



Deliverable 2.13

**Recycling and separation strategies
for catalyst and high-boiling
components**

**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

The hydrogenation of levulinic acid (LVA) to 1-methyl-1,4-butanediol (MeBDO) represents a challenging transformation and within GreenSolRes, a tailored catalyst system and reactor setup should be developed, integrating catalyst recovery and product separation. In previous work, an effective catalyst systems for the hydrogenation of levulinic acid (LVA) in batch experiments could be established and subsequently optimised for the envisaged application in continuous stirred tank reactor (CSTR) applications. The developed tailored ruthenium/triphos complexes represent active and stable molecular catalysts, allowing integration in thermal separation processes. Consequently, in combination with the high boiling organic products, a separation of the catalyst by distillation can be envisaged. Herein, selected thermal separation strategies for catalyst recycling and product isolation have been investigated, finally allowing developing an efficient integrated separation process. The present investigation yielded ruthenium/triphos complexes with high activity in the consecutive hydrogenation of LVA and possibility of integrated thermal separation, producing γ -valerolactone (GVL) and 1-methyl-1,4-butanediol (MeBDO) from LVA. Fractional vacuum distillation was discovered as the most efficient way for separation of the organic products and the molecular catalyst.

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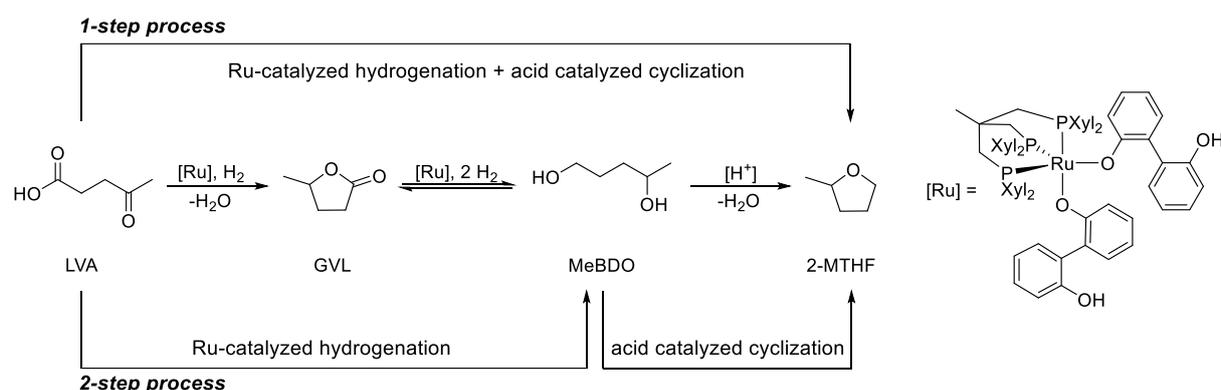
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Abbreviations

| | |
|-------------|---|
| bph | 2- <i>ortho</i> -Phenylophenolato |
| cod | 1,5-Cyclooctadiene |
| CSTR | Continuous stirred tank reactor |
| δ | Chemical shift |
| eq | Equivalent [mol/mol] |
| 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 |
| S | Sump |
| STY | Space-time-yield |
| T | Temperature [°C] |
| THF | Tetrahydrofuran |
| TON | Turn over number [mol/mol] |
| tmm | Trimethylenemethane |
| Xyl | 3,5-Dimethylphenyl |
| Xyl-triphos | 1,1,1-Tris(di(3,5-dimethylphenyl)phosphinomethyl)ethane |

1 Introduction

In Deliverable 2.1 selected molecular catalysts were developed and investigated in the hydrogenation of levulinic acid (LVA) and γ -valerolactone (GVL) towards 1-methyl-1,4-butanediol (MeBDO). With [Ru(xyl-triphos)(bph)₂], a highly active complex could be established, meeting the requested performance criteria. In detail, high turnover numbers (TON \geq 250 000) and high space-time-yields (STY \geq 1000kg/(L·h) could be obtained for the desired products in batch mode. Additionally, in Deliverable 2.2 the advantage of a 2-step process over a 1-step process was discussed (see **Error! Reference source not found.**). It turned out that the separation of the ruthenium-catalyzed hydrogenation and the acid-catalyzed cyclization steps is beneficial in terms of reactor design, as both processes require different process parameters (e.g. temperature, pressure, inert atmosphere vs. air). In a 2-step process, both reaction steps can be tailored and optimized according to their dedicated requirements.



Scheme 1: Process scheme for the conversion of LVA to GVL, MeBDO and 2-MTHF.

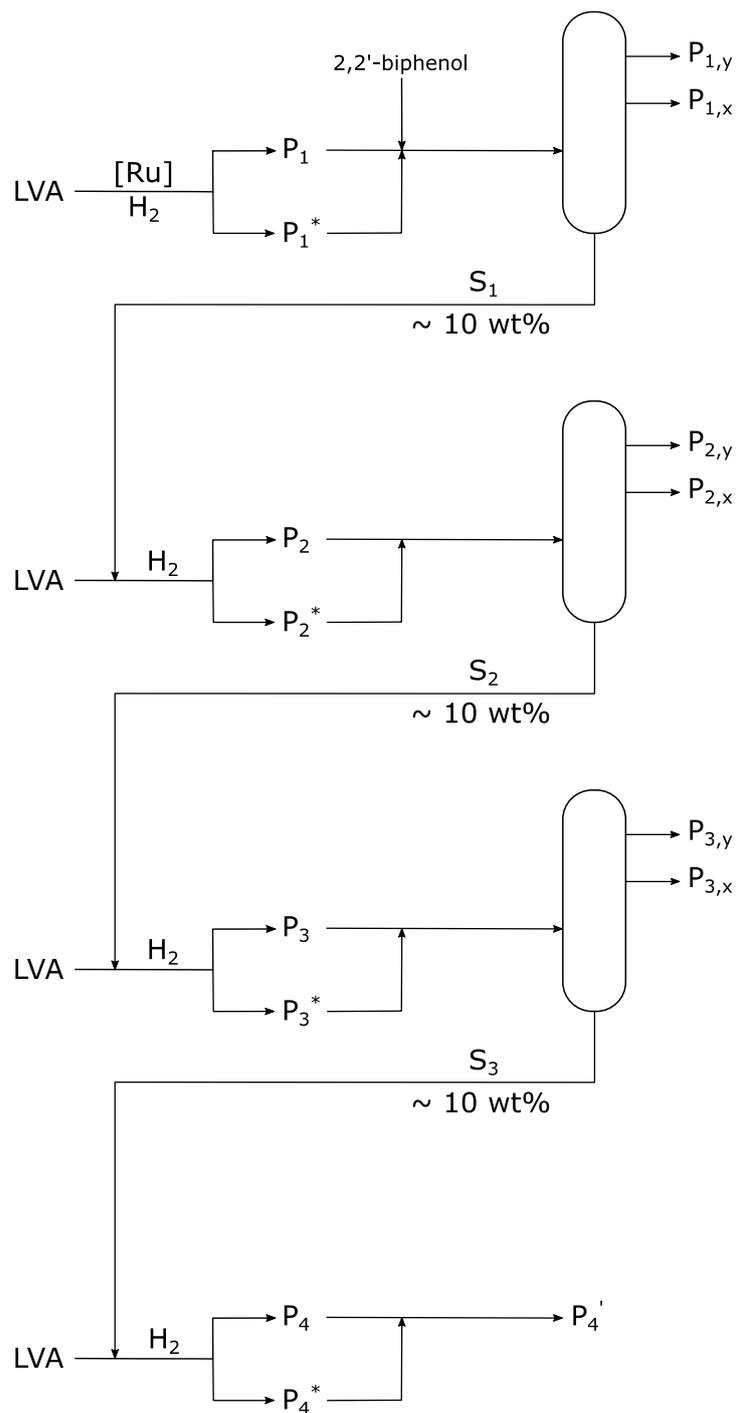
To reach high TON and to develop an economically reasonable process, the separation and recycling of the molecular catalyzed is a crucial step in this process. The separation of the catalyst from the reaction solution by vacuum distillation and re-use of the recycled catalyst is investigated in the following. The recycled catalyst is reused to test its long-term stability, recyclability over multiple steps and stability under the applied product separation conditions. Moreover, the product separation is investigated via vacuum distillation.

2 Separation Strategies

2.1 Catalyst Recycling

Recent investigations on the hydrogenation of LVA demonstrated the ruthenium/triphos-complex $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ as a suitable catalyst (Deliverable 2.1). Reactions were performed in 500 mL autoclaves equipped with glass liner and magnetic stir bar using 100 mL LVA and 0.02 mol% of the catalyst. The optimized reaction conditions could be identified at 160 °C, a constant H_2 pressure of 50 bar and reaction times of 20 h yielding in 39% GVL and 56% MeBDO. This product mixture comprises a good composition for recycling experiments, because the recovery of the catalyst from 100% MeBDO could lead to the formation of inactive catalyst species by decarbonylation of intermediate aldehydes or alcohols, due to the absence of hydrogenatable substrates.^[1-3]

To investigate the catalytic properties of $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ over several consecutive hydrogenation cycles, recycling experiments were performed in 500 mL stainless steel autoclaves. The recycling scheme of the catalyst is shown in **Error! Reference source not found.** For the first hydrogenation cycle, $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ was dissolved in 100 mL LVA and hydrogenated under the optimized reaction condition. The obtained product mixture (P_i) was then transferred into the distiller in argon counter stream *via* canula. Part of the product solution (P_i^*) was found to accumulate between the glass liner and the autoclave material and was added to distiller in air using a funnel in argon countercurrent flow. After collecting a GC sample, the product mixture was concentrated to about 10wt% by vacuum distillation ($p = 10^{-3}$ mbar) and at a maximum temperature of 110 °C. The first fraction was obtained at room temperature containing 2-MTHF and H_2O ($P_{i,x}$), which was collected in a cooling trap. The second fraction containing GVL was obtained at ~30 °C and the third fraction containing MeBDO was obtained at ~66 °C. To minimize the exposition of the catalyst to oxygen and moisture, the reaction mixture was distilled in one step without further product purification (the GVL and the MeBDO fraction were collected together as $P_{i,y}$). Next, 100 mL fresh LVA was added to the distillation sump (S_i) containing the catalyst and transferred into a clean autoclave, which was previously evacuated and flushed with argon for a subsequent hydrogenation cycle under identical conditions. After the last hydrogenation cycle the reaction mixture P_i and the accumulated solution P_i^* were combined and analyzed by GC. Optionally, 10 mol% 2,2'-biphenol, relative to the catalyst, was added to the reaction mixture after the first hydrogenation and before the first distillation step to increase the catalyst activity.



Scheme 2: Recycling Scheme for catalyst recovery.

The first recycling experiment was carried out with 3 hydrogenation and separation cycles. The product composition of each cycle is shown in Figure 1. The amount of the co-product H₂O was calculated corresponding to the obtained amounts of GVL, MeBDO and 2-MTHF. The corresponding values can be found in the appendix (Table 3).

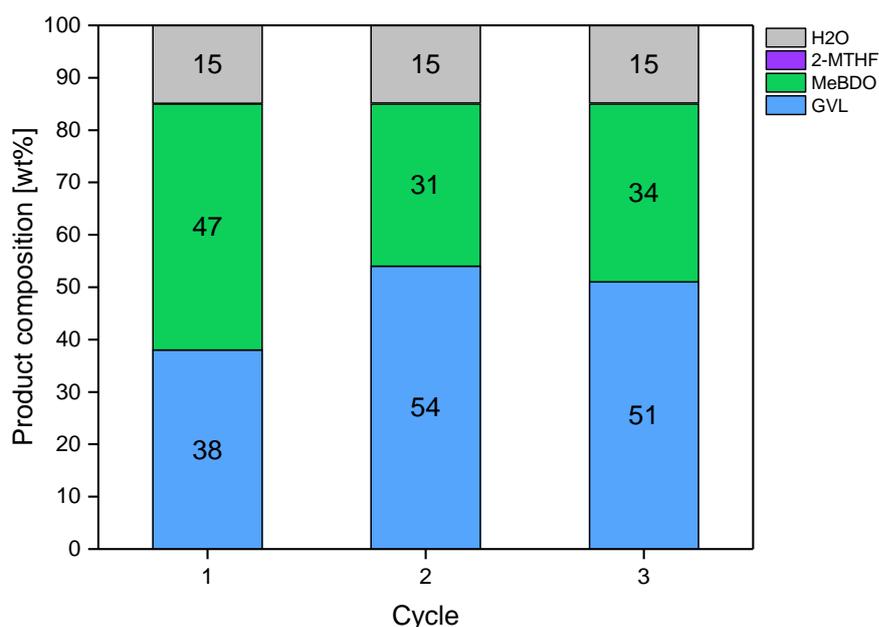


Figure 1: Product composition for the recycling of [Ru(xyl-triphos)(bph)₂] in the hydrogenation of LVA. Reaction conditions: LVA (100 mL, 0.973 mol), [Ru] (0.1946 mmol, 0.02 mol%), H₂, 160 °C, 800 rpm, 20 h. Product yields determined by GC using 1-hexanol as internal standard.

The first hydrogenation run led to a product mixture containing 38 wt% GVL, 46 wt% MeBDO, 0.1 wt% 2-MTHF and 15 wt% H₂O (P₁) with a LVA conversion of 99%. After the second hydrogenation run, the obtained amount of MeBDO decreased to 31 wt%, while the amount of GVL increased to 54 wt%. The third hydrogenation led to a product composition with full conversion of LVA and a product composition similar to these of the second hydrogenation run.

A second recycling experiment was carried out with four hydrogenation and separation cycles. After the first hydrogenation run, a product composition with a lower amount of MeBDO compared to the first recycling experiment was obtained. To increase the catalyst activity, 10 mol% of 2,2'-biphenol, relative to the catalyst, was added after the first hydrogenation run and before the first distillation step. The product composition of the obtained product mixtures for each hydrogenation are shown in Figure 2 and the corresponding values can be found in the appendix (Table 4).

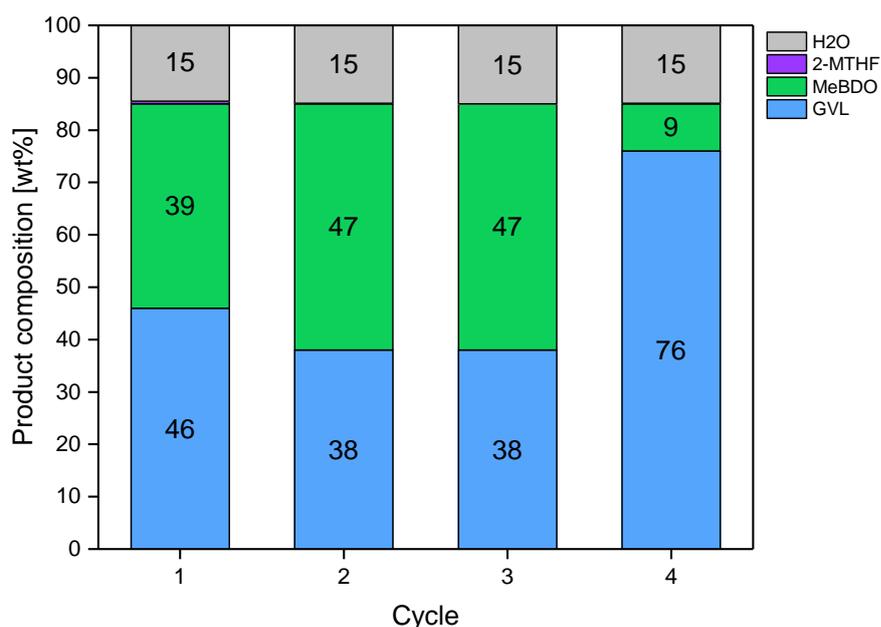


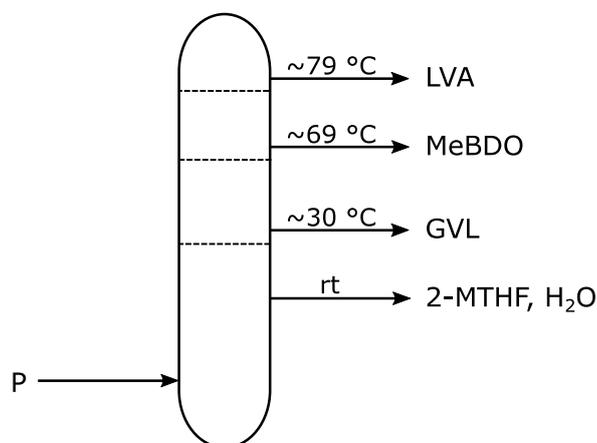
Figure 2: Product composition for the recycling of $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ in the hydrogenation of LVA. Reaction conditions: LVA (100 mL, 0.973 mol), $[\text{Ru}]$ (0.1946 mmol, 0.02 mol%), H_2 , 160 °C, 800 rpm, 20 h. Product yields determined by GC using 1-hexanol as internal standard.

Full conversion of LVA could be achieved within the first hydrogenation run leading to a product composition of 46 wt% GVL, 39 wt% MeBDO, 0.3 wt% 2-MTHF and 15 wt% H_2O . Within the second and third hydrogenation run, the obtained amount of MeBDO increased to 47 wt%, while the amount of GVL decreased to 38 wt%. Full conversion of LVA could be achieved in the third hydrogenation run. The fourth hydrogenation step led to a lower amount of MeBDO (9 wt%) and a higher amount of GVL (75 wt%) with 99% conversion of LVA. Compared to the first hydrogenation run, the increased amounts of MeBDO obtained after the second and third run can be explained by the addition of 2,2'-biphenol, successfully increasing the catalyst activity. In contrast, the first recycling experiment without addition of 2,2'-biphenol led to decreased amounts of MeBDO within the second and third run, confirming the increased activity of the catalyst in the second recycling experiment.

In summary, the $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ catalyst could be successfully applied in recycling experiments and used in several consecutive hydrogenation and distillation experiments. To investigate the long term stability and to estimate possible deactivation effects of the complex, recycling experiments need to be carried out over more than four hydrogenation cycles.

2.2 Product Separation

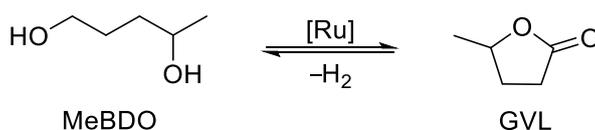
The product mixture obtained from the hydrogenation of LVA containing GVL, MeBDO, 2-MTHF and H₂O could successfully be separated from the catalyst in a single distillation step under reduced pressure ($p = 10^{-3}$ mbar, $T = \leq 110$ °C). The separation of the organic compounds was investigated independently from catalyst recovery and can be performed without the need of inert atmosphere. Regarding CSTR applications, these two processes needs to be combined. For product separation, fractional distillation experiments were performed using a distiller equipped with packing column and glass helices as packing material under reduced pressure ($2.7 \cdot 10^{-2}$ mbar). The distillation scheme is shown in Scheme 3.



Scheme 3: Distillation scheme for product purification.

The product solution P was added to the distiller. Under reduced pressure ($2.7 \cdot 10^{-2}$ mbar) 2-MTHF and H₂O could easily be removed at room temperature under stirring. Heating the solution (≤ 160 °C) led to the separation of the GVL fraction at ~ 30 °C and the MeBDO fraction at ~ 70 °C. Non-converted LVA was retrieved at ~ 80 °C. The difference between the observed head temperatures of the GVL and the MeBDO fraction is big enough to ensure an effective separation step by fractional distillation.

During the distillation process the dehydrogenation/cyclization of MeBDO to GVL can occur, due to the presence of the catalyst in the product solution (Scheme 4). To proof this assumption, a solution of MeBDO containing 0.1 mol% of [Ru(xyl-triphos)(bph)₂] was distilled under reduced pressure.



Scheme 4: Ru-catalyzed dehydrogenation of MeBDO to GVL.

The solution was slowly heated and the first fraction containing MeBDO was obtained at 70 °C. Thus, the dehydrogenation of MeBDO did not occur under distillative conditions. Next, the solution was further heated up to 160 °C and NMR-samples were taken every 20 min after reaching thermodynamically equilibrium at selected temperatures (Figure 3).

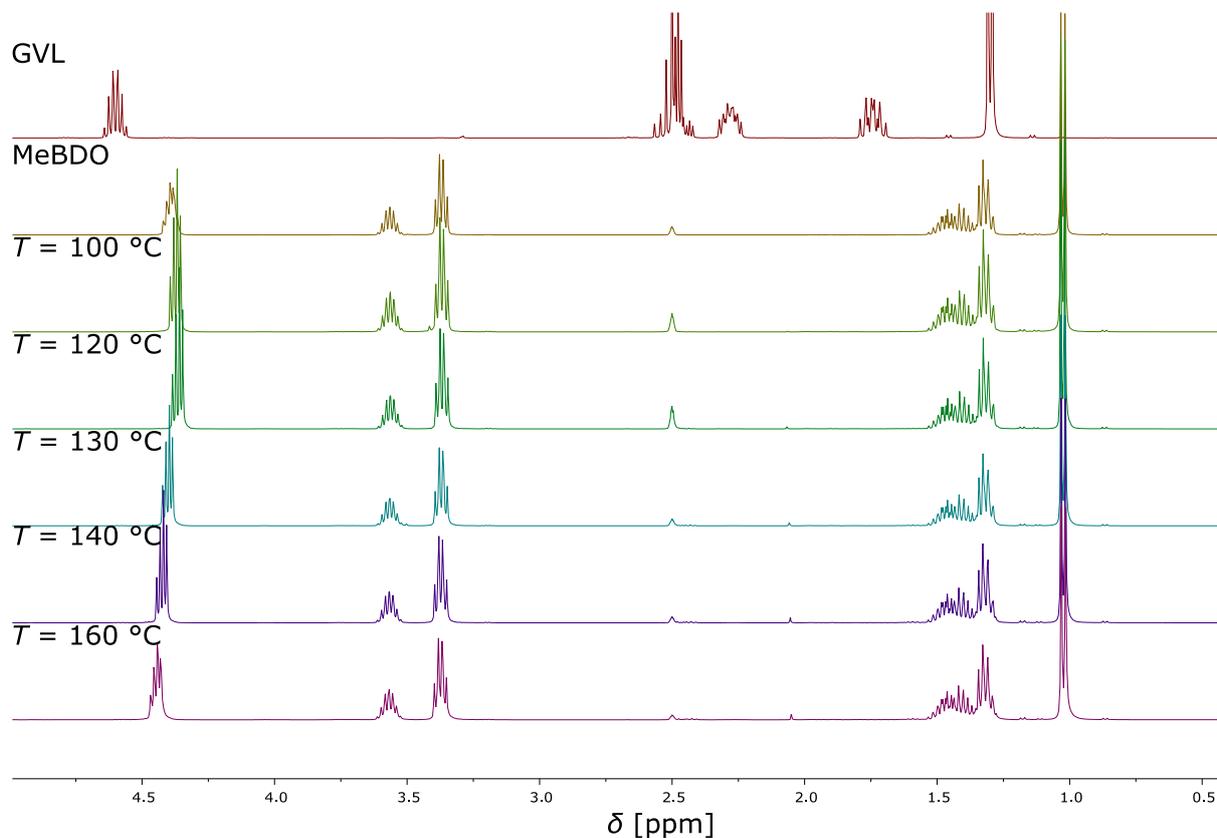


Figure 3: ¹H-NMR-spectra (400 MHz, DMSO-*d*₆) of the fractions obtained after the distillation of MeBDO in the presence of [Ru(xyl-triphos)(bph)₂].

Comparing the reference spectra of GVL and MeBDO to the spectra of the reaction mixture at different temperatures reveals that no significant formation of GVL from 100 °C to 160 °C.

3 Conclusions

Recycling concepts for the molecular catalyst $[\text{Ru}(\text{xyl-triphos})(\text{bph})_2]$ in hydrogenation of LVA were investigated and correlated with selected options for combined product purification. In the initial investigations, thermal separation of catalyst and product via distillation was targeted, finally allowing the recovery of the catalyst in a single distillation step reduced pressure. Thus, four consecutive hydrogenation and separation cycles could be established at largely maintained catalyst activity. Moreover, the addition of 2,2'-biphenol increased the catalyst activity, resulting in higher yields of MeBDO after the second and the third hydrogenation cycle. After the fourth hydrogenation cycle, decreased yields of MeBDO could be observed.

In summary, a tailored separation of catalyst and products from the hydrogenation of LVA could be achieved by fractional distillation under reduced pressure. Using a packed column with glass helices led to an efficient product purification, yielding pure fractions of GVL and MeBDO, in combination with catalyst recycling. Moreover, with the present setup the challenging dehydrogenation of MeBDO could be circumvented, allowing the development of an integrated reaction and purification concept.

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. Levulinic acid was degassed *in vacuo* prior to use.

Catalytic reactions were performed in 500 mL stainless steel autoclaves manufactured in the mechanical workshop of the ITMC RWTH Aachen. All autoclaves were equipped with borosilicate glass liner and magnetic stir bars, which were previously baked out in oven at 120 °C. 500 mL autoclaves were shortly heated at 400 °C prior to use. For the preparation of the autoclaves, a glass liner was placed into the autoclave along with a magnetic stir bar. The autoclave was closed and subsequently evacuated and flushed with argon three times. 500 mL autoclaves were heated by heating cuffs on a 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).^[4]

Table 1: Chemical shift of used deuterated solvents.

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

For the signal splitting the 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-

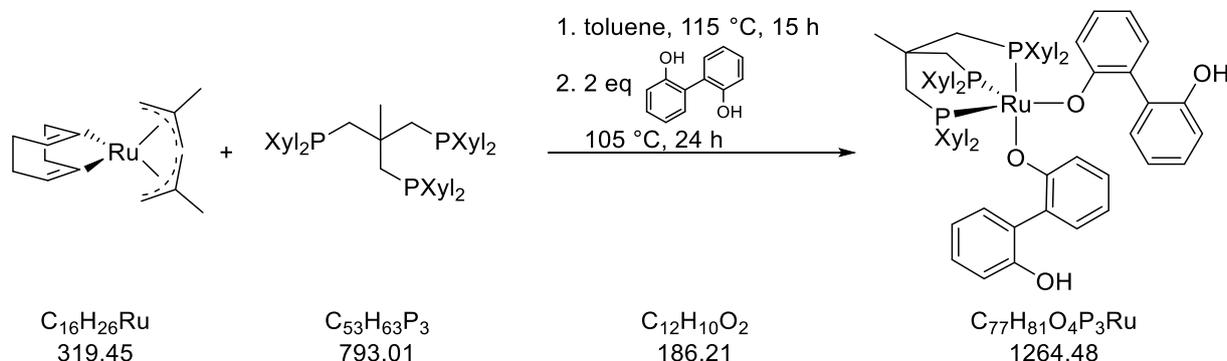
WAX column (60 m, inner diameter 0.25 mm, film thickness 0.25 μm) and flame ionization detector (250 $^{\circ}\text{C}$) using helium as carrier gas. An exemplary chromatogram is attached to the appendix (**Error! Reference source not found.**). The retention times and correction factors are shown in 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-Butandiol | 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 Synthesis of Ruthenium(1,1,1-tris(di(3,5-dimethylphenyl)phosphino-methyl)ethane)(2-ortho-phenylphenolato)₂



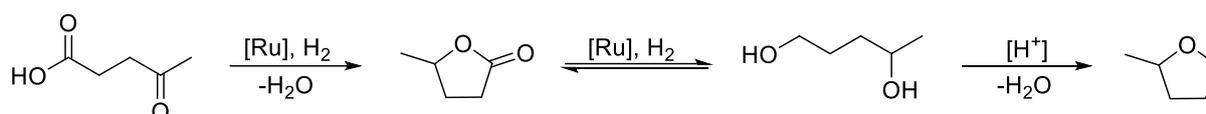
[Ru(cod)(2-methylallyl)₂] (242 mg, 0.758 mmol, 1.00 eq) and 1,1,1-tris(di(3,5dimethylphenyl)-phosphinomethyl)ethane (601 mg, 0.758 mmol, 1.00 eq) were suspended in 15 mL toluene and stirred of 15 h at 115 $^{\circ}\text{C}$. After cooling to room temperature, 2,2'-biphenol (282 mg, 1.52 mmol, 2.00 eq)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

$^1\text{H-NMR}$ (400MHz, THF- d_8): δ = 8.53 (s, 2H, OH), 7.19-7.11 (m, 16H, $\text{C}_{\text{Ar}}\text{H}$), 6.88-6.78 (m, 6H, $\text{C}_{\text{Ar}}\text{H}$), 6.68 (s, 5H, $\text{C}_{\text{Ar}}\text{H}$), 6.68-6.60 (m, 5H, $\text{C}_{\text{Ar}}\text{H}$), 2.30 (s, 6H, $3\times\text{CH}_2$), 1.97 (s, 36H, $\text{C}_{\text{Ar}}\text{CH}_3$), 1.55-1.54 (m, 3H, CCH_3) ppm.

$^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (162MHz, THF- d_8): δ = 44.1 (s, $3\times\text{PXyl}_2$) ppm.

Synthesis according to the literature.^[5]

4.4 Catalyses



[Ru(xyl-triphos)(bph) $_2$] (246 mg, 0.195 mmol, 1.00 eq) was dissolved in levulinic acid (100mL, 0.973 mol, 5000 eq). The reaction mixture 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 20 bar H_2 at room temperature while stirring. The autoclave was heated to 160 °C and pressurized with 50 bar H_2 . The H_2 pressure was kept constant by a MFC and the reaction mixture stirred at 800 rpm for 20 h. After cooling to room temperature, the reaction mixture was transferred in into a Schlenk flask. The solution was then heated and concentrated to ~10 wt% by vacuum distillation ($p = 10^{-3}\text{mbar}$, $T = \leq 110$ °C). The reaction mixture was transferred into a clean autoclave, which was previously evacuated and flushed with argon three times. The autoclave was placed into heating cuffs and pressurized with 20 bar H_2 at room temperature while stirring. The autoclave was heated to 160 °C and pressurized with 50 bar H_2 using a MFC. The H_2 pressure was kept constant by a MFC and the reaction mixture stirred at 800 rpm for 20 h. After cooling to room temperature, the reaction mixture was transferred in into a Schlenk flask and concentrated to 10 wt% by vacuum distillation (10^{-3}mbar). This procedure was repeated for the desired number of cycles.

5 Literature

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

6 Appendix

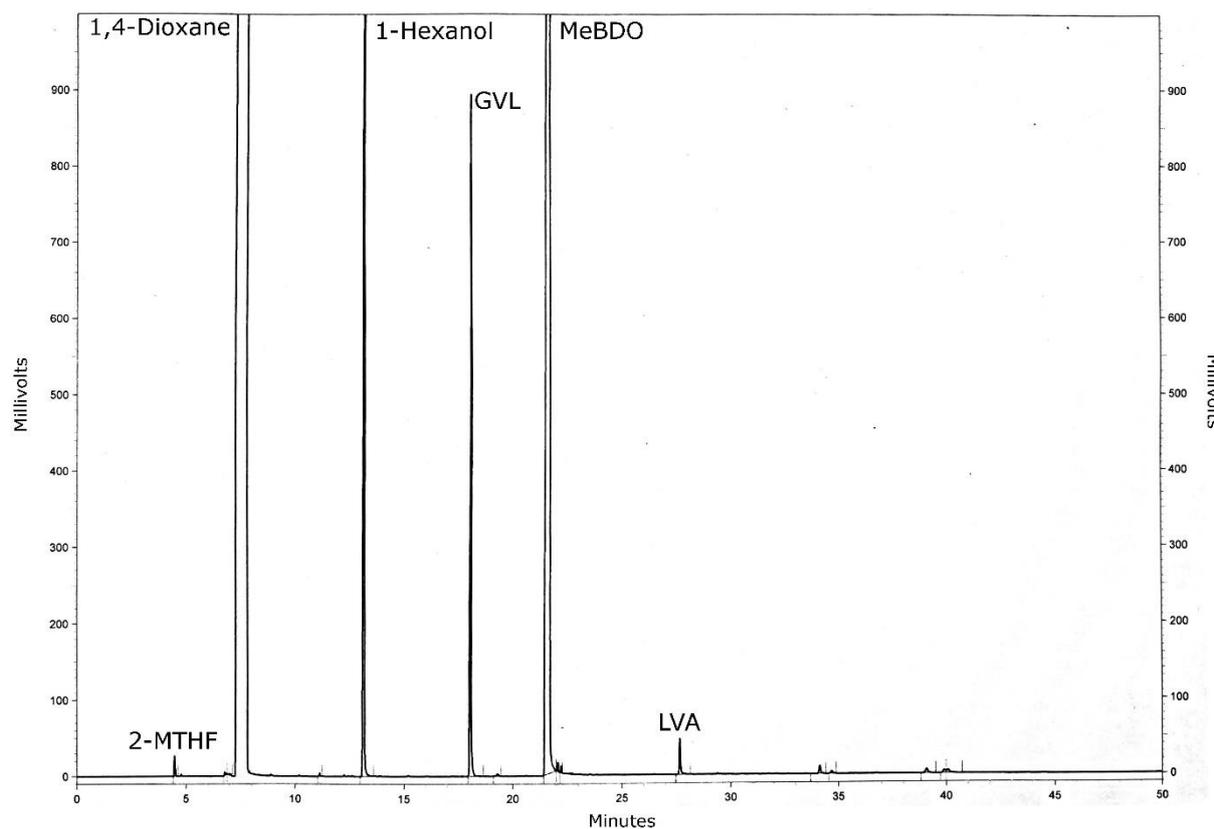


Figure 4: Exemplary gas chromatogram of the hydrogenation of LVA using 1-hexanol as internal standard.

Table 3: Recycling of [Ru(xyl-triphos)(bph)₂] in the hydrogenation of LVA ($p = const.$).

| Cycle | Product composition ^[a] [wt%] | | | | Conversion [%] |
|-------|--|-------|--------|------------------|----------------|
| | GVL | MeBDO | 2-MTHF | H ₂ O | |
| 1 | 37 | 46 | 0.1 | 15 | 99 |
| 2 | 52 | 30 | 0.2 | 15 | 98 |
| 3 | 51 | 33 | 0.2 | 15 | 100 |

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

Table 4: Recycling of [Ru(xyl-triphos)(bph)₂] in the hydrogenation of LVA with additive ($p = const.$).

| Cycle | Product composition ^[a] [wt%] | | | | Conversion [%] |
|-------|--|-------|--------|------------------|----------------|
| | GVL | MeBDO | 2-MTHF | H ₂ O | |
| 1 | 39 | 46 | 0.3 | 15 | 100 |
| 2 | 47 | 38 | 0.1 | 15 | 99 |
| 3 | 47 | 38 | 0.0 | 15 | 100 |
| 4 | 75 | 9 | 0.1 | 15 | 100 |

Reaction conditions: LVA (100 mL, 0.973 mol) [Ru] (0.195 mmol, 0.02 mol%), 2,2'-biphenol (1.95 mmol, 10 mol%), 50 bar H₂, 160 °C, 800 rpm, 20 h. ^[a] Determined by GC using 1-hexanol as internal standard.