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THE GREEN SYNTHESIS OF gamma-VALEROLACTONE USING HOMOGENEOUS AND HETEROGENEOUS CATALYSTS SYSTEMS

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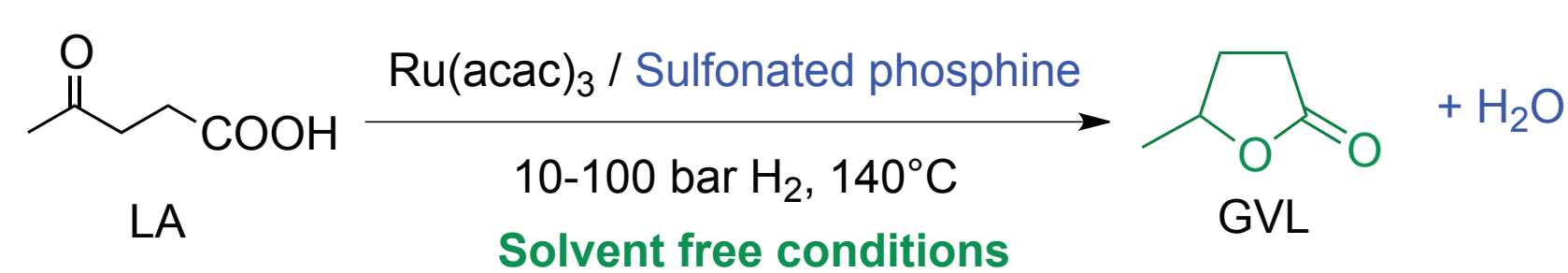
INTRODUCTION

Currently, fossil resources provide more than 95% of our energy needs and feedstock of chemical industry. Their replacement is one of the most challenging tasks of this generation. Especially, the production of carbon-based chemicals from sustainable resources has become a key issue for the chemical industry. The intensive research activities on biomass conversion has led to the identification of unique platform chemicals such as 5-hydroxymethyl furfural (5-HMF) [1], levulinic acid (LA) [2], and gamma-valerolactone (GVL) [3]. These molecules can replace the currently used fossil-based chemicals or serve as renewable feedstock for their production.

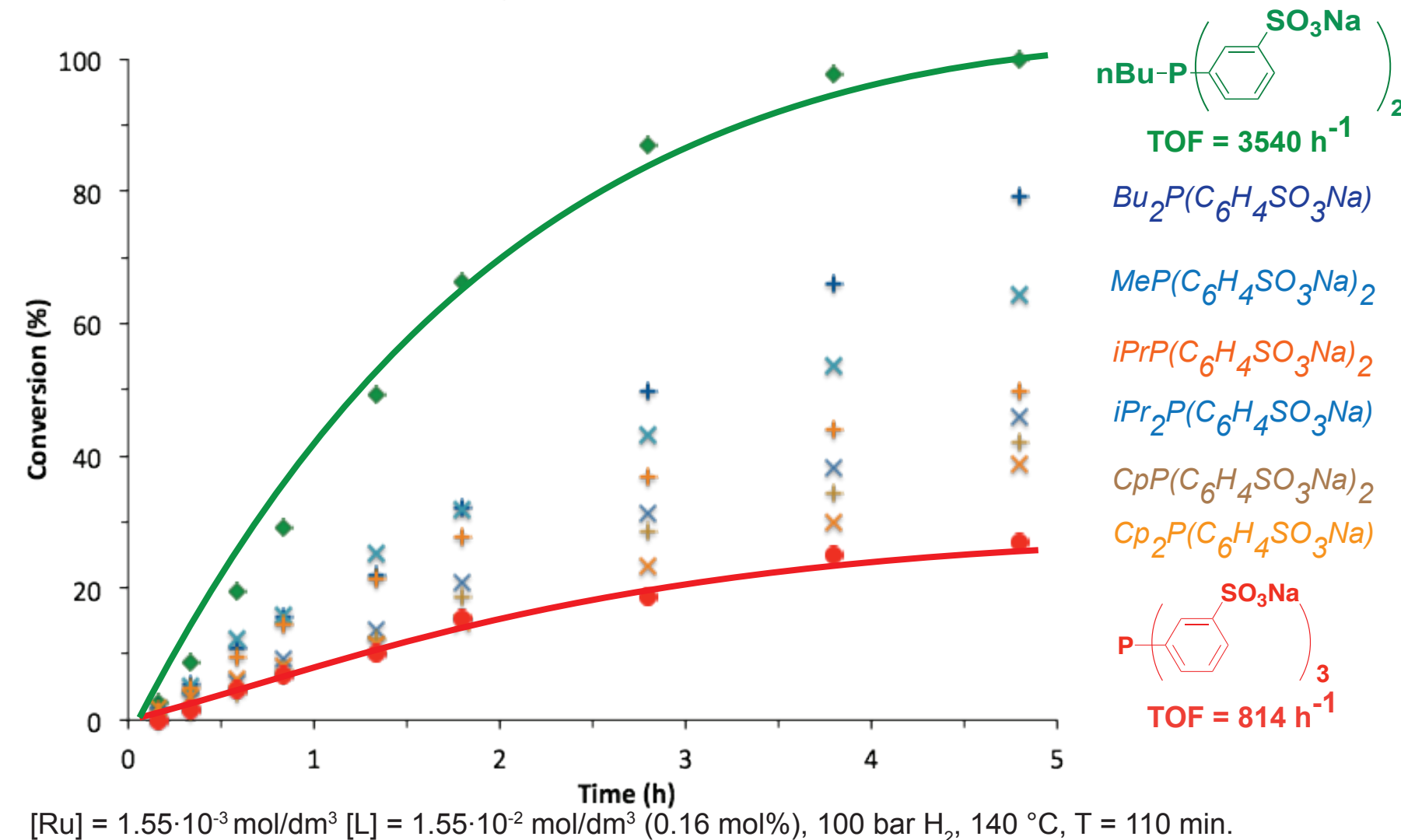
Due to its outstanding physical and chemical properties, GVL was suggested to be a sustainable liquid by Horváth *et al* in 2008 [1]. Since then, GVL has been successfully used for the production of transportation fuels, butane isomers, octane booster, alkanes, 2-methyl-tetrahydrofuran, pentane-1,4-diol, ionic liquids, adipic acid, alkyl valerates, polymers, pentanoic acid, or as a solvent.

Since, the most effective protocol to manufacture GVL is the selective reduction of LA to 4-hydroxyvaleric acid, which subsequently turns to GVL *via* ring closure dehydration, we investigated the Ru catalyzed homogeneous and heterogeneous hydrogenation of LA to GVL to develop an efficient and environmentally benign catalytic systems.

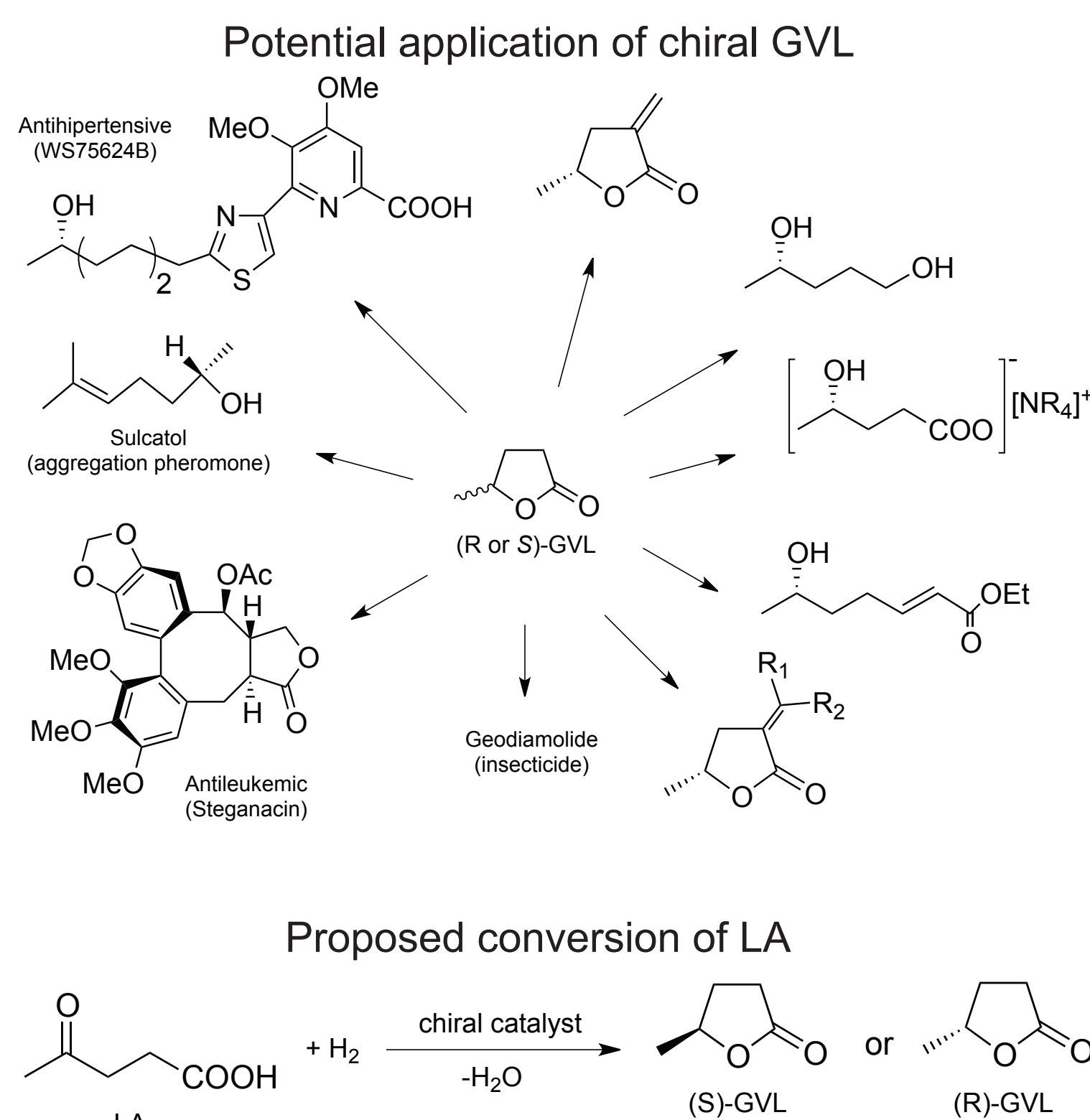
Hydrogenation of LA in the presence of catalyst *in situ* formed from Ru(acac)₃ and R_nP(C₆H₄-m-SO₃Na)_{3-n} (n = 1, 2; R = Me, Pr, iPr, nBu, Cp) ligands under solvent- and promoter-free reaction conditions



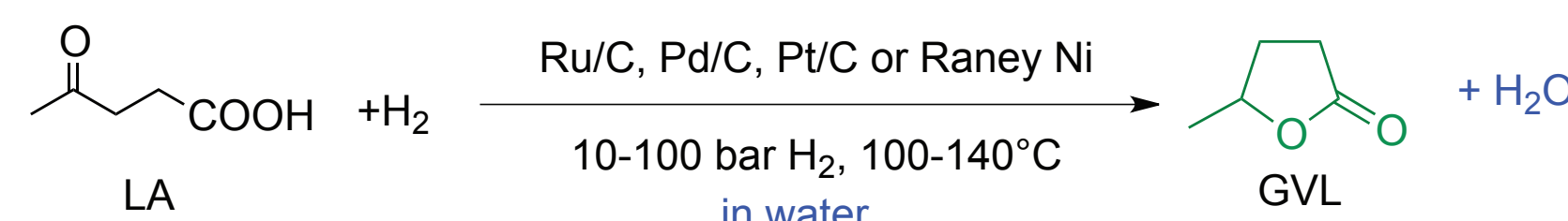
Effect of different ligand on the conversion of levulinic acid



Asymmetric hydrogenation of LA to form optically active GVL using Ru-based chiral catalyst systems.



Heterogeneously catalyzed hydrogenation of LA to GVL using continuous flow reactor, H-Cube® and H-Cube Pro® equipped with 5% Ru/C, 10% Pd/C, and Raney-Ni CatCart®

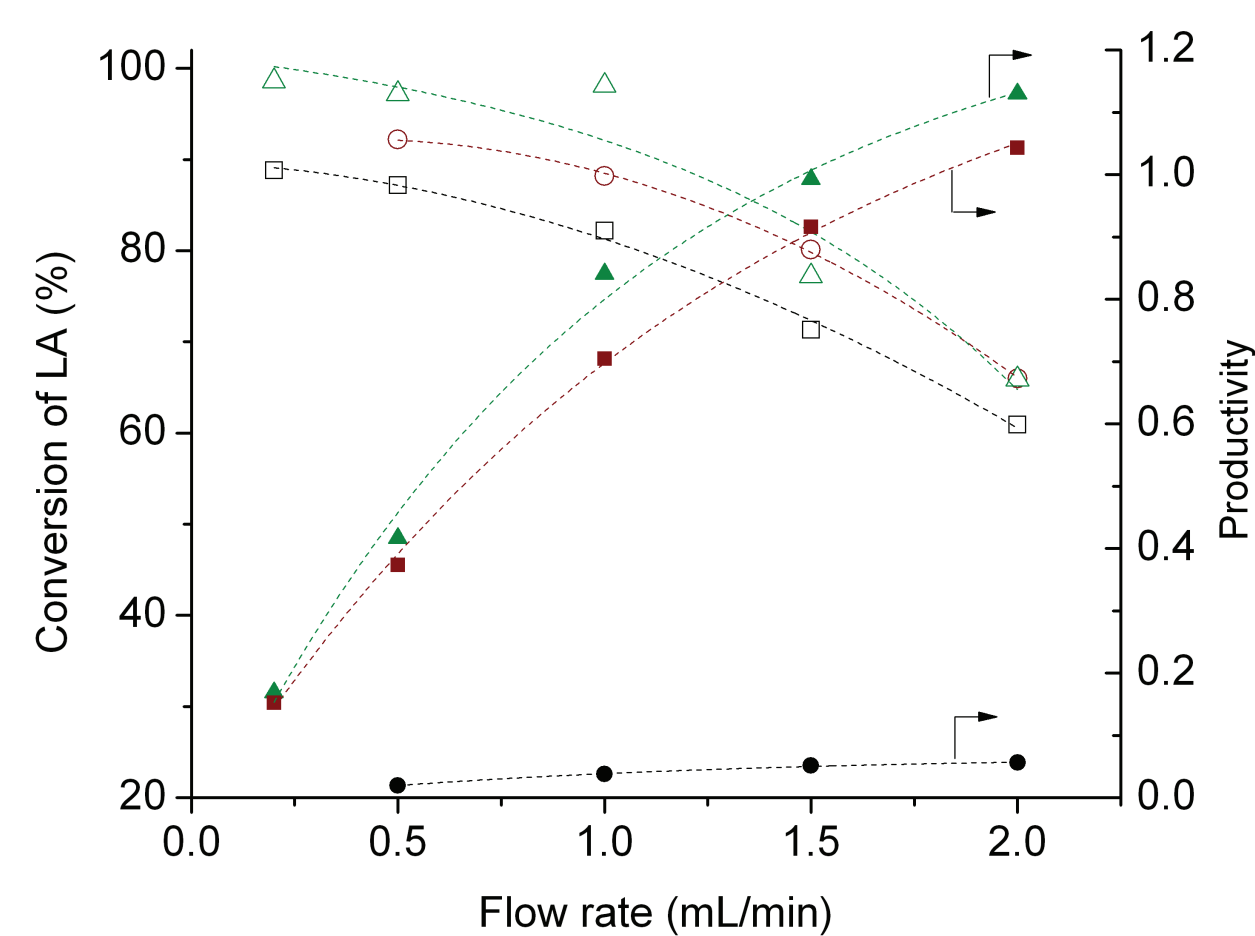


Continuous-flow hydrogenation of LA to GVL using H-Cube®

Entry	Catalyst	p (bar)	T (°C)	Conv. (%)	Productivity (mol _{GVL} × g _{Metal} ⁻¹ × h ⁻¹)
1	Pd/C	10	100	2.6	0.011
2	Pd/C	50	100	4.5	0.019
3	Pd/C	100	100	15.9	0.068
4	Pd/C	100	140	44.5	0.190
5	Ru/C	10	100	25.1	0.215
6	Ru/C	50	100	68.0	0.582
7	Ru/C	100	100	82.9	0.710
8	Ru/C	10	140	97.1	0.832
9	Raney-Ni	10	100	76.1	0.032
10	Raney-Ni	50	100	83.8	0.035
11	Raney-Ni	100	100	88.9	0.038

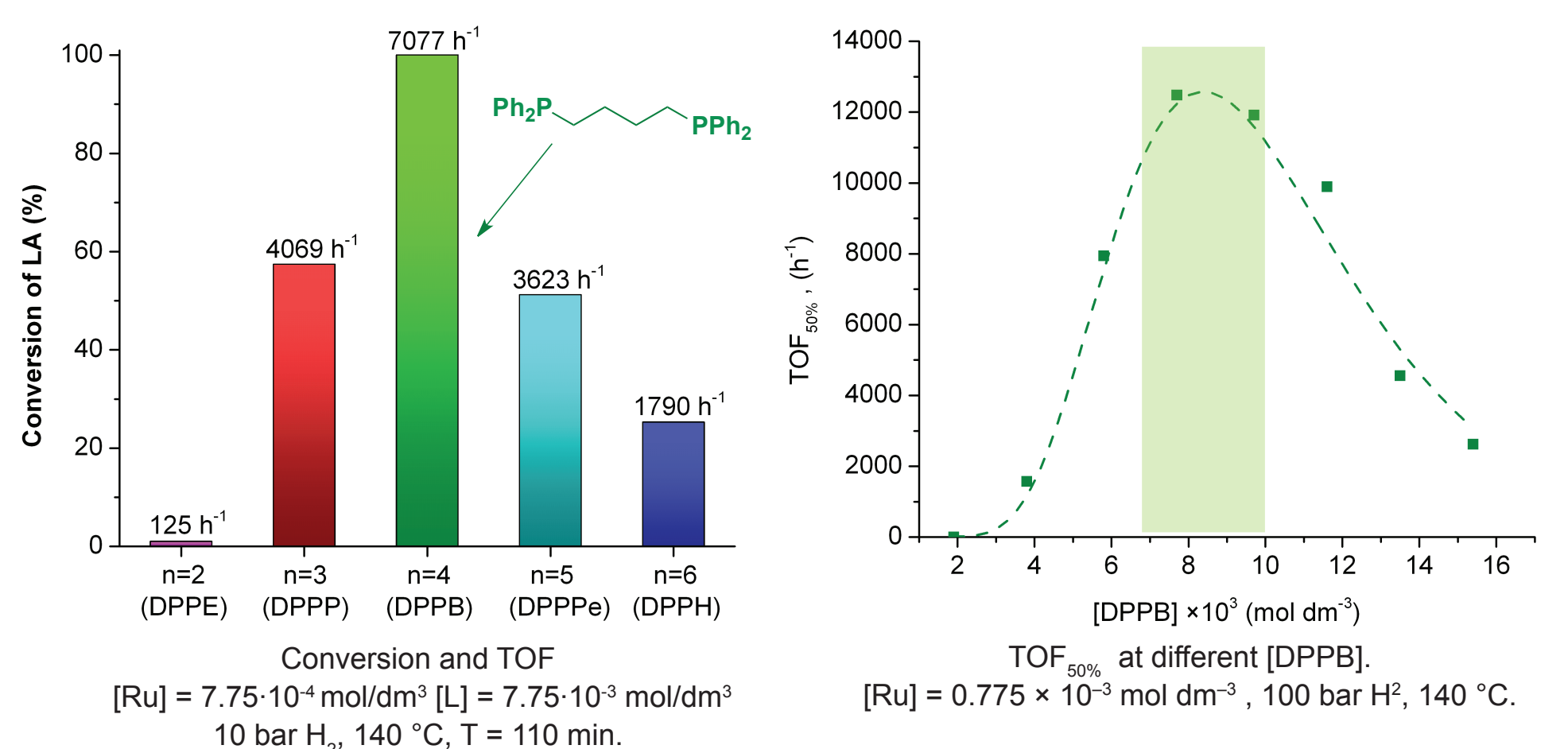
Reaction Conditions: Flow rate: 1.0 mL/min, 0.232 g (1.997 mmol) LA in 20 mL water (0.1 M).

The effect of the flow rate on the conversion and productivity (mol_{GVL} × g_{Metal}⁻¹ × h⁻¹)

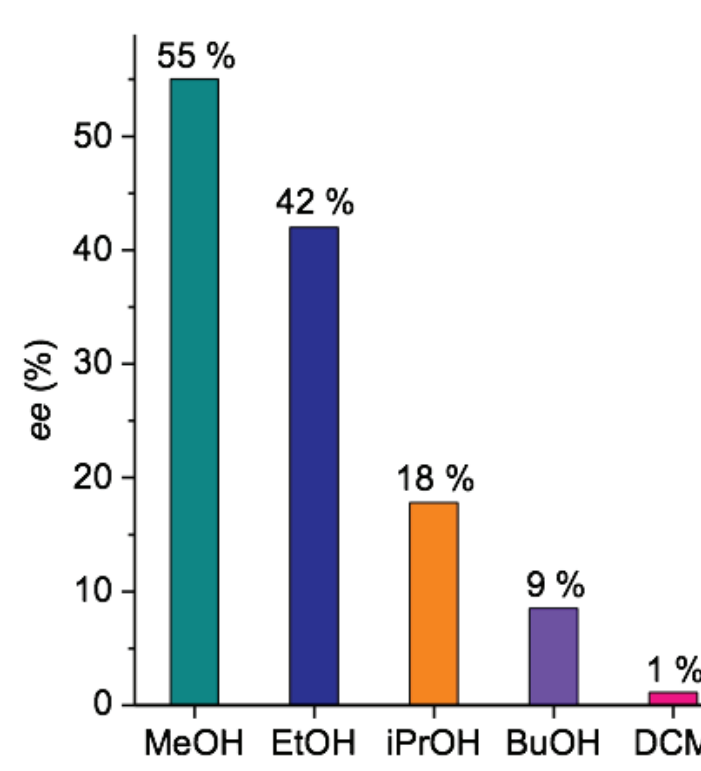


Conversion & productivity: Ru/C (□ & ■); Raney Ni (○ & ▲); Ru/C + BuDPPDS (△ & ▲).
Reaction conditions: 0.232 g (1.997 mmol) LA in 20 mL H₂O (0.1 M), 100 bar, 100 °C.

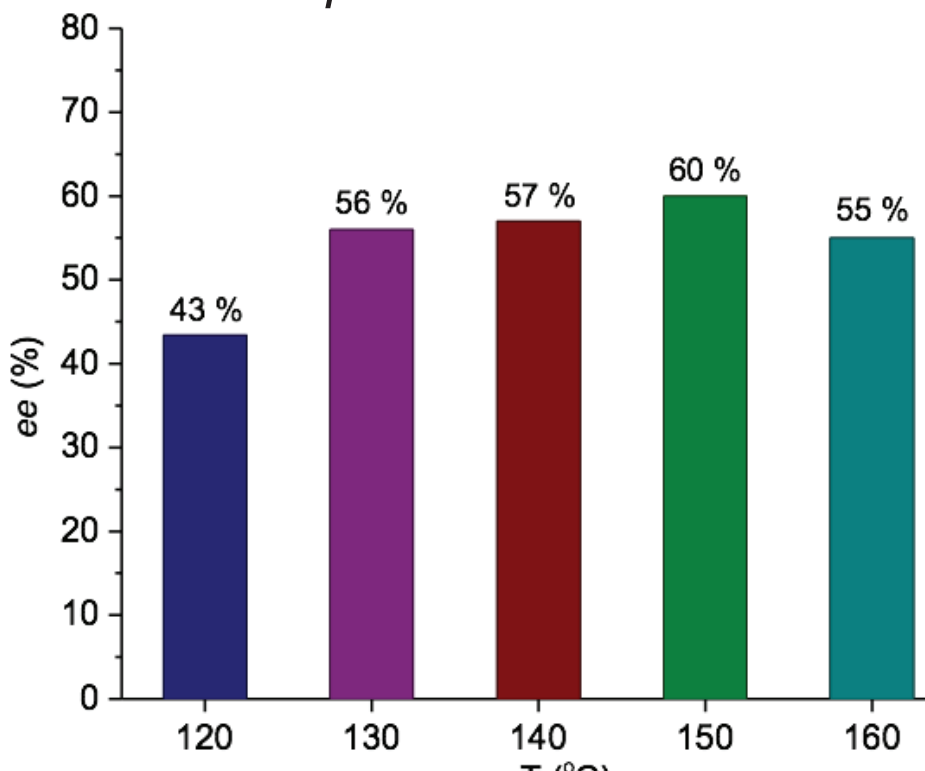
The activity of the catalyst can be improved by the application of Ph₂P-(CH₂)_n-PPh₂ (n = 2 - 6) type bidentate ligands



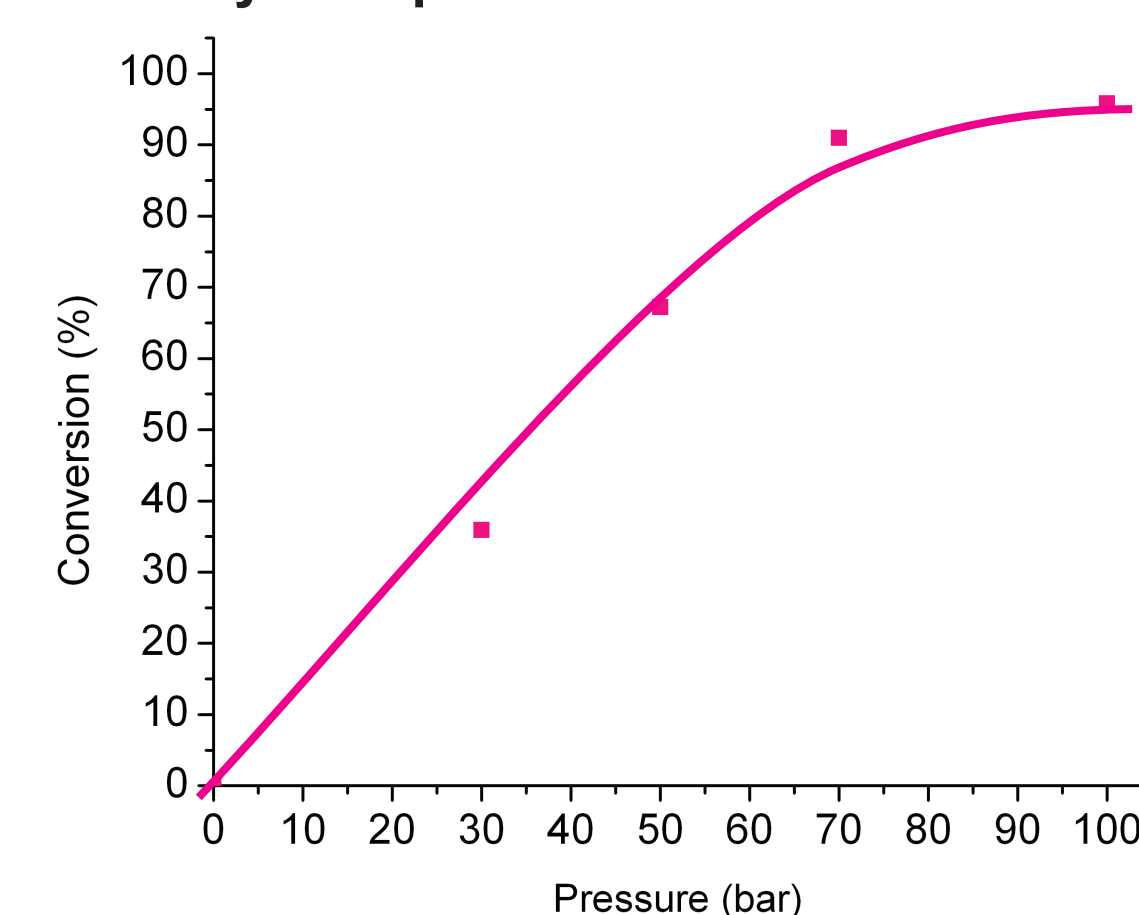
Solvent Effect



Temperature Effect

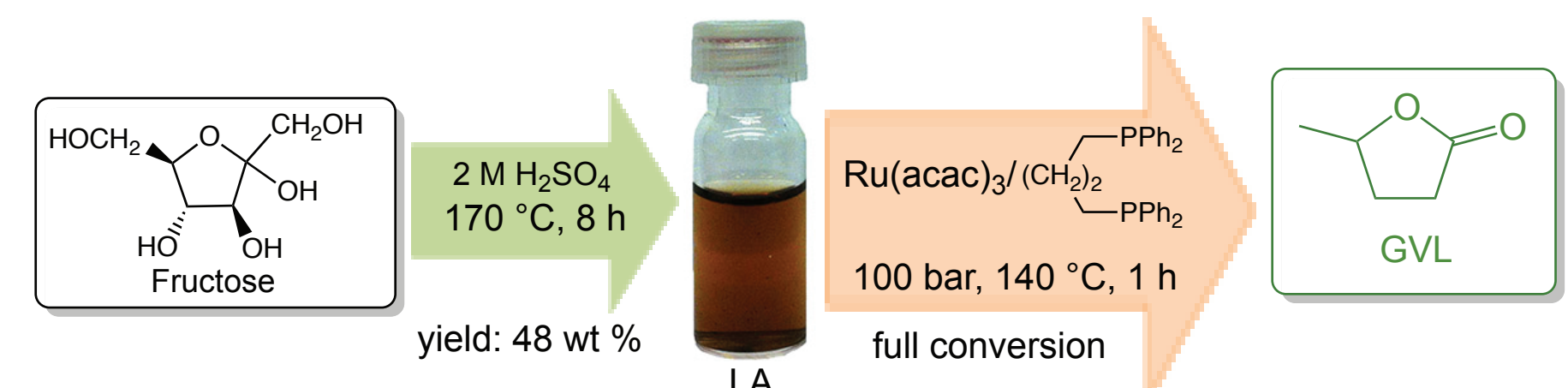


The effect of system pressure on the conversion of LA

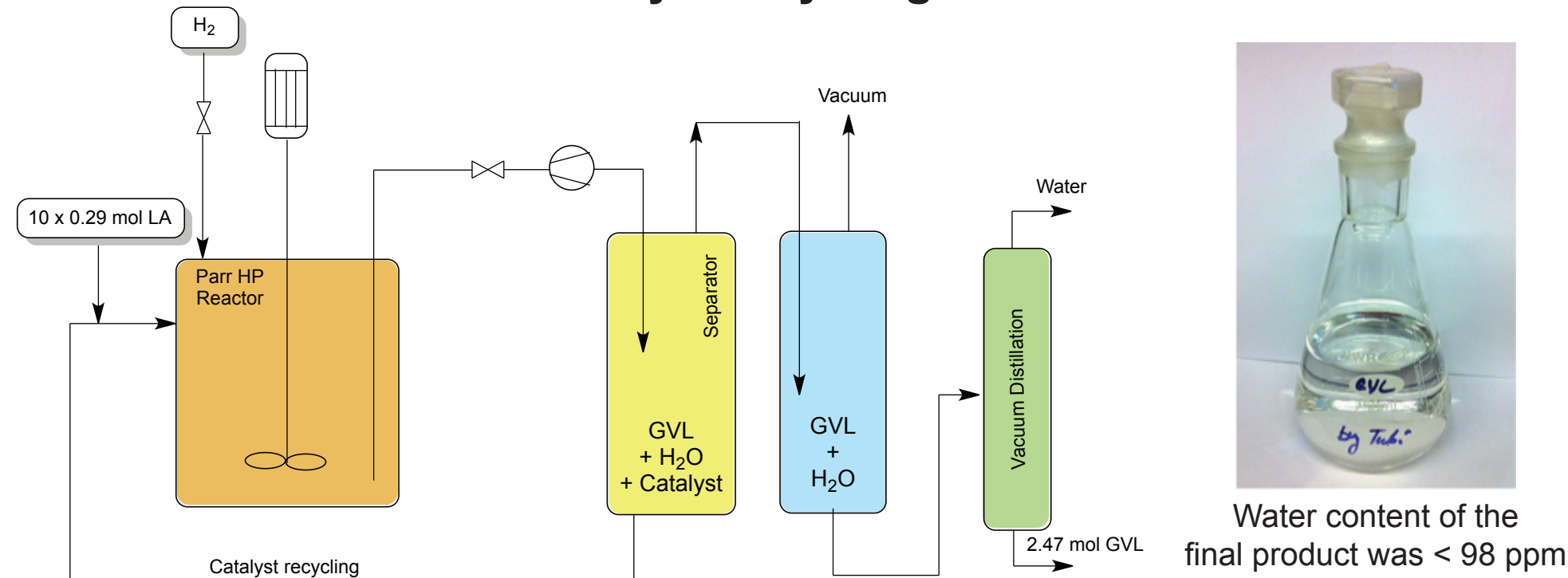


Reaction conditions: flow rate: 1.0 mL/min, 0.232 g (1.997 mmol) LA in 20 mL water (0.1 M), [Bu-DPPDS] = 0.15 mmol/L, 100 °C.

Conversion of “real” biomass based levulinic acid to GVL



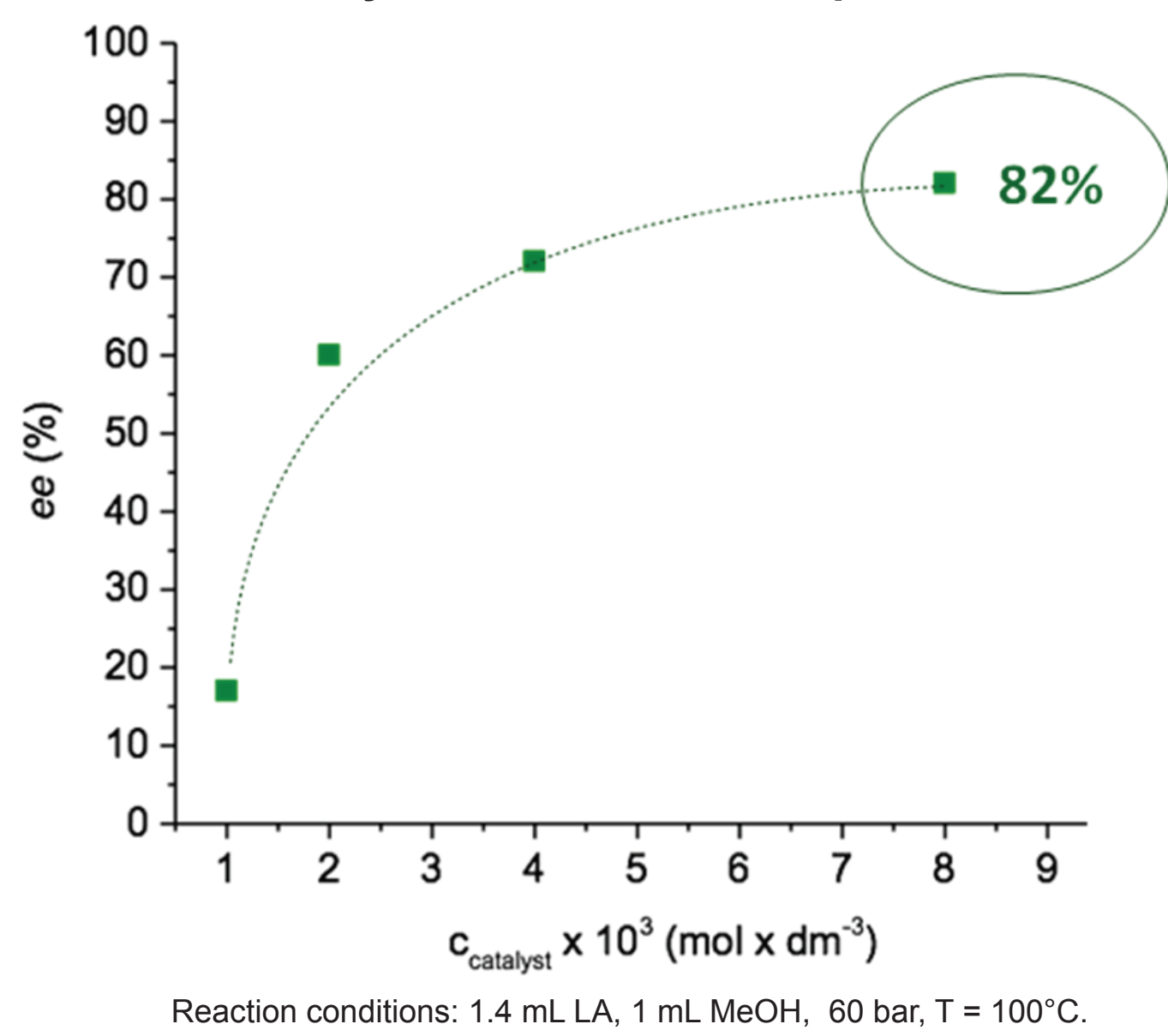
Catalyst recycling



In conclusion: the LA can be quantitatively converted to GVL in the presence of catalyst *in situ* formed from Ru(acac)₃ & DPPB under 10 - 100 bar H₂ at 100 - 160 °C. The highest TOF = 21300 h⁻¹ [4, 5].

In conclusion: It was revealed that LA can be converted in the presence of chiral (S)-[(RuCl(SEGPHOS®))₂(μ-Cl)]₂[NH₂Me]₂ catalyst in MeOH as solvent to GVL with the highest ee of 82% in the under 60 bar H₂ at 150 °C.

Catalyst concentration dependence



The effect of ligand concentration on the conversion of LA

Entry	Catalyst	[Bu-DPPDS] (mmol/L)	Conv. (%)	Productivity (mol _{GVL} × g _{Metal} ⁻¹ × h ⁻¹)
1	Ru/C	0	82.9	0.710
2	Ru/C	0.075	94.2	0.807
3	Ru/C	0.15	95.6	0.820
4	Ru/C	1.5	96.4	0.826
5	Ru/C	5	97.3	0.834
6	Ru/C	10	97.0	0.831
7	Ru/C	15	98.5	0.844
8	Raney Ni	0.15	99.3	0.042
9	Pd/C	0.15	16.3	0.069

Reaction conditions: flow rate: 1.0 mL/min, 0.232 g (1.997 mmol) LA in 20 mL water (0.1 M), 100 bar, 100 °C.

In conclusion: We demonstrated that both H-Cube® and H-Cube Pro™ can be used successfully for the continuous production of gamma-valerolactone from levulinic acid under 100 bar hydrogen at 100 °C. High conversion was achieved by using 5% Ru/C and Raney Ni CatCart®. The conversions exceeded 82.9% with 5% Ru/C catalyst, which was further increased to 98.5% by the addition of Bu-DPPDS ligand [6].

Acknowledgement

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