



abiosus e.V.

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

5th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

**March 18-20, 2012
Karlsruhe, Germany**

in Cooperation with:

Karlsruhe Institute of Technology (KIT)

German Society for Fat Science (DGF)

German Chemical Society (GDCh), Division of Sustainable Chemistry

Agency of Renewable Resources (FNR)



Scientific and Organizing Committee

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Michael A. R. Meier, Karlsruhe Institute of Technology (KIT), Germany

Acknowledgement

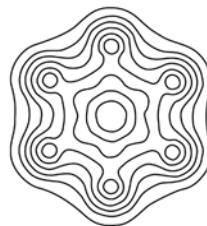
Financial Support by the German Federal Ministry of Nutrition, Agriculture and Consumer Protection (BMELV) and the Fonds der Chemischen Industrie (FCI) is gratefully acknowledged.

Supported by:



Federal Ministry of
Food, Agriculture
and Consumer Protection

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Program

Lectures and Posters

Sunday, March 18, 2012

Registration

Registration will be opened from 13:00 - 19:00

15.30 Welcome and Opening

Jürgen O. Metzger, *abiosus* e.V.

Hans-Jürgen Froese, Federal Ministry of Food, Agriculture and Consumer Protection

Stefan Bräse, Vice Dean for Research of Faculty of Chemistry and Biosciences, KIT

Michael A. R. Meier, Division of Sustainable Chemistry of GDCh and KIT

16.00 – 18.00 First Session

Chair: Michael A. R. Meier

**16:00 – 16:30
L1**

Isomerizing transformations of fatty acids (M)

Lukas J. Gooßen, Dominik M. Ohlmann, University of Kaiserslautern, Germany

**16.30 – 17.00
L2**

Advances in the Chemocatalytic Conversion of Oleochemicals (M)

Bert Sels, K.U.Leuven, Heverlee, Belgium

**17.00 – 17.30
L3**

Polymers from vegetable oils by click chemistry (M)

Zoran Petrovic, Jian Hong, Bipin K. Shah, Pittsburg State University, Kansas, USA

**17.30 – 18.00
L4**

Sustainability evaluation as key factor for the selection of processes and materials (M)

Peter Saling, BASF, Germany

18.00 – 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 19, 2012

9.00 – 10.30 *First morning session*

Chair: Bert Sels

9.00 – 9.30 **Ruthenium catalysis for cross metathesis and sequential reactions adding value to renewable oils (M)**

L5 Christian Bruneau, Pierre Henri Dixneuf, Cédric Fischmeister, Xiaowei MIAO, Université de Rennes 1, Sciences Chimiques, Rennes, France

9.30 – 9.50 **Polymer precursors from catalytic reactions of natural oils (D)**

L6 Marc R. L. Furst¹, David J. Cole-Hamilton¹, Ronan Le Goff¹, CatherineH. Botting¹, Dorothee Quinzler², Stefan Mecking²
¹St. Andrews, Scotland, UK ; ²University of Konstanz, Konstanz, Germany

9.50 – 10.10 **Novel Monomers and Polymers from Plant oils via ADMET and ROMP (D)**

L7 Hatice Mutlu, Michael A. R. Meier, Karlsruhe Institute of Technology, Karlsruhe, Germany

10.10 – 10.30 **Synthesis of fatty acid derived monomers and polymers thereof via efficient catalytic and non-catalytic approaches (D)**

L8 Oguz Türlüncü, Michael A. R. Meier, Karlsruhe Institute of Technology, Karlsruhe, Germany

10.30 – 11.00 **Coffee break**

11.00 – 13.00	<i>Second morning session</i>
	<i>Chair: Lucas J. Gooßen</i>
11.00 – 11.30 L9	Renewable materials @Bayer MaterialScience (M) <u>Gesa Behnken</u> , Bayer MaterialScience, Germany
11.30 – 12.00 L10	Utilization of vegetable oils and fats in the Brazilian Chemical Industry (M) Sergio Teixeira, <u>Ulf Schuchardt</u> Universidade Estadual de Campinas (UNICAM), Campinas-SP, Sao Paulo, Brasilien
12.00 – 12.20 L11	Synthesis of 3,6-disubstitued-1,2,3,6-tetrahydro phthalic acid anhydride derivatives by Rhodium catalyzed addition of maleic anhydride to fatty acids (D) <u>Steven Eschig</u> , Tunga Salthammer, Claudia Philipp, Fraunhofer-Institute for Wood Research, Wilhelm-Klauditz-Institute, Braunschweig, Germany
12.20 – 12.40 L12	Design of Ru-Zeolites for Hydrogen-free Production of Conjugate Linoleic Acids and Conjugated Oils (D) <u>An Philippaerts</u> ¹ , Steven Goossens ¹ , Moniek Tromp ² , Stuart Turner ³ , Oleg I. Lebedev ³ , Gustaaf van Tendeloo ³ , Pierre Jacobs ¹ , Bert Sels ¹ , ¹ K.U.Leuven, Heverlee, Belgium; ² Technische Universität München, München, Germany; ³ University of Antwerp, Antwerpen, Belgium
12.40 – 13.00 L13	Supported ionic liquid phase catalysis with supercritical flow (D) <u>Ruben Duque</u> , Eva Öchsner, Herve Clavier, Marc Mauduit, Steven P. Nolan, David J. Cole-Hamilton, St. Andrews, Scotland, UK
13.00 – 14.00	Lunch break

14.00 – 15.30	<i>First afternoon session</i>
	<i>Chair: Stefan Buchholz</i>
14.00 – 14.30 L14	Optimizing wax ester production in oil seed-crops (M) Mareike Heilmann, Tim Iven, <u>Ivo Feußner</u> , University of Göttingen, Göttingen, Germany
14.30 – 15.00 L15	Pathways for the chemo-catalytic transformation of sugars (M) <u>Regina Palkovits</u> ¹ , Marcus Rose ¹ , Tajvidi Kameh ² , Jens U. Oltmanns ¹ , Stefan Palkovits ³ , Mohammad G. Al-Shaal ¹ , William H.R. Wright ¹ , ¹ Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Aachen, Germany; ² Max-Planck-Institut für Kohlenforschung, Mülheim, Germany; ³ Center of Molecular Transformations, RWTH Aachen, Aachen, Germany
15.00 – 15.30 L16	Transformation of terpenes into fine chemicals (M) <u>Wilfried Schwab</u> , Biotechnology of Natural Products, Technical University München, Freising, Germany
15.30 – 16.00	Coffee break
16.00 – 17.30	<i>Second afternoon session</i>
	<i>Chair: Christian Bruneau</i>
16.00 – 16.30 L17	Sustainable Fatty Acid Derivates (M) <u>Stefan Buchholz</u> , Evonik, Germany
16.30 – 16.50 L18	Lipophilic Antioxidants from Fatty Acids (D) <u>Hans J. Schäfer</u> , Christian Kalk, Universität Münster, Germany
16.50 – 17.10 L19	New Generation Cationic Amphiphiles for Use as Surfactants and Ionic liquids (D) <u>Sukhprit Singh</u> , Avinash Bhadani, Raman Kamboj, Vinay Chauhan, Dev University, Amritsar, India
17.10 – 17.30 L20	Epoxidation with hydrogen peroxide of unsaturated FAMES over Nb(V)-silica catalysts (D) Vladimiro Dal Santo, Alessandro Gallo, Rinaldo Psaro, Cristina Tiozzo, <u>Matteo Guidotti</u> , CNR-ISTM, Milan, Italy
19.30	<i>Conference Dinner</i>
	Renaissance Karlsruhe Hotel

Tuesday, March 20, 2012

9.00 – 10.40 *First morning session*

Chair: Zoran Petrovic

9.00 – 9.30 **Functional group metathesis polymerization of biorenewable feedstocks (M)**

L21 Stephen A. Miller, Department of Chemistry, University of Florida, Gainesville, Florida, USA

9.30 – 10.00 **Strategies for polymerizing cyclohexadiene from plant oils (M)**

L22 Robert T. Mathers, Penn State, New Kensington, USA (M)

10.00 – 10.20 **Vegetable-based building-blocks for the synthesis of renewable polyurethanes and polyesters (D)**

L23 Henri Cramail^{1,2}, Carine Alfos³, Lise Maisonneuve^{1,2}, Thomas Lebarbé^{1,2}, Arvind More^{1,2}, Eric Cloutet^{1,2}, Benoit Gadenne^{3, 1}, Université de Bordeaux, Pessac, France; ² CNRS, Pessac, France ; ³ ITERG, Pessac, France

10.20 – 10.40 **Impact of functionality on properties of vegetable oil-based thermosetting coatings (D)**

L24 Thomas J Nelson, Dean C. Webster, North Dakota State University, Fargo, ND, USA

10.40 – 11.10 *Coffee break*

11.10 – 13.00	<i>Second morning session</i>
	<i>Chair: Stephen A. Miller</i>
11.10 – 11.40 L25	Oleochemicals in Personal Care (M) <u>Markus Dierker</u> , BASF, Germany
11.40 – 12.00 L26	Glycerol-Based Polymers Bearing Acetal and Carbonate Groups: Switchable physical and thermal properties (D) <u>Dien P. Pham</u> , Vincent Lapinte, Sophie Monge, Yann Raoul, Prolea, Jean Jacques Robin, Université de Montpellier, France
12.00 – 12.20 L27	Formic acid as hydrogen donor molecule in the glycerol hydrogenolysis to 1,2-propanediol (D) <u>Andreas Martin</u> , Udo Armbruster, Inaki Gandarias, Pedro Arias, Leibniz-Institut für Katalyse e.V., Rostock, Germany
12.20 – 12.40 L28	Preparation of asymmetric chlorohydrin esters from glycerol (D) <u>Carmen E. Solarte</u> , Mercè Balcells, Mercè Torres, Núria Sala, Jordi Eras, Ramon Canela-Garayoa, Universitat de Lleida, Spain
12.40 – 13.00 L29	Novel catalysts derived from hydrothermally synthesized phyllosilicates for the selective preparation of glycerol ethers or esters (D) <u>Joel Barrault</u> , Sabine Valange, Matte V. Sivaiah, Sabine Petit, CNRS, Poitiers, France
13.00 – 14.00	Lunch break

14.00 – 16.00	<i>Afternoon session</i>
	<i>Chair: Ulf Schuchardt</i>
14.00 – 14.30	New routes for the catalytic valorisation of biomass-derived oxygenates (M)
L30	<u>Pieter C. A. Bruijninx</u> , Bert M. Weckhuysen, Utrecht University, Utrecht, The Netherlands
14.30 – 14.50	The relevance of the anhydride reaction pathway for selective deoxygenation of stearic acid in the absence of H₂. (D)
L31	<u>Stefan Hollak</u> ¹ , J. H. Bitter ² , J. van Haveren ¹ , K. P. de Jong ² , D. S. van Es ¹ , ¹ Wageningen, The Netherlands; ² Utrecht University, Utrecht, The Netherlands
14.50 – 15.10	Ethanolysis of Jathropa Curcas L. oil in a centrifugal contactor separator (D)
L32	<u>Muhammad Yusuf Abduh</u> ¹ , Wouter van Ulden ¹ , Vijay Kalpoe ¹ , Robert Manurung ² , H.J. Heeres ¹ , ¹ University of Groningen, The Netherlands; ² Institut Teknologi Bandung, Indonesia
15.10 – 15.40	An assessment of the potential of critical fluids to support sustainable integrated biorefining, with a focus on oleochemistry (M)
L33	Muhammad Noman BAIG ^{1,2,3} , Regina Santos ¹ , Carsten Zetzl ⁴ , Jerry King ⁵ , Steve Bowra ² , <u>Daniel Pioch</u> ³ , ¹ University of Birmingham, UK; ² Phytatec; ³ CIRAD, France; ⁴ Technical University Hamburg-Harburg, Germany; ⁵ University of Arkansas, USA
15.40	Poster Award and Closing Remarks
	Best Poster Award
	<i>Award committee: Ivo Feußner, Pieter C.A. Bruijninx, Markus Dierker, Robert Mathers, Wilfried Schwab</i>
	Closing remarks
	Michael A. R. Meier
16.00	End of Workshop

Posters

- P1 **Diesel fuel generation from fats and oils with homogeneous catalysts**
Paul F. Schulz^{b)}, Eckhard R. Paetzold^{a)}, Udo Kragl^{a,b)}
^{a)}Leibniz-Institut für Katalyse an der Universität Rostock e. V., Rostock, Germany
^{b)} Institut für Chemie, Universität Rostock e. V., Rostock, Germany
- P2 **Palladium catalyzed C-H activation: a versatile method for the functionalization of fatty acid compounds**
Marc von Czapiewski¹, Oliver Kreye², Michael A.R. Meier²
¹University of Potsdam, Potsdam, Germany
² KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P3 **Camelina oil as an alternative feedstock for oleochemicals production**
Paola Pecchia,¹ Sergio Mapelli,¹ Incoronata Galasso,¹ Federica Zaccheria,² Nicoletta Ravasio²
¹ National Research Council (CNR-IBBA), Milan, Italy; ² National Research Council (CNR-ISTM), Milan, Italy
- P4 **Optimization of Oil Extraction from Beniseed (Sesame indicum) Oilseed Using Response Surface Methodology and Quality Characterization**
Eriola Betiku, Tunde Folorunsho Adepoju, Akinbiyi Kola Omole, Seyi Emmanuel Aluko, Obafemi Awolowo University, Ile-Ife, Nigeria
- P5 **Methanolysis of Beniseed oil to Biodiesel using Statistical Approach and Fuel Quality Characterization**
Eriola Betiku, Tunde F. Adejoju, Akinbiyi K. Omole, Seyi E. Aluko, Obafemi Awolowo University, Ile-Ife, Nigeria
- P6 **Renewable Monomers and Polymers Derived from Terpenes via Thiol-Ene Additions**
Maulidan Firdaus, Lucas Montero de Espinosa, Michael A.R. Meier
KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P7 **Characterisation of Lagenaria siceraria Seed Oils by Fourier Transform Infrared Spectroscopy**
Eunice M Ogunbusola, Tayo N. Fagbemi, Oluwatooyin F. Osundahunsi
The Federal Polytechnic, Ado-Ekiti, Nigeria
- P8 **Synthesis and Investigation Ester Group Containing Cationic Surfactants from Renewable Feed Stocks**
Avinash Bhadani, Sukhprit Singh, Department of Chemistry, Guru Nanak Dev University, Amritsar, India.
- P9 **Synthesis, Characterization and Aggregation Behavior of Renewable Ester Functionalized Gemini Imidazolium amphiphiles**
Vinay Chauhan, Sukhprit Singh, Department of Chemistry, Guru Nanak Dev University, Amritsar, India.

- P10 **Monomer Generation and Synthesis of Linear Polycondensates from Unsaturated Fatty Acids by Isomerizing Alkoxy carbonylation**
Josefine T Christl, Philipp Roesle, Florian Stempfle, Gerhard Müller, Stefan Mecking, University of Konstanz, Konstanz, Germany
- P11 **Rheological and material properties of hyperbranched polymer prepared by ATMET polymerization of Plukenetia conophora oil**
Cecilia Olufunke Akintayo, Hatice Mutlu, Michael Kempf, Manfred Wilhelm, Michael A. R Meier
¹ The Federal Polytechnic, Ado-Ekiti, Nigeria; ² KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P12 **Polyurethane cast resins synthesized from rapeseed oil polyols**
Piotr Rojek¹, Tomáš Vlček², Aleksander Prociak¹
¹Cracow University of Technology, Cracow, Poland
²Synpo a.s., Pardubice, Czech Republic
- P13 **Biodegradable lubricants from vegetable oils through solid acid catalyzed reactions**
Federica Zaccheria,^a Simona Brini,^{b,c} Gabriele Ricchiardi,^c Rinaldo Psaro,^a Nicoletta Ravasio^a
^a Istituto di Scienze e Tecnologie Molecolari del CNR, Milano, Italy; ^b Dipartimento CIMA, Università di Milano, Milano, Italy; ^c NISLabVCO, Verbania, Italy
- P14 **Ugi four component reactions to build structurally diverse polyamides derived from castor oil**
Ansgar Sehlinger, Oliver Kreye, Oğuz Türlünç, Jenny Rackwitz, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P15 **ENONE-CONTAINING HIGH SUNFLOWER OIL TRIGLYCERIDES AS PRECURSORS OF FLAME RETARDANT THERMOSETS**
Maryluz Moreno, M. Moreno, Gerard Lligadas, G. Lligadas, Juan Carlos Ronda, J.C. Ronda, Marina Galià, M. Galià, Virginia Cádiz, V. Cádiz
Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Tarragona, Spain
- P16 **P16 AB – TYPE POLYADDITION APPROACH TO SEMI-CRYSTALLINE POLYURETHANES BASED ON FATTY ACID DERIVATIVES**
Arvind Sudhakar More,¹ Benoit Gadenne,² Carine Alfos,² Henri Cramail¹
¹ Université Bordeaux, Laboratoire de Chimie des Polymères Organiques, Pessac, France; CNRS, Laboratoire de Chimie des Polymères Organiques, Pessac, France ; ² ITERG, Pessac, France
- P17 **Monomers and commodity chemicals via TBD catalyzed transesterification of dimethyl carbonate**
Johal Ruiz,¹ Hatice Mutlu,² Susanne C. Solleder,² Michael A.R. Meier,²
¹ Université Joseph Fourier, Grenoble, France; ² KIT, Institute of Organic Chemistry, Karlsruhe, Germany

- P18 **The Shape-Selective Hydrogenation of FAMES and Vegetable Oils**
An Philippaerts,¹ Sabine Paulussen,¹ Stuart Turner,² Gustaaf Van Tendeloo,² Bert Sels,¹ Pierre Jacobs¹
¹K.U.Leuven, Heverlee, Belgium; ²University of Antwerp, Belgium
- P19 **Polyurethane foams modified with various natural oil polyols**
Henryk Pawlik, Aleksander Prociak, Crakow University of Technology, Crakow, Poland
- P20 **NOVEL THERMOPLASTIC POLY(ESTER/AMIDE URETHANE)S FROM FATTY ACID METHYL ESTERS**
L. Maisonneuve^{1,2} T. Lebarbé^{1,2}, N. Nguyen^{1,2}, B. Gadenne³, C. Alfos³ and H. Cramail^{1,2}
¹ Université de Bordeaux, Pessac, France; ² CNRS, Pessac, France ; ³ ITERG, Pessac, France
- P21 **Fumed Silica Reinforced Biohybrid Polyurethane Nanocomposites as Surface Coating Materials**
Deewan Akram^{a,b}, Eram Sharmin^a, Sharif Ahmad^a
^aDept. of Chemistry, Jamia Millia Islamia, New Delhi-5, India; ^bDepartment of Chemistry, Faculty of Science, Jazan University, Jazan, KSA
- P22 **Biolubricant synthesis using immobilised lipase: Optimisation of trimethylolpropane oleate production**
Cecilia Orellana Åkerman, Anna E.V. Hagström, Amin Mollaahmad, Stefan Karlsson, Rajni Hatti-Kaul, Department of Biotechnology - Kemicentrum - Lund University, Lund, Sweden
- P23 **Heteropoly Acids as Catalysts for Biodiesel Production**
ALI M ALSALME,¹ Elena F Kozhevnikova,² Ivan V Kozhevnikov²
¹KING SAUD UNIVERSITY, RIYADH, Saudi Arabia; ² University of Liverpool, Liverpool, United Kingdom
- P24 **Fatty-acids as renewable feedstocks in the synthesis of thermoplastic polyesters and poly(ester-amide)s**
Thomas Lebarbe,^{1,2} Lise Maisonneuve,^{1,2} Thi Hang Nga Nguyen,^{1,2} Benoit Gadenne,³ Carine Alfos,³ Henri Cramail ^{1,2}
¹ Université de Bordeaux, Pessac, France; ² CNRS, Pessac, France ; ³ ITERG, Pessac, France
- P25 **New Non-Isocyanate Polyurethanes upon catalytic carbon dioxide conversion of epoxidized plant oils and limonene**
Moritz Bähr, Rolf Mülhaupt, Makromolekulares Institut Albert-Ludwigs-Universität-Freiburg, Freiburg, Germany
- P26 **Palladium/Ruthenium catalyzed isomerizing metathesis of fatty acids** Lukas J. Gooßen, Dominik M. Ohlmann, Technische Universität, Kaiserslautern, Germany; Markus Dierker, Care Chemicals Technology, BASF, *Düsseldorf, Germany*

- P27 **Synthesis of monomers on the basis of diglycerol**
K. Volpert, A. Martin, A. Köckritz, Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Rostock, Germany
- P28 **Production of Bio lubricants from Castor oil and higher chain alcohols by enzymatic transesterification**
Chandu Madankar, Subhalaxmi Pradhan, S N Naik, Indian Institute of Technology, Delhi, New Delhi, India
- P29 **Monomers from renewable resources**
Nicolai Kolb, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P30 **Biocompatible Polymers from Renewable Sources: Linear Polyesters from Seed Oils of Flax and Hemp**
Laura Boggioni, Nella Galotto galotto, Incoronata Tritto, CNR-ISMAL, MILANO, Italy
- P31 **New dimer diamine bio-based solutions for flexibility, moisture resistance and low polarity in high-performance polymer systems**
Angela LM Smits, Tanja van Bergen, Bas Wels, Croda, Gouda, Netherlands
- P32 **NEW ESTOLIDES – FUNCTIONAL INDUSTRIAL FLUIDS FROM RENEWABLE VEGETABLE BASED OILS**
Hermine HNM NSA MOTO, Emeline Vedrenne, Sophie Thiebaud-Roux, Pascale De Caro, Zéphirin Mouloungui, Université de Toulouse, INPT-INRA-Ensiacet, Laboratoire de Chimie Agro-Industrielle, France
- P33 **Oxidative Cleavage of Oleic Acid by RuO₄ Catalyst under Ultrasonic Irradiation. Valorization of Pelargonic Acid as a New Reactant for Selective Precipitation of Metallic Cations**
Nicolas Oget, Eric Meux, Michèle Sindt, Sandrine Rup, University of Lorraine, Metz, France
- P34 **Comparison of chemo-enzymatic epoxidation of oleic acid with different immobilized lipases**
Fabian Haitz, Thomas Hirth, Steffen Rupp, Susanne Zibek, Fraunhofer IGB Stuttgart, Stuttgart, Germany
- P35 **Enrichment of unsaturated fractions in a Linseed oil based fatty acid mixture by melt crystallisation**
Sunanda Dasgupta, Nadine Dreijack, Peter Ay, Brandenburg University of Technology, Cottbus, Germany
- P36 **Highly functionalized and structurally diverse polyamides derived from castor oil by applying Ugi four component reactions**
Oliver Kreye, Ansgar Sehlinger, Oguz Turunc, Jenny Rackwitz, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P37 **Organocatalytic modification of sorbitol and isosorbide**
Susanne Carina Solleder, Sarah Wald, Hatice Mutlu, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany

- P38 **Amphiphilic Hyperbranched Polymers from a Castor Oil Derived Monomer**
Oğuz Törünc, Kai Pahnke, Michael A.R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P39 **Catalyzed Crosslinking of Highly Functional Biobased Resins**
Thomas J. Nelson, Dean C. Webster, North Dakota State University, Fargo, ND, USA
- P40 **Process characterization of microbial oil production by *Cryptococcus curvatus***
Ines Schulze, Anke Neumann, Christoph Syldatk, KIT - Technische Biologie, Karlsruhe, Germany
- P41 **Defined and Functional Polymers via Head-to-tail ADMET polymerization**
Matthias Winkler, Lucas Montero de Espinosa, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
- P42 **Renewable Dendrimers via Thiol-Ene Click Reactions**
Kai-Anders Hansen, Lucas Montero de Espinosa, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany

Abstracts

Part 1: Lectures

Isomerizing transformations of fatty acids

Lukas J. Gooßen, Dominik M. Ohlmann, University of Kaiserslautern, Germany
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Double-bond migration is often encountered as an unwanted side reaction in metal catalyzed transformations. However, when integrated with other catalytic transformations, the overall process may open up new synthetic opportunities. Several types of processes are conceivable, depending on whether the second transformation is possible with only one, with some, or with all double-bond isomers.

Most known examples of selective single-site isomerizing functionalizations of oleic acid provide the omega-functionalized products. [1] We have recently shown that isomers with the double-bond in alpha,beta- and beta,gamma-position can also be singled out. In this context, we developed a silver-catalyzed isomerizing lactonization that allows the selective synthesis of the 5-ring lactones from unsaturated fatty acids regardless of the initial double-bond position. [2] We also demonstrated the feasibility of processes in which double-bond isomerizations are combined with aza-Michael reactions or rhodium-catalyzed 1,4-arylations. This opened up perspectives for the synthesis of long-chain beta-aryl and beta-amino acid derivatives. [3]

The isomerizing olefin metathesis of fatty acids is an example of a process in which all double-bond isomers possess comparable reactivity in the functionalization step. We have developed a bimetallic catalyst that reaches a new level of activity in this type of transformation. [4] This allows the isomerizing self-metathesis of technical-grade oleic acid, leading to olefins as well as mono- and dicarboxylic acids with tunable, well-defined chain-length distributions. The new catalyst system even allows isomerizing cross-metatheses with various olefin types. The opportunities held by the new technology for the integration of fatty acids into the chemical value-creation chain will be discussed.

References:

- [1] a) K. Y. Ghebreyessus, R. J. Angelici, *Organometallics* 2006, 25, 3040–3044. b) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* 2005, 8, 878–881. c) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton *Chem. Commun.* 2004, 1720–1721. d) D. Quinzler, S. Mecking, *Angew. Chem.* 2010, 122, 4402–4404. e) A. Behr, D. Obst, A. Westfechtel, *Eur. J. Lipid Sci. Technol.* 2005, 107, 213–219.
- [2] a) L. J. Gooßen, D. M. Ohlmann, M. Dierker, *Green Chem.* 2010, 12, 197–200. b) L. J. Gooßen, D. M. Ohlmann, M. Dierker, T. Löhl, patent EP 22411562, 2009.
- [3] a) L. J. Gooßen, D. M. Ohlmann, M. Dierker, patent EP 10189314, 2010. b) L. J. Gooßen, D. M. Ohlmann, M. Dierker, *Chem. Eur. J.* 2011, 17, 9508–9519.
- [4] a) D. M. Ohlmann, L. J. Gooßen, M. Dierker, patent application, 2011. b) D. M. Ohlmann, L. J. Gooßen, M. Dierker, publication in preparation, 2012.

Advances in the Chemocatalytic Conversion of Oleochemicals

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Triglyceride molecules are grateful molecules for an organic chemist because of their multifunctional character. Accordingly, many catalytic success have been realized today to stir the efficiency and selectivity of the various reaction types among them oxidation, hydrolysis, transesterification, isomerization, hydrogenation, conjugation etc.. Processed vegetable oils are commonly used in food and industrial applications. This presentation concentrates on the latest (catalytic) advances realized in our centre.

A first part highlights a new concept to convert the double bond of unsaturated fatty acids (as acid, esters or triglyceride mixture) into a ketone [1]. The chemical reaction uses nitrous oxide (N₂O), a greenhouse gas and side product of industrial activity, as oxidant, which interacts with the double bond according to a 1,3-bipolar mechanism, followed by rearrangement and expulsion of N₂ [2]. Such ketones are very aluable chemicals, which are conventionally synthesized according to a two-step process (epoxidation and rearrangement), and which are easily hydrogenated into the hydroxy compounds, useful in polyurethane applications for example.

The second case focuses on the partial hydrogenation of vegetable oils. Such hardening is useful to stabilize the oils against autoxidation. Hydrogenation is also a required step to control the physical properties of the fat product. Importantly, the competitive isomerization leading to trans fatty acids, needs to be eliminated as much as possible, because of their negative health aspects such as cardiovascular diseases. Reducing trans levels has been studied intensively, and many process-related parameters such pressure and temperature, are already helpful. However, such process changes in presence of conventional Ni catalysts also reduces the hydrogenation selectivity, fully saturated triglyceride such as StStSt being formed significantly. A new catalytic concept (with Pt/ZSM-5), based on zeolite-related chemistry making use of shape selectivity, will be presented that is able to decouple the isomerization/hydrogenation selectivity [3,4]. Chemical and physical analysis of the new fat products against commercial benchmarks will be given to show its ideal physical melt properties despite its essentially trans-free composition [5].

A final part discusses the catalytic conjugation of PUFAs and their corresponding triglycerides. Such conjugates are interesting chemicals in the polymer and food industry. The ultimate challenge here is to develop a heterogeneously catalyzed process to replace the current soluble base process [6]. A new catalyst, based on a modified zeolite USY and Ru, will be presented. The catalytic

system is able to conjugate double bonds with high rate without the requirement of a hydrogen-rich environment [7]. Modification of the pore structure and absence of acidity was essential in order to allow diffusion of large molecules such triglycerides, and thus to lead to efficient, selective and fast heterogeneous conjugation catalysis.

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Polymers from vegetable oils by click chemistry

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Novel cast resins based on vegetable oils of different degree of unsaturation (castor, canola, corn, soybean, and linseed oil) were prepared using 'click' chemistry. Azidated and alkynated oils were first prepared by the reaction of epoxidized oils with NaN₃ and propargyl alcohol, respectively. Thermal polymerization of these azidated and alkynated oils yielded a range of polymers with different crosslinking density. Irrespective of the number of functional groups, the products were low modulus polymers (rubbers) due to relatively low crosslinking density. On the other hand, thermal polymerization of azidated oils with short dialkynes gave glassy polymers with relatively high glass transitions when the number of the functional group (azide) was high. However, cross-linking of alkynated oils with short diazides produced low modulus polymers.

Sustainability evaluation as key factor for the selection of processes and materials

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BASF has pioneered the assessment of the sustainability of chemical products and production processes through the development and use of its Eco-Efficiency Analysis as well as SEEBALANCE analysis. The tools are used by BASF and its customers to assist strategic decision-making, facilitate the identification of product and process improvements, enhance product differentiation as well as to support the dialogue with opinion makers, NGOs and politicians.

Both Eco-Efficiency Analysis and SEEBALANCE analysis are comparative methods; the advantages and disadvantages of several alternatives are assessed according to a predefined customer benefit. The analyses uses a Life Cycle Assessment approach with the whole life cycle of a product – from cradle to grave – being considered. Next to the environmental impact, which is assessed based on ISO14040 and ISO14044 norms, all economic factors are taken into account. The SEEBALANCE also considers social impacts of products and processes.

Products derived from renewable resources are most likely to be competitive in the marketplace if they demonstrate comparable or better product quality and price versus the synthetically produced alternatives. There is significant opportunity for growth as these technologies mature, further improving their environmental fingerprint, and consumers become more aware of the environmental impacts of products. However, a key factor is educating both the public and industry as to the actual advantages and disadvantages of bio-based vs. traditionally synthesized petrochemical based products. The answer is not obvious, and must be evaluated on a case-by-case basis. Different Case studies will explain how bio-based processes can be assessed.

BASF has the experience of over 450 analyses and is increasingly applying Eco-Efficiency analysis to measure sustainability also in the agri-food sector and the sector using renewable materials from agriculture.

For these applications, a new method was developed based on the existing methods, considering specific factors for this sector like biodiversity, social parameters, water consumption as well as social factors like Residues in feed & food, fair trade, social security etc.. This method, the AgBalance enables experts to increase the knowledge on sustainable agriculture, use results as guidance for R&D and for the design of innovative, more sustainable solutions for the production and use of renewables in different applications.

These multicriterial, holistic life cycle based approaches in combination with a defined aggregation and summary of single results ends in easy understandable graphs. Different scenarios can be worked out additionally to support decision-making processes.

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Ruthenium catalysis for cross metathesis and sequential reactions adding value to renewable oils

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Plant oils constitute a class of renewable raw materials which can produce a large variety of chemicals useful for industry. The numerous applications of polyamides motivate the search of new routes to their monomers from renewable resources.

The cross-metathesis of unsaturated fatty esters, derived from plant oils, with functionalized olefins has potential to generate bifunctional compounds, as it has already been shown by reactions with acrylates.[1] The objective of the presentation will be to describe the cross-metathesis reactions of both terminal and internal double bond containing esters with acrylonitrile. This metathesis was performed with bifunctional nitrile esters— ω,α —using ruthenium catalysts and led to high conversions. [2] Some investigations on the process aiming at improving the TONs will be presented.[3]

It will also be shown that the ruthenium catalyst residue can be used as a hydrogenation catalyst in a sequential cross-metathesis/hydrogenation process leading to saturated nitrile esters and amino esters according to the experimental conditions.[4]

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Polymer precursors from catalytic reactions of natural oils

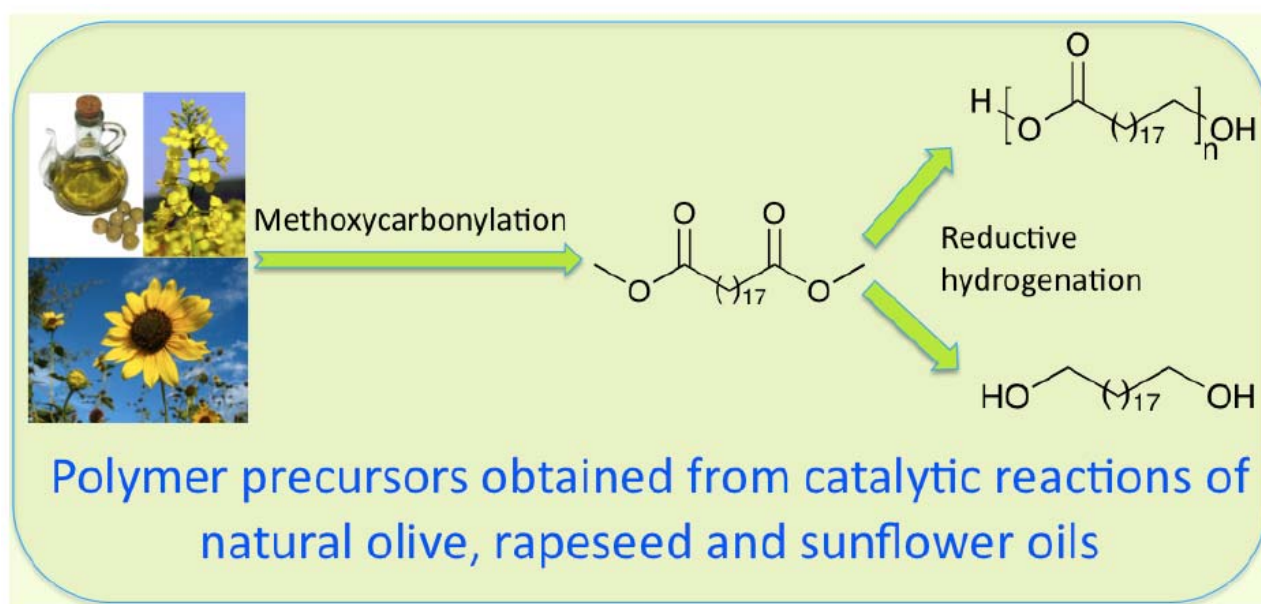
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As oil feedstocks dwindle, there will be a need for alternative fuels, but also for alternative feedstocks to produce the many chemicals that so enhance our lives. Polymeric materials have revolutionised our lives over the last 100 years, not only replacing scarce, expensive and sometimes toxic metals, cloths, etc, but also allowing the development of wholly new applications that were not contemplated until plastics were introduced on a large scale.

The search for renewable raw materials from agricultural resources, which can afterwards be synthesised into environmentally friendly polymers at lower costs, is a burgeoning area.

We shall describe the production of dimethyl 1,19-nonadecanedioate from the methoxycarbonylation of commercial olive, rapeseed or sunflower oils in the presence of a catalyst derived from [Pd₂(dba)₃], bis(ditertiarybutylphosphinomethyl)benzene and methane sulphonic acid. The diester is then hydrogenated to 1,19-nonadecanediol using Ru/1,1,1-tris- (diphenylphosphinomethyl)ethane. The corresponding carboxylic acid is easily obtained by a simple acid hydrolysis. Hydrogenation of 1,19-nonadecadienoic acid leads to short chain oligoesters, which can themselves be hydrogenated to 1,19-nonadecanol by hydrogenation in the presence of water.



Novel Monomers and Polymers from Plant oils via ADMET and ROMP

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The structural diversity of plant oils and derived platform chemicals allows for their use with many different synthetic purposes. Among them, the synthesis of polymers is an active and important research field with the objective of minimizing the strong dependence of the polymer industry on petrol-derived raw materials.[1] Regarding the direct use of plant oils, it has been shown that plukenetia conophora oil can be used for the synthesis of hyperbranched polyesters, with interesting rheological properties, via acyclic triene metathesis (ATMET) polymerization.[2] In a different approach, the introduction of styrene moieties into the structure of sunflower oil has been used to obtain a multifunctional monomer for the synthesis of hyperbranched polymers also via ATMET.[3] On the other hand, plant oil derived platform chemicals such as fatty acids, esters and alcohols are versatile building blocks for the synthesis of polymers of higher complexity. Thus, different monomers for ring opening metathesis polymerization (ROMP) have been prepared and polymerized by functionalization of a hydroxyl containing norbornene with different fatty acids.[4] Moreover, the synthesis of fatty acid based polyamides has been studied following two different approaches, namely acyclic diene metathesis (ADMET) polymerization of amide-based dienes, and TBD-catalyzed polycondensation of fatty diester and diamines.[5] Furthermore, TBD has been efficiently applied as polymerization catalyst for the synthesis of fatty acid-based polycarbonates from (E) icos-10-ene-1,20-diol and dimethyl carbonate. In addition, for the first time, ADMET polymerization has been successfully applied for the polycarbonate synthesis of terpene based monomers containing trisubstituted terminal-olefins.

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Synthesis of fatty acid derived monomers and polymers thereof via efficient catalytic and non-catalytic approaches

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Owing to their tunable mechanical properties and much lower densities, plastics have gradually become one of the most required and used materials, and substituted clay and metal. The recent awareness of sustainability, not only in energy, but also in plastic synthesis, has made mankind seek substitutes to mineral oil. We believe that plant oils have a very high potential to instantly deliver diverse functionality among other sustainable feed-stocks, such as cellulose and starch. Moreover, fatty acid derived monomers and the biopolymers synthesized thereof are excellent materials for the chemical industry.[1] Not only the starting materials, but also efficient (catalytic and non-catalytic) synthetic methods have been considered to achieve green chemistry requirements and to reduce the environmental impact of the chemical industry. Both metathesis and thiol-ene&yne reactions meet these requirements and therefore receive enduring interest, allowing the chemist to obtain a large variety of polymers. Considering the mechanisms of these reactions, 10-undecenoic acid, a castor oil derived platform chemical, is perfectly suited to be used as a renewable monomer for plant oil derived polyesters,[2] polyamides,[3] polyethylenes[4], and polythioethers.[5]

The two major classes of biopolymers are polyesters and polyanhydrides, which undergo bulk and surface erosion degradation, respectively. We applied thiol-ene click and ADMET polymerization reactions for the polymerization of two very similar fatty acid based monomers, which differ only by the ester and anhydride functionality, in order to establish and compare the efficiency of these methods for biopolymer syntheses. Moreover, the polymers derived thereof were evaluated via a set of hydrolytic stability essays in different conditions, e.g. acidic and enzymatic.[6] On the other hand, the same polymerization routes were applied to 10-undecenoic acid derivatives in order to introduce renewable methods towards polyethylenes and polythioethers.[4] In addition, we will report results on the functionalization of methyl-10-undecenoate with different thiols to yield a set of renewable monomers in an efficient manner.[2] The thus derived monomers were also polymerized to yield renewable linear and hyperbranched polyesters; also these results will be discussed within this contribution.

In summary, we will show that both olefin-metathesis and thiol-ene&yne chemistry are very versatile tools for fatty acid functionalization as well as polymerization and thus broaden the application possibilities of plant oils.

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Due to climate change and resource scarcity the importance of more renewable raw materials is increasing. Besides other solutions like e.g. recycling or the direct usage of carbon dioxide as carbon source the use of biobased raw materials is one option. Existing products, new developments and remaining challenges will be discussed.

Utilization of Vegetable Oils and Fats in the Brazilian Chemical Industry

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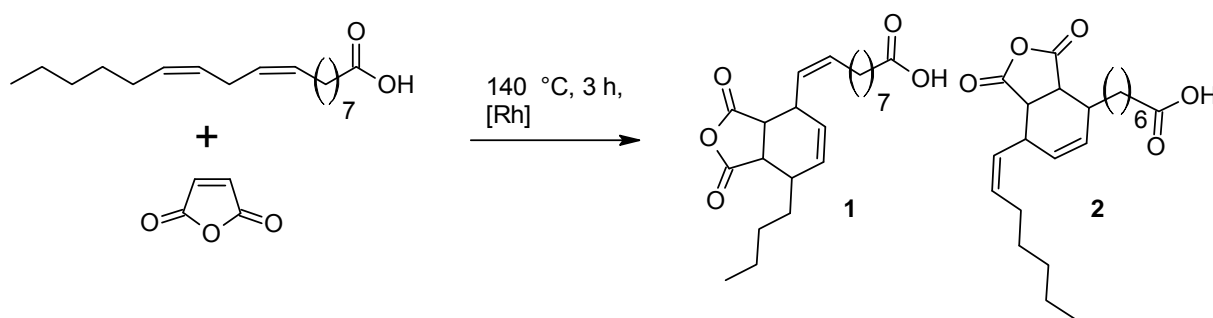
Thanks to the good performance of Brazilian agribusiness, the production of fats and vegetable oils, especially soybean oil, has experienced a constant growth in recent years. Plantations of soybean and other oilseeds also give rise to abundant amounts of animal fats, since part of the meals obtained during oil extraction is used as livestock feed. A substantial portion of the fats and vegetable oils is consumed by the domestic market. More recently, the domestic consumption is increasing mainly driven by biodiesel production. As result of the predominance of soybean oil (> 85 %), and to a lesser extent palm and cottonseed oils, the Brazilian oleochemical platform is mainly based on C16 and C18 fatty acids. These fractions, also obtained from tallow and lard, are used to make products like resins, paints, lubricants, plasticizers, etc. Despite the fact that the production of babassu and palm kernel oils is also growing, it is very small at the moment. As a consequence, Brazil needs to import large amounts of oils or fatty acids rich in C12 and C14 fractions, which are mainly used to produce cosmetics and personal care products. A number of initiatives concerning non-food uses for vegetable oils are in progress due to the favorable scenario for biomass derivatives and good expectations for the Brazilian economy. Industrial facilities with high production capacities are being installed in order to produce fuels and chemical products, like polyols, special esters, and tailored oils, among others.

Synthesis of 3,6-disubstituted-1,2,3,6-tetrahydro-phthalic anhydride derivatives by Rhodium catalyzed addition of maleic anhydride to fatty acids

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The synthesis of fatty acid based 3,6-disubstituted-1,2,3,6-tetrahydrophthalic anhydrides (THPA) is a promising opportunity to receive biobased substitutes for monomers like phthalic anhydride, trimellitic acid and their di-, tetra- or hexahydroderivates, which are commonly used in polycondensation processes. In that case the substructure of the 6-membered carbon rings is of great relevance for the properties of the resulting polyesters, especially for the final hardness. The synthesis of such rings can be achieved on different pathways. Well known and frequently studied are the Diels-Alder reactions, where the fatty acids are used as diene component and converted with a dienophile like maleic anhydride to give the corresponding 3,6-disubstituted-1,2,3,6-THPA.^[1] The main disadvantage of these reactions is the limitation to conjugated fatty acids.

An alternative synthesis route to create 6-membered carbon rings is the transition metal catalysed addition of e. g. maleic anhydride to non-conjugated fatty acids. In case of oleic acid, the Rh-catalysed reaction has already been studied by Behr and Handwerk.^[2] As in natural oils oleic acid is often existent as a mixture with linoleic acid, e. g. in sun flower or rapeseed oil, the Rh-catalyzed addition has to be considered for linoleic acid, too.



Scheme 1: Rh-catalysed addition of maleic anhydride to linoleic acid

It was found that the resulting cyclic addition products **1** and **2** correspond to the Diels-Alder adducts of the natural trienoic acids calendic and α -eleostearic acid with maleic

anhydride having a *cis*-configured allylic double bond.^[3] This could be confirmed via HPLC- (see Fig. 1). and NMR-analysis.

Furthermore, reaction times, yields of cyclic products and conversions of pure oleic and pure linoleic acid were compared. Moreover, the transition metal catalysed addition of maleic anhydride to a natural fatty acid mixture containing mainly linoleic acid and oleic acid was accomplished to determine the optimum reaction conditions for the highest yields of cyclic monomers.

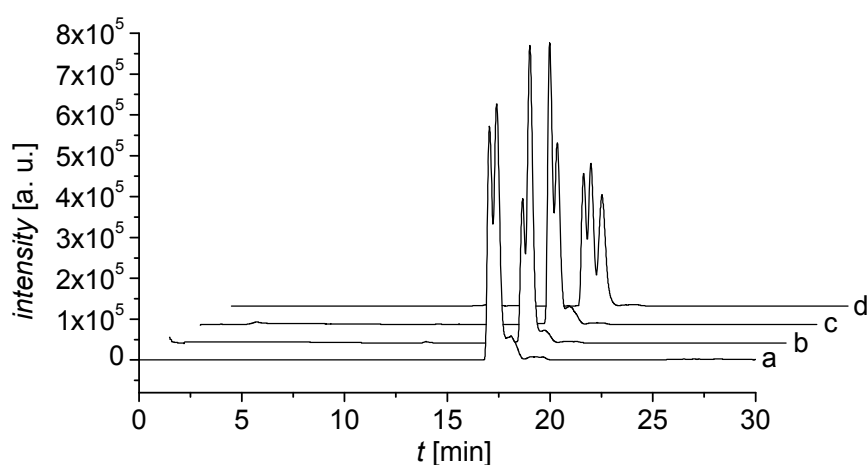


Fig. 1: HPLC-chromatograms: products **1** + **2** of monomaleinated linoleic acid (a), coinjection of **1** + **2** with the Diels-Alder-products of maleic anhydride and calendic acid (b), α -eleostearic acid (c) and β -eleostearic acid (d)

In further studies the synthesized monomers will be used in polycondensation processes to investigate the resulting polyesters which may open the door towards advanced biobased products e. g. for lacquers and coatings.

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Design of Ru-Zeolites for Hydrogen-free Production of Conjugate Linoleic Acids and Conjugated Oils

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Conjugated linoleic acids (CLAs) and conjugated vegetable oils are interesting compounds in the coatings, paints and polymer industries[1] as well as in the food industry[2]. While the isomer distribution is not important for the industrial applications, the type of CLA isomer is crucial for their beneficial effects on physiological properties. Today, CLAs are synthesized in free fatty acid form from vegetable oils rich in linoleic acid using soluble base catalysts[3]. Besides the ecological drawbacks, competitive hydrolysis of the ester linkages is the major limitation of the commercial process. The use of heterogeneous metal catalysts seems a more attractive route for industrial production of CLAs and conjugated oils. However, it does not seem easy to design a catalyst with high CLA selectivity as the competing hydrogenation reaction limits the CLA yield. Moreover, obtained productivity generally is low[4]. This contribution presents the direct production of CLAs over Ru supported on hierarchical zeolites.

Ru/Cs-USY was identified as the most active and selective catalyst for isomerisation of methyl linoleate to CLA at 165 °C[5]. Interestingly, no hydrogen pre-treatment of the catalyst or addition of H-donors is required to achieve industrially relevant isomerisation productivities. Moreover, the biologically most active CLA isomers, viz. c9,t11, t10,c12 and t9,t11, were the main products. Catalyst characterization with CO-chemisorption, EXAFS measurements, TEM analysis and TPO, reveals highly dispersed RuO₂ species in Ru/Cs-USY. It is assumed that such clusters in reaction conditions are transformed into highly dispersed Ru metal clusters via a reaction of autoxidation of methyl linoleate by Ru-O. Conjugation seems to be performed by means of hydrogen transfer between the fatty acids and the active Ru metal clusters on the catalyst, i.e. according to a classical Horiuti-Polanyi mechanism, since cis,trans CLAs at positions 9,11 and 10, 12 were shown to be primary products converted consecutively into trans,trans isomers with double bonds at the same and finally other positions.

The Ru/USY catalyst was also tested in the isomerization of vegetable oils. Because of the particular synthesis procedure, extra mesopores are created in the USY support facilitating transport of the bulky triglyceride molecules to the active centers of the catalyst[6]. As an example, the isomerization of safflower oil at 180 °C under N₂, yielded after 2 hours 75 mg CLA/g oil with a very high specific yield, viz. 377 g(CLA)/(g(metal).h). Moreover, only very low amounts of undesirable C18:1 trans were analyzed.

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SUPPORTED IONIC LIQUID PHASE CATALYSIS WITH SUPERCRITICAL FLOW

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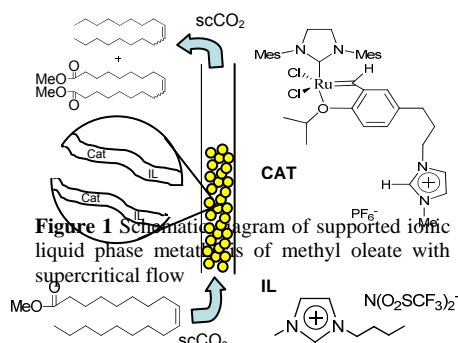
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The separation of catalysts from the solvent and reaction products remains one of the major disadvantages of homogeneous catalytic reactions, which are otherwise advantageous because of their high activity, tuneable selectivity and ease of study. In recent years a large number of different strategies has been employed to address this problem.^{1, 2} Ideally, the reactions would be carried out in continuous flow mode with the catalyst remaining in the reactor at all times, whilst the substrates and products flow over the catalyst. A variety of continuous flow reactions has been proposed,³ but in this presentation we shall highlight the use of supported ionic liquid phase catalysts, over which the substrates flow dissolved in supercritical carbon dioxide (scCO₂). The products are also removed by the flowing scCO₂ stream.⁴

The catalyst is supported within a thin film of an ionic liquid supported within the pores of a microporous silica. This catalyst is then placed in a tubular flow reactor, similar to that used for heterogeneous reactions. The use of pressurised CO₂ as the transport medium offers certain advantages, including:

- A wider substrate selection than is possible for all gas-phase reactions;
- Lower solubility of the ionic liquid and the catalyst in the flowing phase than when using all liquid flow;
- Better transport of gases to the catalytic centres than for liquid flow;
- Fast diffusion of all species to the catalytic centres;

Potentially, these advantages allow for high reaction rates, high rates of transport of substrate over the catalyst and low leaching of both the catalyst and the ionic liquid. We shall describe work on various different reactions including metathesis⁵ (see Figure 1), nowadays considered as one of the most powerful synthetic tools in organic chemistry, as well as discussing effects of different reactant parameters – pressure, flow rates etc. on the reaction activity, as well as on the lifetime of the catalyst.



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Optimizing wax ester production in oil seed-crops

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The use of plant oilseed crops for the production of chemicals of industrial value has received increased attention in light of diminishing resources of fossil hydrocarbons. Of particular interest for technical applications are lubricants that are characterized by thermic stability and constant lubrication properties over a wide temperature range. A class of hydrocarbon-based chemicals with desirable lubrication properties are wax esters. Only few plant species, such as jojoba (*Simmondsia chinensis*), naturally produce wax esters, so in order to produce wax esters on a large scale in oilseed crops a suitable reaction sequence must be established by transgenic technology. Wax esters can be formed from plant-endogenous fatty acids by action of fatty acid reductase (FAR), which reduced fatty acids to their corresponding fatty alcohols, followed by wax synthase (WS), which condenses a fatty acid and a fatty alcohol to form the wax ester. For different industrial applications, wax esters of varying chain lengths are desirable and, thus, one task is to isolate FAR and WS enzymes with suitable catalytic specificities. Another task is to ensure proper cooperativity of FARs and WSs in the host organism in order to maximize catalytic efficiency. Here, the interplay of FARs with WS is systematically tested to optimize wax ester production. Enzymes from different biological sources have been identified and introduced in yeast (*Saccharomyces cerevisiae*) to establish wax ester production. Rational modification of enzymes has been attempted to optimize the interplay of FARs and WSs with the aim to provide a range of possible combinations tailored to the production of different species of wax esters. This project is supported by the EC FP7 project “Industrial Crops producing added value Oils for Novel chemicals” (ICON).

Pathways for the chemo-catalytic transformation of sugars

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The crude oil-based society as we know it is drawn to a close since peak oil will be reached soon. The utilization of biomass to replace crude oil as a feedstock is essential to maintain the current status in energy management, mobility and industrial production. Especially cellulose and cellulose derived sugars present a promising feedstock for the production of novel platform chemicals and biofuels.[1]

Different pathways for the valorization of cellulose are possible. Therein, the direct transformation of cellulose via hydrogenolysis catalyzed by supported metal catalysts gives access to sugar alcohols such as sorbitol. Analyzing reaction kinetics and the impact of the catalyst on product selectivity, the reaction can be optimized to yield the dehydration products of sorbitol such as sorbitan and isosorbide. For instance, simple combination of silico tungstic acid with supported ruthenium catalysts for the hydrogenolysis of cellulose in water yield – dependent on the reaction conditions and the acid to metal ratio – up to 40 % sorbitol or even 20 % isosorbide in a simple one-pot reaction.[2,3]

Isosorbide is a colourless solid with a low melting point of 60-63 °C that decomposes at a temperature higher than 270 °C. This compound is discussed as potential platform chemical derived from cellulose.[4] By addition of aliphatic compounds to the hydroxyl groups the intermolecular hydrogen bonds between the hydroxyl groups are avoided, resulting in a lower melting and boiling point. Additionally, such a substitution increases the energy density of the substance by reducing the relative oxygen content. Isosorbide dimethyl ether is a commercially available chemical that is produced by etherification of isosorbide with chloromethane according to the Williamson ether synthesis. So far, only few works on the synthesis of other isosorbide alkyl ethers using the same method have been published, but no work on the chemo-catalytic etherification of isosorbide, e.g. for the formation of tert-butyl ethers of isosorbide has been described. Instead of halogen compounds in the Williamson ether synthesis also alkenes or alcohols can be used as reagents. In this work, we present the results of the transformation of cellulose into sugar alcohols as well as the etherification of isosorbide with isobutene and tert-butanol using solid catalysts.

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Transformation of terpenes into fine chemicals

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The chemical industry has flourished in the 20th century due to the massive supply of cheap crude oil. However, in the meantime growing concerns about the dependence on imported oil and the awareness that the world's oil supplies are not limitless have prompted interest in exploring nature's richness of plant sources. Plants offer enormous potential as cost-effective, unlimited, environmentally-friendly production systems that make efficient use of light energy and supply raw materials for the production of fuels, bulk and fine chemicals. One of the largest and most diverse class of organic compounds produced by all plants are the terpenes. They are derived biosynthetically from isoprene units which consist of five carbon atoms. Due to their high abundance they have attracted attention as a class of natural products that can be converted into novel and valuable compounds commercially important for the industrial production of fragrances, perfumes, flavours, and pharmaceuticals as well as useful synthetic intermediates and chiral building blocks. The lecture reviews the use of terpenes available from renewable resources in the fine chemicals industry. Chemical and biotechnological approaches will be highlighted.

Sustainable Fatty Acid Derivates

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Sustainability means securing quality of life for a growing world population on the long run. This objective can only be achieved, if we reduce the environmental footprint of our production processes and products while at the same time we increase welfare in the poor and developing countries.

Resource efficiency, health and nutrition and globalization of technologies, the three megatrends Evonik Industries AG is focusing on, can contribute to this societal goal. To achieve it, however, we have to set clear targets. Evonik set targets for its specific CO₂ emissions, specific water consumption and specific waste production.

In 2008 we founded our Science-to-Business Center Eco2, where we develop new systems solutions for increasing resource efficiency. The Science-to-Business Center Eco2 has developed the new CFE-Methodology (Carbon Footprint Estimation) to estimate the carbon footprint of new products, processes and applications in very early stages of development as part of our effort to take into account sustainability criteria early on. The methodology will be explained and sustainability aspects of fatty acid derivatives like emollient esters and of production processes like the biodiesel production will be discussed.

Lipophilic Antioxidants from Fatty Acids

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Antioxidants retard the undesired oxidation of fatty acids to hydroperoxides. Thereby radical intermediates are converted into less reactive species that discontinue the chain reaction. Antioxidants can be hydrogen donating compounds or reducing agents, whereby the first ones can be phenols, the second ones enediols. Fatty phenols were prepared as conjugates of phenols and fatty acids; fatty enediols were synthesized by introducing the enediol - structure into the fatty acid chain.

Conjugates of fatty acids with phenols: The conjugates were prepared by a thermal Claisen rearrangement of allyl phenyl ethers. These ethers were made from fatty allylic alcohols that were obtained by either photooxygenation of unsaturated fatty acids or by isomerization of methyl ricinoleate. The phenoxy group was introduced by a Mitsunobu reaction with phenolic nucleophiles, DEAD and triphenylphosphine or by palladium(0)-catalyzed substitution of fatty allyl carbonates with different phenols. The thermal Claisen rearrangement of the allyl aryl ethers at 150°C to 175°C afforded the corresponding methyl 11-aryl-9-octadecenoates and their regioisomers in 52 - 90 % yield. Furthermore methyl oleate could be arylated in a simple one-step reaction with p-cresol in presence of conc. sulfuric acid at 100 °C, which afforded methyl 2-hydroxy-5-methyl-phenyloctadecanoate and three regioisomers in 46% yield. The activities of the antioxidants were determined with the Rancimat-test. The conjugates with p-cresol and p-hydroquinone methyl ether attached to methyl octadecenoate and octadecanoate were more efficient than the commercial antioxidants: α -tocopherol, t-butylhydroquinone or t-butylhydroxyanisol. The results of further Rancimat-tests are presented and discussed in relation to the structure of the antioxidant.

Fatty acids with reducing properties as antioxidants: Phenoxy radicals can be reduced by L-ascorbic acid (vitamin C). This way the cycle of a fatty acid oxidation to peroxides can be interrupted. The use of vitamin C is limited, because it is a hydrophilic compound that cannot penetrate the cell membrane and is only sparingly soluble in lipophilic media. To overcome this solubility problem we synthesized lipophilic reducing agents from fatty acids. Potential reductones were: methyl 9-oxo-10-hydroxy octadecanoate, methyl 9-oxo-10,11-dihydroxy octadecenoate and methyl 9,12-dimethoxy-9,11-octadecadienoate. They were prepared by epoxidation of methyl oleate and oxidative epoxide ring opening or photooxygenation of methyl ricinoleate. Their activity as antioxidant can be estimated from their reduction potential that was determined by cyclic voltammetry. The reduction potentials of the reductones are discussed in relation to their structure.

Conclusion: Phenols of different structure were covalently attached to methyl oleate. The antioxidant activity was determined with the Rancimat-test. The activity is partly substantially higher than this of the commercial antioxidants α -tocopherol or t-butylhydroxyanisol. In methyl oleate or methyl ricinoleate α -hydroxy- β -ketone structures could be integrated; their reduction potential is partly close to L-ascorbic acid that indicates lipophilic reductone structures with a similar activity as vitamin C.

Support by the Fachagentur Nachwachsende Rohstoffe is gratefully acknowledged.

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New Generation Cationic Amphiphiles for Use as Surfactants and Ionic liquids

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The use of cationic amphiphiles as ionic liquids and surfactants continues to increase with time. Ionic liquids are considered to be room temperature liquid organic salts that find countless applications in varieties of fields [1-5]. Similarly, cationic amphiphiles have great potential in varieties of fields like emulsion polymerization, liquid crystals, oil recovery and protection of metals from corrosion, road repair, mineral flotation [6], household detergents and fibers [7]. Cationic amphiphiles also have biological applications, they show antimicrobial activity and several cationic surfactants are also used in DNA extraction methods [8]. With the continuation of our work on surfactants [9-14] several new ester functionalized heterocyclic cationic amphiphiles and ether functionalized short chain ionic liquids have been synthesized. Ring opening of methyl 9-(oxiran-2-yl)nonanoate and epihalohydrins(chloro and bromo) by imidazole and short chain alcohols in the presence of zincperchlorate hexahydrate catalyst gives valuable intermediates viz., methyl 10-hydroxy-11-(1H-imidazol-1-yl)undecanoate and β -hydroxyhaloethers respectively. The intermediate methyl 10-hydroxy-11-(1H-imidazol-1-yl)undecanoate on reacting with different alkyl dibromides and haloalkanol at 80°C give valuable renewable gemini and monomeric cationic imidazolium amphiphiles respectively. Similarly, on reacting the β -hydroxyhaloethers with N-methylimidazole at 80°C give short chain ether functionalized imidazolium ionic liquids. The surface properties of these new cationic amphiphiles like critical micelle concentration (cmc), Γ_{max} (maximum surface excess), A_{min} (minimum surface area/ molecule), C20 (surfactant concentration required to reduce the surface tension of the solvent by 20 mN•m⁻¹), Gibbs free energy of the micellization ($\Delta G_{0\text{mic}}$) and Gibbs free energy of adsorption ($\Delta G_{0\text{ads}}$) have been measured by surface tension and fluorescence and electrical conductivity method. TGA (thermogravimetric analysis) technique has been used to explore the thermal behavior of these new short chain and long chain cationic amphiphiles.

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Epoxidation with hydrogen peroxide of unsaturated FAMES over Nb(V)-silica catalysts (D)

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Pure alpha-monoglycerides (MGs) , and glycerol carbonate esters (GCEs) are two families of lipochemical molecules composed of a polar building block, glycerol for MGs, glycerol carbonate for GCEs, and a fatty acid lipophilic part. These molecules glycerol derived take part to the valuation of the produced glycerine in the process of lipochemical synthesis such as that of the biodiesel.

From a chemical point of view, MGs include 2 free oxygen in the hydroxyl functions and one ester function between the fatty acid and the glycerol parts, GCEs contain 2 blocked oxygen in the cyclic carbonate backbone and 3 esters functions, 2 endocyclic in the five-membered cyclic carbonate function , 1 exocyclic between the fatty acid and glycerol carbonate parts. At the physico-chemical level, MGs and GCEs³ are bifunctional molecules with amphiphilic structures: a common hydrophobic chain to the both families and a polar head, glycerol for MGs and glycerol carbonate for GCEs. The physico-chemical properties of these both families of oleochemical biomolecules, containing chain lengths comprised between 7 and 18 atoms of carbon, are determined and compared. Differential scanning calorimetry and optical polarized light microscopy allow us to highlight the self-assembling properties of the glycerol carbonate esters alone and in presence of water. We demonstrated by thermal analysis the polymorphic behaviour of GCEs, and the correlation between their melting points versus the chain lengths. The solvo-surfactant character of MGs and overall GCEs were discussed through the measurements of critical micellar concentration (CMC) or critical aggregation concentration (CAC). These surface active glycerol/glycerol carbonate esters were classified following their hydrophilic/hydrophobic character correlated to their chain length ($\text{LogP octanol/water} = f(\text{atom carbon number})$). To conclude, polymorphic GCEs present a different sensitivity than MGs to the cooling rate (controlled phase behavior). Carbonation decreases melting points : 2 OH functions of MGs involved in intra and intermolecular hydrogen bonds. Carbonation decreases the hydrophilic character of the polar head of surface-active GCEs.

Functional group metathesis polymerization of biorenewable feedstocks

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Olefin metathesis polymerization is an established route for converting olefins into polymers with an all-carbon mainchain. We have applied the principles of Acyclic Diene Metathesis (ADMET) polymerization to the development of an analogous methodology that converts acyclic bisacetals into high molecular weight polyacetals. This Acetal Metathesis Polymerization (AMP) approach is a general method for converting diols—especially those from biorenewable triglycerides—into polymers particularly degradable via acid-catalyzed hydrolysis [1]. Thus, the polymers have sustainable origins and are designed to degrade even in the absence of microbial action (abiotic degradation). The AMP process is a subset of a generalized carbon-oxygen metathesis (COMET) polymerization method that our group has successfully applied to other functional groups, yielding a variety of novel polymeric structures derived from sustainable monomers—but designed to replace petroleum-based plastics.

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Strategies for polymerizing cyclohexadiene from plant oils

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Polyunsaturation in plant oils provides options for the renewable-based synthesis of cyclic dienes. Initially, metathesis reactions with soybean oil, corn oil, and canola oil were conducted in the absence of organic solvents to form 1,4-cyclohexadiene (1,4-CHD). These reactions required low catalyst loading, no plant oil purification, and simple product recovery by distillation. After treating soybean oil with a ruthenium metathesis catalyst, the resulting 1,4-CHD was isomerized with a ruthenium hydride (RuH) catalyst. The isomerization reaction was conducted for 1 h in neat 1,4-CHD with [1,4-CHD]/[RuH] ratios as high as 5000. The isomerization and subsequent polymerization of the renewable 1,3-CHD was examined as a two-step sequence and as a one-step cascade reaction. The polymerization was catalyzed with a nickel(II) catalyst in neat monomer, hydrogenated d-limonene, and toluene.

Vegetable-based building-blocks for the synthesis of renewable polyurethanes and polyesters

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Due to the depletion of petroleum resources and their escalating prices, polymer chemists have turned their attention to obtain monomers and polymers from renewable resources.¹ Plant-derived fats and oils bear a large potential as substituents of currently used petrochemicals. Vegetable oils have a large potential to substitute currently used petrochemicals, thanks to their availability, sustainability and biodegradability. Vegetable oils bring different functional groups (ester functions, double bonds) that can be derivatized to design new functional building-blocks for the synthesis of novel polymers. Many recent efforts have been directed towards replacing entire or part of petroleum-based polyols as main precursors of polyurethane (PU) and polyester materials.

First, this presentation will focus on the synthesis of new diols, from castor and sunflower oils, containing ester, esteramide and amide linkages through transesterification, amidation and thiol-ene reactions. A series of amorphous and semi-crystalline polyurethanes and polyesters have been obtained that exhibit different thermo-mechanical features with respect to the diol structure. ^{2,3} The relationship between the diol structure and the properties of the so-formed polyurethanes and polyesters will be presented and discussed in the light of DSC, DMA, TGA and X-ray analyses as well as tensile experiments.

Second, this presentation will present non-isocyanate and greener pathways to PU. A first route deals with the reaction between diamines and biscarbonates, the latter obtained by reaction of the fatty ester bis-epoxides.⁴ A second route concerns a unique approach to the synthesis of PU through the self-polyaddition of new monomers containing acyl azide-hydroxyl functionalities.⁵ The structure-property relationship of these various monomers and the respectively so-formed polyurethanes will be also discussed during the presentation.

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Impact of functionality on properties of vegetable oil-based thermosetting coatings

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Highly functional polyol resins of sucrose esters derived from soybean oil were synthesized and the properties of thermosets were determined after crosslinking with a commercial melamine-formaldehyde (MF) resin using an acid catalyst. As controls, a commercial soybean oil polyol resin and a typical commercial polyester polyol were used. A series of thermosets were made using MF loadings of 20%, 25%, 30% and 35% (wt. polyol) for all polyols studied. The high functionality of polyols from sucrose esters afforded much higher crosslink densities than the controls as determined by dynamic mechanical analysis (DMA). Interestingly, the storage moduli (E') of sucrose ester-based thermosets was about an order of magnitude higher than that of the soybean oil-based thermosets. The glass transition temperature (T_g) of sucrose ester-based thermosets was about 90°C higher at 35% MF loading compared to the soybean-oil which was attributed to the high crosslink density. Coatings properties were also determined and the sucrose ester-based thermosets were found to be much harder in terms of König and pencil hardness versus the soybean oil thermosets and had a comparable hardness to the commercial polyester thermosets.

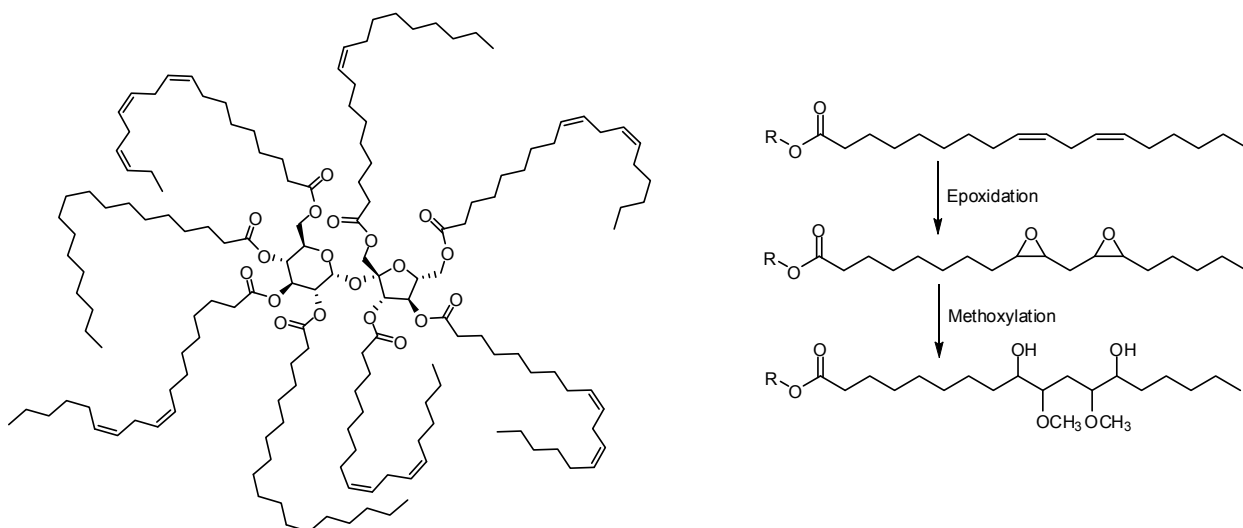


Figure 1. Sucrose soyate (left) and sucrose soyate polyol formation process (right).

Oleochemicals in Personal Care Industry

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Oleochemicals have been used for personal care applications for a very long time. Since the ages of soap boiling the know-how increased more experience in specialty chemistry based on natural, renewable raw materials has been gathered.

Currently we face a demand for sustainable solutions in several industries, for the personal care market a focus on ingredients made from renewable resources can be recognized. The use of nature based ingredients is favored by many cosmetic companies, although there are different approaches how far the use of renewable resources based ingredients is followed. Suppliers of cosmetic ingredients are providing different solutions for these approaches. Besides the trend towards more sustainable formulations it is common understanding that there is no willingness to compromise on performance. Every new nature based product is competing with the performance of existing solutions and has to be convincing to the market.

In this lecture several examples for the utilization of natural, renewable raw materials in personal care ingredients will be presented. It will be shown how chemical conversions, product performance tests and formulation requirements complete each other in the product development process and finally lead to a convincing package for the customer.

Glycerol-Based Polymers Bearing Acetal and Carbonate Groups: Switchable physical and thermal properties

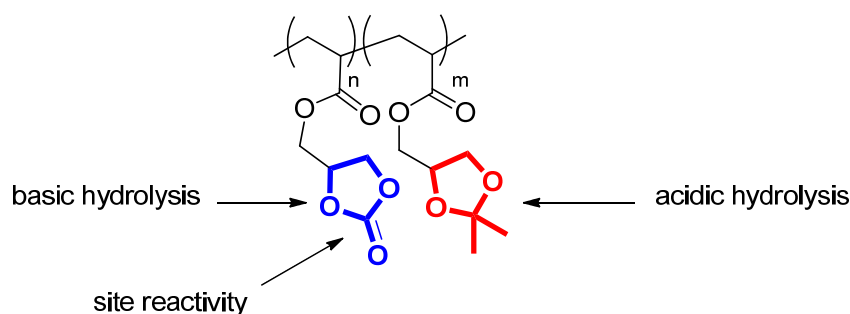
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A major scope of our team is the chemical modification of the vegetable oils^{1,2} and their derivatives including glycerol.³ This communication deals with the valorization of glycerol derivatives: Solketal Acrylate (SolA) and Glycerol Carbonate Acrylate (GCA) in polymer field. In order to overcome the poor solubility of the polyGC in the common organic solvents, two approaches have been investigated: i) the synthesis of low mass polymers (oligomers) by radical telomerization, and ii) the copolymerization of GCA with SolA using the high SolA solubility. Several oligo(GC-*stat*-Sol)s were synthesized by varying GCA/SolA ratio. The kinetic studies have been carried out identifying the reactivity of acetal and cyclocarbonate-based monomers in the radical telomerization process and determining the transfer constant of telogen agent (2-mercaptoethanol) in both cases. In conclusion, the incorporation of SolA in GCA structure by cotelomerization solved GCA problem of solubility as well as offered a large scope in the thermal behavior. On the one hand, selective hydrolyses of cyclocarbonate and acetal protective groups of glycerol-based oligomers were performed under acidic and basic conditions. By this methodology, functionalized (co)telomers were synthesized with alcohol, cyclocarbonate and/or acetal pendant groups. The influence of each one on Tg value and the solubility was clearly demonstrated. On the other hand, the cyclocarbonate group permitted to obtain various branched polymers by modification of this reactive site with nucleophilic reagents.



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Formic acid as hydrogen donor molecule in the glycerol hydrogenolysis to 1,2-propanediol

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Biodiesel production from vegetable oils through transesterification processes cogenerates glycerol at an approximate rate of 1 kg for every 10 kg of biodiesel. Excess glycerol disposal is an expensive and environmentally problematic process, especially in this new era of green chemistry in which the waste concept needs to be changed by the idea of raw material. One promising and valuable compound that can be obtained from glycerol is 1,2-propanediol (1,2-PDO). 1,2-PDO is widely used as an anti-freeze agent, as a monomer for polyester resins and in paints, cosmetics, food, etc [1]. Glycerol hydrogenolysis to obtain 1,2-PDO involves C-O bond dissociation and simultaneous addition of hydrogen [2]. In our previous works, it was observed that in situ production of hydrogen under inert atmosphere via catalytic transfer hydrogenation was a promising process for glycerol hydrogenolysis, avoiding expensive and dangerous high pressure processes with molecular hydrogen [3]. Moreover, Ni and Cu based catalysts and formic acid as hydrogen donor revealed to be suitable for the system.

The objective of this work was the development of a semi-continuous process for glycerol hydrogenolysis to obtain 1,2-PDO under N₂ atmosphere using Ni-Cu/Al₂O₃ catalysts. In order to achieve this objective, four main tasks were fulfilled. (i) The experimental batch reactor set-up, that allowed continuous addition of formic acid and liquid sampling during the reaction time, was designed and tuned up. (ii) The optimized Cu:Ni ratio, in the range of 0.7, was obtained by testing different catalysts, prepared by sol-gel method with constant metal content and different metal ratio. Moreover, deep characterization of the catalysts by N₂-physisorption, transmission electron microscopy (TEM), temperature programmed reduction (TPR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), together with activity and selectivity results allowed deeper understanding in the role played by Cu and Ni. This characterization showed that Ni ended well dispersed and with a significant interaction with the support. The optimum Cu:Ni ratio seems to be controlled on the one side by the activity of Ni in transfer hydrogenation between formic acid and glycerol and on the other side by the accelerated C-C bond cleavage with increasing Ni content. (iii) The optimized Cu + Ni metal content, around 35 wt. %, was obtained by preparing and testing several catalysts with constant metal ratio

but different metal content. The results from the catalyst characterization and activity tests indicate that not only metal sites, but also acid sites play a role in the transfer hydrogenation process. It is suggested that 1,3-dihydroxy isopropoxide formation, an intermediate alkoxide in glycerol conversion to 1,2-PDO, occurs on the acid sites of the alumina support. Previous studies in catalytic transfer hydrogenation by in situ spectroscopy analyses already observed the role of alumina support in the alkoxide formation [4]. (iv) Activity tests performed with the optimized catalyst (20Ni-15Cu/Al₂O₃, 200-220 °C, 45 bar N₂ pressure, 4 wt-% of glycerol in 135 ml aqueous solution) revealed a decreasing glycerol reaction rate with time due to competitive adsorption of 1,2-PDO on catalytically active sites. All these information were used to optimize the process, achieving 90 % glycerol conversion with 80 % selectivity to 1,2-PDO after 24 hours reaction time in semi-batch operation.

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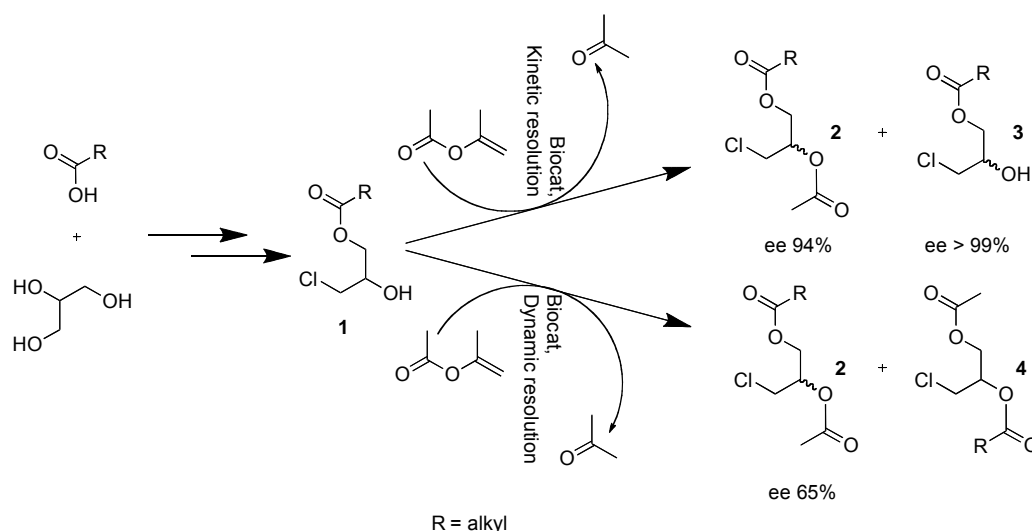
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Preparation of asymmetric chlorohydrin esters from glycerol

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Chlorohydrin esters have been used in the preparation of drugs, surfactants, epoxides, allyl esters and epichlorohydrins. Some of them can be synthesized from crude glycerol, a by-product from the biodiesel industry. Our research group has already developed new procedures to prepare racemic chlorohydrin esters from glycerol and carboxylic acids or fatty material. All these facts prompted us to investigate the preparation of asymmetric chlorohydrin esters by using both kinetic and dynamic kinetic biocatalytic resolutions of the corresponding racemates. Starting from these racemic mixtures the preparation of the corresponding enantiomers was studied using methylvinyl acetate, various chlorohydrin esters (1) and biocatalysts, and several reaction conditions. Finally, we obtained 2-acetoxy-3-chloropropyl 1,1-dimethylphenylacetate (2) with a 94 % enantiomeric excesses (ee) ($E = 42$). The corresponding 3-chloro-2-hydroxy-1-propyl alkanoate (3) presents an ee >99%. A rearrangement process was observed using a dynamic kinetic resolution. In consequence, the 2-acetoxy-3-chloropropyl pivaloate (2) was synthesised with a 100% conversion and 65 % ee.

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Novel catalysts derived from hydrothermally synthesized phyllosilicates for the selective preparation of glycerol ethers or esters

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The increasing availability of glycerol coupled to its high functionalization possibilities makes it one of the most promising platform chemicals of the near future. In fact glycerol is the by-product with the largest economic impact in the modern oleochemical industry, being formed in numerous processes. Among the large panel of applications, the selective synthesis of polyglycerols (PGs) followed by polyglycerol esters (PGEs) preparation is gaining more importance. These products, because of the possibility of controlling their hydrophilic-lipophilic balance (HLB) are of great interest in cosmetics, food and pharmaceutical industry. The synthesis of PGs starting from glycerol and esterification of PGs are generally carried out in the presence of homogeneous basic catalysts (eg. Na_2CO_3). However, active solid base catalysts that are selective and easily recovered/recycled are better suited for environmentally friendly catalytic processes. Recently, alkaline earth based oxides/hydroxides have been emerging as heterogeneous catalysts for the etherification of glycerol to polyglycerol. For example, Mg supported or incorporated in MCM-41-based materials were successfully used as catalysts for this reaction, despite significant amount of acrolein (side product) was generated for some of them. Moreover, rather long reaction times were necessary for Mg incorporated MCM-41 catalysts to reach a significant glycerol conversion even at high temperature (260 °C). Very recently, it was also observed that alkali earth based oxides readily reacted with glycerol, which resulted in the formation of the corresponding metal-glyceroxide phases during glycerol etherification reaction.

We therefore evaluated the ability of hydrothermally synthesized Mg-containing phyllosilicates as novel catalysts to increase the catalytic performances (selectivity and stability) for glycerol etherification to polyglycerols. Such phyllosilicates (PS) are layer structured materials and are mostly represented as 1:1 or 2:1 phases. In 1:1 phyllosilicates, each layer consists in one tetrahedral sheet (with tetracoordinated cations) and one octahedral sheet (with hexacoordinated cations). In the case of 2:1 phyllosilicate type, the octahedral sheet sandwiched in between two tetrahedral sheets.

We will show that these new Mg-based phyllosilicates, in particular the 1:1 analogs, are more active in the selective synthesis of glycerol ethers or esters than the previously used catalysts, while keeping a high selectivity to a (di-tetra glycerol) fraction. We will also demonstrate that such Mg 1:1 PS phases are reusable, which is also a crucial property in catalysis.

Acknowledgements

This work was supported by ANR under the NANOCAT consortium (ANR-06-MAPR-0023-01). The author (MVS) gratefully acknowledges the CNRS/ANR for the awarding of postdoctoral fellowship.

New routes for the catalytic valorisation of biomass-derived oxygenates

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The sustainable production of valuable bulk chemicals from biomass as an alternative to petrochemicals is an important and pressing scientific challenge. New routes have to be found and new catalysts have to be developed to convert the renewable platform molecules that can be obtained from various biomass sources into existing ('drop-in' replacements) or new products. (Poly)saccharides, alcohols, polyols, glycerol in particular, fatty acids and lignin-derived phenols all offer many opportunities for valorization. We have been exploring different catalytic routes for the valorization of glycerol and other renewable oxygenates, including Pd-catalyzed telomerization and solid-acid catalyzed etherification for the production of cosmetics additives or non-ionic surfactants. Other routes, involving oligomerization and conversion to renewable monomers for the polymer industry are also under study in our laboratory. Alternatively, glycerol and other sugar alcohols can also be selectively converted to hydrogen via so-called aqueous phase reforming. Indeed, many of the routes proposed for the valorization of renewable platform molecules involve a hydrogenation step, for which the hydrogen should preferably be renewably produced. Here, we present our recent results on the catalytic conversion of glycerol and other oxygenates to valuable bulk chemicals and hydrogen. Emphasis will be on catalyst development, mechanistic insights, heterogenization of the catalyst and capability to cope with real feeds, such as crude glycerol.

The relevance of the anhydride reaction pathway for selective deoxygenation of stearic acid in the absence of H₂

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Introduction:

The aim of this research is to develop a new, low temperature catalytic decarboxylation procedure for (unsaturated) fatty acids in the absence of external hydrogen. This should not only result in the formation of 2nd generation biodiesel with superior fuel properties, but also generate new feedstocks for high value chemicals production. Obtaining new insights in the deoxygenation reaction pathways is expected to be essential to improve catalyst performance.

Experimental:

Metal supported oxidic materials are used as catalyst, which offer the advantage of thermal regeneration. At this stage, Pd/Al₂O₃ catalyst was investigated in the deoxygenation reaction of stearic acid using dodecane as solvent at 7 bar N₂ pressure.

Results:

We report on strong indications for the existence of stearic anhydride as reactive intermediate in the hydrogen free deoxygenation of stearic acid at a relative low reaction temperature of 523 K. Since stearic anhydride is readily converted under reaction conditions, the rate limiting step in the formation of unsaturated C₁₇ hydrocarbons would be the in-situ formation of stearic anhydride. Stearic anhydride decarbonylation is shown to also proceed at 473 K which creates new openings for a novel low temperature decarbonylation reaction by stimulation anhydride formation from stearic acid at this low reaction temperature. Model reactions also show that ketonization to stearone proceeds via the same stearic anhydride intermediate and that decarbonylation-dehydration via 1-octadecanol does not occur under these conditions.

Overall, the knowledge of the existence of stearic anhydride as reactive intermediate in the decarbonylation and ketonization reaction could be a key in improving catalyst performances and in tuning product selectivities towards paraffins or olefins.

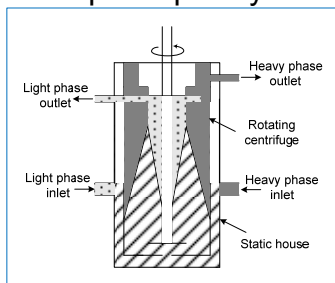
ETHANOLYSIS OF *JATROPHA CURCAS* L. OIL IN A CENTRIFUGAL CONTACTOR SEPARATOR

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Biodiesel is an alternative fuel that can be produced from organically derived oil or fats which has received significant attention due to its numerous benefits and applications [1]. Production of biodiesel via transesterification with alcohol and catalyst has been extensively studied [2]. New reactor and process conditions have also been developed since the last decade such as Centrifugal Contactor Separators (CCS) that efficiently intensified reaction and separation of liquid-liquid systems.



Scheme 1 A schematic diagram of a CINC. Dark and light grey areas represent the heavy and light liquid whereas the hatched area corresponds to the dispersion.

We have previously demonstrated the potential application of CCS type CINC V-02 to produce fatty acid methyl ester (FAME) from sunflower oil and methanol with a reproducible yield of 96 %-mol [3]. In comparison to methanol, ethanol has a better solvent properties, lower toxicity, higher heat content and cetane number and can be obtained from renewable resources. Currently, there is a growing interest to use ethanol, as it is mainly derived from agricultural production [4]. This study tries to explore the potential application of *Jatropha curcas* L. and ethanol to produce biodiesel in a centrifugal contactor separator (CCS). The effect of flow rates, rotational speed, catalyst concentration and molar ratio of ethanol: oil was investigated. An optimized yield of 98 %-mol fatty acid ethyl ester (FAEE) was achieved at an oil feed rate of 28 ml/min with six-fold molar excess ethanol containing 1 %-w/w/of sodium ethoxide with respect to the oil. The system was operated at a jacket temperature of 70 °C and a rotational frequency of 35 Hz. The corresponding volumetric productivity of FAEE was higher as compared to a conventional batch process.

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An assessment of the potential of critical fluids to support sustainable integrated biorefining, with a focus on oleochemistry

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Daniel Pioch³

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Integrated biorefining is an emerging concept that is analogous to refining and fractionation of petroleum oil except the substrate is biomass, and it is envisioned that full utilisation of biomass will reduce the global dependence on fossil carbon.

Processing sustainable renewable biomass requires technology which itself does not elicit an environmental footprint, therefore the choice of solvents is important.

Critical fluids, in particular sub-critical water (SCW) and supercritical carbon dioxide (SCCO₂) are considered 'green' environmentally benign solvents and have been used, successfully, for extraction of a range of biomass derived compounds but have also been shown to support catalytic reactions mediating hydrolysis and synthesis.

In this work we investigate the versatility of critical fluids as solvents to support integrated processing of rice bran, which is dominated by lignocellulose, and rice bran oil which is composed of triacylglycerols. Both substrates are considered 'models' components of biomass therefore providing the opportunity to evaluate the impact of parameters such as pressure, temperature and residency time on processing efficacy. Conducting multi-factorial experiments, using a central composite rotatable design for both batch and continuous flow SCW mediated hydrolysis of rice bran and rice bran oil, illustrated the overall efficiency and efficacy of the medium to support the breakdown of -lignocellulosic oleaginous- biomass into its constituent biopolymers, cellulose, and hemicellulose but also the structurally diverse, triacylglycerols into glycerol and free fatty acids. Results indicate that both carbohydrate polymers and triacylglycerols can be efficiently hydrolysed within 1 hour.

Having assessed the utility of critical fluids to support the so called pre-treatment although a very important step, based on above results, and critical fluids having also shown convenient properties for the recovery and downstream transformation of intermediate products (i.e. free fatty acids bio-catalytically transformed to ethyl esters under continuous flow SCCO₂ environment), the data were combined, and using Superpro Desing, an Integrated multiple step simulation of the production costs of ethyl esters was generated. In summary our results and literature data illustrate the utility of environmentally benign critical fluids such as water and carbon dioxide, to enhance the use biomass and to support a new era of oleochemistry.

Abstracts

Part 2: Posters

Diesel fuel generation from fats and oils with homogeneous catalysts

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Introduction:

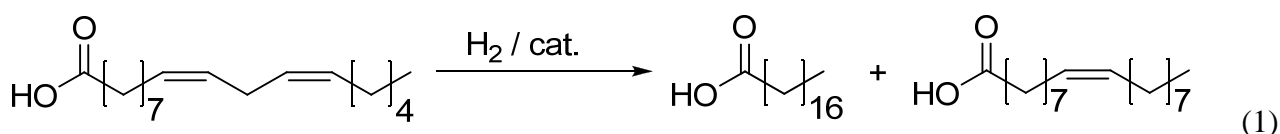
Natural fats consist of glycerol esters of long chain mostly unsaturated carboxylic acids. These Acids can be hydrogenated and decarboxylated to gain diesel fuels. Most popular example is Neste Oils NexBTL, which is produced in scales around two million tons per year. For these reactions heterogeneous catalyst and rigorous conditions (450 °C and 150 bar) are used. Using homogeneous catalysts can provide milder conditions like lower temperatures and pressures.

Aim:

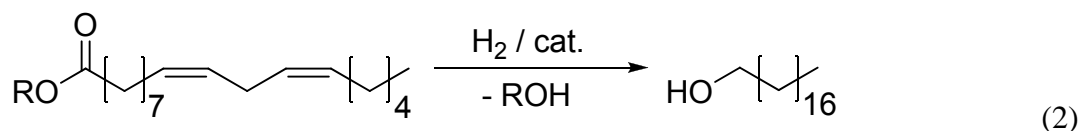
Conversion of fats and oils by hydrogenation and decarboxylation with homogeneous noble metal catalysts at essential milder conditions for different applications as hydrotreated vegetable oil.

Results:

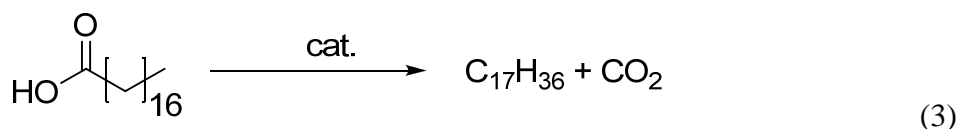
The reactions were studied by model compounds. Linoleic acid was hydrogenated as model compound for unsaturated fatty acids, using palladium nanoparticles as catalyst. It was found, that the nanoparticles provide a conversion of nearly 100 % with a gain of 47,5 % stearic acid and 52,5 % oleic acid at 20 bar hydrogen pressure and 80 °C. At the same conditions dispersed Raney-Nickel or activated palladium on carbon show a conversion around 100 % stearic acid. Using Tris(triphenylphosphine)-chlororhodium (Wilkinson's catalyst) leads to 33,4 % stearic acid [Eq.1].



Using the analog esters as substrates leads with Wilkinson's catalyst and palladium nanoparticles to the saturated ester. With Raney-Nickel or activated palladium on carbon as catalyst, fatty alcohols should be the product:



The decarboxylation was studied with stearic acid as model compound. Up to now, palladium nanoparticles and Raney-Nickel only showed low catalytic activity at high temperatures:



Palladium catalyzed C-H activation: a versatile method for the functionalization of fatty acid compounds

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The goal of this research was the functionalization of unsaturated fatty acid compounds via palladium catalyzed C-H activation. For this purpose methyl 10-undecenoate und methyl oleate were used. These compounds were functionalized with palladium(II)-acetate and acetic acid in DMSO as solvent. The catalyst system activates the allylic C-H bond, followed by reaction with acetic acid. The catalytic reaction of methyl 10-undecenoate resulted in a product mixture of linear, branched and ketone structure with high conversion. In opposite to the first reaction, the functionalized methyl oleate offered only one product though with a lower conversion.

Camelina oil as an alternative feedstock for oleochemicals production A catalytic treatment to improve the quality of polyunsaturated oil

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A growing interest in bioenergy and bioproducts at national and global level strongly promotes the use of renewable resources. A new example of alternative and sustainable oilseed plant is *Camelina sativa* (L.) Crantz, a member of the Brassicaceae family. It's an annual plant with both autumn and spring sowing cycle and capable to grown in different climatic condition and soil type. Due to its wide adaptability the cultivation is under expansion in different climate worldwide. Several *C. sativa* genotypes were grown in Northern Italy, in hilly marginal area at low agricultural input condition. Seed yield ranged from 0.4 to 3.4 t/ha with an oil content between 28 and 37%, depending of genotypes and annual climate conditions. This would give from 0.1 to 1 ton of oil/ha. Camelina oil is composed mainly by unsaturated fatty acids (FAs) and shows a specific pattern composition with different amounts among genotypes. The most abundant polyunsaturated FA is the linolenic acid (34% to 40% and more). The high level in linolenic acid is an issue for the use of camelina oil as raw material in chemical industry. Thus, the presence of three double bond not only influences oxidative stability but also leads to multiple products when the oil is subjected, e.g., to epoxidation or metathesis reactions.

Here we wish to report that a brush hydrogenation process, based on a non toxic and non-pyrophoric heterogeneous copper catalyst (Cu/SiO_2 , $\text{Cu}/\text{Al}_2\text{O}_3$) allows one to reduce the linolenic content to <1 % while increasing selectively the monounsaturated one.

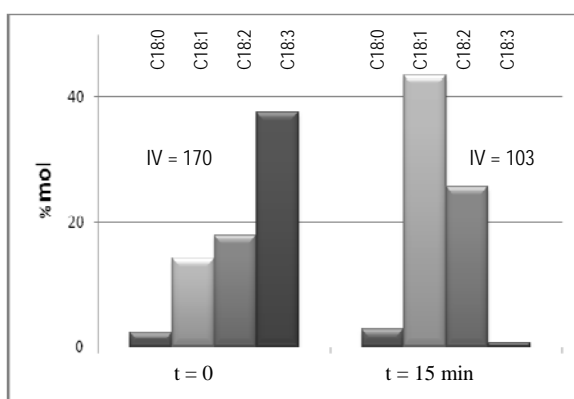


Figure 1 - Effect of the brush hydrogenation process on the C18 *C. sativa* var. calena methyl esters by using Cu/SiO_2 (180°C, 6 atm H_2).

These results showed that independently of camelina genotypes chosen, climate condition and FAs composition detected, the solid catalyst use improves the fatty acid esters quality traits and encourages the cultivation of this new oilseed plant as suitable renewable raw materials for biodiesel and oleochemicals production.

Optimization of Oil Extraction from Beniseed (*Sesame indicum*) Oilseed Using Response Surface Methodology and Quality Characterization

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Solvent extraction of oil from beniseed oilseed was investigated in this work. Response Surface Methodology (RSM) was applied to optimize effects of three independent variables, which include extraction time, solvent volume and sample weight on oil yield. The least square regression analysis, test of variance and the ANOVA test showed the model obtained to be significant ($p < 0.05$). All the linear, quadratic and cross-product terms were markedly significant at 95% confident level. The optimal extraction condition for the beniseed oil was established as extraction time of 50 min, sample weight of 30 g and solvent volume of 300 ml, which gave oil yield of 86.67% (w/w). Fatty acid profile of the oil showed that it contained 12.6% palmitic acid, 10.9% stearic acid, 32.1% oleic acid and 44.4% linoleic acid. The physicochemical analysis of the beniseed oil indicated physical state of the oil to be liquid/golden yellow, refractive index, 1.470, moisture content, 0.09%, specific gravity, 0.88, viscosity, 35.08 cP, acid value, 0.5 (mg KOH/g oil), saponification value, 190 (mg KOH/g oil), iodine value, 108 (g I₂/100g oil), peroxide value, 7.8 (meq O₂/kg oil), higher heating value, 40.02 (MJ/kg), cetane number, 50.73 among others. Hence, the oil could have important food and industrial applications.

Methanolysis of Beniseed oil to Biodiesel using Statistical Approach and Fuel Quality Characterization

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In this work, statistical approach was employed to optimize biodiesel production from beniseed oil. Specifically, Response Surface Methodology (RSM) was applied, and the effects of four factors viz. reaction temperature, catalyst amount, reaction time and methanol/oil molar ratio, and their reciprocal interactions were determined. Central Composite Rotatable Design (CCRD) was used to generate a total of 30 individual experiments, which were designed to study the effects of these factors during alkaline-catalyzed methanolysis of beniseed oil. Optimum beniseed biodiesel yield of 95.86% (w/w), at the following conditions: reaction temperature of 70 oC, a catalyst amount of 0.7 wt. %, and a methanol/oil molar ratio of 8, with a reaction time of 60 min was obtained. The fuel properties of biodiesel produced such as moisture content, specific gravity, viscosity, acid value, saponification value, iodine value, higher heating value, density, aniline point and cetane number of beniseed biodiesel were found to be within the ASTM D6751 and EN 14214 biodiesel specifications.

Renewable Monomers and Polymers Derived from Terpenes via Thiol-Ene Additions

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Addition of thiols to terpenes ((R)-(+)- and (S)-(-)-limonene, and (-)- β -pinene) are described as a simple approach to obtain a wide range of alcohol, ester, and/or amine functionalized renewable monomers. Solvent and radical initiator-free additions of alcohol and ester functional thiols to terpenes presenting different reactivity at the endocyclic and exocyclic double bonds can be regioselective, and can thus be controlled to yield monofunctional, difunctional, or hetero-difunctional monomers by simple variation of the thiol feed ratio. In the same manner, (-)- β -pinene derived alcohol and ester monomers have been prepared. It was found that the addition of thiols to terpenes is also diastereoselective, reaching a ratio of 5:1 for this radical reaction in the addition of 2 mercaptoethanol to (-)- β -pinene. This effect was related to steric hindrance making hydrogen abstraction more favorable from one of both terpene faces. Addition of cysteamine to (R)-(+)- and (S)-(-)-limonene was also performed using DMPA as UV photoinitiator in ethanol at room temperature in order to obtain diamine derivatives for polyamide synthesis. The monomers, which are interesting renewable building blocks, have been characterized and their behavior in polycondensation reactions has been studied. It has been found that long chain diesters or diols, which were synthesized from a castor oil derived platform chemical, are suitable comonomers and result in polyesters with number average molecular weights up to 25 kDa. Polycondensation of the diamine products resulted polyamides with molecular weights up to 10 kDa. Thus, terpene/fatty acid based polyesters and polyamides were prepared and their structure-thermal property relationships were studied.

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Characterisation of *Lagenaria siceraria* Seed Oils by Fourier Transform Infrared Spectroscopy

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Fourier Transform Infrared (FTIR) Spectroscopy was used to characterise two varieties of *Lagenaria siceraria* seed oils. The absorption bands of the spectra were assigned to different functional groups and discussed intensively. The results showed that wave numbers of many of bands were independent on the nature of the seed oils while the IR values of bands at approximately 3008cm^{-1} and 1098cm^{-1} were found to be dependent on the nature of the oil. The intensities of the bands at 3008cm^{-1} , 2922cm^{-1} and 2853cm^{-1} were function of the composition of the *Lagenaria siceraria* seed oils.

Synthesis and Investigation Ester Group Containing Cationic Surfactants from Renewable Feed Stocks

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Surfactants which find countless application in various industries and commodity products are now being developed by sustainable approach. However, for the success and commercialization of these new products, their cost of production should be less compared to the existing products available in the market. Cationic surfactants are important category of surfactants which find infinite uses in several consumer and industrial products. Apart from their conventional uses such as in cosmetic formulations, fabric softeners and as antimicrobial agent these surfactants now find application as soft templates for the synthesis of mesoporous materials, capping agents for the synthesis of nanoparticles and nanorods, and biomedical applications including gene delivery, drug delivery [1-3]. With the continuation of our previous work [4-5] we here report series of new heterocyclic ester group containing cationic surfactants synthesized by sustainable, cost effective and green approach starting from linear fatty alcohols. These new gemini surfactants have been characterized by spectroscopic techniques and evaluated for their surface properties by surface tension, conductivity and fluorescence method. These new surfactants have been found to have superior surface properties compared to most of the petrochemical based conventional cationic surfactants being utilized in several technical areas.

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Synthesis, Characterization and Aggregation Behavior of Renewable Ester: Functionalized Gemini Imidazolium amphiphiles

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In present world renewable commodities found countless applications in a variety of fields. Gemini surfactants are a new generation of surfactants which have lower critical micelle concentration (cmc) than their monomeric counterparts. In recent years much emphasis have been given to synthesize surfactants based on renewable structure moieties i.e. sugar [1], amino acids [2], fatty esters [3] due to the environmental concern. With the continuation of our work on renewable commodities [4-7] six new cationic imidazolium gemini amphiphiles viz., 3,3'-(alkane-1,n-diyl)bis(1-(2-hydroxy-11-methoxy-11-oxoundecyl)-1H-imidazol-3-ium)bromides ($n = 2,3,4,5,6,8$) based on 10-undecenoic acid have been synthesized by energy saving and cost effective methodology. The zincperchlorate hexahydrate catalysed ring opening of methyl 9-(oxiran-2yl)nonanoate gives an valuable intermediate methyl 10-hydroxy-11-(1H-imidazol-1-yl)undecanoate, which on further reacting with different aliphatic alkyl dibromides under solvent free conditions gives new renewable gemini amphiphiles. These new cationic gemini bromides have been characterized by several spectroscopic techniques such as NMR, FTIR and Mass spectroscopy. Interfacial behavior of these new amphiphiles like critical micelle concentration (cmc), Γ_{max} (maximum surface excess), A_{min} (minimum surface area/molecule), C20 (surfactant concentration required to reduce the surface tension of the solvent by 20 mN•m⁻¹), have been explored by surface tension and fluorescence method. Thermal stability of these renewable amphiphiles has been measured by using TGA (thermogravimetric analysis) technique.

Monomer Generation and Synthesis of Linear Polycondensates from Unsaturated Fatty Acids by Isomerizing Alkoxycarbonylation

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Thermoplastic polymers are currently prepared almost exclusively from fossil feedstock. In view of the limited availability of such feedstock, alternative renewable resources are desirable in the long term.¹⁻³ Unsaturated fatty acids from plant oils contain long-chain, crystallizable linear -CH₂- segments, and are attractive substrates for monomer generation.⁴ By means of isomerizing alkoxycarbonylation such unsaturated fatty acids are converted into long-chain linear diesters in polycondensation grade purity (> 99.5 %).^{5,6} These diesters are the basis for novel polycondensation monomers such as long-chain diols or diamines, as well as for novel polycondensates such as aliphatic polyesters and polyamides with melting and crystallization points suitable for thermoplastic processing.^{6,7} We here present an overview of our current research activities in this field: the design and evaluation of novel catalysts for the isomerizing alkoxycarbonylation, based on mechanistic understanding of the reaction, is presented. The fate of impurities in technical feedstock (double and triple unsaturated fatty acids as methyl linoleate and methyl linolenate) were investigated and polycondensates from methyl oleate and ethyl erucate were synthesized.

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Rheological and material properties of hyperbranched polymer prepared by ATMET polymerization of Plukenetia conophora oil

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Highly branched three dimensional macromolecules are considered as good candidates for tailor made materials with high performance and novel functionality due to their unusual and original physical and chemical characterization. In this work the melt and solution material behavior and rheological properties of highly branched polymer obtained by acyclic triene metathesis polymerization of Plukenetia conophora were investigated. Results of the static and dynamic light scattering analysis as well as rheological measurements indicated imperfectly branched tree like structure which had special structural and rheological properties that might lead to potential application in various areas such as rheological modifiers and drug delivery

Polyurethane cast resins synthesized from rapeseed oil polyols

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Four different rapeseed oil polyols were synthesized using epoxidation followed by ring opening method. Methanol, isopropanol and diethylene glycol were used as nucleophilic agents for ring-opening of fully epoxidized rapeseed oil. Additionally, diethylene glycol was applied to open partially epoxidized oil. The rapeseed oil polyols were characterized by hydroxyl, acid and epoxy values, water content, molecular weight and viscosity.

The polyols were used for preparation of four polyurethane (PUR) cast resins in reaction with polymeric MDI. Chemical structure of PUR resins was identified by IR spectroscopy. The network structure was analyzed by means of mechanical properties, glass transition temperature and cross-linking density as well as water absorption and solvent resistance.

Acknowledgement: The work was supported by the European Union through the European Social Fund within „Cracow University of Technology development program - top quality teaching for the prospective Polish engineers; University of the 21st century” project (contract no.UDA-POKL.04.01.01-00-029/10-00)

Biodegradable lubricants from vegetable oils through solid acid catalyzed reactions

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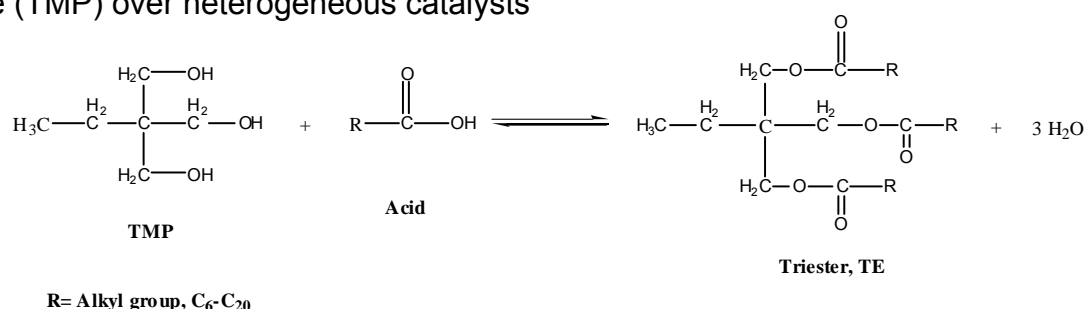
In some applications the requirements for biodegradable hydraulic fluids and lubricants can be met by the use of vegetable oils. Natural oils have some good lubricant properties, including high viscosity indices and **high flash points**. However they have a limited viscosity range because of their limited range of structures and they suffer from poor low temperature fluidity and very poor thermal and oxidative stability, which leads to rapid degradation, thickening and deposit formation in use.

Thermal stability depends on the presence of H atoms located in the beta position of ester groups, thus making the glycerol esters susceptible to elimination reaction and subsequent degradation of the native molecule. That is why so called hindered esters, that is esters of fatty acids with alcohols without H atoms in beta position, are preferred for lubricants that have to withstand high temperature and pressures. Methodologies actually in use for the production of biobased esters from the corresponding fatty acids (mainly) rely on the use of homogeneous acidic catalysts such as sulfuric, p-toluene-sulfonic and hydrochloric acid. All of them show corrosion problems and need to be neutralized after the reaction, thus producing significant amounts of inorganic salts containing effluents to be disposed of.

We recently reported that silica alumina mixed oxides can be effectively used for the esterification of highly acidic oils with methanol [1]. The catalysts are heterogeneous in nature, are stable to leaching and are not poisoned by the water formed during reaction, therefore giving high yield in esters without producing any inorganic waste.

In the present communication we wish to report results obtained on the synthesis of new lubricants with improved performances through heterogeneous catalyzed esterification over solid acidic materials. This would allow one to produce lubricants starting from vegetable oils through a low impact process that does not produce inorganic wastes. These lubricants will be not only more environmentally friendly due to their high biodegradability, but also very much safer to use due their high flash point.

We will report results obtained in the direct esterification of Palm Oil Fatty Acids Distillates, a by product of Palm Oil refining containing 95% Free Fatty Acids, with Tri Methylol Propane (TMP) over heterogeneous catalysts



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Ugi four component reactions to build structurally diverse polyamides derived from castor oil

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The Ugi four component reaction (Ugi-4CR) is a powerful tool to synthesize a vast number of structurally diverse amides in a straightforward way.[1] The use of platform chemicals derived from ricinoleic acid, on the one hand 10-undecenoic acid and on the other hand 10-undecenal, led, by combination with different primary amines and -diene monomers, to a library of α ,

These monomers were polymerized via acyclic diene metathesis (ADMET)[2] or thiol-ene addition polymerization.[3] Thus, it was possible to generate poly-1-(alkylcarbamoyl) carboxamides, a new class of substituted polyamides with amide moieties in the polymer backbone as well as in its side chains.[4]

Moreover o-nitrobenzylamide substituted polymers show a photo-responsive bearing by irradiation of light. It dramatically affects the physical properties of the polyamide.

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ENONE-CONTAINING HIGH SUNFLOWER OIL TRIGLYCERIDES AS PRECURSORS OF FLAME RETARDANT THERMOSETS

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Plant oils and their derivatives have been used by polymer chemists due to their renewable nature, world wide availability, relatively low price, and their rich application possibilities.¹ Recently, their use has received particular attention due to environmental and economic concerns.²

The massive use of polymer materials is driven by their remarkable combination of properties, low weight and ease of processing. However, polymers are also known for their relatively high flammability; most often accompanied by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications.³ Phosphorus based polymers are a well established class of flame retardant materials which are preferred to the widely applied halogenated flame retardants due to health and environment reasons.⁴

The aim of our research is to synthesize new phosphorus-containing plant oil derived thermosets with flame retardant properties. We described a new environmentally friendly route to obtain enone-containing triglyceride from high oleic sunflower oil.⁵ This derivative can react with aromatic primary amines via aza-Michael addition. We reported the formation of quinoline-containing triglyceride-based thermosets when this reaction is carried out at high temperatures.⁶

In an attempt to obtain new phosphorus containing triglyceride derivatives, in this work we describe the phospho-Michael addition of secondary phosphine oxides to the enone derivative of high oleic sunflower oil. When using monofunctional diphenylphosphine oxide, partial modification of enone groups was carried out, allowing further crosslinking by aza-Michael addition of 4,4-diaminodiphenylmethane. In this way, thermosets with phosphorus contents ranging from 0.4 to 1.6 w% were obtained in one pot modification/crosslinking process. Alternatively, the difunctional 1,3-bis(phenylphosphino)propane dioxide has been studied, thus obtaining the phosphorus containing thermosets by phospho-Michael crosslinking. The thermal, dynamomechanical and flame retardant properties of the synthesized polymers were evaluated showing that the incorporation of phosphorus improves the flame retardant behaviour of these materials.

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AB – TYPE POLYADDITION APPROACH TO SEMI-CRYSTALLINE POLYURETHANES BASED ON FATTY ACID DERIVATIVES

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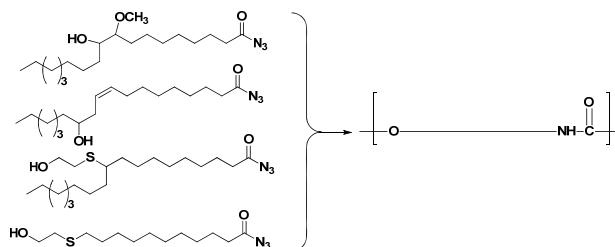
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In our daily life, we are unavoidably, constantly surrounded with polymer materials. To date, most of the monomers that are used to prepare polymers are derived from petroleum (fossil) sources. These fossil resources particularly, petrol and natural gas, will arguably be depleted within one or three generations. Due to the depletion of petroleum resources and their escalating prices, polymer chemists have turned their attention to obtain the monomers and polymers from renewable resource materials.^{1,2} Plant-derived fats and oils bear a large potential as substituents of currently used petrochemicals. Oleochemicals or vegetable oils owing their versatile nature, ability to undergo various organic transformations explored and utilized efficiently in almost every polymeric system.¹⁻⁵ Among them polyurethane (PU) is one of most studied class of polymeric materials due to its large scope of applications as foams, thermoplastic elastomers, adhesives, fibers, etc. Many recent efforts have been directed towards replacing entire or part of petroleum based polyols with vegetable oils.^{6,7} However, not as much attention is paid to the non-isocyanate chemistry, greener pathways to PU.

In the light of above, the present work deals with a unique approach to the synthesis of PU – an AB – type polyaddition.^{4,8} The adaptation of AB – approach has been advantageous in many ways like – (i) the reaction proceeds in one pot, simply by heating; (ii) the stoichiometry is ensured; (iii) indirect use of isocyanate, etc. We have prepared several new monomers containing acyl azide-hydroxyl functionality or methyl carbamate-hydroxyl group starting from methyl oleate, ricinoleic acid and methyl -10-undecenoate. These AB-type monomers have been polymerized to obtain moderate to high molar mass PU. The effect of catalyst and temperature on building of molar mass has been studied. Tuning of amorphous to semi-crystalline properties has been achieved with the systematic choice and polymerization of AB- type monomers. The structure-property relationship of the monomer and the resulting polymer will be discussed during the presentation.



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Monomers and commodity chemicals via TBD catalyzed transesterification of dimethyl carbonate

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The aim of this study was to contribute to solve some of the important challenges of the chemical industry, such as the development and study of highly efficient and greener chemical processes that allow the selective transformation of raw (natural) substances into high added value products.

Organic carbonates are important intermediates for the chemical industry, where they are used as chemical intermediates (for example, as “green” alkylating agents), or as solvents, for instance, in the manufacture of lithium batteries. The conventional synthesis of organic carbonates involves the reaction of alcohols with phosgene, a highly toxic and corrosive substance. In order to overcome these limitations and to develop a new green method, 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD) mediated one step synthesis of alkyl carbonates from alcohols and dimethyl carbonate (DMC) was attempted under solvent-free conditions. Both, the catalyst and carbonylating agent, DMC, are non-toxic and can be generated through clean production processes. Along with 1,3- and higher diols, the fatty acid-based diol, (E) icos-10-ene-1,20-diol, yielded polycarbonates almost exclusively in the presence of TBD as polymerization catalyst.

Moreover, a particularly interesting goal was the transformation of bio-based unsaturated alcohols, such as 10-undecen-1-ol and citronellol, into carbonate functionalized alpha,omega-dienes, which were further polymerized via acyclic metathesis polymerization (ADMET).

The Shape-Selective Hydrogenation of FAMES and Vegetable Oils

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Different zeolite topologies were tested for selective removal of methyl elaidate (trans isomer) from its equimolar mixture with methyl oleate (cis isomer). Both sorption experiments of the geometric isomers and hydrogenation experiments using Pt show that only ZSM-5 samples with low Al content in the framework highly discriminate among the bent cis and the linear trans FAMES in the hydrogenation process [1].

In order to prepare an outstanding shape-selective Pt/ZSM-5 catalyst, the influence of the Pt addition and activation on the Pt-distribution and Pt particle size was investigated using SEM, bright-field and HR TEM, electron tomography, CO-chemisorption, XPS, XRD and UV-VIS measurements.

In a next step some of the Pt/ZSM-5 catalysts were tested in the hydrogenation of model triglycerides and vegetable oils. Next to the preference for trans over cis, a second type of shape-selectivity was found in the hydrogenation of triglycerides: because of the regioselective property of Pt/ZSM-5, central unsaturated fatty acids are hydrogenated faster, resulting in an enrichment of intermediately reduced triglycerides [2]. The melting characteristics of this unique fat composition perfectly match those of commercial bakery shortenings, however, with the important advantage of having only traces of trans fatty acids [3].

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Polyurethane foams modified with various natural oil polyols

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Nowadays, rising prices of petrochemical products and trends to apply environmental friendly components have caused the interest in the applications of biodegradable and renewable materials. Natural oils have gained a lot of interest in recent years due to their environmental friendliness and their availability from different sources. Modified vegetable oils with hydroxyl groups are excellent compounds to replace the petrochemical polyols which are applicable in polyurethane products ^[1,2].

This paper describes the effect of the modification of polyurethane system with palm oil polyol, rapeseed oil polyol and castor oil on the cell structure and physical-mechanical properties of viscoelastic polyurethane foams. Palm and rapeseed polyols were synthesized in the two-step process. Firstly, the double bonds in palm oil were epoxidized by using hydrogen peroxide as an oxidizing agent. Next, the oxirane rings were opened using ethylene glycol as an opener agent^[3]. Polyurethane foams were prepared by substituting a part of petrochemical polyether-polyol with the palm oil polyol^[4], rapeseed oil polyol or castor oil. Selected physical-mechanical properties of these foams were examined and compared with each other and related to the properties of reference foam. The properties such as apparent density, tensile strength, elongation at break, resilience, compressive stress and thermal stability were analyzed. It was found that the modifications of polyurethane formulation with use various natural oil polyols allow to improve selected properties of final products.

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NOVEL THERMOPLASTIC POLY(ESTER/AMIDE URETHANE)S FROM FATTY ACID METHYL ESTERS

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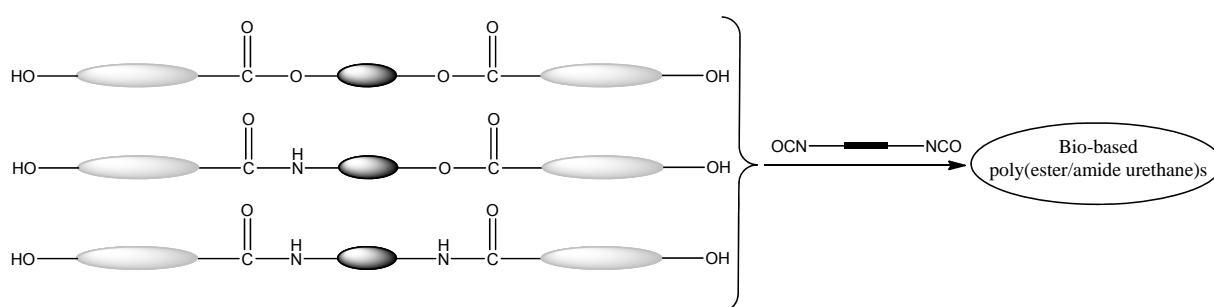
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Due to fossil resources depletion and global warming, there is nowadays a growing interest on sustainable chemistry using biomass as raw material. Among the various polymeric systems derived from renewable resources, polyurethanes are one of the most studied and exploited materials as a consequence of their very large mechanical properties and versatile processability. Vegetable oils have a large potential to substitute currently used petrochemicals, thanks to their availability, sustainability, variability and also biodegradability. Vegetable oils and fatty acid derivatives can be functionalized through several reactive sites (double bonds, ester function and hydroxyl group) to design new functional building-blocks for the synthesis of novel polyurethanes.

In this present work, new diols containing ester, esteramide and amide linkages from castor and sunflower oils were obtained by transesterification, amidation and thiol-ene reaction.^{[1][2][3][4][5]} The starting bio-sourced 'synthons' used are methyl undecenoate and methyl oleate, 1,3-propanediol, isosorbide and 1,4-diaminobutane. The former three can be respectively obtained from glycerol, starch and glutamic acid. A series of amorphous and semi-crystalline polyurethanes have been obtained by varying the diol structure. The relationship between the diol structure and properties of the so-formed polyurethanes will be discussed in the presentation in the light of DSC, DMA, TGA and X-ray analyses as well as tensile experiments.



Synthesis of bio-based poly(ester/amide urethane)s.

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Fumed silica reinforced organic–inorganic hybrid nanocomposites as surface coating materials

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In recent years, considerable attention has been paid on the development of renewable resource based coating materials to reduce the cradle-to-grave pollution. Vegetable seed oils (VSO) are considered to be one of the most important classes of renewable resource for the production of biobased materials. Use of VSO as starting materials has numerous advantages such as low toxicity, inherent biodegradability, high purity and costeffectiveness [1-3]. Organic-inorganic hybrid materials possess advantages of organic polymers such as lightweight, flexibility, good impact resistance and good process ability as well as advantages of inorganic materials such as good chemical resistance and high thermal stability [4-5]. Organic-inorganic hybrid composites are widely used in coating applications.

In this work, attempt has been made for hydroxylation of linseed oil through non-isolable epoxide intermediate forming polyol [Lpol]. Lpol was treated with TEOS resulting in Si/Lpol; the latter underwent polyaddition reaction with toluene-2, 4-diisocyanate [TDI] to develop Si/LPU. Si/LPU matrix was further reinforced with nano-sized fumed silica particles (2wt% and 5wt%) as fillers to develop FS-Si/LPUs (2-Si/LPU and 5-Si/LPU) and their coatings. The physico-mechanical and chemical resistance performance in various corrosive media such as 3.5%HCl, 3.5%NaOH, Xylene, and Salt mist test were conducted to evaluate the coating properties of synthesized 2-Si/LPU and 5-Si/LPU.

Thermogravimetric analysis showed improved thermal stability of Si/LPU and FS-Si/LPUs. The polymers exhibit mild to moderate antibacterial activity against Gram negative bacteria (*Escherichia coli*) and Gram positive bacteria (*Staphylococcus aureus*). Our results display that FS-SiLPUs system exhibits improved coating performance over Si/LPU and can be safely employed upto 240 °C.

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Biolubricant synthesis using immobilised lipase: Optimisation of trimethylolpropane oleate production

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Synthetic lubricants based on esters of polyols and fatty acids from renewable resources are attracting attention nowadays mainly owing to their superior technical, physico-chemical and ecological properties compared to conventional mineral oil based lubricants [1, 2]. Biocatalytic synthesis of fatty acid polyol esters from trimethylolpropane (TMP) and oleic acid was investigated under solvent-free conditions using immobilized *Candida antarctica* lipase B (Novozym® 435). The impact of different reaction parameters on the reaction efficiency was studied. It was observed that higher temperatures (80-100 °C) and biocatalyst load of 2-5%, and stoichiometric amount of substrates as well as continuous removal of the produced water under lowered pressure favor the formation of TMP tri-ester. The product containing the highest tri-ester amount (98%) showed the lowest pour point (-42 °C), which is a desired property for application of the biolubricant at sub-zero temperatures. The results also showed that operating temperatures higher than 70 °C and mechanical stirring lead to the loss of biocatalyst activity due to thermal inactivation and leaching of the enzyme from the matrix. During recycling of the biocatalyst, washing with 2-propanol between the batches prolonged the half-life of the enzyme activity by 71% as compared to the case when the biocatalyst was not washed. [2, 3]

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Heteropoly Acids as Catalysts for Biodiesel Production

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Esterification and transesterification reactions have attracted much interest recently in connection with the development of new synthetic routes to fuels and chemicals based on renewable feedstocks. In particular, the synthesis of biodiesel via transesterification of triglycerides with methanol 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 for the transesterification of triglycerides could potentially overcome these drawbacks.

Keggin heteropoly acids (HPAs) have been reported to have the potential for biodiesel synthesis. The aim of this work is to study homogeneous and heterogeneous catalysis by tungsten HPAs, H₃PW₁₂O₄₀ (HPW) and H₄SiW₁₂O₄₀ (HSiW), in a series of model liquid-phase (trans)esterifications with methanol: esterification of hexanoic acid and transesterification of ethyl propanoate and ethyl hexanoate. Our main focus is on the HPW, the strongest acid among the Keggin HPAs. Solid acid catalysts under study include HPW supported on Nb₂O₅, ZrO₂ and TiO₂, as well as bulk acidic heteropoly salt Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW). The performance of HPA catalysts is compared with that of the conventional acid catalysts such as H₂SO₄, Amberlyst-15, zeolites HY and H-Beta. In heterogeneous systems, leaching of HPA from the catalysts into solution is thoroughly evaluated to estimate the contribution of homogeneous catalysis.

FATTY-ACIDS AS RENEWABLE FEEDSTOCKS IN THE SYNTHESIS OF THERMOPLASTIC POLYESTERS AND POLY(ESTER-AMIDE)S

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World-wide potential demands for replacing petroleum-derived raw materials with renewable ones are quite significant from the societal and environmental points of view. Among the various polymeric systems derived from renewable resources, polyesters gained a widespread interest over the last decades since new semi-crystalline and biodegradable thermoplastics are needed. Poly(lactic acid) is commonly considered as one of the best candidates to replace polymers from petroleum. However, since few decades, vegetable oils (triglycerides) are also gaining widespread interest thanks to their availability, sustainability and biodegradability. From these triglycerides, different fatty acids can be isolated by transesterification or saponification. The latter brings different functional groups (ester functions, double bonds, hydroxyl groups...) that can be derivatized to design new functional building blocks for the synthesis of novel polymers. In this present work, original "synthons" with various functionalities were synthesized. By combining transesterification, amidation and thiol-ene reactions, new diols from castor and sunflower oils were designed for step-growth polymerization^{1,2,3}. Depending on the monomer structure, a large range of polyesters with various thermomechanical properties were obtained. Due to the purely aliphatic character of fatty-acids, polymers made from vegetable-oils generally exhibit poor thermo-mechanical properties such as low T_g, melting point and Young's Modulus. In order to overcome this drawback, amide functions were introduced in the polymer structure in order to enhance the cohesion of the polymer chains. The structure-properties relationship of the so-formed polyesters and poly(ester-amide)s will be discussed in the presentation regarding to DSC, TGA and DMA measurements as well as tensile tests.

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New Non-Isocyanate Polyurethanes upon catalytic carbon dioxide conversion of epoxidized plant oils and limonene

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The increasing shortage of fossil resources and global warming due to carbon dioxide emissions stimulate the development of carbon dioxide neutral plastics manufacturing processes which are not based upon crude oil. Our special aim is to develop non-isocyanate-polyurethanes (NIPU), which are produced based on renewable resources and direct carbon dioxide conversion (Figure 1). Important intermediates for NIPUs are cyclic carbonates, which are readily available by carbon dioxide conversion of epoxides. Conventional approaches employ carbonated soybean oil (CSBO) for NIPU synthesis.¹⁻³ In contrast to the known synthesis we used carbonated linseed oil (CLSO) as new building block, because it has a higher cyclic carbonates functionality and leads to an increased network density.⁴ Furthermore the carbonate content can be varied by blending together both carbonated plant oils. This results in higher Tg's and Young's modulus with increased carbonate content. A disadvantage of these plant oil based NIPUs is that the cure reaction is accompanied by cleavage of the ester groups, thus reducing network density and lowering tensile strength. Therefore, we have developed a new route towards ester-free carbonate monomer for NIPU's. We have employed terpene such as limonene dioxide to produce ester-free carbonates. Structure/properties relationships of NIPUs are reported.

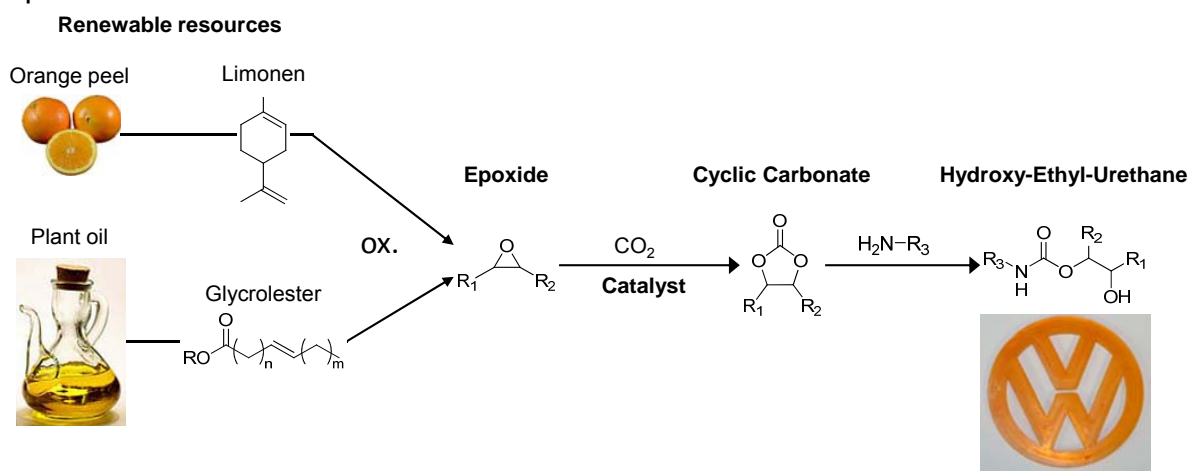


Figure 1: NIPUs based on renewable resources.

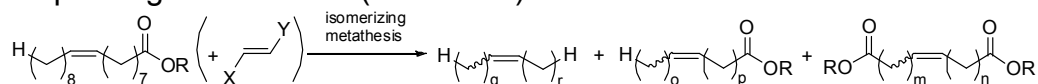
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Palladium/Ruthenium catalyzed isomerizing metathesis of fatty acids

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A new palladium / ruthenium catalyzed method facilitates the synthesis of industrially useful multi-component blends, consisting of functionalized olefins with tunable chain length distributions.^[1]

The use of such mixtures as monomers can be advantageous, but they are hitherto exclusively accessed from petrochemical resources.^{[2],[3]} Our process facilitates the efficient conversion of uniform bio-based starting materials, i.e. readily available fatty acids, into the desired mixtures of olefins, unsaturated mono- and dicarboxylates, surpassing the literature (Scheme 1).^[4]



Scheme 1. Isomerizing metathesis of fatty acid derivatives.

In the presence of a bimetallic system consisting of a palladium dimer and a common metathesis catalyst, a technical quality fatty acid can be employed in an isomerizing self-metathesis, ethenolysis, or cross-metathesis with another functionalized olefin. The chain length distribution can be influenced by the catalyst ratio and the reactants' stoichiometry, leading to product blends of different compositions with quantitative conversions (Figure 1). This way, olefin blends of tailored medium chain lengths become available from renewable resources rather than from crude oil, yielding valuable mono- and dicarboxylates as side products.

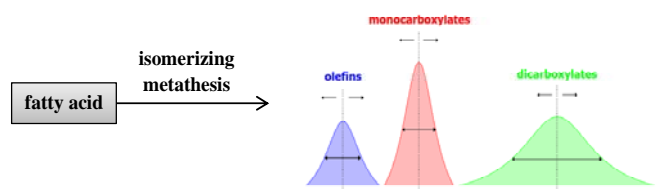


Figure 1. Product distributions accessible from isomerizing metathesis of fatty acids.

The new methods disclosed above extend the chemist's toolbox for the utilization of oleochemicals by making use of bimetallic catalysis, contributing to the necessary change from uncatalyzed to greener catalytic processes.

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Synthesis of monomers on the basis of diglycerol

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Introduction

A new area of application for linear diglycerol [1, 2] easily obtained from glycerol may be its conversion into suitable monomers for polymer synthesis. Polymers achieved from these monomers maintain their hydrophilicity originating from free hydroxyl groups of the diglycerol. New prospects may be opened to get water soluble polymers, which, for example, can be used for encapsulation of drugs.

In this study, diglycerol (contained 84% α,α -diglycerol and 14% α,β -diglycerol) was reacted with several unsaturated derivatives of 10-undecenoic acid, acrylic acid and methacrylic acid as well as with 10-undecenol in different molar ratios. Catalytic and non-catalytic procedures were investigated, their scopes and limitations were shown. Attention was dedicated to a careful analytical characterization of the reaction products.

Experimental

Exemplary procedure for reaction with acid chlorides: The desired amount of diglycerol (0.5-2 mmol) was dissolved in 15 ml of tetrahydrofuran. Then the mixture was stirred for 30 min and the solution was purged triply with argon. Further processing was carried out under argon at room temperature (10-undecenoyl chloride) or at 5 °C (acryloyl chloride, methacryloyl chloride). 10-undecenoyl chloride (n_{10-UC}/n_{Digi} 1:1 – 4:1) was added slowly via a syringe. The 1.5fold surplus of triethyl amine (calculated on the basis of acid chloride) in 5 ml tetrahydrofuran was dropped slowly to the reaction solution. The stirring was continued for 5h. Then the triethyl ammonium hydrochloride was filtered off and washed. The filtrate was concentrated in vacuum at 10-2 mbar.

Results

The aim of the investigations was the synthesis of mono- or disubstituted diglycerols because the solubility of the products in water should be possible also after functionalization. However, also a three- and fourfold surplus of the acylating or etherifying agents was used to get informations about the reactivity of the primary and secondary OH groups of diglycerol.

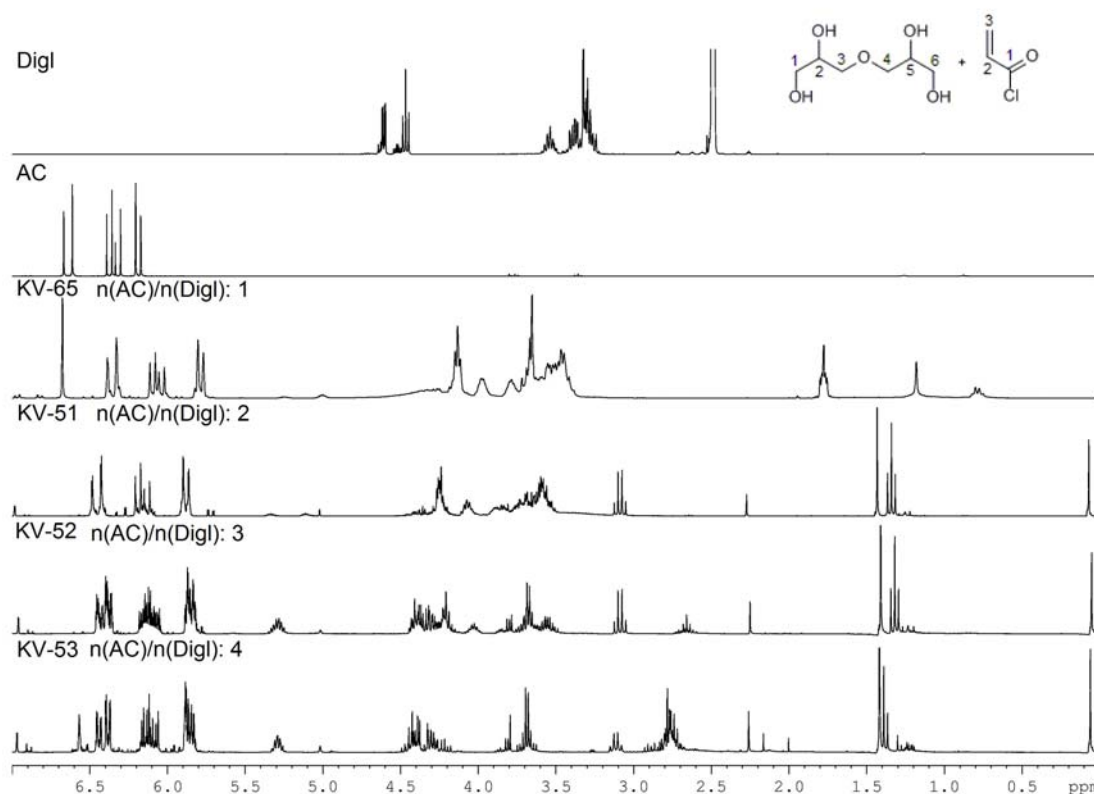


Figure 1. ^1H NMR spectra of the reaction products of acryloyl chloride (AC) and diglycerol (Digl) with molar ratios between 1:1 and 4:1

The reaction of 10-undecenol as well as of 10-undecenoic acid, acrylic acid, methacrylic acid, methyl acrylate and methacrylate with diglycerol failed. The necessary activation at higher temperatures was not possible due to the propensity of the unsaturated educts to polymerize, some of them polymerized even at very low temperatures. Only methyl 10-undecenoate could be transesterified successfully with diglycerol at higher temperatures, and mono and diacylated diglycerols resulted from the reaction with methacrylic anhydride, both in the presence of basic catalysts. The best results were achieved by the reaction of diglycerol with unsaturated acid chlorides at low temperatures. All acylation patterns at the diglycerol, from one- to fourfold substitution, could be identified using elemental analysis, NMR spectroscopy (see Fig 1), and mass spectrometry.

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Production of Bio lubricants from Castor oil and higher chain alcohols by enzymatic transesterification

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During recent years the interest in environment friendly and readily biodegradable lubricant based on vegetable oil has increased. The use of environmentally acceptable vegetable oil-based product as lubricants has many advantages as they are nontoxic, biodegradable, derived from renewable resources, and have a reasonable cost when compared to other synthetic fluids. Castor oil content about 87% of ricinoleic acid which is a hydroxy acid and having high viscosity as compared to other vegetable oils, thus the use of castor oil in lubricants is more prevalent. We have made an attempt to develop a green process for the production of bio lubricants. The transesterification reaction of castor oil catalyzed with Lipozyme TL-IM and Novozyme- 435 with propanol, butanol, amyl alcohol and lauryl alcohol in solvent and solvent free medium led to the production of fatty acid alkyl esters, which can be used as biolubricants. In this study, the reaction parameters investigated were the reaction time, temperature, enzyme loading, mixing speed and molar ratio (alcohol to triglycerides), and their effect on the alkyl esters formation. The lubricity of the alkyl esters were measured using High frequency reciprocating rig (HFRR).

Monomers from renewable resources

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Due to the ongoing shortage of fossil resources it is one of today's biggest challenges of chemistry to develop procedures towards renewable commodity chemicals. In this context, fatty acids have been shown to be a very promising starting material for renewable, bio-based polymers. However, these reactions have been performed almost exclusively for unsaturated fatty acids since the double bond is used for modifications. Modifications of saturated fatty acids towards renewable monomers has been reported only once using a biochemical approach.

On the other hand, by C-H functionalization it should be possible to modify also saturated fatty acids towards sustainable monomers for the synthesis of bio-based polymers. One possibility is the usage of the α -acidity of esters. After deprotonation such esters can undergo a (Cross)-Claisen condensation or be arylated with various aromatics. Another possible way to activate the chain is by terminal dehydrogenation or borylation. Although these reactions have been presented only for alkanes, they seem very promising for fatty acid esters.

Biocompatible Polymers from Renewable Sources: Linear Polyesters from Seed Oils of Flax and Hemp

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Currently, most of thermoplastic polymers are derived almost exclusively from petroleum derivatives. However, given the prospect of a future depletion of fossil fuels, whose prices continue to rise, the need to switch to alternative raw materials derived from renewable sources is a desirable long-term perspective.

In recent years, short-chain aliphatic polyesters based on renewable resources have been launched, such as polyhydroxyalkanoates and polylactic acid, both derived from cellulose. In view of the aforementioned challenge, among the renewable raw materials, fatty acids from plant oils are attractive substrates as they contain long chain linear segments which can provide crystallinity.¹

Among the various methods of polymerization of vegetable oils, the polymerization by means of an acyclic diene metathesis (ADMET) seems to be the most promising.²⁻⁴

Within a project related to utilization of *Cannabis sativa* and *Linum usitatissimum*, we have become interested in exploiting the common fatty acids from their oil seeds for the synthesis of polyesters with high molar masses. An α,ω -diene (building block) has been constructed, the diene was subjected to ADMET polymerization, and the polymer was subsequently hydrogenated (Scheme 1) Ethenolysis⁵ of methyloleate, from oleic acid present in abundance in the oil seeds, by (PCy₃)₂Cl₂Ru=CHPh (first generation) and -C-C₃H₄N₂Mes₂)Cl₂Ru=CHPh (second generation)⁶ Grubbs catalysts⁷(PCy₃)₂ yielded the methyl-9-decenoate. The methyl-9-decenoate obtained was transformed in the 9-decenoic acid and then in the chlorinate derivative. The α,ω -diene was generated by condensation of 1,6-hexanediol with the chlorinate derivative of the 9-decenoic acid. The ADMET polymerization of the α,ω -diene with -C-C₃H₄N₂Mes₂)Cl₂Ru=CHPh catalyst followed by exhaustive⁷(PCy₃)₂ hydrogenation yielded an aliphatic C₁₆ long-chain polyester with high molar mass.

The polymer was characterized by ¹H NMR and ¹³C spectroscopy to determine its structure. The molecular characterization, by Gel Permeation Chromatography (GPC), measured a molecular mass (M_w) of about 14000 Da. The polymer was then hydrogenated in the presence of toluene-4-sulfonylhydrazide in toluene, in order to obtain a crystalline polymer. The DSC analysis shows a melting point and the point of crystallization, respectively of 67 °C and 58 °C.

The synthesis of α,ω -diene with diols with different methylene chain length will allow to modulate the polyester molar masses and thermal properties.

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New dimer diamine bio-based solutions for flexibility, moisture resistance and low polarity in high-performance polymer systems

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Public concerns about climate change and limitation to fossil resources have increased the interest in bio-based raw materials and environmental solutions. Croda has been active in oleochemistry for over 150 years, using natural oils as feedstock for various chemicals. Besides the renewable nature of these products, emphasis is on the unique properties and specific quality benefits they bring.

Dimerised fatty acids are C36 building blocks used in coatings, adhesives and polymers, where the low T_g and hydrophobic nature induce flexibility, hydrolytic resistance and adhesion to a wide range of substrates. Croda has developed new bio-based, amine-functional building blocks, extending the range of dimer acids, dimer diol and Priplast dimer-based polyester polyols.

In Polyamide hot-melts, this extends the freedom in formulating, allowing wider melting point adjustment, while improving hydrophobicity. In epoxy coatings, it brings moisture protection and allows reduced use of solvents or high-solids formulations. The reduced moisture absorption brings dimensional stability to polyamide plastics, while the excellent flow and wetting properties result in strong adhesion to various substrates, including plastic reinforcement fibres.

NEW ESTOLIDES – FUNCTIONAL INDUSTRIAL FLUIDS FROM RENEWABLE VEGETABLE BASED OILS.

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Estolides are natural polyesters derived from oils and fats. They are dimers or oligomers formed by homopolymerization hydroxyl fatty acids or unsaturated fatty acids. The secondary ester linkages formed on estolides are more resistant to hydrolysis than those of triglycerides. Estolides have high viscosity, cold temperature, good oxidative stabilities and are biodegradable. These compounds have shown great promise for use in a wide variety of products with varying physical properties, such as: edible applications, cooling fluids, cosmetics, plastics, hydraulic fluids, inks, crankcase lubricants and coatings.¹

The Estolide Number (EN) is defined as $n + 1$ indicating the extent of oligomerization of the molecule. Viscosity and other physicochemical properties are functions of the degree of oligomerization.

In this study, we investigated, in first, the synthesis of 9,10-dihydroxy stearic acid (DHSA) and 13,14-dihydroxy docosanoic acid (DHDA) from high oleic sunflower oil (>90% oleic acid) and erucic rapeseed oil through catalytic chemical procedure^{2,3}. And second part, we carried out the estolides synthesis, where oleic acid, erucic acid, DHSA and DHDA were used as model substrate, using *p*-toluenesulfonic acid as the catalyst. A reaction temperature of 150°C was used to azeotropically remove the water of esterification⁴. All of the estolide products synthesized were run at stoichiometry such that the fatty acids hydroxyl groups would all be esterified to estolide. This is unique products because they involve estolides synthesis from very-long-chain hydroxyl fatty acids, and this has never yet been described. Using this approach, chemical and physical properties of new estolides were also analyzed.

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Oxidative Cleavage of Oleic Acid by RuO₄ Catalyst under Ultrasonic Irradiation. Valorization of Pelargonic Acid as a New Reactant for Selective Precipitation of Metallic Cations

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The sustainable developments are more and more important for the chemistry. In this area, the use of renewable raw materials, the recycling of metals and the wastes management are concerns for the chemical industry. Therefore, there is an increasing interest in recovering metal from industrial liquid effluents, hydrometallurgical leachates or lixiviates. Chemical precipitation is the most common technology used to remove dissolved metals from industrial lixivate or wastewater. But generally, these chemical precipitation processes lead to sludge without any commercial or industrial values which are stored in specialized landfill. Previous works showed that sodium carboxylates can be used for the selective precipitation of metallic cations (Chemosphere 69 (2007) 763–768; J. Chem. Eng. Data, 50 (2005) 1833-1836). In addition, metallic carboxylates have considerable commercial importance and find applications in many fields: their selective precipitation is researched. The aim of this communication is (i) the oxidative cleavage of oleic acid to lead pelargonic acid and (ii) the using of sodium pelargonate as precipitant to perform selective precipitation of metallic cations. The oxidative cleavage of oleic acid was realised under 20 KHz ultrasonic irradiation with the catalytic RuCl₃/NaIO₄. Associated with Aliquat® 336, this system allowed the free organic solvent oxidative cleavage (Tetrahedron Lett. 51 (2010) 3123–3126). However, the optimal mixture of solvents was H₂O/MeCN (1/1): azelaic and pelargonic acids were obtained in 30 min with 81% and 97% yields respectively (Ultrason. Sonochem. 16 (2009) 266–272 ; Ed. David B. Watson (2011) Edition Nova Science Publishers, Inc. ISBN: 978-1-61761-550-4, Chapter 10, pp311-328).

Comparison of chemo-enzymatic epoxidation of oleic acid with different immobilized lipases

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Epoxidized fatty acids (EFA) and triacylglycerides (ETAG) can be used as precursors for bioplastics and bio-based thermoset materials, as additives for biocompatible lubricants or as plasticisers in further polymer applications.

Industrially produced ETAG are still synthesized via a chemical procedure using harsh reaction conditions. The chemical epoxidation reaction is the most common way to produce plant oil based epoxides. This method uses a peracid for the oxygen transfer to the double bonds in the unsaturated fatty acid chain. The peracid is usually formed *in situ* from hydrogen peroxide and acetic or formic acid with a strong mineral acid or ion exchange resin as catalyst. The presence of strong acids in the reaction mixture and the reaction temperature are considered to cause undesired side reactions, leading to diols, hydroxyesters, estolides and other dimers.

An alternative epoxidation process is provided by a biotechnological approach using enzymes. Under milder reaction conditions peroxy fatty acids can be produced directly from fatty acids and hydrogen peroxide. This peroxy group reacts with the double bond of the unsaturated fatty acid autocatalytically to the corresponding epoxide. For these reactions commonly the commercially available immobilized *Candida antarctica* lipase B is used. Recently other enzymes, like the lipase from *Rhizomucor miehei*, which have also been shown to catalyze the epoxidation reaction, are available as immobilized preparation. We studied different commercially available immobilized lipases which were linked onto various carrier materials and used in the epoxidation of oleic acid (OA). The *Candida antarctica* lipase B (CalB) was immobilized on an acrylic resin (Novozym[®] 435) and on Immobead 150 (copolymer of methacrylate, cross-linked and carrying oxirane groups). Both preparations showed almost complete conversion of OA to epoxystearic acid (ESA) after 24 hours whereas Lipozyme[®] (lipase from *Mucor miehei*, immobilized on a macroporous ion-exchange resin) showed online very low conversion. Interestingly, lipase from *Rhizomucor miehei* (formerly called *Mucor miehei*) immobilized on Immobead 150 showed higher conversion to ESA than Lipozyme[®] but was less efficient than CalB. Furthermore, a lipase from *Rhizopus oryzae* (immobilized on Immobead 150) did transform OA to ESA with high conversion within 24 hours.

Acknowledgement: The work was performed within the project Integrierte BioProduktion funded by BMELV (Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz, Germany) and FNR (Fachagentur Nachwachsende Rohstoffe; FKZ 22027407).

Enrichment of unsaturated fractions in a Linseed oil based fatty acid mixture by melt crystallisation

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Naturally occurring oils and fats are not only widely used as ingredients in various kind of food and cosmetics but they also have potential as renewable resource to synthesize chemically new products. Oils are triglycerides which are basically tri-esters, made of one glycerol and three fatty acids. The physical and chemical properties of oils can be varied by various techniques such as hydrogenation, interesterification or fractionation [1], which was used in this work.

Melt crystallisation is a very common method used for separation and further purification of products to improve their properties [2]. With regard to this investigation, it is applied to crystallise saturated fatty acids out of a Linseed oil fatty acid mixture, thereby obtaining a mother liquor enriched of unsaturated fractions. This product, for example, can be used for the polymerisation of epoxy resins [3]. The high efficiency per separating step, the high purity and the very low energy needed in comparison to other separation methods like distillation makes it attractive to utilize this technique in industrial processes. The big difference in the melting points of saturated in comparison to unsaturated fatty acids, makes it possible to crystallise the saturated content directly in the mixture by altering the system temperature and thereby enrich the melt with unsaturated fractions. Parameters like temperature and cooling rate can hugely influence nucleation and crystal growth. Hence an optimal temperature profile can lead to effective melt crystallisation and hence post separation an enrichment of desired product. A poly-unsaturated fatty acid mixture with high concentration of Linolenic acid (C 18:3) was chosen for this study. This mixture was subjected to different temperature profiles in order to optimize maximum yield of unsaturated fatty acid in the mother liquor post isothermal centrifugal separation. Upon optimisation of the crystallisation temperature, saturated fatty acid content comprising of Palmitic acid: 2.1% (5.4 % in feed) and Stearic acid: 0.8% (3.8% in feed) were achieved. This enables the enriched mother liquor to be used in industrial processes even at very low temperatures.

To monitor the quality of the product, various thermal analyses could be used to determine the temperature depended properties like the mass (Thermogravimetry TG) or the linear expansion of the sample (thermo mechanical analysis TMA) [10]. In this study, the method of measuring the change in enthalpy (Differential Scanning Calorimetry - DSC) was chosen, as it is a effective method to examine sensitive phase transitions like crystallisation, is very rapid and also because only small amounts of sample (few milligrams) are necessary [4].

To characterize the exact composition of the product, gas chromatography methods were modified and applied [5, 6].

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Highly functionalized and structurally divers polyamides derived from castor oil by applying Ugi four component reactions

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The Ugi four component reaction (Ugi-4CR), the most famous isonitrile based multicomponent reaction (IMCR), was used with 10-undecenoic acid, its reduced product 10-undecenal, an incombination with several different primary amines and isonitriles.^{[1],[2]} Undecenoic acid is a valuable platform chemical derived from castor oil by pyrolysis of ricinoleic acid, the main fatty acid of castor oil.^[3]

The obtained versatile carboxamide monomers with α,ω -diene moiety were polymerized via acyclic diene metathesis polymerization (ADMET) and thiol-ene addition polymerization to create a library of a new class of highly substituted polyamides^{[4],[5],[6]} The procedures of polymerizations were intensively optimized and the new polymers well characterized regarding thermal behaviour and molecular weight. Moreover, it was possible to synthesize polymers with photoresponsive behaviour derived from photocleavable o-nitrobenzylamide containing polyamides. After irradiation with sunlight a dramatic change of its properties was observed.

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Organocatalytic modification of sorbitol and isosorbide

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Biomass derived sugars are potential precursors for new and renewable platform chemicals, which are required to establish chemistry based on non-fossil resources. The US Department of Energy reported a list of twelve building blocks, mainly derived from sugars, which can be converted to a number of high value bio-based chemicals or materials.[1] One of these building blocks is sorbitol, which is a hydrogenation product of glucose. Sorbitol itself is used as sugar substitute, but it can also be converted to isosorbide and other renewable platform chemicals. Since, isosorbide is the dehydration product of sorbitol, isosorbide is a potentially valuable renewable and sustainable monomer due to its non-toxic, rigid and chiral properties.[2] However, in polymerisation reactions employing isosorbide, one is facing problems concerning the solubility of isosorbide in organic solvents and an unequal reactivity of the two hydroxyl groups. Considering the solubility-problems, it is obvious that derivatization of isosorbide is required. Our idea is to carbonylate the hydroxy-functionality using dimethylcarbonate (DMC) as methoxycarbonylation agent using an organic catalyst and thus to improve the solubility and to synthesise a fully renewable polycarbonate in a subsequent polymerisation.

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Amphiphilic Hyperbranched Polymers from a Castor Oil Derived Monomer

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Since amphiphilic hyperbranched polymers were shown to be useful as drug-carriers for controlled delivery applications, a large number of studies have been reported on diverse synthetic approaches, peripheral modifications, and their drug delivery essays.[1] As hyperbranched polymers have a three dimensional, branched structure, they can behave as a host for smaller guest compounds. Depending on the polar characteristics of the inner (core) and outer (shell) part of the polymer, guest compounds with different polarity can be encapsulated in the hyperbranched polymer. In the case of drug delivery, a water soluble system with a hydrophobic core is needed, since many drugs are hydrophobic, but the physiological medium is hydrophilic.

At the moment, a very major percentage of polymers are synthesized from monomers that are derived from mineral oil. Considering the urgent necessity for more sustainable and greener synthetic processes, the use of renewable resources for the production of hyperbranched polymers was our goal. We believe that plant oil derived fatty acids are great candidates as a feedstock for the polymer industry, as they offer a wide variety of linear aliphatic chains with carbonyl functionality at one end and C=C double bonds at different number and locations on the chain, giving chemists the chance to generate diverse renewable platform chemicals.[2] For instance, it was already shown that linear polyesters and polyanhydrides, and their copolymers, with finely-tuned degradation properties can be synthesized from castor oil derivatives.[3]

In an earlier report, we showed that hyperbranched polymers can be synthesized from a monomer that was synthesized from a castor oil derivative without the need of any metallic catalysts, which is crucial for medical applications.[4] Furthermore, this monomer was polymerized with glycerol as core material via single-pot polycondensation, where triazabicyclodecene was used as a non-metallic organic catalyst. However, the optimization of some parameters to improve the performance of those hyperbranched polymers, e.g. more uniform structures, higher branching, and peripheral modification for the study of the water solubility characteristics remained missing. Therefore, within this contribution, we report on our newest results regarding the synthesis of a water soluble amphiphilic hyperbranched polymer as a potential substitute to the current mineral oil derived drug carriers.

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Catalyzed Crosslinking of Highly Functional Biobased Resins

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Crosslinking reactions involving the thermal polymerization of 100% biobased epoxidized sucrose esters (ESEs) were studied and the resulting coatings properties were compared against epoxidized soybean oil (ESO) and petrochemical-based soybean ester resins. The low viscosity of ESEs allowed for formulations to be developed with negligible volatile organic content (VOC). ESEs were found to have superior coatings properties compared to ESO and the petrochemical-based soybean esters which was attributed to a higher glass transition temperature (T_g) and a higher modulus. In order to further enhance the coatings properties, small amounts of bisphenol A (BPA) epoxy resin were added which resulted in higher moduli and T_g s. The degree of conversion and optimization of the curing conditions were studied using differential scanning calorimetry (DSC) techniques.

Process characterization of microbial oil production by *Cryptococcus curvatus*

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Many consumer products like plastics or petrol are dependent on raw oil, but the depletion of raw oil in the near future requires an ecological alternative.

The production of Single Cell Oil (SCO) by oleaginous microorganisms enables sustainable lipid production using renewable feedstock. Several yeasts, fungi, bacteria and microalgae belong to that group of microorganisms and contain more than 20 % intracellular fat which is produced as carbon storage in the form of triacylglycerids (TAG) when a carbon source is in excess, but other limitations like depletion of nitrogen source prevent further cell division. Depending on the culturing conditions the percentage of SCO can be increased up to 70% in some strains.

The major aim of this project is the setup of a coupled process for the economical production of Single Cell Oil (SCO) with one heterotrophic and one autotrophic microorganism whereby carbon dioxide emission should be minimized. For this purpose the oleaginous yeast *Cryptococcus curvatus* is taken as a model strain for the heterotrophic part of the process.

The purpose of this study is to characterize a 5-L fermentation process with the model yeast strain which should serve as a platform process. One intention is the development of an "online-measurement" for the determination of lipid percentage in the cells during the fermentation run. The outcome should be later transferred to other oleaginous microorganisms.

Defined and Functional Polymers via Head-to-tail ADMET polymerization

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We present the synthesis of sophisticated polymers from renewable resources via acyclic diene metathesis (ADMET) polymerization. Thus, a castor oil derived monomer (undec-10-enyl acrylate) has been used to directly synthesize diblock copolymers, homo polymers and star block copolymers via our newly developed ADMET polymerization technique.[1] In this context, the well-known cross-metathesis selectivity between terminal olefins and acrylates was used to obtain well defined polymers by selective head-to-tail addition.[2] Since mono- or multifunctional acrylates react selectively with just one chain end (terminal olefin), the molecular weight can be controlled by adding the desired amount of a monofunctional acrylate (selective chain transfer agent). The control over the block sizes was thus achieved by using different amounts of selective chain transfer agent in relation to the amount of monomer. Poly(ethylene glycol)monomethyl ether acrylate and poly(ϵ -caprolactone)acrylate of different molecular weights were thus synthesized and employed as chain transfer agent in the ADMET polymerization. Although a catalyst loading of 0.5 mol% to monomer is generally sufficient to produce the desired polymers with monomer conversions over 95%, we found that higher loadings (1-2 mol%) provide the products in shorter reaction times (typically 3h). These higher loadings minimize the occurrence of acrylate self-metathesis which, even at ratios below 2% with respect to cross-metathesis, results in slightly less defined polymers. Analysis of these polymers by ^1H NMR showed molecular weights close to the theoretical values (calculated from the monomer/chain-transfer agent ratio), good correlation between the end-group integrals, and only a small amount of self-metathesis between 0.2 and 3.0%. Moreover, SEC analysis revealed homogeneous molecular weight distributions and PDIs close to 2. These polymers represent some of the first examples of head-to-tail ADMET polymerization, and confirm the usefulness of this approach for the preparation of block- or star copolymers with high structural control.

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Renewable Dendrimers via Thiol-Ene Click Reactions

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The synthesis of dendrimers based on renewable resources via consecutive thiol-ene “click” chemistry and esterification steps as well as the functionalization of the outer shell via cross-metathesis were investigated. Subsequent steps of esterification of 10-undecenoic acid with glycerol and the addition of 1-thioglycerol to the 10-undecenoic moieties were applied to synthesize the dendrimers. The investigation was focused on the optimization of each step, primarily the limitation of side-products by coupling processes during the thiol-ene addition. The terminal double-bonds of generation 1.5 were successfully functionalized with PEG-chain- and fluoruous-chain-containing acrylates via cross-metathesis. Optimum conditions were found by a screening of reactions conditions.

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