



abiosus e.V.

Non-Profit Association for the Advancement of Research on Renewable Raw Materials

11th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

**May 30 – June 1, 2022
Dortmund, Germany**

in Cooperation with

Agency of Renewable Resources (FNR)
TU Dortmund University

German Society for Fat Science (DGF)

German Chemical Society (GDCh), Division of Sustainable
Chemistry



Fachagentur Nachwachsende Rohstoffe e.V.

tu technische universität
dortmund



Deutsche Gesellschaft für Fettwissenschaft e.V.



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MONDAY
 May 30, 2022
 Dorint, Picasso 1-3

15:45		Welcome & Opening	
16:00	L1	Meier	M
16:30	L2	Cole-Hamilton	D
17:00	L3	Dierker	D
18:30		Opening Mixer & Poster Session (18:30-21:00)	

TUESDAY
 May 31, 2022
 Dorint, Picasso 1-3

9:00	L4	Seidensticker	M
9:30	L5	Vondran	D
9:50	L6	von Vietinghoff	D
10:10	L7	Di Serio	D
10:30	L8	Schunck	D
10:50		Coffee Break	
11:20	L9	Gröger	M
11:50	L10	Myrtollari	D
12:10	L11	Seo	D
12:30	L12	Kanter	D
12:50		Lunch Break	
14:00	L13	Wiedemann	M
14:30	L14	Kelly	D
14:50	L15	Solduga	D
15:10	L16	Di Serio	D
15:30		Coffee Break	
16:00	L17	Mecking	M
16:30	L18	Kirchberg	D
16:50	L19	Caillol	D
17:10	L20	Zaccheria	D
19:00		Conference Dinner	

WEDNESDAY
 June 01, 2022
 Dorint, Picasso 1-3

9:00	L21	Averous	M
9:30	L22	Mutlu	D
9:50	L23	Quienne	D
10:10	L24	Winnacker	D
10:30		Coffee Break	
11:00	L25	Brück	M
11:30	L26	de Vries	M
12:00	L27	Gooßen	M
12:30		Poster Award & Closing Remarks	
12:45		End of Workshop	
13:00		Closing Lunch	

Program

Lectures and Posters

Monday, May 30, 2022

15.00 Registration and Welcome Coffee

15.45 **Welcome and Opening**

Jürgen O. Metzger, *abiosus* e.V.

Markus Dierker, President of German Society of Fat Research (DGF)

Thomas Seidensticker, TU Dortmund

16.00 – 17.30 *First Session*

Chair: Thomas Seidensticker

16.00 – 16.30 **A personal journey through 15 years of Oleochemistry (M)**
L1 Michael A. R. Meier, KIT, Karlsruhe, Germany

16.30 – 17.00 **The role of chemists and chemical engineers in a sustainable world (M)**
L2 David Cole-Hamilton, University of St. Andrews, UK

17.00 – 17.30 **Industrial applications of plant-based hydrocarbons (M)**
L3 Markus Dierker, BASF, Düsseldorf, Germany

18.30 – 21.00 **Opening Mixer and Poster Session**

(M) Main Lecture 30 min. including discussion

(D) Discussion Lecture 20 min including discussion

Tuesday, May 31, 2022

9.00 – 10.50 *First morning session*

Chair: Mike Meier

9.00 – 9.30 **Homogeneous Catalysis for the Functionalization of Oleochemicals: From Laboratory to Miniplant Scale (M)**
L4 Thomas Seidensticker, TU Dortmund University, Germany

9.30 – 9.50 **Homogeneously transition metal catalyzed oxidation of methyl oleate with H₂O₂ – selectivity control and catalyst separation (D)**
L5 Johanna Vondran, Thomas Seidensticker, TU Dortmund University, Germany

9.50 – 10.10 **Triphasic gas/liq/liq segmented slug flow reactor for selectivity control in continuous reactions (D)**
L6 Niclas von Vietinghoff, Thomas Seidensticker, David W. Agar, TU Dortmund University, Germany

10.10 – 10.30 **Chemical Reaction Engineering of Vegetable Oils Epoxidation (D)**
L7 Vincenzo Russo, Tommaso Cogliano, Rosa Turco, Pasi Tolvanen, Adriana Freites Aguilera, Tapio Salmi, Riccardo Tesser, Martino Di Serio, Università di Napoli Federico II, Napoli, Italy

10.30 – 10.50 ***In vivo* Synthetic Olefin Metathesis Catalysis in Microalgae Lipid Droplets**
L8 Natalie S. Schunck, Stefan Mecking, University of Konstanz, Konstanz, Germany

10.50 – 11.20 **Coffee break**

11.20 – 12.50 *Second morning session*

Chair: Thomas Brück

11.20 – 11.50 **Conversion of unsaturated fatty acids into industrial speciality and fine chemicals using chemo- and biocatalysts (M)**
L9 Harald Gröger, University of Bielefeld, Bielefeld, Germany

11.50 – 12.10 **Biocatalytic synthesis of oleochemicals (D)**
L10 Robert Kourist, Elia Calderini, Yue Sun, Kamela Myrtollari, Technische Universität Graz, Graz, Österreich

12.10 – 12.30 **H₂O₂ tunnel engineering for making robust BVMO to produce oleochemicals efficiently (D)**
L11 Eun Ji Seo^{a,b}, Uwe T. Bornscheuer^b, Jin-Byung Park^{a*},
^a Ewha Womans University, Seoul, Republic of Korea; ^b Greifswald University, Greifswald, Germany

- 12.30 – 12.50 **Biotechnological production of odour-active fatty aldehydes by α -dioxygenase and aldehyde dehydrogenase (D)**
L12 Jean-Philippe Kanter¹, Philipp J. Honold¹, Andreas K. Hammer², Christoph Harms³, Egon Gross³, Uwe Bornscheuer⁴, Marco A. Fraatz¹, Jakob P. Ley³, Holger Zorn^{1,2}
¹Justus Liebig University Giessen, Giessen, Germany. ²Fraunhofer Institute for Molecular Biology and Applied Ecology Giessen, Germany. ³Symrise AG, Holzminden, Germany. ⁴University of Greifswald, Greifswald, Germany
- 12.50 – 14.00 **Lunch break**
Restaurant Davidis
- 14.00 – 15.30 *First afternoon session*
Chair: Markus Dierker
- 14.00 – 14.30 **A Review of the Solid-Catalysed Isomerisation of Oleic Acid to Iso-Oleic Acid - How understanding of the reaction at molecular level has led to improved catalyst design and efficiency (M)**
L13 Sophie C.C. Wiedemann, Tanja van Bergen-Brenkman, Roel Moonen, Croda Nederland B.V., Gouda, The Netherlands
- 14.30 – 14.50 **Montmorillonite clay catalysts for oleochemical processing (D)**
L14 Oscar Kelly, Callum Morris, Adam Mudashiru, Adam Brookbanks, BYK Additives Limited, Widnes, Cheshire, United Kingdom
- 14.50 – 15.10 **Sustainable bio-based surfactants (D)**
L15 Gemma Solduga¹, Niklas Thiel², Clariant, Frankfurt¹, Burgkirchen², Germany
- 15.10 – 15.30 **Epoxidized Vegetable oils as additive for Bioplastics (D)**
L16 Rosa Turco^{1,2}, Gabriella Santagata², Cinzia Pezzella³, Riccardo Tesser¹, Martino Di Serio¹; ¹Department of Chemical Sciences, University of Naples Federico II, Naples, Italy; ² Institute for Polymers, Composites and Biomaterials, CNR, Pozzuoli, Italy; ³ Department of Agricultural Sciences, University of Naples Federico II, Portici, Italy
- 15.30 – 16.00 **Coffee break**

- 16.00 – 17.30 *Second afternoon session*
- Chair: Luc Averous*
- 16.00 – 16.30 **Plant oil-based polymers for closed loop recycling and non-persistence** (M)
L17 Stefan Mecking, University of Konstanz, Konstanz, Germany
- 16.30 – 16.50 **Sustainable Syntheses of Non-Isocyanate Polyurethanes based on Renewable 2,3-Butanediol** (D)
L18 Anja Kirchberg, Masood Khabazian Esfahani, Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- 16.50 – 17.10 **Plant oil based radically polymerizable monomers for sustainable polymers** (D)
L19 Sylvain Caillol, ICGM, Univ Montpellier, CNRS ENSCM, Montpellier, France
- 17.10 – 17.30 **Styrene-free thermosetting resins from vegetable oils** (D)
L20 Fabio Bertini, Adriano Vignali, Nicoletta Ravasio, Federica Zaccheria, CNR SCITEC “G. Natta”, Milano, Italy
- 19.00 **Conference Dinner**
- Restaurant Davidis

Wednesday, June 01, 2022

9.00 – 10.30 *First morning session*

Chair: Johannes de Vries

9.00 – 9.30 **Biobased polyurethanes based on different macromolecular architectures from different resources (M)**

L21 Luc Averous, University of Strasbourg, Strasbourg, France

9.30 – 9.50 **A more sustainable chemistry with elemental sulfur surplus: towards the design of novel polymers (D)**

L22 Timo Sehn,¹ Daniel Döpping,¹ Patrick Theato,^{1,2} Hatice Mutlu¹,
¹Soft Matter Synthesis Laboratory, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany, ²Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

9.50 – 10.10 **Synthesis of fully biobased and reprocessable polyurethane foams (D)**

L23 Baptiste Quienne, Florian Cuminet, Julien Pinaud, Sylvain Caillol*, Institut Charles Gerhardt Montpellier, Université Montpellier, CNRS, ENSCM, Montpellier, France

10.10 – 10.30 **Terpene-Based Biopolymers as Novel Functional Biomaterials - Synthesis, Analysis and Applications (D).**

L24 Malte Winnacker, Magdalena M. Kleybolte, Andreas J. G. Beringer, Technische Universität München, München, Germany

10.30 – 11.00 **Coffee Break**

11.00 – 12.30 *Second morning session*

Chair: Sophie Wiedemann

11.00 – 11.30 **Synthetic biotechnology for material innovation- CO2 conversion to carbon fiber composites and innovative lightweight materials (M)**

L25 Thomas Brück, Technical University of Munich, Munich, Germany

11.30 – 12.00 **Sustainable polymers. Use of renewable resources and recycling (M)**

L26 Johannes de Vries, LIKAT, Rostock, Germany

12.00 – 12.30 **Isomerizing Metathesis as a Concept for the Valorization of Fatty Acid Derivatives (M)**

L27 Lukas J. Gooßen, Ruhr-Universität Bochum, Bochum, Germany

12.30 – 12.45 **Poster Award and Closing Remarks**

Best Poster Award

Award committee: Lukas Gooßen, Harald Gröger, Stephan Mecking

Closing Remarks

Thomas Seidensticker

12.45

End of Workshop

13.00

Closing Lunch

Restaurant Davidis

Poster

- P1 **The role of Stabilizers in H₂O₂ for the Peroxyformic Acid Synthesis and Decomposition Kinetics**
Riccardo Tesser, Vincenzo Russo, Tommaso Cogliano, Rosa Turco, Rosa Vitiello, Tapio Salmi, Martino Di Serio, Department of Chemical Science, Università di Napoli Federico II, Napoli, Italy
- P2 **Büchi „Miniclave“ A suitable tool for the downscale process development of Fatty Acid Ethyl Ester – Biodiesel**
Axel Ingendoh, Inachem GmbH, Odenthal, Germany
- P3 **Optimized reaction conditions for the synthesis of 12-opda**
Tim Lukas Guntelmann^{1*}; Karl-Josef Dietz²; Harald Gröger¹, ¹Faculty of Chemistry, Bielefeld University, Bielefeld, Germany, ²Faculty of Biology, Bielefeld University, Bielefeld, Germany
- P4 **Ruthenium catalyzed oxidative cleavage of high oleic sunflower oil**
Luis Santos Correa, Michael A. R. Meier, Institute of Organic Chemistry (IOC) and Institute of Biological and Chemical Systems– Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- P5 **Functionalization of oleo chemicals: Developing sustainable processes by integrated catalyst recycling**
Astrid I. Seifert¹, Johanna Vondran², Thomas Seidensticker², Kerstin Wohlgemuth¹, ¹TU Dortmund University, Laboratory of Plant and Process Design, Dortmund, Germany, ²TU Dortmund University, Laboratory of Industrial Chemistry, Dortmund, Germany
- P6 **Synthesis of linoleic acid hydroperoxides using immobilized LOX for the application in a flow reactor system**
Valentin Gala Marti, Ulrich Schörken, Faculty of Applied Natural Sciences, TH Köln, Leverkusen, Germany
- P7 **Semi-Hydrogenation of Poly-Unsaturated Fatty Acid Derivatives in Multiphase Catalysis**
Maximilian Spiekermann, Florian Lehmann, Thomas Seidensticker, Laboratory of Industrial Chemistry, Department of Biochemical and Chemical Engineering, TU Dortmund University, Dortmund, Germany
- P8 **Organic Solvent Nanofiltration: Recycling of an unmodified Grubbs-Hoveyda catalyst in the self-metathesis of cardanol**
Alexander Kühn, Daniel Fakesch, Dieter Vogt, Thomas Seidensticker, Laboratory of Industrial Chemistry, Department of Biochemical and Chemical Engineering, TU Dortmund University, Dortmund, Germany
- P9 **Synthesis of amino-functionalized oleochemicals via hydroaminomethylation with integrated catalyst recycling**
Anna Kampwerth, Dieter Vogt, Thomas Seidensticker, Laboratory of Industrial Chemistry, Department of Biochemical and Chemical Engineering, TU Dortmund University, Dortmund, Germany

- P10 **Synthesis of fatty amines by homogeneously catalyzed amination of fatty alcohols**
Christian Heider, Dominik Pietschmann, Alina Winter, Dieter Vogt, Thomas Seidensticker, Technical University Dortmund, Laboratory of Industrial Chemistry, Dortmund, Germany
- P11 **Intensification strategies for homogeneously catalyzed hydroformylation of oleo chemicals in aqueous multiphase systems: Utilizing the "chaos"**
T. Roth, M. Heyng, D. Vogt, T. Seidensticker, TU Dortmund University, Laboratory of Industrial Chemistry, Dortmund, Germany
- P12 **Hydroaminomethylation of oleochemicals in a continuously operated miniplant**
Tim Riemer, Thomas Seidensticker, Dieter Vogt, Laboratory of Industrial Chemistry, Department of Biochemical and Chemical Engineering, TU Dortmund University, Dortmund, Germany
- P13 **Application of multiphase systems for the intensified production of furans from biomass**
Nico Thanheuser¹, Jesús Esteban², Andreas J. Vorholt¹, ¹Max-Planck-Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany, ²Department of Chemical Engineering. The University of Manchester, Manchester, United Kingdom
- P14 **Catalysis and Chemical Reaction Engineering for Biolubricants Productions**
Rosa Vitiello, Francesco Taddeo, Rosa Turco, Vincenzo Russo, Riccardo Tesser, Martino Di Serio Department of Chemical Science, Università di Napoli Federico II, Napoli, Italy
- P15 **Pulsed Electric Field (PEF) Treatment for Lipid Extraction from Microalgae**
Aude Silve, Natalja Nazarova, Rüdiger Wüstner, Wolfgang Frey, Institute for Pulsed Power and Microwave Technology, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P16 **Polythiomalonamides: Renaissance of Industrial Waste, i.e. Elemental Sulfur, in Functional Materials**
Timo Sehn¹, Patrick Theato^{1,2}, Hatice Mutlu¹, ¹ Soft Matter Synthesis Laboratory, Karlsruhe Institute of Technology (KIT)Eggenstein-Leopoldshafen,Germany.² Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- P17 **Cost Effective Marriage of Poly(dithiocarbonates) with Elemental Sulfur**
Timo Sehn, Hatice Mutlu, Soft Matter Synthesis Laboratory, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany
- P18 **Synthesis of vinyl monomers from commercial olive oil via transesterification with N-hydroxyethyl acrylamide**
Oliver J. Harris and Fiona L. Hatton, Department of Materials, Loughborough University, Loughborough, LE11 3TU

Abstracts

Part 1: Lectures

A personal journey through 15 years of Oleochemistry

Michael A. R. Meier

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The use of fats and oils as starting materials for the chemical industry is well established. A personal retrospect on the development within the last 15 years, mainly based on own research results, will be given, highlighting advantages as well as limitations of fats and oils as renewable feedstocks. Especially fatty acid derived monomers and their polymers will be discussed, including recent examples on the advantageous combination of fatty acids with other renewable resources, such as lignin or carbohydrates. Throughout, sustainability aspects will be highlighted, as renewability is not enough to improve overall sustainability.

L2

The role of chemists and chemical engineers in a sustainable world¹

David J. Cole-Hamilton

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The world is at a crossroads. It has come from a time where fossil fuel resources provided the raw materials for almost everything and most things were used and thrown away. Because fossil fuels are finite and their burning causes global changes in climate, and because most other resources are finite, we must move to a world where renewable resources are used to make reusable and recyclable objects in a circular economy for sustainable development. The renewable resources must not compete for land with food production.

The United Nations has defined seventeen goals for sustainable development. In this talk we shall explore how chemistry can contribute to achieving all of these goals.

In a special section, our own work using organometallic homogeneous catalysts for the formation of performance chemicals from bio-oils will be described. We shall show how Tall Oil, a by-product from making paper from pine trees, which is available at 2 M tonnes per year, can be used to make a biodegradable substitute for polyethylene² as well as diamines for use in polyamides (nylons).³

We shall further describe how cashew nut shell liquid, a mildly toxic by-product from cashew nut processing, available at >500,000 tonnes per year can be used to make a variety of high added value products.⁴⁻⁸

References:

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2. M. R. L. Furst, T. Seidensticker and D. J. Cole-Hamilton, *Green Chem.*, 2013, **15**, 1218-1225.
3. Y. P. Shi, P. C. J. Kamer and D. J. Cole-Hamilton, *Green Chem.*, 2017, **19**, 5460-5466.
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7. S. Baader, P. E. Podsiadly, D. J. Cole-Hamilton and L. J. Goossen, *Green Chem.*, 2014, **16**, 4885-4890.
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L3

Industrial applications of plant-based hydrocarbons

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Abstract not available.

Homogeneous Catalysis for the Functionalisation of Oleochemicals: From Laboratory to Miniplant Scale

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Unsaturated oleochemicals have shown to be promising feedstocks in the synthesis of biobased chemical intermediates in the production of, e.g. polymers, lubricants and surfactants. Homogeneous transition metal catalysis certainly possesses great potential in this regard, considering selectivity, atom economy and mild reaction conditions by selectively attaching various functional groups to C=C double bonds

In a nutshell: Homogeneously catalysed reactions may contribute to the success of the necessary transformation process of the chemical industry towards sustainability.

However, for such transformations to become competitive to existing synthesis routes and attractive to be run on a continuous and larger scale, different major challenges remain in the downstream process beyond chemistry: efficient product separation considering sufficient purity, recovery of the precious homogeneous catalyst including recycling, etc., only to name a few. Established concepts already operated in the chemical industry addressing these points are not applicable one-to-one to the conversion of oleochemicals due to their generally higher boiling points, polarity, and the usually very sensitive nature of the applied transition metal catalytic system.

Hence, for all the numerous homogeneously catalysed transformations of oleochemicals towards the synthesis of biobased platform intermediates, novel solutions for sustainable processes must be developed to allow a successful and economically viable transfer on a larger scale.

Some of these concepts developed at TU Dortmund will be highlighted in the present contribution. Among these are thermomorphic solvents (TMS) systems and the innovative approach of selective product crystallisation. Additionally, these concepts will be discussed concerning their implementation into continuous miniplant processes.

L5

Homogeneously transition metal catalyzed oxidation of methyl oleate with H₂O₂ – selectivity control and catalyst separation

Johanna Vondran, Thomas Seidensticker
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The oxidation of unsaturated oleochemicals, such as methyl oleate, offers wide potential towards the production of bio-based value products. Depending on the reaction conditions, versatile products such as epoxides, diols and carboxylic acids are obtained. However, taking control of selectivity is often challenging due to potential over-oxidation and side-reactions of products and intermediates. Homogeneous transition metal catalysis is a powerful tool in this regard, allowing for selectivity control and activation of the oxidant. The application of hydrogen peroxide as the sole oxidant is beneficial since it is easy to handle in aqueous solution and, contributing to the green chemistry, the only by-product is water.

In addition to selectivity control, the main challenges for homogeneously catalyzed oxidation are the separation and recycling of an active catalyst to save cost and resources, and the purification of the product to allow for potential subsequent application in the synthesis of e.g. polymers. These aspects are considered for first, Ru-catalyzed epoxidation of technical grade methyl oleate. A recycling approach of combined extraction of the product epoxide and pervaporation to retain the active catalyst and separate water from the reaction solution is successfully developed. The epoxide is a valuable product, and by controlled hydrolysis it is further converted to a vicinal diol. This two-stage reaction is transferred into continuous flow to increase space-time-yield. Hereby, the diol is isolated as a stable intermediate from the reaction mixture by simple precipitation. Finally, the diol is oxidized to pelargonic acid and mono methyl azelate using a cost-efficient W-catalyst, which can be retained *via* organic solvent nanofiltration.

Triphasic gas/liq/liq segmented slug flow reactor for selectivity control in continuous reactions

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² Laboratory for Industrial Chemistry, TU Dortmund, Dortmund, Germany
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The combination of renewable fats and oils with homogeneous multiphase catalysis shows promising results in gas-liquid reactions that may provide a significant contribution to a greener and future-oriented chemical industry. A transfer of such multiphase reactions from a discontinuous reactor to a continuous operation involves a high equipment requirement, especially on laboratory scale. Particularly for consecutive reactions, where the intermediate is the value product, a use of continuous stirred tank reactors (CSTR) entails a drastic reduction in selectivity compared to the discontinuous mode. Plug flow reactors are more suitable from a process engineering perspective. Beside large scale bubble columns, segmented slug flows in micro capillaries (≤ 1 mm) not only allow three-phase gas-liquid-liquid systems, but also offer small-scale application in addition with a narrow residence time distribution and high phase interfaces. This makes this kind of reactor very suitable for investigations of multiphase reactions in flow and may lead to high selectivities.

In this contribution, the applications and challenges of a lab-scale capillary reactor with a three-phase segmented slug flow are presented and discussed. Using a homogeneously catalyzed selective hydrogenation of C18:2-rich sunflower oil, solutions for solids formation, flow stabilization and feeding of reaction gas along the capillary will be presented. As this reaction represents a gas-consuming reaction, a focus will be set on different technologies for gas feeding, as gas permeation or a pulsed addition of new gas droplets. At the same time, the great potential of this type of reactor for other reactions in the field of renewable feedstocks will be outlined.

Chemical Reaction Engineering of Vegetable Oils Epoxidation

Vincenzo Russo, Tommaso Cogliano, Rosa Turco, Pasi Tolvanen, Adriana Freitas Aguilera, Tapio Salmi, Riccardo Tesser, Martino Di Serio
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Epoxidized vegetable oils are used as chemical intermediates and bio-based lubricants. Epoxidation of unsaturated fatty acids in vegetable oils by the Prileschajew method is a complex multiphase reaction system, which consists of an oil phase and a continuous aqueous phase. The main route for the perhydrolysis is the catalyzed process on the active sites present on the heterogeneous acid catalyst immersed in the aqueous phase. The epoxidation reaction takes place in the oil phase as the percarboxylic acid reacts with the double bonds of the vegetable oil forming an oxirane ring. Besides these reactions, ring-opening of oxirane takes place, which leads to a spectrum of secondary products. It is very evident that advanced mathematical modelling is needed to describe the multiphase system of the epoxidation process. Mathematical models with various degree of sophistication were developed and compared in the present work, starting with a real multiphase model based on fundamental principles. The chemical reactions were assumed to proceed in an isothermal stirred batch reactor operated under atmospheric pressure. The system consists of an aqueous phase, a solid catalyst phase and an oil phase. The aqueous phase is the continuous one, while the oil droplets are dispersed in the aqueous milieu. Chemical reactions were presumed to proceed in the aqueous bulk phase, in the pores of the solid catalyst, i.e. on the surface sites of the catalyst and in the oil droplets. The governing mechanism in the porous catalyst particles and in the oil droplets is the coupled reaction-diffusion process. The diameters of the oil droplets can change because of chemical reactions and the change of physical properties during the progress of the reaction. The numerical approach was based on the method of lines: the spatial coordinates of the components in the oil droplets and in the porous catalysts were discretized with central difference formulae because a diffusion problem was concerned.

***In vivo* Synthetic Olefin Metathesis Catalysis in Microalgae Lipid Droplets**

Natalie S. Schunck, Stefan Mecking

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The chemical machinery of cells is extremely efficient, yet its scope is limited. Synthetic catalysis could enable transformations complimentary to those found in nature and achieving such bio-orthogonal catalytic reactions inside living cells is therefore an appealing target. Here, photoautotrophic cells are of special interest as they sustain on atmospheric carbon dioxide and sunlight as a carbon and energy source, respectively. This ability is key for future carbon neutral production schemes. However, synthetic catalysis in photoautotrophic organisms remained elusive to date.

In this contribution, we show that organometallic catalysts enable *in vivo* catalytic olefin metathesis inside photoautotrophic microalgae cells. The small molecule catalysts with lipophilic fluorescent moieties can cross the cell wall of the single-cell organisms. This internalization does not adversely affect the cells' viability or destroy the catalyst exposed to the intracellular environment. Olefin metathesis catalysis is a new-to-nature transformation central to today's industrial upgrading of natural plant oils.¹⁻⁴ Here, it converts the stored fatty acids in the microalgae cells' lipid droplets to alkenes and long-chain dicarboxylates that are valuable building blocks for polymers.⁵ This bioorthogonal synthetic catalysis in photoautotrophic cells provides pathways for the production of desired chemicals in intact cells as reactors.

References:

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L9

Conversion of unsaturated fatty acids into industrial speciality and fine chemicals using chemo- and biocatalysts

Harald Gröger

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Today's "product tree" of industrial chemicals is still mainly based on fossil feedstocks, and accordingly there is a strong need for novel processes as well as novel industrial products, which are produced from renewable raw materials. Among them, fats and oils serve as a valuable feedstock source. The use of unsaturated fatty acids enables further functionalization, which is of interest for the synthesis of industrial products for various industrial segments ranging from the "high-volume low-price" (e.g., plastics and specialty chemicals) to the "low-volume high-price" (e.g., fine chemicals) range.

In this presentation, various transformations of unsaturated fatty acids into molecules of industrial interest by means of chemo- and biocatalysts is given. One example is the synthesis of a new generation of fatty acid esters as lubricants starting from oleic acid, which has been developed within an academic-industrial research project.^[1] A second example consists of the chemoenzymatic synthesis of fatty nitriles and fatty amines.^[2] Starting from bio-based alkenes, hydroformylation in combination with aldoxime formation and dehydration furnishes fatty nitriles, which were hydrogenated to fatty amines used as, e.g., lubricant and detergent components.^[2] The fatty aldoxime dehydration is conducted enzymatically at a high substrate loading of up to 1.4 Kg/L and without organic solvent.^[2a] As a third example, the synthesis of the jasmonic acid precursor and plant hormone 12-OPDA is described, which is obtained within a one-pot process in three enzymatic steps utilizing linolenic acid as a starting material.^[3]

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Biocatalytic synthesis of Oleochemicals

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Decarboxylases are emerging as sustainable catalytic tools for C-C bond breaking under mild reaction conditions [1]. The bacterial CYP450 monooxygenase OleT shows promiscuous activity in the decarboxylation of fatty acids into terminal olefins in aqueous systems and at room temperature. The investigation of the conversion of ω -functionalized fatty acids revealed a high functional group tolerance. The resulting α,ω -alkenols and α,ω -vinylcarboxylic acids are possible precursors for the synthesis of bio-based polymers. The α,ω -alkenols produced by the decarboxylation of ω -hydroxy fatty acids can be further converted into alkenylamines and diols. The combination of enzymatic decarboxylation with a ruthenium catalyst in a chemo-enzymatic cascade gave access to long-chain diols [2]. The recently discovered photodecarboxylase CvFAP from the alga *Chlorella varabilis* catalyzed the direct conversion of fatty acids to the corresponding alkanes. Combination with the addition of water to the double bond of unsaturated fatty acids catalyzed by oleate hydratase provided a new route for the synthesis of optically pure long-chain secondary alcohols from inexpensive starting material [3].

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H₂O₂ tunnel engineering for making robust BVMO to produce oleochemicals efficiently

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Unsaturated fatty acids (e.g., oleic acid and linoleic acid) can be converted into high-value C9 chemicals by Baeyer-Villiger monooxygenases (BVMO)-based whole cell biocatalysts. However, many of these BVMOs suffer from H₂O₂-induced oxidative stress, which is generated by uncoupling reactions in the active site. Here engineering of H₂O₂ access tunnels of BVMOs was examined to improve their robustness against H₂O₂. The potential H₂O₂ tunnels in BVMOs (i.e., Phenylacetone monooxygenase variant (PAMO_C65D) from *Thermobifida fusca* and the BVMO from *Pseudomonas putida* KT2440) were predicted using CAVER and Protein Energy Landscape Exploration (PELE) software. After that, the amino acids in vicinity of the tunnels, which are vulnerable to oxidation by H₂O₂, were changed into inert ones. This led to the design of BVMO variants with remarkably improved H₂O₂ resistance. Especially, a C302L/M340L/M380L mutant of *P. putida* BVMO showed 2.8-fold greater turnover number for the BV-oxygenation of 4-decanone than the parent enzymes. Furthermore, it allowed the PpBVMO-based whole cell biocatalyst to produce ester fatty acids, which can be easily hydrolyzed into C9 chemicals by a lipase, from oleic acid, with 2-fold enhancement titer. This study demonstrated that CAVER/PELE-based H₂O₂ tunnel engineering can be an efficient rational approach for generating H₂O₂-resistant BVMO biocatalyst to produce value-added oleochemicals. Also, this approach may be useful for improving other H₂O₂-dependent biocatalysts.

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Biotechnological production of odour-active fatty aldehydes by α -dioxxygenase and aldehyde dehydrogenase

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Aliphatic aldehydes with a carbon chain length between 8 and 18 represent an important class of compounds widely applied in aroma and fragrance preparations of the food and cosmetic industry. Their odour impressions are many-faceted and described as fruity and citrus-like as well as green, soapy and waxy¹. Most of these fatty aldehydes can be found ubiquitously in nature, but for instance (*Z*)-unsaturated as well as *iso*- and *anteiso*-methyl-branched aldehydes are typically present in trace concentrations. Moreover, chemical synthesis as an alternative is rather complex and inconvenient in terms of energetics, solvent disposal, ecology and consumers' acceptance². Therefore, alternative approaches for the generation of odour-active fatty aldehydes are highly desired. Fermentation based flavour generation is of great interest to the food, cosmetic and pharmaceutical industry. In the current studies, the oxidoreductases α -dioxxygenase (α -DOX) and fatty aldehyde dehydrogenase (FALDH) were applied as biocatalysts, by which long-chain fatty acids were converted to homologous chain-shortened aldehydes. As substrates, isolated fatty acids as well as natural lipid extracts from fungi were applied. Generated fatty aldehydes were identified, sensorially examined and (semi-) quantified by means of gas chromatography-mass spectrometry-olfactometry (GC-MS-O). Furthermore, structure elucidation of double-bond positions was implemented using the nanoESI-online-Paternò-Büchi-MS/MS method. The established method allows the selective and efficient conversion of several middle- and long-chain fatty acids to homologous chain-shortened fatty aldehydes with interesting odour. The bioconversion of naturally abundant lipids to odorous fatty aldehyde mixtures represents a promising technology for generation of flavour/fragrance ingredients.

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A Review of the Solid-Catalysed Isomerisation of Oleic Acid to Iso-Oleic Acid - How understanding of the reaction at molecular level has led to improved catalyst design and efficiency

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Commercial “isostearic acid” is a complex mixture of mainly saturated methyl-branched C18 fatty acids, and is a valuable ingredient in many consumer, lubricant, polymer additive and industrial products. It is a coproduct in the clay-catalyzed polymerization of unsaturated fatty acids (with an overall yield of about 25%) and although it is possible to steer the isomerization process to achieve somewhat higher yields of isostearic acid, supply remains strongly dependent on polymerized fatty acid demand. Decoupling isomerization from oligomerization, in order to meet the growing demand for isostearic acid independently of polymerized fatty acids, has been a research topic for the last 40 years.

Manufacturing of saturated branched fatty acids and their esters by hetero- and homogeneous catalysis has been comprehensively reviewed by Haßelberg and Behr in 2016^[1]. This presentation focuses on the use of shape-selective heterogeneous catalysts, which were first investigated in the mid-1990s^[2-3]. The benefits of specific frameworks such as Ferrierite^[4] will be explained, before discussing more recent work on zeolites and zeotypes whose morphology, microstructure and acidity can be tailored to optimize branched acid yields while minimizing oligomerization reactions. Understanding the catalysis at the molecular level has been a key factor in recent progress, and advanced spectroscopic techniques have provided valuable support in investigating the isomerization reaction and optimizing the manufacturing process.

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Montmorillonite clay catalysts for oleochemical processing

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Oleochemicals are an important and growing sector of the chemical industry. However, they are not without their problems; significantly the (un)sustainable production of palm oil, and therefore should be considered a limited resource. In spite of these ongoing concerns, with considerate farming practices and improved processing efficiency oleochemicals are going to be an important pillar of a sustainable chemical industry for years to come. Clay based materials have an opportunity to provide clean and efficient heterogeneous catalyst solutions for the oleochemical industry. BYK, as both a user of oleochemical feedstocks and a producer of acid and natural FULCAT® clay catalysts, has a vested interest in supporting this sector.

The ionising effect of the charged montmorillonite clay surfaces generates Hammett acidities of up to -3 and acid activation can push this as low as -8. These properties mean that montmorillonite clays have been used for many years as clean, cost effective solid acid catalysts. For example in the oleochemical industry, both acid treated and natural montmorillonite clays have been used as Diels-Alder cycloaddition catalysts in the production of dimer acids from tall oil. Recent research within the catalyst division at BYK has focused on further diversifying the FULCAT® clay catalyst applications and sales in oleochemical production. As well as demonstrating excellent catalytic performance in dimer acid production, this talk will discuss how FULCAT clay based catalysts can also be used as excellent heterogeneous esterification and alcohol dehydration catalysts, for the production of such oleochemicals as fatty acid esters and dehydrated castor oil.

Sustainable bio-based surfactants

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Chemistry and materials are at the heart of the specialty chemicals industry. Challenging cost-performance balance, ecology and safety demands, from consumers and legislation, determine the way towards more sustainability. The key to solve the challenges is innovation. Sustainable products must remain competitive and deliver the required performance for very specific industry needs and applications while committing to environmental requirements as well as meeting social demands. A holistic thinking from raw materials to disposal is necessary. Based on fats and oils as renewable feedstock, bio-based surfactants are prominent examples of how carbon footprint can be reduced compared to their petrochemical based counterparts. Beside excellent performance in diverse applications such as e.g. cosmetics, cleaning agents or coatings, bio-based surfactants offer an outstanding environmental profile. Within Clariant's Portfolio Value Program, our products undergo a systematic, in-depth screening process using 36 criteria covering the three sustainability dimensions people, planet and performance. Products providing sustainable benefits above market standards are awarded with our EcoTain® label. This talk will summarize our latest developments towards a fully bio-based surfactants portfolio.

Epoxidized Vegetable oils as additive for Bioplastics

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Cardoon, *Cynara cardunculus* L. from Asteraceae family, represents a challenging, non-food chain competitive crop, able to grow in dry, marginal lands and/or polluted soils of many Mediterranean regions, already exploited for industrial pulp and paper production. The recently founded national Italian project “CARDIGAN” aims at exploiting a “Cardoon biorefinery model” by a holistic approach. The idea is to valorize all fractions derived by cardoon to obtain high added value products. In this scenario, the CARDIGAN project aims to design bioplastics from Cardoon, by biological and chemical transformation of its different fractions, such as roots and seeds. Cardoon seeds contain high oil content (25–33%), and their composition in fatty acids of the Cardoon oil (CO) is like that of the soybean oil. Therefore, CO represents an interesting potential non-food plant oil. The aim of this work concerns the study of bio-plasticizers for bioplastics such as poly(lactic acid) (PLA) and Poly(3-hydroxybutyrate) (PHB) to improve the overall properties and broaden their industrial applications as a biodegradable packaging material. Bio-plasticizers were prepared by epoxidation reaction of this cost-effective and environmentally friendly oil, using both peracids and hydrogen peroxide directly as an oxidizing agent. PHB has also been obtained by a simultaneous Saccharification and Fermentation (SSF) of inulin derived from cardoon roots. Hence, ECO and CO, PLA, or PHB have been formulated in blends to develop bio-based films with optimized, chemical-physical, and mechanical properties. The cardoon biomass recovery, separations into different components, and their following recombination in upgraded materials can be framed in a holistic approach of zero waste circular economy.

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Plant oil-based polymers for closed loop recycling and non-persistency

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An introduction of low densities of functional groups in the main chain can endow polyolefins with desirable additional traits while retaining their mechanical strength and durability. Particularly, recyclability and environmental persistency can be improved upon. An access to such materials can be gained by a number of conceptually different approaches. Catalytic conversions of olefinic substrates and carbonylations are commonly a key step. These can utilize fossil or plant-based feedstocks, like seed or microalgae oils. This talk discusses recent findings on main-chain functionalized polyolefins, with an emphasis on recycling and relevant materials properties.

Sustainable Synthesis of Non-Isocyanate Polyurethanes based on Renewable 2,3-Butanediol

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In this work, three different cyclic carbonates were obtained from renewable diols and transformed into carbamates by reacting them with 11-amino undecanoic acid methyl ester in order to synthesize non-isocyanate poly(ester urethane)s in a sustainable manner. A procedure using 2,3-butanediol (2,3-BDO) as renewable starting material to synthesize a cyclic carbonate with dimethyl carbonate (DMC) is introduced, catalyzed by 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Three purification strategies, i.e. column chromatography, extraction, and distillation, were compared regarding their E-Factors. Propylene glycol (PG) and ethylene glycol (EG) were used as alternative starting materials to broaden the substrate scope and compare material properties. Their cyclic carbonates likewise reacted to carbamates with 11-amino undecanoic acid methyl ester. All carbamates were then polymerized in a bulk polycondensation reaction, yielding mainly fatty acid based non-isocyanate polyurethanes (NIPUs), specifically poly(ester urethane)s, with molecular weights (M_n) >10 kDa. Full characterization is reported using differential scanning calorimetric (DSC), size exclusion chromatographic measurements (SEC), ¹H-NMR as well as IR spectroscopy. The rheological properties of the poly(ester urethane)s were investigated in the framework of small amplitude oscillatory shear (SAOS) and uniaxial elongation.

Plant oil based radically polymerizable monomers for sustainable polymers

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Current depletion of conventional fossil fuels, instability of petroleum prices, environmental concerns and more stringent environmental regulations are encouraging the design and synthesis of biobased monomers and polymers from renewable stocks. Several goals are pursued: the increase of biogenic carbon in polymeric materials, the replacement of toxic and hazardous monomers and the production of materials with suitable chemical and mechanical properties, which could mimic or even surpass the properties exhibited by their petrochemical counterparts. If the synthesis of biobased monomers for step growth polymerization has been largely reported, including by our team, the synthesis of biobased monomers for chain growth polymerization is still an interesting challenge, particularly with radically polymerizable monomers. Acrylic acid, ethylene and styrene can be synthesized from renewable sources. Nevertheless, the syntheses of monomers usually derived from fossil fuels but which can now be prepared from renewable sources (drop in) are beyond the scope of our works. We have focused our studies on the synthesis of novel biobased monomers designed for free radical polymerization which could increase the biomass carbon content pursuing to equal or improve the performance of existing polymers from non-renewable sources.

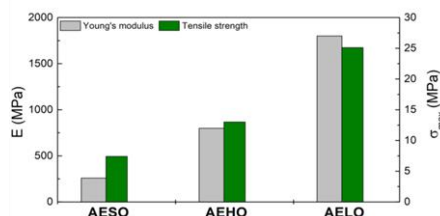
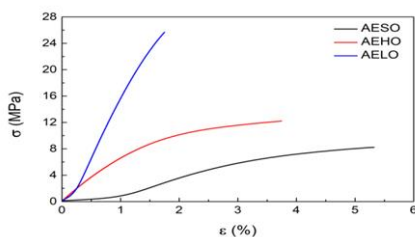
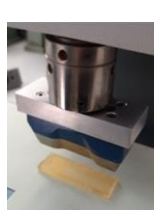
Cardanol, which is a natural phenolic oil, is issued from Cashew Nutshell Liquid (CNSL), a non-edible renewable resource, co-produced from cashew industry in large commercial volumes (1Mt p.a.). Cardanol is non-toxic and particularly suitable for the addition of aromatic renewable resources in polymers and materials. We recently reported various routes for the synthesis of di- and poly-functional building blocks derived from cardanol thereafter used in polymer syntheses. We especially synthesized a new radically polymerizable cardanol-derived monomer. Hence, we synthesized cardanol-based aromatic latex by radical aqueous emulsion (and miniemulsion) polymerization. We also synthesized UV-reactive cardanol-derived latex for styrene-free coating applications. The latexes were colloidally stable with monomodal particle size distributions and mean particle diameters ranging from 100 to 250 nm. Eugenol (4-allyl-2-methoxyphenol), a major component of clove oil, is an aromatic renewable resource with potential to replace some petroleum-based aromatic monomers. We interestingly synthesized a new platform of eugenol-derived methacrylates and studied for the first time their reactivity in radical aqueous emulsion (and miniemulsion) polymerization. The resulting latexes were stable and featured an average particle diameter of 40-50 nm. These results open the door to the formulation of new bio-based aromatic latexes with potential applications in adhesives and coatings. Vegetable oils and their fatty acids (FAs) derivatives have become the most promising alternative solution to design performant bio-based polymers. However, considering the poor reactivity of the internal unsaturation of FAs through radical process, most currently available synthesis of monomers reported in literature are limited to polycondensation. Therefore, the objective of our work was to synthesize monomers from fatty acids bearing reactive function through radical process and evaluate their resulting methacrylate polymers as viscosity modifiers in various oils such as mineral or vegetable oils.

Styrene-free thermosetting resins from vegetable oils

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The exploitation of oils as building blocks for the preparation of bio-materials offers the great opportunity to tap into a pool of varied monomers in terms of double bonds availability that is the starting point for the preparation of thermosetting resins. In our experience this was found to be the case when using soybean, hempseed and linseed oil, that present a different composition in terms of fatty acid profile. All of them are highly unsaturated oils and give the chance to obtain highly reticulated materials due to the significant amount of double bonds that via epoxidation can be properly functionalised depending on the desired final resin. Our strategy was based on the preparation of acrylic resins starting from these sources by curing the fatty based monomer in the presence of terpenes of different nature as the co-monomers.

The materials obtained can be shaped upon needs and present mechanical properties that depend on the unsaturation degree of the starting oil. As an example in the figure is shown the series of



homopolymers obtained with acrylated soybean (AESO), linseed (AELO) and hempseed oil (AEHO). The comparison with a resin prepared with acrylated soybean oil and styrene shows that it is possible to obtain strength even superior by using linseed oil based resins, thus showing that the proper choice of the oil and of the co-monomer allows one to tune the properties and the final material. Performances of this kind of resins can be also improved by designing

composite materials with fibers others than the traditionally used carbon or glass ones, such as hemp or flax fibers. A seven layered composite obtained by impregnating AEHO with limonene as the co-monomer and hemp fibers has been prepared. SEM analysis clearly shows that complete adhesion of the resin to the fibers is observed, even without any previous chemical compatibilisation process. The present research puts in light the great potential of oils and natural fibers for the design of a range of materials with properties that can be modulated according to the composition of the starting fat and of the terpenic co-monomer. This allows one to think about the preparation of resins that can be used in a wide variety of applications, ranging from the automotive or marine material industry to the interior design.

Biobased polyurethanes based on different macromolecular architectures from different resources

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Nowadays, the use of renewable biobased carbon feedstock from different resources, such as vegetable oils, is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint with an improved life cycle analysis (LCA), in agreement with a sustainable development. Besides, compared to conventional fossil-based materials, innovative macromolecular architectures with improved or additional properties can be obtained.

In this presentation, we report two decades of active researches on the synthesis and characterization of several innovative and renewable polyurethanes (PUR, PIR, TPU and NIPU), with controlled macromolecular architectures to elaborate different designs and morphologies (membranes, foams,), for a large range of applications. These materials are synthesized from different biobased building blocks, which can be directly extracted from biomass or obtained from white biotech (fermentation,):

- (i) Aliphatic structures from different glycerides and derivate (dimer fatty acids,), sugar-based molecules, bacterial polyesters ...
- (ii) Aromatic structures from lignins, tannins and furans.

A large range of materials with improved properties and durable applications are developed/synthesized in our team, for a greener and durable future. Besides, the end of life of these materials is now also considered, by e.g. bio-recycling, from cradle to cradle.

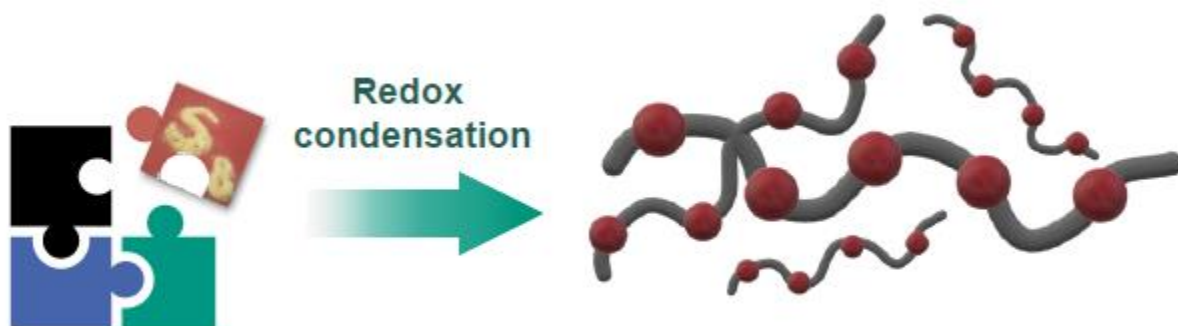
A more sustainable chemistry with elemental sulfur surplus: towards the design of novel polymers

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The possible depletion of non-renewable raw materials and the overall increase in pollution has promoted the search for other sources for the synthesis of polymers. Thus, one of the most challenging problems to be solved of modern macromolecular chemistry is to enable access to the targeted polymers from simple and readily available starting materials with higher efficiency and minimal waste. With this idea in mind, we have been concentrating on the use of elemental sulfur – an abundant waste of oil and gas industry with annual product up to 70 Million tones – as a polyvalent synthetic tool. Accordingly, in the present contribution, we will highlight an innovative polymerization method involving this element as a new synthetic strategy that satisfies most of the requirements of a more sustainable chemistry to deliver potential alternatives to traditional polymers derived from fossil fuels.



Synthesis of fully biobased and reprocessable polyurethane foams

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Polyurethanes (PU) are one of the most used polymer in the world in many applications but especially as foams with two thirds of the 18 Mt produced per year, representing a market of more than \$26 Billion in 2019. They are obtained from the reaction of diisocyanates with polyols, the large panel of available structures of these monomers leads to soft or rigid foams, which find their applications as thermal insulation, bed mattresses or automotive seats... Biobased polyols are very common nowadays but it is still not the case for polyisocyanates, very few are actually available. For that reason, polyurethane foams are only partially biobased. Therefore, the synthesis of fully biobased PU foams still stay a major challenge to this field.

In this study, four fully biobased PUFs were synthesized with monomers derived from fatty acids, saccharides and amino-acids. A biobased carbon content up to 93 % was achieved and the thermomechanical and physical properties of foams were studied. The development of new biobased monomers and polymer materials is an essential step to increase the sustainability of plastic industries. However, not only the first synthesis step needs to be improved, but the whole life cycle of polymers and especially their end-life. To this aim, transcarbamoylation was used to recycle the PUFs by compression molding in the pursuit of a greener consumption model, the PUFs were reshaped over five cycles. Their vitrimer properties were fully characterized.

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Terpene-Based Biopolymers as Novel Functional Biomaterials - Synthesis, Analysis and Applications

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Nature can provide a variety of building blocks for the synthesis of sustainable and functional polymers and materials from renewable resources, whose exploration and utilization is a key issue in modern polymer chemistry. This natural pool of compounds is interesting and important in terms of alternative feedstock and green chemistry in general, but also and especially with regards to the significant molecules and structures, that can thus be utilized and that are not so conveniently accessible via fossil-based pathways.^[1,2] In this context, terpenes are very important building blocks due to their abundance, low costs and in particular in terms of their interesting structures comprising e.g. side groups, stereocenters and/or additional functionalities.^[3] Generally, polyamides are very important polymers for applications in many fields (consumables, biomedicine, automotive, ...), and their impact is growing. They are mainly synthesized via polycondensation of dicarboxylic acids and diamines or via ring-opening polymerization (ROP) of lactams (cyclic amides). In this whole context, we e.g. investigate the transformation of cyclic biobased terpenoid ketones (e.g. *L*-Menthone, Nopinone, ...) to polyamides.^[4] This procedure works thus in analogy to the established fossil-based Nylon 6 (Polycaprolactam) synthesis and leads to novel sustainable (co)polymers with side groups and stereocenters, which results in very interesting properties.^[4,5] We also investigate the applications of suchlike polymers with regards to high-performance materials, and for biomaterials and bioconjugates for the interactions with living cells.^[6]

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Synthetic biotechnology for material innovation- CO₂ conversion to carbon fiber composites and innovative lightweight materials

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Biotechnological processes enable fixation, valorisation and terminal removal of atmospheric/ industrial CO₂ and hence contribute to mitigate global climate change. Synthetic biotechnology combining technological aspects of chemical biology, systems- and synthetic biology with targeted bioprocess engineering offers a consolidated approach to design new, mass- and energy efficient routes for the generation of sustainable chemical entities.

The talk will convey advances in the synergistic development of oleaginous photoautotrophic and heterotrophic microbial platforms for conversion of CO₂ in biofuels, and polymers materials and sustainable carbon fibers. A particular focus will be the use of microalgae based oil, for generation of CO₂ based carbon fibers and resulting sustainable carbon fibre composites that include sustainable bio based resin formulations. Further the application of sustainable carbon fibre composites in generation of new carbon fiber: stone applications, which are a sustainable, lightweight replacement of steel and aluminium in the aviation, automotive and building industry will be discussed.

Sustainable polymers. Use of Renewable Resources and Recycling

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In the foreseeable future, all chemicals will have to be produced from renewable resources. A number of different approaches can be taken when converting lignocellulose into chemicals. Using platform chemicals that can be obtained in good yield from renewable resources via fermentation or thermochemical reactions allows us to retain at least part of the oxygen substituents that were originally present in the biomaterials. In the lecture, I will present our recent research on the catalytic conversion of the platform chemicals levulinic acid and 5-hydroxymethylfurfural (HMF) into monomers for polymers. A number of these monomers were also converted into relatively short-chain polymers that were used as components for adhesives.

Currently, the largest part of the polymers that we rely on for our daily lives wind up in landfills or is released into the environment where it eventually winds up in the oceans. It is clear that this unsustainable practice can only be countered by recycling the polymers. This is easier said than done as physical recycling usually leads to damage to the polymer chains, allowing their use only for low-value applications. Chemical recycling back to the monomers is possible for most polymers, but the monomers thus obtained are usually more expensive than the virgin monomers. A solution to this problem could be the use of *upcycling*, i.e. the conversion of a polymer to a material with a higher added value. We have recently shown that it is possible to convert polyesters to valuable polyether polyols by using methodology developed by Beller and co-workers. The polyether polyols can be used as components for adhesives.

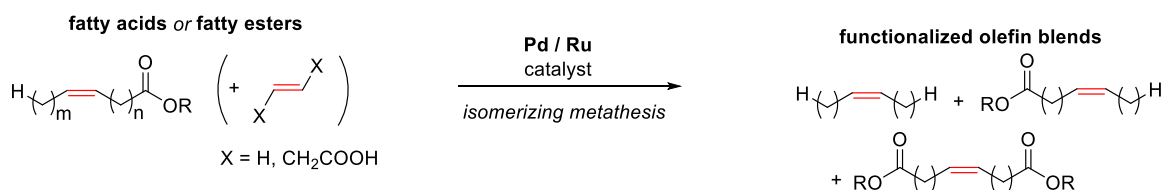
Isomerizing Metathesis as a Concept for the Valorization of Fatty Acid Derivatives

L. J. Gooßen

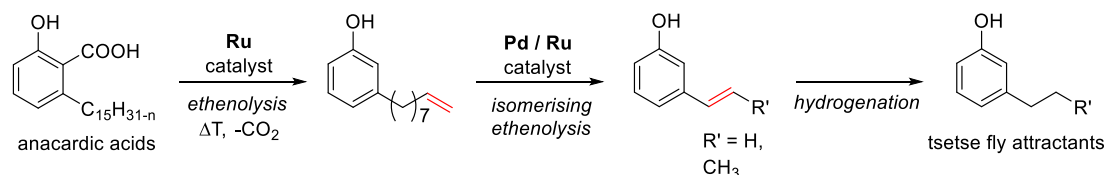
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Within recent years, we have investigated isomerizing metathesis reactions as tools for the valorization of vegetable oils as renewables resources that are available not only available to industrial but also to developing countries.¹ A bimetallic palladium² / ruthenium catalyst system enables the synthesis of industrially useful functionalized olefin blends of tailored medium chain lengths from renewable resources rather than from crude oil. In this context, technical quality fatty acids were successfully employed in isomerizing self-metathesis, ethenolysis, and cross-metathesis processes.³ Potential applications of this technology will be discussed, e.g., its use for the generation of biodiesel.⁴ Our current focus is set on the development of heterogeneous catalysts that selectively promote double-bond migration within fatty acid derivatives.



A cascade of isomerizing metathesis was used in a concise synthesis of the tsetse fly attractants 3-ethyl- and 3-propylphenol from anacardic acid, the main component of cashew nutshell extract.⁶ Further applications to the synthesis of bioactive materials will be discussed.⁷



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Abstracts

Part 2: Posters

P1

The role of Stabilizers in H₂O₂ for the Peroxyformic Acid Synthesis and Decomposition Kinetics

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The kinetics of the formation and decomposition of peroxyformic acid was studied. From experimental evidence taken from literature, we noticed that the decomposition reaction depends on the source of the hydrogen peroxide used as a reactant, so we focused on the idea that stabilizing agents present in the hydrogen peroxide solutions affect the reaction rate, inhibiting the peracid decomposition. The nature of the stabilizing agents and the concentration used might in fact change from a supplier to another. A kinetic model was proposed, in which the decomposition model considers this effect and, as a first approximation, the stabilizing agent concentration is quantified indirectly through the initial concentration of hydrogen peroxide loaded in the reactive system. The present model aims to lay the foundations for a new approach to the study of the decomposition of peracids in reactive systems. So, the present work aims to propose a new approach to the study of the performic acid formation and decomposition taking into account the effect of stabilizing agents on the decomposition rate.

**Büchi „Miniclave“
A suitable tool for the downscale process development
of Fatty Acid Ethyl Ester – Biodiesel**

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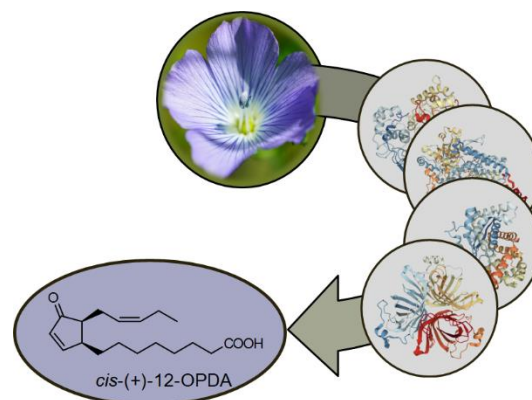
We like to report on inachem's laboratory process development of Fatty Acid Ethyl Ester - FAEE- with bio-ethanol. 99% of all industrial biodiesel plant use an alkali catalysed process, although it has certain drawbacks like soap formation. The alkali process is not applicable to ethanol and higher alcohols. Inachem's new Biodiesel process uses the acid catalysis which avoids soap formation. It has proved its industrial suitability at the Tecosol plant in Ochsenfurt near Würzburg. The MSA catalyst unit runs on 30.000 kt/y producing DIN EN 14 214 quality Biodiesel for the European market since 2019. To increase the Green house gas savings on biodiesel, it is useful to use renewable bio-ethanol in replacement of fossil methanol. Our downscale approach in process development uses the Büchi „Miniclave“ to mimic an industrial plant scale reactor equipment. Variables on reaction temperature, concentration of catalyst, free fatty acids and water content were run in a statistical approach. The correlations will be presented and a conclusion for the best protocol of the process will be given. Further investigations are planned to introduce C3-C6 alcohols which should lead to fatty acid ester useful as renewable and sustainable bio-organic solvents.

Optimized reaction conditions for the synthesis of 12-opda

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The jasmonic acid and its precursor *cis*-(+)-12-oxo phytodienoic acid (12-OPDA) are signal hormones for stress regulation and growth in plants.^[1] There is a high demand of jasmonic acid in the fragrance industry but at the same time a complex chemical synthesis for both compounds.^[2] Therefore, Löwe *et al.* introduced a biocatalytic cascade that result in 12-OPDA starting from α -linolenic acid (α -LA) by using a reaction cascade with commercial Gm-13-LOX and a WCC containing AtAOS and AtAOC2.^[3] However, drawbacks are the formation of the α -ketol as side product, difficult work-up, reduced conversion at increased substrate concentrations and to some extent an isomerization of the *cis*-(+)-12-OPDA to the *trans*-isomer.

In this work, inspired by the work of Löwe *et al.*, the whole cell catalyst was changed to a one-plasmid-system to better adjust the balance between the AOS- and AOC-catalyzed reactions and, thus, to



reduce the formation of the labile intermediate 12,13-EOT. Furthermore, a change of reaction conditions leads to a decrease of isomerization of the product. Additionally, the conversion at increased substrate concentrations could be strongly enhanced and the work-up is now simplified. In addition, we were able to change the substrate to linseed oil. In an extended cascade, the lipase from *Candida rugosa* can release the fatty acids before the known system can convert the α -LA to the 12-OPDA in a one-pot process.

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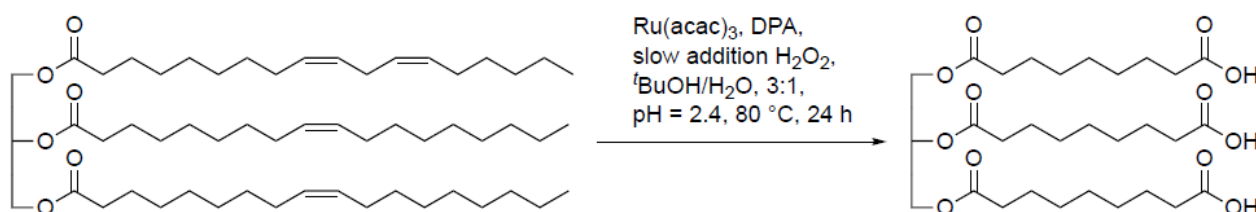
Ruthenium catalyzed oxidative cleavage of high oleic sunflower oil

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Nowadays, due to the depletion of fossil resources, there is a growing interest in fats and oils as renewable resources to produce more sustainable chemicals and polymers. Fatty acid derived substances, such as pelargonic acid and azelaic acid, have already been used for decades for the manufacture of plasticizers, lubricants and polymers.^[1] However, the industrial synthesis of these valuable carboxylic acids still relies on ozonolysis, a process with a high energy demand and safety risks owing to the use of toxic and explosive ozone.^[2-3] BEHR *et al.* developed a promising alternative to the conventional ozonolysis of methyl oleate.^[4] Both cleavage products were obtained in yields higher than 80% by homogenous catalysis using commercially available ruthenium(III) acetylacetonate ($\text{Ru}(\text{acac})_3$) as catalytic precursor, pyridine-2,6-dicarboxylic acid (DPA) as ligand, and hydrogen peroxide as oxidant.

In this work, the reported procedure was investigated *via* quantitative gas chromatography to develop a further understanding of the formed intermediates and their relevance regarding the proposed reaction pathway. The oxidative cleavage was then employed on high oleic sunflower oil to synthesize a renewable monomer bearing multiple carboxylic acid moieties (Scheme 1). This monomer may be suitable for the synthesis of sunflower oil based polymers, for instance *via* PASSERINI reaction.^[5]



Scheme 1: Synthesis of a renewable monomer from high oleic sunflower oil.

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Functionalization of oleo chemicals: Developing sustainable processes by integrated catalyst recycling

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New sustainable processes towards biopolymers based on renewable resources are in focus of current research. By means of homogeneous transition metal catalysis, oleo chemicals from natural fats and oils can be efficiently transferred to polymer pre-stages. With regard to an ecological and economical application of these reactions, a downstream separation of product and catalyst is essential - on the one hand, to meet product purity specifications and on the other hand, to enable a recycling of the usually expensive precious metal catalysts. However, common separation methods can be limited regarding the achievable product purity and recovery while maintaining catalyst activity and stability throughout the recycling process. In a collaborative project, selective product crystallization as novel recycling method is systematically investigated using the example of Pd-catalyzed methoxycarbonylation of methyl 10-undecionate, largely obtained from natural castor oil, to linear dimethyl dodecanedioate.

In this contribution, we present our strategy for developing an integrated catalyst recycling process, equally considering the homogeneously catalyzed reaction and the subsequent product isolation by selective crystallization from the reaction mixture [1]. By investigating both process steps in parallel, reciprocal influences are determined and the integrated process is optimized towards maximum catalyst turnover number.

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P6

Synthesis of linoleic acid hydroperoxides using immobilized LOX for the application in a flow reactor system

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Lipoxygenases catalyze the hydroperoxidation of linoleic acid with molecular oxygen leading either to the 9- or 13-hydroperoxides, which are interesting precursors for further processing. Splitting of the 13-hydroperoxide by e.g. hydroperoxide lyase leads to volatile C6-aldehydes, alcohols and C12-oxoacids. The volatiles are marketed by the flavor and fragrance industry as green notes and the bifunctional oxoacids are interesting bio-based intermediates for the chemical industry.

Lipoxygenase conditions were optimized for the development of an enzymatic cascade for a green synthesis route towards hydroperoxides utilizing safflower oil in combination with lipase hydrolysis and catalase mediated *in situ* oxygen supply to suppress foaming caused by gasification. Results of a combined system of LOX-1 and catalase reveal that peroxidation is comparable to that of gas bubbling experiments. A combined lipase and LOX-1 system using lipase from *P. fluorescens* showed to be most promising with near quantitative conversion at a substrate concentration of up to 100 mM. Implementing catalase from *M. lysodeikticus* and H₂O₂ dosing for *in situ* oxygen generation, a three enzyme system consisting of lipase, LOX and catalase was employed allowing nearly full conversion of free linoleic acid up to a concentration of 300 mM.

Industrial processes aim to be as cost-efficient as possible. In this sense, one-step processes with the cheapest and non-toxic substrates and catalysts possible at moderate temperatures and high throughput are the goal. The immobilization of enzymes, is suitable to further reduce costs of the catalysts. Immobilization of LOX was investigated on several carriers with different functionalizations. Functionalized Immobead P turned out to be the most promising option. It was shown that this immobilizate was able to maintain its activity for 16 hours in a fluidized bed reactor.

Semi-Hydrogenation of Poly-Unsaturated Fatty Acid Derivatives in Multiphase Catalysis

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Dwindling fossil resources increase the demand for sustainable alternatives, i.e. oleochemicals.^[1] Increasing the degree of saturation to mono-unsaturated fatty acid derivatives paves the way for various chemical reactions like epoxidation. The major part of these reactions depends on mono-unsaturated oleochemicals independent of the terminal functionalization of the molecule to ensure a stable catalyst or a high selectivity to the desired product.^[2] Most promising results in terms of heterogeneous catalysis have utilized Pd catalysts at reaction temperatures of 80°C and 75 atm Hydrogen or needed high catalyst loading of 4,94 wt.% with reaction times over 1 hour.^[3] This research focuses on an approach that utilizes a multiphasic reaction system which consists of a polar solvent containing a transition metal and a non-polar substrate phase. The non-polar phase only consists of the fatty substrate and is solvent free. Hydrogen at different pressures is provided as gas phase. Intense stirring is key to ensure proper phase interaction.^[4] The catalyst shows high activity already at temperatures up to 50°C and high selectivity to the monounsaturated fatty compound in the mixture. Optimization of reaction conditions led to reaction times below 15 minutes. First tests were performed using a mixture of fatty acid methyl esters (FAMES). After promising results reactions were performed using refined soybean oil that was esterified with methanol. Since the reaction performance is already on a high level, whilst utilizing a multiphasic approach, the separation of the reaction mixture should be the less demanding task which makes this approach more viable for industrial application.

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Organic Solvent Nanofiltration: Recycling of an unmodified Grubbs-Hoveyda catalyst in the self-metathesis of cardanol

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Due to the dwindling fossil resources, chemicals from renewable sources are more attractive than ever. Unfortunately, renewable resources compete with the production of food for agricultural areas. Hence, the usage of agricultural waste, which is otherwise disposed of, is most sustainable.^[1] Cardanol, a component of cashew nut shell liquid (**CNSL**), a waste product of cashew kernel production, is one such waste. Self-metathesis using the homogenous Grubbs-Hoveyda catalyst selectively yields 3-non-8-enylphenol under mild reaction conditions with low reaction times. Since this reaction avoids ethylene as a byproduct catalyst deactivation is less of an issue.^{[2],[3]} 3-Non-8-nonylphenol could potentially replace 4-nonylphenol in the detergent production, thereby increasing the value of cardanol.^[3] Organic solvent nanofiltration (**OSN**) exploits the different molecular weights to remove the catalyst. In contrast to most studies on recycling metathesis catalysts with membranes, this work aims at using unmodified catalyst, i.e. no additional catalyst tags, and commercial membranes. This improves transferability of the research presented without the need to consider complex synthesis to provide a catalyst or membrane. Moreover, the full catalytic activity can be exploited. Thus, we strive to efficiently remove the substrate and reaction products from the reaction solution to reuse the catalyst in further reaction. In this context, we identified the composite membrane Borsig oNF-1, with a molecular weight cut off of 600, as a suitable membrane. To build upon the seen potential and to improve the catalyst service life it is desirable to perform continuous experiments and thereby increase the productivity of the catalyst.

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Synthesis of amino-functionalized oleochemicals via hydroaminomethylation with integrated catalyst recycling

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Amines are of great importance for the chemical industry having a wide range of applications in surfactants and fine chemicals.^[1] Using catalysis enables more energy and resource efficient processes. In addition to advantages such as high activity and selectivity under mild reaction conditions, many homogeneously catalyzed amination reactions exhibit high atom economy, like hydroaminomethylation (HAM) with only water as byproduct. However, the key challenge with homogeneous catalysts is the difficult separation from the valuable product. One proven way is by immobilization in a liquid phase. Here the catalyst resides in one phase, whereas the products are in a different phase. To avoid mass transport problems, thermomorphic multiphase systems (TMS)^[2] can be applied. Here, a temperature-dependent miscibility gap is utilized, so that although the separation takes place in a two-phase system, the reaction is monophasic.

Herein, we present the HAM of methyl 10-undecenoate with different amines in the TMS of methanol and dodecane. The use of the renewable raw material methyl 10-undecenoate, produced from castor oil, is in line with green chemistry and enables the production of α,ω -bifunctional products. In two-phase systems, bifunctional substances can have a significant influence on the separation and thus also on catalyst leaching into the non-polar product phase. In this work, we want to show the differences in phase behavior, catalyst leaching and catalyst activity that arise for each amine used. In addition, a catalyst recycling for the HAM with diethylamine was performed over 10 runs, with Rhodium leaching less than 1.2% of the initial amount of catalyst used in each run.

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Synthesis of fatty amines by homogeneously catalyzed amination of fatty alcohols

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Various amines are important compounds for the chemical industry. They find use in the production of pharmaceuticals, fine chemicals, polymers, dyes, and agrochemicals. But especially primary and tertiary amines are of particular importance. For the synthesis of amines various synthesis paths incorporating catalytic steps, like the BUCHWALD-HARTWIG reaction, hydroamination (HA), hydroaminomethylation (HAM), reductive amination (RA), reduction of nitriles and the amination of alcohols have thus been explored. However, for the synthesis of primary fatty amines a reaction of fatty acids with ammonia, followed by the hydrogenation of the nitrile, is the most common method. These amines are used directly, or methylated to obtain tertiary alkyl amines, like cetyltrimethylammonium bromide. But alkylating agents such as alkyl halides are mostly toxic, so that each alkylation step should be avoided.

In this work we present the alcohol amination (Figure 1) for the synthesis of long-chain primary and tertiary amines, by the homogeneously, ruthenium-catalyzed amination of fatty alcohol with ammonia to primary amines and dimethylamine to tertiary dimethylalkylamines. In all cases high yields and selectivities, greater 90 %, are achieved.

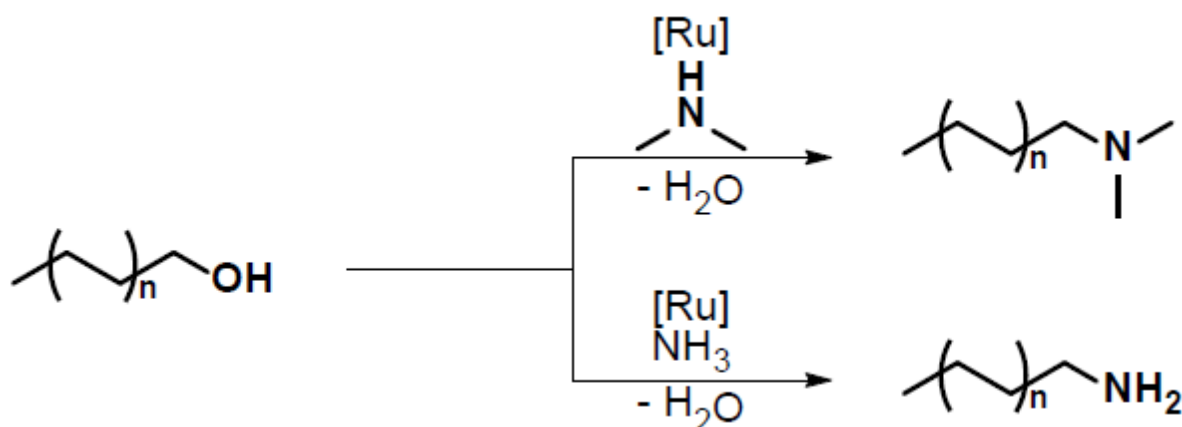


Figure 1: Amination of fatty alcohols ($n = 3-8$) with ammonia and dimethylamine for the synthesis of tertiary (top) and primary fatty amines (bottom)

Intensification strategies for homogeneously catalyzed hydroformylation of oleo chemicals in aqueous multiphase systems: Utilizing the "chaos"

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As recycling of homogeneous transition metals is indispensable for the economic and ecological sustainability of the processes the development of efficient separation and recycling concepts is required to exploit their full potential. The immobilization of the catalyst in one phase of a multiphase system offers a promising approach in this respect. The use of water as a solvent in combination with co-solvents is in these cases particularly beneficial from economic and environmental impact viewpoints. To increase the phase boundary area in order to reduce mass transport limitations an advanced reactor concept like the jet loop could be used.

Those concepts have now been applied for the hydroformylation of methyl oleate (Fig. 1, left). Preliminary investigations and a setup for the continuous application of this reaction system were established (Fig. 1, right) which resulted in the first continuous hydroformylation of methyl oleate in a jet loop reactor. To establish a more integrated value chain, a substrate change to triolein was being tested in aqueous multiphase systems as well.

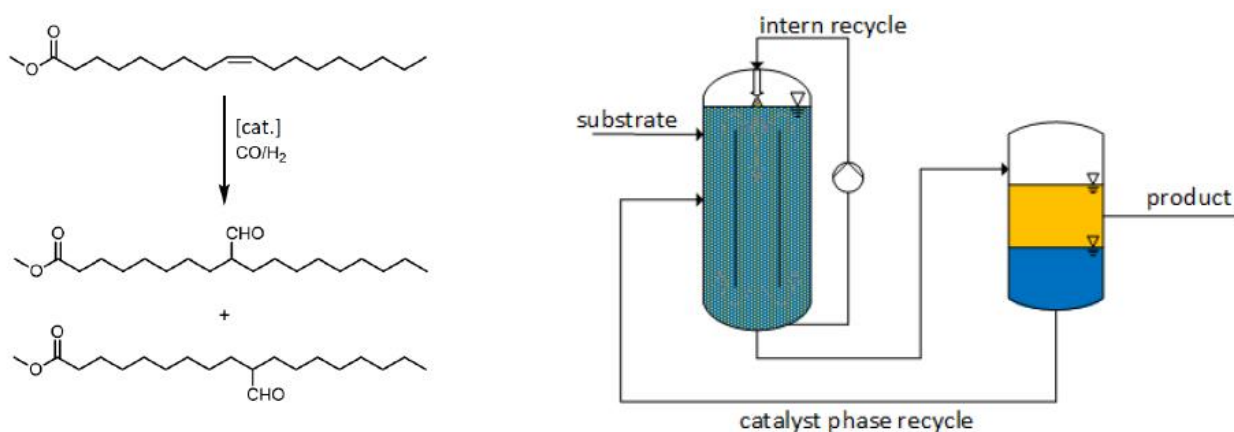


Figure 1: Hydroformylation of methyl oleate (left) Concept for continuous setup of hydroformylation in aqueous multiphase systems utilizing a jet loop reactor (right)

Hydroaminomethylation of oleochemicals in a continuously operated miniplant

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One of the major challenges of chemical industry is the decreasing stock of fossil feedstocks. A possible approach is to substitute them with bio-based, renewable materials. However, one difficulty in their incorporation is their higher degree of functionalization compared to petrochemicals. Homogeneous transition metal catalysis offers an effective approach to still achieve high selectivities to the desired products.

To provide a homogenous reaction mixture during reaction and still enable a simple separation of the catalyst is the application of thermomorphic multiphase systems (TMS). At reaction temperature, the solution is monophasic allowing reaction without transport limitation. Cooling after reaction shifts the miscibility gap and two phases are formed. One phase ideally contains the product and the second phase the catalyst, which therefore can be recycled through simple decantation. Our group already successfully performed the hydroaminomethylation (HAM) with 1-decene and diethylamine as model substrates in a TMS consisting of methanol and dodecane.[1] In this work, we address the conversion of bio-based feedstocks in TMS. Methyl 10-undecenoate, obtained from castor oil, is used as a model component in the HAM (Figure 1). To proceed further towards potential industrial application, this system is studied in a continuously operated miniplant. Crucial insights on the accumulation of components, catalyst performance and on the long-term stability are gained. Since water is produced as by-product, water must be continuously removed from the system to enable a stable long-term operation. In this work, we present the water removal via selective organic solvent nanofiltration. This widens the scope of TMS by providing a new application with renewable and bio-based raw materials.

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Application of multiphase systems for the intensified production of furans from biomass

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The valorization of lignocellulosic biomass derived sugars has gained more interest for the production of chemicals. 5-hydroxymethylfurfural (HMF) and furfural are highly valued building blocks that can be obtained by the dehydration of glucose, fructose and xylose. To prevent the formation of undesired humins and other by-products that occur in monophasic systems, a multiphase approach can be followed, whereby a reaction with *in situ* extraction takes place. With regard to Green Chemistry, the choice of solvents is a matter of interest. Therefore, environmental, health and safety (EHS) as well as the performance of the chosen solvent have to be considered. Several solvent selection guides have been established taking the EHS parameters into account. To assess the performance, the Conductor-like Screening MOdel for Real Solvents (COSMO-RS) is a proven tool for screening different candidates based on structural information of the molecules. COSMO-RS screenings among a pool of selected solvent candidates gave methyl propionate and ethyl acetate as best performing extraction phases. In addition, methyl isobutylketone (MIBK) also showed a promising performance with the advantage of not undergoing hydrolysis under the typical acidic conditions of the reaction. Dehydration reactions were conducted in a biphasic system with MIBK as extracting phase, with ethylene diaminetetraacetic acid (EDTA) as a catalyst due to its thermomorphic behaviour at temperatures above 140 to 170 °C. In addition, autocatalytic reactions are very promising although they are less productive, since catalyst removal is no longer needed as a further workup step. Furthermore, highly advantageous partition coefficients for furfural in MIBK and water can be observed, emphasizing the suitability of MIBK for this reaction setup.

Catalysis and Chemical Reaction Engineering for Biolubricants Productions

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Waste raw materials obtained by several sources of both food and agro industries could be considered for biomaterials production. In the last years, this topic has growing in interest, in particular considering the oleins, mixtures of free fatty acids (FFAs) and glycerides. The biolubricants based on esters, in the last years have generated a great interest in the scientific community and represent an alternative to the petrochemical lubricants. Their properties are similar to those of the petrochemical lubricants but at the same time they are more degradable and less toxic respect to mineral lubricants. The classical catalysts used for the esterification reaction are acid homogeneous catalysts such as p-toluenesulfonic acid, phosphoric acid, sulfuric acid [1]. On the contrary, the use of classical heterogeneous catalysts, such as the acid resins, is limited by the fact that they are not stable at temperature higher than 120°C [2]. In this work we studied the biolubricants synthesis by esterification reaction between fatty acid and several polyols using a synthetic materials as acid catalyst. This synthetic material is stable at high temperature (about 180°C) and in this way we have the advantage of using a relatively high temperature favouring the stripping of water formed during the esterification. The esterification reaction was performed using different polyalcohols with saturated monocarboxylic acids.

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Pulsed Electric Field (PEF) Treatment for Lipid Extraction from Microalgae

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Pulsed Electric Field (PEF) treatment induces permeabilisation of cell's membrane and is already being used successfully in the food-industry at very large scale for improving extraction or drying processes. PEF-treatment has been successfully transposed to microalgae downstream processing especially for lipid extraction. Several intrinsic advantages of the PEF technology can guarantee lipids of high quality at reasonable price: the possibility to operate on wet biomass and therefore bypass extremely costly drying steps, the easiness to work in continuous mode even at very large scale, the absence of damages on the mechanical cell structure, which considerably facilitates further processing, and the absence of over-heating which preserves integrity of lipids and of other valuable cell components. Experiments performed on *Auxenochlorella protothecoides*, have shown that PEF-treatment followed by a solvent assisted lipid extraction enabled to recover up to 97% of the evaluated lipid content. Energy input remains low, typically between 0.25 MJ/kg_{DW} and 1.5 MJ/kg_{DW} depending on other processing parameters. Current work focuses on upscaling of the currently laboratory-scale experiments to achieve a volume of lipids of 100mL.

Polythiomalonamides: Renaissance of Industrial Waste, i.e. Elemental Sulfur, in Functional Materials

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“Ensure sustainable consumption and production patterns.” (Global Goal number 12 for Sustainable Development)¹ At the outset of the current millennium human society understandably benefited from the arising industrialization in terms of career, living standards and mobility.² Nevertheless, the non-existent farsightedness in regard to sustainability in daily life as well as in industry yielded in the climate change along dramatic environmental concerns.³ Hence, sustainable production of polymeric materials and their respective consumption have been currently receiving an increased importance in the human society.^{4,5} Accordingly, at the interface of organic synthesis and polymer chemistry, a cost-effective avenue towards a novel class of polymers (i.e. polythiomalonamides) from readily available starting materials and industrial waste, i.e. elemental sulfur, has been developed. Specifically, the highly efficient avenue employs a mild, metal free, DMSO-oxidized redox decarboxylation polycondensation using maleic anhydride, diamine derivatives and the waste material elemental sulfur as monomers. Indeed, we were able to assemble a library of novel polythiomalonamides by incorporating diverse diamine derivatives (varying from linear aliphatic to aromatic and heteroatom containing ones, i.e. sulfur, oxygen and silicon) into the polymerization approach. Importantly, an in-depth structural characterization, i.e. 1D, 2D NMR, ATR-IR and SEC, of all synthesized polymers has been performed. Last but not at least, in order to get an awareness for a potential applicability of the novel polymer class, the materials properties of polythiomalonamides were investigated by DSC, TGA, WCA, UV/Vis and fluorescence measurements.

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Cost Effective Marriage of Poly(dithiocarbonates) with Elemental Sulfur

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The incorporation of sulfur atoms into polymer backbone can significantly tune the properties of polymeric materials, i.e., refractive index, self-healing tendency or coordination towards heavy metal ions.¹ Thus, it is not surprising that sulfur containing polymers exhibit nowadays a high applicability in optoelectronic applications as well as in Li-S batteries as cathode materials.^{1,2} Keeping the former mentioned tunability of polymeric materials by introducing sulfur in mind, i.e., in terms of refractive index, selfhealing properties and metal ion complexation,¹ especially the sulfur analogous of industrial relevant polymers, i.e., polythioethers,^{3,4} polythioesters^{3,5} or polythioamides,^{3,6} were in-depth investigated within the last years. Although, Polycarbonates are currently widespread in engineering, biomedical and packaging applications,⁷ which underpins the industrial importance of this polymer class, the corresponding disubstituted sulfur derivatives, i.e., poly(dithiocarbonates), are rarely reported in the current literature. Therefore, a novel superbase (i.e., 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)) catalyzed step growth polymerization approach using commercially available starting materials, i.e., dithiols and 1,1'-carbonyldiimidazole (CDI), has been developed. Besides the synthesis of homopolymers from a single dithiol derivative, a sequential addition of two structural disparate dithiols yielded in the formation of alternating copolymers, which broaden the toolbox of poly(dithiocarbonates) significantly. Furthermore, the incorporation of an industrial waste material, i.e., elemental sulfur, into the polymerization approach, afforded the synthesis of high sulfur content poly(dithiocarbonates). The incorporation of linear sulfur chains (-S-(S)_x-S-) next to the functional dithiocarbonate groups additionally enhanced the potential for an efficient photo degradability of the polymer class. All synthesized polymers were characterized by 1D, 2D NMR, ATR-IR, SEC, DSC, UV/Vis and fluorescence measurements.

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Synthesis of vinyl monomers from commercial olive oil via transesterification with N-hydroxyethyl acrylamide

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Plant oils are an abundant renewable resource that have been demonstrated in the literature^{1,2} to be a suitable feedstock for polymers with interesting properties (low T_g, hydrophobicity, functionalisation of unsaturations in pendant groups). The aim of this project is to synthesise plant oil based monomers (POBMs) and investigate the properties and applications of the resulting polymers³. A one-step transesterification reaction of commercial olive oil with N-hydroxyethyl acrylamide (40°C, 3h, NaOH catalyst, THF cosolvent)¹ was performed to obtain a high purity monomer (>95%) suitable for radical polymerisation. A free radical polymerisation was conducted in toluene using 2,2'-azobis(2-methylpropionitrile) as an initiator with 25% w/w olive oil monomer at 70°C for 3h^{1,3}. A conversion of 87% was achieved and ¹H NMR spectroscopy confirmed that unsaturations in the fatty chain were not significantly affected by the polymerisation. A range of monomers with different molecular weights or different degrees of unsaturation can be synthesised based on the choice of oil feedstock which could allow for simple tuning of the polymer's properties. Copolymerisation of POBMs with higher T_g or hydrophilic blocks will be performed to produce materials that may be of interest in applications such as adhesives, bulk thermoplastic elastomers and as rheology modifiers.

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