abiosus e.V.
Non-Profit Association for the Advancement of Research on Renewable Raw Materials

8th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

March 29-31, 2015
Karlsruhe, Germany

in Cooperation with

Agency of Renewable Resources (FNR)

FACHAGENTUR
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Scientific and Organizing Committee

Ursula Biermann, University of Oldenburg, Oldenburg, Germany
Norbert Holst, Agency of Renewable Resources (FNR), Gülzow, Germany
Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
Jürgen O. Metzger, *abiosus* e.V. and University of Oldenburg, Oldenburg, Germany

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Program

Lectures and Posters

Sunday, March 29, 2015

Registration

Registration will be opened from 14:30 - 19:00

15.45	**Welcome and Opening**
	Jürgen O. Metzger, *abiosus* e.V.
	Michael A. R. Meier, KIT
16.00 – 17.30	*First Session*
	Chair: Michael A. R. Meier
16.00 – 16.30 L1	**Single cell oil – realistic and unrealistic perspectives** (M) Alexander Steinbüchel, Institut für Molekulare Mikrobiologie und Biotechnologie, Westfälische Wilhelms-Universität Münster, Münster, Germany
16.30 – 17.00 L2	**Catalytic Functionalisation of Oleochemicals – New Developments in Laboratory and Miniplants** (M) Arno Behr, Lehrstuhl für Technische Chemie, Fakultät Bio- und Chemieingenieurwesen, Technische Universität Dortmund, Dortmund**,** Germany
17.00 – 17.30 L3	**New Value Chains from Oil Crops to Long Chain Polyamides** (M) Jean-Luc Dubois, Arkema France, Colombes, France
17.30 – 20.30	**Poster Session and Opening Mixer** Posters will be displayed until the end of the workshop

(M) Main Lecture 30 min including discussion
(D) Discussion Lecture 20 min including discussion

Monday, March 30, 2015

9.00 – 10.30 *First morning session*

Chair: Stefan Mecking

9.00 – 9.30 **In-situ Spectroscopy of Liquid-phase Catalytic Processes with Biomass-derived Compounds** (M)
L4 Bert M. Weckhuysen**,** Xavier Ruiz Martinez, Inorganic Chemistry and Catalysis, Utrecht University, Utrecht, The Netherlands

9.30 – 9.50 **Synthesis of Saturated Branched Fatty Derivatives using a Process Combination of Homogeneous and Heterogeneous Catalysis in Miniplant Scale** (D)
L5 Jennifer Haßelberg, Arno Behr, Carsten Weiser, Jan Billy Bially, Technische Universität (TU), Dortmund, Germany

9.50 – 10.10 **Isomerizing Metathesis as an Efficient Tool for the Generation of Biodiesel from Rapeseed Oil** (D)
L6 Kai F. Pfister, Sabrina Baader, Lukas J. Gooßen, Technical University of Kaiserslautern, Kaiserslautern, Germany

10.10 – 10.30 **Unravelling the Mechanism of the Isomerizing Alkoxycarbonylation of Plant Oils** (D)
L7 Verena Goldbach[1], Philipp Roesle[1], Josefine T. Christl[1], Florian Stempfle[1], Lucia Caporas[2], Stefan Mecking[1], [1] Department of Chemistry, University of Konstanz, Konstanz, Germany;
[2] Department of Chemistry, University of Salerno, Italy

10.30 – 11.00 **Coffee break**

11.00 – 12.50 *Second morning session*

Chair: Jean-Luc Dubois

11.00 – 11.30 **Symbiosis of Chemistry and Biology: BASF´s Biodegradable and Renewable Polymers** (M)
L8 Andreas Künkel, Robert Loos, Carsten Sinkel, BASF, Ludwigshafen, Germany

11.30 – 11.50 **Catalytic Copolymerization of Methyl 9,10-Epoxystearate and Cyclic Anhydrides** (M)
L9 Ursula Biermann[1], Ansgar Sehlinger[2], Michael A. R. Meier[2], Jürgen O. Metzger[1], [1] Institute of Chemistry, University of Oldenburg, Oldenburg, Germany; [2] Institute of Organic Chemistry, KIT, Karlsruhe, Germany

11.50 – 12.10 L10	**Regioselective Acetoxylation of Limonene: Access to Renewable Building Blocks via Catalysis and the Passerini Three-component Reaction** (D) Marc von Czapwieski, Michael A.R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany
12.10 – 12.30 L11	**Vegetable Plant Oils as a Versatile Source of Greener Thermoplastics: Example of Non-isocyanate Polyurethanes** (D) Etienne Grau, Henri Cramail, Bordeaux University – CNRS, Bordeaux, France
12.30 – 12.50 L12	**New Bio-based Hyperbranched Polyesters** (D) Blandine Testud, Etienne Grau, Daniel Taton, Henri Cramail, Bordeaux University – CNRS, Bordeaux, France
12.50 – 14.00	**Lunch break**
14.00 – 15.30	*First afternoon session* *Chair: Charlotte Williams*
14.00 – 14.30 L13	**Sustainable Synthesis of Amines – Direct Amination of Alcohols with NH_3** (M) Dieter Vogt, School of Chemistry, University of Edinburgh, Edinburgh, UK
14.30 – 14.50 L14	**Reductive Amination of Dodecanol with NH_3 over Heterogeneous Catalysts** (D) Atte Aho, Åbo Akademi University, Åbo Finland
14.50 – 15.10 L15	**Reactions of Methyl 9-Oxo-10-undecenoate** (D) Hans J. Schäfer, Ludger Hinkamp, Organisch-Chemisches Institut, University of Münster, Münster, Germany
15.10 – 15.30 L16	**Sugar Derived Amphiphiles as Crude Oil Thickening Agents – Influence on Type and Complexity** (D) Malick Samateh, Swapnil R. Jadhav, George John, City College of New York, City University of New York, New York, USA
15.30 – 16.00	**Coffee break**

16.00 – 17.20 *Second afternoon session*

Chair: Arno Behr

16.00 – 16.30 **Catalyst Selection for Development of Chemical Processes Based on Fats and Oils** (M)
L17 Aalbert Zwijnenburg, Johnson Matthey Chemicals GmbH, Emmerich, Germany

16.30 – 16.50 **Skeletal Isomerisation of Oleic Acid over Ferrierite: Influence of Acid Site Number, Accessibility and Strength on Activity and Selectivity** (D)
L18 Sophie C.C. Wiedemann[1], Ramon Oord[2], Tanja van Bergen-Brenkman[1], Bas Wels[1], Pieter C. A. Bruijnincx[2], Bert M. Weckhuysen[2], [1] Croda Nederland BV, The Netherlands; [2] Utrecht University, Utrecht, The Netherlands

16.50 – 17.10 **Rhodium-Catalyzed Hydroformylation of Triglycerides in Aqueous Media Using Supramolecular Emulsifiers (D)**
L19 Théodore Vanbésien, Frédéric Hapiot, Eric Monflier, Université d'Artois, Lens Cedex, France

17.10 – 17.30 **Rhodium-Catalyzed Functionalization of Mono-Unsaturated Fatty Acids (D)**
L20 S. Eschig, C. Schirp, T. Salthammer, Fraunhofer Institute for Wood Research, Wilhelm-Klauditz-Institut WKI, Braunschweig, Germany

19.30 *Conference Dinner*

Renaissance Karlsruhe Hotel

Tuesday, March 31, 2015

9.00 – 10.40 *First morning session*

Chair: Aalbert Zwijnenburg

9.00 – 9.30 **Vegetable Oils as Raw Materials for Polymer Nanoparticles** (M)
L21 Pedro H. H. Araújo, Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Florianópolis, Brazil

9.30 – 9.50 **Reactivity and Release of Plant Oils from Loaded Poly(styrene-co-maleimide) Nanoparticles** (D)
L22 Pieter Samyn, Dirk Stanssens, Leo Vonck, Henk Van den Abbeele, University of Freiburg, Freiburg, Germany

9.50 – 10.10 **From Plant Oils to Plant Foils: Straightforward Functionalization and Crosslinking of Natural Plant Oils with Triazolinediones** (D)
L23 Kevin De Bruycker, Oğuz Türünç, Stijn Billiet, Samira Ouardad, Johan Winne, Filip E. Du Prez, Ghent University, Ghent, Belgium

10.10 – 10.40 **Using Fatty Acid Derived Epoxides to Prepare New Polyesters and Polycarbonates** (M)
L24 Charlotte K. Williams[1], M. A. R. Meier[2], Mathias Winkler[2], Charles Romain[1], [1] Department of Chemistry, Imperial College London, London, UK; [2] Institute of Organic Chemistry, KIT, Karlsruhe, Germany

10.40 – 11.10 **Coffee Break**

11.00 – 12.50 *Second morning session*

Chair: Dieter Vogt

11.10 – 11.40 **Glycerol Valorisation Example in the Context of Oil Plants Biorefineries Design** (M)
L25 Franck Dumeignil, Lille University, UCCS UMR CNRS 8181, Villeneuve d'Ascq, France

11.40 – 12.00 **High Intensified Selective Synthesis of Partial Diglycerol Esters of Undecylenic Acid in Direct Esterification Reaction Melted Gel Conditions** (D)
L26 Gildas Nyame Mendendy Boussambe, Romain Valentin, Zéphirin Mouloungui, Laboratoire de Chimie Agro-Industrielle, INP-ENSIACET Toulouse, France and INRA, UMR 1010 CAI, Toulouse, France

12.00 – 12.20 **One Step Biodiesel Manufacture of Acid Oils via MSA Catalysis** (D)
L27 Axel Ingendoh, Ralf Tuerck, InaChem GmbH, Odenthal, Germany

12.20 – 12.40 L28	**Biodiesel Production via Catalytic Hydrodeoxygenation of Fatty acids derived from Chlorella algae and tall oil** Imane Hachemi, Åbo Akademi University, Åbo, Finland
12.40 – 14.00	**Lunch break**
14.00 – 15.30	*Afternoon session* *Chair: Alexander Steinbüchel*
14.00 – 14.30 L29	**Algae Oils as a Unique Source of Chemicals** (M) Florian Stempfle, Philipp Roesle, Sandra K Heß, Julia Zimmerer, Carolina Rio-Bartulos, Bernard Lepetit, Angelika Eckert, Peter Kroth, Stefan Mecking, Department of Chemistry, University of Konstanz, Konstanz, Germany
14.30 – 14.50 L30	**Synthesis and Characterization of Innovative Materials Based on Triglycerides from Microalgae** (D) Alice Arbenz, Luc Averous, ICPEES, CNRS UMR 7515, Strasbourg, France
14.50 – 15.20 L31	**Algae for the Production of Advanced Biofuels** D. Behrendt, C.Schreiber, A.Müller, U.Schurr, IBG-2: Pflanzenwissenschaften, Forschungszentrum Jülich GmbH, Jülich
15.20	**Poster Award and Closing Remarks** **Best Poster Award** Award committee (Pedro Araujo, Franck Dumeignil, Xavier Ruiz Martinez) **Closing remarks** Michael A. R. Meier
15.30	**End of Workshop**

Posters

P1 **Jatropha curcas hydroxylated and urethanated polymeric material – Preparation and characterization**

Cecilia Olufunke Akintayo[1], Emmanuel Temitope Akintayo[2], Habibat Omolara Adubiaro[1], [1] Federal University, Oye Ekiti, Ekiti State, Nigeria, [2] Ekiti State University, Ado Ekiti, Ekiti State, Nigeria

P2 **Solid acid catalysts based on polyoxometalate for esterification of acetic acid with heptanol**

ALI M. ALSALME, Abdulaziz Alghamdi, King Saud University, RIYADH, Saudi Arabia

P3 **Synthesis of Nickel Nanoparticles From N,N’-Dialkylimidazolium Chloronickel(II) Ionic Liquid and their application as catalysts for bio-diesel production**

Abdulaziz Ali Alghamdi, Ali M. Alsalme, King Saud University, RIYADH, Saudi Arabia

P4 **Synthesis and Antimicrobial properties of Citronellol Based Surface Active Ionic Liquids (SAILs)**

Vinay Chauhan, Sukhprit Singh, Department of Chemistry, Guru Nanak Dev University, Amritsar, India

P5 **Hydrophobe-free miniemulsion polymerization: towards high solid content of fatty acid-based poly(urethane-urea) latexes**

Estelle Rix, Etienne Grau, Henri Cramail, LCPO CNRS Bordeaux University, Bordeaux, France

P6 **Statistical quantification of vegetable oils based on PCA and PLS analysis of vibrational spectra**

Pieter Samyn, University of Freiburg, Freiburg, Germany

P7 **Bio-based additives for PLA- A case study of oleo-product development**

THOMAS LEBARBE[1], ETIENNE GRAU[2], HENRI CRAMAIL[2], CARINE ALFOS[1], [1] ITERG, Pessac, France; [2] LCPO CNRS Bordeaux University, Bordeaux, France

P8 **Towards Resource Efficient Synthesis of novel Long-Chain-Polyesters from Renewable Feedstocks via hydroformylation**

Thomas Seidensticker, Andreas J. Vorholt, Arno Behr, Technische Universität (TU) Dortmund, Dortmund, Germany

P9 **Synthesis and Characterization of New Polymers from Adenopus breviflorus benth oil, Styrene and Divinyl Benzene by Cationic Polymerization**

Emmanuel T Akintayo[1], Sabine Beuermann[2], [1] Ekiti State University, Ado-Ekiti, Nigeria; [2] Institut für Technische Chemie, TU Clausthal, Clausthal-Zellerfeld, Germany

P10 **Synthesis of macrocyclic lactones with musk odor by ring closing metathesis using oleic and 9-decenoic acids as building blocks**

Adrian Sytniczuk, Karol Grela, Biological and Chemical Research Centre, Department of Chemistry, Warsaw University, Warsaw, Poland

P11 **Chemical Valorization of Cashew Nut Shell Liquid by Isomerizing Metathesis**
Sabrina Baader[1], Stefania Andrada Trita, Patricia E. Podsiadly, David J. Cole-Hamilton[2], Lukas J. Gooßen[1], [1] Technische Universität Kaiserslautern, Kaiserslautern, Germany; [2] University of St. Andrews, St. Andrews,Scotland, UK

P12 **Synthesis of plant oil derived polyethers by the $GaBr_3$-catalyzed reduction of carboxylic acid esters**
Patrick-Kurt Dannecker[1], Ursula Biermann[2], Jürgen O. Metzger[2], Michael A.R. Meier[1], [1] Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; [2] University of Oldenburg, Oldenburg, Germany

P13 **Triazolinediones as a rapid functionalization and crosslinking tool of plant oil-based step-growth polymers**
Laetitia Vlaminck, Kevin De Bruycker, Oguz Türünç, Samira Ouardad, Filip E. du Prez, University of Gent, Gent, Belgium

P14 **Process Development for the Hydroformylation of Methyl 10-Undecenoate Using Water/Butanol-Solvent Systems – From Laboratory to Miniplant Scale**
Tom Gaide, Jens Dreimann, Arno Behr, Andreas J Vorholt, Technische Universität (TU) Dortmund, Dortmund, Germany

P15 **Long-chain unsymmetrical α,ω-difunctional compounds from fatty acids with complete feedstock molecule utilization**
Timo Witt, Florian Stempfle, Philipp Roesle, Stefan Mecking, Department of Chemistry, University of Konstanz, Konstanz, Germany

P16 **Synthesis of Polyethers from Fatty Alcohols by Allyl-Activation**
Veronika R. Huber, Herbert M. Riepl, Weihenstephan-Triesdorf University of Applied Sciences, Straubing, Germany

P17 **Electrochemistry for the conversion of free fatty acids and triglycerides in organic and aqueous media**
Tatiane R. dos Santos[1], Uwe Schröder[2], Falk Harnisch[1], [1] Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, Leipzig, Germany; [2] Technische Universität Braunschweig, Braunschweig, Germany

P18 **Linear Long-Chain Aliphatic Polyamides – Fatty Acid Based Polycondensates and Novel Approaches via ADMET Copolymerization**
Justus Walter, Patrick Ortmann, Tobias A Lemke, Brigitta Schemmer, Stefan Mecking, Department of Chemistry, University of Konstanz, Konstanz, Germany

P19 **Liquid solid phase behavior of ternary fatty acid systems of palmitic, stearic, oleic and linoleic acid**
Karl Andreas Eckert, Sunanda Dasgupta, Benjamin Selge, Peter Ay, Brandenburg University of Technology, Cottbus-Senftenberg, Germany

P20 **A modified Wacker Oxidation process: efficient oxyfunctionalization of renewable raw materials**
Marc von Czapwieski, Michael A.R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P21 **Epoxidized vegetable oils as glycerol based alkyd resins modifiers**
Hanna Nosal, Janusz Nowicki, Marek Warzała, Jan Mosio-Mosiewski, Dorota Stańczyk, Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland

P22 **Efficient and Sustainable Synthesis of High Vicosity Fatty Acid Esters**
Dorota Stańczyk, Janusz Nowicki, Jan Mosio-Mosiewski, Marek Warzała, Hanna Nosal, Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland

P23 **Syntheses and Characterization of Crosslinked High-Oleic Sunflower Oil for Biolubricant Applications**
Franziska Huß, Werner Pauer, Hans-Ulrich Moritz, University of Hamburg, Hamburg, Germany

P24 **Amphiphilic ionic liquids with dual functions – surfactant and catalyst**
Dorota Stańczyk, Janusz Nowicki, J. Łuczak, Hanna Nosal, Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland

P25 **Modified starch and β-cyclodextrin obtained from Ugi five-component reactions with carbon dioxide**
Rebekka Schneider, Ansgar Sehlinger, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P26 **Catalytic Decarbonylation of Biosourced Substrates**
Jeremy Ternel[1], Thomas Lebarbe[2], Eric Monflier[1], Frederic Hapiot[1], [1] Université d'Artois, Lens Cedex, France; [2] ITERG, Pessac, France

P27 **Synthesis of Modified Polycaprolactams Based on Renewable Resources**
Stefan Oelmann, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P28 **Pressure Sensitive Adhesives from Plant-based Oils: Synthesis and Adhesive Properties**
Wiebke Maassen[1,2], Norbert Willenbacher[2], Michael A. R. Meier[1], [1] Institute of Organic Chemistry, KIT; [2] Institute for Mechanical Process Engineering and Mechanics, KIT, Karlsruhe, Germany

P29 **Renewable Polymers from Itaconic Acid by Polycondensation and Ring-Opening-Metathesis Polymerization**
Matthias Winkler[1], Talita M. Lacerda[1,2], Felix Mack[1], Michael A. R. Meier[1], Institute of Organic Chemistry, KIT, Karlsruhe, Germany; [2] São Carlos Institute of Chemistry and Department of Materials Engineering/São Carlos School of Engineering, University of São Paulo, São Carlos, SP, Brazil

P30 **Modified Poly(ε-caprolactone)s: An Efficient and Renewable Access via Thia-Michael Addition and Baeyer−Villiger Oxidation**
Matthias Winkler, Yasmin S. Raupp, Hanna E. Wagner, Lenz A. M. Köhl, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P31 **Sustainable and Environmentally Friendly Alkylations of Phenols with Organic Carbonates and its Application on Organosolv Lignin**
Lena Charlotte Over, Oliver Kreye, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P32 **Glycerol-mediated liquefaction of lignin residue for preparation of lignol**
Eun Yeol Lee, Department of Chemical Engineering, Kyung Hee University, Gyeonggi-do, Republic of Korea

P33 **Catalytic Carbonylation of Crude Algae Oil Lipids**
Sandra K. Hess[1], Philipp Roesle[1], Florian Stempfle[1], Julia Zimmerer[1], Stefan Mecking[1], Daniela Ewe[2], Carolina Río-Bártolus[2], Bernard Lepetit[2], Angelika Eckert[2], Peter Kroth[2], [1] Department of Chemistry, [2] Department of Biology, University of Konstanz, Konstanz, Germany

P34 **Synthesis of defined star polymers using ADMET-polymerization and post-polymerization modification via thiol-click chemistry**
Maike Unverferth, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P35 **A SUSTAINABLE ROUTE TO TERMINAL EPOXIDES FROM FAMEs**
Chiara Palumbo, Cristina Tiozzo, Rinaldo Psaro, Nicoletta Ravasio, Matteo Guidotti, CNR-Institute of Molecular Sciences and Technologies, Milano, Italy

P36 **Thermoplastic polyester elastomers based on plant-oil derived long-chain crystallizable aliphatic hard segments**
Brigitta Schemmer, Florian Stempfle, Stefan Mecking**,** Department of Chemistry, University of Konstanz, Konstanz, Germany

P37 **Use of waste frying oil for the biotechnological production of surface-active hydrolysates of industrial interest**
Ignacio Moya-Ramírez, Alejandro F. Arteaga, Manuela M. Lechuga-Villena, Encarnación Jurado, Miguel García-Román, University of Granada, Granada, Spain

P38 **Two-phase olive mill waste as feedstock for biosurfactant production by Bacillus subtilis DSM 3526**
Danielle Maass[1], Ignacio Moya Ramírez[1], Alejandro F. Arteaga[2], Deisi Altmajer Vaz[2], S. M.A. Guelli U. De Souza[1], R.C. S.C. Valle[1], Miguel García Román[2], [1] Federal University of Santa Catarina, Florianópolis, Brazil; [2] University of Granada, Granada, Spain

P39 **The Sustainable Derivatization of Starch with Organic Carbonates: Renewable Feedstock for the Chemical Industry**
Zafer Söyler, Michael A. R. Meier, Institute of Organic Chemistry, KIT, Karlsruhe, Germany

P40 **New approach to monomer synthesis for polyamide production from local plant oils**
Christian Beck, Herbert M. Riepl, Weihenstephan-Triesdorf University of Applied Sciences, Straubing, Germany

P41 **Kinetics and mechanism of Jatropha curcas biodiesel decomposition by oxidation reaction**
S. Supriyono [1], H. Sulistyo [1], J.M.Dias [2], [1] Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada, Indonesia; [2] LEPABE, Department of Metallurgic and Materials Engineering, FEUP, Portugal

Abstracts

Part 1: Lectures

L1

Single cell oil – realistic and unrealistic perspective

Alexander Steinbüchel
Institut für Molekulare Mikrobiologie und Biotechnologie,
Westfälische Wilhelms-Universität Münster, Münster, Germany
steinbu@uni-muenster.de

Although we experience at present a transient decrease of the crude oil prize, the global economy heads for a severe energy crisis in the future: Comparing the forecasted energy demand and accessible resources of crude oil, it is obvious that the future energy demand cannot be solely and forever met by fossil fuels. The energy demand is going to rise, whereas well accessible sources of crude oil are expected to decrease in the future. Consequently, it is inevitable to resolve the dependency on crude oil by establishing sustainable and competitive alternatives. One part of a solution could be the biotechnological production of lipids by using microorganisms and the subsequent conversion of the lipids into fuels. These microbial lipids are often referred to as single cell oil. The lecture describes the potential of single cell oil which could be produced by enzymatic processes or by fermentation of microorganisms in biotechnology. The lecture will include a comparison of the various naturally occurring microorganisms and also microalgae, which are capable of synthesizing lipids and which occur frequently, as well as genetically engineered microorganisms. It will also include the various carbon sources from which single cell oil could be produced. The pros and in particular the cons of the currently available biological systems for production of single cell oil will be discussed.

L2

Catalytic Functionalization of Oleochemicals – New Developments in Laboratory and Miniplants

Arno Behr
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This contribution will give a short survey about the research results at our Chair of Technical Chemistry in recent years in the field of catalytic oleochemistry. We are especially interested in the development of new reactions with homogeneous transition metal catalysts and their recycle via different physicochemical methods. These reactions are optimized in the lab scale by chemical researchers and are then scaled-up into the miniplant scale via engineers. These miniplants represent the real chemical flow in a production plant and simulate all recycling streams of solvents, non-reacted starting compounds and catalysts.
We are especially engaged in investigations of unsaturated fatty compounds as e.g. oleic acid, linoleic acid, linolenic acid, erucic acid and undecylenic acid, which are well suited for homogeneous catalyzed functionalization reactions on the CC-double bond. A survey will be given about the following reaction types:

- Selective catalytic oxidation of fatty esters to epoxides and diols
- Oxidative cleavage of fatty compounds to dicarboxylic acids
- A reaction sequence of homogeneous co-oligomerisation of linolenic acid with ethylene followed by hydrogenation to saturated branched fatty compounds
- Metathetic conversions of unsaturated oleochemicals
- Carbonylation reactions with fatty compounds, especially hydroformylations, hydroesterifications and hydroaminomethylations

Recent literature:

A. Behr, N. Tenhumberg, A. Wintzer, „Selective Oxidation and Functionalisation of Renewables“ DGMK-Tagungsbericht **2014**-3, 11-15.
A. J. Vorholt, T. Seidensticker, K. A. Ostrowski, A. Behr, „Hydroformylation – Door Opener to Highly Efficient Tandem Reactions to Bifunctional Molecules“, DGMK-Tagungsbericht **2014**-3, 47-50.
A. Behr, A. J. Vorholt, „Neue Trends in der homogenen Übergangsmetallkatalyse“, Chem. Ing. Tech. 86 (**2014**), 2089-2104
A. Behr, T. Seidensticker, A. J. Vorholt, „Diester monomers from methyl oleate and proline via tandem hydroaminomethylation-esterification sequence with homogeneous catalyst recycling using TMS-technique", Eur. J. Lipid Sci. Technol. 116 (**2014**), 477-485
A. Behr, S. Toepell, S. Harmuth, "Cross-metathesis of methyl 10-undecenoate with dimethyl maleate: an efficient protocol with nearly quantitative yields", RSC Adv. 4 (**2014**), 16320-16326
A. Behr, H. Witte, A. Kämper, J. Haßelberg, M. Nickel, "Entwicklung und Untersuchung eines Verfahrens zur Herstellung verzweigter Fettstoffe im Miniplant-Maßstab", Chem. Ing. Tech. 86 (**2014**), 458-466
A. Behr, A. J. Vorholt, K. A. Ostrowski, T. Seidensticker, „Towards recource efficient chemistry: tandem reactions with renewables", Green Chem. 16 (**2014**), 982-1006.
A. J. Vorholt, P. Neubert, A. Behr, "Katalytische Funktionalisierungen von Oleyalkohol in thermomorphen Lösungsmittelsystemen zur Synthese potenzieller Biotenside und -Monomere" Chem. Ing. Tech. 85 (**2013**), 1540-1547.
A. Behr, H. Witte, Z. Bayrak„Homogeneous metal complex catalyzed conjugation of methyl linoleate", Eur. J. Lipid Sci. 115 (**2013**), 721-728.
A. Behr, A.J. Vorholt, N. Rentmeister, „Recycable homogeneous catalyst for the hydroesterification of methyl oleate in thermomorphic solvent systems", Chemical Engineering Science 99 (**2013**) 38-43
A. Behr, J. Gomes-Jelonek, H. Witte, "Katalysatorrecycling in der homogenkatalysierten Kreuzmetathese von Ölsäuremethylester und 4-Octen", Chem. Ing. Tech. 84 (**2012**), 2174-2181
A. Behr, S. Krema, A. Kämper, „Ethenolysis of ricinoleic acid methyl ester - an efficient way to the oleochemical key substance methyl dec-9-enoate", RSC Advances, 2 (**2012**), 12775-12781
A. Behr, N. Tenhumberg, A. Wintzer, „Efficient ruthenium-catalysed oxidative cleavage of methyl oleate with hydrogen peroxide as oxidant", RSC Advances, 3 (**2012**), 172-180.
A. Behr, N. Tenhumberg, „Aufbau einer Versuchsanlage zur katalytischen Spaltung des 9,10-Dihydroxystearinsäuremethylesters mit Luftsauerstoff", Chem. Ing. Tech. 84 (**2012**), 1559-1567.
A. Behr, N. Tenhumberg, A. Wintzer, „An efficient reaction protocol for the ruthenium-catalysed epoxidation of methyl oleate", Eur. J. Lipid Sci. Technol. 114 (**2012**), 905-910.

L3

New Value Chains from Oil crops to long chain polyamides

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The EuroBioRef project, a 7th Framework Program project, was one of the 3 major Integrated BioRefinery projects which started nearly 5 years ago. The project was targeting both lignocellulosic and oils seed crops, and aims for a valorization of the whole crops. For long chain monomers, fatty acids are a naturally attractive starting material. Within the project, several oil crops have been field tested in Greece, Poland and Madagascar. In the later case, the objective was also to include tropical crops in the project, but also to generate a Business Plan for the combined production of food and non-food crops in an African environment. Castor, Crambe but also Safflower proved to be attractive crops for Europe.

Castor Oil, a non-edible vegetable oil, is rather unique since it has a high concentration of a hydroxyfatty acid (ricinoleic acid, (C18:1,OH, δ-9)). Crambe has a unique fatty acid profile with a high concentration of erucic acid (C22:1, δ-13), while safflower can have either a high linoleic or a high oleic acid (C18:1, δ-9), profile.Several chemical processes have been developed including improved thermal cleavage, cross-metathesis, conversion of fatty acids to fatty nitriles, but also oxidative cleavage and hydroformylation in order to produce monomers for long chain polyamides.

In all cases, the functionalizations of the fatty acids, such as unsaturation and hydroxyl groups, are used and their position determines the monomer which can be obtained. Arkema already produce renewable (Polyamide-11, Polyamide-10.10) and non-renewable (Polyamide-12) polymers. Although having similar chain length, they have different properties. Polyamide-11 and 10.10 are produced from castor oil. For the PA-11 monomer, aminoundecanoic acid, the synthesis involves the formation of 10-undecylenic acid (and methyl ester).

In EuroBioRef, this ω-unsaturated fatty acid has been converted to the corresponding nitrile. Reaction through cross metathesis of either the unsaturated ester or unsaturated nitrile leads to diacid, dinitrile and subsequently diamine, or nitrile-ester and after hydrogenation amino-acid, depending of the other reactant, methyl acrylate or acrylonitrile. Cross metathesis reaction is straightforward, but there is limited availability of expensive catalysts.

Alternative routes have also been investigated, using other fatty acids, but also the same fatty acid and nitrile. For example, through hydroformylation ω-unsaturated fatty nitrile are converted to the corresponding aldehyde-nitrile, which after oxidation and reduction is turned into the 12 carbon atoms amino-acid, monomer of Polyamide-12. Like for cross metathesis, this route uses homogeneous catalysts, but at much higher turnover numbers (lower catalyst consumption).

Oxidative cleavage of fatty unsaturated nitrile leads to a nitrile-acid and a saturated short chain acid. After hydrogenation of the former, an amino-acid is obtained whose chain length depends on the position of the double bond in the initial material. The main advantage of this route results from the absence of expensive catalyst, and the limited number of steps. Effective collaboration between partners enabled the creation of Value Chains from various non-edible oil crops to high value monomers through several different chemistries.

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007- 2013) under grant agreement n°241718 EuroBioRef.

L4

In-situ spectroscopy of liquid-phase catalytic processes with biomass-derived compounds

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The last decade has witnesses the blooming of in-situ and operando spectroscopy for the characterization of heterogeneous catalysts. These advances allow scientists to investigate the working principles of solid catalyst with time- and space-resolution and high chemical sensitivity. Now we are in the position to understand, to a greater extent, the nature and dynamics of active sites, reaction intermediates and porosity/accessibility of catalyst at the molecular and microscopic level. Advances in this field have been mostly obtained in catalytic processes occurring in the gas phase. However, spectroscopic studies examining heterogeneous catalyst in the liquid phase are scarce in the open literature. These studies are highly relevant in biomass valorization, where conversion processes are often inevitably limited to be carried out in liquid phase. Many reasons hamper the development of tools to investigate the chemistry of solids in the liquid phase. Challenges when using spectroscopy include the discrimination between the liquid and solid phase and the transparency of beam probe through the liquid. Be that as it may, a significant number of tools are suitable or have been adapted to investigate solid catalyst in the liquid phase. These include vibrational spectroscopy, UV-Vis and X-ray-based techniques. This lecture highlights the latest developments in this area of research, with especial emphasis on research conducted in our own group.

L5

Synthesis of Saturated Branched Fatty Derivatives using a Process Combination of Homogeneous and Heterogeneous Catalysis in Miniplant Scale

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Branched oleo derivatives have a huge potential, particularly in cosmetics and lubricants industry which is based, among other advantages, on the low melting point and the high thermal and oxidative stability. A process for synthesis of saturated branched oleo derivatives from renewable raw materials and a new method for catalyst recycling were developed including a combination of homo- and heterogeneous catalysis.

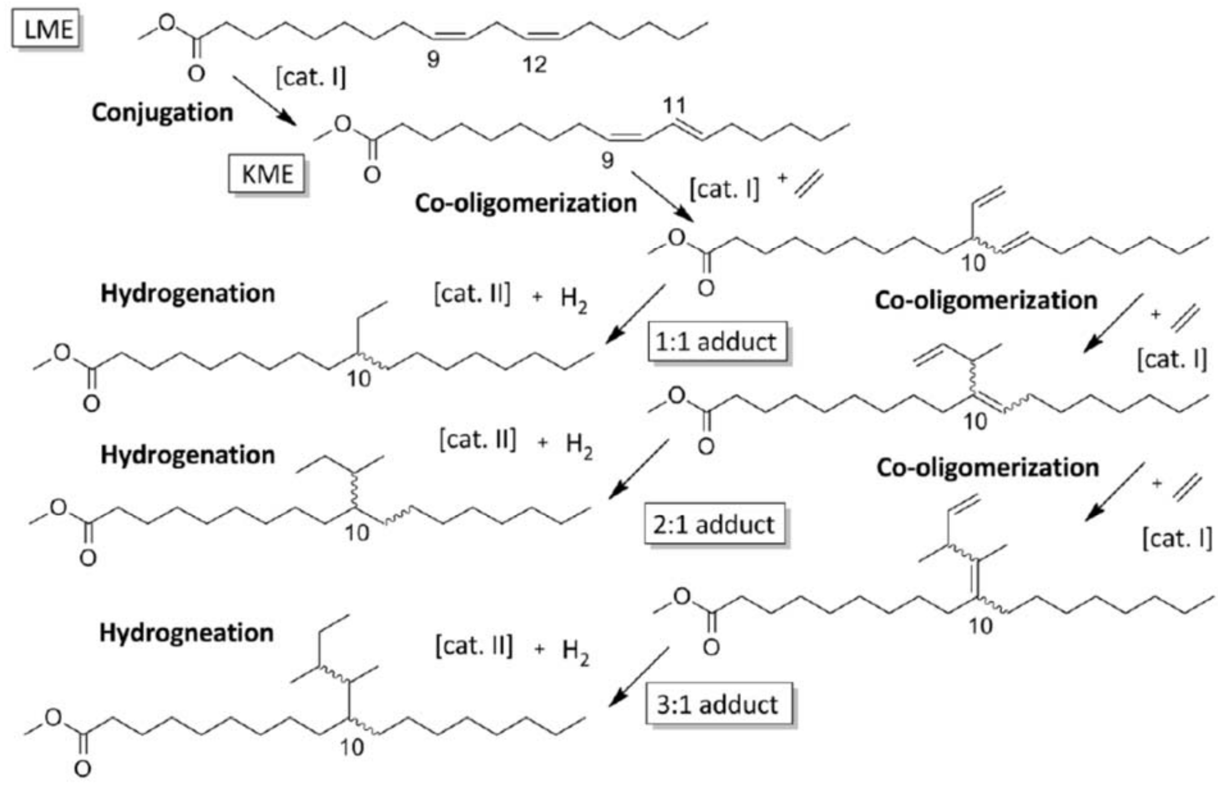

Figure 1: Conjugation and Co-oligomerization of methyl linoleate with ethylene and hydrogenation forming saturated branched oleo derivatives

Starting from methyl linoleate (LME) or linolenic acid with a tandem-reaction consisting of conjugation and co-oligomerization with ethylene branched derivatives were formed with a yield up to 92% using a homogeneous RhCl3•3H2O precursor which has to be recycled

[1]. A biphasic liquid reaction system for this process step is unfavorable due to high mass transfer limitations.

The use of temperature-controlled multicomponent solvent systems (TMS) as catalyst recycling method is one possible solution. The homogeneously catalyzed reaction takes place in a monophasic liquid reaction system at reaction temperature (70 °C) using one polar and one medium polar solvent. In the following separation step (10 °C), due to the temperature dependent miscibility gap two liquid phases are formed, one contains the homogeneous catalyst, the other one the product. The polar catalyst phase can then be recycled back to the reaction.

The problem concerning the above-mentioned tandem-reaction is that after heating up to reaction temperature, the catalyst cannot be totally separated from the fatty compounds by reason of coordination of the homogeneous rhodium catalyst to the double bonds of the oleo compounds. The coordination to the double bonds of the product could be verified by examination of the extraction behavior of the rhodium catalyst from several oleo derivatives that differ in their amount and position of double bonds. Hydrogenation of the product is required in order to recycle the homogeneous rhodium catalyst. From saturated branched oleo derivatives the rhodium amount was reduced to 2 ppm (0.2 %) by extraction.

Hydrogenation was tested in a miniplant including a trickle bed reactor and the iodine value was optimized to 4.5 using Pd/C as heterogeneous catalyst. During hydrogenation, the homogeneous rhodium catalyst was adsorbed by the heterogeneous one. This adsorption was dramatically reduced from 76.3% to 9.6% by revealing unique correlation of the adsorption behavior to the reaction conditions.

The presentation will highlight the synergy of homo- and heterogeneous catalysis and new opportunities for catalyst recycling demonstrated on a process for synthesis of saturated branched oleo derivatives.

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Chem. Ing. Tech. 2014, 86, No. 4, 458–466

L6

Isomerizing Metathesis as an Efficient Tool for the Generation of Biodiesel from Rapeseed Oil

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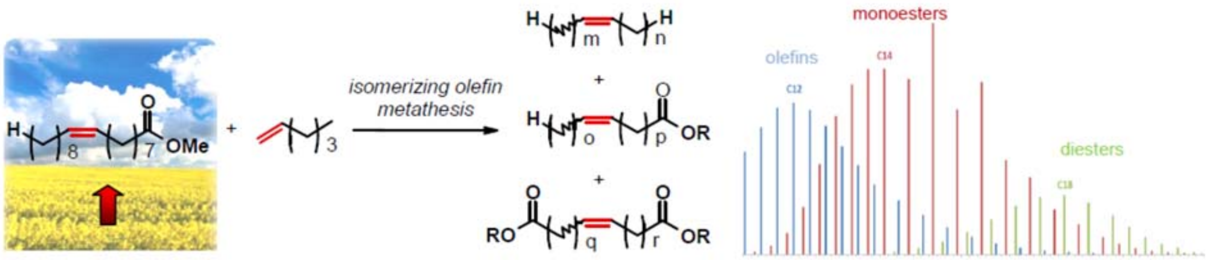
Plant oils, e.g. rapeseed oil, are the most common renewable feedstock for the replacement of petrodiesel.[1] However, this natural resource based fuel suffers from several drawbacks, such as instability towards oxidation, high viscosity and pour point. Another issue that becomes important when using larger percentages of biodiesel in fuel blends is the boiling behavior. Protocols based on the cross metathesis of rapeseed methyl ester (RME) with short olefins show improvement, but still do not match the boiling curve of petrodiesel. Our recently developed isomerizing olefin metathesis process converts rapeseed oil into multi-component blends, consisting of olefins, mono- and dicarboxylates.[2] When the cross-metathesis partner is 1-hexene, the resulting mixtures show a uniform product distribution with a distillation curve similar to commercial diesel. Unlike the mixtures obtained by non-isomerizing crossmetathesis,[3] they exhibit a more homogeneous distillation curve, making them suitable for use in engines. Therefore, this procedure represents a promising alternative to fossil-based fuel in the future (Scheme 1).



Scheme 1. Isomerizing cross metathesis of RME.

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L7

Unravelling the mechanism of the isomerizing alkoxycarbonylation of plant oils

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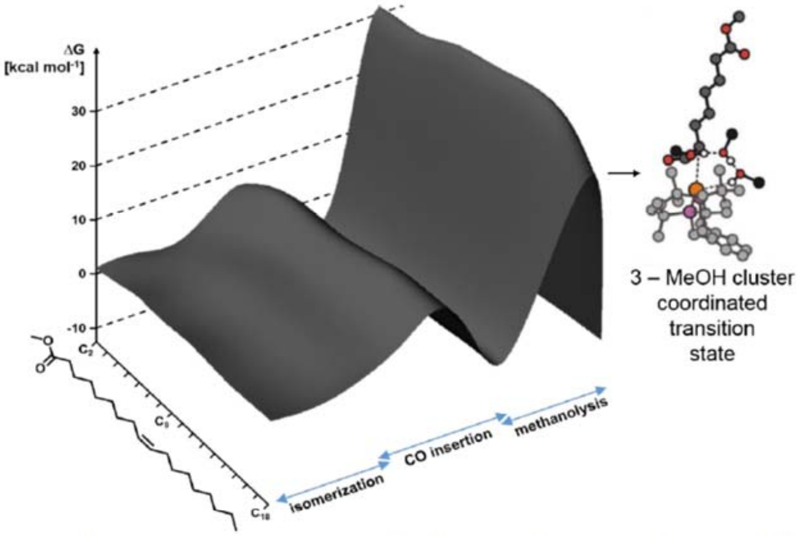
Fatty acids from plant oils are attractive alternative sources for chemicals and materials due to their long-chain linear methylene segments in combination with a reactive double bond.[1] A complete conversion to α,ω-functionalized compounds is of particular interest, for example, for the utilization as monomers for polycondensation reactions.[2] This requires the conversion of an internal double bond deep in the fatty acid chain to a terminal functional group in order to incorporate the complete fatty acid chain. The utilization of the linear fatty acid chain in polyesters or polyamides results in polymers with excellent thermal and mechanical properties.[3]

The conversion of the double bond can be brought about in principle by an isomerization-functionalization approach. This is particularly difficult, however, as terminal olefins are thermodynamically strongly disfavored vs. the internal double bonds of the substrate. The state of the art in terms of terminal selectivity and lack of undesired side reactions is Pd(II)-catalyzed isomerizing alkoxycarbonylation.[2,4] Hereby, methyl oleate can be converted to 1,19-nonadecanedioate with 95% conversion and selectivity, respectively, at the same time.[5] A key within this approach are electron-rich bulky diphosphine ligands.

Very recently we unraveled the full mechanism and energy landscape of the isomerizing alkoxycarbonylation of plant oils.[6] In this contribution we present the origin of the selectivity and reaction rates by direct observation of relevant intermediates with NMR spectroscopy, studies under pressure reactor conditions (20 bar CO, 90°C) and DFT calculations.

Essentially, sterically congested metal centers result in higher selective systems due to pronounced energy differences between the pathways leading to the linear *versus* the branched products of the rate-determining methanolysis steps. In addition, these systems are generally more productive, as the energetic barrier of this rate-determining step is lower compared to less encumbered systems, which may not be active catalysts at all for methoxycarbonylation due to an unfavorable barrier.

As a general picture of this isomerization-functionalization reaction sequence, the rate determining step is preceded by a diverse relatively flat energy landscape of the various reversible reaction pathways. This applies to the isomerization sequences, but also to the first functionalization steps. Effectively, these isomerization-functionalization steps are in mutual equilibrium vice versa. Selectivity arises from differentiation of pathways in the final and highest barrier step of functionalization, here by extreme steric congestion about the active site.



Scheme 1: Energy landscape of an isomerization-functionalization approach of methyl oleate with $[Pd(dtbpx)(OTf)_2]$ as catalyst precursor.

Further, theoretical studies show that bulky diphosphine ligands favor a transition state with a cluster of three methanol molecules for the linear acyl species while the branched alkyl species exhibit a single methanol coordinated transition state. This energy difference contributes to the high selectivity towards linear products for bulky diphosphine ligands. Higher alcohols slow down the alcoholysis step, as observed in both pressure reactor experiments and NMR studies with a model Pd-acyl compound. Theoretical studies also indicate that iso-propanol exhibits a single molecule transition state versus a three molecule transition state for methanol.

These features define the essential prerequisite in designing isomerization-functionalization schemes with a single type of active sites, and this picture identified may also provide inspiration for multi-component catalyst systems in which equilibrium landscapes may extend over the different types of sites.

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L8

SYMBIOSIS OF CHEMISTRY AND BIOLOGY: BASF’S BIODEGRADABLE AND RENEWABLE POLYMERS

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INTRODUCTION

Manmade plastics amount to an annual world production of roughly 250 million metric tons. Biopolymers – biobased and/or biodegradable polymers - are an alternative to conventional polymers if they possess a better life-cycle assessment and/or improved properties. For certain applications (e.g. food packaging) biodegradability can be such a new functional property.[1] Today the capacity for biopolymers is still below 1% of global polymer production, capacity, but strongly growing. Formation of alliances between different players in the value chain and significant investments in large scale production plants are the most visible sign for the dynamic growth of biodegradable and biobased polymers. Prominent examples for biodegradable polymers are polylactic acid by NatureWorks and the ecoflex® polyesters by BASF. Partly biobased Polytrimethylterephthalate by DuPont and biobased polyethylene by Braskem are commercialized durable polymers.

The field of biopolymers requires the close cooperation of chemistry and biology on the level of renewable monomers, polymers and end of life mechanism (e.g. composting) respectively. Using BASF as an example, this symbiosis of chemistry and biology will be presented (see figure 1).

RENEWABLE MONOMERS

Renewable monomers can be obtained by conversion of renewable feedstocks either by classical chemical catalysis (e.g. adipic acid from glucose) or via a direct fermentation process (e.g. succinic acid from glucose). Potential advantages of these processes based on renewable resources are i.) improved sustainability profile (e.g. lower carbon footprint), ii.) improved cost position and iii.) new performance characteristics. Succinic acid will be the BASF example to show the opportunities of such new processes.

POLYMER – COMPOUND – APPLICATION

ecoflex® F, the aliphatic-aromatic BASF polyester, is made from terephthalic acid, butanediol and adipic acid. Due to the composition the polymer is biodegradable under industrial composting conditions. This structure is also the reason why ecoflex® F combines excellent mechanical properties with the good processability of synthetic thermoplastics. ecoflex® F is the preferred blend partner for biobased and biodegradable polymers which typically do not exhibit good mechanics and processability for film applications by themselves – ecoflex® F therefore is a synthetic polymer which enables the extensive use of renewable raw materials (e.g. starch, PLA). The BASF brand name for compounds of ecoflex® with PLA is ecovio®.

This compounding and the introduction of biobased monomers in ecoflex® F leads to different property profiles. The application range[2] is very broad: from film applications like organic waste bags, shopping bags or agricultural mulch films to stiff foamed packaging, thermoforming (e.g. lids for biopolymer coated paper cups) and injection molding applications like coffee capsules.

END OF LIFE

Biodegradability and renewability are strongly associated with natural polymers (e.g. starches, cellulose, chitin, and lignin) and in fact evolution has established closed systems were carbon is recycled over and over again. But biodegradability, which is ideally the conversion of a given substance into carbon dioxide (and methane), water and biomass, and renewability are two properties that are not necessarily connected. Polymer biodegradation commonly begins with the (hydrolytic) breakdown of the main chain – often enzymatically catalyzed – followed by the aforementioned mineralization by microorganisms present in the respective habitat. Whether a polymer degrades under certain environmental conditions (e.g. microflora, temperature, humidity) is a question of the polymer microstructure. When talking about biodegradation it is important to be precise, because biodegradation in a controlled process like industrial composting is something totally different compared to biodegradation in soil. Therefore elucidation of the interaction of microorganisms and their respective enzymes with polymer substrates in different environments and deducing relevant structure-property relationships is an important task of BASF biopolymer research.

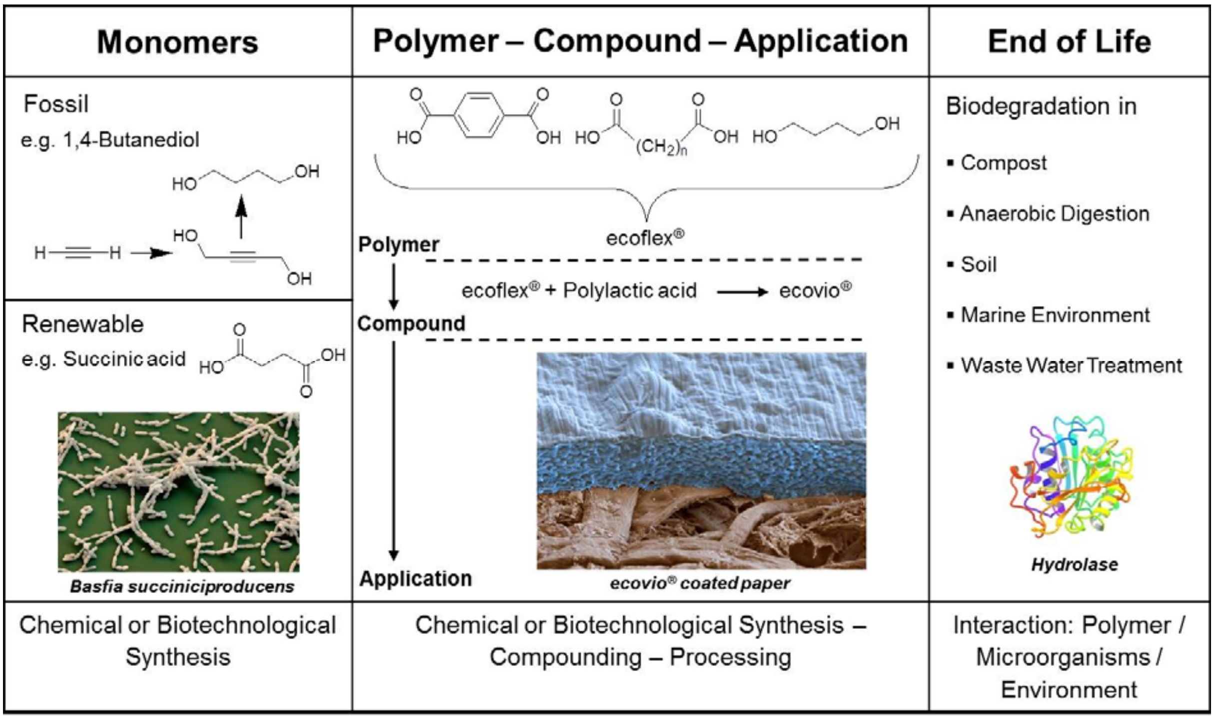

Figure 1. From monomers to end of life – Symbiosis of chemistry and biology.

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L9

Catalytic Copolymerization of Methyl 9,10-Epoxystearate and Cyclic Anhydrides

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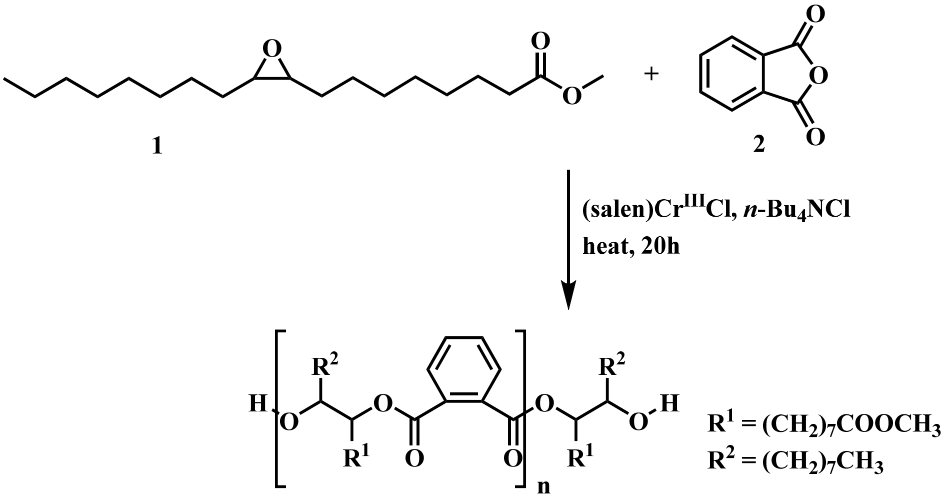
Plant oil derived compounds are attractive as raw material for the production of environmentally friendly and in many cases biodegradable consumer products. A great challenge is the production of polymers based on renewable feedstock. We have reported the alternating ring-opening copolymerization of methyl 9,10-epoxystearate **1** (scheme) with various cyclic acid anhydrides such as phthalic anhydride **2**, succinic anhydride and maleic anhydride to afford polyesters of narrow molecular weight distributions using a (salen)Cr$^{(III)}$Cl catalyst in the presence of *n*-Bu$_4$NCl.



In this way, polyesters (M_n = 2000-10000 g/mol) with low glass transition temperatures were formed. The reaction is characterized by sustainable aspects, for instance, the use of starting materials derived from renewable resources (> 60 %), low catalyst loadings and no added solvent. The pending long chain alkyl groups introduced in the polyesters by the fat derived substrates attribute amorphous properties to the polymers. Various fatty epoxides are easily available and open up the possibility for the synthesis of new highly branched polyesters.

L10

Regioselective Acetoxylation of Limonene: Access to Renewable Building Blocks via Catalysis and the Passerini Three-component Reaction

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The development of sustainable processes using renewable feedstocks is an important and urgent challenge, not only due to the depletion of fossil resources.[1] Among the available renewable materials, terpenes constitute a valuable and cheap biomass resource, which are available in large amounts from various essential oils or as by-product from diverse industrial processes.[2] Within this contribution a direct catalytic and regioselective acetoxylation of limonene was investigated.[3] The obtained acetoxylated limonene derivative, selectively functionalized at the exocyclic double bond, was saponified and subsequently isomerized under mild conditions into the corresponding aldehyde using an hydrogen-activated palladium catalyst. Subsequently, the thus obtained limonene aldehyde was applied in the Passerini three-component reaction (Passerini-3CR) using acrylic acid and a variety of isocyanides to produce several acrylate monomers. In subsequent free radical polymerizations polyacrylates with molecular weights up to 13 kDa were obtained (Figure 1).

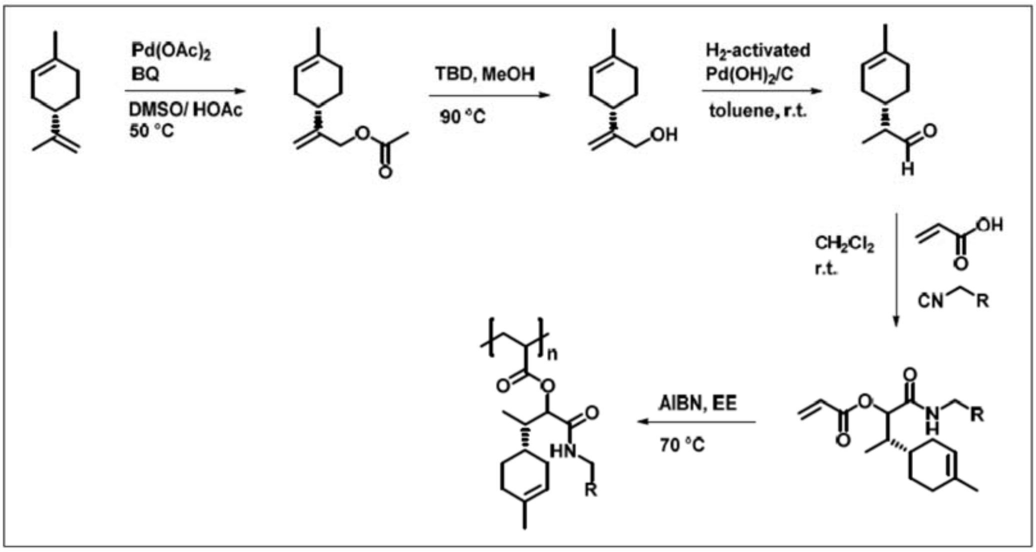

Figure 1: Synthesis route to renewable based polyacrylates using (*S*)-(-)-limonene.

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L11

Vegetable plant oils as a versatile source of greener thermoplastics: example of non-isocyanate polyurethanes

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Nowadays the use of vegetable oils as polymer precursors is the subject of growing interest in the academic and industrial communities. Many synthetic pathways can be pursued from natural vegetable oils to yield different functionalized derivatives – also called synthons – and polymers, such as polyesters, polyurethanes, polyamides, etc.[1]

In this context, polyurethanes (PUs) is commodity or technical material representing an important market, estimated around 8 %, of the current synthetic polymer production around the world (~ 300 million tons in 2012), finding applications in many fields, including medicine, fibbers, automotive, coatings, foams, etc. A challenging problem in designing poly(urethane)s is to avoid the use of isocyanate monomers which are obtained from phosgene, a highly hazardous reactant. Synthesis of PUs can now be achieved using CO2, an abundant starting material and valuable surrogate of toxic and corrosive phosgene. Here, we develop eco-friendly synthetic routes to bio-sourced PUs using fatty acid methyl esters and CO_2 as starting renewable raw materials, while resorting to organic (non-metallic) catalysts. This project thus leans on the three following pillars: i) precursors from vegetable oils, ii) CO_2 as a reactant avoiding the use of carcinogenic intermediates, iii) and organocatalysts as substitutes of metal-based catalysts.

L12

New Bio-based Hyperbranched Polyesters

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Hyperbranched polymers are a special type of dendritic materials and have as common features a high branching density as well as a globular and compact architecture. In contrast to their perfectly branched analogues, the dendrimers, hyperbranched materials are prepared in a one-pot route. This process limits the control on molar masses and branching accuracy. Nevertheless, hyperbranched polymers exhibit equivalent properties: a lower viscosity and a higher solubility than their linear analogues of the same molecular weights, as well as a high functionality.

Hyperbranched polymers are considered as suitable products for large scale applications as additives, materials for encapsulation in a wide range of fields including paintings, coatings, cosmetics and even in the medical field. All the commercially available hyperbranched polymers are petroleum-based.

The present work is dedicated to the synthesis of bio-based equivalents to replace them. Were used as raw materials some vegetable oils. Multifunctional precursors were prepared by chemical modification of fatty acids derivatives. Environmentally friendly processes were developed to polymerize them by polycondensation, leading to hyperbranched polymers. Insights into the fine structures obtained were performed by NMR spectroscopy, their macromolecular characteristics and thermo-mechanical properties investigated.

L13

Sustainable Synthesis of Amines – Direct Amination of Alcohols with NH_3

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The recently developed direct amination of alcohols with ammonia opens new possibilities for the transformation of renewable feedstocks for building-block synthesis.[1-4]
A range of biomass-derived alcohols was converted into primary amines in high to excellent selectivity, deriving interesting potential building blocks for polymers, intermediates and fine chemicals. The catalysts proved to be stable in a couple of consecutive runs without product removal. In order to improve the catalyst performance, mechanistic insight has to be gained. The $RuHCl(CO)(PPh_3)_3$/Xantphos system shows excellent activity in this reaction.[4] Varying the Ru-precursor and the ligands, and the use of various additives provided new insight on the reaction mechanism. Catalytically active and inactive intermediates have been identified by NMR studies. It was shown how inactive dihydrido species formed during the reaction can be reactivated.[5-7]
Additives like bases or ketones have a profound effect, which can lead to total deactivation or increase in reaction rate. Based on these insights, a possible mechanism for the direct amination of alcohols will be suggested.

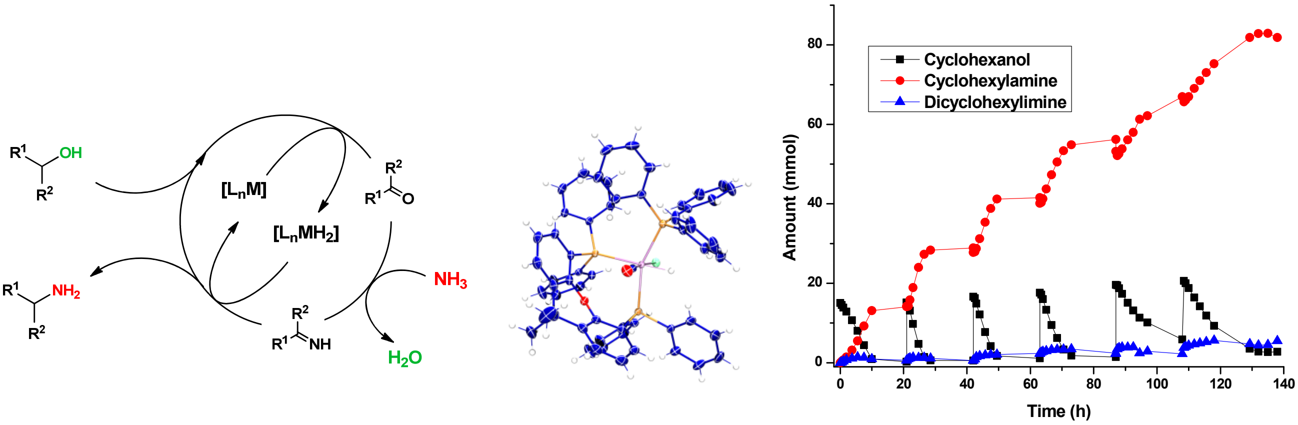

Figure: Hydrogen shuttling concept (left), the $RuHCl(CO)(PPh_3)(Xantphos)$ catalyst structure in the crystal (middle), and repetitive batch conversion of cyclohexanol with a $Ru_3(CO)_{12}$/acridine-based diphosphine system (right).

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L14

Reductive amination of dodecanol with NH_3 over heterogeneous catalysts

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Reductive amination of fatty alcohols with ammonia can be an efficient way of synthesizing fatty amines. The latter can be used as corrosion inhibitors, fabric softeners and surfactants [1]. In this work, reductive amination of dodecanol over heterogeneous catalysts was carried out over platinum, ruthenium, and palladium supported on carbon. The concentrations of the reactant and the products were analyzed by GC-FID.

The reductive amination of dodecanol consists of three consecutive reversible reactions namely, catalytic dehydrogenation of the alcohol forming an aldehyde, condensation of the formed aldehyde and ammonia forming an imine, and, finally catalytic hydrogenation of the imine to an amine.

In theory no extra hydrogen is needed for hydrogenation of the imine. In practice, some extra hydrogen is required for the reaction and for maintaining the catalyst activity [2]. Besides the formation of the primary amine, secondary and tertiary amines can also be formed as well as hydrogenolysis to dodecane can occur.

In this work, the influence of temperature and active metal on the reductive amination of dodecanol is studied. Furhtermore, an attempt of revealing the true reaction scheme is undertaken by studying reactions with aldehyde, alcohol, primary and secondary amines under different reaction conditions.

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L15

Reactions of methyl 9-oxo-10-undecenoate (1).

Synthesis of a C-glycolipid by a vitamin B_{12}-catalyzed addition of α-acetobromglucose to **1** and cathodic hydrodimerization of **1** to dimethyl 9,14-dioxodocosanedioate

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Methyl 10-undecenoate, which is available from ricinoleic acid, can be converted by allylic oxidation with *t*-butyl hydroperoxide and substoichiometric amounts of selenium dioxide to methyl 9-oxo-10-undecenoate (**1**). Michael additions of CH-acidic compounds as 1,3-dicarbonyl compounds, nitroalkanes, hydrogen cyanide and cyanohydrins with enone **1** have been described [1].

We report a vitamin B_{12}-catalyzed addition of α-acetobromglucose to enone **1**. As adduct, a C-glycolipid is obtained in 77% yield and high diastereoselectivity. In contrast to O-glycolipids, C-glycolipids are stable in acidic media and in the presence of enzymes. Their stability and important biological and medicinal effects are well documented in many recent publications, one of them is reference [2]. Further routes to C-glycolipids and to fatty acids attached to steroids are presented.

1,n-Diacids can be prepared by metathesis or anodic coupling of fatty acids. We report here a further access by an electrochemical hydrodimerization. The terminal oxo-ene group in enone **1** is electroactive and **1** yields in a cathodic hydrodimerization 78 % of dimethyl 9,14-dioxodocosanedioate. This way a 1,22-diester with a 1,6-dione group is formed. 1,6-Diones can be converted in an acid catalyzed reaction into acylcyclopentenes [3]. The keto groups can be hydrogenated to hydroxy and in the presence of amines to amino groups yielding monomers for polyesters and polyamides. Further cathodic couplings of derivates from methyl ricinoleate and citric acid are given.

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L16

Sugar Derived Amphiphiles as Crude Oil Thickening Agents – Influence on Type and Complexity

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Oil spills have negative impacts on the ecosystem, particularly aquatic lives, prompting the desire for their effective containment on water bodies. Unlike refined oils like diesel, crude oils have complex compositions, which vary from one crude oil type to another. Hence, an ideal material for crude oil thickening should be versatile enough to be applied to various crude oil types. We hereby present a class of crude oil thickening material that is a bio-based, phase-selective gelator (PSG); forms a thermoreversible gel; is derived from abundant biomass; and gels different crude oil type. Prior to testing for phase-selectivity, different amphiphiles were generated via a combinatorial search approach using different combinations of sugar-alcohols and fatty acids and tested for gelation in just crude oil (the conventional method); this led to M-8 and S-8 as the best two. Subsequently, M-8 and S-8 were subjected to phase-selective gelation test, which revealed M-8 to be the best. Overall, M-8 exhibited the ability to efficiently gel crude oil (up to over 62-times its mass of crude oil) and proved versatile towards gelling different crude oils types; its gel remained thermally stable up to 106 °C and hence exhibited thermo-reversibility between the gel and sol states, and underwent phase-selective gelation even while being strongly agitated. Hence, M-8 has been demonstrated to be an effective crude oil thickening material and, hence, a contender for an ideal crude oil recovery material.

L17

Catalyst Selection for Development of Chemical Processes Based on Fats and Oils

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Production of chemicals from naturally derived resources is receiving more attention. Bio-synthetic pathways can be used for making new products, it is shown that in many cases under industrial conditions these still need chemical transformations. Catalyst selection and design can be guided by following a consecutive approach looking at catalyst performance (activity/selectivity) but also price, availability, handling and recycling conditions.

L18

Skeletal Isomerisation of Oleic Acid over Ferrierite: Influence of Acid Site Number, Accessibility and Strength on Activity and Selectivity

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Branched-chain unsaturated fatty acids (BUFA) derived from vegetable oils are used extensively, in hydrogenated form, for the production of lubricants, cosmetics and surfactants. They combine liquidity, good thermal and oxidative stability, and exhibit useful interfacial properties. The current commercial process uses vegetable fatty acids as feedstock, and montmorillonite clay as catalyst [1]; yields in BUFA are 50% or less, the balance being mainly polymerised acids. Recently, improvements in both conversion and selectivity to BUFA have been reported using a commercial protonated ferrierite [2-3].
In this paper, we present our study of the skeletal isomerisation of oleic acid (OA) in the presence of various ferrierite catalysts. Five samples, four of which have very similar Si/Al ratios, were tested in order to explore how subtle differences in morphology and acidity, including type, strength, location and accessibility of the acid sites, influence the activity and selectivity to BUFA. A number of complementary characterisation techniques have been combined to measure these key parameters.
After normalization for the catalyst external surface area, initial activity correlates well with the Brønsted acidity of the larger channels as determined by adsorption / desorption of pyridine and FTIR. A low density of external acid sites reduces undesired oligomerisation of fatty acids, while a high ratio of Brønsted to Lewis acid sites explains the observed high BUFA yield. The strength of the Brønsted acid sites (as measured by temperature-programmed desorption with ammonia) influences the extent of branching per molecule (single or multiple). Our results suggest that the second (and subsequent) branching occurs via a hydride extraction step, and therefore requires a stronger acidity.

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L19

Rhodium-Catalyzed Hydroformylation of Triglycerides in Aqueous Media Using Supramolecular Emulsifiers

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Concerns about the environmental impact of chemical transformations prompted chemists to develop clean chemical processes using water as a solvent. Although appropriate for small partially water-soluble molecules, these processes are not suitable for the transformation of hydrophobic substrates due to the mass transfer limitation between the aqueous and the organic phase.

In this context, we have developed a process capable of converting naturally occurring triglycerides in water through supramolecular means in the presence of cyclodextrins (CDs). During the course of the hydroformylation reaction, a transient supramolecular complex is formed between triglyceride alkyl chains and appropriate CDs in a well-defined range of concentrations. The resulting CD/triglyceride supramolecular emulsifiers help converting the triglyceride C=C double bonds in biphasic conditions using a water soluble organometallic Rh-catalyst. Thus, through inclusion of their alkyl chains within the CD cavity and the subsequent formation of supramolecular emulsifiers, the triglycerides drive their own transformation into hydroformylated products. Once the reaction is complete, the unstable emulsion is broken rapidly. The hydroformylated products are recovered in the upper organic phase while the catalyst-containing aqueous phase can be recycled. Thus, this biphasic process can truly be considered as a clean process. Moreover it is applicable to a wide range of vegetable oils.

Through the presentation, the key parameters influencing this novel catalytic process will be described and commented.

L20

Rhodium-Catalyzed Functionalization of Mono-Unsaturated Fatty Acids

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Cyclic maleinated fatty acids are interesting monomers for the synthesis of sustainable polyester resins, which might be used for lacquers, paints or adhesives. The rhodium catalysed maleinisation of fatty acids, e. g. oleic acid, was reported first by Behr and Handwerk.[2] They found that the Rh-catalysis enables the synthesis of cyclic, Diels-Alder-like products from mono-unsaturated fatty acids, e. g. oleic acid.

This work focused on the mechanistic aspects of the catalytic addition of maleic anhydride and the selectivity of the used catalysts, $RhCl_3(H_2O)_3$ and $Rh(OAc)_2$, towards the cyclic Diels-Alder like products. Moreover, it was found that during the reaction an isomerisation of the cis-configurated oleic acid towards its trans-isomer occurs. Therefor the influence of the double bond configuration of the fatty acid component on the product composition was investigated. The resulting product mixtures were determined by HPLC and NMR-analysis. It will be shown that the amount of acyclic, Ene-like products will increase significantly, when the trans-configurated elaidic acid was used as starting material. In consideration of the stereochemistry of the formed acyclic products, it was found that from oleic acid mainly the syn-diastereomers were formed, whereas from elaidic acid also the anti-isomers were obtained.[2] This observation was proved by comparison with the results from Metzger and Biermann.[3] Based on the results a mechanism was proposed to explain the formation of the observed products.

In further experiments the Rh-catalysed additions of fumaric acid dimethylester and maleic acid dimethylester were performed to investigate the influence of the double bond configuration of the non-fatty acid component on the final products.

All in all the presentation will sum up the product spectrum and the opportunities of the Rh-catalysed functionalization of mono-unsaturated fatty acids.

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L21

Vegetable Oils as Raw Materials for Polymer Nanoparticles

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In the past few years, renewable monomers have been investigated in replacement to the current petroleum derived ones. In this context, vegetable oils show a high potential as alternative resource for the production of polymeric materials because of their renewability, world wide availability, relatively low prices, and value added application possibilities as they possess specific sites feasible of chemical modification, which in turn leads to a vast pool of obtainable monomers fit for different applications. Due to its versatility, miniemulsion technique can be applied to produce polymer nanoparticles from very different compounds by different polymerization mechanisms. Besides that, miniemulsion polymerization is a suitable technique for the polymerization of very hydrophobic monomers like most of those derived from vegetable oils as the nanodroplets in the size range between 50-500 nm are the locus of polymerization and no aqueous phase transfer between the monomer reservoir and the locus of polymerization is needed. Another advantage is that very hydrophobic monomers can act as an osmotic pressure agent (or co-stabilizer) preventing diffusional degradation of the small droplets resulting in quite stable dispersion of nanodroplets.

In this work, results concerning the synthesis of polymeric nanoparticles from vegetable oils by miniemulsion technique are presented. Its show that large amounts of vegetable oils can be employed in the synthesis of polymer nanocapsules by free radical polymerization being the particle morphology dependent on the degree of unsaturation of the fatty acid chain. Vegetable oils, like linseed oil and castor oil can also be used in natura to produce stable polymeric nanoparticles by acyclic triene metathesis reaction and urethane formation, respectively. The chemical modification of vegetable oils increases the application possibilities and results are shown for the synthesis of polymer nanoparticles obtained from monomers derived from castor oil like new polyols from castor oil glycerolysis reaction and undecenoic acid, derived from the pyrolysis reaction of castor oil. These monomers were polymerized by different miniemulsion polymerization reactions, like urethane reaction, metathesis and thiol-ene reactions. These examples show the versatility of miniemulsion technique and the possibility of obtaining new polymer nanoparticles with defined morphology and surface functionality that can be designed in a single step.

L22

Reactivity and Release of Plant Oils from Loaded Poly(styrene-co-maleimide) Nanoparticles

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In view of developing renewable protective barrier coatings for packaging papers, vegetable oils are ideal resources for replacing traditional extruded films because of their reactivity and hydrophobic properties. In order to better locate the vegetable oils at the coating surface and protect them against degradation, new nanotechnological approaches allow to encapsulate the vegetable oils into organic nanoparticles of poly(styrene-*co*-maleimide) or SMI and provide them in a compatible waterborne dispersion. The encapsulation process of different vegetable oils in presence of poly(styrene-*co*-maleic anhydride) precursors and ammonium hydroxide has been optimized for different oil types such as soy-, corn-, rapeseed-, castor-, sunflower, coconut, groundnut, palmkernel and palm-oil. The presence of oils favourably reduces viscosity during ammonolysis of the anhydride moieties and increase the maximum solid content of the dispersed imidized SMA to maximum 65 wt.-%, compared to a maximum of 35 wt.-% for pure imidized SMA. The maximum amount of encapsulated oil is 70 wt.-% relatively to the poly(styrene-*co*-maleic anhydride). After reaction, the morphology of SMI/oil nanoparticles depends on the oil type and reactivity, having homogeneous spherical shapes (20 to 60 nm) with sponge-like structures for poly-unsaturated oils, core-shell shapes for mono-unsaturated oils, or containing free oil at the surface for the most saturated oils. The interactions of oil and organic phase were studied by FTIR, indicating qualitative variances between different oils, the amount of SMI and remaining fraction of ammonolyzed SMA without leakage of oil upon diluting the dispersion and precipitation at low pH. A quantitative analysis with calculation of imide contents, amounts of reacted oil and chemical interactions was made by FT-Raman spectroscopy and ToFSIMS suggesting that binding between the oil and organic phase happens around the unsaturated oil moieties and ammonolyzed anhydride parts. The thermal properties of the nanocapsules with different incorporated oils were investigated by DSC and DMA, indicating a glass transition temperature between 160 to 170°C.

Upon thermal heating at temperatures of 120 to 250°C, progressive release of the oil from the nanocapsules is controlled by selecting the required heating temperature and time. The amount of released oil depends on the type of encapsulated oil and resulting morphology of the nanocapsules. It is evident that the release of oils from sponge-like nanoparticle structures happens more gradually compared to the release from core-shell nanoparticles, showing a diffusion-like dependency. Moreover, the stability of the organic nanoparticles against oil release depends on the reaction conditions, especially the degree of imidization that directly relates to the molar ratio of ammonium hydroxide to maleic anhydride. The thermal release of vegetable oils from nanoparticle coatings on paper has been followed by AFM and chemical Raman mapping of the coated surfaces, allowing to quantify the amount of vegetable oils present at the surface of the coating as a function of the thermal curing conditions. From chemical Raman mapping of progressive oil release, different trends of surface coverage with oil are observed depending on the type of vegetable oil.

L23

From Plant Oils to Plant Foils: Straightforward Functionalization and Crosslinking of Natural Plant Oils with Triazolinediones

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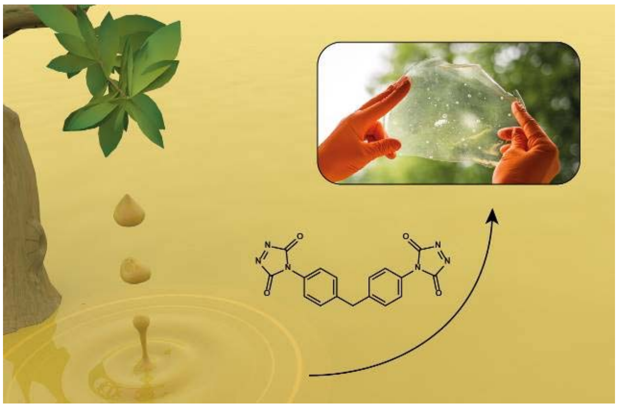
Non-sustainable chemical manufacturing processes have recently been an important subject of discussions not only for the chemical industry, but also among scientist.[1] Plant oils, for example, can be transformed into fatty alcohols or fatty amines on industrial scale, which have applications such as surfactants or additives for lubricants and coatings. Moreover, when the chemical structure of these products are evaluated, one easily realizes that they provide different amounts of double bonds that are available for chemical functionalization. However, while established chemical pathways exist to use plant oils as such, these typically require harsh reaction conditions or a transition metal catalyst.

Triazolinediones (TAD's), on the other hand, are known to be one of the strongest ene- and diene-ophiles in organic chemistry, allowing for a wide range of additive-free and atom efficient reactions at ambient conditions.[2] However, the low commercial availability of those compounds limited the use of TAD chemistry in a plant oil context to niche-type applications, such as pre-treatment method for fatty acid analysis *via* GC-MS or viscosity modification of soybean oil.

In this work, triazolinedione chemistry is used for the straightforward and additive-free crosslinking of numerous natural plant oils. In a first step, free fatty acids were functionalized with different TAD compounds. The reactivity of the different fatty acids in this model study could be rationalized by the structure thereof. In a next step, a large variety of polymer networks could be obtained by reacting crude plant oils with bifunctional TAD compounds. The resulting materials showed a wide range of thermal properties, which can be tuned and rationalised by the chemical structure of both the used plant oil and crosslinker.



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L24

Using Fatty Acid Derived Epoxides to Prepare New Polyesters and Polycarbonates

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The production of polymers from renewable resources continues to attract significant attention. One attractive and controlled polymerization route is the ring-opening copolymerization (ROCOP) of epoxides and carbon dioxide to produce polycarbonates.[1] Another option is to use controlled ROCOP of epoxides/anhydrides to produce polyesters.[2] Currently most of the epoxides used in these ROCOP reactions are derived from petrochemicals, however, there have been some interesting recent reports of using terpene derived epoxides.[3]

This presentation focusses on the use of cyclohexadiene, derived from fatty acids, to prepare new epoxides. The application of these cyclohexadiene epoxides for ROCOP, with various different catalyst systems, will be described as an interesting route to prepare partially and fully bio-based polycarbonates and polyesters.[4] The presentation will describe the polymerization process and the properties of the resulting polymers. Furthermore, the opportunities to combine ROCOP processes with lactone ring-opening polymerization, using a novel 'Switch' catalysis will be highlighted.[5]

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L25

Glycerol Valorisation Example in the Context of Oil Plants Biorefineries Design

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Introduction. Oil plants biorefineries design obviously involves the advanced use of fatty compounds, but also of the generated co-products. In such concepts, after oil extraction, cleavage of the triglycerides glycerol backbone is one of the first reactions that is usually envisioned before chemical upgrading of the as-obtained fatty acids/esters. Valorisation of glycerol has been already widely studied notably due to the oversupply of the latter from biodiesel production, obtained by triglycerides catalytic transesterification with methanol. Among the different upgrading reactions, dehydration to acrolein is of high interest due to the importance of acrolein as an intermediate for polymer industry (*via* acrylic acid) and for feed additive (synthon for *DL*-methionine). We developed catalytic systems for efficient glycerol dehydration to acrolein in a first step, before extending the concept to conversion of acrylonitrile, a compound especially used in the carbon fibres industry.

Glycerol conversion to acrolein. The catalysts used for glycerol dehydration to acrolein suffer from deactivation by coking. We studied the regeneration of spent catalysts based on Keggin-type silicotungstic acid (STA). A 20 wt.% STA sample supported on bare SBA-15, and a specifically developed 20 wt.% STA sample supported on SBA-15 containing 20 wt.% of ZrO_2 nanoparticles were prepared. Their performances were determined at 275 °C in a fixed bed reactor. STA/ZrO_2/SBA-15 showed significantly increased long-term performances (69 % *vs.* 24 % acrolein yield after 24 h), which was explained by a decrease in the acid strength of the STA due to a modified active phase/support electronic interaction, which further increased its thermal stability and prevented STA decomposition during one-shot regeneration of the catalyst by coke burning under air. Over the ZrO_2-free catalyst, the regeneration step led to a significant loss in acrolein yield (30 %) due to thermal destruction of STA. As this decomposition proceeds *via* the loss of constitutional water from the Keggin-structure, addition of water in the regeneration feed enabled recovering a slightly higher yield in acrolein (42 %), due to equilibrium displacement. Finally, cyclic regeneration of the catalyst was performed using iso-chronical cycles of 10 min for reaction and coke burning. STA/ZrO_2/SBA-15 exhibited poor performances (35 % yield in acrolein) due to the longer activation period needed for this catalyst. The ZrO_2-free catalyst exhibited stable performances (74 % acrolein yield) without STA destruction. We then patented an integrated process for simultaneous reaction and regeneration, based on a Two-Zone Fluidized Bed Reactor.

Glycerol conversion to acrylonitrile. For this reaction, we examined two different routes: *(1)* In Route 1, acrolein was selected as the intermediate reactant using a previously optimized WO_3/TiO_2 catalyst for the first step (glycerol dehydration to acrolein) and a Sb-Fe-O catalyst for the second step. The reaction conditions were optimized for the catalyst with an Sb/Fe molar ratio of 0.6. A maximum yield in acrylonitrile of 40 % (based on glycerol) could be achieved. *(2)* In Route 2, allyl alcohol was selected as the intermediate reactant. According to the litterature, allyl alcohol can be obtained from glycerol.[1,2] We then studied ammoxidation of allyl alcohol as a new alternative. Ammoxidation of allyl alcohol was demonstrated over optimized antimony-iron mixed oxide catalysts with Sb/Fe ratios of 0.6 and 1. Both catalysts showed a high acrylonitrile yield (*ca.* 84%) at the steady state.

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L26

High Intensified Selective Synthesis of Partial Diglycerol Esters of Undecylenic Acid in Direct Esterification Reaction Melted Gel Conditions

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Few papers describe the synthesis and characterization of diglycerol esters fatty acids. All of them use solvent or a mixture of solvents to resolve the problem of mass transfer in the system diglycerol/fatty acid (Kumar et al., 1989; Padmaja et al., 2012; Brito et al., 2014). Mass transfer problem is mainly due to the diglycerol viscosity and the biphasic system. Because of this problem, the reaction system diglycerol/fatty acid gave very low yield in fatty acid partial diglycerol esters.

We have studied the relation between the number of hydroxyl functions and the number of carboxylic acid functions to control the yield in partial diglycerol esters. Direct partial esterification of diglycerol by pure undecylenic acid in different molar ratios. It has been shown that the ratio OH/COOH must be more than 1 to obtain selectively in high yield in diglycerol partial esters of undecylenic acid. Selectivity in partial esters remained constant at 73% whatever the ratio OH/COOH, only the composition in diglycerol partial esters was modulated. The equilibrium of the reaction time was reached in 100 minutes.

To control the direct esterification of undecylenic acid with linear diglycerol without solvent, a physico-chemical study of the reaction system was carried out. Optical microscopic analysis have carried up on different reaction systems such as the diglycerol/undecylenic acid system, the diglycerol/DBSA /undecylenic acid system, the diglycerol/undecylenic acid/water system and the diglycerol/DBSA /undecylenic acid/water system. This allows to understand the physico-chemical phenomena throughout the direct esterification reaction. The system diglycerol/undecylenic acid gives a dispersion of one phase in the other. Adding DBSA, the system diglycerol/DBSA/undecylenic acid gives an emulsion with particles sizes are around 10 µm. Introducing water decrease more the drop size less than 10 µm. Temperature's rising induce a sharp change in behaviour and the pass from an emulsified heterogeneous two-phase system to a homogeneous melted gel, which improves the mass transfer in the complex reaction of direct esterification. The effect can be due to the surfactant properties of the DBSA which acts as catalyst and compatibilizing agent. Also, partial diglycerol esters produced during the evolutive esterification reaction played a role in the *in-situ* self-assembling of this system containing water (Nyame Mendendy Boussambe et al., 2014) and permit the improvement of the yield and selectivity in partial diglycerol esters.

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L27

One Step Biodiesel Manufacture of Acid Oils via MSA Catalysis

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Industrial biodiesel technology follows exclusively base catalysed transesterification of plant oils. Major drawback is that free fatty acids from cheap raw materials like acid oils have to be preesterified seperately prior to transesterification, formation of alkali salts of fatty acids is unavoidably and leads to emulsification at the phase separation step and finally only methanol is usable, higher alcohols like bioethanol do not react sufficiently.

The new patented MBT-Technology applies for the first time a sulfonic acid transesterification in one step, even for free fatty acids containing used cooking oils. Emulsification does not occur and phase separation is instantaneously due to acid environment. Bioethanol does react equally well as methanol even in the presence of up to 5% water.

The MBT-technology is currently beeing explored on industrial level in the tecosol biodiesel plant in Würzburg.

Details of the chemistry and technology is reported as well as information on improved efficiency over existing alkaline technology.

L28

Biodiesel Production via Catalytic Hydrodeoxygenation of Fatty acids derived from Chlorella algae and tall oil

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It has become increasingly obvious that sustainable energy is becoming more engaging owing to the depletion of the world reserves of fossil resources of energy and to the increase of the greenhouse gas emissions. Numerous feedstocks are being utilized to produce biofuels and biodiesel, however, it is vital that the production should not be competitive with food resources. Algae as a feedstock for biomass is not competitive with food supply, their growth rate is faster compared to terrestrial plants and they do not require arable lands to be cultivated. Tall oil fatty acid (TOFA) as another source of biomass is a byproduct of the pulp and paper industry which is obtained in the third largest quantity, containing mainly C18 acids with different degrees of instauration (1.5 wt% 18:0, 25.1 wt% 18:1, 53.4 wt% 18:2 and 18 wt% 18:3). The use of TOFA as a feedstock for the production of biodiesel is of a large interest since it does not compete with food production. The aim of this work is to convert fatty acids methyl esters (FAME) obtained from in situ transesterification of chlorella algae (Fuqing King, Drarmsa Spirulina Co, Ltd, China) and TOFA into biodiesel by adapting hydrodeoxygenation (HDO) reaction over a sulfur-free Ni/H-Y catalyst.

FAME was produced via in situ transesterification process. Due to a high content of oxygen in the later and TOFA, HDO step is required to upgrade the biodiesel feedstocks. HDO was performed in a semi-batch reactor at 300 °C in hydrogen at the total pressure of 30 bars. The products were analyzed by gas chromatography. 5 wt% Ni/H-Y 80 was synthetized by a wet-impregnation method and characterized by N2-physisorption, NH3-TPD, CO2-TPD, SEM, EDXA, TEM.

The results revealed that Ni/H-Y allows a complete conversion of FAME and TOFA in approximately 2 hours resulting in aliphatic hydrocarbons (C15, C16, C17, C18 in HDO of FAME and C17, C18 in HDO of TOFA). Ni catalyst appeared to have a two-fold higher selectivity to hydrodeoxygenation than to decarboxylation.

L29

Algae Oils as a Unique Source of Chemicals

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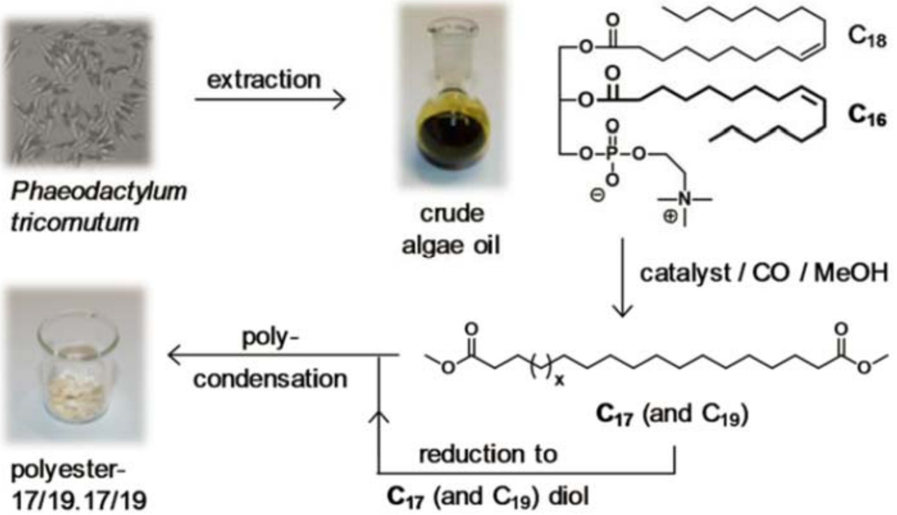
Microalgae are attractive as a potential feedstock as they contain unique compositions of, for example, fatty acids. Beneficially, they gain energy from photosynthesis like higher plants, but they can grow in brackish or salt-water independent from season and they do not compete with food production by consuming arable land. Microalgae can double within 24 hours and their lipid content can reach up to 70 wt.-% of their dry weight.[1] Current efforts to technically use microalgae oil focus on the generation of fuels with a molecular structure ideally identical to crude oil based products.[2] In this contribution we discuss a different approach for the utilization of algae by translating the unique molecular structures of algae oil fatty acids into higher value chemical intermediates and materials.



Scheme 1: Utilization of algae as exemplified by the generation of an aliphatic long-chain polyester.[3]

Anticipated issues are not only the efficiency of algae production, but also the algae mass workup and the compatibility of catalytic conversions with the particular multicomponent mixtures present. The latter two issues are discussed for the specific example of an isomerization-functionalization via carbonylation (Scheme 1). The compatibility with non-lipid components and with phosphocholines, and the behavior of multiple unsaturated fatty acids is of particular interest here. To this end, fatty acids with a specific chain length as well as multifunctional fatty acids could be enriched in *Phaeodactylum tricornutum* without compromising yields via genetic modification. Moreover, the fatty acid composition can be optimized only via the algaes' growth conditions also for the wildtype.[4] The resulting lipids are further investigated in different selective reactions.

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L30

Synthesis and Characterization of Innovative Materials Based on Triglycerides from Microalgae

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Nowadays, replacing petroleum-based raw materials with renewable resources is a major concern, both in terms of economic and environmental viewpoints.[1] An alternative developed these last decades is based on the oleochemistry, principally focused on vegetable oils. Due to their high functionality, the triglycerides and the corresponding fatty acids react easily to elaborate materials without any modifications e.g., thermosets resins, or they can be chemically modified like in the case of polyols for polyurethanes synthesis.[2] An interesting way to produce polyols is based on the epoxidation of the double bonds.[3] Then, the corresponding epoxide groups can be opened with alcohol or water in presence of catalysts, with acids, or by hydrogenation to give secondary alcohols.[4]

However often, the use of vegetable oils generates a competition with food production, with some additive issues such as the mobilization of arable land surfaces and the water consumption. In this context, microalgae offer currently an amazing opportunity.[5] Indeed, these single cell microscopic species are rich in triglycerides (around 20–50% of the dry weight) which can be useful for oleochemistry. Microalgae can be cultivated in salt or fresh water, on non-arable land and moreover, sunlight and CO2 can be used as energy source and raw material, respectively. In addition to produce a large amount of lipids, microalgae are also a unique resource for infrequent lipids and fatty acids differing from those available from plant organisms.[6] The algal oil profile depends of the algae species. Compared to vegetal resource, several microalgae species develop long fatty chains (typically up to C24) with a high unsaturation level.

The objective of this preliminary study was (i) to elaborate innovative and biobased macromolecular architectures and (ii) to demonstrate (as a proof of concept) that microalgae triglycerides derivatives can be used for the synthesis of polyurethane-modified isocyanurate (PUIR) foams. In this study rapeseed oil was used as a reference, for comparison purposes. The corresponding modified triglycerides were used to replace a conventional polyol i.e., a polyether polyol based on oxypropylated glycerol (OPG). The double bonds from triglycerides were chemically converted into epoxides and open with methanol to elaborate biobased polyols. From these latter, PUIR foams were synthesized and characterized. Algal oil was transformed in fully biobased epoxides and polyols as was the case for rapeseed oil. In terms of kinetics and morphology, all elaborated foams were close to the PUIR reference (only based on OPG). Results demonstrated that OPG can be replaced by algal triglycerides thus doubling the biobased content of foams.

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L31

Algae for the Production of Advanced Biofuels

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The governmental funded project AUFWIND investigates the large scale production of algae, the conversion into bio-kerosene and the impact over the whole value-chain. Focus is laid on the following aspects: Algae production (1), best method for cell-disruption and extraction (2), highest conversion- and refinement rates (3), identification and analysis of by-products (4), and a complete system analysis - including economic and ecological aspects. 1,500m² (0.37 acres) of algae Photobioreactors (PBRs) were built in Jülich representing three different concepts for algae cultivation.

Currently AUFWIND is the largest facility in Germany to produce algae-fuel. It is contributing as a first facility to analyze and evaluate the technical production of algae-fuel. It's the first step out of the research lab towards a commercial production of algae-fuel.

Abstracts

Part 2: Posters

P1

Jatropha curcas hydroxylated and urethanated polymeric material – Preparation and characterization

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Jatropha curcas oil was hydroxylated with formic acid in the presence of excess hydrogen peroxide to give polyhydroxylated oil with hydroxyl value of 170mgKOH/g. Through the hydroxyl group of the polyhydroxylated oil, urethane moieties were successfully appended on to the triacylglycerol to obtain the urethanated oil. The reactions were followed by both Infrared and nuclear magnetic resonance. Infrared analysis was performed on a Nicolet 380 Fourier-transform infrared (FTIR)

spectrophotometer using NaCl cells. 1H-nuclear magnetic resonance (NMR) and 13C-NMR were obtained on a Bruker Avance 400 NMR spectrophotometer. Physico-chemical characterisation of the samples for iodine value (IV), saponification value (SV) and hydroxyl value (HV) were carried out titrimetrically. Thermal transitions of the products were studied on a differential scanning calorimeter (DSC). The grafting process, spectroscopic characterisation, film and solvent properties of the resulted product are hereby discussed.

P2

Solid acid catalysts based on polyoxometalate for esterification of acetic acid with heptanol

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Synthesis of biodiesel via esterification reactions has attracted much interest recently. Esterification of heptanol with acetic acid has been investigated in detail. Commercial production of biodiesel employs homogeneous alkali catalysts. These catalysts, although highly active, are sensitive to water and suffer from poisoning by fatty acids that are present in the feedstock. Their separation also presents an environmental problem. Use of solid acid catalysis could potentially overcome these drawbacks. The aim of this work is to study homogeneous and heterogeneous catalysis by tungsten Heteropoly acids (HPAs), H3PW12O40 (HPW). Solid acid catalysts under study include HPW supported on different clays (Kaolinite, Bentonite and Montmorillonite).

Catalysts were characterized using different techniques including nitrogen adsorption using the BET method, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) and Transmission electron microscopy (TEM). It was observed that the Keggin structure remains intact even after calcined at 300^{o}C for three hours.

HPAs were found to be active catalysts for the esterification of acetic acid with heptanol in both homogeneous and heterogeneous liquid-phase systems. The performance of HPA catalysts is compared with that of the conventional acid catalysts such as Amberlyst-15 and zeolites. In heterogeneous systems, leaching of HPA from the catalysts into solution is thoroughly evaluated to estimate the contribution of homogeneous catalysis.

P3

Synthesis of Nickel Nanoparticles From N,N'-Dialkylimidazolium Chloronickel(II) Ionic Liquid and their application as catalysts for bio-diesel production

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A new N,N'-dialkylimidazolium salts of the type [RMIM]2[MCln], where [RMIM+] = 1-alkyl-3-methylimidazolium and M = Ni(II) have been prepared by refluxing the imidazolium with nickel chloride in an ethanolic solution. The resulting salt has been characterized by FT-IR, 1H, 13C and 2D COSY NMR, UV-Vis spectroscopy and elemental analysis. TGA and DSC measurements show that the salt melts around 40oC and decomposes in air in several steps eventually to form the corresponding metal, the onset of decomposition being observed around 220°C, clearly indicating an ionic liquid window from 40 – 220oC. This ionic liquid was then used as a precursor for the synthesis of nickel nanoparticles using NaBH4 as a chemical reductant and also by calcining the ionic liquid at 500oC for four hours. The nanoparticles have been characterized by powder X-Ray diffraction, Scanning electron microscopy and transmission electron microscopy. These results indicate that nickel nanoparticles of similar morphology are formed from both the chemical and thermal methods.

The activities of ionic liquid as well as nickel nanoparticles have been tested for esterification of heptanol with acetic acid and modelling biodiesel production. These materials were found to be active catalysts for the reaction under study. Performance of catalysts is compared with that of the conventional acid catalysts such as Amberlyst-15 and zeolites.

P4

Synthesis and Antimicrobial properties of Citronellol Based Surface Active Ionic Liquids (SAILs)

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The momentum gained by the use of eco-friendly synthetic motifs and enhanced interest in the synthesis of oleo-chemicals led us to look for alternate natural products. In the present research we have made an attempt to synthesize surface active ionic liquids (SAILs) by carrying out structural modifications to the terpineol (Citronellol). A variety of SAILs having renewable structural moieties like amino acids,1 fatty acids,2 and fatty alcohols3 etc have been reported in literature in the past. They have been found to possess better bio-physicochemical properties than traditional ionic liquids. Citronellol is a natural acyclic monoterpenoid that is used in perfumes, insect repellents and as a mite attractant. Pursuant to continue research on surface active molecules,2-8 we here synthesized a series of citronellol based surface active ionic liquids (SAILs) by catalytic regioselective ring opening reaction. The structure of these ionic liquids has been confirmed by NMR and mass spectroscopy. Surface properties of citronellol based SAILs have been examined by state of the art techniques such as tensiometry, conductometry, spectrofluometry and isothermal calorimetry. Surface properties and thermal stability of the investigated SAILs were found to be better than earlier reported conventional ILs. These citronellol based SAILs were also shown sensible biological activity towards gram negative and gram positive bacteria as judged by antimicrobial study. The investigated SAILs were found to be non-cytotoxic in a prescribed range for biological application as compared to conventional IL as judged by MTT assay towards C6 glioma cells. This work put prominence on the use of natural feedstock for the synthesis of surface active molecules having better properties than traditional amphiphile and considered to be environmentally safe.

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P5

Hydrophobe-free miniemulsion polymerization: towards high solid content of fatty acid-based poly(urethane-urea) latexes

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Due to the depletion of fossil carbon resources, biomass as a sustainable resource is gaining importance. Among them, vegetable oils are interesting molecules for polymer synthesis through the derivatization of their functional groups.[1,2] They are easily converted into diols or polyols that can be used for the synthesis of polyurethanes (PU).[3] This work focuses on aqueous dispersions of PU obtained through the miniemulsion polymerization process.

A ricinoleic acid derived diol is coupled with isophorone isocyanate in order to formulate polyurethane latexes with solids content up to 50wt%. These latexes could be obtained without the use of a hydrophobic agent. The study of their thermomechanical properties will be discussed.

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P6

Statistical quantification of vegetable oils based on PCA and PLS analysis of vibrational spectra

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In this work, the quality of palm-, soy-, sunflower-, corn-, castor-, and rapeseed oil was evaluated by means of spectroscopy methods. Different batches of vegetable oils were classified on the basis of FTIR and Raman spectroscopy in combination with statistical analysis of the spectra, in order to build a calibration model as a reference for quality evaluation. This method was successfully applied as an alternative for wet-chemical characterization of oil parameters. The percentages of mono- and polysaturated fatty acids are calculated from FTIR spectra and quantitatively observed from the absorption band in Raman spectra. The degree of saturation and iodine value can be directly measured by a linear correlation of Raman absorption bands, while it is not as clear in FTIR spectra. The relation was confirmed by checking with a hydrogenated oil. The evaluation of the entire spectra based on statistical procedures enables automatic classification of vegetable oils according to two statistical parameters. A calibration model was developed for classification of the oils by principal component analysis (PCA) and partial least squares (PLS) regression. The statistical analysis of Raman spectra favourably distinguishes according to the iodine value, while the FTIR spectra are most sensitive to hydroxyl moieties and progressive degradation of the oil, e.g., by oxidation processes. The supplementary analysis of oil samples that were aged for 12 months confirms the classification in regions with 90% confidence. There is very good agreement between the predicted values of the statistical model and actual values from Raman spectroscopy ($R^2 > 0.97$), while the statistical significance is lower for data from FTIR ($R^2 > 0.93$). A more robust and convincing classification of oils is obtained from two-parameter statistical models, which allows automatically classifying the oil types according to their quality. Therefore, both spectroscopic techniques should be used in combination with each other, as they contain different information that influences the statistical model. In future, this calibration model will be used to check vegetable oil qualities before using them in polymerization processes and/or following the variation in oil quality during reaction.

P7

Bio-based additives for PLA- A case study of oleo-product development

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Vegetable oils, which are annually renewable, are one of the most important sustainable raw materials for the chemical industry. Indeed, vegetable oils are already heavily used as raw materials in industry for surfactants, as cosmetic products, lubricants, in paint formulations, as flooring materials and for coating and resin applications. Vegetable oils or fatty acid derivatives are raw materials of great promise and offer new tailor-made structures with variable functionalities. Being easy to obtain and having ability to mimic petroleum-based products, there has been a plethora of examples in the synthesis of molecules, resins and polymers issued from plant oils(1). In order to bridge the gap between the development of innovative biomolecules and their potential industrial applications, an extensive investigation of the scaling-up is required. The scale-up and process validation includes industrial viability, economic and environmental evaluation.

In this context, ITERG (French technical research centre for fats and oils industries) has created the European Oil-Products Development Centre (CEDOP) in order to drive academic researches toward semi-industrial level and to help companies to innovate while limiting the risks during the scaling-up of an oleo-product.

CEDOP is a highly skilled department with expert know-how in environmentally friendly synthesis processes for oil-and-fat (vegetable and animal) processing. The CEDOP platform is part of a global strategy aimed at achieving synergy and developing pilot-scale biorefining based on the tools and technological means (from 1kg to 2000kg) available on our site in Pessac (France), which include: the CREOL, Centre for Research and Experimentation on Oilseed and Protein Crops (a division of CETIOM and SOFIPROTEOL) and the refining unit of the ITERG, which is equipped with all the necessary facilities for fat and oil chemical and physical refining unitary processes.

This technological platform dedicated to the valorization of plant oils biomass in industrial applications will be described in this presentation to illustrate the unique facilities that allow the development of a bio-product from the native plant oil refining to the pre-industrial production thanks to oleochemistry transformations.

To illustrate the challenges of product development, this presentation will highlight the scaling-up approach of bio-based additives originated from plant oils for the improvement of poly(lactic acid) (PLA) mechanical properties(2)(3).

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P8

Towards Resource Efficient Synthesis of novel Long-Chain-Polyesters from Renewable Feedstocks via Hydroformylation

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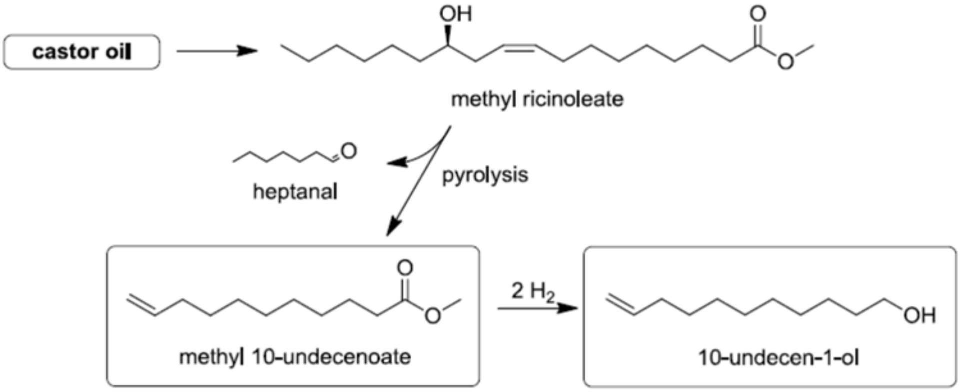
The conversion of substrates derived from renewable resources into polymer precursors has gained much attention during the last years.[1] In this regard, the transformation of fatty compounds yielding α,ω-bifunctional molecules seems particularly promising. Especially the implementation of homogeneous transition metal catalysts is one key for achieving high selectivities towards the desired linear molecules. Different approaches have been developed for the synthesis of e.g. diesters, amino esters, etc. Metathesis of internal and terminal fatty compounds with either itself or with short-chained unsaturated esters is one important means of producing linear long-chain diesters. Additionally, the Pd-catalyzed tandem sequence consisting of isomerization of internal double bonds to the end of the fatty chain with subsequent methoxycarbonylation furnishes saturated linear diesters with high selectivities.[2,3] This example demonstrates the synergy of tandem catalytic systems in the conversion of renewables.[4]

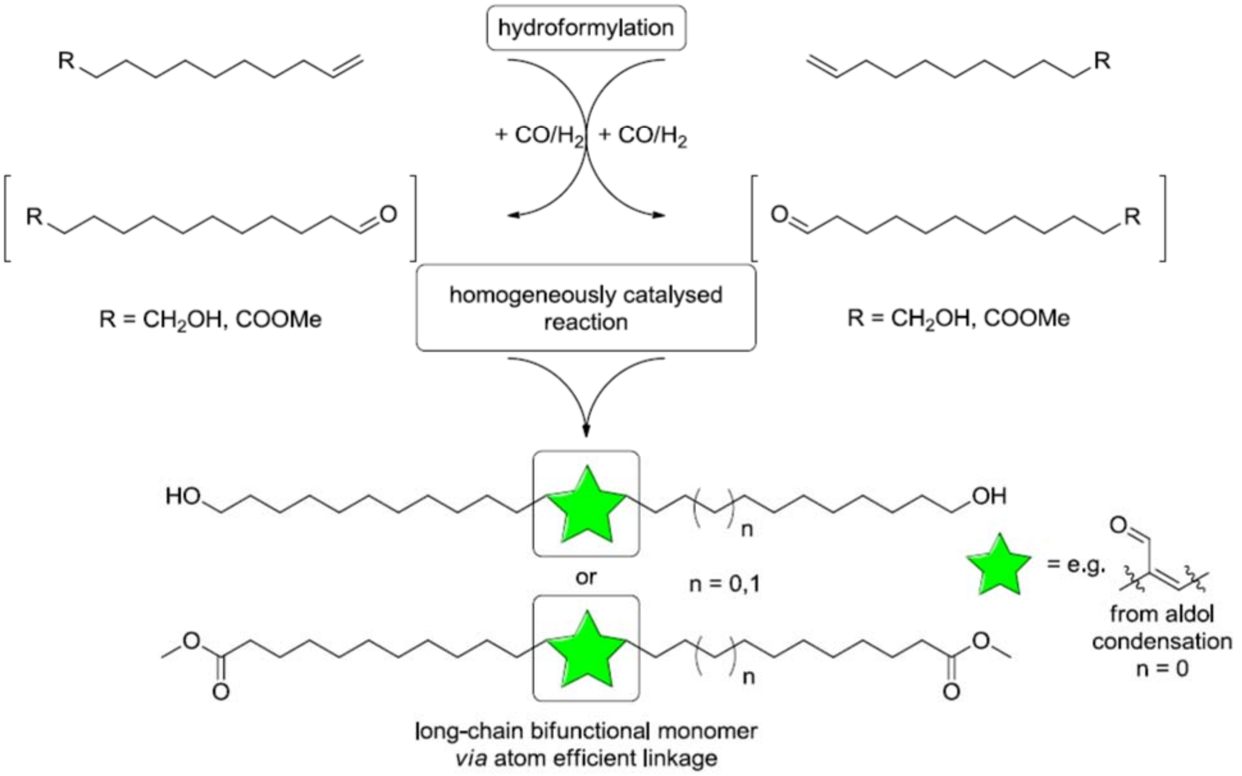
Hydroformylation as the key step for the tandem catalytic or one-pot preparation of potential polyester monomers has not yet gained much attention. Although this type of reaction features multiple advantages:

- fast - functional group tolerant
- highly regioselective - recyclable catalyst system
- aldehyde moiety undergoes many possible reactions

Herein we present different routes to selectively yield linear long-chain monomers from renewable compounds, in which *n*-selective hydroformylation represents the key step. Methyl 10-undecenoate and 10-undecen-1-ol are applied, which both are accessible from cracking methyl ricinoleate derived from castor oil (**Scheme 1**). The intermediate linear ω-functionalized aldehyde products react homogeneously catalyzed without intermittent work-up, to give rise to the desired long-chain products *via* atom efficient linkages (**Scheme 2**).



Scheme 1: Pathway for the production of terminal unsaturated substrates from renewable castor oil



Scheme 2: Hydroformylation as the key step for the synthesis of intermediate aldehydes, which undergo homogeneously catalyzed linkage, to yield potential polyester monomers.

Different strategies for the linkage of the intermediate aldehydes are presented, which differ in the required catalytic system, the kind of operational procedure and the resulting functional group in the linkage. (E.g. aldol condensation furnishes an α,β-unsaturated formyl-group as linkage).

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P9

Synthesis and Characterization of New Polymers from Adenopus Breviflorus Benth Oil, Styrene and Divinyl Benzene by Cationic Polymerization

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A variety of new polymers ranging from soft to hard plastics were prepared by cationic polymerization of Adenopus breviflorus oil with styrene and divinyl benzene initiated by modified boron trifluoride etherate. The fully cured thermosets were found to contain between 78 – 92% crosslinked materials possessing crosslink densities of between 2.39×10^3 to 2.09×10^4 mol/m^3 and glass transition temperatures of 12 – 80°C. The tensile moduli of the materials ranged from 1.47 to 404 MPa, the ultimate tensile stress varied from 0.18 to 7.78 MPa and the elongation at break varied between 2 and 34%. Depending on composition, some of the materials possessed good damping and shape memory properties. Overall the newly prepared materials from Adenopus breviflorus oil hold a lot of promise as new polymeric materials.

P10

Synthesis of macrocyclic lactones with musk odor by ring closing metathesis using oleic and 9-decenoic acids as building blocks

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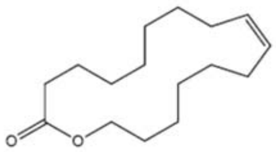
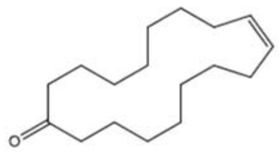
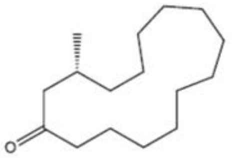
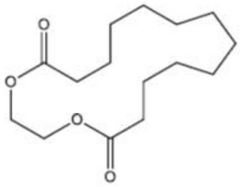
Musk is a class of aromatic substances commonly used as base notes in perfumery[1]. They include glandular secretions from animals or plants secretions with similar odors. The musk was recognised in ancient times and has became one of the most attractive and expensive substance.


Ambrettolide

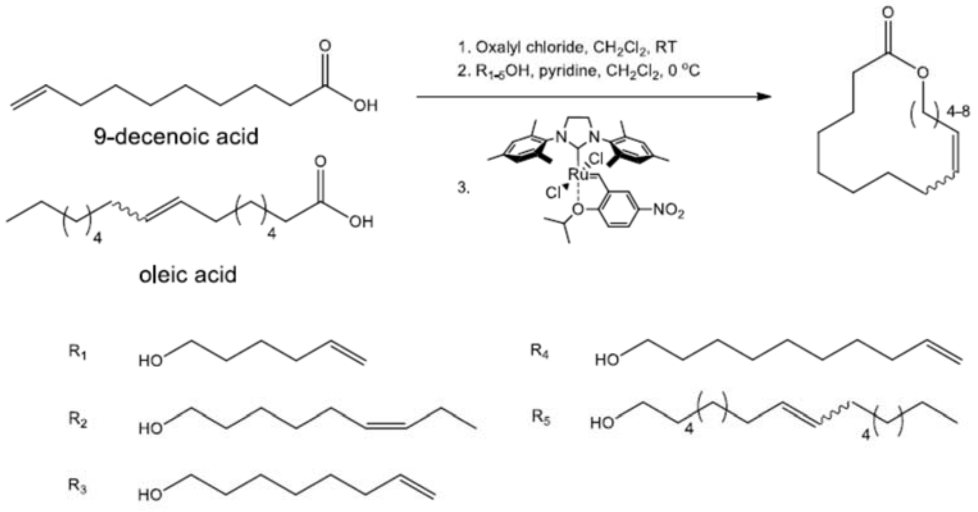

Civetone


Muscone


Ethylene Brassylate

Natural macrocyclic musks, especially *Muscone* and *Civetone* are attractive ingredients in many perfumes and fragrances. The natural sources are limited and products from them receive very high prices. Natural musk is mainly derived from animals (*Viverra Civeta* and *Moschus Moschiferus*), whose death is sometimes prerequisite for the harvesting of musk scent. There are ways to obtain similar scents from plants like *Ambrette Seed* and *Angelica Root*.

The macrocyclic lactones such as Ambrettolide are valuable synthetic musks. The above compounds can be easily synthetized from the biodegradable mass which makes them very attractive for industrial companies to produce.



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P11

Chemical Valorization of Cashew Nut Shell Liquid by Isomerizing Metathesis

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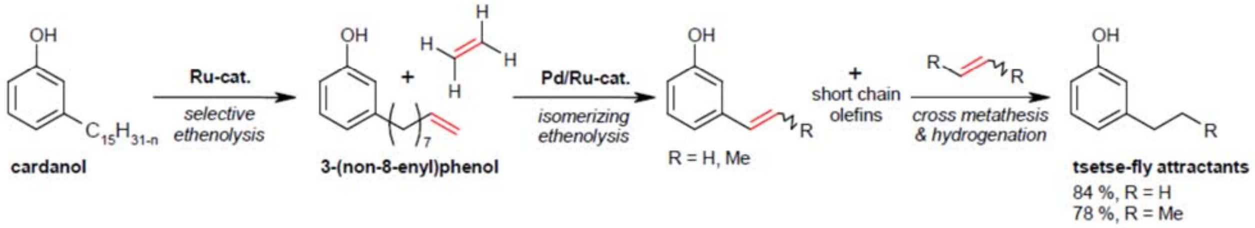
Isomerizing olefin metathesis reactions have recently emerged as valuable tools for the valorization of renewables.[1] In the presence of a bimetallic palladium/ruthenium catalyst system, fatty acids were converted into industrially useful multi-component blends, consisting of functionalized olefins with tuneable chain length distributions.[2] This synthetic approach was also applied on the selective transformation of naturally occurring allylarenes (e.g. eugenol, estragol or safrol) into the corresponding styrenes.[3]

Cashew nut shell liquid (CNSL) is obtained as a waste by-product of cashew nut processing (450.000 t/a).[4] Therefore, it is an excellent representative of an inedible renewable resource for which no competition occurs between land use for food or raw material production. After distillation at above 140 °C the liquid consists mainly of cardanol, a mixture of *m*-alkenylphenols. Starting from this technical CNSL, we have developed a concise synthesis of the tsetse-fly attractants 3-ethylphenol and 3-propylphenol with the isomerizing metathesis reaction being the key-step: In order to obtain a homogeneous starting material, the cardanol mixture was first converted into 3-(non-8-enyl)phenol *via* selective ethenolysis and distillation. The olefinic side chain was then shortened by isomerizing ethenolysis. This process was efficiently mediated by the combination of the isomerization catalyst $[Pd(\mu\text{-}Br)^{t}Bu_3P]_2$ and a second-generation Hoveyda-Grubbs metathesis catalyst. An additional non-isomerizing butenolysis or ethenolysis followed by hydrogenation furnished the target molecules in one pot.[5]



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P12

Synthesis of plant oil derived polyethers by the $GaBr_3$-catalyzed reduction of carboxylic acid esters

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Recently, a $GaBr_3$/TMDS (1,1,3,3-tetramethyldisiloxane) system was introduced as an efficient method for the reduction of esters of long-chain fatty acids and polyols, such as triglycerides to the corresponding ethers.[1] While the reducing agent TMDS is used in stochiometric amounts, GaBr3 can be used in catalytic amounts of 0.5-1 mol%. The reaction is carried out at mild conditions without solvent giving full conversion of the substrate. Since the reducing agent TMDS is a byproduct of the silicon industry[2] and gallium has a widespread and future availability,[3] this method gains a highly sustainable character.

Here, the GaBr3/TMDS system is applied to monomeric and polymeric plant oil derived carboxylic acid esters in order to have a partial or full reduction and obtain high-performance polymers.

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P13

Triazolinediones as a rapid functionalization and crosslinking tool of plant oil-based step-growth polymers

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Linear, branched and cross-linked plant oil derived polymers have recently attracted great interest among polymer chemists, as evidenced by the increasing number of publications and reviews.[1] Moreover, since fatty acids consist of long linear aliphatic chains, those polymers are promising candidates to substitute some platform plastics.[2] However, the chemical pathways applied to synthesize such plastics rely on the only available functionalities, *i.e.* carboxylic acids and/or double bonds, which results in limited post-functionalization opportunities. Nevertheless, we recently demonstrated that triazolinediones (TAD's) are highly reactive towards both dienes and isolated alkenes,[3] and utilized this new click chemistry platform to functionalize fatty acids and to crosslink a wide range of crude plant oils in an atom efficient and additive-free manner at ambient conditions.[4] Unfortunately, the complex nature of those crude oils limited the unambiguous rationalization of the reaction kinetics and the achievable material properties.

In this work, the given limitations are avoided by using plant oil derived products, rather than the crude oils themselves. Therefore, the first stage consisted of synthesising linear polymers following via various recently published step-growth procedures.[5][6] These macromolecules contain a quantifiable amount of double bonds, which were used in a first step for functionalization with TAD molecules. In a second step, a bis-TAD crosslinker was added to the functional TAD compounds, resulting in functionalized bio-based networks. Moreover, we have shown that the functionalized polymers and networks can be saturated via classical hydrogenation processes without loss of the introduced functionalities.

Within this contribution, we would like to discuss these results, demonstrating that TAD-chemistry is a very powerful tool for the efficient functionalization and crosslinking of plant oils derived renewable polymers.

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P14

Process Development for the Hydroformylation of Methyl 10-Undecenoate Using Water/Butanol-Solvent Systems – From Laboratory to Miniplant Scale

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The implementation of renewable feedstocks in industrial chemistry is of great interest due to the shortage of fossil fuels. Oleocompounds like fatty acids or their methyl esters are promising raw materials for synthesis of chemicals based on renewable resources. The hydroformylation is the most important industrial-scale application of homogenous catalysis. In this reaction more than 10 million tons of olefins are converted with synthesis gas to aldehydes each year. Hydroformylation of oleocompounds enables access to compounds with potential use for bio-based polymers. In hydroformylation recovery of the valuable rhodium catalyst is one of the main challenges. An important process variant for the conversion of C3-C5 olefins to aldehydes is the Ruhrchemie/Rhône-Poulenc process, wherein an efficient catalyst recycling can be realized with the principle of an aqueous two phasic reaction system. While this technique is well suited for short chain olefins, higher olefins and oleocompunds suffer from mass transfer issues in this reaction system. This is why the design of new reaction systems, which allow high reaction rates, selectivities and easy catalyst separation, is necessary for the hydroformylation of oleocompounds.

In this context we developed in the common research project “InPrompt” (SFB/Transregio 63) a new reaction concept for the hydroformylation of methyl 10-undecenoate in laboratory scale batch experiments. A reaction system consisting of an aqueous phase containing the water soluble rhodium catalyst and 1 butanol containing the substrate allows high reaction rates and good catalyst recovery in several recycling experiments. Furthermore, this knowledge was conducted to develop a continuous process in miniplant scale so that circulating aqueous catalyst phase was achieved and the product was extracted by 1-butanol. A continuously operated and stable hydroformylation process could be realized for 20 h with a yield of 70% of the linear aldehyde without any intervening in the process.

P15

Long-chain unsymmetrical α,ω-difunctional compounds from fatty acids with complete feedstock molecule utilization

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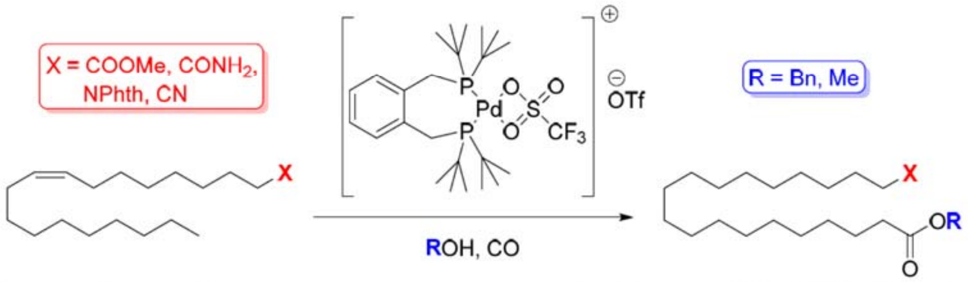
Isomerizing alkoxycarbonylation has been proven to be to be a powerful tool for the synthesis of a range of mono- and dicarboxylic acid esters of different chain lengths.[1] Application of this reaction to unsaturated fatty acids with their long-chain crystallizable methylene sequences provides access to long-chain *α,ω*-dicarboxylic acid esters, allowing for the preparation of new materials inaccessible through non-catalytic multistep approaches.[2] However, currently from the catalytically obtained *α,ω*-dicarboxylic acid esters still up to four successive steps may be required for the preparation of long-chain polyamides, for example.[3]

An approach to unsymmetrically *α,ω*-difunctionalized long-chain compounds has recently been reported by Cole-Hamilton with aminocarbonylation of terminally unsaturated esters.[4] This offers potential for a more straightforward route to polyamide precursors, though it is restricted to substrates with a terminal double bond since selectivity towards the linear, terminally disubstituted regioisomer is low when starting from internal olefins.

In this contribution we present the direct selective synthesis of valuable long-chain unsymmetrically *α,ω*-disubstituted compounds, starting from commercially available fatty acid derivatives. Isomerizing alkoxycarbonylation is applied to various substrate functionalities in a fashion that both groups - the alcohol functionality introduced as ester as well as the existing, chemically orthogonal functionality of the starting material stay intact and an unsymmetrically *α,ω*-disubstituted compound is formed (**Scheme 1**).



Scheme 1. The isomerizing alkoxycarbonylation to unsymmetrically *α,ω*-disubstituted compounds based on fatty acid derivatives as starting material.

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P16

Synthesis of Polyethers from Fatty Alcohols by Allyl-Activation

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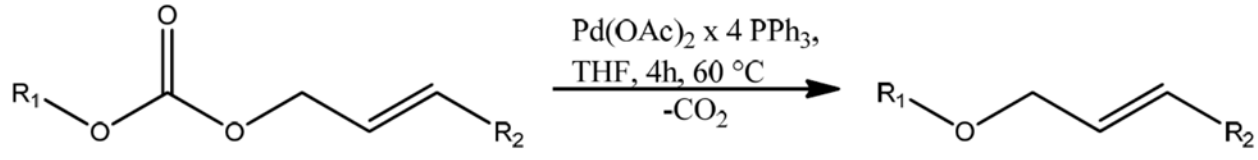
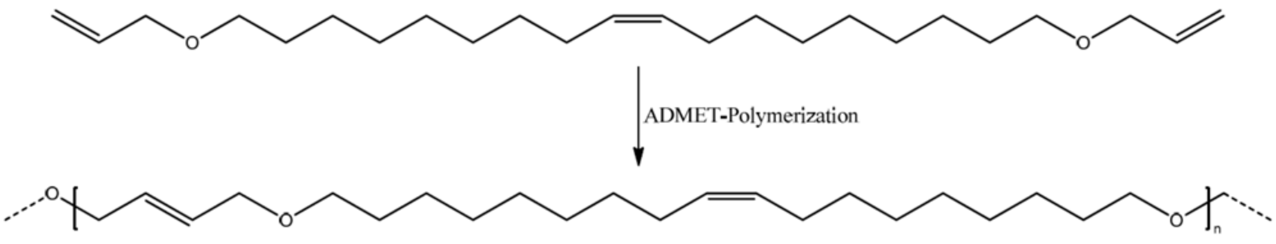
Ether-monomers for thermoplastic elastomers would be desirable because of their low polarity. The efficient synthesis of ethers without using hazardous chemicals like bromine is a challenging field. In this work, we describe a sustainable method of synthesis for long chained ethers by using fatty alcohols, from renewable resources. The fatty alcohols are coupled with alkyl chloroformates to give the corresponding alkyl carbonates, which can be easily converted to the ethers by Pd-catalysed decarboxylation (Scheme 1). A double bond in an allyl-position is required, which can be at the terminal position like in allyl alkyl carbonates or inside a long alkyl chain.



R_1 = unsaturated alkyl chain
R_2 = H, saturated or unsaturated alkyl chain

Scheme 1: Pd-catalysed ether synthesis from various alkylcarbonates

A variety of long chained unsaturated alkyl ethers can be synthesized by this method. ADMET-Polymerization of these ether monomers yielded unsaturated ether-polymers with a defined chain length between the oxygen-atoms and therefore with a defined polarity. Scheme 2 shows the metathesis reaction of the diallyloctadec-9-enyldiether to an oligomer with alternate chain length of four or eighteen carbon-atoms.



Scheme 2: Metathesis of a diallyldiether

P17

Electrochemistry for the conversion of free fatty acids and triglycerides in organic and aqueous media

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In this study we propose an electrochemical route for the transformation of fats and oils in into olefins and ethers by electrochemical decarboxylation. The electrochemical conversion was studied on the example of stearic acid (C18, saturated – octadecanoic acid) and oleic acid (C18, mono-unsaturated – (9Z)-Octadec-9-enoic acid) and on the triglyceride rapeseed oil. Thereby the electrochemical conversion of the free fatty acids is demonstrated in methanol and ethanol, whereas the decarboxylation of the triglyceride is shown in aqueous emulsions using sonoelectrochemistry. The proposed method may be applicable for the conversion of a large variety of fatty acids and triglycerides, present in different natural resource ranging from vegetable oils via animal fats to algae. The products of the conversion could potentially be used as biofuels or as precursors for chemical processes.

P18

Linear Long-Chain Aliphatic Polyamides – Fatty Acid Based Polycondensates and Novel Approaches via ADMET Copolymerization

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Polyamides (or nylons) are one of most important classes of today's industrially produced polymers.[1] They are generally characterized by high melting points and mechanical strength as a result of interchain hydrogen bonding. Thus, polyamide-6,6 melts between 265 °C and 270 °C and displays a Young's modulus of ca. 3000 MPa.[1,2] The polar nature of amide groups is also beneficial for resistance to apolar solvents, like hydrocarbon fuels. On the other hand, it results in a substantial water uptake such that swelling varies with the humidity of the environment. Long-chain, less hydrophilic polyamides therefore can possess an advantageously higher dimensional stability. The utilization of fatty acids can provide long-chain aliphatic chemical building blocks, which are not accessible otherwise.[3]

Via isomerizing alkoxycarbonylation of high oleic sunflower oil,[4] followed by ester hydrolysis, 1,19-nonadecanedioic acid was obtained and used for A2+B2 polycondensation with shorter-chain diamines to yield polyamides PA-6,19, PA-7,19, PA-8,19 and PA-12,19 with molecular weights Mn around 2x10^4 g mol^-1. As anticipated, melting points decrease with decreased contents of amide groups in the aliphatic chains, from 190 °C (for PA-6,19) to 171 °C (for PA-12,19). A comparable trend was found regarding the mechanical properties, the Young's modulus decreases from ca. 1500 MPa to 1000 MPa.

To fill the gap between long-chain aliphatic polyamides (from A2+B2 polycondensation approaches) and linear polyethylenes, ADMET copolymerizations of an amide and a non-functionalized alpha,omega-diene were applied,[5] since the availability of even longer-chained diacid monomers is limited. After post-polymerization hydrogenation of the remaining carbon-carbon double bonds, further 'diluted' polyamides were obtained. A distinct melting point minimum (predicted qualitatively from theoretical considerations since the 1950s) was observed around 110 °C for polyamides containing ca. 35 amide groups per 1000 methylene units, going in hand with a change of the crystalline structure for polyamides (dominated by hydrogen bonding) to polyethylene (regulated by van-der-Waals interactions).

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P19

Liquid solid phase behavior of ternary fatty acid systems of palmitic, stearic, oleic and linoleic acid

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Enrichment of natural unsaturated fractions by melt crystallization processes has already been proved to be effective in prior investigations [1]–[3]. Palmitic, stearic, oleic, linoleic and linolenic acid are the five main fatty acids present in most of these plant based natural oils. There is quite a bit of information about the liquid solid phase behavior of binary mixtures such as palmitic-oleic, stearic-oleic and palmitic-stearic acid mixtures in literature [4]–[6]. Recent investigations have shown phase diagrams of real natural oil based fatty acid systems containing up to 19% saturated content (11% stearic acid and 8% palmitic acid) [7]. Yet, there is hardly any information regarding ternary systems as those of palmitic-stearic-oleic and palmitic-stearic-linoleic acids.

In this work, synthetic mixtures have been used in order to obtain a complete overview of the liquid solid phase diagrams of these ternary mixtures. To imitate naturally occurring mixtures, a mixture with 1:1 ratio of palmitic stearic acid was prepared. Varying amounts of either oleic or linoleic acids were added to this mixture in order to obtain the entire range required for the phase diagrams. These mixtures were then subjected to a specific profile with a wide temperature range in a Differential Scanning Calorimeter (DSC) so as to record every phase transition.

This study successfully concludes that these complex mixtures could be treated as binary mixtures of their saturated and unsaturated contents. This is because there were essentially two main peaks noted in the DSC thermograms. It is to be noted that there was a third peak, assumed to represent the solid transition, in mixtures containing oleic acid. This has already been shown in detail and discussed in prior investigations [6], [7].

Another major discovery was that the solidus line depends on the type of the unsaturated content, that is, the degree of unsaturation, in the mixture.

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P20

A modified Wacker Oxidation process: efficient oxyfunctionalization of renewable raw materials

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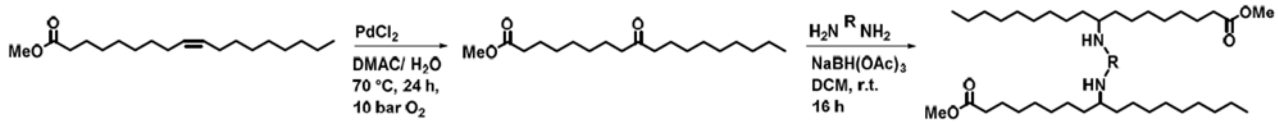
The use of fats and oils as renewable feedstock in the field of organic synthesis and especially for polymer chemistry has become ever more important during the last decades, since these materials provide many different application possibilities and a sustainable as well as an economic alternative to depleting fossil resources.[1] Moreover, the development of processes using catalytic amounts of transitions metals and stoichiometric environmentally friendly oxidants, such as molecular oxygen, is one major goal in organic chemistry. The Wacker Oxidation process has become one of the most important industrial processes, which demonstrates efficiently the manufacturing of acetaldehyde from ethylene. For this reason, the process represents a promising catalytic procedure for the oxyfunctionalization of olefins.

Within this contribution, a modified Wacker Oxidation process was applied for ketone functionalization of tryglycerides (e.g. olive oil) and thereof derived unsaturated fatty acid methyl esters (e.g. methyl oleate, methyl erucate) using a high pressure reactor system.[2,3] For this purpose, catalytic amounts of palladium chloride were used in the presence of a dimethylacetamide/ water mixture and either molecular oxygen or synthetic air as re-oxidant.

Furthermore, the catalytic system provides some advantages regarding the sustainability, if compared to the original Wacker Oxidation process, since the utilization of a co-catalyst (i.e. copper) can be avoided and dimethylacetamide can retain the palladium catalyst in solution, which allows a straightforward recycling. Moreover, the obtained ketone FAMEs represent an interesting class of starting materials for further chemical modification, e.g. dimerization by reductive amination (Scheme 1).



Scheme 1: Wacker Oxidation of methyl oleate and subsequent dimerization of its ketone derivative *via* reductive amination.

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P21

Epoxidized vegetable oils as glycerol based alkyd resins modifiers

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1. Introduction – Alkyd resins are an important group of synthetic polymers, widely used in coatings and paints technologies. The most commonly used raw materials for production of drying alkyd resins are soybean oil, linseed oil, pentaerythritol and phthalic anhydride. One of the key challenges of modern chemistry is development of new varieties of polymers using renewable raw materials. Potentially a promising great renewable resource for the synthesis of alkyd resins could be glycerol – a cheap and easily available raw material. Unfortunately, alkyd resins obtained from polyols having three or less hydroxyl groups like glycerol give coatings with poor crosslinking properties. As solution of this problem, we propose to use epoxidized vegetable oil as modifier in the resin synthesis. Epoxidized oils, due to the high reactivity of the epoxide rings can form additional branches in the structure of the resin and the obtained coatings are characterized by better properties.
This work describes synthesis of alkyd resins, which are based on new renewable raw materials like camelina oil, glycerol as polyol and with addition epoxidized camelina oil.

2. Experimental – Epoxidation of camelina oil was carried out using peracid forming in-situ, by reacting formic acid with hydrogen peroxide at the temperature of 60°C. Alkyd resins synthesis was performed in two stages. In the first stage the purified oil was subjected to alcoholysis reaction with polyol, epoxidized camelina oil and lithium hydroxide as catalyst. In the second stage, carried out at 220°C, the intermediate product was subjected to esterification with phthalic and maleic anhydride.

3. Results and Discussion – Table 1 presents properties of the obtained epoxidized camelina oil and table 2 presents physicochemical properties of the synthesized resins.

Table 1 Physicochemical properties of epoxidized camelina oil, linseed oil and rape oil.

Properties	Camelina oil
Acid value (mg KOH/g)	1.13
Oxirane value (mol/100g)	0.45
Hydroxyl number (mg KOH/g)	22.6
Iodine value (g I_2/100 g)	8.8

Epoxidized camelina oil was characterized by a low iodine value - 8.8 gJ_2 / 100g compared to initial 144 gJ_2 / 100g and a relatively high oxirane value 0.45 mol / 100g. This means that the conversion of unsaturated bonds contained in camelina oil is 94 %.

Table 2 Physicochemical properties of alkyd resins.

Properties	Without additive	Camelina oil	
		10 wt%	20 wt%
Acid value (mgKOH/g)	1.3	8.8	6.3
Flow time (s)[I]	27	58.5	87
Drying time (h)[II]	27	10	8.5

[I] Determined as Ford cup efflux time (Ø 4mm), 55% naphta solution, temperature 22°C.
[II] The drying time of resins (55% naphta solution) was studied with drying agents.

As shown in table 2 the films based on alkyd resins that were synthesized from camelina oil, glycerol and with addition of epoxidized camelina oil dried faster and were characterized by higher viscosity than the films of alkyd resins which did not contain any modifier.

4. Conclusions - The epoxidized camelina oil had a significant effect on the properties of the alkyd resins. A real possibility was determined for the synthesis of glycerol based alkyd resins with properties better than those manufactured without any additive.

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P22

Efficient and Sustainable Synthesis of High Vicosity Fatty Acid Esters

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Esters of fatty acids of vegetable origin and polyols are one of the most important and biocomponents of oils and greases. Thanks to these features this ester is one of the most valuable biocomponents for the manufacture of ISO Class 68 hydraulic fluids and Class VG-68 engine oils. Equally valuable properties have also fatty acid esters of trimethylolpropane (TMP), TMP dimer (DiTMP) and pentaerythritol (PE). The common method of synthesis of esters of this type is direct esterification of the fatty acid and polyols conducted in the presence of acid catalysts, mainly homogeneous sulfonic acids (ptsa), heterogeneous and selected organic phosphates. Unfortunately, the crude product was characterized with a very dark color and requires purification including the cumbersome film distillation under high vacuum. The developed method of the synthesis of fatty acid esters and polyols is devoid of these disadvantages. This method is very convenient and highly effective. Conversion of fatty acid is ca. 99.5 with high selectivity to full esterified product. As a catalyst were used the readily available organotin esterification catalyst, which does not require the removal and the crude product does not require additional purifying distillation.

P23

Syntheses and Characterization of Crosslinked High-Oleic Sunflower Oil for Biolubricant Applications

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Introduction:
Vegetable oils had been used as lubricants over a long time. During industrialization the specifications of lubricants became more complex and diverse. Therefore, mainly due to their lower production costs petroleum products replaced vegetable oil products. However, strategies are often focused on renewable feedstock because of biodegradability, environmental sustainability and recyclability of biolubricants. Nowadays biolubricants have become more relevant due to their sometimes better lubricating properties.1,2
One possible procedure to produce biolubricants is the crosslinking reaction of unsaturated fatty acids or fatty acid esters with peroxides as initiators.3,4 Here, the use of highly monounsaturated fatty acids or fatty acid esters is recommended, high-oleic sunflower oil with more than 60 % oleic acid is mentioned in particular.
This study focusses on crosslinking reaction of high-oleic sunflower oil to receive products with dynamic viscosity in the range of 1000 mPas and low peroxide content. In order to transfer the reaction into a continuous loop reactor the reaction mechanism and the chemical structure of crosslinked high-oleic sunflower oil is investigated in dependence of the reaction conditions.

Materials and methods:
High-oleic sunflower oil with a content of 75 – 90 % oleic acid was crosslinked with peroxide initiators e.g. 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane. Experiments were carried out under nitrogen in a 1 l stirred tank reactor as a solvent free process with up to 10 wt-% initiator. Rheological studies were used to measure the dynamic viscosity. A rotational viscosimeter and a cone and plate system at 40 °C were utilized.
For identifying the chemical structure of crosslinked high-oleic sunflower oil infrared spectroscopy in attenuated total reflection (ATR-IR) and nuclear magnetic resonance spectroscopy (NMR) were used to provide detailed information about the chemical structure and environment of molecules.

Results and Discussion:
Results of NMR research technique will be presented. 1-dimensional proton and carbon-13 NMR spectroscopy was used as well as 2-dimensional technique (HSQC, HMBC) to identify the reactive centers. It was expected that crosslinking reaction takes place at the double bond of oleic acid. With passing reaction time merely little changes in chemical shift and integral of the double bond peak were found. A small intensity peak with a chemical shift of 2.77 ppm was identified as the methylene group in the middle of the two double bonds of linoleic acid which is part of high oleic sunflower oil with a content of 2 – 17 %. In the course of reaction the integral of this peak decreases which likely means that crosslinking takes place at methylene groups next to the double bond and not at the double bond itself.
ATR-IR spectroscopy was used to identify functional groups because of their characteristic bands. Double bonds can be detected as well as peroxides by this technique. While reaction is passing the double bond bands remain unchanged which indicates too that

crosslinking doesn’t take place at the double bond. The amount of the initiator 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane was quantified while crosslinking reaction with ATR-IR spectra and the decrease of initiator concentration was followed with this method. As expected the initiator reacts in first-order.

The reaction conditions were varied over a wide rage. Results of rheological measurements of the crosslinked high-oleic sunflower oil will be presented. The crosslinked high-oleic sunflower oils behave like Newtonian Fluids. The changes in dynamic viscosity in the course of the reaction will be shown. Variation in initiator starting concentrations show that low initiator concentrations lead to low dynamic viscosities. The increase of dynamic viscosity with passing reaction time correlates with the decrease of initiator concentration. The higher the reaction temperature the faster dynamic viscosity increases and initiator concentration decreases due to the lower half-value time of the initiator. The supposedly high initiator content is needed to receive dynamic viscosities over 1000 mPas.

The crosslinking reaction was transferred into a continuous loop reactor with optimized recipe. The backmixing was varied by different residence times. Crosslinked products and their chemical structures from stirred tank and continuous loop reactor were compared by the analytical methods described above.

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P24

Amphiphilic ionic liquids with dual functions – surfactant and catalyst

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Most of ionic liquids is characterized by relatively strong ionic asymmetry and can by described as amphiphilic compounds with specific hydrophilic and lipophilic centers. Studies on the surfactant properties of ionic liquids in aqueous solutions have been developed intensively for many years, and revealed that by changing the alkyl chain length, the head group type, as well as the counterions nature, the aggregation behavior of the ionic liquids can be modified. Ionic liquids, especially imidazolium ones, cannot be considered only as common cationic surfactants. One of the important properties of ammonium salts is their use as interfacial phase transfer catalysis. Selected ionic liquids also can be applied as PTC catalysts. In contrast to the "classical" PTC catalysts, ionic liquids may be subjected to targeted modification (TSIL). TSIL may play a dual role: catalyst (co-catalyst) and the surfactant, which has a significant impact on the efficiency of the catalyst. In our study, the 1-alkyl-3-methylimidazolium hydrogen sulfate homologous series (C6-C12) ionic liquids were used both as a phase transfer (co-)catalyst and surface active agent in the oxirane ring opening reaction. Oxirane ring opening of fatty acid derivatives (eg. FAME) in the presence of water as oppening reactant is good model reaction for evaluation of dual functionality of amphiphilic IL.

P25

Modified starch and β-cyclodextrin obtained from Ugi five-component reactions with carbon dioxide

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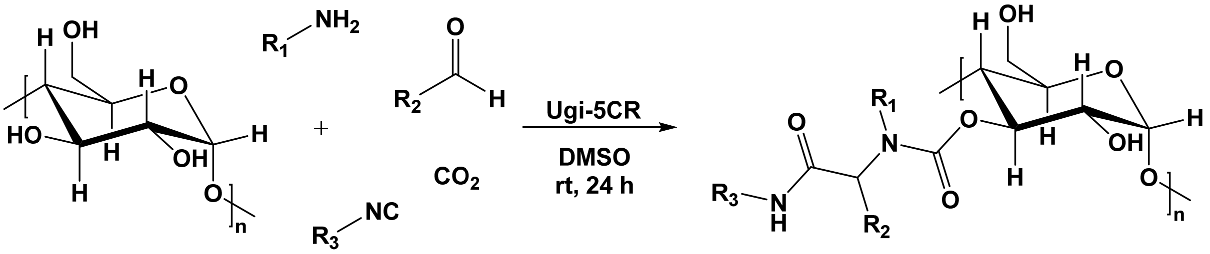
Modified starches are promising biomaterials, as they lead to biodegradable polymers from a renewable feedstock.[1] Also β-cyclodextrin, one decomposition product of starch, is highly demanded in pharmaceutical, food and cosmetic industry.[2] Here, an easy one-pot synthesis for the modification of β-cyclodextrins and starch is introduced. A variation of the Ugi reaction, the Ugi five-component reaction (Ugi-5CR), is used for this matter.[3] Whereas the Ugi four-component reaction has already been performed with polysaccharides,[4] the Ugi-5CR has only recently found its way into polymer chemistry.[5] The Ugi-5CR requires carbon dioxide and an alcohol (carbohydrate) instead of an acid component. Thus, not only the scaffold is based on renewable resources, but CO_2 as alternative carbon source is incorporated. Moreover, only secondary hydroxyl groups are substituted, enabling a regiospecific substitution. The modified starches and cyclodextrins exhibit a better thermal stability and the solubility behaviour of cyclodextrins is improved as well.



Scheme 1: Modification of starch and β-cyclodextrin *via* Ugi-5CR.

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P26

Catalytic Decarbonylation of Biosourced Substrates

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Linear alpha olefins (LAO) are currently one of the main target in the field of surfactants, lubricants and polymers. Facing the depletion of petroleum resources, production of LAO from renewable feedstock is gaining increasing interest in recent years. In the present study, we demonstrated that Ir-catalysts were suitable to decarbonylate a wide range of biosourced substrates under rather mild conditions (160 °C, 5 h reaction time) in the presence of potassium iodide and acetic anhydride. The resulting LAO were obtained in good conversion and selectivity provided that the purity of the substrate, the nature of the ligand and the amounts of the additives were accurately controlled. The catalytic system could be efficiently recovered using a Kugelrhor distillation apparatus and recycled.

P27

Synthesis of Modified Polycaprolactams Based on Renewable Resources

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Polycaprolactam is a polyamide with specific properties mainly used as a synthetic fiber marketed under the trade name Perlon®. These polyamides are produced on an industrial million tons scale at high temperatures (240°C) utilizing petroleum base chemicals. Current research endeavors to replace petroleum based feedstocks with renewable materials and furthermore to achieve polymerization at lower temperatures.

This work evaluates the ability to produce polyamides from renewable monomers at lower temperatures (150 °C). Caprolactam monomers were modified to obtain novel polyamides with tuneable properties.

By using polyunsaturated fatty acid methyl ester mixtures, it is possible to obtain the diesters to create AA-type-monomers. 1,4-cyclohexadiene is obtained as a byproduct due to intramolecular self-metathesis of linolenic acid derivatives.[2] In a sustainable three step synthesis, the 1,4-cyclohexadiene can be further converted to 2-cyclohex-1-enone.[3, 4] Starting from 2-cyclohex-1-enone, a Thia-Michael-Addition and three additional steps are used to synthesize modified monomer derivatives. The monomer synthesis is further optimized in order to achieve high yields utilizing environmentally benign synthesis procedures. Of particular importance is the use of less toxic reagents and the minimization of chemical waste in order to meet the requirements of environmentally friendlier chemistry. *Via* coordination-insertion ring-opening polymerization with a tin(II)2-ethylhexanoat (Sn(Oct)2) catalyst, it is possible to create common, high molecular weight polyamides.

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P28

Pressure Sensitive Adhesives from Plant-based Oils: Synthesis and Adhesive Properties

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Pressure-sensitive adhesives represent an important segment of adhesives and are used in different applications, such as labels, tapes and foils, or special construction adhesives, which are employed for both industrial and domestic purposes. Currently ongoing research, both in academia and industry, is trying to replace petrochemical adhesives with those incorporating natural and renewable materials.[1, 2] Along this general idea, this work investigates the synthesis of bio-based pressure sensitive adhesives and their characterization in terms of mechanical properties relevant to processing and application.

The synthesis of monomers was based on various fatty acids derived from vegetable oils as renewable feedstock and proceeded *via* a one-step, a two-step, or a three-step synthesis route.[3, 4, 5] These monomers were polymerized *via* free radical polymerization resulting in high molecular weight polymers with adhesive properties. Focus was laid on the pure homopolymers, which were easily tunable in their adhesive properties. Synthesized polymers displayed the typical dependence of molecular weight and degree of crosslinking on the adhesive properties, described by rheological studies as well as tack and peel measurements. By variation of curing time at given temperature, it was possible to show the change in the debonding behavior from cohesive towards adhesive failure. The same trend could also be shown in peel tests and by rheology. The described polymers generally showed good PSA performance compared to a common industrial standard.

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P29

Renewable Polymers from Itaconic Acid by Polycondensation and Ring-Opening-Metathesis Polymerization

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Itaconic acid, a renewable feedstock obtained by fermentation of carbohydrates, is a very interesting substrate to prepare renewable unsaturated polymers with interesting material properties.[1-4] Herein, itaconic acid is used as a key substrate to produce aliphatic unsaturated polyesters as well as polynorbornenes.[5] Renewable unsaturated polyesters were prepared by direct polycondensation of dimethyl itaconate (DMI) with diols, whereas the ring-opening metathesis polymerization (ROMP) of a DMI derived norbornene led to polynorbornenes. The direct polycondensation of DMI was performed with tin(II) ethylhexanoate as catalyst, 4-methoxyphenol as radical inhibitor, and different diols to yield linear unsaturated polyesters with a molecular weight up to 11 500 Da without isomerization or cross-linking of the vinylic double bond. Further modification of the unsaturated polyesters by thia-Michael addition yielded polysulfides, which were subsequently oxidized to polysulfones. Moreover, the solvent-free and straightforward Diels−Alder reaction of DMI and cyclopentadiene was used to prepare a partially renewable norbornene monomer, which was used in ROMP with different catalysts to prepare polymers with low dispersities and adjustable molecular weights.

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P30

Modified Poly(ε-caprolactone)s: An Efficient and Renewable Access via Thia-Michael Addition and Baeyer−Villiger Oxidation

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The preparation of a novel class of ε-caprolactone (CL) monomers, modified at the β-position of the ester function, is described.[1] 1,4-Cyclohexadiene, obtained as by-product from the self-metathesis of polyunsaturated plant oils,[2-4] was used as renewable key substrate. The efficient thia-Michael addition to cyclohex-2-en-1-one and subsequent Baeyer−Villiger oxidation provided the regioselectively modified CL monomers. To enable a sustainable Baeyer−Villiger oxidation, several reaction procedures were investigated. In order to prove a controlled ring-opening polymerization of the prepared monomers, the kinetics were studied and the monomer to initiator ratios were varied in order to prepare poly(ε-caprolactone)s with different molecular weights and different side groups.

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P31

Sustainable and Environmentally Friendly Alkylations of Phenols with Organic Carbonates and its Application on Organosolv Lignin

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Lignin is one of the most abundant biopolymers on earth, third only after cellulose and chitin.[1] Thus, it is a highly available renewable resource. Especially for the production of aromatic compounds, lignin probably is the most promising alternative to petroleum-based materials. The functionalization of both the phenolic and aliphatic hydroxyl groups in lignin is essential for applications in polymer chemistry.[2]

The alkylation of phenols with organic carbonates is shown to be non-toxic, sustainable and effective in the presence of under-stoichiometric quantities of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and potassium carbonate.[3] Different phenols, serving as model substances for lignin, were etherified with diethyl carbonate (DEC), diallyl carbonate (DAC), and dibenzyl carbonate (DBC). It was found that methoxy group-containing phenols show an increased reactivity towards alkylation reactions. Moreover, comparative studies of different bases and temperatures were performed to optimize the solvent-free allylation of organosolv lignin (OL) with diallyl carbonate. Due to a better solubility, the reactivity of OL is significantly higher towards the allylation of phenolic and aliphatic hydroxyl groups using tetrabutylammonium bromide (TBAB) as a base. Up to now, 87% of all lignin hydroxyl groups were reduced by allylation.

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P32

Glycerol-mediated liquefaction of lignin residue for preparation of lignol

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Lignin residue from various lignocellulosic biomass was solvothermally liquefied to prepare lignols. Lignol can be used as the monomer for production of polyester and polyurethane. Glycerol or PEG-blended glycerol was used as the liquefaction solvent and sulfuric acid was used as the catalyst. The effects of various liquefaction reaction conditions, such as biomass loading, sulfuric acid loading, liquefaction temperature and reaction time, on lignol production was investigated and optimized. The hydroxyl and acid numbers of the lignol were analyzed, and the resulting lignol was suitable for polymer synthesis on the basis of Fourier transform infrared spectroscopy. Acknowledgement: This work was supported by the R& D Program of the Ministry of Trade, Industry & Energy (MOTIE)/the Korea Evaluation Institute of Industrial Technology (KEIT) (Project # 10049675).

P33

Catalytic Carbonylation of Crude Algae Oil Lipids

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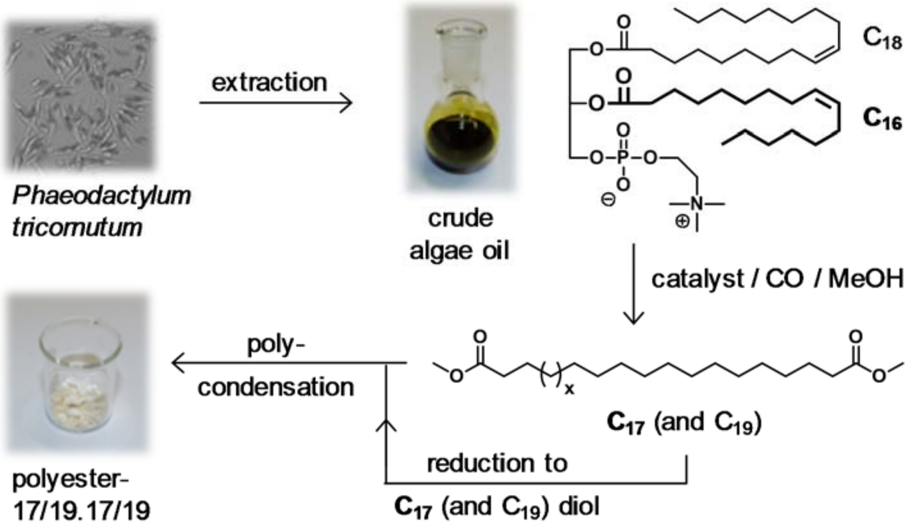
Microalgae are attractive as a feedstock as they contain unique compositions of, for example, fatty acids. Beneficially, they gain energy from photosynthesis like higher plants, but they have the advantage to grow in brackish or salt-water independent from season and they do not compete with food production by consuming arable land. Additionally, microalgae can double within 24 hours and their lipid content can reach up to 70 wt-% of their dry weight.[1] Current efforts to technically use microalgae oil focus on the generation of fuels with a molecular structure ideally identical to crude oil based products.[2] In this contribution we discuss a different approach for the utilization of algae by translating the unique molecular structures of algae oil fatty acids into higher value chemical intermediates and materials.



Scheme 1: Utilization of algae as exemplified by the generation of an aliphatic long-chain polyester.[3]

The issues of algae mass workup and the compatibility of catalytic conversions with the specific multicomponent mixtures obtained are discussed for the example of carbonylation (Scheme 1). These direct practical considerations are aided by a mechanistic understanding. The behavior of multiple unsaturated components is of particular interest here. To this end, multifunctional intermediates could be enriched in *Phaeodactylum tricornutum* without compromising yields via genetic modification. Moreover, it was possible to tune the fatty acid composition only via the algaes' growth conditions.[3,4] These intermediates are further investigated in different selective reactions.

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P34

Synthesis of defined star polymers using ADMET-polymerization and post-polymerization modification via thiol-click chemistry

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The synthesis of star polymers with 4 and 6 arms was accomplished using ADMET polymerization of a core unit with acrylate endgroups and fatty acid derived 10-undecenyl acrylate as unsymmetric α,ω-diene monomer. Thereby, the selectivity of olefin cross-metathesis between acrylates and terminal olefins allows the buildup of defined polymer architectures.[1,2] The core-first approach was applied to synthesize stars having arms of ten or twenty monomer units exhibiting an α,β-unsaturated ester backbone suitable for post-polymerization functionalization. Subsequent modification of internal as well as external α,β-unsaturated esters was realized via base-catalyzed thia-Michael addition. For this, five different thiols were employed in a simple and efficient procedure, without observing degradation of the polymer backbone. The polarity of these modified star-shaped polymers could thus be tuned by choosing different thiols for this modification, as it was shown by determining the octanol water partition coefficients of these polymers by high pressure liquid chromatography (HPLC).[3] Functionalization of only acrylate endgroups was performed by thio-bromo click chemistry of thioglycerol-functionalized 4-arm star polymer.[4] Combination of esterification and thio-bromo click reaction provides star polymers bearing a dendritic corona with a variable quantity of hydroxyl groups on the surface.

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P35

A SUSTAINABLE ROUTE TO TERMINAL EPOXIDES FROM FAMEs

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Plant oils are among the most useful raw materials from vegetable sources for the chemical industry. Over the last decades, the derivatization of the fatty acids alkyl chains have been extensively explored. A noteworthy example is the catalytic epoxidation of unsaturated fatty acid methyl esters (FAMEs) such as methyl oleate.[1] The cross-metathesis has been applied to unsaturated FAMEs to give linear terminal olefins, as in the case of the ethenolysis of methyl oleate, which produces 1-decene.[2] In this context, a derivatization of the mentioned terminal, non-activated olefins through epoxidation, appears of great interest even though it represents a challenge for chemists. Here we report about a selective catalytic epoxidation of terminal (non-activated) and internal linear alkenes, such as 1- and *trans*-2-octene by titanium containing silica catalysts. Ti- and Nb-based catalysts with similar characteristics, grafted on mesoporous SiO2, had been previously employed in the selective epoxidation of functionalized bulky alkenes.[3,4] In the present work, a series of Ti-containing catalysts was prepared via liquid-phase grafting (ca. 2% wt. metal), starting from a selection of silica supports. In particular, commercial Davisil and Aeroperl amorphous non-ordered silica and the ordered mesoporous MCM-41 material were used as supports for the catalytic species, in order to evaluate the influence of the silica nature on the catalytic performances. The catalytic activity was tested in batch reactor in heterogeneous phase, in various solvents. Remarkably, in trifluorotoluene (PhCF3), which has been considered as a green alternative to dichloromethane, the formation of side-products was significantly reduced and good results were achieved in the presence of the whole catalysts selection, with *tert*-butyl hydroperoxide (TBHP) as oxidant. In particular, in the epoxidation of the internal olefin *trans*-2-octene, 98% selectivity and almost complete conversion were achieved after 24 hours over Ti-SiO2 Davisil catalyst. Comparable conversion and selectivity were observed on the same substrate after just 6 hours, in the presence of Ti-MCM-41 catalyst. Surprisingly, the use of PhCF3 led to high selectivity and good conversions (93% conversion, 93% selectivity to epoxide), even in the case of the less active terminal alkene, 1-octene. These results suggest that the selective electrophilic epoxidation is feasible and may be extended to other linear and poorly activated substrates directly derived from alkene metathesis of unsaturated FAMEs.

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P36

Thermoplastic polyester elastomers based on plant-oil derived long-chain crystallizable aliphatic hard segments

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Plant-oil derived long-chain dicarboxylic acids and their corresponding diols are utilized as entirely aliphatic hard segments in the synthesis of segmented thermoplastic polyester elastomers. Hereby, physical crosslinking is provided by their polyethylene-like crystallinity. Together with stoichiometric amounts of oligomeric polyethers like poly(tetramethylene glycol) (PTMG) and corn sugar derived poly(trimethylene glycol) (PPDO), copolymers were prepared in a one-pot polycondensation procedure. The obtained polyester-polyether copolymers show high melting points up to 94 °C and significantly enhanced thermal properties compared to polycondensates based on the commercially available short-chain analogues, namely dodecanedioic acid/dodecane diol. Material testing of the renewable resource based thermoplastic elastomers shows high ductility values in combination with characteristic elastomeric behavior.

P37

Use of waste frying oil for the biotechnological production of surface-active hydrolysates of industrial interest

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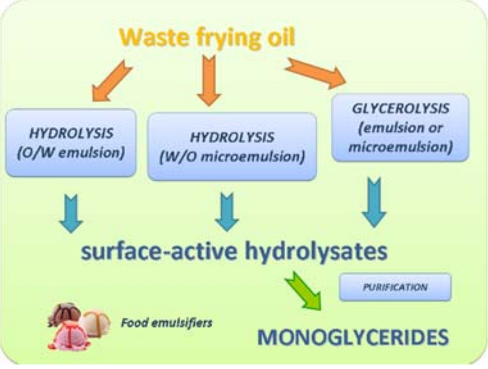
Oily products are widely used in both industry and houses, with high risk of uncontrolled spilling, especially in household activity because softer control. At that respect, waste frying oils are generated in considerable amounts worldwide (i.e. 2.5 millions of tons are produced yearly in the EU). They present a high pollutant potential and cannot be handled by biological wastewater standard treatment processes, which becomes a threat to the environment. Thus the development of new strategies is necessary for its valorisation. One promising solution to this problem is the use of waste frying oils as feedstock for the production of biofuels and high added-value chemicals. Among them, free fatty acids and mono- and diacylglycerols have interesting interfacial properties and are used in a wide range of applications from food and dairy products to cosmetics. Furthermore monoacylglycerols are the most used emulsifiers in the food, cosmetic and pharmaceutical industries and are considered as GRAS (Generally Recognized as Safe) by the Food and Drugs Administration.

Traditionally, the industrial production of monoacylglycerols is carried out by glycerolysis with inorganic catalysts, at 220-250°C. However this path implies high energy consumption and the appearance of undesired by-products. Thus the development of enzymatic processes, which implies milder hydrolysis conditions and higher selectivity and specificity, seems to be an interesting path for the valorisation of renewable oily substrates, yielding high-quality products, which could not be obtained by conventional chemical procedures.



This work is focused on the enzymatic hydrolysis of oils to yield monoacylglycerols. Free commercial lipases are used and two reaction media were tried in order to evaluate their feasibility: i) an oil in water emulsion, the oily phase being previously emulsified in the aqueous phase using an emulsifier or a surfactant; ii) a water in oil microemulsion or reverse micellar system, that contains AOT as surfactant, an aqueous phase and a mixture of isooctane and waste oil as the oily phase.

In a first step the conditions for the preparation of the reaction media were optimized, considering several factors such as oil phase volume fraction, emulsifier-to-oil phase mass ratio and applied energy/volume to form the emulsion. Then, we carried out several assays to study the effect of enzyme concentration, pH, oil-to-solvent ratio, etc. on hydrolysis extent and product distribution.

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P38

Two-phase olive mill waste as feedstock for biosurfactant production by Bacillus subtilis DSM 3526

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Spain is the world's largest producer of olive oil, with 1.8 million of metric tons in 2013. Currently, the predominant method for the extraction of the oil in this country is a two-phase centrifugation, obtaining olive oil and the two-phase olive mill waste (TPOMW), also known as "alperujo". The purpose of this work is to evaluate the potential of TPOMW as the main carbon source for the production of biosurfactants with Bacillus subtilis DSM 3526. To do that, the time course of the fermentation was followed by measuring pH and surface tension of the cell-free supernatant, as well as biosurfactant and biomass concentration throughout the process. The chemical structure of the biosurfactant, as well as its interfacial properties (such us the critical micelle concentration, surface and interfacial tension) and the ability to produce stable emulsions were also evaluated.

Our experimental results demonstrate that Bacillus subtilis DSM 3526 is able to produce surface active compounds using TPOMW as carbon source. The biosurfactant produced using TPOMW was able to reduce surface tension considerably (<32 mN/m) and exhibit low CMC values (0.03 g/L). The highest concentration of biosurfactant was obtained at 36 hours of fermentation, and the specific production rate was 0.07 gbiosurfactant/gbiomass. FTIR determinations indicate that the biosurfactant produced by this strain is surfactin. Moreover, it was found that a small part of phenolic compounds present in TPOMW were extracted together with the biosurfactant from the culture medium. The presence of phenolic compounds in the partially purified biosurfactant may be advantageous for certain applications, particularly in the alimentary, pharmaceutical and cosmetic sectors, as they can benefit from the combination of both compounds in the same product. Further studies are needed to optimize the lipopeptide production and to explore the advantages of the presence of phenolic compounds in the final product.

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P39

The Sustainable Derivatization of Starch with Organic Carbonates: Renewable Feedstock for the Chemical Industry

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The global production of plastics raised approximately 20 million tons within the last 5 years reaching 300 million tons by 2015 mainly derived from fossil resources. The excessive consumption of fossil resources and the global awareness of the high pollution caused by petroleum-based waste products gave rise to the need of the development of environmentally friendly, non toxic and biodegradable bio-based materials and procedures in the industry.[1,2]

Starch is one of the major alternative renewable feedstocks that can be isolated from several raw materials including corn, wheat, pea and potato. There is considerably increasing interest for the preparation of industrial products from starch due to its low cost, eco-friendly and non-toxic nature. However, it has limited applications because of its inherent properties like low solubility, viscosity and brittleness. Chemical modification of starch is often necessary and achieved by modifying its free hydroxyl groups to enhance the mechanical and other properties, which opens various strategies to substitute the conventional synthetic plactics derived from petroleum feedstock.[3] In order to achive a sustainable production, the reagents that are being used in the modification are also required to be non-toxic and eco-friendly. The development of a new class of solvents, ionic liquids (ILs), enabled new approaches for the modification of starch and also cellulose. ILs are described as ‘green’ solvents, mainly due to their very low vapor pressures.[4] It is proposed that the use of ILs can sufficiently interrupt the intramolecular hydrogen bonding and thus lead to activation of the hydroxyl groups.[5]

In our work, dimethyl, diethyl and diallyl carbonate which are shown to be non-toxic, sustainable and efficient reagents[6] are utilized for the homogeneous modification of starch in the presence of sub-stoichiometric quantities of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5,7 triazabicyclo[4.4.0]dec-5-ene (TBD) as a base in two different solvent systems: DMSO and BMIMCl/DMSO as co-solvent. The higher degree of substititon (DS) was obtained in the BMIMCl/ DMSO system (DS >1). The method performed in this work was an important step forward for sustainability and represents a new approach for carbohydrate modification. The BMIMCl–DMSO mixture can be recycled and reused for the further reactions.

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P40

New approach to monomer synthesis for polyamide production from local plant oils

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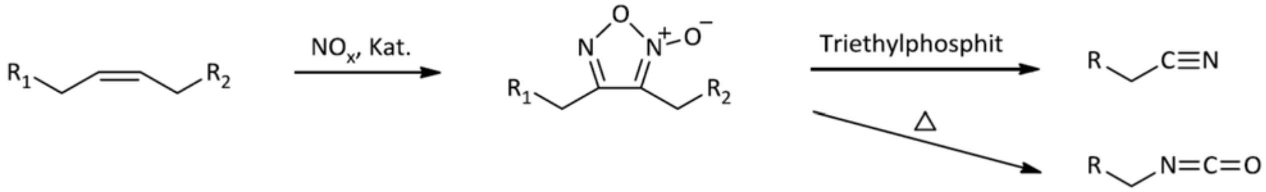
In this study we focused on a new nitrogen related transformation of oleochemicals, in order to obtain necessary monomers for the generation of polyamides & polyurethanes. The cleavage of the double bond in oleic acid and insertion of the nitrogen function in an atom economic fashion is highly desirable. To achieve this, a useful means is to convert the unsaturated compound into a furoxane, which serves as a key intermediate. These heterocycles can be splitted into mono- or bi-functionalized compounds.



We have transformed this methodology to the reaction of oleic acid esters. Possible products resulting from the cleavage of the furoxanes are isocyanates and nitriles, depending on the cleavage conditions.

The addition of the nitrogen oxides was successful at low temperatures and could be confirmed with spectroscopic and literature data.

P41

Kinetics and mechanism of Jatropha curcas biodiesel decomposition by oxidation reaction

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Biodiesel is start to use in a world as an alternative fuel for substitution of petrodiesel.. The advantage of biodiesel is well known in sustainability and renewability, short carbon cycle, fat and non edible oil as source for the feedstock and in case of micro algae oil, cultivation of micro algae could reduce carbon dioxide and developed better environment. However due to the characteristic of biodiesel in application should be mixed with petrodiesel. Mixing between biodiesel and petrodiesel should be done in order to optimize technical and economical value of the fuel and to reduce disadvantage of biodiesel itself. Disadvantage of biodiesel is tends to degradable and decompose by biological activities, physical exposure and chemical reaction and in some cases these will be simultaneous effect.

Under environment temperature, biodiesel decomposition is mainly by activities of oxygen which is tends to react with double bond on the fatty acid. Position and quantities of double bond on the fatty acid molecular chain is different one to other feedstock sources, thus believed that different biodiesel feedstock will resulted on different stability of biodiesel due to decomposition by oxidation.

In this work, purified *Jatropha curcas* biodiesel was treated by accelerated reaction on Rancimat Test Equipment, in which 3 grams of biodiesel was exposed by 10 L.min-1 dry air flow on the different temperature and time. Quantity of double bond on biodiesel was analyzed by determining the iodine number on the tested biodiesel. The similar treatment also applied to *Jatropha curcas* biodiesel with pyrogallol as antioxidant agent.

It was found that decomposition due to oxidation reaction on *Jatropha curcas* biodiesel was determined by mass transfer rate of Oxygen to the body of biodiesel., while the value of k in room temperature 20 OC is 0.125 /10 days, and kG. 0,019 m.s-1.

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