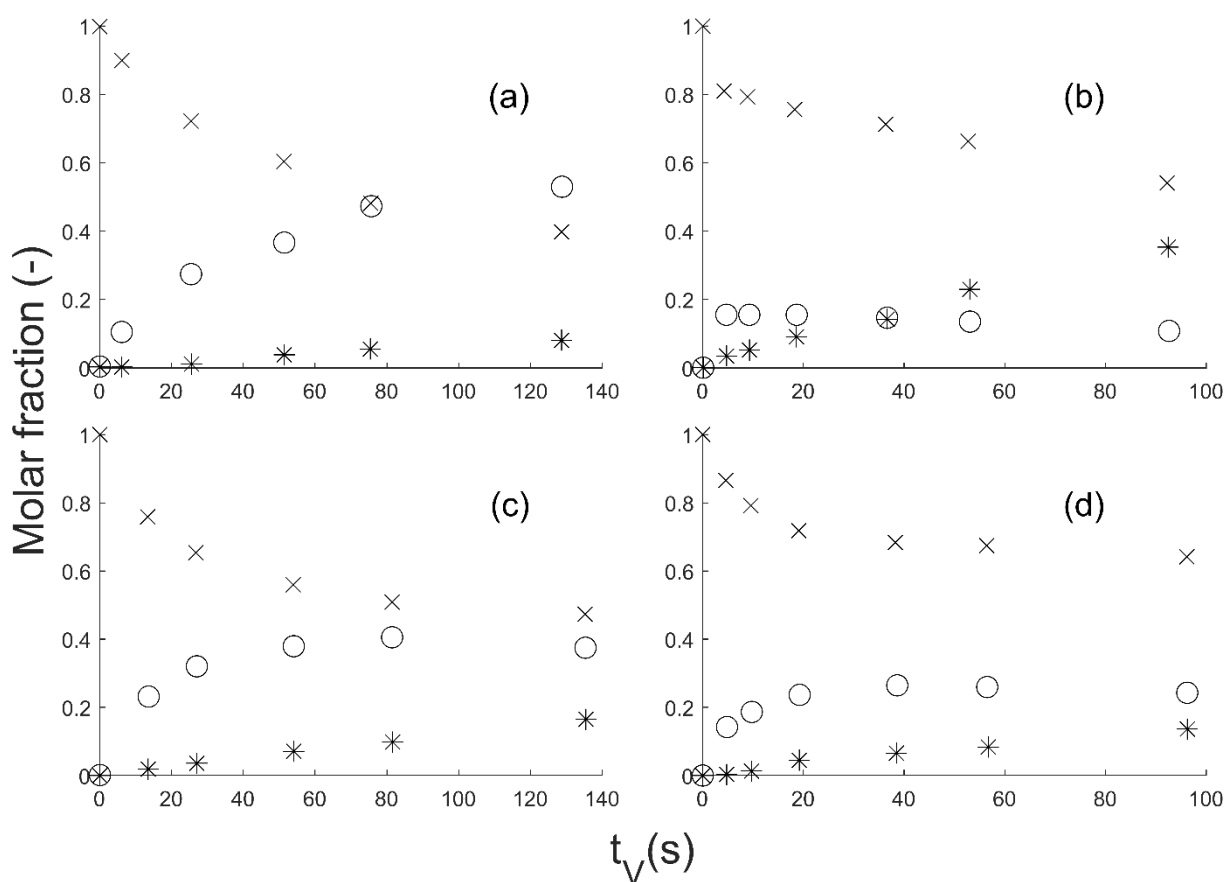
The GBL hydrogenation was performed in gas phase on a CuZnO catalyst (see Table S2) in an isothermal tubular reactor. The reactor was an electrically heated stainless steel tube reactor with 13 mm inner diameter and 200 mm length. The fixed bed includes crushed glass to carry the catalyst and was loaded on a reactor length of 80 mm (Figure S1), making the total volume of the reactive section 9.3 cm<sup>3</sup>. The catalyst loading was about 8g. The mean particle size ( $d_p$ ) was given at about 400  $\mu$ m. Concentrations of the output flow were measured by an online gas chromatograph and concentrations of the input flow were measured by bypassing the reactor. In order to vaporize the reactants at those conditions, reactants were stripped in a H<sub>2</sub> flow. This led to a large excess of hydrogen in the reactor (molar ratio H<sub>2</sub>/GBL = 90). Data were obtained by adjusting the gas flow rate in the reactor to obtain output concentrations at different residence times. Temperature ranges from 200°C to 240°C and pressure ranges from 25 bar to 35 bar were screened. The catalyst was prepared by co-precipitation along the method proposed by Herman et al. [28] and contained 15mol% Cu and 85mol% ZnO. J.H. Schlender presented his results with  $t_{mv} = t_v \frac{m_{cata}}{V_R}$  the modified residence time. In this paper, we will use  $t_v = \frac{V_R}{Q}$

**Table S2.** Chemical and geometrical properties of the copper-zinc catalyst used for the kinetic measurements [25]

Synthesis method	Co-precipitation
Chemical composition	15mol% Cu - 85mol% ZnO
Particle diameter (cm)	4·10 <sup>-2</sup>
Characteristic length (cm)	6.67·10 <sup>-3</sup>
Mean pore radii (cm)	2·10 <sup>-8</sup>
Porosity (-)	0.26
Tortuosity (-)	3
Specific surface area of the catalyst grains (m <sup>2</sup> .g <sup>-1</sup> )	30.1
Specific surface area of the copper particles (m <sup>2</sup> .g <sup>-1</sup> )	4.2



**Figure S1.** Scheme of the active part of the reactor.



**Figure S2.** GBL (X) BDO (O) and side products (SP) (\*) molar fraction vs. time on stream ( $t_V$ ) (a) 35 bar, 200°C (b) 25 bar, 240°C (c) 35 bar, 220°C (d) 25 bar, 220°C. Data were extracted from the PhD thesis of J.H. Schlender [25].

### Section S3: Intraparticle diffusion and capillary condensation

The experimental data showed that the reaction rates are slower at higher pressure. Diffusion of reactants and capillary condensation inside the catalyst pores were investigated to explain this aspect.

The effect of reactant diffusion was discussed inside the PhD thesis of J.H. Schlender, where Thiele modulus was evaluated for pressures of 5 and 35 bar. The results showed that diffusion played no role in the limitation of the reaction kinetics with Thiele modulus ranging between 0.004 for 5 bar and 0.005 for 35 bar. Our calculation with the extrapolated Model 3 for 35 bar and 240°C, resulted in a Thiele modulus of 0.01. Indeed, the resulting Thiele modulus values being below 0.09, the diffusion of reactants inside the catalyst pores does not affect the observed reaction kinetics and cannot explain the

difference in reaction rates between 25 and 35 bar. Further calculation details can be found in the PhD thesis of J.H. Schl nder.

Capillary condensation was then investigated for GBL, BDO, THF, BuOH and water through Kelvin’s law:

$$R_{\text{crit}} = \frac{2\gamma v_m}{RT \ln\left(\frac{P}{P_{\text{sat}}}\right)} \quad \#(37)$$

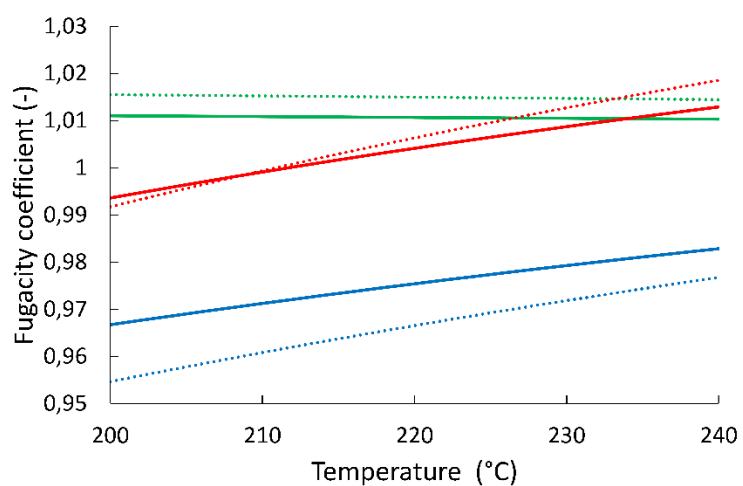
Capillary condensation describes the liquefaction of a gas through capillary forces inside a small channel (the catalyst pores in this case). This could explain the gap in reaction kinetics with pressure changes, because the diffusion of chemicals in liquid phase is much slower than in gas phase, resulting in slower reaction rates caused by a liquid film hindering the access of reactants towards active sites. Kelvin’s law gives the critical radius for which capillary condensation starts to appear. If the radius of the catalyst is greater than the critical radius, then capillary condensation will not happen inside the catalyst. Thermodynamic properties for each component were extracted through the software ProPhyPlus for pressures ranging from 25 to 35 bar and temperatures ranging from 200 C to 240 C. J.H. Schl nder estimated a mean pore radius of  $2 \cdot 10^{-8}$  m. Table S3 shows that critical radius for each component is well below the mean pore radius and, therefore, rules out the possibility of a condensation of compounds inside the catalyst pores.

**Table S3.** Critical radius for catalytic pores below which condensation of compounds can occur. Thermodynamic properties were extracted from ProPhyPlus database.

Pressure (bar)	Temperature (�C)	Critical radius (m)				
		GBL	BDO	Water	BuOH	THF
25	200	$3.0 \cdot 10^{-10}$	$3.2 \cdot 10^{-10}$	$8.3 \cdot 10^{-10}$	$6.0 \cdot 10^{-10}$	$1.6 \cdot 10^{-9}$
	220	$3.1 \cdot 10^{-10}$	$3.4 \cdot 10^{-10}$	$4.5 \cdot 10^{-9}$	$8.6 \cdot 10^{-10}$	0
	240	$3.3 \cdot 10^{-10}$	$3.7 \cdot 10^{-10}$	0	$2.0 \cdot 10^{-9}$	0
35	200	$2.7 \cdot 10^{-10}$	$3.0 \cdot 10^{-10}$	$4.9 \cdot 10^{-10}$	$4.4 \cdot 10^{-10}$	$6.3 \cdot 10^{-10}$
	220	$2.8 \cdot 10^{-10}$	$3.1 \cdot 10^{-10}$	$8.4 \cdot 10^{-10}$	$5.3 \cdot 10^{-10}$	$9.6 \cdot 10^{-10}$
	240	$2.9 \cdot 10^{-10}$	$3.3 \cdot 10^{-10}$	$6.4 \cdot 10^{-9}$	$7.1 \cdot 10^{-10}$	0

#### Section S4: Ideal gas hypothesis

Every model in this paper (either kinetic or thermodynamic) is built under the assumption of the ideal gas hypothesis. However, with pressure ranging from 25 bar to 35 bar, it becomes reasonable to challenge that assumption. In order to study the validity of the application of the ideal gas hypothesis under the conditions studied, fugacity coefficients were calculated for a mixture close to those presented in this article using the thermodynamic property calculation software ProPhyPlus. The closest a fugacity coefficient is to one, the closest the behaviour of a gas is to ideal. In absence of experimental data on liquid-gas phase equilibria, a predictive model using a homogeneous approach is used for the calculations. The Soave-Redlich-Kwong (PSRK) predictive model presented in ProPhyPlus uses a Redlich-Kwong equation of state, with a Mathias-Copeman alpha function and PSRK mixing rules. The model used for the calculation of activity coefficients is UNIFAC PSRK. Fugacity coefficients are calculated at 25 bar and 35 bar for a temperature range of 200 C to 240 C. The mixture used in the simulation consists of 99 mol% H<sub>2</sub>, 0.5 mol% GBL and 0.5 mol% BDO.



**Figure S4.** Calculated fugacity coefficient for GBL (blue), BDO (red) and H<sub>2</sub> (green). Full lines: 25 bar ; dotted lines: 35 bar. Calculations are done using a PSRK model. Gas composition (mol%) : 99% H<sub>2</sub>, 0.5% GBL, 0.5% BDO.

Figure S4 shows that the fugacity coefficients are close to those of the studied conditions, especially for hydrogen, which constitutes up to 99 mol% of the gas. Therefore, it is reasonable to assume the ideal gas in this paper.