



Abschließender Sachstandsbericht  
Leibniz-Wettbewerb

**Agro and Paper Industry Waste to Bulk Chemicals.  
Levulinic Acid and Furfural as Platform Chemicals.**  
Antragsnummer: SAW-2016-LIKAT-1

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**Projektleiter/in:** Prof. Dr. Johannes G. de Vries

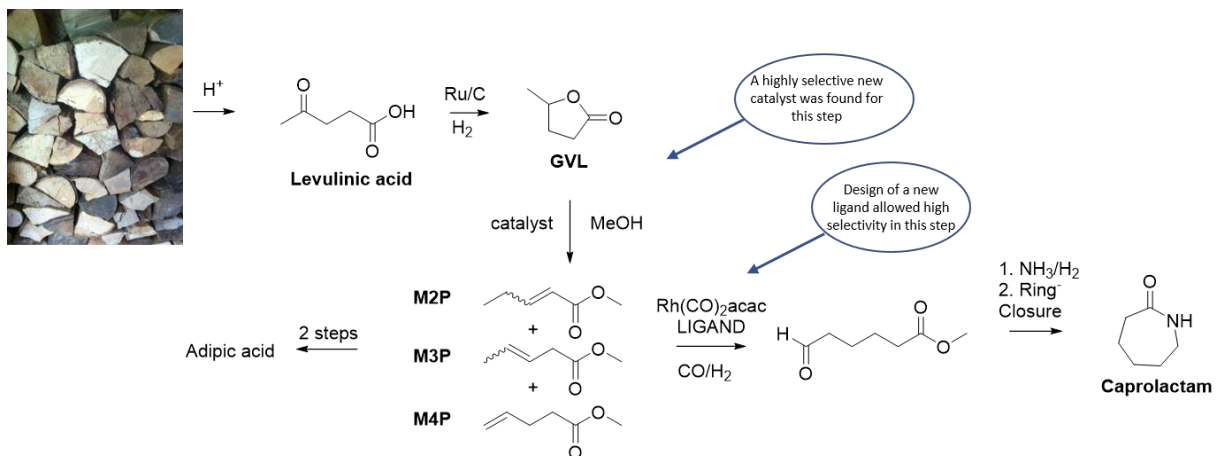
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## 1. Zielerreichung und Umsetzung der Meilensteine

The goal of the project was the development of new catalytic methods to convert biomass, ideally in the form of waste from the agro and the paper industry, via the platform chemicals levulinic acid (LA), 5-hydroxymethylfurfural (HMF) and furfural (FA) into useful chemicals that can serve as monomers for polymers, solvents or building blocks for the agro- and pharma industry. The original proposal was divided in 9 work packages which in the end was reduced to 8 as a result of a 10% reduction in funding with respect to the requested amount.

The project has been highly successful in that it has developed two new routes that will enable the economic conversion of bio-based levulinic acid into the Nylon monomers caprolactam and adipic acid. Both routes have been patented. The new routes to caprolactam counts 6 steps, whereas the current fossil-based route counts 7 steps.



**Scheme 1** Conversion of biomass-derived levulinic acid into caprolactam and adipic acid

In addition, the current route to caprolactam has a relatively high carbon footprint, part of which is related to rather large  $\text{NO}_x$  emissions caused by the production of hydroxylamine. As the new routes are based on the use of ammonia instead of hydroxylamine, there are no  $\text{NO}_x$  emissions associated with these new processes.

Other highlights are the development of new building blocks from bio-based 5-hydroxymethylfurfural, that may find application in the pharma- agro- and F&F industries as well as the development of a new route to dimethyl 2,5-furandicarboxylate, which can be used as monomer for the new bio-based polyester poly-ethylenefuranodioate (PEF). These inventions will be described in detail in the next section.

## 2. Aktivitäten und Hindernisse

**WP1** (PI: PD Dr. Detlef Heller) This WP was reduced in size because of the reduction in funding. The aim was the development of a better and cheaper catalyst for the *isomerisation of glucose to fructose*. This is a key step in the conversion of biomass to both HMF and LA. An efficient catalyst could allow lower temperatures to be used in these processes, thus leading to higher selectivities. Current best catalysts are either enzymes or tin-based zeolites. The first milestone, the development of an accurate analysis protocol was achieved. However, in spite of extensive tests, no catalysts were found that improved upon the state-of-the-art. A major stumble block was the self-redox reaction of glucose, induced by most homogeneous catalysts, leading to 50/50 mixtures of sorbitol and glucono-delta-lactone.

**WP2** (PI: Dr. Uwe Rodemerck) In this WP the goal was to find a gas-phase process for the *hydrogenation of methyl levulinate to 1,4-pentanediol* (1,4-PDO), a bio-based monomer for

polyesters. Here, extensive high throughput testing (140 catalysts) has been performed to find a good catalyst. With most catalysts gamma-valerolactone was formed with selectivities > 80%. In some reactions 1,4-PDO was formed. However, because of the high temperatures, in most cases the desired product reacted further to form 2-methyl-tetrahydrofuran (2-MeTHF). This was aggravated by the presence of acidic carrier materials. When Al<sub>2</sub>O<sub>3</sub>-based catalysts were used methyl valerate was formed in up to 70% selectivity. Although the goals have not been reached, these findings could form the basis of new processes towards 2-MeTHF, a renewable solvent, or methyl valerate.

**WP3** (PI: Dr. Norbert Steinfeldt) *Conversion of gamma-valerolactone (GVL) into butadiene.* Butadiene is an import monomer for rubbers as well as for Nylon 6,6. There is currently a shortage in the market caused by the use of American shale gas in crackers, leading to a very low output of C-4 hydrocarbons. LA can be hydrogenated to GVL in > 99% yield. The current project was aimed at finding catalysts for first, the decarboxylation of GVL to butene and second, the dehydrogenation of butene to butadiene using CO<sub>2</sub> as oxidant. Since good catalysts had already been reported for the first step, the focus of the research was on the second step with a further aim to combine steps 1 and 2 in a single process. Catalysts have been found that catalyzed the conversion of butene into butadiene with 30-35% selectivity. Use of CO<sub>2</sub> did lead to higher selectivities. It was impossible to combine the two processes in view of the large difference in temperature of the two processes.

**WP4** (PI's: Dr. Sebastian Wohlrab, Dr. Narayan Kalevaru) The goal of this WP was the catalyzed *ring-opening of GVL in the gas-phase to a mixture of methyl pentenoates (MP)* with a content of methyl 4-pentenoate (M4P) in excess of 80%. This in turn would allow the application of an older DSM patent that describes the selective hydroformylation of M4P from the mixture to methyl 5-formylvalerate, an intermediate that can be converted into caprolactam in two simple steps. The best known catalysts achieved selectivities to M4P of around 45%. In this WP we have found a catalyst based on ZrO<sub>2</sub> that is capable to catalyse the desired conversion to 95% of a mixture of MP's containing 81% of M4P. The catalyst was proven in an experiment with 100 h run time. This invention has been patented. The selective hydroformylation of M4P from this mixture using Rh/TPPTS as catalyst in a two-phase system worked indeed very well on this mixture and the 5-formylvalerate intermediate to caprolactam was obtained with very high selectivity. The remaining 2- and 3-pentenoate esters could be converted into dimethyl adipate with very high selectivity by isomerizing methoxycarbonylation.

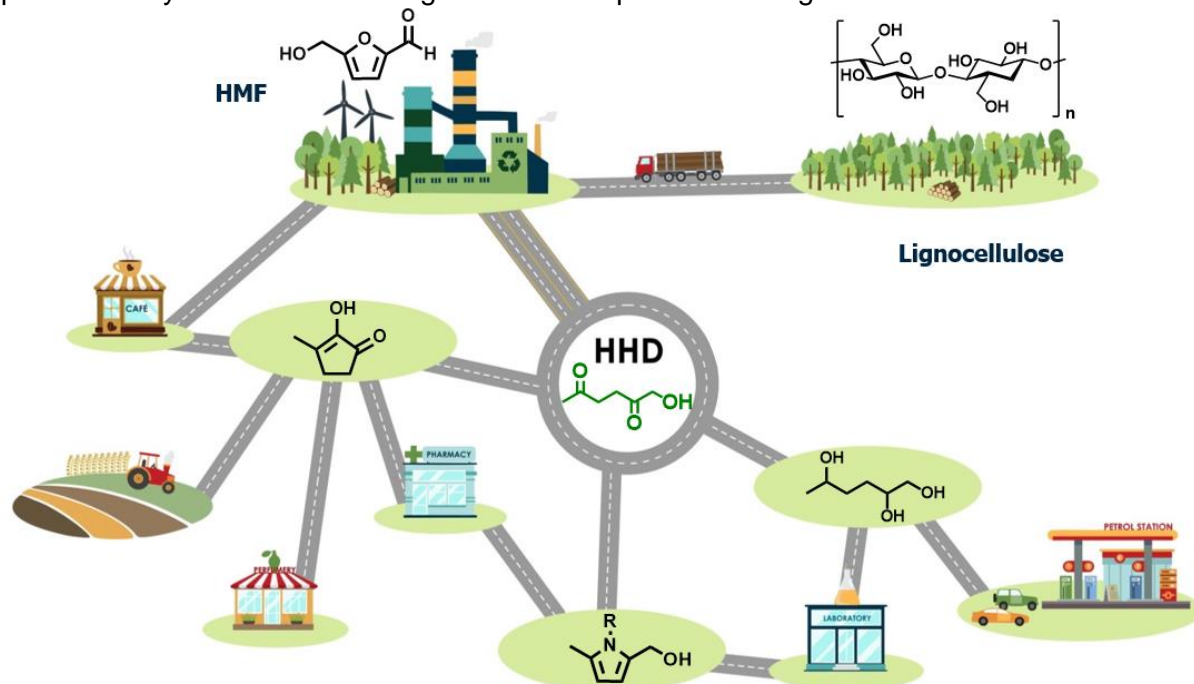
**WP5** (PI: Prof. Dr. Armin Börner) In this WP a range of *hydroformylation activities on building blocks derived from LA and FA* were foreseen. In the end, most of the work has concentrated on the selective isomerising hydroformylation of the mixture of methyl pentenoates. Other than in the procedure of WP4, here the entire mixture of M2P, M3P and M4P is converted into the desired 5-formylvalerate. New ligands were found, the use of which led to exceptional selectivities in this hydroformylation reaction. This invention was patented together with Evonik Performance Materials GmbH.

**WP6** (PI's Dr. Norbert Steinfeldt and PD Dr. Thomas Werner) This WP aimed at the development of *new routes to 2,5-furandicarboxylic acid (FDCA) based on furfural (FA) and on 5-chloromethyl-furfural* (an analogue of HMF). One project aimed at the catalytic conversion of the potassium salt of 2-furancarboxylic acid with CO<sub>2</sub> in a liquid phase reaction to form FDCA. A number of hydrotalcites and metal oxides were tested, but none of these led to useful yields of FDCA. Another approach was the conversion of 5-chloromethylfurfural, which can be obtained by dehydrating fructose (or even glucose) with HCl/LiCl. This was first oxidized to 2,5-diformylfuran using catalytic *N*-methyl-morpholine *N*-oxide and hydrogen peroxide in a modest 50% yield. This compound could be oxidized to FDCA, however, the two steps could not be combined in one pot as planned as the second oxidation requires basic conditions.

**WP7** (Dr. Esteban Mejia) In this WP it was attempted to find a new method to produce *phthalic acid* by an inverse electron demand *Diels-Alder reaction* between *dimethyl 2,5-furandioate* (see WP6) and N-vinyl-piperidine. Unfortunately, this reaction did not work. More successful was the oxidative esterification of HMF with methanol to dimethyl 2,5-furanidoate. This conversion was achieved with 99% selectivity at 100% conversion using a novel Co/Ru catalyst. This material is an intermediate in Avantium's production process for the renewable polymer PEF.

**WP8** In this WP the *decarbonylation of furfural to furan* was going to be investigated. This project was cancelled as a result of the 10% budget reduction.

**WP9** (PI's Prof. Dr. Johannes G. de Vries, Dr. Sergey Tin, Dr. Yuehui Li) This was the most ambitious of all the work packages. The proposal aimed at the conversion of the aldehyde group of FA or HMF in a dehydrogenative reaction with nucleophiles catalyzed by *N*-heterocyclic carbenes. Some preliminary investigations were performed, including some mechanistic NMR studies, which led to the conclusion that this reaction could not work. Instead in this WP we have investigated the chemistry of 1-hydroxy-2,5-hexanedione (HHD), which can be obtained in a single step in good yield from HMF. Attempts to convert this six-atom building block into aromatics did not work. However, base-catalysed ring-closure of HHD gave rise to the formation of 3-methyl-2-hydroxy-cyclopent-2-ene-1-one, which is a known flavouring compound found in coffee and maple syrup. Reaction of HHD with primary amines in ethanol at room temperature led to >99% yields of the 1-alkyl-2-hydroxymethyl-5-methyl-pyrroles. This exceptionally mild and selective reaction can be classified as a *Click-Reaction*. And finally, in the same project we have subjected the triols that can be obtained from HHD to the deoxydehydrogenation reaction, leading to the unsaturated alcohols in good yields. The products may find use as building blocks in the pharma and agro industries.



**Scheme 2.** Use of bio-based HHD for the production of pharma-, agro- and flavours & fragrances

One of the Ph.D's paid by the project has supported all other projects with DFT calculations. Mostly to solve mechanistic issues. (PI: PD Dr. Haijun Jiao).

### 3. Ergebnisse und Erfolge

The project has led to:

#### *Patents*

1. S. Behrens, G. Torres Morales, A. Börner, R. Franke, D. Selent, DE 102017206200 (2017). Hydroformylierung von Pentensäureestern.
2. A. Marckwordt, H. Amani, Hadis, V. N. Kalevaru, S. Wohlrab, P. C. J. Kamer, J. G. de Vries, DE 10 2018 114 441 (2019), Verfahren zur Herstellung von endständig ungesättigtem Alkencarbonsäureester aus Lactonen.

#### *Publications*

25 publications in peer-reviewed journals, 4 of which are open access. A number of publications are still forthcoming.

#### *Scientific qualifications (Ph.D.'s, Habilitations)*

Dr. Esteban Mejian has submitted all the necessary documents for his habilitation; two of the publications he submitted were related to the research done in this project.

Dr. Bartosz Wozniak, Dr. Zhihong Wei and Dr. Stephan Behrens obtained their Ph.D. based on the research performed in this project. Annemarie Marckwordt and Abel Salazar will defend their theses this year.

#### *Additional funding obtained as a result of this project:*

Based on the results of WP9 a proposal was written aimed at the conversion of sugars into aromatics. This proposal was part of the larger proposal for a Leibniz Campus “ComBioCat” (PI Prof. Dr. Paul C. J. Kamer) which was funded as of 01.10.2019.

De Vries and Kalevaru have written a proposal for a joint call of the Indian Science Foundation and the DFG based on the results of WP4.

The Wohlrab group has started research on the oxidation of propenoic acid to acrylic acid, based on the results of WP3.

#### *Dissemination*

In addition to the publications mentioned above, all PI's have presented lectures at international conferences on the results obtained in this project. The Ph.D. students that were participating in this project have presented posters and have given oral presentations at conferences (Katalytikertagung Weimar, International Symposium on Homogeneous Catalysis (Amsterdam), Green Catalysis symposium (Rennes), International Symposium on Green Chemistry (La Rochelle), bi-annual meetings of the American Chemical Society. One publication has appeared in Leibniz Nord-Ost.

A station on the Theme of the project is in preparation for Die Lange Nacht der Wissenschaften, Rostock.

### 4. Chancengleichheit

All new positions were advertised. In these advertisements the following text is a standard part: LIKAT supports professional equality of women and men and so applications from women are most welcome. As women are underrepresented in this sector of LIKAT preference will be given to women with equal qualification. Disabled applicants with equal qualification and aptitude will be given preferential consideration.

## 5. Qualitätssicherung

All publications contain an electronic supplementary information containing the description of the experiments as well as copies of all relevant spectra as well as the data on the electronic calculations.

Till recently the extra cost associated with publishing open access was between € 1500-4000,- per publication. This extra cost was not provided as part of the funding by the Leibniz Association. In the mean time we have agreements with Wiley and Springer regarding open access. Negotiations with the American Chemical Society and Elsevier are still ongoing.

All students and co-workers have been taught on the different aspects of responsible scientific conduct. There also is a clause in the contract of all scientists relating to good scientific conduct.

## 6. Zusätzliche eigene Ressourcen

For project management (hours of the PI's): 36 man months

The current overhead per researcher month is € 2700. For the project as a whole this would amount to ca. € 750 000,- This amount includes analysis services as well as administration.

## 7. Strukturen und Kooperation

The project was pre-structured by de Vries and the individual groups in LIKAT could submit proposals for the separate parts. In this way the project was integrated from the start. The entire project group had bi-annual meetings, but separate clusters (for instance nylon intermediates) had more regular contacts. In the last year of the project contacts were made with the Leibniz Institute für Plasmaforschung und Technologie (INP Greifswald). In this informal collaboration we have investigated the use of low temperature plasma for the pretreatment of cellulose and lignocellulose.

## 8. Ausblick

The catalytic conversion of renewable resources into chemicals remains an extraordinary important field. The current relatively low oil prices, caused for a large part through the production of cheap shale gas in the USA, makes the traditional chemical companies reluctant to invest in new plants based on renewables. Nevertheless, virtually all chemical companies would like to switch at least part of their product portfolio to bio-based products. Opportunities exist for simple one-step processes that lead to a lower cost price than the current fossil-based process.

Scientifically, there is still a need for better catalysts and processes for the conversion of sugars into chemicals. In particular, dehydration, hydrogenolysis, hydrogenation, decarbonylation and decarboxylation are chemical conversions that are needed to convert sugars into useful chemicals. Also processes based on the use of CO<sub>2</sub> are extremely important.