



Deliverable 2.6

Report on implementation of optimal catalyst conditions in CSTR system

Demonstration of solvent and resin production from lignocellulosic biomass via the platform chemical levulinic acid

The project leading to this application has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation programme under grant agreement No 720695



Horizon 2020
European Union Funding
for Research & Innovation

About GreenSolRes

The need to establish economic and sustainable large-scale operations for the conversion of renewable resources to chemical building blocks is becoming increasingly urgent in the context of climate change and depleting fossil fuel reservoirs. Pathways for manufacturing of bio-based fuels and chemicals have been developed but most of them rely on sugar and starch crops for feedstock. GreenSolRes aims at a sustainable and competitive industrial production of the platform chemical levulinic acid (LVA) from non-food lignocellulosic biomass. Further, the conversion of LVA and LVA esters into industry relevant building blocks γ -valerolactone (GVL), 1-methyl-1,4-butanediol (MeBDO) and 2-methyltetrahydrofuran (2-MTHF) will take place by new catalytic methods developed during the course of this project. Finally, these chemicals will be upgraded to solvents and resin monomers for the production of high added value adhesives and consumer products. This project was started in September 2016 and has a duration of five years.

Project Coordinator



Project Office



Consortium



About this document

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Publishable Summary

Ruthenium/triphos catalysts have been found as promising catalyst lead structure for the hydrogenation of Levulinic acid (LVA) to γ -valerolactone (GVL), 1-methyl-1,4-butanediol (MeBDO) and 2-methyltetrahydrofuran (2-MTHF). The envisaged application of the system in a continuous stirred tank application (CSTR) requires detailed tailoring of the molecular catalyst for application in a reaction system on enlarged scale. Consequently, catalytic hydrogenation of LVA was performed in 500 mL autoclaves with selected catalyst systems, resulting in good yields of GVL and MeBDO as the main product. The investigation on optimized reaction parameters were made at combined variation of the hydrogen pressure, the reaction solvent and the selected ruthenium/triphos catalyst structures, resulting in suitable reaction parameters for the CSTR application.

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List of Schemes

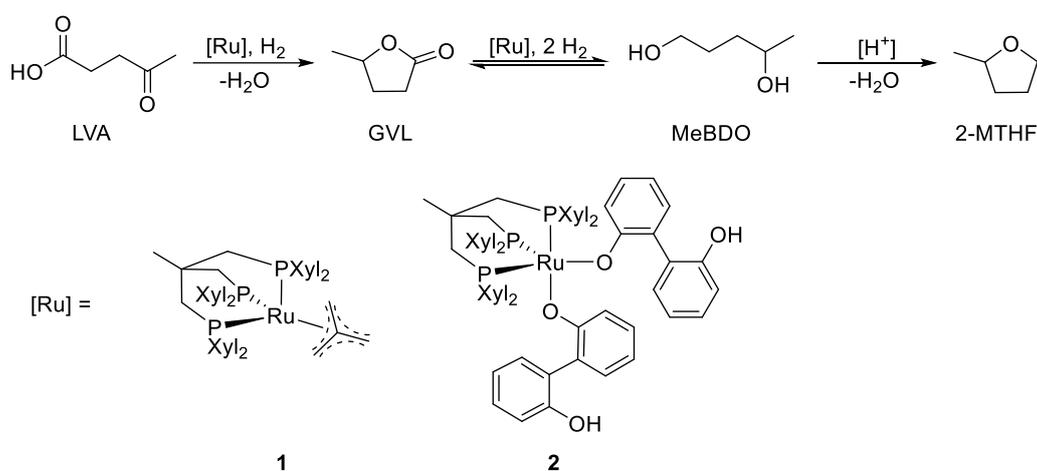
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Abbreviation

2-naph	2-Naphtholato
bph	2- <i>ortho</i> -Phenylolphenolato
cod	1,5-Cyclooctadiene
CSTR	Continuous stirred tank reactor
eq	Equivalent [mol/mol]
δ	Chemical shift
GC	Gas chromatography
GVL	γ -Valerolactone
LVA	Levulinic acid
MeBDO	1-Methyl-1,4-butandiol
MTHF	Methyltetrahydrofuran
NMR	Nuclear magnetic resonance
p	Pressure [bar]
ppm	Parts per million
rpm	Rotations per minute
T	Temperature [°C]
THF	Tetrahydrofuran
tmm	Trimethylenemethane
TON	Turn over number [mol/mol]
Xyl	3,5-Dimethylphenyl
Xyl-triphos	1,1,1-Tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane

1 Introduction

The transition metal complexes $[\text{Ru}(\text{xyl-triphos})(\text{tmm})]$ (**1**) (xyl-triphos = 1,1,1-Tris-(di(3,5-dimethylphenyl)phosphinomethyl)ethane, tmm = trimethylenemethane) and $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ (**2**) could be established as suitable molecular catalysts for the selective hydrogenation of levulinic acid (LVA) and γ -valerolactone (GVL) (see Scheme 1). Specifics on this development process were already reported in Deliverables 2.1 and 2.16. In initial investigations, high TONs were obtained for the formation of MeBDO with catalysts **1** and **2**.



Scheme 1: Reaction system of the hydrogenation of LVA to GVL and MeBDO, using the molecular catalysts **1** and **2**. Included is the subsequent acid catalyzed cyclization to 2-MTHF with acid co-catalyst.

In the present deliverable, the detailed catalyst compositions and reaction conditions for the hydrogenation of LVA to MeBDO were established in batch mode, enabling in the next development step the development of a tailored CSTR setup. Additionally, catalyst and product solution were after the experiments separated by distillation, allowing to generate additional important information with respect to catalyst recycling, finally described in more detail in Deliverable 2.13.

2 Optimization of Reaction Conditions

In Deliverable 2.1, the activity of novel ruthenium/triphos complexes in the hydrogenation of GVL were investigated. Reactions were carried out in 10 mL stainless steel autoclaves at 50 bar H₂ using 0.1 mol% catalyst relative to the substrate.^[1] Besides [Ru(xyl-triphos)(tmm)] **1** (xyl-triphos = 1,1,1-Tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane, tmm = trimethylene-methane), the [Ru(xyl-triphos)(bph)₂] complex **2** (bph = 2-*ortho*-phenylolphenolato) (Figure 1) showed high activities in the conversion of GVL to MeBDO under the investigated conditions. Moreover, with catalyst **2** consecutive hydrogenation reactions could be performed by adding additional portions of GVL after each hydrogenation cycle without further product separation. In these experiments an increased activity of the catalyst **2** could be observed in the second and third cycle compared to experiments with the catalysts **1**. Thus, complex **2** will be used as catalyst for the optimization study in 500 mL stainless steel autoclaves, while complex **1** is used as the reference catalyst.

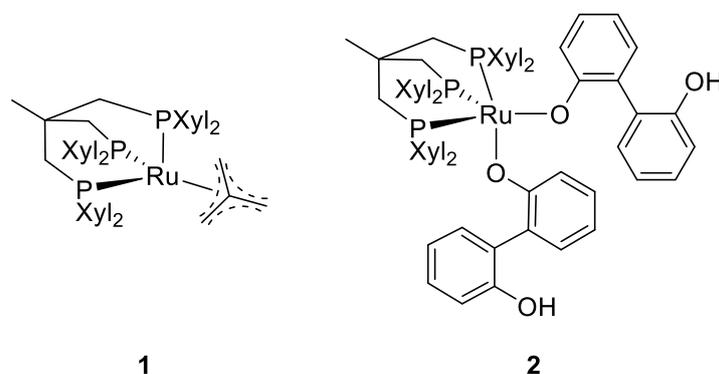


Figure 1: Structure of [Ru(xyl-triphos)(tmm)] **1** and [Ru(xyl-triphos)(bph)₂] **2**.

2.1 Variation of Hydrogen Pressure

Promising results in the hydrogenation of GVL could be obtained at a temperature of 160 °C as reported in Deliverable 2.1, which is the starting point of the present optimization study for the CSTR setup.^[1] It is known that the addition of acid co-catalysts lead to the formation of 2-MTHF, due to the acid catalyzed dehydration/cyclization of MeBDO. Therefore, reactions were performed in 500 mL stainless steel autoclaves under solvent-free conditions in the absence of acid co-catalysts, allowing obtaining MeBDO as the main product. Before the experiments, the autoclave was shortly heated at 400 °C and the glass liner and magnetic stir bar were baked out in the oven at 120 °C prior to be placed into the autoclave. Next, the autoclave was closed, subsequently evacuated and flushed with argon three times. The catalyst was dissolved in LVA, which was degassed *in vacuo* prior to use and the solution was transferred into the autoclave under argon countercurrent flow. Reaction conditions were

controlled by *LabView* and the H₂ pressure was kept constant using a mass flow controller (MFC).

The first hydrogenation reactions were performed using 100 mL LVA and 0.01 mol% of **1** as catalyst at 160°C for 40 h under variation of the H₂ pressure ($p = \text{const.}$). The obtained product yields were analyzed by gas chromatography (GC). The results are shown in Figure 2 and in the appendix (Page 21, Table 3).

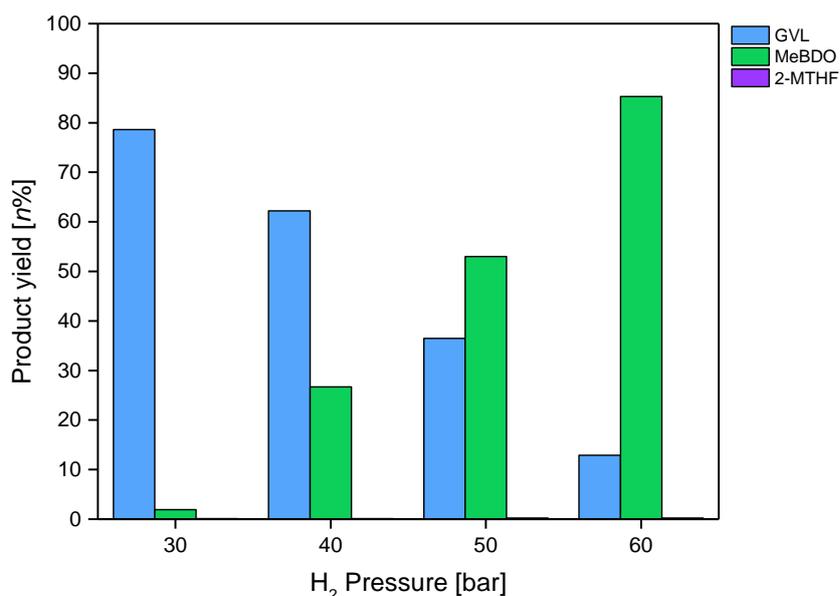


Figure 2: Hydrogenation of LVA with 0.01 mol% **1** under variation of the H₂ pressure. Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.0973 mmol, 0.01 mol%), H₂, 160 °C, 800 rpm, 40 h. Product yields determined by GC using 1-hexanol as internal standard.

Applying a H₂ pressure of 30 bar led to 92% conversion of LVA obtaining 79% GVL with a turn over number (TON) of 7611 for the conversion to GVL. At a H₂ pressure of 40 bar, full conversion of LVA obtaining 62% GVL and 27% MeBDO was achieved. A further increase of the H₂ pressure up to 60 bar led to 13% GVL and 85% MeBDO with full conversion of LVA. When increasing the H₂ pressure from 30 to 60 bar constant marginal 2-MTHF yields were obtained (0.1-0.2%). The yield of GVL decreased and the yield of MeBDO increased in a linear correlation with increasing the H₂ pressure.

Under the same reaction conditions (100 mL LVA, 0.01 mol% [Ru], 160 °C, 40 h), hydrogenation reactions were performed using complex **2** as catalyst under variation of the H₂ pressure. The results are shown in Figure 3 and in the appendix (Page 22, Table 4).

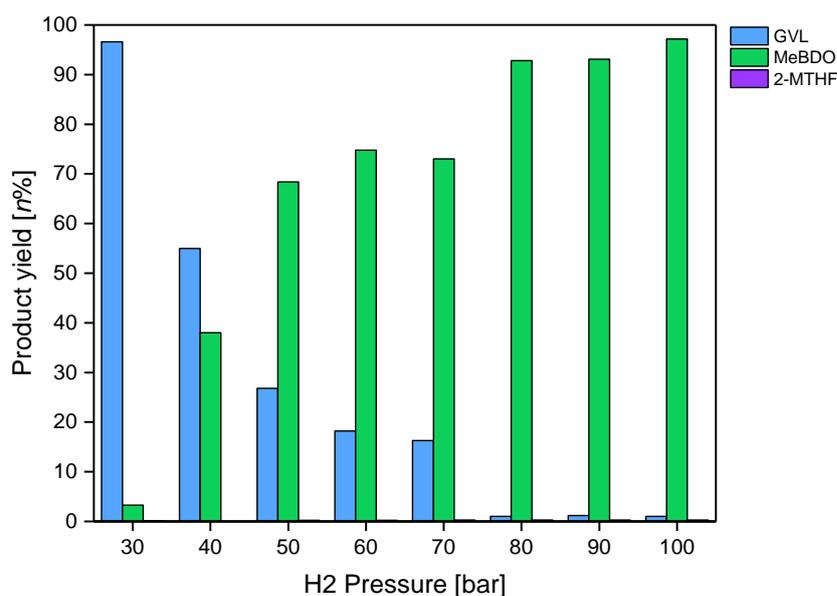


Figure 3: Hydrogenation of LVA with 0.01 mol% **2** under variation of the H₂ pressure. Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.0973 mmol, 0.01 mol%), H₂, 160 °C, 800 rpm, 40 h. Product yields determined by GC using 1-hexanol as internal standard.

At a H₂ pressure of 30 bar, already 99% conversion of LVA could be achieved obtaining 97% GVL with a TON_{GVL} of 10326, demonstrating a higher activity of **2** compared to **1** under the same conditions. Applying a H₂ pressure of 40 bar decreased the yield of GVL (55%), while the yield of MeBDO increased from 3% to 38%. Increasing the pressure to 50 bar led to 27% GVL and a good yield of MeBDO (68%) with a TON of 7294 for the conversion of LVA to MeBDO. Applying H₂ pressures of 60 bar and 70 bar did not change the product composition significantly. Only a slight increased yield of MeBDO could be observed (75%). A possible explanation might be the high viscosity of MeBDO entailing H₂ transport limitations. Diluting the reaction solution by addition of an additional solvent could solve this problem. Increasing the H₂ pressure to 80 bar resulted in 93% MeBDO with a TON_{MeBDO} of 9392. A further increase of the H₂ pressure up to 100 bar led to an almost quantitative yield of MeBDO (97%) with a TON_{MeBDO} of 9721. Thus, a pressure of 50 bar seems to be a suitable parameter to obtain a high yield of MeBDO at milder reaction conditions. Nevertheless, the reaction time of 40 h is quite long.

To achieve similar results in a shorter time scale, hydrogenation reactions were performed using double catalyst concentration (0.02 mol%) and half of the reaction time (20 h) under otherwise same conditions. The results are shown in Figure 4, the corresponding values can be found the appendix (Page 22, Table 5).

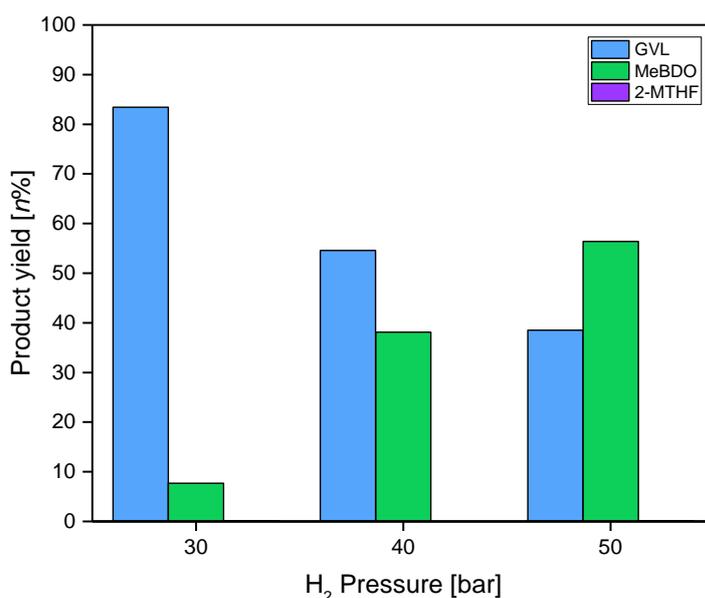


Figure 4: Hydrogenation of LVA with 0.02 mol% **2** under variation of the H₂ pressure. Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.1946 mmol, 0.02 mol%), H₂, 160 °C, 800 rpm, 20 h. Product yields determined by GC using 1-hexanol as internal standard.

Hydrogenation at a H₂ pressure of 30 bar gave 83% GVL with a TON_{GVL} of 4175. Increasing the H₂ pressure to 40 bar led to a mixture of 55% GVL and 38% MeBDO with a TON of 2786 for the conversion to GVL and 1937 for the conversion to MeBDO. A further increase of the H₂ pressure to 50 bar 39% GVL (TON_{GVL} = 1946) and 56% MeBDO (TON_{MeBDO} = 2849). The product mixture obtained at a H₂ pressure of 50 bar comprises a good composition for recycling experiments. However, the catalyst recovery from 100% MeBDO could lead to the formation of inactive catalyst species by decarbonylation of intermediate aldehydes or alcohols in the absence of substrates.^[2-4] Thus, a H₂ pressure of 50 bar and a reaction time of 20 h are considered the optimized reaction conditions.

2.2 Variation of Solvents

Hydrogenation reactions were performed using complex **2** under the optimized reaction conditions (50 bar H₂, 0.02 mol% [Ru], 160 °C, 20 h) by variation of the solvent in ratio 1:1 mL/mL with LVA and a total volume of 100 mL. The ethereal solvents 1,4-dioxane and THF were investigated due to their good miscibility with all present compounds. The results are shown in Figure 5. The corresponding values can be found in the appendix (Page 22, Table 6).

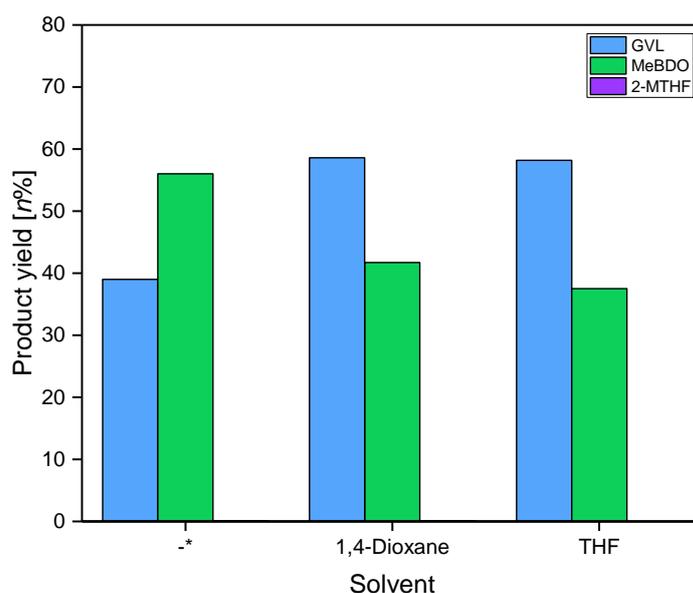


Figure 5: Hydrogenation of LVA with 0.02 mol% **2** under variation of the solvent in ratio 1:1 (mL/mL) with LVA. Reaction conditions: LVA (50 mL, 0.487 mol), [Ru] (0.0974 mmol, 0.02 mol%), solvent (50 mL), 50 bar H₂, 160 °C, 800 rpm, 20 h. Product yields determined by GC using 1-hexanol as internal standard. * LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.02 mol%),

The hydrogenation of 100 mL LVA under solvent-free conditions led to 39% GVL and 56% MeBDO. Hydrogenation of LVA in 1,4-dioxane (1:1 mL/mL) led to a reduced MeBDO yield of 42%. Performing the reaction in THF resulted in a comparable yield of MeBDO (38%). In both cases, a yield of 59% GVL was obtained. For the reaction in THF, the yield of 2-MTHF could not be determined by GC, due to its elution along with THF. The hydrogenation of 50 mL LVA in solution using 1,4-dioxane and THF in ratio 1:1 mL/mL led to lower yields of MeBDO, compared to the hydrogenation of 100 mL LVA under solvent-free conditions. A possible explanation might be the coordinative nature of the ethereal solvents, influencing the kinetics of the reaction by ligand exchange processes with coordinated substrate molecules. However, more promising results could be achieved under solvent-free conditions using 100 mL LVA, which were thus kept as the optimized reaction condition.

2.3 Variation of Catalysts

Under the optimized reaction conditions (100 mL LVA, 0.02 mol% [Ru], 50 bar H₂, 160 °C, 20 h) the activity of complex **1** and the bis-2-naphtholato complex **3**, were investigated in comparison to complex **2** (Figure 6). The results are shown in Figure 7 and can be found in the appendix (Page 22, Table 7).

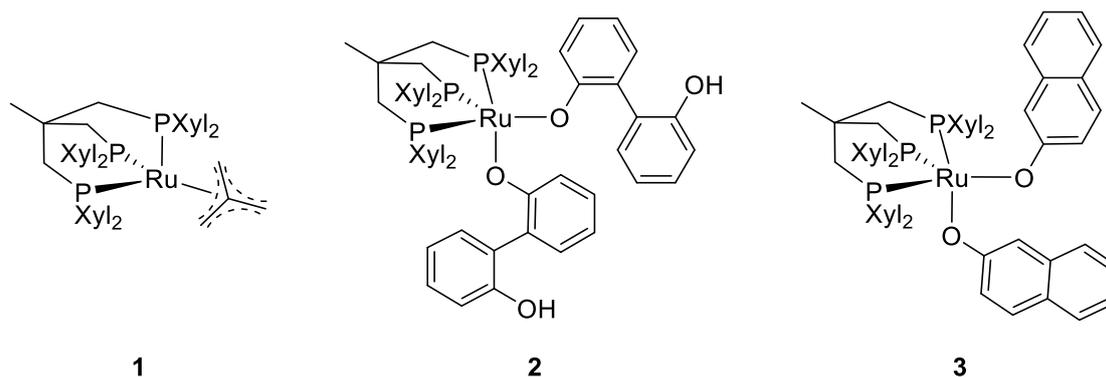


Figure 6: Used catalysts for the hydrogenation of LVA under the optimized reaction conditions: [Ru(xyl-triphos)(tmm)] (**1**), [Ru(xyl-triphos)(bph)₂] (**2**), [Ru(xyl-triphos)(2-naph)₂] (**3**).

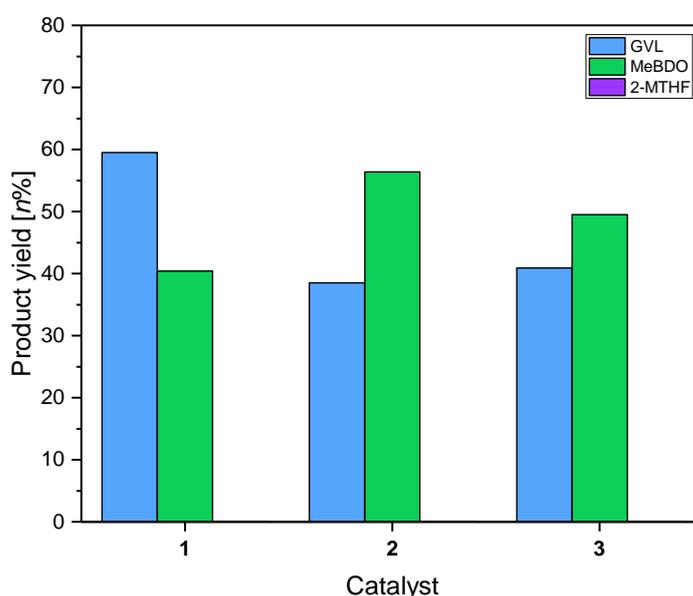


Figure 7: Hydrogenation of LVA under variation of the catalyst. Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.1946 mmol, 0.02 mol%), H₂, 160 °C, 800 rpm, 20 h. Product yields determined by GC using 1-hexanol as internal standard.

Using complexes **1-3**, full conversion could be achieved in all cases under the optimized reaction conditions. The hydrogenation of LVA using **1** as catalyst led to a low yield of MeBDO (38%), achieving a TON of 1874 for the conversion to MeBDO. Hydrogenation with complex **2** led to a high yield of MeBDO with a TON_{MeBDO} of 2849. Applying complex **3** to the reaction led to similar results compared to the reaction with complex **2**, although obtaining a slightly lower yield of MeBDO (50%) with a TON_{MeBDO} of 2576. Comparing the results of the hydrogenation with complexes **1-3**, the highest yield of MeBDO as well as the highest TON_{MeBDO} could be achieved with complex **2**, which will thus be kept as catalyst for upcoming hydrogenation experiments.

3 Conclusions

The catalytic study on the hydrogenation of levulinic acid (LVA) was carried out in large 500 mL stainless steel autoclaves using the developed molecular catalysts [Ru(xyl-triphos)(tmm)] (**1**) and [Ru(xyl-triphos)(bph)₂] (**2**). In the initial set of experiments, the reactions were conducted under solvent-free conditions with variation of the H₂ pressure. Hydrogenation with complex **1** at selected H₂ pressures showed an almost linear correlation between the H₂ pressure and the obtained yields of GVL and MeBDO, achieving 53% MeBDO with a TON_{MeBDO} of 5477 at a pressure of 50 bar. Under the same conditions using complex **2**, 68% MeBDO with a TON_{MeBDO} of 7294 could be achieved, demonstrating a higher activity of this catalyst system in the hydrogenation of LVA. In the subsequent investigations at 100 bar H₂, nearly quantitative yield of MeBDO could be obtained with a TON_{MeBDO} of 9721.

Based on this detailed information on the performance of the catalysts in large reactor setups, experiments with a doubled catalyst concentration of 0.02 mol% **2** and condensed reaction time of 20 h were performed. Herein, also a linear correlation between the obtained product yield and the H₂ pressure could be observed, enabling to largely estimate the reaction conditions for the planned CSTR setup. In detail, at a pressure of 50 bar a product mixture of 39 n% GVL and 56 n% MeBDO was obtained. This optimized amount of MeBDO in the mixture is beneficial for the envisaged continuous reaction setup, as this product composition minimizes catalyst deactivation and facilitates recycling experiments with a distillation setup. For the CSTR setup a reaction mixture with reduced viscosity at decreased reaction temperature would strongly reduce the reactor complexity and allowing a simplified feed of LVA. Thus, additional hydrogenation experiments with 50 mL LVA in 1,4-dioxane and THF (ratio 1:1 (mL/mL)) led to lower yields of MeBDO compared to hydrogenation reactions under solvent-free conditions. Consequently, for the CSTR setup the handling of neat substrates has to be integrated.

In summary, optimized reaction conditions and catalyst compositions for the envisaged construction of a CSTR setup could be developed. In detail, after the finalization of the CSTR system, initial catalytic reactions will be performed at 50 bar H₂, 160°C and 20 h using 100 mL neat LVA and 0.02 mol% of the tailored [Ru(xyl-triphos)(bph)₂] catalyst **2**.

4 Experimental Section

4.1 Reaction Techniques

All syntheses were carried out in preheated glass equipment under exclusion of oxygen and moisture using Schlenk techniques. Argon 4.8 was used as inert gas. Solvents and reagents were transferred in argon countercurrent flow using Teflon cannulas and syringes.

All solvents were degassed, dried and stored under argon atmosphere over molecular sieves (4 Å), which have been previously activated at 500 °C for 4 h. Levulinic acid was degassed *in vacuo* prior to use.

Reactions were performed in 500 mL stainless steel autoclaves, manufactured in the mechanical workshop of the ITMC RWTH Aachen University, equipped with borosilicate glass liners and magnetic stir bars, which were previously baked out in oven at 120 °C. The autoclaves were heated at 400 °C prior to use and subsequently heated by heating cuffs on a conventional stirring plate. Reaction conditions were controlled by *LabView* and the H₂ pressure was kept constant using a mass flow controller (MFC).

4.2 Analytics

4.2.1 Nuclear Magnetic Resonance Spectroscopy

¹H-NMR-spectra were measured on a *BRUKER Advance II Ultrashield Plus 400* spectrometer using deuterated solvents shown in table 1. The spectra were analyzed with *MestReNova* (v12.0.0).^[5]

Table 1: Chemical shift of used deuterated solvents.

Solvent	δ (¹ H) [ppm]
DMSO- <i>d</i> ₆	2.50
Methylenchloride- <i>d</i> ₂	5.32
THF- <i>d</i> ₈	1.72/3.58

For the signal splitting following abbreviations are used in the experimental section: s for singlets and m for multiplets.

4.2.2 Gas Chromatography

Measurements by gas chromatography (GC) were performed on a *ThermoFischer SCIENTIFIC Trace GC Ultra* chromatograph with SSL Inlet (250 °C, Split 40 mL·min⁻¹), CP-

WAX column (60 m, inner diameter 0.25 mm, film thickness 0.25 μm) and flame ionization detector (250 $^{\circ}\text{C}$) using helium as carrier gas. An exemplary chromatogram is attached to the appendix (Figure 8). The retention times and correction factors are shown in the following table:

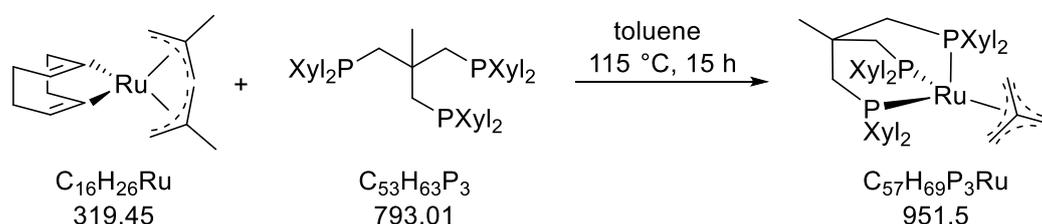
Table 2: GC retention times and correction factors of detected compounds.

Compound	Retention time [min]	Correction factor [a.u.]
2-Methyltetrahydrofuran	4.55	1.12
γ -Valerolactone	18.30	1.56
1-Methyl-1,4-Butanediol	21.73	1.59
Levulinic acid	28.08	2.52

For the preparation of GC-samples, 100–250 mg of the reaction solution was filtrated into a small glass vial. 15–25 mg 1-hexanol was added as internal standard and the vial filled with 1,4-dioxane.

4.3 Syntheses

4.3.1 Synthesis of Ruthenium(1,1,1-tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane)(trimethylenemethane) **1**



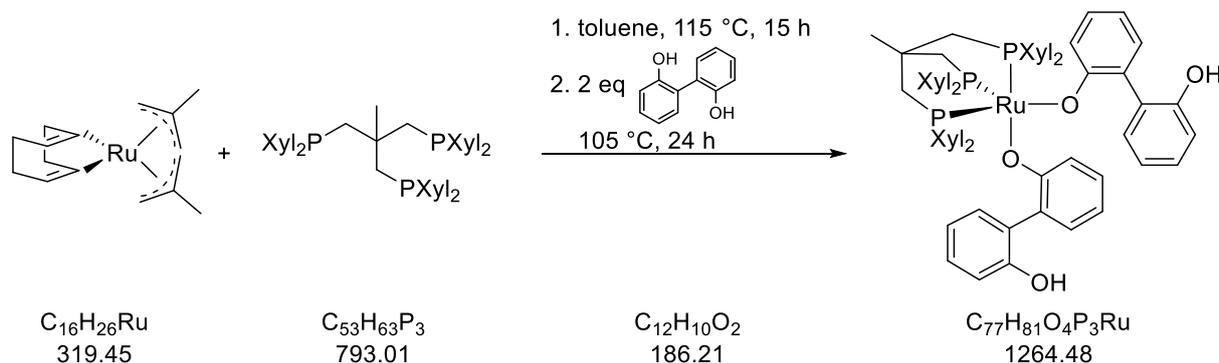
[Ru(cod)(2-methylallyl)₂] (242 mg, 0.758 mmol, 1.00 eq) and 1,1,1-tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane (601 mg, 0.758 mmol, 1.00 eq) were suspended in 15 mL toluene and stirred for 15 h at 115 $^{\circ}\text{C}$. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo*. After adding 10 mL *n*-pentane, a yellow precipitate was formed and the solvent removed by filtration. The residue was washed three times with 10 mL *n*-pentane and dried at 60 $^{\circ}\text{C}$ *in vacuo*. The complex was obtained as yellow powder (568 mg, 0.597 mmol, 79%).

¹H-NMR (400 MHz, methylene chloride-*d*₂): = 6.74-6.70 (m, 18H, C_{Ar}H), 2.24-2.22 (m, 6H, 3xCH₂), 1.99 (s, 36H, C_{Ar}CH₃), 1.70 (s, 6H, C(CH₂)₃), 1.45-1.41 (m, 3H, CCH₃) ppm.

³¹P{¹H}-NMR (162 MHz, methylene chloride-*d*₂): δ = 31.7 (s, 3xPXyl₂) ppm.

Synthesis according to literature.^[1]

4.3.2 Synthesis of Ruthenium(1,1,1-tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane)(2-*ortho*-phenylolphenolato) 2



[Ru(cod)(2-methylallyl)₂] (242 mg, 0.758 mmol, 1.00 eq) and 1,1,1-tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane (601 mg, 0.758 mmol, 1.00 eq) were suspended in 15 mL toluene and stirred for 15 h at 115 °C. After cooling to room temperature, 2,2'-biphenol (282 mg, 1.52 mmol, 2.00 eq) was added and the reaction mixture stirred for 24 h at 105 °C. The reaction mixture was cooled to –20 °C and the solvent removed by filtration. The obtained red crystals were washed three times with 5 mL *n*-pentane and dried at 60 °C *in vacuo*. The complex was obtained as red powder (804 mg, 0.636 mmol, 84%).

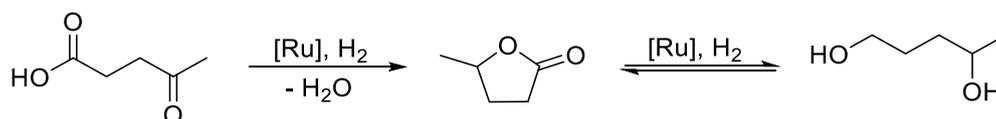
¹H-NMR (400 MHz, THF-*d*₈): δ = 8.53 (s, 2H, OH), 7.19-7.11 (m, 16H, C_{Ar}H), 6.88-6.78 (m, 6H, C_{Ar}H), 6.68 (s, 5H, C_{Ar}H), 6.68-6.60 (m, 5H, C_{Ar}H), 2.30 (s, 6H, 3xCH₂), 1.97 (s, 36H, C_{Ar}CH₃), 1.55-1.54 (m, 3H, CCH₃) ppm.

³¹P{¹H}-NMR (162 MHz, THF-*d*₈): δ = 44.1 (s, 3xPXyl₂) ppm.

Synthesis according to literature.^[1]

4.4 Catalytic Experiments

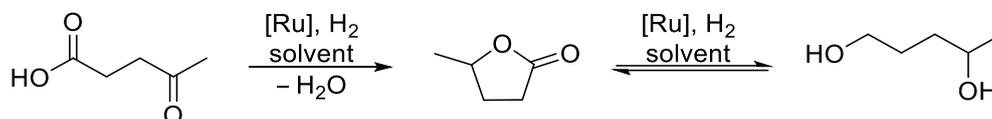
4.4.1 Hydrogenation of Levulinic Acid



In a typical reaction, 1.00 eq [Ru] was dissolved in levulinic acid (100 mL, 0.973 mol, 5000–10000 eq). The solution was transferred into an autoclave which was previously evacuated and flushed with argon three times. The autoclave was placed into heating cuffs and preheated to 40 °C. After pressurizing with 10–35 bar H₂ while stirring the autoclave was heated to 160 °C

and the desired H₂ pressure was kept constant using an MFC. The reaction mixture was stirred at 800 rpm for the desired reaction time. The obtained product mixture was analyzed by GC.

4.4.2 Hydrogenation of Levulinic Acid in Solution



In a typical reaction, [Ru] (0.195 mmol, 1.00 eq) was dissolved in levulinic acid (50 mL, 0.487 mol, 5000 eq) and 50 mL solvent. The solution was transferred into an autoclave which was previously evacuated and flushed with argon three times. The autoclave was placed into heating cuffs and pressurized with 10-35 bar H₂ while stirring. The autoclave was heated to 160 °C and the desired H₂ pressure was kept constant using an MFC. The reaction mixture was stirred at 800 rpm for the desired reaction time. The obtained product mixture was analyzed by GC.

5 Literature

- [1] Deliverable 2.1, GreenSolRes
- [2] F. M. A. Geilen, *Am. Chem. Soc.* **2011**, 133, 14349-14358.
- [3] T. vom Stein, *Am. Chem. Soc.* **2014**, 136, 13217-13225.
- [4] M. Meuresch, *Angew. Chem. Int. Ed.* **2016**, 55, 1392-1395.
- [5] Mestrenova v12.0.0, Mestrelab S.L. **2017**.

6 Appendix

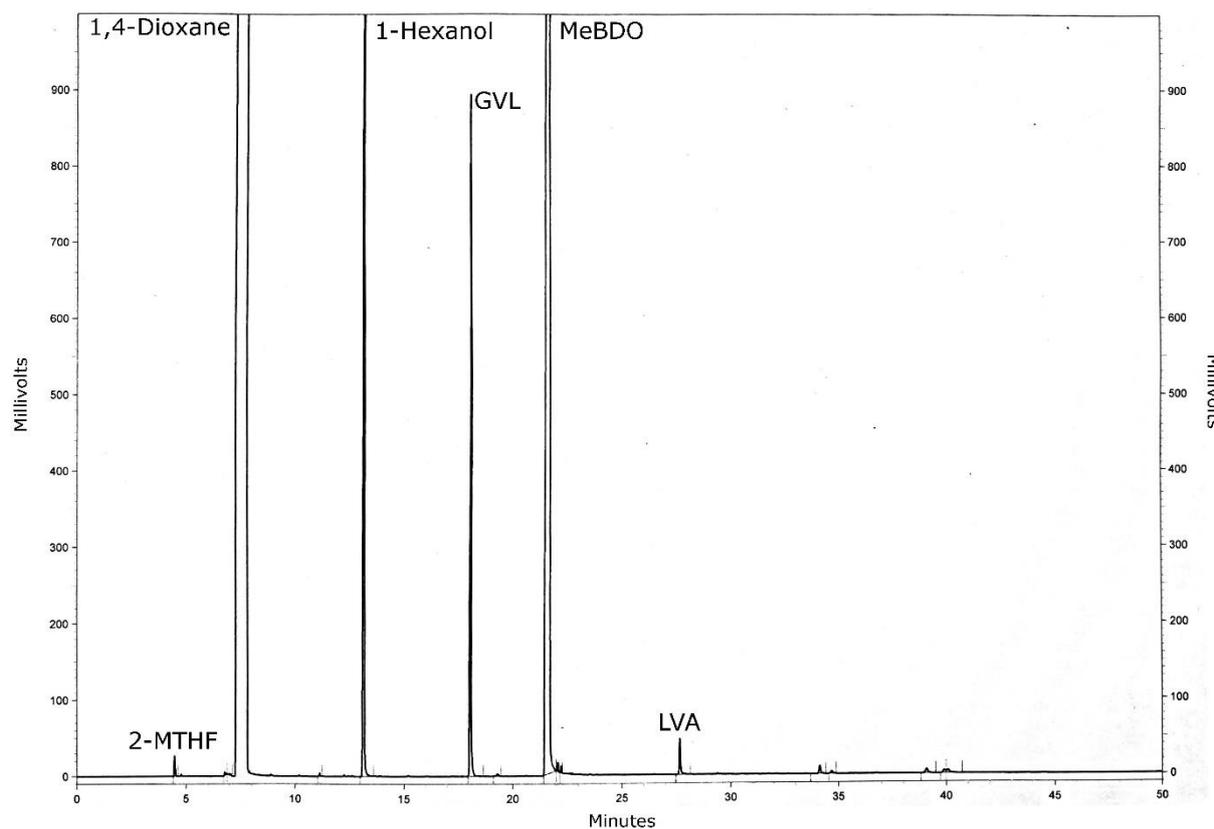


Figure 8: Exemplary gas chromatogram of the hydrogenation of LVA using 1-hexanol as internal standard.

Table 3: Hydrogenation of LVA with 0.01 mol% **1** under variation of the H₂ pressure ($p = \text{const.}$).

Entry	H ₂ Pressure [bar]	Yield ^[a] [%]			TON			Conversion [%]
		GVL	MeBDO	2-MTHF	GVL	MeBDO	2-MTHF	
1	30	79	2	0.1	7611	186	11	92
2	40	62	27	0.1	6310	2707	11	100
3	50	37	53	0.2	3771	5477	20	100
4	60	13	85	0.2	1291	8541	22	100

Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.01 mol%), H₂, 160 °C, 800 rpm, 40 h.

^[a] Determined by GC using 1-hexanol as internal standard.

Table 4: Hydrogenation of LVA with 0.01 mol% **2** under variation of the H₂ pressure ($p = \text{const.}$).

Entry	H ₂ Pressure [bar]	Yield ^[a] [%]			TON		
		GVL	MeBDO	2-MTHF	GVL	MeBDO	2-MTHF
1 ^[b]	30	97	3	0.1	10326	353	13
2	40	55	38	0.0	2780	1937	2
3	50	27	68	0.2	2862	7294	26
4	60	18	75	0.2	1856	7615	19
5	70	16	73	0.3	1685	7553	26
6	80	1	93	0.3	106	9392	27
7	90	1	93	0.3	128	9733	30
8	100	1	97	0.3	196	9721	31

Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.01 mol%), H₂, 160 °C, 800 rpm, 40 h. Conversion = 100%, ^[a] Determined by GC using 1-hexanol as internal standard. ^[b] Conversion = 99.

Table 5: Hydrogenation of LVA with 0.02 mol% **2** under variation of the H₂ pressure ($p = \text{const.}$).

Entry	H ₂ Pressure [bar]	Yield ^[a] [%]			TON		
		GVL	MeBDO	2-MTHF	GVL	MeBDO	2-MTHF
1	30	83	8	0.1	4175	387	3
2	40	55	38	0	2786	1937	5
3	50	39	56	0.1	1946	2849	5

Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.01 mol%), H₂, 160 °C, 800 rpm, 40 h. Conversion = 100%, ^[a] Determined by GC using 1-hexanol as internal standard.

Table 6: Hydrogenation of LVA with 0.02 mol% **2** under variation of the solvent in ratio 1:1 ($p = \text{const.}$).

Entry	Solvent	Yield ^[a] [%]			TON		
		GVL	MeBDO	2-MTHF	GVL	MeBDO	2-MTHF
1 ^[b]	-	39	56	0.1	1946	2849	5
2 ^[c]	1,4-Dioxane	59	42	0.1	2878	2047	3
3	THF	58	38	0	2856	1855	-

Reaction conditions: LVA (50 mL, 0.487 mol), [Ru] (0.0974 mmol, 0.02 mol%), Solvent (50 mL), 50 bar H₂, 160 °C, 800 rpm, 20 h. Conversion = 100%, ^[a] Determined by GC using 1-hexanol as internal standard, ^[b] LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.02 mol%), ^[c] Yield > 100%.

Table 7: Hydrogenation of LVA under variation of the catalyst ($p = \text{const.}$).

Entry	Catalyst	Yield ^[a] [%]			TON		
		GVL	MeBDO	2-MTHF	GVL	MeBDO	2-MTHF
1	1	55	38	0.1	2764	1874	5
2	2	39	56	0.1	1946	2849	5
3	3	41	50	0.1	2125	2576	6

Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.195 mmol, 0.02 mol%), 50 bar H₂, 160 °C, 800 rpm, 20 h. Conversion = 100%, ^[a] Determined by GC using 1-hexanol as internal standard