



abiosus e.V.

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

6th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

**March 17-19, 2013
Karlsruhe, Germany**

in Cooperation with:

Karlsruhe Institute of Technology (KIT)

German Society for Fat Science (DGF)

German Chemical Society (GDCh), Division of Sustainable Chemistry



Scientific and Organizing Committee

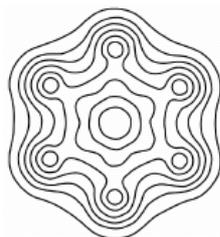
Ursula Biermann, University of Oldenburg, Oldenburg, Germany

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

Jürgen O. Metzger, *abiosus* e.V. and University of Oldenburg, Oldenburg, Germany

Acknowledgement

Financial Support by the Fonds der Chemischen Industrie (FCI), BASF – The Chemical Company and by Clariant Produkte (Deutschland) GmbH is gratefully acknowledged.



FCI
FONDS DER
CHEMISCHEN
INDUSTRIE



CLARIANT 

Content

Program Lectures	6
Posters	15
Abstracts of lectures	19
Abstracts of posters	55
List of participants	89

Program

Lectures and Posters

Sunday, March 17, 2013

Registration

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

- 15.45 **Welcome and Opening**
- Jürgen O. Metzger, *abiosus* e.V.
- 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 **Polyurethanes from renewable resources and carbon dioxide (M)**
L1 Rolf Mülhaupt, Freiburg Materials Research Center and Institute for Macromolecular Chemistry, Freiburg, Germany
- 16.30 – 17.00 **Novel high molecular weight vinyl ether polymers based on plant oils (M)**
L2 Samim Alam, Harjyoti Kalita, Satyabrata Samanta, Andrey Chernykh, Bret J. Chisholm, North Dakota State University, Fargo (ND), USA
- 17.00 – 17.30 **Protein engineering and application of enzymes in lipid modification (M)**
L3 Uwe T. Bornscheuer, Institute of Biochemistry, Greifswald University, Germany
- 17.30 – 18.00 **Epicerol[®] and the environmental challenges of bio-based chemistry (M)**
L4 Thibaud Caulier, Solvay, Brussels, Belgium
- 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 18, 2013

9.00 – 10.30 *First morning session*

Chair: Ursula Biermann

9.00 – 9.30 **Metathesis: Commercialization of specialty chemicals from lipids (M)**

L5 Mel Luetkens, Elevance Renewable Science, Woodridge , IL, USA

9.30 – 9.50 **News from the isomerizing alkoxy-carbonylation (D)**

L6 Philipp Roesle¹, Timo Witt¹, Florian Stempfle¹, Josefine T. Christl¹, Ilona Heckler¹, Gerhard Müller¹, Lucia Caporaso², Stefan Mecking¹,
¹ Department of Chemistry, University of Konstanz, Konstanz, Germany;
² Department of Chemistry, University of Salerno, Fisciano (SA), Italy

9.50 – 10.10 **Polyesters and polyamides precursors from natural and waste oils (D)**

L7 Marc R. L. Furst¹, David J. Cole-Hamilton¹, Thomas Seidensticker¹, Ronan Le Goff¹, Catherine H. Botting¹, Dorothee Quinzler², Stefan Mecking²
¹ St. Andrews, Scotland, UK; ² Department of Chemistry, University of Konstanz, Konstanz, Germany

10.10 – 10.30 **Access to value-added products via metathesis of fats and terpene derivatives (D)**

L8 Christian Bruneau, Cédric Fischmeister, Antoine Dupé, Hallouma Bilel, Université de Rennes 1, Sciences Chimiques, Rennes, France

10.30 – 11.00 **Coffee break**

- 11.00 – 12.50 *Second morning session*
- Chair: George John*
- 11.00 – 11.30 **Fatty alcohols from triglycerides via catalytic hydrogenation (M)**
L9 Dmitry G. Gusev, Denis Spasyuk, Wilfrid Laurier University, Waterloo, Ontario, Canada
- 11.30 – 11.50 **Fe-catalyzed oxidative cleavage of olefins towards aldehydes with hydrogen peroxide (M)**
L10 Peter Spannring, Pieter C. Bruijninx, Bert M. Weckhuysen, Bert Klein Gebbink, Utrecht University, Utrecht, Netherlands
- 11.50 – 12.10 **The first catalytic Lossen rearrangement: Sustainable access to fatty acid derived nitrogen containing monomers and polymers (D)**
L11 Oliver Kreye, Sarah Wald, Maike Unverferth, Alexander Prohammer, Michael A. R. Meier, KIT, Karlsruhe, Germany
- 12.10 – 12.30 **Regioselective hydrogenation of vegetable oils with Pt/ZSM-5 catalysts (D)**
L12 An Philippaerts, Pierre Jacobs, Bert Sels, K.U.Leuven, Heverlee, Belgium
- 12.30 – 12.50 **Catalyst selection for conversion of fats and oils to renewable chemical products (D)**
L13 Aalbert Zwiijnenburg, Johnson Matthey Chemicals GmbH, Emmerich, Germany
- 12.50 – 14.00 **Lunch break**

14.00 – 15.30 *First afternoon session*

Chair: Mel Luetkens

14.00 – 14.30 **ADM's Green Chemistry - platform chemicals based on renewable feedstock (M)**

L14 Jürgen Fischer, Paul Bloom,
ADM Research GmbH, Hamburg, Germany

14.30 – 14.50 **Isosorbide-based value products (D)**

L15 Claudia Stoer, Markus Dierker, Claus Nieendick, Catherine Breffa,
BASF Personal Care and Nutrition GmbH, Düsseldorf, Germany

14.50 – 15.10 **Polyurethane dispersions based on renewable resource materials – off to pasture new! (D)**

L16 Manfred Diederich, Markus Dimmers, Maria Ebert,
Alberdingk Boley GmbH, Krefeld, Germany

15.10 – 15.30 **Development of transformer oils based on renewable raw materials (D)**

L17 Günther Kraft, FUCHS Europe Schmierstoffe, Mannheim, Germany

15.30 – 16.00 **Coffee break**

16.00 – 17.30 *Second afternoon session*

Chair: Dmitry G. Gusev

16.00 – 16.30 **Biorefinery: A sustainable design platform for green surfactants and soft materials (M)**

L18 George John, Department of Chemistry, The City College of the City University of New York, New York, USA

16.30 – 16.50 **Synthesis of fatty ethers: Catalytic reduction of fatty acid esters (D)**

L19 Ursula Biermann, Jürgen O. Metzger, Universität Oldenburg and abiosus e.V., Oldenburg, Germany

16.50 – 17.10 **Additions to unsaturated fatty acid esters: Electrophilic additions via boron compounds and [2+2]-cycloadditions with N-chlorosulfonyl ethanimine to β -lactams (D)**

L20 Hans J. Schäfer, Theodor Lucas, Christian Kalk, Organisch-chemisches Institut der Universität Münster, Münster, Germany

17.10 – 17.30 **Singlet oxygenation of unsaturated monoglycerides in single-phase and multiphase systems using hydrogen peroxide catalyzed by molybdate anions (D)**

L21 Hermine HNM NSA Moto, Zephirin MOULOINGUI, Université de Toulouse, ENSIACET-INRA-INP Toulouse, Laboratoire de Chimie Agro-Industrielle, Toulouse, France

19.30 *Conference Dinner*

Renaissance Karlsruhe Hotel

Tuesday, March 19, 2013

9.00 – 10.40 *First morning session*

Chair: Jürgen O. Metzger

9.00 – 9.30 **Synthesis of biobased building blocks from vegetable oils:
towards platform chemicals (M)**
L22 Sylvain Caillol, Remi Auvergne, Bernard Boutevin, ICGM - ENSCM,
Montpellier, France

9.30 – 10.00 **Biobased polyamides past, present and future (M)**
L23 Jürgen Herwig, Jasmin Nitsche, Harald Häger, Evonik, Marl,
Germany

10.00 – 10.20 **Plant oil based renewable polyamide monomers and their
polymers via efficient (catalytic) processes (D)**
L24 Matthias Winkler, Oğuz Türünç, M. A. R. Meier, KIT, Karlsruhe,
Germany

10.20 – 10.40 **Dimer fatty acids: Building blocks for a multitude of new
macromolecular architectures (D)**
L25 Luc Averous, ICPEES-ECPM University of Strasbourg, France

10.40 – 11.10 *Coffee break*

11.10 – 13.00 *Second morning session*

Chair: Uwe Bornscheuer

- 11.10 – 11.40
L26 **Enzyme-catalyzed reactions for fatty acids modification (M)**
Pierre Villeneuve, Erwann Durand, Jérôme Lecomte, Eric Dubreucq,
UMR IATE, CIRAD, Montpellier, France
- 11.40 – 12.00
L27 **Fine-tuning fatty acids length chain by metabolic engineering for
“Single Cell Oils” strategies in *Ashbya gossypii* (D)**
Rodrigo Ledesma-Amaro, José Luis Revuelta, Universidad de
Salamanca, Salamanca, Spain
- 12.00 – 12.20
L28 **Bio-catalytic synthesis of small molecule oil structuring
agents from renewable resources (D)**
Julian Silverman, George John, Department of Chemistry, The City
College of New York, and The Graduate Center of The City
University of New York, New York, New York
- 12.20 – 12.40
L29 **Online analysis of polycondensations in a bubble column
reactor using ATR-FTIR spectroscopy (D)**
Jakob Gebhard, Lutz Hilterhaus, Andreas Liese, Hamburg
University of Technology, Hamburg, Germany
- 12.40 – 13.00
L30 **Application of fatty acid chlorides in iron and zinc catalyzed
depolymerization reactions (D)**
Stephan Enthaler, TU Berlin, Department of Chemistry, Cluster of
Excellence “Unifying Concepts in Catalysis”, Berlin, Germany
- 13.00 – 14.00 **Lunch break**

14.00 – 16.00 *Afternoon session*

Chair: Sylvain Caillol

14.00 – 14.20 **Synthesis of Palm oil based ethylhexyl ester for drilling fluid application** (D)

L31 Robiah Yunus, Nur Saiful Hafiz Habib, Zurina Zainal Abidin, Universiti Putra Malaysia, Selangor, Malaysia

14.20 – 14.50 **Biobased adhesives: when green chemistry meets the material science of sticky things** (M)

L32 Richard Vendamme, Nitto Denko Corporation's European Research Committee (ERC), Nitto Europe NV, Belgium

14.50 – 15.10 **Microwave-assisted heterogeneous catalysis in esterification and etherification reactions** (D)

L33 Sabine Valange¹, Gina Hincapie², Diana Lopez², Clement Allart¹, Joel Barrault¹, ¹ IC2MP, UMR CNRS 7285, ENSIP, Poitiers Cedex, France; ² Institute of Chemistry, University of Antioquia, Medellin, Colombia

15.10 – 15.30 **Synthesis and application of cyclic carbonates of fatty acid esters** (M)

L34 Benjamin Schöffner¹, Matthias Blug¹, Daniela Kruse¹, Benjamin Woldt¹, Mykola Polyakov², Angela Köckritz², Andreas Martin², Sebastian Jung³, David Agar³, Bettina Rüngeler⁴, Andreas Pfennig⁵, Karsten Müller⁵, Wolfgang Arlt⁵, ¹ Evonik Industries AG, Germany; ² Leibniz-Institute for Catalysis e.V., Rostock, Germany; ³ TU Dortmund, Dortmund, Germany; ⁴ RWTH Aachen, Aachen, Germany; ⁵ TU Graz, Graz, Austria; ⁶ University of Erlangen-Nuremberg, Erlangen, Germany

15.30 **Poster Award and Closing Remarks**

Best Poster Award

Award committee: Bret J. Chisholm, Pierre Villeneuve, Richard Vendamme

Closing remarks

Michael A. R. Meier

16.00 **End of Workshop**

Posters

- P1 **Green synthesis of biolubricants from castor oil and higher chain alcohols**
Chandu S. Madankar, Subhalaxmi Pradhan, S.N. Naik, Indian Institute of Technology, Delhi, India
- P2 **Potassium fluoride impregnated CaO/NiO: An efficient heterogeneous catalyst for transesterification of triglycerides**
Mandeep Kaur, Amjad Ali, Thapar University, Patiala India
- P3 **In-situ monitoring and induction time measurements during melt crystallization of plant based fatty acid mixtures in V-form reactor**
Sunanda Dasgupta, Peter Ay, Chair of Mineral Processing, Processing of Biogenous Resources, Brandenburg University of Technology, Germany
- P4 **Biomass conversion: Preparation of glycerol carbonate esters by esterification with hybrid Nafion-silica catalyst**
Sergio Martínez Silvestre, Maria José Climent Olmedo, Avelino Corma Canós, Sara Iborra Chornet, Instituto de Tecnología Química, Valencia, Spain
- P5 **Time-resolved characterization of aging products from fatty acid methyl esters**
Stephanie Flitsch, Sigurd Schober, Martin Mittelbach, Institute of Chemistry, University of Graz; Graz, Austria
- P6 **Solvent Assisted Hydraulic Pressing of Dehulled Rubber Seeds**
Muhammad Yusuf Abduh, Erna Subroto, Robert Manurung, Hero Jan Heeres, University of Groningen, Groningen, Netherlands
- P7 **Hydrotreating of Non-Food Fat and Oil Derivatives for the Production of Biofuels**
Alexander F. H. Studentschnig, Sigurd Schober, Martin Mittelbach, Institute of organic/bioorganic Chemistry, Karl-Franzens University Graz, Graz., Austria
- P8 **Enhancing the acyltransferase activity of *Candida antarctica* lipase A**
Janett Müller, Henrike Brundiek, Birte Fredrich, Uwe T. Bornscheuer, University of greifswald, Greifswald, Germany
- P9 **Temperature and composition dependence of density for soybean oil, epoxidized soybean oil and acetic acid binary mixtures**
Milovan Jankovic¹, Olga Govedarica¹, Snezana Sinadinovic-Fiser¹, Vesna Rafajlovska²
¹ Faculty of Technology, University of Novi Sad, Serbia; ² Faculty of Technology and Metallurgy, SS Cyril and Methodius University in Skopje, Macedonia
- P10 **Renewable co-polymers derived from limonene and fatty acid derivatives**
Maulidan Firdaus, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

- P11 **Biphasic kinetic model of in situ epoxidation of castor oil with peracetic acid**
Milovan Jankovic, Snezana Sinadinovic-Fiser, Olga Govedarica, Faculty of Technology, University of Novi Sad, Serbia
- P12 **Thiol-yne approach to biobased polyols: polyurethane synthesis and surface modification**
Cristina Lluch, Gerard Lligadas, Joan Carles Ronda, Marina Galià, Virginia Cádiz, Universitat Rovira i Virgili, Tarragona, Spain
- P13 **Heteropoly acids for conversion of renewable feedstocks**
Ali M. Alsalme, Abdulaziz A. Alghamdi, King Saud University, Riyadh, Saudi Arabia
- P14 **Flexible polyurethane foams modified with selectively hydrogenated**
Sylwia Dworakowska¹, Dariusz Bogdal¹, Federica Zaccheria², Nicoletta Ravasio²,
¹ Cracow University of Technology, Cracow, Poland; ² Institute of Molecular Science and Technologies, National Research Council (CNR-ISTM), Milano, Italy
- P15 **Synthesis, purification and modification of abietic acid dimer, an interesting source of (co)monomers for the design of novel renewable polymers**
Audrey Llevot, Stephane Carlotti, Stephane Grelier, Henri Cramail, LCPO, PESSAC, France
- P16 **Rhodium-catalyzed hydroformylation of unsaturated fatty esters in aqueous media assisted by activated carbon**
Jérôme Boulanger, Frédéric Hapiot, Anne Ponchel, Eric Monflier, UCCS Artois, Lens, France
- P17 **Effect of some medicinal tea extracts on some oxidative parameters of sesame oil**
Mehmet Musa Özcan¹, Nurhan – Uslu¹, Fahad Al Juhaimi²,
¹ Selçuk University, Konya, Turkey; ² King Saud University, Riyadh, Saudi Arabia
- P18 **Self-metathesis of fatty acid methyl esters: Full conversion by choosing the appropriate plant oil**
Robert Hofsäß, Hatice Mutlu, Rowena E. Montenegro, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P19 **Synthesis and characterization of new biodegradable poly(linoleic acid) / poly(linolenic acid) graft copolymers**
Abdulkadir Allı¹, Pınar Geçit¹, Sema Allı², Baki Hazer²,
¹ Department of Chemistry, Düzce University, Düzce, Turkey; ² Bülent Ecevit University, Turkey

- P20 **Diversity in ADMET monomer synthesis via Passerini three component reactions with 10-undecenal as key building block**
Ansgar Sehlinger, Lucas Montero de Espinosa, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P21 **Malate production by *Aspergillus oryzae***
Katrin Brzonkalik, Marina Bernhardt, Christoph Syldatk, Anke Neumann, KIT Technical Biology, Karlsruhe, Germany
- P22 **Monitoring of glyceride synthesis in multiphase system by ATR-Fourier transform infrared spectroscopy**
Sören Baum¹, Martin Schilling², Fabien Cabirol², Lutz Hilterhaus¹, Andreas Liese¹,
 Institute of Technical Biocatalysis, TH Hamburg, Hamburg, Germany; ² Evonik Industries AG
- P23 **Pressure sensitive adhesives from renewable resources**
Wiebke Maassen, Norbert Willenbacher, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P24 **Renewable aromatic aliphatic copolyesters derived from rapeseed**
Stefan Oelmann, Oliver Kreye, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P25 **Influence of the double bond configuration on the product composition of Rh-catalyzed maleinisation of monounsaturated fatty acids**
Steven Eschig, Tunga Salthammer, Claudia Philipp, Fraunhofer Institute for Wood Research, Wilhelm-Klauditz-Institut, Braunschweig, Germany
- P26 **α -Arylation of saturated fatty acids: a sustainable approach to renewable monomers?**
Nicolai Kolb, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P27 **New transformations of ricinoleic acid derivatives**
Manuel Hartweg, Hatice Mutlu, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P28 **Self-metathesis derived renewable 1,4-cyclohexadiene and its potential applications**
 Sarah Wald, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
- P29 **Mesoporous niobium-silica materials for the epoxidation of vegetable oil-derived mixtures of unsaturated fatty acid methyl esters (FAMES)**
Cristina Tiozzo¹, Nicoletta Ravasio¹, Rinaldo Psaro¹, Dariusz Bogdal², Sylwia Dworakowska², Matteo Guidotti¹,
¹ CNR-Institute of Molecular Sciences and Technologies, Milan, Italy; ² Cracow University of Technology, Cracow, Poland

- P30 **Isomerizing ethenolysis of functionalized olefins**
Sabrina Baader, Dominik M. Ohlmann, Lukas J. Gooßen, Fachbereich Chemie,
Organische Chemie, TU Kaiserslautern, Kaiserslautern, Germany
- P31 **Synthesis of oleic acid based-polymeric lattices through emulsion and miniemulsion polymerization**
Alan T. Jensen¹, Claudia Sayer², Pedro H. H. Araújo², Fabricio Machado¹,
¹ University of Brasilia, Brasilia, Brazil; ² Federal University of Santa Catarina,
Florianópolis – SC, Brazil
- P32 **Synthesis of polyurethane nanoparticles from renewable resources by miniemulsion polymerization**
Alexsandra Valerio¹, Sandro R. P. da Rocha², Claudia Sayer¹, Pedro H. H. Araújo¹
¹ Federal University of Santa Catarina, Florianópolis – SC, Brazil; ² Wayne State University

Abstracts

Part 1: Lectures

Polyurethanes from renewable resources and carbon dioxide

Rolf Mülhaupt

Freiburg Materials Research Center and Institute for Macromolecular Chemistry,
Freiburg, Germany

rolf.muelhaupt@makro.uni-freiburg.de

Since the pioneering advances by Otto Bayer, polyurethanes are well recognized as very versatile class of materials, which can be tailored to meet the demands of highly diversified applications, ranging from low weight engineering plastics to elastomers, fibers, foams, coatings and adhesives. The quest for green economy and growing concerns regarding global warming are stimulating the development of biobased polyurethanes and polyurethanes derived from the greenhouse gas carbon dioxide. Traditionally, renewable resources play an important role in polyurethane technology, particularly in manufacturing of polyols and prepolymers. For example, polyols are produced by propoxylation of various sugars and natural oils such as soybean and castor oil. Owing to progress in propoxylation chemistry, odor and color problems, have been eliminated, improving properties of such biobased polyurethanes. A variety of biobased polyols are commercially available. New routes are developed to produce propyleneoxide from glycerol, which is a byproduct of the biodiesel production. Intermediates of biorefineries are attractive components for making polyurethanes. Instead of using biocatalytic carbon dioxide conversion and biomass, new processes employ the direct chemical fixation of carbon dioxide. For instance, copolymerization of propylene oxide with carbon dioxide affords polypropylenecarbonates as new polyols for polyurethanes. In green polyurethane chemistry the use of isocyanates is eliminated. Key intermediates are cyclic carbonates, prepared by reacting polyepoxides with carbon dioxide, which are cured with amines. Both epoxidized unsaturated natural oils and epoxidized terpenes are used as raw materials, aiming at preventing competition with food production. This presentation will give an overview on trends and prospects of biobased polyurethanes, focusing on the direct conversion of carbon dioxide and the prospects of green polyurethanes.

L2

Novel high molecular weight vinyl ether polymers based on plant oils

Samim Alam, Harjyoti Kalita, Satyabrata Samanta, Andrey Chernykh, Bret J. Chisholm,
North Dakota State University, Fargo (ND), USA
bret.chisholm@ndsu.edu

A platform technology that has been developed that involves the production of a vinyl ether monomer using simple base-catalyzed transesterification of a plant oil triglyceride with a hydroxy-functional vinyl ether such as 4-(vinyloxy)butanol or 2-(vinyloxy)ethanol, to produce a mixture of vinyl ether monomers that possess fatty acid ester groups in their structure. This process is essentially the same as that used to produce biodiesel (i.e. methyl esters of plant oil fatty acids) with the exception that the hydroxy-functional vinyl ether is used in place of methanol. A key aspect of the technology involves the polymerization process that allows for high molecular weight polymers to be produced by polymerization exclusively through the vinyl ether double bonds. This feature enables polymers to be produced that possess unsaturation in the fatty acid ester pendent groups derived from the plant oil starting material. As has been done for conventional plant oil triglycerides, the double bonds can be used to produce thermoset materials either directly through an oxidative process or by derivatization to produce other functional groups, such as epoxides, acrylates, and hydroxyls, that can be subsequently used to produce crosslinked networks. The polymerization process also results in a “living” polymerization that allows for control of polymer molecular weight, narrow molecular weight distributions, and the production of unique polymer architectures such as block copolymers and multi-arm star polymers. Another very important feature of the technology involves the ability to copolymerize the plant oil-based vinyl ether monomers with other monomers to tailor polymer properties such as glass transition temperature, mechanical properties, and solubility/compatibility with other materials.

L3

Protein engineering and application of enzymes in lipid modification

Uwe T. Bornscheuer

Institute of Biochemistry, Greifswald University, Germany
bornsche@uni-greifswald.de

Protein engineering has developed in the past decade to an important technology to alter the properties of enzymes [1-3]. Whereas initially rational protein design was the method of choice, directed evolution (in essence a random mutagenesis followed by screening or selection of desired mutants) became an important alternative. More recently, researchers used combinations of both methods. We applied extensive protein engineering guided by advanced bioinformatic tools in combination with high-throughput screening to alter the fatty acid selectivity of lipase A from *Candida antarctica* (CAL-A). This resulted in the creation of mutants with excellent selectivity for trans- and saturated fatty acids in the hydrolysis of partially hydrogenated plant oil [4]. Hence, this lipase variant now enables to substantially reduce the trans-fatty acid content providing access to healthy oil for human nutrition. Furthermore, we identified by sequence comparison a lipase from *Ustilago maydis*, which also shows trans-fatty acid selectivity [5]. Another mutant of CAL-A was found to show distinct selectivity for medium chain fatty acids [6]. We also developed a process to reduce the monoglyceride content in commercial biodiesel by applying a monoglyceride-selective lipase from *Penicillium camembertii* [7].

- [1] Kazlauskas, R.J., Bornscheuer, U.T. (2009) *Nature Chem. Biol.*, 5, 526-529
- [2] Bornscheuer, U.T., Huisman, G., Kazlauskas, R.J., Lutz, S., Moore, J., Robins, K. (2012), *Nature*, 485, 185-194.
- [3] Kourist, R., Brundiek, H., Bornscheuer, U.T. (2010) *Eur. J. Lipid Sci. Technol.*, 112, 64-74,
- [4] Brundiek, H.B., Evitt, A.S., Kourist, R., Bornscheuer, U.T. (2012) *Angew. Chem. Int. Ed.*, 51, 412-414.
- [5] Brundiek, H., Sass, S., Evitt, A., Kourist, R., Bornscheuer, U.T. (2012), *Appl. Microb. Biotechnol.*, online; DOI: 10.1007/s00253-012-3903-9.
- [6] Brundiek, H., Padhi, S.K., Evitt, A., Kourist, R., Bornscheuer, U.T (2012), *Eur. J. Lipid Sci. Technol.*, 114, 1148-1153.
- [7] Padhi, S.K., Haas, M., Bornscheuer, U.T. (2012), *Eur. J. Lipid Sci. Technol.*, 114, 875-879.

L4

Epicerol® and the environmental challenges of bio-based chemistry

Thibaud Caulier, Solvay, Brussels, Belgium
thibaud.caulier@solvay.com

The use of more renewable resources is an important trend in the chemical industry. This evolution is well illustrated by Epicerol®, the Solvay patented process to manufacture bio-based epichlorohydrin (ECH) from natural glycerin.

To better understand the environmental footprint of this technology, we performed a life cycle assessment benchmarking Epicerol® with the traditional propylene-based ECH manufacturing process. This comparative eco-footprint shows that, for the same quantity of ECH produced, Epicerol®:

- reduces the non renewable energy demand and the impact on climate change;
- has a detrimental impact on the quantitative land use and the eco-toxicity;
- does not significantly modify the water consumption.

The Epicerol® process allows the chemical industry to reduce its direct environmental footprint (from gate to gate) thanks to an optimization of the resources (less consumption of energy, chlorine and water), and a reduction of the emissions (CO₂, chlorides and water effluents) and by-product formation (chlorinated organics).

From cradle to gate, the use of renewable glycerin reinforces the Epicerol® gate to gate advantages on non renewable energy consumption and CO₂ balance (thanks to the biogenic carbon capture). Paradoxically, renewable glycerin also contributes to a degradation of other environmental parameters. It is true not only for the quantitative land use (impact of farmlands) and the eco-toxicity (impact of plant protection products released in the environment), but also for the water consumption (impact of irrigation) which appears neutral from cradle to gate despite the fact that Epicerol® saves a lot of process water from gate to gate.

The Epicerol® sustainability issues inherited from the agriculture are fundamentally different from the sustainability issues faced by the petrochemical route. They are usually managed by the agro-companies who face pressure in their mainstream food businesses and by the biodiesel industry where authorities are progressively setting strict sustainability criteria.

A lot of improvements are still to be expected in the production of glycerin. They are in the crop yield, in the water consumption and in the general farming operations. The bio-based chemical industry can contribute to this evolution, by the development of sustainable sourcing policies involving a close collaboration with raw material suppliers.

L5

Metathesis: Commercialization of Specialty Chemicals From Lipids

Mel Luetkens, Elevance Renewable Science, Woodridge , IL, USA
Mel.Luetkens@elevance.com

Elevance produces high-performance, cost-advantaged green chemicals from renewable oils. Its process uses Nobel Prize-winning innovations in metathesis catalysis, consumes significantly less energy and reduces greenhouse gas (GHG) emissions compared to petrochemical technologies. The process use a highly efficient, selective catalyst to produce olefins and novel fatty ester fragments from natural oils. The core process technology is based on the work of Nobel Laureate Dr. Robert H. Grubbs. In 2011, Elevance expanded its proprietary technology in metathesis with a licensing agreement with XiMo AG to use proprietary molybdenum and tungsten metathesis catalysts based on the work of Nobel Laureate Dr. Richard Schrock.

The resulting products from its biorefinery are high-value, difunctional chemicals with superior functional attributes previously unavailable commercially. These molecules combine the functional attributes of an olefin, typical of petrochemicals, and a monofunctional ester or acid, typical of biobased oleochemicals, into a single molecule. Conventional producers have to blend petrochemicals and biobased oleochemicals in attempts to achieve these functional attributes simultaneously, which when possible, increase their production costs. Elevance's difunctional building blocks change this paradigm by creating specialty chemical molecules which simultaneously include desired attributes enabled by both chemical families

Elevance's products enable novel surfactants, lubricants, additives, polymers, and engineered thermoplastics. Elevance has completed validation of its several processes in toll manufacturing and it is completing its world-scale biorefinery in Gresik, Indonesia. Elevance has also secured strategic partnerships with value chain global leaders to accelerate deployment and commercialization for these products. In this presentation, the biorefinery process, the biorefinery products, and some markets for the products will be discussed.

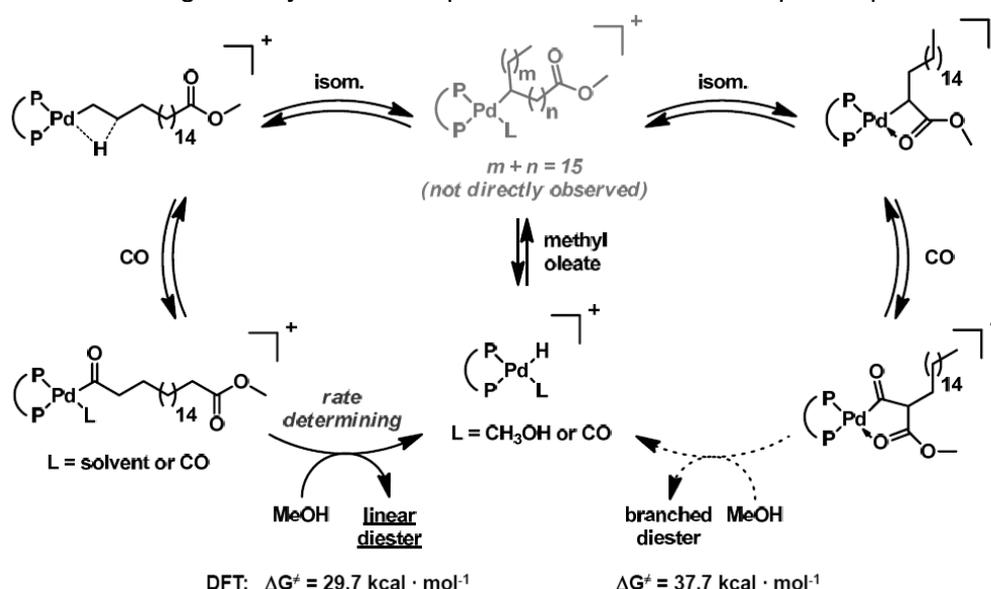
News from the isomerizing alkoxy carbonylation

Philipp Roesle¹, Timo Witt¹, Florian Stempfle¹, Josefine T. Christl¹, Ilona Heckler¹,
Gerhard Müller¹, Lucia Caporaso², Stefan Mecking¹,

¹Department of Chemistry, University of Konstanz, Konstanz, Germany;

² Department of Chemistry, University of Salerno, Fisciano (SA), Italy
Philipp.Roesle@uni-konstanz.de

Thermoplastic polymers are currently prepared almost exclusively from fossil feedstocks. In view of the limited availability of such feedstocks, alternative renewable resources are desirable in the long term.¹ Due to their unique long methylene sequences, fatty acid esters from plant oils are attractive substrates for monomer generation.² By means of isomerizing alkoxy carbonylation such unsaturated fatty acids are converted into long-chain linear diesters in polycondensation grade purity (> 99 %).^{3a,3b} 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.^{3b,3c}



In the discussion lecture we want to present an overview of our current research activities in the field of the isomerizing alkoxy carbonylation of fatty acid esters: a full mechanistic study of this unusual, highly selective reaction, by direct observation of the relevant intermediates with NMR spectroscopic methods, supported by DFT calculations and X-ray structure analysis (identification of the intermediates was performed by various NMR spectroscopic methods assisted by the use of ¹³C enriched compounds).⁴ Moreover, structure-activity relationship of the diphosphine Pd(II) catalysts, as well as the scope and limitations of this reaction will be discussed.

[1] a) D. R. Dodds, R. A. Gross, *Science* **2007**, *318*, 1250 - 1251. b) S. Mecking, *Angew. Chem. Int. Ed.* **2004**, *43*, 1078 - 1085. c) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1788 - 1802. d) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, *Angew. Chem. Int. Ed.* **2011**, *50*, 3854 - 3871.

[2] a) U. Biermann, W. Friedt, S. Lang, W. Lühs, G. Machmüller, J. O. Metzger, M. Rüscher-Klaas, H. J. Schäfer, and M. P. Schneider, *Angew. Chem. Int. Ed.* **2000**, *39*, 2206 - 2224. b) C. Vilela, A. J. D. Silvestre, M. A. R. Meier, *Macromol. Chem. Phys.* **2012**, *213*, 2220 - 2227. c) F. Stempfle, P. Ortman, S. Mecking, *Macromol. Rapid Commun.* **2013**, *34*, 47 - 50.

[3] a) C. Jiménez-Rodríguez, G. R. Eastham, D. J. Cole-Hamilton, *Inorg. Chem. Commun.* **2005**, *8*, 878 - 881. b) D. Quinzler, S. Mecking, *Angew. Chem. Int. Ed.* **2010**, *49*, 4306 - 4308. c) F. Stempfle, D. Quinzler, I. Heckler, S. Mecking, *Macromolecules* **2011**, *44*, 4159 - 4166.

[4] P. Roesle, C. J. Dürr, H. M. Möller, L. Cavallo, L. Caporaso, S. Mecking, *J. Am. Chem. Soc.* **2012**, *134*, 17696 - 17703.

Polyesters and polyamides precursors from natural and waste oils

Marc R. L. Furst¹, David J. Cole-Hamilton¹, Thomas Seidensticker¹, Ronan Le Goff¹,
Catherine H. Botting¹, Dorothee Quinzler², Stefan Mecking²

¹St. Andrews, Scotland, UK ; ² Department of Chemistry, University of Konstanz, Konstanz,
Germany
mrlf2@st-andrews.ac.uk

As oil feedstocks dwindle, there will be a need for alternative feedstocks to produce the many chemicals that so enhance our lives. The search for renewable raw materials from agricultural resources, which can be synthesised into environmentally friendly low cost polymers, is a burgeoning area.

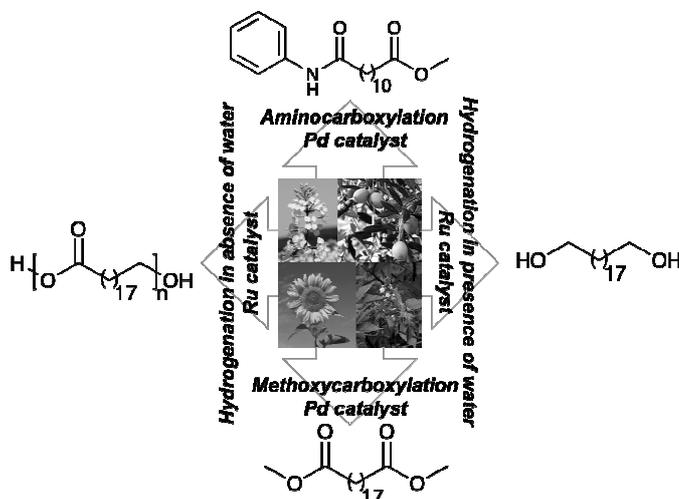
We describe the production of different monomers for the production of polyesters and polyamides. Dimethyl 1,19-nonadecanedioate is obtained from the methoxycarbonylation of commercial olive, rapeseed or sunflower oils in the presence of a catalyst derived from [Pd2(dba)3], bis(ditertiarybutylphosphinomethyl)benzene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

One of the key aspirations of Green Chemistry is to produce useful chemicals from renewable resources, but it is also important to use feedstocks which are available as side products from other processes so that the Chemical syntheses does not require land which could be used for food production.

Dimethyl 1,19-nonadecanedioate can then be obtained from Tall Oil fatty Acids (TOFA), a side product from paper manufacture from pine trees using the Kraft process.

Moreover, we show that methoxycarbonylation of TOFA can give isomeric triesters, trimethyl 1,n,17-heptadecanetricarboxylate, which are isolated in moderate yield from methoxycarbonylation of linoleic acid. The methoxycarbonylation of methyl linoleate is used to gain understanding of the products obtained from TOFA and to optimise that reaction.

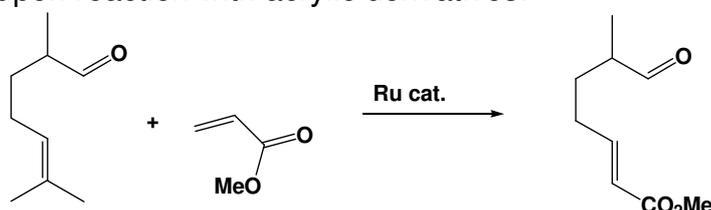
Moreover, a derivative from castor oil, methyl undecen-10-enoate, is aminocarboxylated into methyl 12-oxo-12-(phenylamino)dodecanoate, in the presence of aniline and the previously described palladium catalyst.



Access to value-added products via metathesis of fats and terpene derivatives

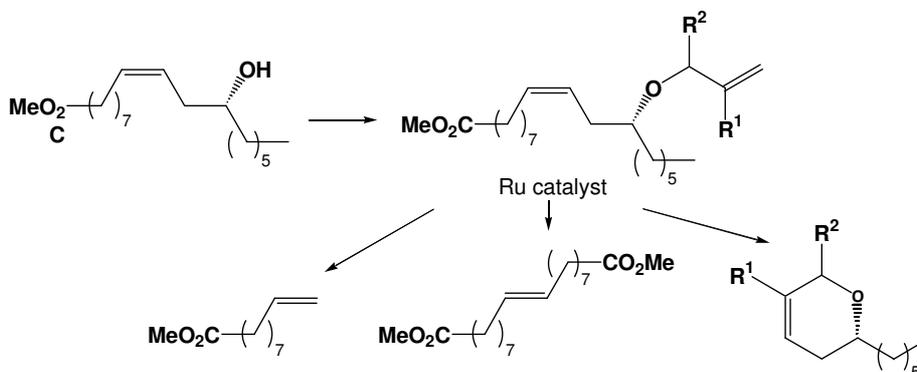
Christian Bruneau, Cédric Fischmeister, Antoine Dupé, Hallouma Bilel,
UMR 6226 CNRS-Université de Rennes 1, Institut Sciences Chimiques de Rennes,
Organométallique : Matériaux et Catalyse, Rennes cedex. France
christian.bruneau@univ-rennes1.fr

Plant oils and terpene derivatives constitute a class of renewable raw materials, which can produce a large variety of chemicals useful for polymer and fine chemical industry. We will show that cross-metathesis of terpenoids produces in one step new functionalized terpene derivatives upon reaction with acrylic derivatives.^[1]



(Scheme 1)

The alcohol functionality of methyl ricinoleate provides a convenient entry to the preparation of dienes. The ring closing metathesis reaction concomitantly leads to dihydropyrans derivatives, which are potentially useful for flavor and fragrance applications, and methyl 9-decenoate and dimethyl octa-9-decenoate (its self-metathesis product), which are polymer precursors (Scheme 2).^[2]



Scheme 2

[1] H. Bilel, N. Hamdi, F. Zagrouba, C. Fischmeister, C. Bruneau, *Green Chem.*, **2011**, 13, 1448.

[2] A. Dupé, M. Achard, C. Fischmeister, C. Bruneau, *ChemSusChem*, **2012**, 5, 2249.

L9

Fatty alcohols from triglycerides via catalytic hydrogenation

Dmitry G. Gusev, Denis Spasyuk, Wilfrid Laurier University, Waterloo, Ontario, Canada
dgoussev@hotmail.com

Reduction of carboxylic esters is typically accomplished with the help of aluminum hydrides. This approach is hazardous and has a challenging work-up protocol due to the highly exothermic hydrolysis step yielding voluminous precipitates. An attractive 'green' alternative to the classical method is the catalytic hydrogenation: $\text{RCOOR}' + 2\text{H}_2 \rightarrow \text{RCH}_2\text{OH} + \text{R}'\text{OH}$, and there has been much recent academic and industrial interest in reduction of esters under hydrogen gas. This presentation concerns the results of catalytic research in our group. In the last two years, we succeeded in developing a series of ester hydrogenation catalysts distinguished by low costs of production, high efficiency, and currently best selectivity for the reduction of unsaturated esters. Examples of applications of the catalytic hydrogenation for reduction of esters of fatty acids, triglycerides and natural oils will be presented. The mechanistic details of the chemical process, practical challenges, and perspectives of the catalytic approach for conversion of fats and oils into fatty alcohols will be discussed.

Fe-catalyzed oxidative cleavage of olefins towards aldehydes with hydrogen peroxide

Peter Spanning, Pieter C. Bruijninx, Bert M. Weckhuysen, Bert Klein Gebbink,
Utrecht University, Utrecht, Netherlands
r.j.m.kleingebink@uu.nl

Olefins can be found in nature as terpenes or unsaturated fatty acids, which are derived from vegetable oils and animal fats. Oxidative cleavage of these bio-based alkenes yields mono- or dicarbonyl compounds, i.e. aldehydes or carboxylic acids, which can be used in polymer, plasticizer and stabilizer production. These compounds are also useful as intermediate building blocks for subsequent reactions.

Industrially, the oxidative cleavage of oleic acid is done by ozonolysis, yet this oxidant is hazardous. Expensive and often toxic transition-metal complexes derived from Ru [1], W [2] or Os [3] are known to catalyze these specific oxidative cleavages, with the help of reactive and relatively hazardous oxidants like NaIO₄ or oxone. On the other hand, first-row transition-metal complexes are primarily known to cleave styrene-derivatives into benzaldehyde [4]. Permanganate may also be used for these reactions, yet it has to be used in stoichiometric amounts.

Here, we present a study towards the use of more benign methods to oxidatively cleave aliphatic double bonds and unsaturated fatty acids into aldehydes, using Fe-catalysts and hydrogen peroxide. Ultimately, such procedures can be seen as green alternatives for the production of chemical building blocks from renewable sources.

[1] Rup, S., Zimmermann, F., Meux, E., Schneider, M., Sindt, M. and Oget, N., *Ultras. Sonochem.* 16 (2009) 266.

[2] Turnwald, S.E., Lorier, M.A., Wright, L.J. and Mucalo M.R., *J. Mat. Sci. Lett.* 17 (1998) 1305.

[3] Ley, S.V., Ramarao, C., Lee, A.L., Oostergaard, N., Smith, S.C. and Shirley, I.M., *Org. Lett.* 5 (2003) 185.

[4] Dhakshinamoorthy, A. and Pitchumani, K., *Tetrah.* 62 (2006) 9911.

The first catalytic Lossen rearrangement: Sustainable access to fatty acid derived nitrogen containing monomers and polymers

Oliver Kreye, Sarah Wald, Maik Unverferth, Alexander Prohammer, Michael A. R. Meier,
KIT, Karlsruhe, Germany
oliver.kreye@kit.edu

A new highly efficient and environmentally benign catalytic variant of the Lossen rearrangement is described.[1] Dimethyl carbonate (DMC) as green activation reagent of hydroxamic acids in presence of catalytic amounts of tertiary amine bases (TBD, DBU, DABCO and triethylamine) and small quantities of methanol initiate the rearrangement.[2] Methyl carbamates were obtained in good to moderate yields if aliphatic hydroxamic acids were employed in this catalytic Lossen rearrangement; under the same conditions aromatic hydroxamic acids yielded anilines. Notably, the mixture of DMC / methanol was recycled several times without observing decreased yields, thus minimizing the produced waste. Moreover, several other organic carbonates (e.g. bis-allyl- or bis-benzyl-carbonate) were successfully employed in the introduced catalytic Lossen rearrangement procedure. The rearrangements of fatty acid derived dihydroxamic acids afforded a facile and sustainable entry to valuable dimethyl carbamate monomers for the synthesis of non-isocyanate polyurethanes (NIPUs).[3] The conversion of these monomers with different aliphatic diols gave structurally diverse thermoplastic NIPUs with molecular weights up to 17 kDa after intensive optimizations regarding the used catalytic system and reaction conditions.

[1] H. L. Yale, Chem. Rev. 1943, 33, 209; L. Bauer, O. Exner, Angew. Chem. Int. Ed. 1974, 13, 376.

[2] O. Kreye, S. Wald, M. A. R. Meier, Adv. Synth. Catal. 2013, DOI: 10.1002/adsc.201200760.

[3] O. Kreye, M. Unverferth, A. Prohammer, M. A. R. Meier, Manuscript in preparation.

Regioselective hydrogenation of vegetable oils with Pt/ZSM-5 catalysts

An Philippaerts, Pierre Jacobs, Bert Sels, K.U.Leuven, Heverlee, Belgium
an.philippaerts@biw.kuleuven.be

Catalytic hydrogenation of vegetable oils is a well-known process in food industry to make the oil more resistant against air autoxidation and/or to obtain fats with a certain melting profile.[1] With the increasing interest of vegetable oils as a renewable feedstock, the selective hydrogenation of triglyceride molecules is also important for industrial applications, as for instance in the production of bio-lubricants.[2] Importantly, the competitive isomerization leading to trans fatty acids needs to be eliminated as much as possible both in food as industrial applications as they are considered a risk factor in coronary heart diseases[3] and/or have a too high melting point, respectively. Unfortunately, literature learns that low cis/trans isomerization is almost always associated with a lower hydrogenation selectivity, implying that the unstable polyunsaturated fatty acids are not selectively converted to the more stable mono-unsaturates.[4]

In this contribution, a new catalytic concept with shape-selective Pt/ZSM-5 catalysts, that is able to decouple the isomerization/hydrogenation selectivity, will be presented.[5] Chemical and physical analysis of the new fat products against commercial benchmarks will be given to show its ideal physical properties despite its essentially trans-free composition.[6]

It will be shown that the improved selectivity obtained with the Pt/ZSM-5 catalyst results from a unique regioselectivity in which the fatty acids located on the central position (sn-2) are preferentially hydrogenated. As vegetable oils contain their polyunsaturated fatty acids mostly at the central position of the triglyceride molecules, these will be preferentially hydrogenated and hence stabilized without significant trans fatty acid formation. Experiments with Pt/ZSM-5 catalysts with different crystal sizes prove that this unprecedented regioselective property is a consequence of pore-mouth catalysis, in which only one fatty acid chain is able to enter the small micropores of the ZSM-5 zeolite where it will be hydrogenated by the internal Pt nanoclusters.

[1] H.B.W. Patterson in "Hydrogenation of Fats and Oils: Theory and Practice, AOCS press, 1994.

[2] a) N. Ravasio, F. Zaccheria, M. Cargano, S. Recchia, A. Fusi, N. Poli, R. Psaro, Appl. Catal. A 2002, 233, 1-6; b) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, Angew. Chem. Int. Ed. 2011, 50, 3854-3871; Angew. Chem. 2011, 123, 3938-3956.

[3] D. Mozaffarian, M. Katan, A. Ascherio, M. Stampfer, Willett, W. N. Engl. J. Med. 2006, 354, 1601-1613.

[4] A. Philippaerts, P.A. Jacobs, B.F. Sels, Angew. Chem. Int. Ed. (accepted)

[5] A. Philippaerts, S. Paulussen, A. Beersch, S. Turner, O.I. Lebedev, G. Van Tendeloo, B. Sels, P. Jacobs, Angew. Chem. Int. Ed. 2011, 50, 3947-3949; Angew. Chem. 2011, 123, 4033-4035.

[6] A. Philippaerts, A. Breesch, G. De Cremer, P. Kayaert, J. Hofkens, G. Van den Mooter, P. Jacobs, B. Sels, J. Am. Oil Chem. Soc. 2011, 88, 2023-2034.

L13

Catalyst selection for conversion of fats and oils to renewable chemical products

Aalbert Zwijnenburg, Johnson Matthey Chemicals GmbH, Emmerich, Germany
bart.zwijnenburg@matthey.com

This contribution will focus on how to select optimal catalysts for the conversion of fats and oils to renewable chemical products. To achieve commercially attractive products, in general, fats and oils need oxygen removal and or hydrogen addition.

These reactions are best carried out via metallic catalysts. The presentation will focus on how to select most promising catalysts, by following design rules on the feedstock acidity, the expected scale of the production plant and the expected purity of the starting material.

By synthetic biology, new feedstocks are becoming available, such as terpenes and fatty alcohols. These new material potentially need less chemical conversion (such as oxygen removal and/or hydrogen addition). It will be shown how these feedstocks differ from the traditional raw materials and how this affects the catalysis. Also the applicability of the general catalyst selection rules will be discussed.

To illustrate the catalyst selection process, an overview of traditional fatty alcohol developments will be given and this will be linked to most recent developments in this area.

ADM's Green Chemistry – Platform Chemicals Based on Renewable Feedstock

Jürgen Fischer, Paul Bloom, ADM Research GmbH, Hamburg, Germany
Juergen.Fischer@adm.com

Archer Daniels Midland, founded in 1902 as a linseed crushing plant, is today one of the world's largest agricultural companies, with its activities covering the whole value chain. The development of new technologies and products is indispensable to make the company fit for the future and to assure its position in the world.

The technical use of bio-based products has a long history. Today, ADM's industrial products cover a wide range comprising biofuels, sugars and specialty chemicals amongst others solvents.

Worldwide research on chemicals from biomass focuses on two major pathways:

1. Direct replacement of existing substances by their "bio" versions

Direct replacement is the preferred option since products and intermediates from conventional production routes can be replaced by their identical biobased version. Good examples are propylene glycol (PG), ethylene glycol (EG) and acrylic acid. PG and EG can easily be produced from biomass by hydrogenolysis of glycerol and sugars. This reaction with hydrogen under mild conditions is a direct replacement for the production from fossil resources. ADM's propylene glycol plant has been in operation since 2010, producing high quality PG with significantly lower CO₂ emissions compared to the petrochemical route. Propylene glycol is used as a key component i.e. in resins, cosmetics, detergents and deicers. Acrylic Acid is a common platform chemical for many applications. ADM is currently piloting a plant for the conversion of biomass to ethanol and acrylic acid/esters.

2. Bioadvantaged molecules: new intermediates from biomass able to replace existing ones from fossil sources.

New intermediate and new products derived thereof are facing a major challenge: they must prove that they perform like their existing alternatives and/or they must provide significant health or environmental benefits.

The production of carbohydrates from biomass is a technology which still offers room for improvement. ADM is running a biorefinery for the conversion of lignocellulosic materials to sugars, which are the main source for new platform materials. Beside substances like Itaconic acid and Succinic acid Isosorbide is a promising molecule which can be used as platform chemical for a variety of products, i.e. polymers, solvents, surfactants etc., thus replacing e.g. Bisphenol A.

ADM will continue to develop the use of biomass and assure feedstock supply by innovations in processing, investment in agricultural infrastructure, thus continuing and/or establishing partnerships.

Isosorbide-based Value Products

Claudia Stoer, Markus Dierker, Claus Nieendick, Catherine Breffa,
BASF Personal Care and Nutrition GmbH, Düsseldorf, Germany
claudia.stoer@basf.com

Isosorbide, a cyclic diol completely obtainable from renewable raw materials, is an ideal candidate for further derivatization that should lead to new, innovative, green products with favourable properties regarding sustainability and performance compared to petrochemical based existing benchmarks.

While Isosorbide has been known for many years, only a few applications have been realized commercially so far. When we started with Isosorbide chemistry we intended to evaluate Isosorbide as building block and starting material for the development of new marketable products for cosmetic and laundry detergents.

Thus the challenge is that fundamental studies are required to come to a conclusion in terms of general and economic feasibility of the synthesis as well as compatibility with typical formulation ingredients. The properties of new synthesized derivatives are not predictable at all and must therefore be evaluated in a broad screening.

Here the syntheses as well as first application test results of neutral and anionic Isosorbide derivatives are presented. In summary, not only the practicability in typical formulations but also the general suitability for the foreseen applications can be demonstrated. The most promising results are currently evaluated and optimized in new projects.

Polyurethane dispersions based on renewable resource materials – off to pasture new!

Manfred Diederling, Markus Dimmers, Maria Ebert,
Alberdingk Boley GmbH, Krefeld, Germany
m.diederling@alberdingk-boleyn.de

With the increasing importance to preserve limited resources and the steadily increasing prices for mineral oil based raw materials, the pressure and will is increasing to utilize more renewable raw materials. Among coating materials, alkyd resins and polyurethanes are important substance classes which can be produced to a significant percentage on a renewable base. Especially water-born polyurethane dispersions are predestined for the application in new fields of applications due to their broad variability regarding the chemical and mechanical properties.

The binder in interior wall paints is typically on the base of styrene acrylics or vinyl acetate ethylene copolymers. These raw material bases make it quite difficult to switch to renewable raw materials as there are hardly any renewable monomers available. In addition, in this product range there are additional requirements and regulations important for a healthy living environment.

Alberdingk Boley shows current developments in an area which is opening up a new application field for polyurethane dispersions: a binder for interior wall paints with a significant part of renewable raw material (based on vegetable oil) which is at the same time free of VOC (volatile organic compound) and amines. The presentation focuses on the application, technological comparison between conventional binders and the new product. It is shown that it is indeed possible to achieve comparable performance and to reduce the mineral oil based organic content by ca. 50%.

Development of transformer oils based on renewable raw materials

Günther Kraft, FUCHS Europe Schmierstoffe, Mannheim, Germany
gunther.kraft@fuchs-europe.de

Since approx. 20 years the increase of the usage of renewable material in substantial and energetical way is promoted by policy, natural sciences and economy. The increasing application of renewable raw materials has various positive consequences, of economical as well as of ecological nature. Fallow acres can be (re)used reasonably to produce renewable raw materials and the products basing on those are potentially less toxic and possess better biodegradability in comparison to mineral oil based products. Additionally the substitution of fossil limited resources, whose CO₂- emissions potential pollutes the environment more distinctively, can have a positive effect on the eco-balance, as renewable raw materials offer a closed cycle of materials.

The development of new transformer oils on the base of plant oils offer the possibility to substitute the hitherto used mineral oil based products. In addition to the higher biodegradability, the renewable based oils can be classified as “not hazardous to waters” according to German legislative, which is especially preferable in a sensible ambience. Besides the argumentation of sustainability and eco-balance, a renewable based ester transformer oil can also offer technical benefits due to optimized properties. Examples are e.g. higher flame and burning points which can reduce the risk of the burning potential explicitly. Optimized cold temperature behaviour with a low pour point allows the application in cold locations, which is not possible with pure plant oils. In comparison to mineral oils, the ester based fluid is able to hold much higher quantities of water, without a decline of the electrical stability. Hereby the risk of snap-through failures at cold starting conditions is reduced. Due to the higher absorption of water by ester oils, the lifetime of the transformer can be extended additionally, as the bio based oil decreases especially the hydrolytic degradation of the cellulose (by water) which is used in the transformer pressboard.

Overall, new transformer ester oils on the base of renewable raw materials can have a share in the substitution of fossil crude materials without cutting back the technical abilities – in contrary, they outclass the mineral oil based transformer oils of today.

L18

Biorefinery: A sustainable design platform for green surfactants and soft materials

George John, Department of Chemistry,
The City College of the City University of New York, New York, USA
gglucose@gmail.com

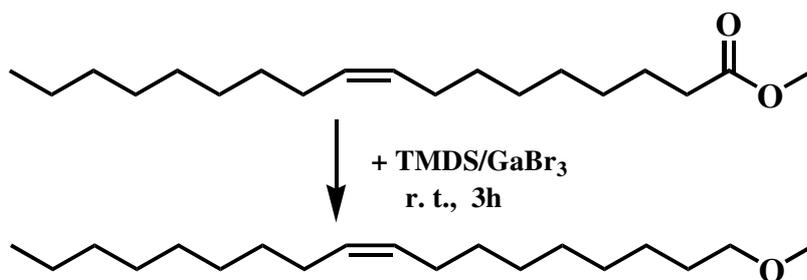
In future research, developing materials from renewable resources would be fascinating yet demanding practice, which will have a direct impact on industrial applications, and economically viable alternatives. This talk presents a novel and emerging concept of generating new chemicals, intermediates and materials in a 'Biorefinery'. Our continuous efforts in this area have led us to develop new amphiphiles and surfactants from industrial by-products, which upon self-assembly produced molecular materials including micelles, emulsions, lipid nanotubes, twisted/helical nanofibers, thickening agents (molecular gels) and liquid crystals. More recently, harnessing the availability of 'chiral pool' of carbohydrates and selectivity of enzymes catalysis, we have produced an array of amphiphilic molecules from simple sugars and sugar alcohols. Intriguingly, by combining biocatalysis, with principles of green and supramolecular chemistry, we have developed building blocks-to-assembled materials. The second part of the talk addresses the templated synthesis of organic-inorganic hybrid materials for targeted use in coatings, liquid crystal templates and energy storage devices. These results will lead to efficient molecular design of supramolecular architectures and multifunctional soft materials from underutilized plant/crop-based renewable feedstock.

Synthesis of fatty ethers: Catalytic reduction of fatty acid esters

Ursula Biermann, Jürgen O. Metzger,
 Universität Oldenburg and abiosus e.V., Oldenburg, Germany
 ursula.biermann@uni-oldenburg.de

Oils and fats are presently the most important renewable feedstock of the chemical industry. The direct reduction of fatty esters and especially of triglycerides to fatty ethers would be a most important reaction because fatty ethers show interesting differences of the properties in comparison to esters. We discuss a novel reaction protocol allowing to convert for example tributyrine, a triglyceride, and methyl oleate, an unsaturated fatty ester (Scheme) to the respective ethers using stoichiometric amounts of 1,1,3,3-tetramethyldisiloxane (TMDS) as reductant and low catalyst loading of 1% GaBr₃ to give in a solvent-free reaction at room temperature after a reaction time of only 3 h 100 % conversion of the starting material and high product yields. The work up procedure is most simple. The products were isolated by simple distillation of the reaction mixture without any additional work-up.

Using the described standard reaction conditions it was also possible to convert lactones to the respective cyclic ethers.



Conversion 100%; Yield 89% (distillation)

Methyl oleate : TMDS : GaBr₃ = 1:1:0.01

Scheme: Gallium-catalyzed reduction of methyl oleate with tetramethyldisiloxane and GaBr₃ as catalyst to give methyl oleylether

[1] WO 2013/010747 A1

Additions to unsaturated fatty acid esters: Electrophilic additions via boron compounds and [2+2]-cycloadditions with N-chlorosulfonylisocyanate to β -lactams

Theodor Lucas, Christian Kalk, Hans J. Schäfer, Organisch- chemisches Institut der Universität Münster, Münster, Germany
schafeh@uni-muenster.de

Unsaturated fatty acids can be modified by electrophilic addition and cycloaddition to form higher value products.

In hydroboration the added boron atom can be replaced in a subsequent oxidation by a hydroxy group [1]. This way methyl linoleate (**1**), methyl ricinoleate (**2**), methyl 10-undecenoate (**3**) and methyl oleate (**4**) could be converted into the corresponding methyl dihydroxy- and hydroxystearates and 11-hydroxyundecenoate in 82-92 % yield [2]. Organoboranes isomerize at higher temperatures [1]. Hydroboration of oleic acid and subsequent heating to 220 oC led after oxidative work-up to 70% of 1,4-octadecandiol [2]. Presumably a 1,4-oxaborinane intermediate determines the interesting regioselectivity of this isomerization.

Organoboranes undergo a dealkylation-coupling with alkaline silver nitrate, presumably via radicals as intermediates, which had been applied to ester **3** [1]. Attempts to transfer the reaction to the internal organoboranes from ester **1** and **4** led to radical disproportionation products, which is the favourable reaction of the intermediate secondary alkyl radicals. Reaction of ester **3** with a terminal double bond and 1-hexene, which involves primary alkyl radicals, led to 25 % of the heterocoupling product: methyl heptadecanoate [2].

Organoboranes can be added to α,β -unsaturated carbonyl compounds [1]; presumably a radical chain reaction is involved. With **3**, borane and methylvinylketone the 1,4-adduct methyl 14-oxopentadecanoate could be obtained in 68% yield [2]. However, attempts to add unsaturated fatty acid methyl esters with internal double bonds as **1** and **4** failed.

With carbon monoxide or the cyanide anion the carbonyl group can be inserted between two alkyl groups of an organoborane. The same result can be achieved in the base initiated reaction of dichloromethyl methyl ether (DCME) with boranes. This is a less toxic alternative to the use of carbon monoxide or cyanide and additionally it has a broader scope [1]. The boranes of **1**, **3** and **4** were treated at -75°C with DCME and then were deprotonated with lithium triethyl carboxide. This way esters **1**, **3** and **4** led to dimers connected by a carbonyl group in 55-80% yield [2].

The [2+2]-cycloaddition of *N*-chlorosulfonylisocyanate (NCSI) to alkenes affords β -lactams [3]. The esters **1**, **2**, **3** and methyl petroselinat (**5**) were reacted at room temperature with NCSI. Thereafter the chlorosulfonyl group was reductively removed with sodium disulfite, which afforded the β -lactams in 59-72% yield [4].

Ring opening of the β -lactams led to partial ester hydrolysis in spite of using different acids and different acid concentrations. To achieve a selective ring opening the ester group was replaced by an acid resistant alkoxy group. Alkoxy ethers from **3** and **4** afforded the β -lactams in 42-57% yield; the lactams were hydrolyzed with aqueous HCl quantitatively to the corresponding amino acids.

The antibiotic activity of the β -lactams from **2**, **3** and **5** was explored with the plate diffusion test. They showed a significant activity against mycobacterium, which also comprises the pathogens of tuberculosis and leprosy. The highest activity was found with the β -lactam from **5**.

[1] H. C. Brown, Hydroboration, 2. ed, Benjamin, 1980.

[2] Th. Lucas, Ph. D. Thesis, University of Münster, 1991.

[3] R. Graf, Chem. Ber. 1956, 89, 1071-1079.

[4] Ch. Kalk, Ph. D. Thesis, University of Münster, 2001.

Singlet oxygenation of unsaturated monoglycerides in single-phase and multiphase systems using hydrogen peroxide catalyzed by molybdate anions

Hermine HNM NSA MOTO, Zephirin MOULOUNGUI, Université de Toulouse, ENSIACET-INRA-INP Toulouse, Laboratoire de Chimie Agro-Industrielle, Toulouse, France
hermine.nsamoto@ensiacet.fr

Monoglycerides are the most polar component of simple lipids. Because of their special chemical structures comprising an aliphatic lipophilic chain and two hydroxyl groups in the hydrophilic part, monoglycerides have detergent-like properties; hence, they easily form micelles in aqueous solutions. Monoglycerides are directly used in a wide range of applications, including surfactants, lubricant additives, plastics, and materials for textile industry. These products are of great interest as emulsifiers in the foods, cosmetic and pharmaceutical industries. Monoglycerides have been synthesized by a variety of substrates with glycerol, an abundant by-product from the biodiesel industries (1). Our research group has already developed new routes to convert the glycerol and glycidol with fatty acid material to 1-monoglycerides (2,3). This fact stimulated the study on monoglyceride as a platform chemical that can be derivatized to design new functional building-blocks for the synthesis of new surfactants or polymers.

The major aim of this project is to use vegetable oils and their derivatives, and to transform them by the simple methods into very rewarding oxygenated products which are products of high added value oleochemicals. To do this, the oxidation of unsaturated fatty acids by singlet oxygen has proved to be considerable more suitable route to the synthesis of the allylic alcohols and epoxides compounds (4).

First, this presentation will highlights a new route to convert selectively double bond of unsaturated monoglycerides into oxygenated monoglycerides using singlet oxygen generated chemically by aqueous hydrogen peroxide (H_2O_2) catalyzed by molybdate anions (MoO_4^{2-}) in single-phase and multiphase emulsion systems (5,6). Such a method involves the synthesis in an organized molecular system which is favorable to in situ production of singlet oxygen and to improve the lifetime of singlet oxygen and the coexistence of singlet oxygen with a molybdate catalyst activated. According to this process, the hydroxy allylic-, epoxy- and dihydroxy-monoglycerides were synthesized and the characteristics of these resultant products were evaluated.

Second, this presentation will present the use of a method for in situ generation of singlet oxygen by heterogeneous molybdate-based catalysts which are consisting with molybdate anions supported on anion exchange resins. This system can be considered as an emulsion or a microemulsion supported on a solid catalytic phase that prevent only the close contact between organic substrates and peroxomolybdates (the intermediate peroxomolybdates generated by H_2O_2/MoO_4^{2-} system) to increase the in situ generation of singlet oxygen and promotes also a large surface exchange for oxidation.

The last part of study deals with the synthesis of estolides (7), where oleic acid and erucic acid and the new oxygenated monoglycerides were used as model substrate. All reactions were run at stoichiometry such that the fatty acids hydroxyl groups would all be esterified to estolide. Using this approach, chemical characteristics of these new estolides compounds were also analyzed.

Synthesis of biobased building blocks from vegetable oils: towards platform chemicals

Sylvain Caillol, Remi Auvergne, Bernard Boutevin,
ICGM - ENSCM, Montpellier, France
sylvain.caillol@enscm.fr

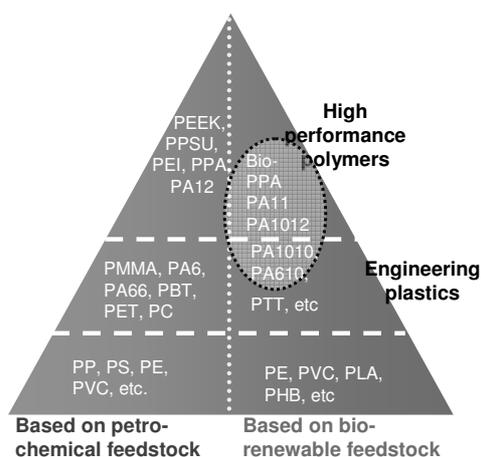
Uncertainty in terms of price and availability of petroleum, in addition to global political and institutional tendencies toward the principles of sustainable development, urge chemical industry to a sustainable chemistry and particularly the use of renewable resources in order to synthesize biobased chemicals and products. A biobased product is a product synthesized from renewable resources (vegetal, animal, or fungal). Vegetable oils come from various plants (soybean, palm, rapeseed, etc.) and mainly contain triglycerides molecules where the three hydroxyl functions of glycerin are esterified with fatty acids. These fatty acids could be saturated, with non-reactive aliphatic chains (stearic or palmitic acids) or unsaturated, with aliphatic chains bearing double bonds (oleic, linoleic, linolenic, ricinoleic acid, etc.). These natural oils, and particularly the unsaturated ones, are of interest since various reactions could be performed from their different groups in order to obtain various building blocks for polymer chemistry. We report the synthesis of various building blocks from vegetable oils in one or two-steps syntheses. Thiol-ene coupling allowed to synthesize new biobased reactants with various function and functionality with reaction conditions in agreement with green chemistry principles: it does not use neither solvent nor initiator or need a simple purification step, feasible at industrial scale. Esterification and amidification were also use to insert ester or amide groups in fatty chains in order to modify properties of thereof synthesized polymers. Building blocks synthesized have various functions and functionality: polyols, polyacids, polyamines and dicyclocarbonates from vegetable oils and from glycerine derivatives. We developed a real chemical toolbox based on thiol-ene coupling and amidification/esterification to synthesize a library of biobased building blocks with various functions and functionality from vegetable oils. The synthesized building blocks reported in this contribution are polyols, polyacids, polyamines and dicyclocarbonates from vegetable oils and from glycerine derivatives. They led to polymer synthesis such as polyurethanes, polyhydroxyurethanes and epoxy resins. These biobased building blocks led to polymers with various properties: low Tg polymers for coating or higher Tg polymers for composites.

Biobased Polyamides past, present and future

Jürgen Herwig, Jasmin Nitsche, Harald Häger, Evonik, Marl, Germany
juergen.herwig@evonik.com

Although the chemical industry stands for less than 10 percent of the overall fossil carbon usage, the chemical industry is nevertheless making a concerted effort to use renewable resources for producing the monomers used in polymer synthesis. One method is to use ethanol obtained from sugar cane (as Braskern and DOW are planning to do in Brazil) to manufacture petrochemical feedstocks such as ethylene, which can then be used for synthesizing polyethylene. The advantage of this method is that it can accommodate existing processes, and does not affect existing approvals. A second approach—one that, while significantly more difficult, is also more promising in the long run—is to convert raw materials using new catalytic or biotechnological processes. This is the strategy that DuPont is pursuing as it uses biotechnology techniques to produce 1,3-propanediol, a compound that yields new material properties in polyesters. While reducing the number of process steps—in some cases dramatically—is yet another advantage, these new materials will, however, need to be relaunched on the market and submitted to relevant chemical registries.

Polyamids based on biorenewable feedstocks, primarily those derived from ricinus oil and/or ricinoleic acid known for over 50 years. sebacic acid, and pyrolytic produces 10-undecylenic converted to 11-PA11. Decanediamine this way, which opens up PA1010. Combining these from petrochemical polyamides such as PA10T based in part on important to remember pathways described produce by-products.



methyl ester, have been Boiling with NaOH yields cleavage at $>500^{\circ}\text{C}$ acid. This, in turn, can be aminocarboxylic acid and can also be synthesized in the door to producing with monomers derived feedstocks yields PA610, PA1012 and biological sources. It is here that the synthesis above necessarily

Major growth in the use of polyamides derived from petrochemical feedstocks has prompted growing interest in sustainable products over the past several years, with the result that more and more fatty acid-based polyamides are being marketed as biopolyamides. This means that polyamides from biorenewable feedstocks are now an issue for the future—the task ahead will be to combine the sustainability of renewable materials with the manufacturing processes of the petrochemical industry.

In addition to discussing methods for synthesizing polyamides from a variety of available monomers, the speaker will also compare the properties of polyamides derived from biorenewable feedstocks to those of their petrochemical counterparts. How can sustainability and green chemistry be combined? Various approaches will be presented.

Plant oil based renewable Polyamide monomers and their polymers via efficient (catalytic) processes

Matthias Winkler, Oğuz Türünç, M. A. R. Meier, KIT, Karlsruhe, Germany
matthias.winkler@kit.edu

Aliphatic polyamides are a class of highly valuable engineering plastics. Their excellent mechanical properties are mainly due to increased chain-chain interactions by hydrogen bonding, which lead to higher tensile strength, impact strength, fracture stress and abrasive resistance as well as chemical inertness and heat resistance. Polyamides are widely applied high-performance polymers, which are used, e.g., as fibers, tubings, form-parts in the automobile-, textile- or electric industry. Particularly, Polyamides from renewable resources are of great interest due to their lower environmental impact. Herein, we present three different strategies for the synthesis of AB-type renewable monomers, which can be used for the preparation of polyamides by simple polycondensation. In this context, methyl oleate and -erucate were utilized as substrates, which were transformed to valuable AB-type monomers via thiol-ene addition of cysteamine[1] and other efficient procedures.[2,3] Both, monomer synthesis and polymerization were studied in detail and the resulting Polyamides were characterized by GPC, NMR, DSC as well as tensile tests. Moreover, the prepared renewable monomers were employed in co-polymerizations with hexamethylenediamine and dimethyl adipate to modify the mechanical and thermal properties of conventional nylon 6,6.

[1]O. Türünç, M. Firdaus, G. Klein, M. A.R. Meier, Green. Chem. 2012, 14, 2577-2583.

[2]M. Winkler, M. A. R. Meier, submitted

[3]M. Winkler, M. Steinbiß, M. A. R. Meier, submitted

Dimer fatty acids: Building blocks for a multitude of new macromolecular architectures

Luc Averous, ICPEES-ECPM University of Strasbourg, France
luc.averous@unistra.fr

At high temperature, double bonds of unsaturated fatty acids may change their position to form conjugated structures, facilitating their dimerisation by Diels-Alder mechanism. This reaction leads to a mixture of compounds, such as dimers and trimers of fatty acids. After purification, the dimer fatty acids can be used as raw materials or modified e.g., for the synthesis of biobased polymers.

The activity of the BioTeam at University of Strasbourg (France) is mainly focused on the development of new biobased polymer systems for environmental and biomedical applications. In this context, we have developed a great variety of new macromolecular architectures based on dimer fatty acids such as (i) TPUs, which can be partially [1-2] of fully biobased [3], (ii) Polyamides [4-5], (iii) polyetheramides ...

The presentation will be mainly focused on the structure-properties relationships for these different architectures, in connection with their synthesis.

From these polymers, different multiphase systems (biocomposites ...) can be formulated [6-8] with specific performances to fulfill the requirements of a large range of applications and numerous fields such as automotive industry, consumer or domestic equipment, construction engineering and biomedical applications.

1. Bueno-Ferrer C., Hablot E., Garrigós M.C., Bocchini S., Averous L., Jiménez A., (2012) "Relationship between morphology, properties and degradation parameters of novative biobased thermoplastic polyurethanes obtained from dimer fatty acids" *Polymer Degradation and Stability*. Vol. 97, N°10, pp. 1964-1969.
2. Bueno-Ferrer C., Hablot E., Perrin-Sarazin F., Garrigós M.C., Jiménez A., Averous L. (2012) "Structure and morphology of new bio-based thermoplastic polyurethanes obtained from dimeric fatty acids" *Macromolecular Materials & Engineering*. Vol. 297, N°8, pp. 777–784.
3. Charlon M., Heinrich B., Donnio B., Matter Y., Avérous L., "Synthesis, structure and properties of fully biobased thermoplastic polyurethanes based on hydrogenated dimer of fatty acids " Under Press.
4. Hablot E., Donnio B., Bouquey M., Avérous L. (2010) « Dimer acid-based thermoplastic bio-polyamides: reaction kinetics, properties and structure ». *Polymer*, Vol. 51, N°25, pp. 5895-5902.
5. Hablot E., Tisserand A., Bouquey M., Avérous L. (2011) "Accelerated artificial ageing of new dimer fatty acid-based polyamides" *Polymer Degradation and Stability*. Vol. 96, pp. 1097-1103.
6. Matadi R., Hablot E., Wang K., Bahlouli N., Ahzi S., Avérous L. (2011) « High strain rate behaviour of renewable biocomposites based on dimer fatty acid polyamides and cellulose fibres » *Composites Science and Technology*. Vol. 71, pp. 674–68.
7. Hablot E, Matadi R, Ahzi S, Avérous L. (2010) "Renewable biocomposites of dimer fatty acid-based polyamides with cellulose fibres: thermal, physical and mechanical properties". *Composites Science and Technology*. Vol. 70, pp. 504–509.
8. Hablot E, Matadi R, Ahzi S, Vaudemond R, Ruch D, Avérous L. (2010) "Yield behaviour of renewable biocomposites of dimer fatty acid-based polyamides with cellulose fibres". *Composites Science and Technology*. Vol. 70, pp. 525–529.

Enzyme-catalyzed reactions for fatty acids modification

Pierre Villeneuve, Erwann Durand, Jérôme Lecomte, Eric Dubreucq
UMR IATE, CIRAD, Montpellier, France
villeneuve@cirad.fr

This presentation will give an overview of the various kinds of reactions that are carried out in our research group regarding the use of enzymes, mainly lipases, to modify oils and fats. Lipases are enzymes that perform very well outside their physiological and natural medium and that can be therefore used as biocatalysts for reactions in limited aqueous systems. Indeed, lipases are widely used in a large variety of reactions such as lipid customizing, corresponding to an adjustment of the fatty acid composition and regiodistribution of oils and fats to obtain new products with designed physical and chemical properties, such as mixtures enrichment and modification of fatty acids or such as the synthesis of new lipophilized compounds with specific physico-chemical or biological properties. Some examples of such reactions will be given with emphasis on lipases specificity and selectivities, and the use of new alternative media to organic solvents for enzyme-catalyzed reactions

**Fine-tuning fatty acids length chain by metabolic engineering for
“Single Cell Oils” strategies in *Ashbya gossypii***

Rodrigo Ledesma-Amaro, José Luis Revuelta,
Universidad de Salamanca, Salamanca, Spain
rodrigoledesma@usal.es

Fatty acids and its derivatives are highly relevant compounds in industry since they have a wide range of applications, from biofuels to fine chemicals such as pharmaceutical or fragrances. Metabolic engineering of microorganisms to produce “Single Cell Oils” (SCOs) seems to be a feasible strategy with promising industrial results in lipid production. *Ashbya gossypii* is an industrial-friendly filamentous fungus, which is being used for large-scale production of vitamins but it is also an oleaginous organism able to accumulate lipids up to 40% of its cell dry weight. Different organisms have distinct fatty acids compositions and two kinds of enzymes: elongases and desaturases are major determinants of lipid profiles. We characterized the elongase and desaturase system in *Ashbya gossypii* by heterologous functional analysis in *S. cerevisiae*, thus we identified two very long chain fatty acid elongases and one $\Delta 12$ desaturase. We used this information to perform metabolic engineering in this pathway and several *Ashbya gossypii* strains with different fatty acid composition were constructed. These strains can be used as both, 1) platform strains for future development of genetic engineering approaches in order to produce a specific fatty acid derivative and 2) as direct source of uncommon fatty acids important for industry since they are enriched in 24:0 and 26:0 or 24:1, which are mainly constituents of wax esters used for polishes, coatings and cosmetics or they are used as high-temperature lubricants and engineering nylons respectively.

Bio-catalytic synthesis of small molecule oil structuring agents from renewable resources

Julian Silverman, George John,
Department of Chemistry, The City College of New York, and The Graduate Center of The
City University of New York, New York, New York, USA
jsilverman@gc.cuny.edu

The synthesis and formation of functional materials from renewable resources is the first step to mitigating an anthropogenic dependence on petroleum-derived products. Biocatalysis allows for the facile synthesis of fatty acid glucosides capable of thickening and solidifying a range of hydrophobic solvents. Various glucosides were selected as sugar-based headgroups and a series of amphiphiles were synthesized by attaching hydrophobic carboxylic acids at one-end of the sugar using an enzyme-mediated regioselective transesterification reaction. For tuning the hydrophobicity of the resulting amphiphile, various carboxylic acids of different chain length were attached [typically (CH₂)₄₋₁₄]. A library of new compounds was easily established by the simple variation of hydrophobic fatty acid chain length, and modification of the hydrophilic glucoside for a variety of applications (food storage and preservation, cosmetics and personal care products). The synthesis of novel structuring agents using biocatalysis from renewable feedstocks is a green methodology that may be used to produce next generation environmentally benign products and chemicals.

Online analysis of polycondensations in a bubble column reactor using ATR-FTIR spectroscopy

Jakob Gebhard, Lutz Hilterhaus, Andreas Liese,
University of Technology of Hamburg, Hamburg, Germany
Jakob.Gebhard@tuhh.de

Synthetic polymers are indispensable for modern society. Since the 1920s polymers are produced from fossil resources, which are being exhausted. Biocatalytic syntheses of polymers via lipase-catalyzed polycondensation of renewable monomers is an alternative but challenging approach. However biocatalysts show higher enantio- and regioselectivity at lower reaction temperatures than chemical catalysts.

The presented work focuses on the solvent free polyester synthesis starting from 1,3-propanediol and 9-((Z)-non-3-enyl)-10-octylnonadecanedioic acid (Pripol™) in a bubble column reactor catalyzed by immobilized lipase B from *Candida antarctica*. The analysis of these biotransformations is usually carried out by size exclusion chromatography.

Therefore monitoring of such processes requires labor intensive sample preparation. The aim of this work is to design chemometric models based on the measured absorption spectra of fourier transform infrared (FTIR) spectroscopy in combination with an attenuated total reflectance (ATR)-probe. This methodology allows the continuous determination of conversion of the reactants as well as the molecular weight (Mw) distribution of the formed polymer. The developed models make use of partial least squares (PLS) algorithm to correlate offline data and spectral information. Mw and conversion from several polymerizations performed at same experimental conditions are used to calibrate two independent models, which showed small root mean square errors of cross validation of 2,14 % and 319 g/mol for conversion and Mw respectively.

Application of fatty acid chlorides in iron and zinc catalyzed depolymerization reactions

Stephan Enthaler, TU Berlin, Department of Chemistry, Cluster of Excellence “Unifying Concepts in Catalysis”, Berlin, Germany
stephan.enthaler@tu-berlin.de

Polymers occupy a significant and omnipresent position in human life. Current polymer feedstocks are based primarily on monomers originated from fossil fuels, which cause clearly a number of problems. On the one hand the confirmed reserves of fossil fuels are progressively decreasing, and their depletion is just a matter of time. On the other hand a huge quantity of polymers is thermally decomposed after they have accomplished their purposes or are converted to low-quality materials. In consequence, a negative impact on the environment is caused, specifically the production of greenhouse gases. Due to these problems, an important issue for current research must address to the invention of protocols for an efficient recycling of polymers. One attractive approach could be the depolymerization of polymeric materials to attain valuable products, which can be applied later on in polymerization processes to produce new polymeric materials. In this regard the utilization of transition metal catalysts presents an efficient opportunity to realize this aim. Here the application of cheap and abundant “bio”metals as catalyst core (e.g., Fe, Zn) will be advantageous. An extensively applied class of polymers or co-polymers are polyethers (e.g., polytetrahydrofuran, polyethylene oxide, polypropylene oxide). The repeating ether units could represent an appropriate functionality to coordinate to the metal and by this an activation of the ether can take place. The addition of fatty acid chlorides, to the activated ether functionality could allow the depolymerization of the polyether to obtain well-defined monomeric chloroesters. The products can be suitable sources for the production of monomers, such as vinyl esters, which can later on polymerize to yield new high-quality semi-biomaterials. Moreover, the carbon carbon double bonds in unsaturated fatty acids can be of interest for cross linked polymers.

Based on this concept and our interest in zinc and iron chemistry we present herein the usefulness of an easy-to-adopt system composed of catalytic amounts of zinc or iron salts and stoichiometric amounts of fatty acid chlorides for the depolymerization of polyethers to yield valuable building blocks for polymer chemistry.[1-4]

References

- [1] S. Enthaler, M. Weidauer, *Catal. Lett.* 2012, 142, 168–175.
- [2] S. Enthaler, M. Weidauer, *Chem. Eur. J.* 2012, 18, 1910–1913.
- [3] S. Enthaler, M. Weidauer, *ChemSusChem* 2012, 5, 1195–1198.
- [4] S. Enthaler, *Eur. J. Lipid Sci. Technol.* 2012, DOI: 10.1002/ejlt.201200301.

Synthesis of palm oil based ethylhexyl ester for drilling fluid application

Robiah Yunus, Nur Saiful Hafiz Habib, Zurina Zainal Abidin,
Universiti Putra Malaysia, Selangor, Malaysia
robiah@eng.upm.edu.my

Recently, the use of ester as a base fluid in synthetic base fluids (SBF) has become a trend in drilling operations due to many advantages compared to the conventional drilling fluids in particular its costs and environmental concern. The synthesis of ester as biodegradable base oil was conducted via transesterification reaction of palm oil methyl ester (POME) with 2-ethylhexanol (EH). The reaction was carried out at different temperatures (70°C to 140°C) and the pressure was fixed at 1.5 mbar. Palm oil based ethylhexyl esters was successfully synthesized in less than 30 minutes under 1.5 mbar pressure, 70°C, and 1:2 molar ratio of POME to EH. The rate constant of the reaction (k) obtained from the kinetics study was in the range of 0.44 to 0.66 s⁻¹. The activation energy of the reaction was 15.6 kJ.mol⁻¹. The preliminary investigation on the lubrication properties of drilling mud formulated with palm based 2EH ester indicated that the base oil has a great potential to substitute the synthetic ester base oil for drilling fluid. Its high kinematic viscosity provides better lubrication to the drilling fluid compared to other ester-based oils. The pour point and the flash point are superior for the drilling fluid formulation. The plastic viscosity, HPHT filtrate loss and emulsion stability of the drilling fluid give acceptable values while, gel strength and yield point can be improved by blending it with proper additives.

Biobased adhesives: when green chemistry meets the material science of sticky things

Richard Vendamme,

Nitto Denko Corporation's European Research Committee (ERC), Nitto Europe NV,
Belgium

richard.vendamme@neuf.fr

The growing awareness of society towards environmental issues combined with the recent governments regulations and incentives towards the reduction of carbon dioxide emissions is pushing the chemical and adhesive industries to develop greener products and to find alternative growth strategies based on more sustainable economical models. Although the use of raw materials derived from renewable feedstock seems a particularly relevant option, finding sustainable and efficient ways to transform biofeedstocks into highly functional materials and coatings is still very challenging.

Pressure sensitive adhesive (PSA) materials are a peculiar class of glues intended to form a reversible bond simply by the application of a light pressure to marry the adhesive with the adherent. Conceptually, PSAs must be designed with a subtle balance between flow and resistance to flow: the bond forms because the adhesive is soft enough to wet the adherent, but the bond also has suitable strength because the adhesive is hard enough to resist the stress of the debonding stage. The formation, development and strength of the adhesive bonds can be tuned by thoughtfully adjusting the bulk viscoelastic properties of the glue and/or by incorporating functional monomers within the base-polymer structure. To date, most commercial PSA are still based on petroleum resources and there is an imperious need to develop more sustainable PSA chemistries.

The development of biobased materials is one solution (among others) used by the Nitto Denko group to tackle environmental problems. In this talk, we would like to demonstrate that Nitto Denko's ambition to make a step-forward in the advancement of biobased adhesives take the form of pragmatic and multi-angle investigations covering both value chain considerations (monitoring and screening of biobased raw material, performing Life-Cycle-Assessment), technical aspects (leveraging the performance and reliability of biobased adhesives) and new business development (unravelling the full business potential of biobased adhesives). The technical part of the presentation will be focused on the development of polyester-based pressure sensitive adhesives derived from various renewable biofeedstocks such as plant oils or sugars.¹

¹ Interplay Between Viscoelastic and Chemical Tunings in Fatty-Acid-Based Polyester Adhesives: Engineering Biomass toward Functionalized Step-Growth Polymers and Soft Networks. R. Vendamme*, K. Olaerts, M. Gomes, M. Degens, T. Shigematsu, W. Eevers, *Biomacromolecules*, 13, 1933-1944 (2012).

Microwave-assisted heterogeneous catalysis in esterification and etherification reactions

Sabine Valange¹, Gina Hincapie², Diana Lopez², Clement Allart¹, Joel Barrault¹,
¹ IC2MP, UMR CNRS 7285, ENSIP, Poitiers Cedex, France ; ² Institute of Chemistry,
University of Antioquia, Medellin, Colombia
joel.barrault@univ-poitiers.fr

Among alternative fuels, monoalkyl (methyl or ethyl) esters issued from vegetable or animal oils and alcohols have some advantages, such as renewability, biodegradability, heat content, availability, ... From these natural oils (triesters of glycerol) monoalkyl-esters are obtained via transesterification with methanol or ethanol, while glycerol being formed as by-product. The use of methanol is more common than ethanol at the industrial scale because of its low cost and high reactivity. There is however an increased interest in the use of ethanol because of its superior solubility for oil coupled to its entirely renewable characteristics. Since the reaction rate of that reaction is much lower than the former one, there is a need for finding more efficient catalysts or/and more efficient processes.

We have shown that starting from a non-edible oil, namely castor oil obtained from *Ricinus communis* L. seeds, a homogeneous base-catalyzed transesterification process in the presence of ethanol can take place at low temperature (60 °C) and atmospheric pressure with a ethyl-ester yield of 78% after 1h of reaction. By contrast, the use of microwaves as a heating medium to drive the transesterification reaction resulted in a strong increase of the reaction rate under the same experimental conditions (1.5 wt% KOH as catalyst and temperature of 60 °C). Such microwave-assisted system allowed us to obtain the same ethyl-ester yield after only 10 min of reaction. Our results indicated that microwave heating can effectively reduce the reaction time probably due to a change in Arrhenius pre-exponential factor.

We next investigated the microwave-assisted glycerol etherification to selectively produce short-chain oligomers in the presence of homogeneous bases at temperatures ranging from 200 to 260 °C. While a complete glycerol conversion was observed after 6h of reaction under conventional heating, the same conversion was attained after only 1h with the microwave-assisted system. More surprisingly, diglycerol was mainly obtained with a yield as high as 90 % under such reaction conditions, whereas a complex mixture of polyglycerols was formed under conventional heating with a diglycerols yield less than 50%.

In summary, we have shown that the microwave-assisted production of ethylesters derived from castor oil was more easily achieved with shorter times compared to conventional methods. A similar trend was observed for the formation of diglycerol where a fairly unexpected yield of 90 % was obtained. Future studies will focus both on a fundamental approach of the alcohol activation and on the scaling up of the microwave-assisted esters or ethers production.

Acknowledgement

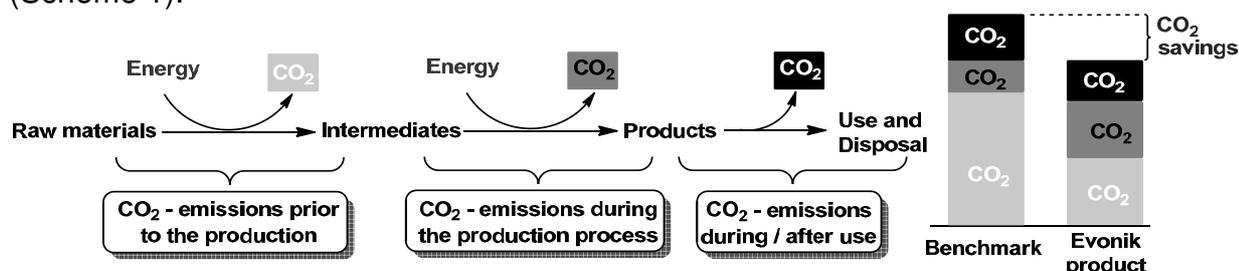
The authors acknowledge CODI - University of Antioquia for financing the project, Colciencias for the Ph.D. scholarship of G.H. and 'VALAGRO Carbone Renouvelable Poitou-Charentes' for fruitful discussion.

Synthesis and application of cyclic carbonates of fatty acid esters

Benjamin Schäffner¹, Matthias Blug¹, Daniela Kruse¹, Benjamin Woldt¹, Mykola Polyakov²,
Angela Köckritz², Andreas Martin², Sebastian Jung³, David Agar³, Bettina Rüngeler⁴,
Andreas Pfennig⁵, Karsten Müller⁵, Wolfgang Arlt⁵,

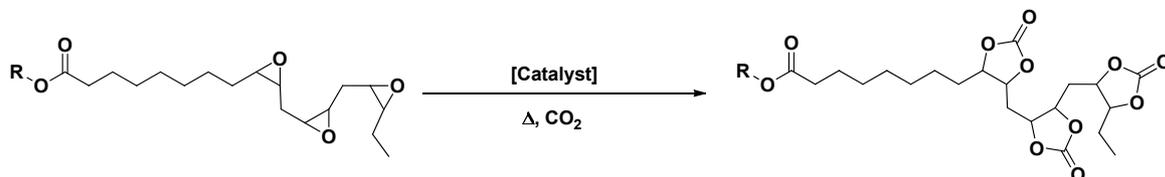
¹ Evonik Industries AG, Germany; ² Leibniz-Institute for Catalysis e.V., Rostock, Germany; ³ TU Dortmund, Dortmund, Germany; ⁴ RWTH Aachen, Aachen, Germany; ⁵ TU Graz, Graz, Austria; ⁶ University of Erlangen- Nuremberg, Erlangen, Germany
benjamin.schaeffner@evonik.com

A cascaded method for the development of new processes using carbon dioxide has been developed in the public-funded project^a H₂ECO₂ coordinated by the Science-to-Business Center Eco² of Creavis, the strategic research and development unit of Evonik. The procedure includes a thermodynamic, ecological and economic analysis as well as the evaluation of the catalytic and process feasibility. Industrial relevant target molecules have been identified with a great CO₂-saving potential. Suitable catalysts and a synthetic route have been designed and a Life-Cycle-Analysis for the new product has been completed (Scheme 1).



Scheme 1: Life-Cycle of a new product in comparison to the benchmark.

The combination of fatty acid derivatives and CO₂ as building block can yield an interesting class of compounds known as fatty acid carbonates. The use of CO₂ as chemical building block has the chance to mitigate CO₂-emissions from power plants and large industrial sites. The consortium established a robust route to synthesize cyclic carbonates from fatty acid epoxides in order to test their potential in applications (Scheme 2). Furthermore, a Life-Cycle-Analysis was performed with an established benchmark to compare the environmental footprint and CO₂-emissions.



Scheme 2: Synthesis of cyclic carbonates of epoxidized fatty acid esters and CO₂.

^a This project is funded by the German state of North Rhine-Westphalia (Ministry for innovation, science and research) and co-financed by the EU (European Regional Development Fund).

Abstracts

Part 2: Posters

Green synthesis of biolubricants from castor oil and higher chain alcohols

Chandu S. Madankar, Subhalaxmi Pradhan, S.N. Naik,
Indian Institute of Technology, Delhi, India
chandumadankar@gmail.com

Renewable raw materials are playing important role in developing environmentally sustainable products. The consumption of oils and fats from vegetable and animal origin is increasing, as the trend is moving towards more eco friendly products. 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 from castor oil. The process includes the enzymatic transesterification of castor oil with higher chain alcohols 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).

Potassium Fluoride Impregnated CaO/NiO: An Efficient Heterogeneous Catalyst for Transesterification of Triglycerides

Mandeep Kaur, Amjad Ali, Thapar University, Patiala India
mandeepthapar@gmail.com

Potassium impregnated CaO/NiO has been prepared by wet impregnation method in nano particle form as supported by powder X-ray diffraction, Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). BET surface area measurements and Hammett indicator studies have done in order to establish the effect of potassium impregnation on catalyst structure, particle size, surface morphology and basic strength. CaO/NiO impregnated with 20 wt% potassium was used as solid catalyst for the transesterification of different triglyceride (Fresh cottonseed oil, Waste cottonseed oil, Karanja oil, Jatropha oil, Soybean oil) having free fatty acid contents in the range of 0.32–8.3 wt %. The variables used for the transesterification were KF impregnated on CaO/NiO, catalyst concentration, reaction temperature, methanol to oil molar ratio, reaction time and free fatty acid content. Reaction parameters have been optimized to achieve the least reaction period for the completion of the reaction. Complete transesterification of waste cotton seed oil with methanol required 4 h in the presence of KF impregnated CaO/NiO nano catalyst at 65 °C with 15:1 methanol to oil and 5 wt% (catalyst/oil) of catalyst.

In-situ monitoring and induction time measurements during melt crystallization of plant based fatty acid mixtures in V-form reactor

Sunanda Dasgupta, Peter Ay, Chair of Mineral Processing, Processing of Biogenous Resources, Brandenburg University of Technology, Germany
dasgupta@tu-cottbus.de

Enriched plant based unsaturated fatty acid mixtures are increasingly finding applications in various fields like those of production of bio-fuels and polymerization of epoxy resins. In the case of production of epoxy resins, they are highly advantageous due to the presence of multiple double bonds in the fatty acids which provide opportunities for cross linking by substitution. On the other hand, bio-fuels need raw materials with very low crystallization temperatures. This special property can also be attributed to these enriched unsaturated fractions due to their weak inter-molecular interactions owing to the kink in their structures. Melt crystallization has long been established as an optimal method for purification and enrichment of fractions from mixtures [1,2]. Previous studies have shown promising results with regard to enrichment of unsaturated fractions by melt crystallization processes [1]. Melt crystallization kinetics of two plant based poly-unsaturated fatty acid mixtures have been investigated in this study [3]. A high oleic and a high linoleic fatty acid mixture were chosen for comparison purposes. A V-form reactor was developed for optimal in-situ analysis with the help of the focused beam reflectance measurement (FBRM®, Mettler Toledo Ltd., Switzerland) instrument [3]. Enhanced heat transfer especially to deal with the heat given out during crystallization was enabled through minimal volume of sample, optimized mixing and the special shape of the reactor. Important parameters like induction time, mixing speed, etc have been determined and compared as functions of degree of supercooling and composition of PUFA mixtures. In accordance to theory, the induction times in both the cases decreased with increasing supercooling and mixer speed. On the other hand, the high linoleic fatty acid mixture required much higher supercooling (4.4K to 5.4K) than the high oleic mixture (2.2K to 3.2K) for favorable induction times.

References

- [1] S. Dasgupta, N. Dreier, P. Ay, presented at the 5th Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry (Eds: J.O. Metzger, M.A.R. Meier), Karlsruhe 2012
- [2] G.F. Arkenbout, Melt Crystallization Technology, Technomic Publishing Company Inc., Pennsylvania 1995
- [3] S. Xu, Master thesis, Chair of Mineral Processing, Processing of Biogenous Resources, Brandenburg University of Technology, Cottbus 2010

P4

Biomass conversion: Preparation of glycerol carbonate esters by esterification with hybrid Nafion-silica catalyst

Sergio Martínez Silvestre, Maria José Climent Olmedo, Avelino Corma Canós, Sara Iborra Chornet, Instituto de Tecnología Química, Valencia, Spain
sermars4@itq.upv.es

Glycerol carbonate esters (GCEs) which are valuable biomass derivative compounds have been prepared by direct esterification starting from glycerol carbonate and long organic acids with different chain length in absence of solvent and using acid organic resins, zeolites and hybrid organic-inorganic acid catalysts as heterogeneous catalysts. The best results in terms of activity and selectivity to glycerol carbonate esters have been obtained using a Nafion-silica composite. A full reaction scheme has been established and it has been found that an undesired competing reaction is the generation of glycerol and esters derived from a secondary hydrolysis of the endocyclic ester group due to water formed during the esterification reaction. The influence of temperature, substrates ratio, catalyst to substrate ratio and use of solvent has been studied and, under optimized reaction conditions, it is possible to achieve 95% selectivity to the desired product at 98% conversion. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain of the carboxylic acid increases for both p-toluenesulfonic acid and Nafion SAC-13. Fitting experimental data to a mechanistically based kinetic model, the reaction kinetic parameters for Nafion SAC-13 catalysis were determined and compared when reacting different carboxylic acids. The enthalpy of adsorption, activation energy and entropy of the surface reaction indicate that the lower reactivity of the carboxylic acid in this reaction when increasing the chain length kinetic study is supported by inductive as well as entropic effects.

Time-resolved characterization of aging products from fatty acid methyl esters

Stephanie Flitsch, Sigurd Schober, Martin Mittelbach,
Institute of Chemistry, University of Graz; Graz, Austria
stephanie.flitsch@uni-graz.at

Fatty acid methyl esters (FAME) are the main components of biodiesel. They are subject to chemical aging and play a major role in fuel aging processes of biodiesel and diesel/biodiesel blends. The occurrence of FAME aging products in standard diesel engines may result in damage to fuel-carrying or engine parts. While numerous sum parameters are available to characterize fuel aging properties, very little research has been done on the analysis of specific aging products.

The aim of this work is to develop a deeper understanding of the processes of FAME aging.

FAMEs were aged by applying high temperatures (110 °C) and a constant stream of air via a Rancimat device. FAME hydroperoxides were identified and characterized as the primary aging products. Secondary aging products include short-chain fatty acids, aldehydes, alcohols, and epoxides.

The formation of aging products is monitored during time-resolved measurements using gas chromatography-mass spectrometry (GC-MS) and ion exchange chromatography (IEC) [1]. Additionally, polymer formation is monitored via size-exclusion chromatography (SEC) [2]. The concentration of hydroperoxides reaches its maximum shortly before the investigated FAME reaches its IP. An increase in the formation of secondary aging products is observed after the investigated FAME reaches its IP.

[1] Morales A, Dobarganes C, Márquez-Ruiz G, Velasco J, 2010: Quantitation of Hydroperoxy-, Keto- and Hydroxy-Dienes During Oxidation of FAMEs from High-Linoleic and High-Oleic Sunflower Oils, *Journal of the American Oil Chemists Society*, 87, 1271-1279

[2] Márquez-Ruiz G, Holgado F, García-Martínez MC, Dobarganes MC, 2007: A Direct and Fast Method to Monitor Lipid Oxidation Progress in Model Fatty Acid Methyl Esters by High-Performance Size-Exclusion Chromatography, *Journal of Chromatography A*, 1165, 122-127

Solvent Assisted Hydraulic Pressing of Dehulled Rubber Seeds

Muhammad Yusuf Abduh, Erna Subroto, Robert Manurung, Hero Jan Heeres,
University of Groningen, Groningen, Netherlands
p262868@rug.nl

Rubber seed oil (RSO) has potential to be used for biodiesel synthesis [1, 2]. We have carried out experimental studies on the solvent assisted hydraulic pressing (SAHP) of rubber seeds with the objective to enhance oil recovery yields. Ethanol was used as the solvent as it is available from renewable resources, non-toxic and poses less handling risks than hexane [3]. Dehulled rubber seeds were pressed in a laboratory scale hydraulic pressing machine. The effect of seed moisture content (0-6 % w.b.), temperature (35-105 oC), pressure (15- 25 MPa) and solvent to seed ratio (0.07- 0.21 % (v/w)) on the oil recovery was investigated. An optimum oil recovery of 74 % d.b. was obtained when 2 % w.b. dehulled rubber seeds were pressed in the presence of ethanol at 20 MPa, 75oC and 10 min pressing time, which is about 8% better than in the absence of ethanol. The experimental dataset was modelled using two approaches, viz i) a regression model using Response Surface Methodology (RSM) and ii) a fundamental model developed by Shirato [4]. Both models give a good description of the effects of process conditions on oil yields. The moisture content of the seeds and temperature has the most significant effect on the oil recovery followed by pressure and solvent to seed ratio (Figure 1).

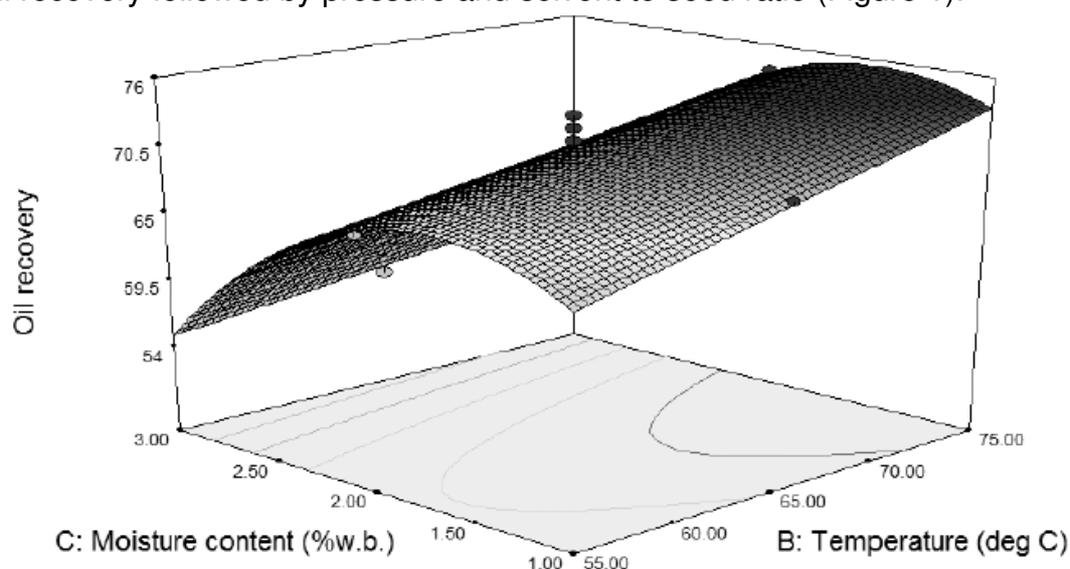


Figure 1 Effect of moisture content and temperature on the oil recovery of SAHP of dehulled rubber seeds as modelled by RSM

In conclusion, we have shown that ethanol assisted hydraulic pressing has a clear beneficial effect on the oil recovery oil yield for dehulled rubber seeds.

- [1] Ikwuagwu, O. E.; Ononogbu, I.C.; Njolu, O.U., *Industrial Crops Products*, 12 (2000), 57–62.
- [2] Morshed, M.; Ferdous, K.; Maksudur, R.K.; Mazumder, M.S.I.; Islam, M.A., Uddin, Md. T., *Fuel*, 90 (2011), 2981–2986.
- [3] Ferreira-Dias, S.; Valente, D.G.; Abreu, J.M.F., *Grasas y aceites* 54 (2003), 378–383.
- [4] Shirato, M.; Murase, T.; Iwata, M.; Nakatsuka, N, *Chemical Engin. Sci.* 41 (1986), 3213–3216.

Hydrotreating of Non-Food Fat and Oil Derivatives for the Production of Biofuels

Alexander F. H. Studentschnig, Sigurd Schober, Martin Mittelbach,
Institute of organic/bioorganic Chemistry, Karl-Franzens University Graz, Graz,, Austria
alexander.studentschnig@uni-graz.at

Fatty acid methyl esters are well established alternative biofuels and have been successfully used as neat diesel fuel or as blend with fossil fuels around the world. However, due to limited stability and an oxygen content of about 10 %, the use in blends is limited by 7 % (vol/vol) due to European specifications. Hydrogenation of vegetable oils in combination with deoxygenation, decarbonylation and decarboxylation could lead to hydrocarbons, which could be used as so-called drop-in fuels with similar properties like fossil Diesel fuel or kerosene.

Hydrotreating is used in conventional oil refineries to remove sulfur, nitrogen and metals from petroleum-derived feedstocks. Also high quality diesel fuel can be produced through this process [1]. Although hydrogenated vegetable oils have already been commercialized as so-called Next-BTL [2] or UOP's Green Diesel™ and Green Jet fuel™ [3] not much is known about the use of non-food feedstocks like waste vegetable oils, animal fat or fatty acids from oil refining.

Fatty acid methyl esters from different non-food sources were successfully converted into n-alkanes in a batch reactor under hydrotreating conditions. Different formulations of self-prepared NiMo/Al₂O₃ were used as catalysts and the reaction kinetics was studied for each of the feedstocks at 360 and 380 °C at a constant initial hydrogen pressure of 90 bars, samples were taken periodically. These samples were analyzed for their composition by GC-MS. It could be found out that there are slight differences in turnover depending on the characteristics of the feedstock that seem to diminish by increasing the reaction temperature. The obtained products were tested on certain fuel properties such as the distillation range by simulated distillation via gas chromatography, cold flow properties and other general fuel parameters. As the main components of these synthetic hydrocarbon mixtures are n-alkanes in the diesel boiling range, blending with diesel fuel can easily be done.

[1] G.W. Huber et al., Applied Catalysis A: General 329 (2007) 120–129

[2] Neste Oil, <http://www.nesteoil.com/>, (accessed 01/2013)

[3] Honeywell UOP, <http://www.uop.com/>, (accessed 01/2013)

Enhancing the Acyltransferase Activity of *Candida antarctica* Lipase A

Janett Müller,¹ Henrike Brundiek,² Birte Fredrich,¹ Uwe T. Bornscheuer,¹

¹University of Greifswald, Greifswald, Germany; ² Enzymicals AG, Greifswald, Germany
janett.mueller@uni-greifswald.de

Fatty acid esters are important compounds in different fields of application. Fatty acid methyl esters can be used as biodiesel and are an alternative to common diesel fuel. Moreover different fatty acid esters e. g. methyl laurate and ethyl laurate can be used as flavoring and fragrance compounds in the cosmetic industries.

The synthesis of these compounds is often achieved by the use of lipases in water-free or low-water transesterification reactions where common oils are used as substrates.[1] But some lipases like the *Candida antarctica* lipase A (CAL-A) also possess an acyltransferase activity that enables the synthesis of fatty acid esters even in the presence of water.

Avoiding the necessity of a water-free system can be an important cost factor concerning the industrial applicability of a certain process. In addition to that the CAL-A exhibits some characteristics, e.g. its thermostability that is favorable for industrial application and the 3D structure of the enzyme is available, which is beneficial for protein engineering.[2]

For an engineering of the acyltransferase activity of CAL-A, the enzyme expression was established in *E. coli* and in *Pichia pastoris*. [3] The expression in *E. coli* is possible in deepwell plates. Thus larger mutant libraries can be screened. For such a screening different high-throughput assays are possible: on one hand the pH-shift caused by fatty acid consumption can be detected, on the other hand the consumption of alcohol can be measured by establishing an enzyme cascade that converts the alcohol further for example with an alcohol dehydrogenase or an oxidase.

[1] Gog, A.; Roman M.; Toşa M.; Paizs C.; Irimie F. D. (2012); Biodiesel production using enzymatic transesterification - Current state and perspectives; *Renew Energ* **39**: 10-16

[2] Ericsson D.J.; Kasrayan A.; Johansson P.; Bergfors T.; Sandström A. G.; Bäckvall J.-E. and Mowbray S. L. (2008); X-ray structure of *Candida antarctica* Lipase A shows a novel lid structure and a likely mod of interfacial activation; *J. Mol. Biol.* **376**: 109-119

[3] Brundiek, H.B., Evitt, A.S., Kourist, R., Bornscheuer U.T. (2011); Creation of a lipase highly selective for *trans* fatty acids by protein engineering; *Angew. Chem. Int. Ed.* **51**: 412-414.

TEMPERATURE AND COMPOSITION DEPENDENCE OF DENSITY FOR SOYBEAN OIL, EPOXIDIZED SOYBEAN OIL AND ACETIC ACID BINARY MIXTURES

Milovan Jankovic¹, Olga Govedarica¹, Snezana Sinadinovic-Fiser¹, Vesna Rafajlovska²
¹ Faculty of Technology, University of Novi Sad, Serbia; ² Faculty of Technology and Metallurgy, SS Cyril and Methodius University in Skopje, Macedonia
 ssfiser@uns.ac.rs

Epoxidized soybean oil is biodegradable replacement for phthalates used in past as PVC stabilizers. By subjecting epoxidized soybean oil to ring opening reactions, high-functionality vegetable oil-based materials applicable for resin preparation may be produced. Industrially, soybean oil is mainly epoxidized with peracetic acid formed in situ from acetic acid and hydrogen peroxide in the presence of an acid catalyst. Mineral acids, such as sulphuric acid, or acidic ion exchange resin are catalysts of choice. Such reaction system is two (oil-water) or three (oil-water-ion exchange resin) phase, depending of applied catalyst. Two main reactions of peracetic acid and epoxy ring formation occur, as well as several side reactions of epoxy ring cleavage. Therefore, a rigorous kinetic model, necessary for process optimization, should include kinetic, thermodynamic and mass transfer parameters. Due to extensive number of the parameters, their simultaneous determination by fitting experimental data for the variation of components concentration with time is inconvenient and incorrect [1]. More appropriate should be to determine some of the parameters in separate experiments designed for investigation of particular phenomenon such as partitioning of components between phases [2]. For the multiphase epoxidation system, partition coefficient of acetic acid, K_A , is the function of a liquid-liquid equilibrium constant for acetic acid, $K_{x,A}$, and molar volumes of compressed liquid for water and oil phase, v_w and v_o , respectively. Molar volume of compressed liquid is a ratio of molar mass, M , and a compressed liquid density, ρ .

In this work, densities of pure components and their binary mixtures related to the oil phase of the reaction system of soybean oil epoxidation with peracetic acid formed in situ were measured and fitted with appropriate correlations found in literature. The aim was to determine temperature and composition dependence of the density. Measurements were done in the temperature range of 20 to 800C and for mixture compositions that correspond to the component ratio in an industrial process. Spencer-Danner-Rackett [3] and COSTALD [4] correlations and Amagat's law for calculation of molar volume of saturated liquid, as well as Yen-Woods [5], Nasrifar-Moshfeghian [6], simplified Nasrifar-Moshfeghian [7] and Iglesias-Silva-Hall [8] correlations for saturated liquid density, were used. Tait equation is further applied to obtain corresponding values of molar volume of compressed liquid. Fitting the experimental data by Marquardt algorithm, a critical temperature, critical pressure, acentric factor and critical compressibility factor for soybean oil, epoxidized soybean oil and acetic acid for each applied correlation were calculated. The best fit model, with an average relative error of 0.59%, was found to be Spencer-Danner modification of Rackett equation. Acknowledgment: This work is part of the Project #III 45022 supported by the Ministry of Education and Science of the R. Serbia. The authors thank the DAAD and INFU, FR. Germany, for instrument donations.

References:

- [1] M. Janković, S. Sinadinović-Fišer, M. Lamshoeft, J. Am. Oil Chem. Soc. (2010) 87:591-600
- [2] S. Sinadinović-Fišer, M. Janković, J. Am. Oil Chem. Soc. (2007) 84:669-674
- [3] C.F. Spencer, R.P. Danner, Chem. Eng. Data (1973) 18:230-234
- [4] R.W.Hankinson, G.H. Thompson, AIChE J. (1979) 26:653-663
- [5] L.C. Yen, S.S. Woods, AIChE J. (1966) 12:95-99
- [6] Kh. Nasrifar, M. Moshfeghian, Fluid Phase Equilib. (1999) 158-160:437-445
- [7] A. Mchaweh, A. Alsaygh, Kh. Nasrifar, M. Moshfeghian, Fluid Phase Equilib. (2004) 224:157-167
- [8] G.A. Iglesias-Silva, K.R. Hall, Fluid Phase Equilib. (1997) 131:97-105

Renewable Co-Polymers Derived from Limonene and Fatty Acid Derivatives

Maulidan Firdaus, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
maulidan.firdaus@student.kit.edu

The limited availability of petroleum resources and their escalating prices has led to an increase interest in the development of new platform chemicals from renewable resources. From the standpoint of cost and availability, fatty acid derivatives and (R)-(+)-limonene are among valuable renewable raw materials of great promise for polymer synthesis. Thus, we present a versatile and effective way to synthesize renewable diolefin and dithiols derived from (R)-(+)-limonene and/or fatty acid derivatives via thiol-ene addition. The monomers thus obtained have been characterized and their behavior in thermal or photochemical thiol-ene polyaddition have been investigated. Thus, through different combinations, (R)-(+)-limonene and fatty acid derivatives copolymers were prepared and their structure-thermal property relationships were studied. GPC results and intensive DSC analysis of the resulting polymers revealed that renewable polysulfides from amorphous to high-melting crystalline polymers with molecular weights up to 31.8 kDa can be obtained. In addition, polysulfones were also prepared by oxidation of corresponding polysulfides with hydrogen peroxide solution. DSC analysis demonstrated an increase in thermal properties when the polysulfides are oxidized into polysulfones. Overall, the combination of (R)-(+)-limonene and fatty acid derived monomers might open an entry to new polymers derived from these renewable resources.

BIPHASIC KINETIC MODEL OF IN SITU EPOXIDATION OF CASTOR OIL WITH PERACETIC ACID

Milovan Jankovic, Snezana Sinadinovic-Fiser, Olga Govedarica,
Faculty of Technology, University of Novi Sad, Serbia
oborota@uns.ac.rs

Castor oil is a natural polyol which has in its fatty acid composition about 90% of monounsaturated hydroxy acid i.e. ricinoleic acid (12-hydroxy-9-octadecenoic acid). This renewable resource can be used for polyurethane production. However, more crosslinked polyurethane network may be obtained by introducing additional hydroxy groups in fatty acid chains of castor oil triglycerides. That can be achieved via epoxidation of double bonds, followed by transformation of epoxy groups to hydroxy groups.

In large scale production of epoxidized vegetable oils common oxidizing agent is percarboxylic acid, such as performic or peracetic acid. It is usually obtained in situ through the acid catalyzed reaction of the corresponding organic acid with hydrogen peroxide. Soluble mineral acid, usually sulphuric acid, or acidic cation exchange resin, is commonly used as catalyst for this reaction [1]. Besides the main reactions of percarboxylic acid and the epoxy ring formation, side reactions of epoxy ring cleavage also occur [2]. Depending on the applied catalyst, the reaction system is either two- (oil-water) or three-phase (oil-water-ion exchange resin). Due to complexity of the reaction system, kinetic models that have been proposed are based on different simplifications [3].

In this work the kinetics of the epoxidation of castor oil in benzene with peracetic acid generated in situ from acetic acid and hydrogen peroxide in the presence of an acidic cation exchange resin as the catalyst was studied. A pseudo-two phase kinetic model was developed. The side reaction of epoxy ring with acetic acid involving the formation of hydroxyl acetate in addition to reactions of the formation of peracid and epoxy groups was considered. Approximate modeling of the peracetic acid formation, assuming that it occurs at the surface of the ion exchange resin, was based on Langmuir-Hinshelwood-Hougen-Watson (LHHW) and Rideal-Eley (RE) postulates. Depending on which reactants/products are adsorbed/desorbed on active catalyst sites and which step of this heterogeneous catalytic reaction determines the overall reaction rate, 18 models were established. Temperature dependency of the reaction rate coefficients k_i and sorption equilibrium constants K_S were expressed by reparameterized Arrhenius equation. The model parameters, i.e. constants of the Arrhenius equation were determined by fitting experimental data for epoxidations run under different reaction conditions using the Marquardt method. After model discrimination the best fit model was accepted. It assumes that acetic acid, hydrogen peroxide, peracetic acid and water are chemisorbed on the active catalytic sites without dissociation and that acetic acid adsorption is the overall rate-determining step. Good agreement between the calculated and experimental values indicated the suitability of the proposed kinetic model.

Acknowledgment: This work is part of the Project #III 45022 supported by the Ministry of Education and Science of the R. Serbia. The authors thank the DAAD and INFU, FR Germany, for instrument donations.

References:

- [1] B.M. Abdullah, J. Salimon (2010) Epoxidation of vegetable oils and fatty acids: catalysts, methods and advantages, *J. Applied Sci.* 10:1545-1553
- [2] A. Campanella, M.A. Baltanás (2006) Degradation of the oxirane ring of epoxidized vegetable oils in liquid-liquid heterogeneous reaction systems, *Chem. Eng. J.* 118:141-152
- [3] S. Sinadinović-Fišer, M. Janković, O. Borota (2012) Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion exchange resin, *Chem. Eng. Process.* 62:106-113

Thiol-yne Approach to Biobased Polyols: Polyurethane Synthesis and Surface Modification

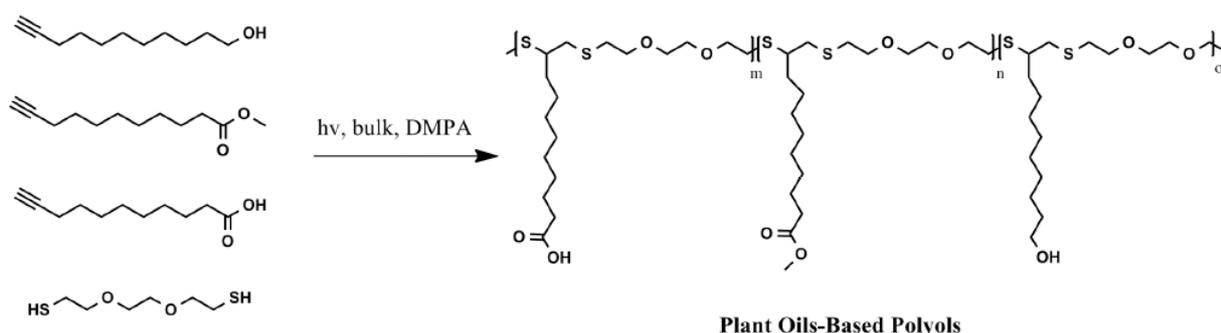
Cristina Lluch, Gerard Lligadas, Joan Carles Ronda, Marina Galià, Virginia Cádiz, Universitat Rovira i Virgili, Tarragona, Spain
cristina.lluch@urv.cat

Nowadays, the use of vegetable oils and their fatty acids for the synthesis of polymers represents an important contribution to sustainable development.¹ In the last few years, click chemistry reactions in combination with renewable resources has attracted a lot of interest in the field of Green Chemistry.

Besides, the unceasingly demands of modern societies for new high performance materials should be translated in fostering higher versatile polymers. The design of smarter polymers with broader application could be accomplished by introduction of auxiliary functional groups onto the polymer backbone, which can be further modified on-demand.²

Thiol-yne click chemistry has shown to be successful to obtain oligothioethers by UV-initiated polymerization of 10-undecynoic acid with dithiols.³ In this work, we aim at preparing oligothioethers from 10-undecynoic acid and its ester and hydroxyl derivatives (methyl 10-undecynoate and 10-undecynol) via a photoinitiated thiol-yne click chemistry approach using 3,6-dioxa-1,8-octanedithiol, as a dithiol. The combination of these monomers in different ratios yields brush-type polyols which have been used in the synthesis of polyurethanes with pendant acid and ester groups. This synthetic route provides the straightforward obtention of functional polyurethanes with no need of time and cost-consuming protection-deprotection steps.

The surface of the resulting thermosets has been tailored via a mild and efficient post-polymerization modification allowing tuning the hydrophobic-hydrophilic properties of the final polymer. This postpolymerization reaction could be easily extended to a wide range of components to provide new value-added characteristics to the polymer.



1 Ronda J. C.; Lligadas, G; Galià, M; Cádiz, V. Eur. J. Lipid Sci. Technol., 2011, 113, 46–58.

2 Fournier, D; De Geest B.G; Du Prez, F.E. Polymer, 2009, 50, 5362-5367.

3 TÜRÜNÇ, O; Meier, M. A. R. J. Polym. Sci. Part A: Polym. Chem., 2012, 50, 1689–1695.

Heteropoly acids for conversion of renewable feedstocks

Ali M. Alsahme, Abdulaziz A. Alghamdi,
King Saud University, Riyadh, Saudi Arabia
aalsahme@ksu.edu.sa

Introduction

Alternative fuels developed from renewable feedstocks have attracted much interest recently. Biodiesel is one of such alternative fuels produced from vegetable oils or animal fats. Commercial production of biodiesel employs homogeneous alkali catalysts. However, alkali catalysts, along with liquid acid catalysts have some limitation. Solid acid catalysts have strong potential to replace liquid acids, eliminating separation, corrosion and environmental problems.

α -Pinene is another important renewable feedstock. It is isomerised to produce camphene and limonene, important intermediates and ingredients in cosmetics, food and pharmaceutical industries. The drawback of commercial catalyst (TiO_2) is its low rate and poor selectivity.

The aim of this work was to study homogeneous and heterogeneous catalysis by heteropoly acids (HPAs) for conversion of renewable feedstocks to fuel and chemicals.

Results and Discussion

The composites under study comprised H₃PW₁₂O₄₀ (HPW) supported on Nb₂O₅, ZrO₂ and TiO₂. Catalyst texture, state of HPW on the surface, catalyst crystallinity, nature and strength of acid sites were investigated using different techniques including nitrogen adsorption using the BET method, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), ³¹P MAS NMR and differential scanning calorimetry (DSC) as well as isopropanol dehydration as a test reaction.

HPAs were found to be active catalysts for the esterification of hexanoic acid and transesterification of ethyl propanoate and ethyl hexanoate with methanol in both homogeneous and heterogeneous liquid-phase systems. In homogeneous system, HPAs were much more active than H₂SO₄ in terms of turnover frequency (TOF). TOF for HPW supported on Nb₂O₅, ZrO₂ and TiO₂ was higher than that of the conventional solid acid catalysts such as Amberlyst-15, HY and H-Beta. However, these catalysts suffered from leaching and exhibited significant contribution of homogeneous catalysis by the leached HPA.

α -pinene over HPW supported on Nb₂O₅, ZrO₂ and TiO₂ isomerisation was carried out in the gas-phase at 200°C. The catalytic activity, selectivity and deactivation resistance of these catalysts were compared with "standard" HPAs such as bulk HPW, CsPW and HPW/SiO₂ and was found to be greatly dependent on the catalyst acidity. The catalysts possessing very strong Brønsted acid sites such as bulk HPW and CsPW suffered from intense deactivation. On the contrary, HPW supported on Nb₂O₅, ZrO₂ and TiO₂, possessing weaker acids, exhibited more stable as well as more selective performance in this reaction.

Flexible polyurethane foams modified with selectively hydrogenated rapeseed oil

Sylwia Dworakowska¹, Dariusz Bogdal¹, Federica Zaccheria², Nicoletta Ravasio²,
¹ Cracow University of Technology, Cracow, Poland; ² Institute of Molecular Science and
 Technologies, National Research Council (CNR-ISTM), Milano, Italy
 sylwiadworakowska@gmail.com

Nowadays, much attention is paid to the use of polyols derived from vegetable oils for the preparation of polyurethane foams due to both environmental as well as economical point of view [1]. Natural oils are valuable renewable raw materials, which can be widely used in synthesis and modification of polymers as an alternative to petrochemical sources [2]. The aim of this study was to apply vegetable oils stabilized through a selective hydrogenation process [3] for their use in the preparation of polyols and therefore in the synthesis of polyurethane foams. Rapeseed oil-based polyols were synthesized using epoxidation followed by ring opening method (Fig. 1).

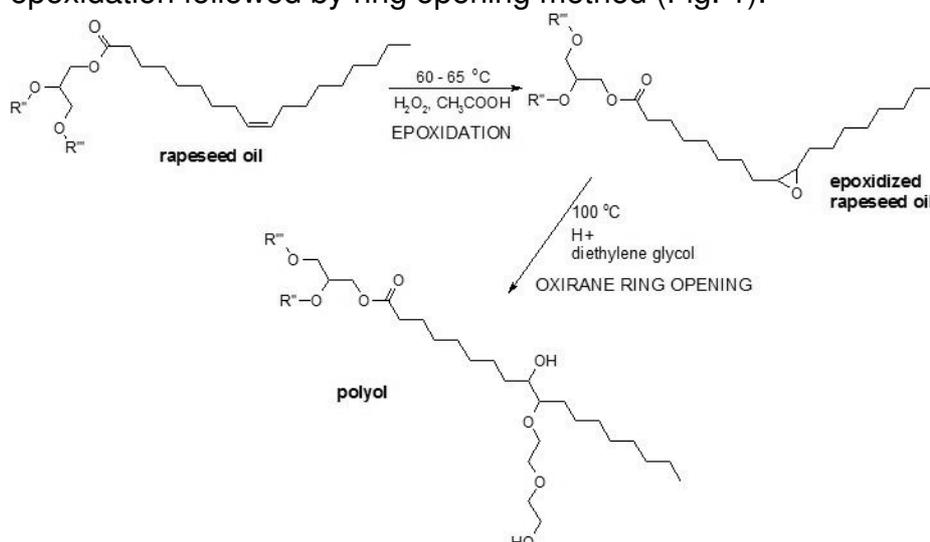


Fig. 1. Synthesis of polyols from rapeseed oil through epoxidation and oxirane ring opening process. R'' and R'''- residues of fatty acids.

Flexible polyurethane foams were synthesized by substituting a portion of base polyether polyol with rapeseed oil-derived polyol. The influence of these modifications on the selected physico-chemical properties of synthesized foams was investigated. Selective hydrogenation represent a valuable tool for vegetable oils composition standardization. Moreover, the use of oils with a homogeneous composition and a very high content in C18:1 improves the final properties of the flexible foams making them more yellowing resistant due to the low level of unreacted double bonds [4]. COST Action CM0903 UBIOCHEM is acknowledged for the support in the Short Term Scientific Missions of Sylwia Dworakowska and Federica Zaccheria.

References

1. Veenendaal B.: *Polyurethanes Magazine International*, 2007, **4**(6) 352-359.
2. Dworakowska S.; Bogdal D.; Prociak A.: *Polymers*, 2012, **4**(3) 1462-1477.
3. Zaccheria F.; Psaro R.; Ravasio N.; Bondioli P.: *Eur. J. Lipid Sci. Technol.*, 2012, **114** 24-30.
4. Heidbreder A.; Gruetzmacher R.; Nagorny U.; Westfechtel A.: US2002/0161161 A1, 2002.

P15

Synthesis, purification and modification of abietic acid dimer, an interesting source of (co)monomers for the design of novel renewable polymers

Audrey LLEVOT, Stephane CARLOTTI, Stephane GRELIER, Henri CRAMAIL,
LCPO, PESSAC, France
llevot@enscbp.fr

As petroleum resources are decreasing and environmental concerns are growing, more attention is paid to the partial replacement of fossil resources by renewable ones. In the plastic industry, vegetable oils are considered as suitable alternative resources thanks to their availability and sustainability. However, the linear aliphatic structure of these monomers is an issue when polymers with high T_g , T_m are requested. The copolymerization of these vegetable-based monomers with cyclo-aliphatic resinic derivatives can be a solution to enhance the material rigidity.

Rosin -or colophony- is mainly obtained by the distillation of a tall oil, a by-product of the Kraft pulp process, or by tapping living pine trees. It is composed of 10% of neutral compounds and 90% of isomeric organic acid mixtures, mainly abietic acid (40-60%). The production of rosin is more than 1 million metric ton per year and is commonly used in adhesives and inks.

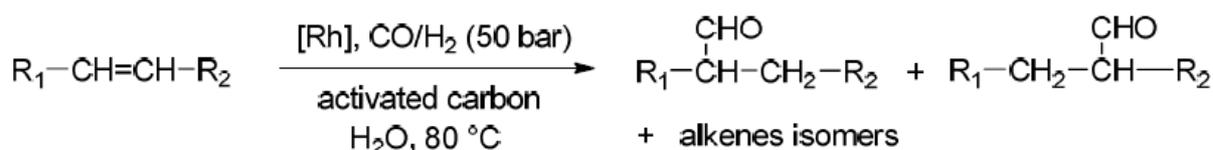
In this study, abietic acid has been first dimerized following the Sinclair's method. A mixture of abietic acid, dimers and trimers of abietic acid have been obtained from the solution. Conditions of separation of the compounds have been determined using HPLC. The adaptation of these conditions on a Flash chromatography apparatus allowed the isolation of the dimers. GC and NMR analyses have been performed before and after the separation. The richer fraction in dimers shows a purity of 92% by GC analyses.

In a second step, the dimers have been esterified with different alcohols under mild conditions. Then several strategies of copolymerizations with fatty acids have been investigated. For instance, after esterification with undecenol, the diester dimer of abietic acid has been readily copolymerized with undecenyl undecenoate by ADMET (acyclic diene metathesis) yielding novel renewable polymers. The chemical structure and features of these polymers have been investigated by means of NMR, SEC, DSC and DMA.

Rhodium-catalyzed hydroformylation of unsaturated fatty esters in aqueous media assisted by activated carbon

Jérôme BOULANGER, Frédéric HAPIOT, Anne PONCHEL, Eric MONFLIER,
UCCS Artois, Lens, France
jerome.boulangier897@laposte.net

Concerns about the environmental impact of chemical transformations prompted chemists to develop clean chemical processes using water as a solvent. Although appropriate for small partially water-soluble molecules, these processes do not allow for the transformation of hydrophobic substrates due to the mass transfer limitation between the aqueous and the organic phase. In this context, we show that activated carbons can be used as mass transfer additives to promote the rhodium-catalyzed hydroformylation of methyl oleate and other unsaturated olefins. Due to its mesoporous and hydrophobic character, the Nuchar®WV-B activated carbon proved to be especially effective as mass transfer promoter. Actually, a significant increase in the conversion was observed. Additionally, more than 90% aldehydes were formed during the course of the reaction. When compared to other mass transfer promoters such as co-solvents or cyclodextrins, Nuchar®WV-B was by far the most efficient. Thus, the use of activated carbons appeared to be a suitable solution for the aqueous rhodium-catalyzed hydroformylation of hydrophobic bio-sourced substrates.



Reference: Jérôme Boulanger, Anne Ponchel, Hervé Bricout, Frédéric Hapiot, Eric Monflier, *European Journal of Lipid Science and Technology*, **2012**, *114*, 1439–1446.
DOI:10.1002/ejlt.201200146

P17

Effect of some medicinal tea extracts on some oxidative parameters of sesame oil

Mehmet Musa Özcan¹, Nurhan – Uslu¹, Fahad Al Juhaimi²,
¹ Selçuk University, Konya, Turkey; ² King Saud University, Riyadh, Saudi-Arabia
mozcan@selcuk.edu.tr

In this study, the antioxidant effect of some medicinal tea extract extracts at different concentrations (0.3 % and 0.5 %) on the oxidation parameters of sesame oil at 80 oC was determined. Butylated hydroxyanisole (BHA) was used as positive control in experiment. All extracts exhibited antioxidant activity compared to BHA upto 14 days. When antioxidant effect of extract concentrations were compared with BHA, the effect of 0.5 % extract concentration was more remarkable for sesame oil upto 14 days. All of seed extracts was effective at 80 oC in comparison with control. On the other hand, an important in both the peroxide and viscosity values during the experiment period increase was observed. It concluded that tea extract could be used as a oxidative inhibitor agent in oil and oil products.

Self-metathesis of fatty acid methyl esters: Full conversion by choosing the appropriate plant oil

Robert Hofsaß, Hatice Mutlu, Rowena E. Montenegro, Michael A. R. Meier
Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe
robert.hofsaess@googlemail.com

New lines of research have been developed since the transformation of renewables has received major research interest both in academia and industry. In this domain, besides carbohydrates, fats and oils are the most commonly employed natural products. Especially the multifunctional character of triglycerides allows plant oils to be considered as valuable alternatives to fossil reserves. Considerable interest and attention has been focused on the transformation of oleochemicals into linear, long-chain α,ω -functionalized compounds in order to obtain the necessary monomers for the generation of diverse aliphatic poly- α,β -unsaturated polymers. In this aspect, olefin-metathesis has the potential to enable a more efficient conversion of renewable and fossil feedstocks to difunctional alkenes.³ Thus, within this study, a sustainable and efficient route to diesters and thereof derived polycondensates from plant oils was established. The high amount of polyunsaturated fatty acids in the investigated plant oils made an efficient self-metathesis reaction possible, since the volatile products cyclohexa-1,4-diene and hex-3-ene can be removed from the equilibrium reaction mixture. The removal of these compounds forced the reaction towards the desired α,ω -diester, leading to high yields (~80%). Also the scale up of the most promising fatty acid methyl ester mixture and catalyst combination was successful, allowing a production of the diester in higher amounts. Furthermore, efficient, quantitative reactions were used to obtain the saturated α,ω -diester and corresponding diol. The following polymerisation led to polyester 18,18 showing high molecular weight and high melting point. Last but not least, it should be emphasized that the by-products of the self-metathesis reaction, cyclohexa-1,4-diene and hex-3-ene, are of great potential synthetic value.

References

- P. Y. Dapsens, C. Mondelli and J. Perez-Ramirez, *ACS Catal.*, 2012, 2, 1487-1499.
U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew Chem Int Ed.*, 2011, 50, 3854-3871.
L. Montero de Espinosa and M. A. R. Meier, Eds. M. A. R. Meier, B. M. Weckhuysen, P. C. A. Bruijninx, Springer, Heidelberg (Germany), 2012.
H. Mutlu, R. Hofsaß, R. E. Montenegro and M. A. R. Meier, *RSC Adv.*, 2013, DOI: 10.1039/C3RA40330K.

Synthesis and Characterization of New Biodegradable Poly(linoleic acid) / Poly(linolenic acid) Graft Copolymers

Abdulkadir Allı¹, Pınar Geçit¹, Sema Allı², Baki Hazer²,

¹ Department of Chemistry, Düzce University, Düzce, Turkey; ² Bülent Ecevit University, Turkey
abdulkadiralli@duzce.edu.tr

Plina / PLinl peroxides were obtained by the auto-oxidation of linoleic acid (Lina) and linolenic acid (Linl) respectively. The autooxidation of Lina and Linl under air at room temperature rendered waxy soluble polymeric peroxide, having soluble fraction more than 98 weight percent (wt%) and containing up to 1.10-1.20 wt % of peroxide. Biodegradable poly (linoleic acid)-g-poly(ϵ -caprolactone) and poly (linolenic acid)-g-poly(ϵ -caprolactone) graft copolymers were synthesized via ring opening polymerization between autoxidized linoleic acid and linolenic acid peroxide initiators's carboxylic acid groups and ϵ -caprolactone monomer.

In the second part of the study, one-step synthesis of graft copolymers by ring-opening polymerization and free radical polymerization by using polymeric linoleic acid peroxide and polymeric linolenic acid peroxide is studied. Graft copolymers having the structure of poly (linoleic acid)-g-p-(N-isopropylacrylamide)-g-poly(D,L-lactid) were synthesized from polymeric linoleic acid peroxide possessing peroxide groups in the main chain by the combination of free radical polymerization of N-isopropylacrylamide and ring opening polymerization of D,L-lactid in one-step. The principal parameters such as monomer concentration, initiator concentration, and polymerization time that affect the one-step polymerization reaction were evaluated.

The graft copolymers obtained were characterized by proton nuclear magnetic resonance (¹H NMR), gel permeation chromatography (GPC), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. These characterization studies of the obtained polymers indicate graft copolymers easily formed as a result of combination free radical polymerization and ring opening polymerization in one-step.

Diversity in ADMET monomer synthesis via Passerini three component reactions with 10-undecenal as key building block

Ansgar Sehlinger, Lucas Montero de Espinosa, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
ansgar.sehlinger@gmail.com

The use of plant oils, fatty acids, and thereof derived platform chemicals in the synthesis of polymers became increasingly important as a result of the limited availability of fossil oil resources.[1] Especially castor oil is a very interesting source of building blocks for organic synthesis. Pyrolysis of ricinoleic acid produces heptaldehyde and 10-undecenoic acid, which can be reduced to the corresponding 10-undecenal.[2] In this work, we focused on the use of 10-undecenal which was, besides acrylic acid and an isocyanide, the starting material for our monomer synthesis.

The monomers were synthesized by a Passerini three component reaction (Passerini-3CR), which is a powerful tool to obtain structurally diverse molecules in a straightforward and atom economic fashion.[3] The one-pot synthesis of the mentioned starting materials leads to a library of asymmetric α,ω -dienes, containing an acrylate and a terminal double bond in the backbone. Such substrates show high cross-metathesis selectivity and thus polymerize strictly head-to-tail in an acyclic diene metathesis (ADMET) polymerization.[4,5] This approach enables us to control the polymer structure and, in combination with the Passerini-3CR synthesis, to vary the functional groups of the repeating unit. Additionally, an amphiphilic block copolymer has been made by adding a PEG480-acrylate to the reaction mixture. This monofunctional acrylate acts as a selective chain-stopper because it reacts only with one end of the polymer. Thus, we could show control over the molecular weight of the growing chain by using different ratios of monomer and chain stopper. Furthermore, the polymers thus obtained present acrylate end-groups, which allow for further post-modifications.

[1] L. Montero de Espinosa, M. A. R. Meier, *Eur. Polym. J.* 2011, 47, 837.

[2] H. Mutlu, M. A. R. Meier, *Eur. J. Lipid Sci. Technol.* 2010, 112, 10.

[3] M. Passerini, *Gazz. Chem. Ital.* 1921, 51, 126.

[4] A. K. Chatterjee, T. L. Choi, D. P. Sanders, R. H. Grubbs, *J. Am. Chem. Soc.* 2003, 125, 11360.

[5] L. Montero de Espinosa, M. A. R. Meier, *Chem. Commun.* 2011, 49, 1908.

Malate production by *Aspergillus oryzae*

Katrin Brzonkalik, Marina Bernhardt, Christoph Syldatk, Anke Neumann,
KIT - Technical Biology, Karlsruhe, Germany
katrin.brzonkalik@kit.edu

L-malic acid is a C₄ dicarboxylic organic acid and considered as a promising chemical building block. It can be applied as food preservative and acidulant, in rust removal because of its chelator properties and as polymerization starter unit due to its bifunctionality. Up to now it is produced chemically from crude oil via maleic anhydride. The mould *Aspergillus oryzae* produces malic acid in large quantities from glucose and other carbon sources. The microbial production of organic acids from renewable sources has the potential to be a sustainable alternative to petroleum and to reduce greenhouse gases as CO₂ fixation is involved in microbial biosynthesis.

In this study the production conditions were optimized in shaking flask experiments and a bioreactor fermentation was established to produce malic acid in large quantities. At 35 °C up to 52 g/L malic acid were produced which corresponds to a molar yield of 1.13.

Monitoring of Glyceride Synthesis in Multiphase System by ATR-Fourier Transform Infrared Spectroscopy

Sören Baum¹, Martin Schilling², Fabien Cabirol², Lutz Hilterhaus¹, Andreas Liese¹,
Institute of Technical Biocatalysis, TH Hamburg, Germany; ² Evonik Industries AG
soeren.baum@tuhh.de

The assay of mono-, di-, and triglycerides in a multiphase system is of great importance in several industrial fields. Mixtures with a high content of monoglycerides with different fatty acid chain lengths are broadly used as emulsifiers and stabilizers for a variety of products in the food and cosmetics industry¹. During synthesis of these components, it is of desirable to achieve a high content of monoglycerides, whereby the di- or triglyceride content should be as low as possible. Therefore the analysis of the product composition and reaction selectivity plays an important role for the process control in the production process of glycerides.

Conventional analytical methods for glycerides are gas chromatography (GC) or highpressure liquid chromatography², which are of limited suitability for multiphase systems. This work demonstrates an *in-situ* differentiation between mono-, di- and triglycerides in a multiphase system by attenuated total reflectance (ATR) Fourier transform infrared spectroscopy. As a model system the enzymatic esterification of glycerol with lauric acid was analyzed. The reaction was carried out in a bubble column reactor containing four phases (two liquid phases of glycerol and lauric acid, air as gaseous phase, and a heterogeneous catalyst as solid phase).

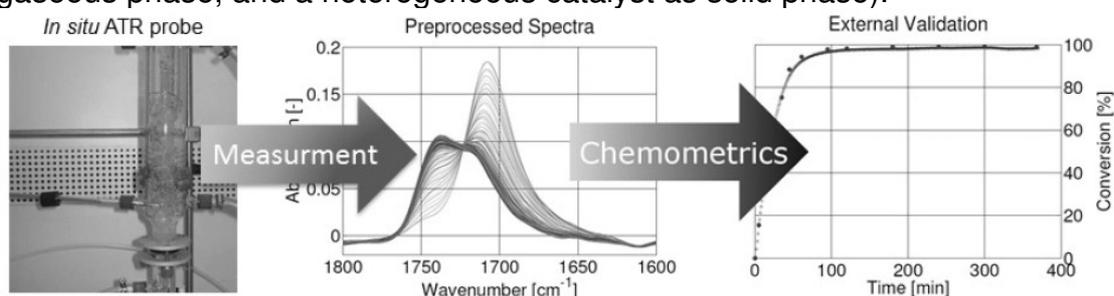


Fig.1: Generation of the chemometric model

For the study of this multicomponent system, a chemometric model was generated based on the calibration of the pure components only³. Deviations from the offline data generated by GC were observed with respect to monoglyceride content during the course of the reaction. Therefore, the calibration was repeated applying detailed GC datasets of real reaction samples. Internal as well as external validation (cross validated and test-set validated) showed significant lower deviations between offline and online data. The quantities of lauric acid and 1-monolaurin, 2-monolaurin, 1,3-dilaurin, 1,2-dilaurin and trilaurin could be monitored over the course of the reaction. Thus, this technology has the potential to give accurate *in situ* results allowing its implementation as process control technology.

(1) Hasenhuettl G.A, Hartel R.W, *Food Emulsifiers and Their Application*, 2nd ed., Springer: New York, 2010.

(2) Indrasti D, Man, Y. B. C, Chin S. T, Mustafa S, Hashim D.M, Manaf M.A, *J. A. Oil Chem. Soc.* **2010**, 87(11), 1255–1262.

(3) Müller J.J, Baum S, Hilterhaus L, Eckstein M, Thum O, Liese A, *Simultaneous Determination of Mono-, Di- and Triglycerides in Multiphase Systems by Online FT-IR Spectroscopy*. *Anal. Chem.*, **2011**, 83(24), 9321-9327.

Pressure sensitive adhesives from renewable resources

Wiebke Maassen, Norbert Willenbacher, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
wiebke.maassen@kit.edu

The so-called pressure-sensitive adhesives represent an important segment, which are used in different applications like labels, tapes and foils or special construction adhesives which are employed both for industrial and domestic purposes. However, these adhesives are almost exclusively petroleum-based synthetic products. Thus, currently ongoing research both in academia and industry is the shift from petrochemical adhesives to those incorporating natural and renewable materials. In line with this concept, the aim of the proposed project is to evaluate the ability to produce such adhesives on the basis of monomers which are synthesized using various fatty acids derived from vegetable oils. Appropriate polymers have been synthesized via standard radical polymerization procedures in bulk and solvent. It has been shown that the adhesion properties of the characterized homo-polymers are as good as equal polymers and co-polymers used in literature before[1]. Regarding a resources-protective and environmental friendly processing, the adhesives were manufactured successfully by means of miniemulsion polymerization as aqueous dispersions showing almost the same adhesive properties[2]. Within the bulk and solvent based polymerization we were able to optimize the adhesive properties by using not only different bio based monomers for the polymer synthesis, but also by varying the degree of polymerization and cross-linking, as well as by using co-monomers to get control over the visco-elastic properties leading to higher values in the storage and loss modulus. The visco-elastic and adhesive properties have been characterized using rheological[3] and mechanical standard measurements e.g. tack and peel tests[4]. For the first time it has been shown that by simple deprotection of the ester end group of the polymer side chain, one can improve the cohesion by generating hydrogen bonds in-between the bio based polymer.

References

- [1] S.P. Bunker, R.P. Wool, *J. Polym. Sci. Part A: Polym. Chem.*, Vol. 40, 451–458, 2002.
- [2] S. Bunker et al., *International Journal of Adhesion & Adhesives*, 23, 29–38, 2003.
- [3] S.-G. Chu, L.-H. Lee, editor., New York: Plenum Press, 1991.
- [4] A. Zosel, *J. Adhes.*, 18, 265-271, 1998.

Renewable aromatic aliphatic copolyesters derived from rapeseed

Stefan Oelmann, Oliver Kreye, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany
stefan-oelmann@versanet.de

Novel (co)polyesters were synthesized from rapeseed as a valuable renewable resource.[1] The aliphatic monomers were obtained from oleic and erucic acid via thiol-ene addition. We already prepared monomers and polymers from renewable sources via this method.[2] Moreover, we demonstrated the facile synthesis of α , a phenolic acid contains in several natural products, and the -diene monomers from oleic and erucic acid by applying ADMET and thiol-ene addition polymerization.[3]

Copolyesters with different ratios of these monomers were prepared via base-catalyzed transesterification reactions under neat conditions with different catalysts. 1,5,7-Triazabicyclo[4.4.0]dec-5-en (TBD), titanium(IV)-isopropoxid (Ti(Oi-Pr)₄) and tin(II) 2-ethylhexanoat (Sn(Oct)₂) were tested as catalysts. The best results regarding high molecular weights were obtained applying TBD as catalyst. Monomers and polymers were fully characterized and the polymers were additionally characterized for their thermal properties. Furthermore, the monomer synthesis was optimized in order to achieve high yielding and environmentally benign synthetic procedures. Particular focus was put on applying less toxic reagents, and to minimize chemical waste, in order to meet the requirements of green chemistry.

[1] O. Kreye, S. Oelmann, M. A. R. Meier, *Macromol. Chem. Phys.* 2013, in preparation.

[2] O. Türünç, M. Firdaus, G. Klein, M. A. R. Meier, *Fatty acid derived renewable polyamides via thiol-ene additions*, *Green Chem.* 2012, 14, 2577-2583.

[3] O. Kreye, T. Tóth, M. A. R. Meier, *Copolymers derived from rapeseed derivatives via ADMET and thiol-ene addition*, *Eur. Polym. J.* 2011, 47, 1804-1816.

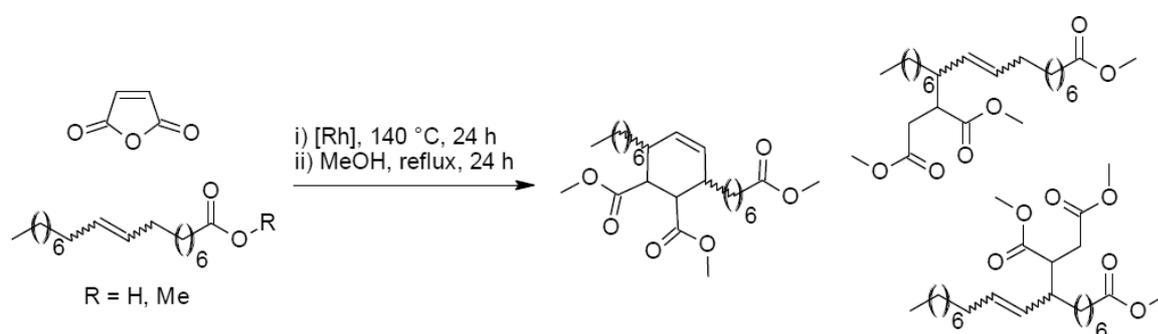
Influence of the double bond configuration on the product composition of Rh-catalyzed maleinisation of monounsaturated fatty acids

Steven Eschig, Tunga Salthammer, Claudia Philipp, Fraunhofer Institute for Wood Research, Wilhelm-Klauditz-Institut, Braunschweig, Germany
 steven.eschig@wki.fraunhofer.de

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. Especially the 6-membered carbon ring is of great interest because it strongly influences the properties of the resulting polyesters, e. g. 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 conjugated 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]

Another possibility to synthesize fatty acid based THPA-derivatives is the Rh-catalyzed maleinisation which has already been investigated for oleic[2] and linoleic acid.[3] Compared to the Diels-Alder-reaction, it is the main advantage of the Rh-catalysis, that it allows synthesizing 6-membered carbon rings from non-conjugated as well as from monounsaturated fatty acids. Our previous work has shown that the Rh-catalyzed maleinisation of linoleic acid leads exclusively to the required cyclic substructures.[3] In contrast to that Behr and Handwerk[2] reported that the maleinisation of oleic acids leads also to acyclic byproducts but without detailed investigations on the selectivity of the different catalysts.

Therefore two different catalysts, $\text{Rh}(\text{OAc})_2$ and $\text{RhCl}_3(\text{H}_2\text{O})_3$, being already mentioned by Behr and Handwerk[2] to be suitable, were investigated. The maleinated oleic acid was esterified with methanol and the resulting product mixtures were analyzed by HPLC. The corresponding chromatograms (reaction a, reaction c) are shown in Fig. 1. Thereby the peaks between 30-32 min can be allocated to the cyclic products, whereas the peaks between 34-36 min belong to the acyclic products.



Scheme 1: Rh-catalyzed addition of maleic anhydride to oleic acid/-methylester (*cis*) and elaidic acid/-methylester (*trans*)

In addition to that it was found that the *cis*-configured double bond of oleic acid was isomerized into the thermodynamically favored *trans*-configuration during the reaction. To investigate the influence of this observed isomerization on the final product composition, the Rh-catalyzed maleinisation was also carried out with elaidic acid followed by an esterification with methanol as shown in scheme 1.

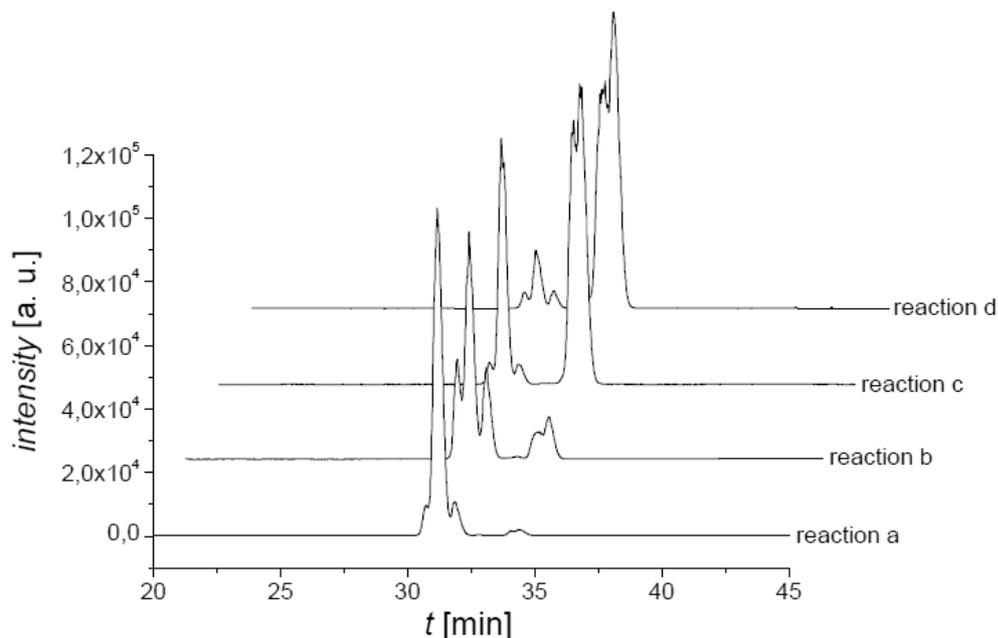


Fig. 1: HPLC-chromatograms of maleinised fatty acids by Rh-catalysis:

reaction a: oleic acid, $\text{Rh}(\text{OAc})_2$	reaction b: elaidic acid, $\text{Rh}(\text{OAc})_2$
reaction c: oleic acid, $\text{RhCl}_3(\text{H}_2\text{O})_3$	reaction d: elaidic acid, $\text{RhCl}_3(\text{H}_2\text{O})_3$

All in all it was found that the selectivity towards the cyclic products is much higher for $\text{Rh}(\text{OAc})_2$ than for $\text{RhCl}_3(\text{H}_2\text{O})_3$. Furthermore it was observed that the amount of elaidic acid decreases the selectivity towards the cyclic products. These results allow deducing new insights of the ongoing mechanism.

A better understanding of this mechanism might give new opportunities to develop new catalysts which may increase the yield of the maleinated products as well as the selectivity towards the preferred, fatty acid based, cyclic THPAs.

References:

- [1] H. J. Schäfer, M. aus dem Kahmen, *Fett/Lipid* 1998, **100**, 227-235
- [2] A. Behr, H.-P. Handwerk, *Fat Sci. Technol.* 1992, **94**, 204-208
- [3] S. Eschig, C. Philipp, T. Salthammer, *Eur. J. Lipid Sci. Technol.* 2013, **115**, 101- 110

α -Arylation of saturated fatty acids: a sustainable approach to renewable monomers?

Nicolai Kolb, Michael A. R. Meier, Institute of Organic Chemistry, Karlsruhe
Institute of Technology, Karlsruhe, Germany
nicolai.kolb@student.kit.edu

With the ongoing limitation of fossil resources, it is today's biggest challenge in chemistry to develop sustainable approaches for daily-life commodity chemicals. In this context, fatty acids have been shown to be a promising feedstock for polymer chemistry since they can be derivatized towards renewable monomers in numerous ways.[1] However, these derivatizations were mainly carried out with unsaturated fatty acids where the double bond can be used for many reactions. Saturated fatty acids on the other hand have been barely used because of their limited modification possibilities.

We have recently presented a method for the direct conversion of saturated and unsaturated fatty acid methyl esters towards malonate derivatives by using the α -acidity of the ester for the derivatization.[2]

Another approach to use the α -acidity would be the α -arylation reaction.[3] During this reaction the ester is deprotonated with a strong base to the corresponding enolate, which can be coupled with aryl halides. This reaction has been intensively studied with short-chain esters, mainly tert-butyl acetate. However, we found that this arylation reaction is also possible with saturated fatty acid esters. Furthermore, we tested the arylation reaction with 1,4-dibromobenzene in order to obtain aryl-bridged diesters for the preparation of renewable monomers or gemini-detergents. The synthesis of these diesters was successful for saturated fatty acid esters of different chain lengths (C8-C18) with isolated yields around 60-70%.

Literature:

[1] a) U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger, H. J. Schäfer, *Angew. Chem. Int. Ed.* 2011, 50, 3854; b) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* 2007, 36, 1788.

[2] a) N. Kolb, M. A. R. Meier, *Green Chem.* 2012, 14, 2429; b) N. Kolb, M. A. R. Meier, *Eur. Poly. J.* 2012, accepted.

[3] F. Bellina, R. Rossi, *Chem. Rev.* 2009, 110, 1082.

New transformations of ricinoleic acid derivatives

Manuel Hartweg, Hatice Mutlu, Michael A. R. Meier, Institute of Organic Chemistry,
Karlsruhe Institute of Technology, Karlsruhe, Germany
manuel.hartweg@gmx.de

In order to replace depleting fossil resources for organic synthesis, and especially for polymer chemistry, an increasing interest in renewable feedstock becomes more important in industry as well as research.[1] Inexpensive, readily available commodity oils containing unusual fatty acids, while having no nutritive value, can be regarded as feedstock of choice. With respect to chemical transformations, ricinoleic acid [(12R,9Z)-12-hydroxyoctadecenoic acid,] – the main component for castor oil – has a broad synthetic potential for both industrial and academic uses, based primarily upon the unique presence of the hydroxyl group.[2] There are several examples for the utilization of ricinoleic acid, both direct and indirect, or its derivatives for the production of a broad range of functional molecules, potentially accessible by using efficient and selective (catalytic) methods.[2] Therefore, the aim of this work was to investigate new routes towards further utilization of methyl ricinoleate. Along this idea, we focused on the development of a more sustainable methodology for the synthesis of conjugated linoleic acids (CLAs) that uses dimethyl carbonate as a green reagent/solvent. The use of TBD as an environmentally friendly base in the dehydration of ricinoleic acid was thus our goal. Our results revealed that in addition to the desired CLAs, different ricinoleic acid derivatives were obtained. Depending on the starting derivative of ricinoleic acid and the applied reaction conditions, we observed ricinoleic acid based lactones and lactams as by-products or major products.

References:

- [1] U. Biermann, U. Bornscheuer, M. A. R. Meier, J. O. Metzger and H. J. Schäfer, *Angew. Chem. Int. Ed.* 2011, 50, 3854.
[2] H. Mutlu and M. A. R. Meier, *Eur. J. Lipid Sci. Technol.* 2010, 112, 10.

Self-metathesis derived renewable 1,4-cyclohexadiene and its potential applications

Sarah Wald, Michael A. R. Meier, KIT, Institute of Organic Chemistry, Karlsruhe, Germany
sarah.wald@student.kit.edu

In the last few years, renewable resources, especially fats and oils, are getting more and more interesting because of decreasing fossil feedstocks and global warming.[1] One important oil for renewable polymers is chia seed oil, which contains, just like linseed oil, high amounts of α -linolenic acid.[2] The methyl-esters of this highly unsaturated oil can be used for self-metathesis reactions to obtain C18-diesters and volatile products, like 1,4-cyclohexadiene and 3-hexene.[3] 1,4-Cyclohexadiene can also be synthesized from soybean oil via olefin metathesis without purification of the oil and simple distillation. The product can, after isomerization to 1,3-cyclohexadiene, be used for polymerization to renewable polycyclohexadiene.[4] The self-metathesis byproduct, 1,4-cyclohexadiene, can also be used to prepare monomers for polysulfides and polysulfones, as will be discussed within this contribution. Therefore, the 1,4-cyclohexadiene was reacted with an excess of thioacetic acid in a thiol-ene addition to obtain a mixture of regioisomers (S,S'-cyclohexane-1,4-diyl diethanethioate and S,S'-cyclohexane-1,3-diyl diethanethioate). After saponification of the mixture, the monomers cyclohexane-1,4-dithiol and cyclohexane-1,3-dithiol, which can be polymerized via thiol-ene-polymerisation with 1,7-octadiene or 1-octyne to polysulfides, were obtained. After oxidation of these polysulfides, the polysulfones were obtained by simple oxidation with hydrogen peroxide.

References

- [1] M. A. R. Meier, J. O. Metzger, U. S. Schubert, Chem. Soc. Rev. 2007, 36, 1788-1802.
- [2] R. Ayerza, W. Coates, Industrial Crops and Products 2011, 34 (2), 1366-1371.
- [3] H. Mutlu, R. Hofsäß, R. E. Montenegro, M. A. R. Meier, RSC Adv. 2013.
- [4] R. T. Mathers, M. J. Shreve, E. Meyler, K. Damodaran, D. F. Iwig, D. J. Kelley, Macromol. Rapid Commun. 2011, 32, 1338–1342.

P29

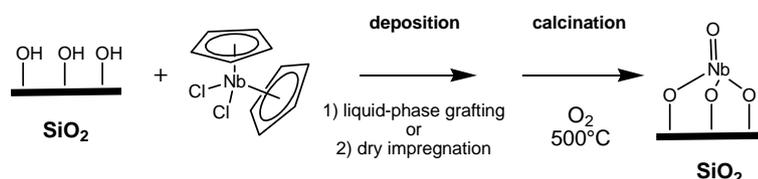
Mesoporous niobium-silica materials for the epoxidation of vegetable oil-derived mixtures of unsaturated fatty acid methyl esters (FAMES)

Cristina Tiozzo¹, Nicoletta Ravasio¹, Rinaldo Psaro¹, Dariusz Bogdal², Sylwia Dworakowska², Matteo Guidotti¹,

¹ CNR-Institute of Molecular Sciences and Technologies, Milan, Italy; ² Cracow University of Technology, Cracow, Poland
c.tiozzo@istm.cnr.it

Functionalized FAMES constitute interesting raw materials for obtaining polyurethane materials suitable for many applications, e.g. coatings as well as flexible and rigid foams. By introducing hydroxyl groups at the position of unsaturated double bonds, it is possible to obtain polyols which are one of the major components in polyurethane synthesis. Vegetable oil-derived unsaturated FAMES are therefore viable building blocks for the production of polymers from renewable resources.^{1,2} Niobium-based silicates have already shown promising performances as heterogeneous catalysts for liquid-phase oxidation epoxidation of alkenes and FAMES.^{3,4} These solids in fact present a high stability and robustness towards metal leaching and hydrolysis. This feature is a noteworthy advantage for their use in the presence of aqueous H₂O₂ or in water-containing media.

The Nb/SiO₂ materials studied in this work were prepared by deposition of Nb(Cp)₂Cl₂ onto the surface of different pure silica supports characterized by various textural features following a dry impregnation (solventless) approach⁵ (Fig. 1). It was thus possible to obtain catalysts with a tailored metal loading and an optimized surface active site density. The catalysts were used as heterogeneous catalysts for the selective epoxidation, in the presence of aqueous hydrogen peroxide, of a set of pure model unsaturated FAMES as well as of FAME mixtures prepared from food-grade high-oleic rapeseed oil, as such or after selective partial hydrogenation, in order to maximize the content of monounsaturated components.⁶



All the catalysts were particularly active in the first hour of reaction. Then, the formation of heavy deposits on the catalyst surface gradually leads to deactivation. The selectivity to epoxide was in all cases excellent and only minor amounts of side-products were found in solution. The catalysts did not show any leaching of active Nb species and proved to be easily recoverable and reusable after a rapid intermediate calcination step.

Yields in methyl epoxystearate as high as 70% were achieved on pure methyl oleate (4:1 oxidant to FAME ratio). On rapeseed-derived FAME mixtures (obtained by direct transesterification of the vegetable oil), yields to monoepoxy-FAMES (epoxystearate and epoxyoleate) up to 55% and 45% were attained, starting from hydrogenated or non-hydrogenated mixtures, respectively. These data are among the best results obtained so far for the epoxidation of unsaturated FAMES over solid oxidic catalysts with hydrogen peroxide.

Regione Lombardia (VeLiCa Project) and COST Action CM0903 UBIOCHEM are acknowledged for financial support.

[1] J.O. Metzger et. al, J. Polym. Sci. Part A: Polym. Chem., 44 (2005) 634

[2] Z.S. Petrovic, I. Cvetkovic, Contemporary Materials, III-1 (2012) 63

[3] M. A. Feliczak-Guzik, I. Nowak, Catal. Today, 142 (2009) 288

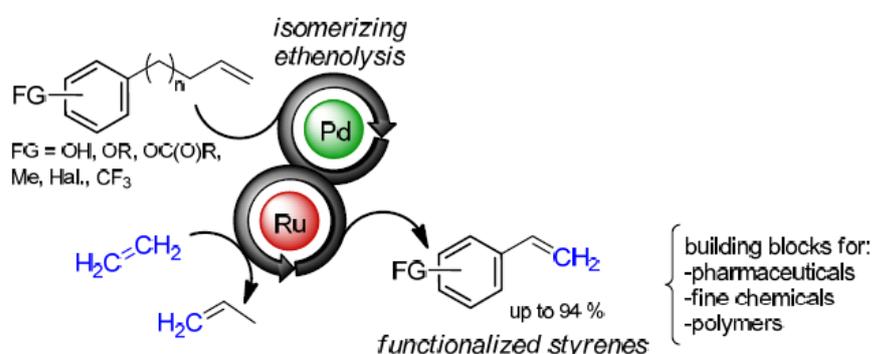
[4] Tiozzo C. et al., Eur. J. Lipid Sci. Tech., 115 (2013) 86 [5] A. Gallo, C. Tiozzo, R. Psaro, F. Carniato, M. Guidotti, J. Catal., 298 (2013) 77

[6] F. Zaccheria, R. Psaro, et al., Eur. J. Lipid Sci. Tech., 114 (2012) 24

Isomerizing ethenolysis of functionalized olefins

Sabrina Baader, Dominik M. Ohlmann, Lukas J. Gooßen, Fachbereich Chemie, Organische Chemie, TU Kaiserslautern, Kaiserslautern, Germany
baader@chemie.uni-kl.de

The combination of $[\text{Pd}(\mu\text{-Br})(\text{tBu}_3\text{P})_2]$ with a Hoveyda-Grubbs II catalyst has been found to efficiently promote the cross-metathesis between substituted alkenes and ethylene, while continuously migrating the double bond along the alkenyl chain.^[1] When allylarenes such as the natural products eugenol, safrol or estragol were treated with this catalyst under ethylene pressure, they were cleanly converted into the corresponding styrenes along with propylene gas (Scheme 1). This process is of particular value in the context of renewable chemical synthesis, i.e. for incorporating naturally occurring allylarenes, some of which are available on ton scale, into the chemical value chain. This conversion of the natural product eugenol is a good example of the potential economic impact of this transformation, as the corresponding vinylarene (465 €/100 g) is of substantially higher commercial value than the eugenol starting material (16 €/100 g).



Scheme 1. Isomerizing ethenolysis as an efficient strategy for styrene synthesis.

Another application of isomerizing metathesis is the efficient conversion of technical quality fatty acids into industrially useful multi-component blends, consisting of functionalized olefins with tuneable chain length distributions.^[2]

References:

- [1] S. Baader, D. M. Ohlmann, L. J. Gooßen, publication submitted.
[2] a) D. M. Ohlmann, L. J. Gooßen, M. Dierker, patent application, **2011**. b) D. M. Ohlmann, N. Tschauer, J.-P. Stockis, K. Gooßen, M. Dierker, L. J. Gooßen, *J. Am. Chem. Soc.* **2012**, *134*, 13716-13729.

Synthesis of Oleic Acid Based-Polymeric Lattices through Emulsion and Miniemulsion Polymerization

Alan T. Jensen¹, Claudia Sayer², Pedro H. H. Araújo², Fabricio Machado¹,
University of Brasilia, Brasilia, Brazil; ² Federal University of Santa Catarina, Florianópolis
– SC, Brazil
pedro@enq.ufsc.br

The use of vegetable oils and their derivatives as precursor monomers in polymerization reactions has increased each day due to their renewable origin, unlike most materials obtained from fossil fuel sources. Among them, oleic acid (OA) deserves special attention due to the high availability and ease of chemical modification, mainly when the double bounds are considered.

This work presents experimental results from copolymerizations of acrylated methyl oleate (AMO) and styrene (Sty) – CAMOSty carried out in both emulsion and miniemulsion polymerization systems. CAMOSty copolymers produced by emulsion polymerization exhibited narrow particle size distributions (PSDs), average particle size in the range from 116 nm to 128 nm and conversions lying in the range of 96 % to 100 %. Despite the high conversion achieved during the emulsion reactions, the amount of AMO in the monomeric organic phase is limited to 15 wt.% to avoid reaction medium destabilization and consequent coagulation of the polymer particles possibly due to the low solubility of methyl oleate in aqueous phase that hinders the diffusion of AMO from the monomer droplets to the growing polymer particles. In order to overcome problems with the low solubility and mass transfer of AMO through the aqueous phase a miniemulsion polymerization process has been employed as the loci of polymerization is the monomer droplets. It was observed that the AMO and Sty can be successfully copolymerized with the additional advantage of using higher amounts of AMO in the organic polymerizing mixture, which permits the incorporation AMO fractions higher than 80 wt.%. In the miniemulsion system, high conversion values were also attained presenting average particle size in the range from 150 nm to 190 nm. Although both processes allow proper copolymerization of AMO and Sty, leading to formation of polymer particles with monodisperse PSDs, comparatively, miniemulsion polymerization process is more attractive due to the high stability of polymerization reactions performed with high concentrations of AMO.

Synthesis of polyurethane nanoparticles from renewable resources by miniemulsion polymerization

Alexsandra Valerio¹, Sandro R. P. da Rocha², Claudia Sayer¹, Pedro H. H. Araújo¹,
¹ Federal University of Santa Catarina, Florianópolis – SC, Brazil; ² Wayne State University
pedro@enq.ufsc.br

Polyurethanes are one of the most versatile polymers being the final product easily tailored, even during the production process. One of the reasons for that is the broad range of polyols (e.g., molecular weight, functionalities) that could be employed. Recently, the development of colloidal delivery systems from biodegradable and biocompatible polyurethanes (PU) has attracted increasing interest as the highly variable synthetic chemistry of PU may be exploited to generate polymers having properties ranging from very soft elastomers to very rigid plastics.

In this work we will report the preparation of PU nanoparticles using isophoronediiisocyanate (IPDI) and different polyols, obtained from renewable resources: castor oil, glycerol and poly(ϵ -caprolactone) (PCL), through miniemulsion polymerization. Poly(ethylene glycol) of different molar masses (PEG 400, PEG 600, and PEG 1000) were also added to the reaction medium partially substituting the other polyols. As those particles were designed for drug delivery, attaching PEG to the outer surface of the particles improves the biodisponibility of the polymeric nanoparticles. Results show that the synthesis of polyurethane nanoparticles by miniemulsion polymerization using polyols from renewable resources is a particularly interesting and facile strategy for the formation of biodegradable and biocompatible nanoparticles, and for the control of the chemistry of the particle shell.

List of participants

Muhammad Yusuf Abduh
University of Groningen
Nijenborgh 4
9747 AG Groningen, Netherlands
p262868@rug.nl

Dr. Khalid A. Alamry
King Abdulaziz University
Aljammah 80203
21589 Jeddah, Saudi Arabia
k_alamry@yahoo.com

Dr. Abdulaziz Ali Alghamdi
King Saud University
King Khaled Street 2455
11451 Riyadh, Saudi Arabia
aalghamdia@ksu.edu.sa

Jessica Allard
NOVANCE
Rue des Rives de l'oise 1
60280 Venette, France
j.allard@novance.com

Dr. Abdulkadir Alli
Department of Chemistry
Konuralp 1
81620 Duzce, Turkey
abdulkadiralli@duze.edu.tr

Dr. Ali M. Alsalmé
King Saud University
College of Science 5
11451 Riyadh, Saudi Arabia
aalsalme@ksu.edu.sa

Thorsten Anders
Fraunhofer ICT
Joseph-von-Fraunhoferstr. 7
76327 Pfinztal, Germany
thorsten.anders@ict.fraunhofer.de

Prof. Dr. Pedro H. H. Araújo
Federal University of Santa Catarina
Departamento de Engenharia Química e
Engenharia de Alimentos
Cx. Postal 476
88040-970 Florianópolis- SC, Brazil
pedro@eng.ufsc.br

Dr. Matthias Arndt
Clariant Produkte GmbH
Industriepark Höchst D 560
65926 Frankfurt am Main, Germany
matthias.arndt@clariant.com

Prof. Dr. Luc Averous
University of Strasbourg
Bio Team
25 rue Becquerel
67087 Strasbourg, France
luc.averous@unistra.fr

Sabrina Baader
TU Kaiserslautern
Fachbereich Chemie, Organische
Chemie
Erwin-Schrödinger-Str. 54
67663 Kaiserslautern, Germany
baader@chemie.uni-kl.de

Prof. Dr. Joel Barrault
CNRS-LACCO
Avenue du Recteur Pineau 40
86022 Poitiers, France
joel.barrault@univ-poitiers.fr

Benjamin Basler
Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
bbasler88@gmail.com

Sören Baum
Technical University Hamburg-Harburg
Denickestr. 15
21073 Hamburg, Germany
soeren.baum@tuhh.de

Christian Beck
Wissenschaftszentrum Straubing
Schulgasse 16
94315 Straubing, Germany
c.beck@wz-straubing.de

Dr. Toine Biemans
Worlée Chemie GmbH
Söllerstr.12
21481 Lauenburg, Germany
tbiemans@worlee.de

Dr. Ursula Biermann
University of Oldenburg
Carl-von-Ossietzky-Str. 9-11
26111 Oldenburg, Germany
ursula.biermann@uni-oldenburg.de

Dr. Rolf Blaauw
Wageningen UR Food & Biobased
Research
Bornse Weilanden 9
6708 WG Wageningen, Netherlands
rolf.blaauw@wur.nl

Prof. Dr. Uwe Bornscheuer
Greifswald University
Institute of Biochemistry
Felix-Hausdorff-Str. 4
17487 Greifswald, Germany
bornsche@uni-greifswald.de

Jérôme Boulanger
UCCS Artois
Jean Souvraz SP 18
62307 Lens, France
jerome.boulanger897@laposte.net

Dr. Christian Bruneau
Université de Rennes 1
Avenue du Général Leclerc 263
35042 Rennes, France
christian.bruneau@univ-rennes1.fr

Dr. Katrin Brzonkalik
Karlsruhe Institute of Technology
Institute for Process Engineering in Life
Science, Section II: Technical Biology
Engler.Bunte-Ring 1
76131 Karlsruhe
katrin.brzonkalik@kit.edu

Dr. Sylvain Caillol
ENSCM
Ecole Normale 8
34296 Montpellier, France
sylvain.caillol@enscm.fr

Priscilla B. Cardoso
Federal University of Santa Catarina
Caixa Postal 476
88010970 Florianopolis, Brazil

Dr. Thibaud Caulier
Solvay
Rue de Ransbeek 310
1120 Brussels, Belgium
thibaud.caulier@solvay.com

Dr. Bret Chrisholm
North Dakota State University
Research Park Drive 1805
58102 Fargo, United States
bret.chrisholm@ndsu.edu

Sunanda Dasgupta
Brandenburg University of Technology
Siemens Halske Ring 8
03046 Cottbus, Germany
dasgupta@tu-cottbus.de

Dr. Manfred Diederich
Alberdingk Boley GmbH
Düsseldorfer Str. 39
47829 Krefeld, Germany
m.diederich@alberdingk-boley.de

Dr. Markus Dierker
BASF Personal Care and Nutrition GmbH
Henkelstr. 67
40589 Düsseldorf, Germany
markus.dierker@basf.com

Dr. Christophe Duquenne
Arkema
Rue Jacques Taffanel Alata
60550 Verneuil-en-Halatte, France
christophe.duquenne@arkema.com

Sylwia Dworakowska
Cracow University of Technology
Warszawska 24
31-155 Cracow, Poland
sylwiadworakowska@gmail.com

Dr. Stephan Enthaler
Technical University of Berlin
Str. des 17.Juni 135/ C2
10623 Berlin, Germany
stephan.enthaler@tu-berlin.de

Steven Esching

Fraunhofer Institute for Wood Research
Wilhelm-Klauditz-Institute
Bienroder Weg 54E
38108 Braunschweig, Germany
steven.esching@wki.fraunhofer.de

Dr. Martin Fängewisch

Croda GmbH
Herrenpfad-Süd 33
41334 Nettetal, Germany
matrin.faengewisch@croda.com

Maulidan Firdaus

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
maulidan.firdaus@student.kit.edu

Dr. Jürgen Fischer

ADM Recherche GmbH
Seehafenstr. 24
21079 Hamburg, Germany
meike.rademacher@adm.com

Stephanie Flitsch

University of Graz
Heinrichstr. 28
8010 Graz, Austria
stephanie.flitsch@uni-graz.at

Marc R. L. Furst

University of St. Andrews
North Haugh 1
KY16 9ST St Andrews, United Kingdom
mrlf2@st-andrews.ac.uk

Jakob Gebhard

Institute of Technical Biocatalysis
Denickerstr. 15
21071 Hamburg, Germany
jakob.gebhard@tuhh.de

Olga Govedarica

University of Novi Sad
Faculty of Technology
Bul. Cara Lazara 1
21000 Novi Sad, Serbia
oborota@uns.ac.rs

Michael Graß

Evonik Industries AG
Paul-Baumann-Str. 1
45772 Marl, Germany
michael01.grass@evonik.com

Prof. Dr. Dmitry G. Gusev

Wilfrid Laurier University
University Avenue West 75
N2L 3C5 Waterloo, Canada
dgoussev@hotmail.com

Prof. Dr. Frédéric Hapiot

UCCS Artois
Rue Jean Souvraz 00
62307 Lens, France
frederic.hapiot@univ-artois.fr

Manuel Hartweg

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-haber-Weg 6
76131 Karlsruhe, Germany
manuel.hartweg@gmx.de

Dr. Jürgen Herwig

Evonik Industries AG
Paul-Baumann-Str. 1
45772 Marl, Germany
juergen.herwig@evonik.com

Robert Hofsaß

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
robert.hofsaess@googlemail.com

Dr. Norbert Holst

Fachagentur Nachwachsende Rohstoffe
Hofplatz 1
18267 Gülzow, Germany
n.holst@fnr.de

Thimo Huber

Wissenschaftszentrum Straubing
Schulgasse 16
94315 Straubing, Germany
t.huber@wt-straubing.de

Veronika Huber

FH Weihenstephan-Triesdorf
Schulgasse 16
94315 Straubing, Germany
v.huber@wz-straubing.de

Bernd Jakob

University
Gausstr. 20
42097 Wuppertal, Germany
bjakob@uni-wuppertal.de

Prof. George John

The City College of CUNY
Department of Chemistry
160 Convent Avenue
10031 New York, United States
gglucose@gmail.com

Mandeep Kaur

Thapar University
Bhadson Road 9465236880
147004 Patial, India
mandeepthapar@gmail.com

Prof. Dr. Bert Klein Gebbink

Utrecht University
Universiteitsweg 99
3584 CG Utrecht, Netherlands
r.j.m.kleingebink@uu.nl

Nicolai Kolb

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
nicolai.kolb@student.kit.edu

Dr. Gunther Kraft

FUCHS Europe Schmierstoffe
Friesenheimerstr. 19
68169 Mannheim, Germany
gunther.kraft@fuchs-europe.de

Dr. Oliver Kreye

Karlsruher Institut of Technologie
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
oliver_kreye@gmx.de

Dennis Kugele

Karlsruher Institute of Technologie
Klosterweg 28
76131 Karlsruhe, Germany
denniskugele@web.de

Dr. Karsten Lange

University of Wuppertal
Gausstr. 20
42097 Wuppertal, Germany
klange@uni-wuppertal.de

Ralph Lange

KIT Karlsruhe
Hagsfelder Allee 10
76131 Karlsruhe, Germany
ralph.lange@student.kit.edu

Rodrigo Ledesma-Amaro

University of Salamanca
Palacio Valdés 19 4A
37007 Salamanca, Spain
rodrigoledesma@usal.es

Dr. Dirk Leinweber

Clariant Produkte GmbH
Industriepark Höchst D 560
65926 Frankfurt am Main, Germany
claudia.weichel@clariant.com

Dr. Gerhard Leinz

Alberdingk Boley GmbH
Düsseldorferstr. 53
478229 Krefeld
dr.leinz@alberdingk-boley.de

Audrey AL LLevot

LCPO
Avenue Pey Verland 16
33607 Pessac. France
llevot@enscbp.fr

Cristina Lluch Porres

Rovira i Virgili University
Marcel.li Domingo s/n
43007 Tarragona, Spain
cristina.lluch@urv.cat

Mel Luetkens

Elevance Renewable Science
Davey Road 2501
Woodridge, 60517 Illinois, United States
vera.zaccariello@elevance.com

Wiebke Maassen

Karlsruhe Institute of Technology
Gotthard-Franz-Straße 3
76131 Karlsruhe, Germany
wiebke.maassen@kit.edu

Chandu S. Madankar

Indian Institute of Technology, Delhi
Hauz Khas
110016 New Delhi, India
chandumadankar@gmail.com

Dr. Claudia Martinez

BASF Personal Care and Nutrition GmbH
Henkelstr. 67
40589 Düsseldorf
claudia.a.martinez@basf.com

Sergio Martinez Silvestre

Instituto de Technoloia Auimicra
Av. Tarongers s/n
46022 Valencia, Spain
sermars4@itq.upv.es

Prof. Dr. Michael A. R. Meier

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
m.a.r.meier@kit.edu

Prof. Dr. Jürgen Metzger

abiosus e.V.
Bloherfelder Str. 239
26129 Oldenburg, Germany
metzger@abiosus.org

Prof. Dr. Martin Mittelbach

University of Graz
Heinrichstr. 28
8010 Graz, Austria
stephanie.flitsch@gmail.com

Dr. Aurélie Morel

Novance
Venette BP 20609
60206 Compiègne, France
a.morel@novance.com

Hermine HNM NSA Moto

Université de Toulouse, INP-Ensiacet
Allée Emilie Monso 4
31030 Toulouse, France
hermine.nsamoto@ensiacet.fr

Zéphirin Mouloungui

INRA
Allé Emile Monso 4
31030 Toulouse, France
zephirin.mouloungui@ensiacet.fr

Prof. Dr. Rolf Mülhaupt

University Freiburg
Institution of Macromolecular Chemistry
Stefan-Meier-Str. 31
79104 Freiberg, Germany
rolf.muelhaupt@makro.uni-freiburg.de

Janett Müller

Universität Greifswald
Schuhhagen 28/29
17489 Greifswald, Germany
janett.mueller@uni-greifswald.de

Dr. Hatice Mutlu

Karlsruher Institut of Technologie
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
hatice.mutlu@kit.edu

Dr. Anke Neumann

Karlsruher Institut of Technologie
Institut für Bio- und Lebensmitteltechnik
Bereich II: Technische Biologie
Engler-Bunte-Ring 1
76135 Karlsruhe, Germany
anke.neumann@kit.edu

Huy Hoang Nguyen

Oleon GmbH
Industriestr. 10
46446 Emmerich am Rhein, Germany
huyhoang.nguyen@oleon.com

Tobias Nitsche

Karlsruher Institut of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
tobiasnitsche@aol.com

Stefan Oelmann

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
stefan-oelmann@versanet.de

Dr. Dominik Ohlmann

BASF Personal Care and Nutrition GmbH
Henkelstr. 67
40589 Düsseldorf, Germany
dominik.ohlmann@basf.com

Prof. Dr. Mehmet Musa Özcan

Selcuk University
Selcuklu 1
42031 Konya, Turkey
mozcan@selcuk.edu.tr

An Philippaerts

K. U. Leuven
Kasteelpark Arenberg 23
3001 Heverlee, Belgium
an.philippaerts@biw.kuleuven.be

Dr. Fernando Portela Cabillo

Freundenberg Forschungsdienste
Hoehnerweg 2-4
69469 Weinheim, Germany
fernando.portelacubillo@freundenberg.de

Dr. Yann M. Raoul

SIA
Rue de Monceau CS 60003 11
75378 Paris, Cedex 08, France
y.raoul@prolea.com

Prof. Dr. Herbert Riepl

Hochschule Weihenstephan-Triesdorf
Schulgasse 16
94315 Straubing, Germany
r.karl@wz-straubing.de

Prof. Dr. Yunus Robiah

Universiti Putra Malaysia
Institute of Advanced Technology UPM
43400 Selangor, Malaysia
robiah@eng.upm.edu.my

Philipp Roesle

Universität Konstanz
Universitätsstraße 10
78457 Konstanz, Germany
Philipp.Roesle@uni-konstanz.de

Dr. Sophie M. Sambou

Novance
Rue les Rives de l'Oise
BP 60206 Compiègne Cedex, France
s.sambou@novance.com

Prof. Dr. Hans J. Schäfer

University
Organisch-Chemisches Institut
Correns-Str. 40
48149 Münster, Germany
schafeh@uni-muenster.de

Dr. Benjamin Schäffner

Evonik Industries AG
Paul-Baumann-Str. 1
45772 Marl, Germany
benjamin.schaeffner@evonik.com

Prof. Dr. Ulrich Schörken

FH Köln
Campus Leverkusen
Kaiser-Wilhelm-Allee 1
51368 Leverkusen, Germany
ulrich.schoerken@fh-koeln.de

Alexander Schenzel

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
schenzel.alexander@gmx.de

Dr. Christof Schmitz

Freundenberg Forschungsdienste
Hoehnerweg 2-4
69469 Weinheim, Germany
christof.schmitz@freundenberg.de

Ansgar Sehlinger

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
ansgar.sehlinger@gmail.com

Stephanie Seidel

Bergische Universität Wuppertal
Gaußstr. 20
42119 Wuppertal, Germany
stephanie.seidel@uni-wuppertal.de

Julian R. Silverman

City College of New York
609 W 135th Street 20
10031 New York, United States
jsilverman@gc.cuny.edu

Prof. Dr. Snezana Sinadinovic-Fiser

University of Novi Sad
Faculty of Technology
Bul. Cara Lazara 1
21000 Novi Sad, Serbia
ssfiser@uns.ac.rs

Susanne Solleder

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
susanne.solleder@student.kit.edu

Dr. Claudia Stoer

BASF Personal Care and Nutrition GmbH
Henkelstr. 67
40589 Düsseldorf, Germany
claudia.stoer@basf.com

Alexander Studentschnig

Karl-Franzens University Graz
Institute of Organic/Bioorganic Chemistry
Heinrichstr. 28/II
8010 Graz, Austria
alexander.studentschnig@uni-graz.at

Prof. Dr. Christoph Syldatk

Karlsruhe Institute of Technology
Technical Biology
Egnler-Bunte-Ring
76135 Karlsruhe, Germany
christoph.syldatk@kit.edu

Dr. Oguz Türünc

Ghent University
Department of Organic Chemistry
Polymer Chemistry Research Group
Krijgslaan 281
9000 Ghent, Belgium
turunc.oguz@gmail.com

Yushin Takahashi

Kao Chemicals GmbH
Kupferstr. 1
46446 Emmerich, Germany
yushin.takahashi@kaochemicals.de

Elke Theeuwes

Ecover Co-ordination Center NV
Steenovenstraat 1A
2390 Malle, Belgium
theeuwes.elke@ecover.com

Dr. Cristina Tiozzo

CNR-ISTM
Via Venezian 21
20133 Milan, Italy
c.tiozzo@istm.cnr.it

Peter J. Tollington

Cargill BV
Jan van Galenstraat 4
3115 JG Schiedam, Netherlands
peter_tollington@cargill.com

Maike Unverferth

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
maike.unverferth@kit.edu

Richard Vendamme

Nitto Europe N.V.
Eikelaartsraat 22
3600 Genk, Belgium
richard.vendamme@neu.fr

Dr. Pierre Villeneuve

CIRAD
2 Place Viala 2
34060 Montpellier, France
villeneuve@cirad.fr

Hanna Wagner

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
hannawagner91@gmx.de

Sarah Wald

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
sarah.wald@student.kit.edu

Matthias Winkler

Karlsruhe Institute of Technology
Institute of Organic Chemistry
Fritz-Haber-Weg 6
76131 Karlsruhe, Germany
svm-winkler@t-online.de

Stefanie Wolf

Clariant Produkte GmbH
Ludwig-Hermann-Str. 100
86368 Gersthofen, Germany
stefanie1.wolf@clariant.com

Motonori Yamamoto

BASF SE
GMT/ B-B001
Carl-Bosch Str. 38
67056 Ludwigshafen, Germany
montori.yamamoto@basf.com

Dr. Aalbert Zwijnenburg

Johnson Matthey Chemicals GmbH
Wardstr. 17
46446 Emmerich am Rhein, Germany
bart.zwijnenburg@matthey.com