

abiosus e.V.

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

3rd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

**March 14-16, 2010
Emden, Germany**

in Cooperation with:

University of Applied Sciences Emden/Leer
German Society for Fat Science (DGF)
Agency of Renewable Resources (FNR)



University of Applied Sciences

**Fachhochschule
EMDEN•LEER**



Deutsche Gesellschaft für Fettwissenschaft e.V.



Scientific and Organizing Committee

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

Michael A. R. Meier, University of Potsdam, Germany

Acknowledgement

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

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Program

Lectures and Posters

Sunday, March 14, 2010

Registration

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

15.30

Welcome and Opening

Jürgen O. Metzger, *abiosus* e.V.

Gerhard Kreutz, Vice-President University of Applied Sciences Emden/Leer

Michael A. R. Meier, University of Potsdam, Germany

16.00 – 17.50 First Session

Chair: Michael A. R. Meier

16:00 – 16:30 L1	Renewable raw materials for the laundry and home care sector (M) <u>Thomas Müller-Kirschbaum</u> , Henkel, Germany
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16.30 – 17.00 L2	Peculiarities of microorganisms for synthesis and production of designed lipids (M) <u>Alexander Steinbüchel</u> , University of Münster, Germany
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17.00 – 17.30 L3	Vegetable oils as platform chemicals for polymer synthesis (M) <u>Juan Carlos Ronda</u> , University of Tarragona, Spain
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17.30 – 17.50 L4	Supplies of Oils and Fats for Non-Food Purposes (M) <u>Frank Gunstone</u> , University of St. Andrews, UK
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17.50 – 20.30	Poster session and Opening Mixer Posters will be displayed until the end of the workshop.
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(M) Main Lecture 30 min including discussion (D) Discussion Lecture 20 min including discussion

Monday, March 15, 2010

9.00 – 10.30 *First morning session*

Chair: Stefan Mecking

- 9.00 – 9.30 **Ruthenium-catalysed cross-coupling of vegetable oils with symmetrical alkenes and conversion of the products into diesters and aminoesters in tandem reaction sequences (M)**
L5 W. Roy Jackson, Monash University, Australia
- 9.30 – 10.00 **Ruthenium catalysts: the providers of added value to plant oils (M)**
L6 Xiaowei Miao, Cédric Fischmeister, Christian Bruneau, Pierre H. Dixneuf, University of Rennes, France
- 10.00 – 10.30 **Synthesis of α -olefins from seed oils (M)**
L7 Richard Pederson, Materia, USA
- 10.30 – 11.00 **Coffee break**

11.00 – 12.30 *Second morning session*

Chair: W. Roy Jackson

- 11.00 – 11.30 **Metathesis and other efficient (catalytic) approaches to renewable monomers and polymers (M)**
L8 Michael A. R. Meier, University of Potsdam, Germany
- 11.30 – 11.50 **Controlling olefin isomerization during olefin metathesis with fatty acid derivatives (D)**
L9 Patrice A. Fokou, University of Applied Sciences, Emden, Germany, Michael A. R. Meier, University of Potsdam, Germany
- 11.50 – 12.10 **Acyclic triene metathesis oligo- and polymerization of oleochemicals (D)**
L10 Ursula Biermann, University of Oldenburg, Jürgen O. Metzger, University of Oldenburg and *abiosus* e.V., Michael A. R. Meier, University of Potsdam, Germany
- 12.10 – 12.30 **Oleochemical uses of oils and biodiesel derived products (D)**
L11 Yann RAOUL, SOFIPROTEOL, Paris, France
- 12.30 – 14.00 **Lunch break**

14.00 – 15.30 First afternoon session

Chair: Alexander Steinbüchel

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| 14.00 – 14.30 | Innovative products from renewables – Opportunities in the field of lipid biotechnology (M) |
| L12 | <u>Ulrich Schörken</u> , Cognis, Germany |
| 14.30 – 14.50 | Optimization of 1,18-octadecenedioic acid synthesis via biotransformation by the use of <i>Candida tropicalis</i> (D) |
| L13 | Sabine Huf, Wenke Wagner, Thomas Hirth, Steffen Rupp, <u>Susanne Zibek</u> , Fraunhofer IGB, Stuttgart, Germany |
| 14.50 -15.10 | Engineering aspects of polyol biotransformations (D) |
| L14 | Simon Strompen, Dennis Kaufhold, Carolin Korupp, Jakob Müller, Andreas Liese, <u>Lutz Hilterhaus</u> , Hamburg University of Technology, Germany |
| 15.10 – 15.30 | Novel emulsifiers, thickeners and antioxidants based on hydroxy carboxylic acids – recent developments (D) |
| L15 | <u>Karsten Lange</u> , B. Jakob, H.J. Altenbach, S. Nandi, R. Ihizane, M.P. Schneider, Universität Wuppertal, Wuppertal, Germany |
| 15.30 – 16.00 | Coffee break |

16.00 – 18.00 Second afternoon session

Chair: Pierre Dixneuf

- 16.00 – 16.30
L16 **Catalytic mono-functionalization of triacylglycerols (M)**
Mark Rüschen gen. Klaas, Romy Wahlandt, Tamas Vari, University of Applied Sciences, Neubrandenburg, Germany
- 16.30 – 16.50
L17 **Alkyne fatty acids. -Preparation, reactions, products (D)**
Hans J. Schäfer, Kim E. Augustin, Claus Rüdiger, Organisch-Chemisches Institut der Universität, Münster, Germany
- 16.50 – 17.10
L18 **Gold-catalyzed aerobic cleavage of methyl 9,10-dihydroxystearate (D)**
Angela K. Köckritz, A. Janz, Andreas Martin, Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Rostock, Germany
- 17.10 – 17.40
L19 **Addition of C1- C8 alcohols to the fatty acid ester C=C double bond under heterogeneous catalytic conditions (M)**
Daniel Pioch, Anh Thoai Nguyen, Clement Lansalot-Matras, CIRAD, Montpellier, Annie Finiels, Claude Moreau, Ecole Nationale Supérieure de Chimie de Montpellier, France
- 17.40 – 18.00
L20 **Synthesis and properties of highly branched jatropha oil derivatives (D)**
Louis Daniel, A. R. Ardiyanti, B. Schuur, R. Manurung, A.A. Broekhuis, and H. J. Heeres, University of Groningen, The Netherlands
- 19.30 **Conference Dinner Upstalsboom Parkhotel**

Tuesday, March 16, 2009

9.00 – 10.50 *First morning session*

Chair: Juan Carlos Ronda

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| 9.00 – 9.30
L21 | From castor oil to a range of renewable polyamides (M)
<u>Patrick Borg</u> , Bernard Pees, Frederic Malet, ARKEMA , Serquigny, France |
| 9.30 – 10.00
L22 | Thermoplastic polymers from renewable ressources via entirely chemical routes (M)
<u>Stefan Mecking</u> , Dorothee Quinzler, Cecile Bouilhac, Anna Osichow, Christoph Dürr, University of Konstanz, Germany |
| 10.00 – 10.30
L23 | Well-defined soy-based poly(2-oxazoline)s: More than just renewable (M)
<u>Richard Hoogenboom</u> , Eindhoven University of Technology, The Netherlands, Ulrich S. Schubert, Friedrich-Schiller-University Jena, Germany |
| 10.30 – 10.50
L24 | Polyurethanes with bio-based and recycled components (D)
<u>Hynek Benes</u> , Institute of Macromolecular Chemistry AS CR, Tomas Vlcek SYNPO a.s., Renata Cerna, Faculty of Science, Charles University in Prague, Czech Republic |
| 10.50 – 11.20 | Coffee Break |

11.20 – 12.30 *Second morning session*

Chair: Mark Rüsch gen. Klaas

11.20 – 11.50 **Glycerol as a sustainable C3 platform: contribution
of 'heterogeneous' catalysis (M)**
L25 Francois Jerome, Joel Barrault, Laboratoire de catalyse en Chimie
Organique, Poitiers, France

11.50 – 12.10 **Glycerol etherification to dimers using basic and acidic catalysts (D)**
L26 Andreas Martin, Manfred Richter, Leibniz-Institut für Katalyse e.V,
Rostock, Germany

12.10 – 12.30 **Oxidative decarboxylation of unsaturated fatty acids (D)**
L27 Rolf Blaauw, Frits van der Klis, Willem Vogelzang, Marinus van den
Hoorn, Daan van Es, Jacco van Haveren, Wageningen UR Food &
Biobased Research, Business Unit Biobased Products, Wageningen,
The Netherlands

12.30 **Poster Award and Closing Remarks**

Best Poster Award

Award committee Daniel Pioch, Richard Hoogenboom, Ulrich
Schörken

Closing remarks

Michael A. R. Meier

12.45 **Lunch**

Poster

- P1 **Clicking renewable resources: Fatty acid derived monomers and related polymers via thiol-ene additions**
Oğuz Türünç, Michael A.R. Meier, University of Potsdam, Germany
- P2 **Clicking Renewable Resources: Thiol-ene Additions as a Versatile Tool for Terpene Modification**
Maulidan Firdaus, Michael A. R. Meier, University of Potsdam, Germany
- P3 **Synthesis of plant oil derivatived polyols via ADMET polymerization**
Enrique del Rio, Marina Galia, Joan Carles Ronda, Virginia Cadiz, Michael A. R. Meier, University of Potsdam, Germany
- P4 **Transformation of unsaturated fatty compounds by ene-yne cross-metathesis**
Antoine Dupé, Virginie Le Ravalec, Cédric Fischmeister, Christian Bruneau, University of Rennes, France
- P5 **Environmentally Friendly Surface Coatings from Renewable Fats and Oils.**
Zuzanna E Kosowski, Roy W Jackson, Andrea J Robinson, Algi Serelis, Chris Such, Monash University, Australia
- P6 **Ring Opening Metathesis Polymerization of Fatty Acid Derived Monomers**
Hatice Mutlu, Michael A. R. Meier, University of Potsdam, Germany
- P7 **Thermoplastic Polyesters from Plant Oils by Carbonylation Chemistry**
Dorothee A. Quinzler, Cécile Bouilhac, Stefan Mecking, University of Konstanz, Germany
- P8 **Towards Sustainable Polymerization: Biodiesel as a Green Polymerization Solvent**
Somaieh Salehpour, Marc A. Dubé, University of Ottawa, Canada
- P9 **Synthesis of 2-(methacryloyloxy)ethyl palmitate by transesterification of tripalmitin with HEMA**
Carla AC Vilela, Armando JD Silvestre, Alessandro Gandini, University of Aveiro, Portugal
- P10 **Catalytic Double Bond Isomerization as a New Way to Valuable Products from Fatty Acids**
Dominik M. Ohlmann, Lukas J. Gooßen, University of Kaiserslautern, Germany
- P11 **Synthesis and Evaluation of Renewable Oil Based Cationic Lipids**
Avinash Bhadani, Sukhprit Singh, Guru Nanak Dev University, Amritsar, India
- P12 **Soap Stock Separation process**
Yousef Fazli, Parisa Kermani, Islamic Azad University- Arak Branch, Arak, Islamic Republic of Iran

- P13 **KINETICS MODELING OF FATTY ACID ESTERIFICATION USING ION EXCHANGE RESIN CATALYST IN THE BIODIESEL PRODUCTION**
Ratna D Kusumaningtyas, Supranto, Rochmadi, Arief Budiman, Suryo Purwono, Gadjah Mada University, Yogyakarta, Indonesia
- P14 **PHENOLIC COMPOUND PRODUCTION FROM LIQUID SMOKE AND ITS POTENCY TO INHIBIT LINOLEIC ACID OXIDATION**
Dimas R.A Muhammad, Purnama Darmadji, Yudi Pranoto, Gadjah Mada University, Yogyakarta, Indonesia
- P15 **The dry fractionation of some adulterated vegetable oils**
Calin Jianu, Ionel Jianu, USAMVB Timisoara, Timisoara, Romania
- P16 **The dry fractionation of fats from piggish fleshing wastage**
Calin Jianu, Ionel Jianu, USAMVB Timisoara, Timisoara, Romania
- P17 **Iron(II)- and Manganese(II)-Induced Oxidation of Limonene by Dioxygen**
Anna Szczepanik, Dorota Naróg, Andrzej Sobkowiak, Rzeszow University of Technology, Rzeszow, Poland
- P18 **Syntheses of natural products from semi-mangrove plants**
Christoph Söffing, Jörg Pietruszka, Institut für Bioorganische Chemie der Heinrich-Heine-Universität Düsseldorf im Forschungszentrum Jülich, Jülich, Germany
- P19 **Used frying oils as a source for supercritical FAME preparation.**
Pasquale Campanelli, Luigi Manna, Mauro Banchero, Silvio Sicardi, Politecnico di Torino, Torino, Italy
- P20 **Transesterification of triglycerides applying zeolitic heterogeneous catalysts**
Oliver Meyer, Frank Roessner, Rainer A. Rakoczy, Richard W. Fischer, University of Oldenburg, Germany
- P21 **Novel Cationic Asymmetrical Gemini Surfactants Based on Tartaric Acid**
Rachid Ihizane, H. J. Altenbach, Karsten Lange, Bernd Jakob, University of Wuppertal, Germany
- P22 **New castor oil derived monomers via Baylis Hillman reactions**
Oliver Kreye, Michael A. R. Meier, University of Potsdam, Germany

- P23 **Adsorbed oils as ABE fermentation substrate**
Nils Tippkötter, Kai Muffler, Steffen Wollny, Kirstin Suck, Friedrich Ruf, Ulrich Sohling, Roland Ulber, University of Kaiserslautern, Germany
- P24 **Chemical structure and thermal properties of polyesters based on renewable resources**
Lidia Jasinska, Cor E. Koning, Eindhoven University of Technology, Eindhoven, Netherlands
- P25 **Continuous deoxygenation of triglycerides on solid catalysts**
Pierre Kube, Udo Armbruster, Manfred Richter, Andreas Martin, Leibniz Institute for Catalysis, Rostock, Germany
- P26 **Enzymatic synthesis of low molecular weight polyols from methylesters of ricinoleic acid**
Tomas Vlcek, SYNPO, a.s., Pardubice, Czech Republic
- P27 **Branched renewable polymers via metathesis and thiol-ene additions**
Lucas Montero de Espinosa, Michael A. R. Meier, University of Potsdam, Germany
- P28 **Hydrocarbon based raw materials from free fatty acids, lipids and soaps**
E. A. Stadlbauer, S. Stengl, B. Weber, S. M. Hossain, A. Frank, Fachhochschule Gießen-Friedberg, Giessen, Germany
- P29 **NEW LINSEED OIL-BASED UV-CURABLE MATERIALS**
Ornella ZOVI, Laurence LECAMP, Claude BUNEL, INSA Rouen- UMR CNRS, Saint-Etienne du Rouvray, France
- P30 **NEW BIOSOURCED POLYAMIDE UV-POWDER COATING**
Marion N'NEGUE MINTSA, Laurence LECAMP, Claude BUNEL, INSA Rouen- UMR CNRS, Saint-Etienne du Rouvray, France
- P31 **Evaluation of Nigerian plant oils for polymer chemistry**
Cecilia Olufunke Akintayo, Michael A. R Meier, University of Potsdam, Emden, Germany
- P32 **How 'Green' Is Your Chemistry?**
Marco Eissen, Gymnasium Ganderkesee, Ganderkesee, Germany
- P33 **Selfmetathesis of ethyloleat – A process engineering approach**
K. Kowollik, M. Zang, P. Schächtele, U. Fehrenbacher, R. Schweppe
Fraunhofer Institut für Chemische Technologie, Pfinztal; T. Adrian, HS Mannheim, Mannheim; J. Pettrak, TU München, H. Riepl, Hochschule Weihenstephan-Triesdorf, Weidenbach, Germany
- P34 **The Development of Palm Methyl Ester Sulfonic Acid (MESA) To Increase Oil Well Recovery**
Siti Mujdalipah, Surfactant and Bioenergy Research Center, Bogor, West Java, Indonesia

Abstracts

Part 1: Lectures

Renewable raw materials for the laundry and home care sector

Thomas Müller-Kirschbaum, Henkel AG & Co. KGaA, Düsseldorf, Germany
Thomas.mueller-kirschbaum@henkel.com

The global laundry and home care business amounts to 86 billion Euro. In those parts of the market where Henkel is active the company holds a global and European #2 position, in Germany the #1 position, of course. Henkel is widely recognized as being the leader in sustainability. Leadership in sustainability is based on the holistic approach of “Performance based on Sustainability”. By that the entire value chain is aligned with the concept of innovative sustainable consumption.

The use of renewable raw materials is one of the pillars within Henkel’s sustainability concept in the laundry and home care business. While on average 20 % of all surfactants used in Western Europe are based on renewable raw materials, namely palm kernel and coconut oil, Henkel’s average amounts to 35%. But using renewable resources is by far not enough since aspects like biodiversity have to be taken into account as well. From its very beginning in 2003 Henkel actively supported the Round Table of Sustainable Palm Oil (RSPO) which was formed by stakeholders from NGOs, governmental organizations and the industry to foster the sustainable sourcing of palm oil and palm kernel oil.

For “TERRA Active”, the first sustainable product range in the laundry and home care market, Henkel used as the unique first mover in the industry specified palm kernel oil certificates within the “book and claim” concept of the RSPO.

The presentation will disclose a look into the future development of our industry, too. Again, Henkel sets the pace by introducing a key performance indicator for sustainable innovations: the Sustainable Consumption Index. As the examples will show this opens new opportunities for bio-based materials.

L2

Peculiarities of microorganisms for synthesis and production of designed lipids

Alexander Steinbüchel, Institut für Molekulare Mikrobiologie und Biotechnologie,
Westfälische Wilhelms-Universität, D-48149 Münster, Germany
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Several bacteria synthesize lipids such as triacylglycerols and wax esters as storage compounds and deposit these hydrophobic compounds as insoluble inclusions in the cytoplasm. Some of bacteria excrete the lipids even into the medium. The key enzyme for synthesis of lipids in bacteria was identified for the first time as a wax ester synthase/diacylglycerol acyltransferase in the Gram-negative bacterium *Acinetobacter baylyi* [1]. Meanwhile, homologues of this promiscuous acyltransferase were detected also in *Rhodococcus opacus*, *Mycobacterium tuberculosis*, *Alcanivorax borkumensis* and in any other lipid synthesizing bacterium. These acyltransferases have been characterized in detail at the biochemical and molecular level and are capable of synthesizing a wide range of different acyloxyesters and even acylthioesters with a widely varying carbon-chain-length of the constituents. The acyltransferase of *A. baylyi* and of other bacteria were heterologously expressed in a functional active form in non-lipid synthesizing bacteria and in yeast. Tailor-made lipids and of fatty acid ethyl esters (FAEEs), which were referred to as 'Microdiesel' [2], were produced in engineered bacteria. The potential of these acyltransferase for the production of fine chemicals and oleochemicals on the one side and of bulk chemicals like lipids for fuel production and FAEEs on the other side [3] will be illustrated and summarized. The source of the used acyltransferase, the physiological background of the acyltransferase, i. e. the bacterium in which this enzyme is active, mutants in fatty acid and/or fatty alcohol metabolism, and the carbon sources during growth are important factors that determine the composition of the synthesized lipids. Production of these lipids requires also high cell density fermentations of bacteria for being able to produce abundant amounts.

Vegetable Oils as Platform Chemicals for Polymer Synthesis

Juan C. Ronda, Gerard Lligadas, Marina Galià, Virginia Cádiz
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The replacement of petroleum-based raw materials by renewable resources constitutes a major contemporary challenge in terms of both economical and environmental aspects.[1] Natural vegetable oils are considered to be one of the most important classes of renewable sources because of the wide variety of possibilities for chemical transformations, universal availability, and low price and they are preferred by the chemical industry as alternative.[2] The main components of the triglyceride vegetable oils are saturated and unsaturated fatty acids which in its pure form are also available as platform chemicals for polymer synthesis.

The purpose of our research is to develop new biobased thermosetting polymers from vegetable oils and its derivatives as renewable resources. Recently there have been many attempts to convert vegetable oils and fatty acids to useful polymers and several different approaches have been described.[3]

The direct polymerization of vegetable oils themselves is generally considered difficult due to their lack of active functional groups. Moreover the aliphatic nature and the light crosslinking that characterize the triglyceride-based materials make them incapable of displaying the necessary rigidity and strength required for structural applications by themselves. These drawbacks can be overcome for instance by cationic copolymerization of natural oils with styrene and divinylbenzene. [4] Even the resulting materials have the appropriate properties for a specific application, they must be inherently safe to be commercialized which involves to possess flame resistance and non toxic characteristics. Vegetable oil-based materials, like many other organic polymeric materials, are inherently flammable and so the use of flame retardant additives or the copolymerization with flame retardant monomers are common strategies used in the industry to overcome this shortcoming. Phosphorus, silicon and boron-containing polymers are well recognized for their flame retardant properties, and they are increasingly becoming more popular than their halogen counterparts, as they generally give off nontoxic combustion products.[5] In this work we describe the preparation and characterization of styrene-soybean oil based copolymers containing phosphorus, silicon or boron as effective environmentally friendly flame-retardant systems.

The functionalization of the triglyceride double bonds is another common strategy for obtaining high performance polymeric materials and various chemical pathways for functionalising triglycerides have been described.[6-8] We developed an environmentally friendly chemical procedure to obtain an enone-containing triglyceride from high oleic sunflower oil that could be an interesting alternative to epoxidized vegetable oils to produce thermosets. We studied their chemical crosslinking through aza-Michael and phospho-Michael reactions using aromatic diamines and aromatic secondary phosphine oxides in order to impart flame retardancy to the final materials. The curing of this enone-containing triglyceride with aromatic amines at high temperatures has been found to proceed through a complex cascade mechanism which leads to the formation of quinoline moieties that notably enhances the physical properties of the resulting thermosets.

The use of fatty acids or its chemical derivatives to obtain useful polymers has been also considered. Starting from 10-undecenoic acid or 10-undecenyl alcohol, we

synthesized a set of glycerol derived α,ω -dienic monomers containing free hydroxylic groups. Acyclic diene metathesis (ADMET) polymerization of α,ω -dienes has been shown as an efficient tool for the synthesis of a wide variety of linear polymers and polymer architectures that are not available using other polymerization methods.[9] It has been demonstrated that ADMET polymerization can proceed in the presence of heteroatoms and a variety of functional groups, as long as the terminal olefins are far enough apart from them.[10] So we used this synthetic procedure to prepare a set of lineal polyether and polyester polyols with different molecular weight and hydroxyl content from the above undecenoyl-based α,ω -dienes. In the case of the 10-undecenoic acid-derived α,ω -diene, the copolymerization with a phosphorus containing α,ω -diene has been also carried out. The resulting P-containing polyester-polyols have been acrylated and radically crosslinked to obtain a set of flame retardant thermosets. In the case of polyether-polyols thermosetting polyurethanes have been prepared.

Finally, 10-undecenoic and oleic acid derivatives have been exploited as platform chemicals to obtain renewable diols and polyols to produce linear and crosslinked polyurethanes. The coupling between a thiol and a carbon double or triple bond has received recently a growing interest.[11] Thiol-ene coupling complies with most of the requirements of the concept of a click reaction [12] and so it has been used with hydroxyl and carboxyl-functionalized thiols such as 2-mercaptoethanol and thioglycolic acid to obtain well defined functionalized structures.

- 1- Bozell J.J., Patel M., eds. ACS Symposium Series 921. Washington DC: American Chemical Society, 2006.
- 2- Biermann U., Friedt W., Lang S., Lühs W., Machmüller G., Metzger J.O., Klaas M.R., Schäfer H.J., Schneider M.P. *Angew Chem Int Ed* 2000; 39: 2206-2224.
- 3- Wool R.P., Sun X.S., eds. London: Elsevier Academic Press, 2005. Sharma V., Kundu P.P. *Prog Polym Sci* 2006, 31: 983-1008. Sharma V., Kundu P.P. *Prog Polym Sci* 2008,33:1199-1215.
- 4- Lu Y., Larock R.C.. *ChemSusChem* 2009, 2:136-147.
- 5- Lu S.Y., Hamerton I. *Prog. Polym Sci* 2002, 27:1661-1712.
- 6- Güner F. S., Yagci Y., Erciyas A. T. *Prog Polym Sci* 2006, 31, 633-670.
- 7- Meier M. A. R., Metzger J. O., Schubert U. S. *Chem Soc Rev* 2007, 36, 1788-1802.
- 8- Khot S. N. , LaScala J. J., Can E. S., Morye S. G., Williams I., Palmese, G. R. S., Küsefoglul H.; Wool R. P. *J Appl Polym Sci* 2001, 82, 703-723
- 9- Schwendeman J. E., Church A. C., Wagener K. B. *Adv Synth Catal* 2002, 344, 597-613
- 10- Wagener K. B., Brzezinska K., Anderson J. D., Younkin T. R., Steppe K., DeBoer W. *Macromolecules* 1997, 30(24), 7363-7369
- 11- Dondoni A. *Angew. Chem. Int. Ed.* 2008, 47, 8995-8997
- 12- Killops K.L., Campos L.M., Hawker C.J. *J. Am. Chem. Soc.* 2008, 130, 5062-5064

Supplies of oils and fats for non-food purposes

Frank D. Gunstone, SCRI, United Kingdom
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This lecture will survey the nature and sources of those fatty acids which are important for non-food purposes. Supply levels of the most important commodity oils will be reported. Figures from the United States Department of Agriculture (USDA) show a marked increase in non-food use in the last ten years. This can be explained in part, but not wholly, by the demand for biodiesel. Finally an attempt will be made to answer the question as to whether increasing supplies can meet the increasing demand for vegetable oils for both food and non-food uses.

**Ruthenium-catalysed cross-coupling of vegetable oils
with symmetrical alkenes and conversion of the products
into diesters and amino esters in tandem sequence reactions**

W. Roy Jackson,
Centre for Green Chemistry, Monash University, Australia
Roy.Jackson@sci.monash.edu.au

Vegetable oils have been shown to react with 2-butene with very high turnover numbers in the presence of metathesis catalysts to give methyl 9-undecenoate in high yields when a large excess of 2-butene is used. The excess 2-butene can easily be recovered and reused for several subsequent reactions. Isomerisation, followed by methoxycarbonylation using palladium catalysis can be carried out in the same pot leading to high yields of dimethyldodecanoate.

A related reaction sequences involving isomerisation, hydroformylation, hydroamination with benzylamine leads to aminoesters of potential use in the polymer industry.

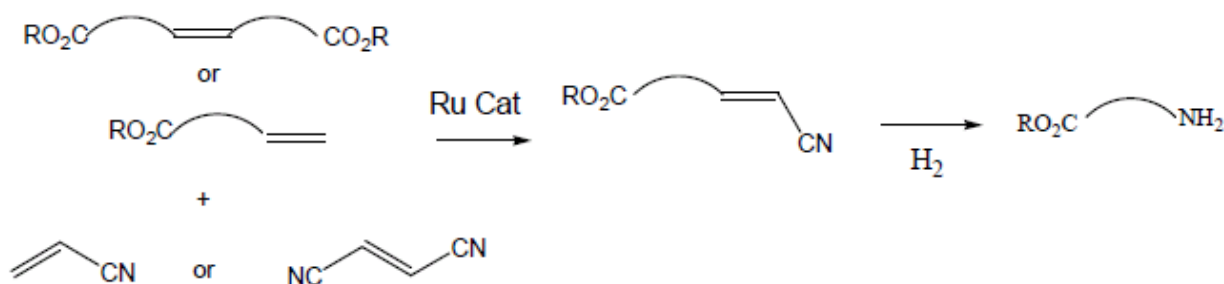
Reactions of vegetable oils with 1,4-diacetoxybut-2-ene and conversion of the products in to useful synthetic intermediates involving palladium catalysis will also be discussed.

L6

Ruthenium catalysts as providers of added value to plant oils: from unsaturated fatty esters to aminoacid precursors

Xiaowei Miao, Cédric Fischmeister, Christian Bruneau, Pierre H. Dixneuf
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UMR 6226 CNRS-Université de Rennes, Rennes cedex. France
pierre.dixneuf@univ-rennes1.fr

Plant oils, the known precursors of a variety of unsaturated acid derivatives, have also the potential to produce, by action of alkene metathesis catalysis, new intermediates useful for chemical industry, from renewable materials.[1] The numerous applications of polyamides motivate the search of new routes to their monomers from renewable resources rather than from petroleum derivatives. The objective of the presentation will be to show our efforts to generate long chain aminoacid precursors from plant oils derivatives.[2,3] The approach is based on the cross-metathesis, promoted by selected alkene metathesis ruthenium catalysts, of unsaturated esters, acids and other oil derivatives with acrylonitrile and fumaronitrile associated to the catalytic hydrogenation of the reaction products.



[1] C. Bruneau *et al*, *Chem. Today*, **2009**, 27, 17

[2] R. Malacea *et al*, *Green Chem.*, **2009**, 11, 152

[3] X. Miao *et al*, *ChemSusChem.*, **2009**, 2, 542

L7

Synthesis of alpha-Olefins from Seed Oils

Richard L Pederson, Materia Inc., United States

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Natural seed oils are an attractive alternative to petroleum based feed stocks due to their low costs, worldwide availability, built-in functionality and renewable supply. The seed oil biorefinery concept has come to fruition with the use of the Grubbs ruthenium olefin metathesis catalyst. Ruthenium olefin metathesis has enabled the conversion of oleochemicals into pharmaceutical intermediates, antimicrobials agents, insect pheromones, waxes, cosmetics, epoxy thermoplastics, thermosets, polyolefin monomers and surfactants.

Early work with traditional ill-defined Mo, W and Re-based metathesis catalysts revealed their incompatibility with the natural seed oil's functional groups; thereby, severely limiting commercialization efforts. Since the invention of highly active and functional group tolerant ruthenium olefin metathesis catalysts, cross metathesis of seed oils with ethylene (i.e. ethenolysis) has received special attention as this process produces alpha-olefins. However the best ethenolysis turnover number for the synthesis of methyl 9-decenoate has been 35,000. Cross metathesis of seed oils with an alpha-olefin of three carbons or higher (i.e. alkenolysis) has produced methyl 9-decenoate with turn over numbers of 200,000. This talk will describe our alkenolysis results and discuss the alkenolysis mechanism.

Metathesis and other efficient (catalytic) approaches to renewable monomers and polymers

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Plant oils bear a large potential for the substitution of currently used petrochemicals, since a variety of value added chemical intermediates can be derived from these renewable resources in a straightforward fashion taking full advantage of nature's synthetic potential.[1,2] Here, new approaches for the synthesis of monomers[3,4,5] as well as polymers[6,7,8,9] from plant oils as renewable resources will be discussed.

Especially olefin cross-metathesis allows an efficient catalytic access to α,ω -difunctional fatty acid derivatives.[3,4,5] Moreover, thiol-ene click chemistry offers a complementary approach for the introduction of a large variety of functional groups to fatty acids in a straightforward and efficient manner. Both approaches are fully along the lines with the principles of green chemistry and offer the possibility to efficiently functionalize fatty acid derivatives. The thus obtained renewable platform chemicals are valuable starting materials for a variety of polyesters and polyamides.[6]

Additionally, acyclic diene metathesis (ADMET) can be used to directly obtain macromolecules from such starting materials.[7,8] Linear as well as highly branched polyesters with interesting application possibilities can be obtained from fatty acid derived monomers in that way. Moreover, we could recently show that this approach is also suitable for the direct polymerization of high oleic sunflower oil.[9]

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Controlling Olefin Isomerization During Olefin Metathesis with Fatty Acid Derivatives

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Olefin metathesis with oleochemicals is a very versatile approach to obtain value added chemical intermediates from renewable raw materials.[1] Moreover, acyclic diene metathesis (ADMET) polymerization has developed into a very versatile technique for the preparation of a variety of macromolecular architectures. Applying this efficient catalytic process to monomers from renewable resources will lead to the development of materials with interesting properties that have the potential to replace existing fossil oil based materials. Despite of this success, it is known from low molecular weight model compounds that especially second generation olefin metathesis catalysts show a temperature dependent double bond isomerization activity.[2,3] The mechanism leading to the formation of the ruthenium-hydride species, which are responsible for these isomerizations, is discussed in detail in the literature.[4] One particular problem of ADMET reactions in this respect is that it is rather difficult to study the occurring side reactions with the resulting polymeric materials.

Within this contribution, the synthesis of novel and degradable monomers from fatty acid derivatives will be described and their subsequent polymerization discussed in detail. We will focus our discussion on the investigation of isomerization side-reactions occurring during ADMET polymerizations. Our approach to study isomerisation side reactions of the prepared polyesters depends on their degradation by transesterification with methanol in order to be able to investigate and quantify isomerization side-reactions that occurred during the polymerizations by GC-MS.[5,6] Furthermore, we will correlate these findings to self- and cross-metathesis reactions of low molecular weight model compounds.[7] Finally, a simple method to suppress these isomerizations during ADMET with second generation ruthenium metathesis catalysts will be described.

Financial support from the German Federal Ministry of Food, Agriculture and Consumer Protection (represented by the Fachagentur Nachwachsende Rohstoffe; FKZ: 22026905) is kindly acknowledged.

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Acyclic Triene Metathesis Oligo- and Polymerization of Oleochemicals

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The synthesis of branched macromolecules from renewable raw materials via olefin metathesis should be of importance because the resulting polymers are expected to show interesting properties e.g. as base materials for coatings, additives or processing aids for linear thermoplastics. The acyclic diene metathesis (ADMET) polymerization is known to be a versatile technique for the preparation of linear polymers, polymers with a defined degree of branchings, telechelics as well as block-copolymers. The acyclic triene metathesis (ATMET) polymerization using glyceryl triundec-10-enoate as starting material has been described to give in a simple one pot one step procedure using different ratios of the triglyceride and methyl acrylate as chain stopper branched macromolecules of different molecular weights.[1] Recently we developed the ATMET polymerization of high oleic sunflower oil, a renewable raw material consisting of triglycerides with internal C,C-double bonds, to yield highly branched and functionalized polyesters.[2] If Hoveyda-Grubbs second generation catalyst was used and methyl acrylate was introduced as a chain stopper, the molecular weight of the obtained polymers could be tuned by varying the ratio of the triglyceride and methyl acrylate. Using the first generation Grubbs catalyst for the polymerization of high oleic sunflower oil, no cross-linking was observed, even without the use of a chain stopper. The resulting branched materials were characterized by GPC, ^1H and ^{13}C NMR and ESI-MS.

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Oleochemical uses of oils and biodiesel derived products

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Renewable resources have long been used to serve the needs of populations to eat, to keep warm, to dress and many others. Oleaginous plants, of which rape and sunflower, have been used and are still used to cater for these needs.

Developing the uses of these vegetable resources is at the heart of the mission of SOFIPROTEOL, financial establishment of the French vegetable oils and proteins organisation.

The SOFIPROTEOL group, through its Diester Industrie subsidiary, is committed to producing 3 million tons biodiesel in 2010, mainly methyl esters derived from rape and sunflower seedoils, and which will also generate 300 000 ton glycerol. Sofiprotéol has also been investing for about 20 years in the development of oleochemicals, a growing market due to regulatory requirements as well as the strong demand for renewable and biodegradable products.

The focus of this talk will be to review the oleochemical developments and possibilities arising from the valorisation of glycerol and fatty acyl chains to produce fatty acids, esters, fatty alcohols, dimers and other specialties to be used as chemical intermediates or as end products.

Those products combine high technical and environmental properties and are used by industrial companies in applications such as lubricants, detergents, cosmetics and hygienic products, coatings, paints, bioplastics and other applications.

Innovative products from Renewables – Opportunities in the field of Lipid Biotechnology

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Nowadays a strong trend towards “green” is seen in the chemical industry as well as in the energy sector. In this respect the oleochemical industry has been ahead of the latest trend for more than 100 years. Cognis utilizes fats and oils from renewable resources since decades with an overall amount of renewables of > 50 %.

The oleochemical industry is traditionally a chemically based industry. Most of the established chemical processes produce little waste and are environmentally friendly, thus they can be called sustainable over the whole value chain.

Biotechnology based processes have been established in oleochemistry since a few years. These processes fit well into the green strategy of Cognis. The presentation will give an overview about biotechnologically produced lipid based products [1] and will discuss chances and limitations for the application of White Biotechnology. The following examples will be discussed in more depth:

- Production of dicarboxylic acids with microbial biooxidation
- Enzymatic synthesis of CLA triglycerides
- Carotenoid production with algae
- Current fields of research: BMELV funded projects with Cognis participation

[1] Ulrich Schörken, Peter Kempers; Lipid biotechnology: Industrially relevant production processes; Eur. J. Lipid Sci. Technol. 2009, vol. 111, no. 7, pp. 627–645.

Optimization of 1,18-octadecenedioic acid synthesis via biotransformation by the use of *Candida tropicalis*

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For the production of polyesters diols and dicarboxylic acids are used. These raw materials usually are made from crude oil. Long-chain dicarboxylic acids (DCA) are promising compounds for the synthesis of polymers with new characteristics, but long-chain DCA are difficult to produce and expensive. Especially unsaturated DCA with more than twelve carbon atoms are currently not available from petrochemical raw materials. For the production of biobased polymers long-chain DCA can be produced via biotransformation for instance with yeast of the genus *Candida*. For this conversion a metabolic pathway called ω -oxidation is required. Alkanes and fatty acids are oxidized at their terminal methyl group in three enzymatic steps. By blocking degradation of DCA via ω -oxidation pathway an enrichment of dicarboxylic acids in the supernatant of the culture is possible.

Candida tropicalis is a known DCA producing strain of long-chain dicarboxylic acids. In our experiments we first screened different substrates like oleic acid methylester derived from rapeseed oil and olein and determined their conversion rates. *Candida tropicalis* was not able to convert crude rapeseed oil into DCA itself, but only when lipase was added into the bioreactor.

Within this work we established the biotransformation of oleic acid into the corresponding 1,18-octadecenedioic acid and the bioprocess in a 30 L fermenter. The process is divided into two main phases: an optimized cell growth phase with different fed batch strategies to avoid crabtree effect as well as production phase which require change of the pH and limiting amounts of C- and N-sources. We achieved biomass concentrations up to 40 g/L and DCA conversion rates of 0,44 g/(L h) and a maximum concentration of 100 g/L. Additionally we observed that the conversion is influenced by the concentration of ammonium in the medium.

In our future work we will focus on the establishment of new strains with even higher productivity.

Engineering Aspects of Polyol Biotransformations

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Enzymes are already successfully used in many fields of life. For example they are applied for starch degradation, for isomerization of glucose, for aroma production and in cosmetic industry. Main advantages are higher product quality, better raw material exploitation, lower production costs and lower environmental impact [1,2]. As enzymes could already replace chemical catalysts in many fields, research is also done with the aim of using enzymes as catalysts in polymer synthesis, ester oil [3] and fatty acid production.

Applying enzymes on preparative scale is a challenging goal for biotechnology which can lead to new reactor setups for biotransformations. These reactor setups must fulfill requirements like catalyst recycling, mixing, and product removal. This will be discussed and exemplified in the lecture. Catalyst recycling is explored since many years and various separation processes have been developed for enzyme recycling such as membrane technologies and immobilization. Product removal is exploited in numerous synthetic applications from lab to industrial scale. As viscosities for solvent free conversions are high, mixing becomes a crucial issue. Mixing influences reaction rate and conversion. If the reaction medium is not ideally mixed, less substrate can get to the active site of the enzyme and fewer product is formed per unit of time.

Polyols represent versatile substrates for biotransformations. Using various reactants under catalysis of enzymes simple esters as well as complex polymers can be formed. Apart from this also polyols can be obtained from renewable resources applying enzymes. Each of these synthetic routes has their specific requirements mentioned above. Several examples showing the engineering aspects of these polyol biotransformations will be highlighted in the lecture. Up scale of biotransformations like hydrolysis of plant oils [4], solvent free synthesis of ester oils and bulk polymerization [5] will be discussed. Exploiting limiting parameters of bioprocesses lead to improvement in conversion and provide novel reaction pathways.

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Novel emulsifiers, thickeners and antioxidants based on hydroxy carboxylic acids – recent developments

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We reported [1] (several times) about the syntheses of O-acylated hydroxy carboxylic acid anhydrides and their use as key intermediates for combination products with several different nucleophiles. Series of novel surface active compounds were obtained, which could be interesting for use as surfactants, emulsifiers, thickeners and antioxidants in cosmetics, nutrition and industrial processes. We tested partly the physical and chemical behavior and the biological activities as well. In this lecture we will report about recent developments in preparation of new combination products based on hydroxy carboxylic acids and their properties as multifunctional molecules.

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Catalytic mono-functionalization of triacylglycerols

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Selective introduction of one functional group in a triacylglycerol molecule is an important target for the utilization of plant oils for polymer applications, e.g. paints and varnishes.

A reported two-step procedure for the introduction of acryl groups in triacylglycerols consists of the epoxidation of C=C-bonds and the subsequent ring-opening of the epoxide with acrylic acid. Thus, a mono-acrylated triacylglycerol can be obtained by mono-epoxidation in the first step. This was carried out by the classic Prileshajev-epoxidation with peracetic acid and by the more selective chemo-enzymatic epoxidation.

A (statistically) mono-epoxidized oil can also be made by the catalytic randomization of a commercial fully-epoxidized soybean oil with an adequate amount of any other triacylglycerol. The interesterification is favorably catalyzed by a lipase, because the epoxide-ring might react under standard conditions with a strong base as catalyst.

An acryl group can be directly introduced in a triacylglycerol by lipase-catalyzed interesterification. The most straightforward way would be the reaction of a triacryl glycerol with an adequate amount of a plant oil. However, triacryl glycerol is not a commercial commodity; therefore we used trimethylol propane (TMP) triacrylate for the same purpose. Starting with butyl acrylate a product of slightly different composition was obtained.

Both two-step and one-step reactions were carried out with various unsaturated plant oils like linseed oil, soybean oil and hemp oil.

Selectivities and product characteristics will be shown; safety concerns and different problems in downstream-processing will be discussed.

Alkyne fatty acids - Preparation, reactions, products

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Whilst alkene fatty acids occur abundantly in nature, acetylene fatty acids are rare. The most important ones are tariric acid (18:1 6a) and crepenynic acid (18:2 9c12a). Furthermore acids with conjugated acetylene groups are known.[1] Alkyne fatty acids are furthermore prepared and used as intermediates in fatty acid synthesis, because they allow the easy assembly of building blocks and the stereospecific hydrogenation to cis- or trans-double bonds.[2].

Alkynes can be prepared from alkenes by bromination/debromination. In this way the one-pot conversion of oleic acid to stearolic acid (1) and of 11-undecenoic acid to 11-undecynoic acid (2) was achieved in 85% and 78%, respectively.[3, 4]

The triple bond allows a number of reactions that are not possible with the double bond. Some of these have been applied here:

Triple bond isomerization offers the possibility to isomerize internal alkyne groups into terminal ones by using the acetylene zipper. This way stearolic acid (1) could be isomerised to 90% methyl 17-octadecynoate (3) and converted to 93% 17-octadecyn-1-ol (4).[4]

Substitution of the acetylenic-CH-bond: 2-Alkyne fatty acids are biologically active. By deprotonation and carboxylation 19-hydroxy-nonadeca-2-ynoate was obtained in 85% yield.[5]

The ester 3 could be dimerized with CuCl, DBU, pyridine and dioxygen to 96% dimethyl hexatriaconta-17,19-diyn-1,36-dioate.[4] The hydrogen in the acetylenic CH-bond in 2 - 4 can be substituted by aryl in nearly 90% yield, when reacted with iodobenzene and CuI, PdCl₂ as catalyst.[5]

Addition to the triple bond: Hydratisation of 3 with Hg(II) as catalyst yielded 98 % methyl 17-oxooctadecanoate. With PdCl₂, CuCl₂, dioxygen and carbon monoxide in methanol the internal triple bonds in 1 could be converted in a methoxycarbonylation to 58% methyl 9(10)-methoxycarbonyloctadeca-9-enoate. Terminal triple bonds in 2 - 4 afforded the bismethoxycarbonyl adducts in 76-83% yield.[5,6]

Cyclotrimerization: With Pd/C, TMSCl as catalyst the octadecynol 4 could be converted into 96% of the cyclotrimers.[5-7]. Terminal alkynes could not be dimerized with this

catalyst, however, a Co(I)-catalyst afforded the cyclotrimer of 2 in 85% yield. From 2 - 4 and different alkynitriles with another cobalt-catalyst pyridine derivatives were obtained in 62 - 93% yield. Phenylisocyanate the ester 1 or the corresponding alcohol could be cyclotrimerized with a Ni-catalyst to pyridones in 98% and 75% yield, respectively.[5,6] The cyclotrimers of 1 and 4 were converted into surfactants by ethoxylation, sulfatation and N-methyl-glucamidation. They show interesting Langmuir-isotherms with similarities to the lung surfactant and exhibit low surface tensions.[8] Support by Henkel KGaA, Düsseldorf and the Fachagentur "Nachwachsende Rohstoffe" is gratefully acknowledged.

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Gold-catalyzed aerobic cleavage of methyl 9,10-dihydroxystearate

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Introduction

Azelaic acid (nonanedioic acid, AA) and its derivatives are used in a broad range of industrial applications such as polymers and synthetic fibres, lubricants, plasticisers or pharmaceuticals. The manufacture of AA is made from oleic acid (OA) via ozonolysis [1]. However, due to safety risks alternative syntheses are highly demanded. 9,10-Dihydroxystearic acid (DSA), obtained by the oxidation of OA, was cleaved under aerobic conditions using cobalt catalysts, also in combination with polyoxometallates or N-hydroxyphthalimide [1,2,3]. In this study, a new gold-catalyzed aerobic cleavage of methyl 9,10-dihydroxystearate (MDS) without any additional co-oxidant is described.

Experimental

In typical screening experiments, 1 mmol substrate, 0.5 mol% catalyst, 2-20 mmol NaOH and 20 ml H₂O were placed in a 100 ml Parr autoclave. Then the autoclave was pressurized with 5 bar O₂ and stirred at 80°C for 260-540 min. Additionally, experiments under optimized conditions were carried out in a 500 ml Buechi glass reactor equipped with double jacket heater, stirrer, oxygen inlet dipping into the liquid, pH-electrode and base (NaOH) inlet for keeping a constant pH. The conversion and yield of products were controlled by GC-MS.

Results

AA **3** and pelargonic acid **2** (PA) were the main products in the Au-catalyzed oxidation of MDS **1** with O₂ (Fig. 1, Table 1).

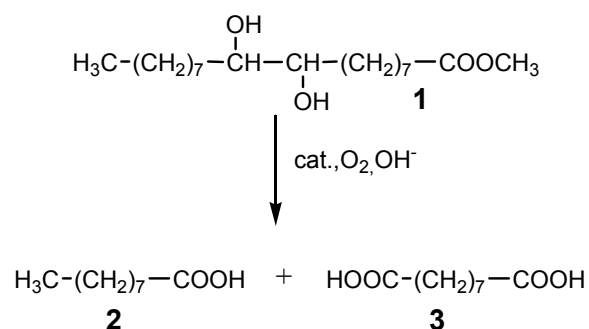


Fig. 1. Cleavage of methyl 9,10-dihydroxystearate

Observed side products were octanoic acid and octanedioic acid as products of chain-degrading further oxidation. Gold nanoparticles supported by different metal oxides were used as catalysts (Table 1, entries 2-6), Highest yields in cleavage products were obtained with Au/Al₂O₃, therefore it was used for further optimizations. Obviously, the pH value of the reaction solution has a main influence on catalytic activity. Even if the actual pH value

could not be detected in the autoclaves under reaction conditions, different molar amounts of NaOH were added to generate a basic environment. The highest yield of **2** and **3** were observed at a molar ratio of 1:NaOH=1:10 (entry 11). Currently, experiments are performed in a glass reactor under constant pH values. 52 % and 44 % of PA and AA, respectively, were received using this equipment at a pH value of 10.4 (Table 1, entry 15).

entry	1 [mmol]	catalyst	Au loading [w%]	n _{Au} [mmol]	n _{NaOH} [mmo]	t [min]	Y (2) [mol%]	Y (3) [mol%]
1	2	blank	-	0.004	4	540	0	0
2	2	Au/CeO ₂	0.36	0.004	4	540	8	5
3	2	Au/Al ₂ O ₃	0.64	0.004	4	540	26	20
4	2	Au/MgO	0.18	0.004	4	540	18	14
5	2	Au/ZrO ₂	0.29	0.004	4	540	23	17
6	2	Au/Fe ₂ O ₃	1.06	0.004	4	540	19	14
7	1	Au/Al ₂ O ₃	0.64	0.002	0	260	0	0
8	1	Au/Al ₂ O ₃	0.64	0.002	2	260	15	13
9	1	Au/Al ₂ O ₃	0.64	0.002	4	260	25	21
10	1	Au/Al ₂ O ₃	0.64	0.002	6	260	29	25
11	1	Au/Al ₂ O ₃	0.64	0.002	8	260	31	27
12	1	Au/Al ₂ O ₃	0.64	0.002	10	260	38	31
13	1	Au/Al ₂ O ₃	0.64	0.002	12	260	28	24
14	1	Au/Al ₂ O ₃	0.64	0.002	20	260	21	16
15*	10	Au/Al ₂ O ₃	0.64	0.02	pH 10,4	240	52	44

Reaction conditions: 20 ml H₂O, 80 °C, 5 bar O₂; * 200 ml H₂O adjusted to pH 10.4 with 1M NaOH (glass reactor).

Table 1. Accomplished catalytic runs

Further investigations in order to improve the yield of AA and to include DSA, 9,10,12-trihydroxy stearic acid and 13,14-dihydroxybehenic acid derivatives are in progress.

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Addition of C1- C8 Alcohols to Fatty Acid Ester C=C Bond under Heterogeneous Catalytic Conditions

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Low thermal and oxidation stability limits the use of vegetable oils and derived esters because of the presence of C=C double bonds. The reactivity of this double bond has been investigated to perform the addition of C1-C8 alcohols, in the presence of H-form zeolites, thus leading to saturated oxygen-containing side chains.

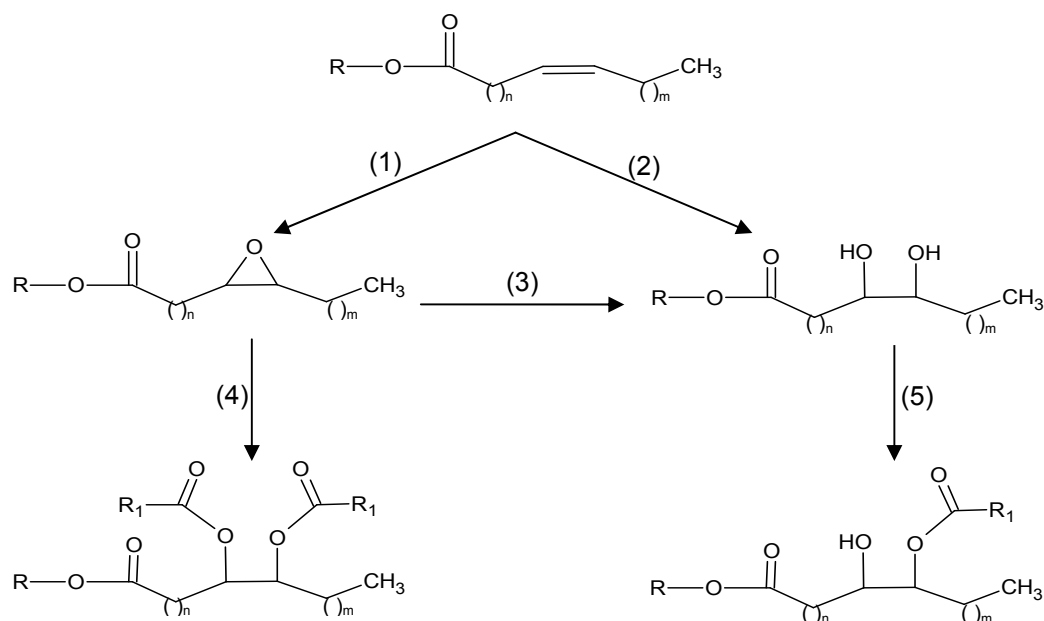
On the chemical side, our previous results relative to the model reaction -addition of methanol to methyl oleate- have shown the influence of key parameters acting on the yield of the target product, methyl methoxy stearate (temperature, methanol excess, Si/Al ratio). The present study deals with an even more complex system: in addition to C=C bond migration and to a thermodynamic limitation related to the reverse reaction (de-methoxylation), already noted, methyl oleate here also undergoes alcoholysis as a parallel reaction, thanks to the acidic properties of the solid catalyst. Selectivity and reaction rates are discussed according to steric and electronic effects, the alcohol being solvent but also reactant upon the case. The initial rate of the alcoholysis being about 4 to 10 times faster than the addition to C=C, the reaction medium first contains the ester with the higher alcohol, which is then alkoxyated at almost constant initial rate whatever the chain length from methanol to n-butanol.

On the applied side, this work opens the way to a range of oleochemicals under “green” conditions; the catalyst yields C=C free alkoxyated long chain esters, including a di-alkoxyated chain when starting from linoleate, with selectivity higher than 70 mole%. The adduct is similar to a branched chain wax when starting from a common unsaturated ester, or is a normal chain wax but bearing an oxygen bridge in place of one CH₂ when starting from undecylenic ester. All these “new” alkoxyated esters –not yet manufactured at industrial scale but accessible- should bring interesting properties for example in lubricant and cosmetic formulations.

Synthesis and Properties of Highly Branched Jatropha Oil Derivatives

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Pure plant oil from *Jatropha curcas* L. is a potentially very attractive source for green chemicals [1]. It is toxic and as such does not compete with the food chain. We here report exploratory studies on the synthesis of highly branched Jatropha oil derivatives using epoxidation/dihydroxylation/esterification methodology (Scheme 1). The products may find applications as biolubricants or as cold-flow improvers in biofuel applications [2]. Two different routes were explored, i.e. esterification of epoxides (Route 1 and 4), and esterification of dihydroxyl groups (Route 2 and 5). Epoxidation was performed using a catalytic Sharpless system, dihydroxylations by either a Swern *trans*-dihydroxylation or an Upjohn *cis*-dihydroxylation. The products were characterized using NMR, GC-MS, GPC, DSC, Cloud/Pour Point Analyses (low temperature properties), and Rancimat analyses (oxidative stability). Compared to virgin Jatropha oil (pour point of about -1 to -3 °C), the branched products showed improved low temperature behaviour. The cold properties of the branched products are a function of the synthetic methodology. The compound from the route 2, 5 showed a pour point of -18 °C, whereas that of route 1, 4 was only -3 °C. Synthetic details, an overview of product properties and explanations for the differences in cold flow properties of the branched derivatives will be provided.



Scheme 1 Modification steps of Jatropha oil (R= remaining of the triglyceride structure, $R_1=CH_3$, C_5H_{11})

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From castor oil to a range of renewable polyamides

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In the middle of the 30's, the French chemists have succeeded to synthesize a polymer from castor oil. This polymer, more commonly called "PA11", is a polyamide marketed under the trade name of Rilsan®. The unique combination of high performance properties allows to use this Bioplastic in a wide range of highly demanding applications including packaging, automotive and truck (air brake tubes, fuel lines), oil and gas (off shore flexible pipes), sporting equipments (soles for sport shoes, ski top layers), textile, cable and electrical components.

As early as 1947, this polyamide, made from renewable sources, was sold under the name of Rilsan®. First, it was used to create long, fine, resistant threads which were converted into synthetic fibres to compete Nylon® 6 and 6.6 oil-based polyamides. Then quickly, the use of Rilsan®, found other applications. Today, the PA11 is widely used in high-value added applications with great technical and resistance requirements ; PA11 delivers an outstanding level of chemical, thermal and impact resistance over a wide range of flexibility. PA11 is used as a cost effective replacement of metal or rubber in highly technical applications.

Present in Castor Oil at 85% in the form of triglyceride ester, ricinoleic acid can be converted according to two separate processes.

First, alkaline pyrolysis process leads to both 2-octanol (8 carbons) and sebacic acid (decanedioic acid - 10 carbons). Both find applications in many fields, i.e. solvent, lubricant, plasticizer, hydraulic fluid, cosmetic, etc.. Sebacic acid is also a component of bio-plastics. A second process currently used by Arkema, consists in cracking methyl ricinoleate to get in one hand heptaldehyde - source of co-products with 7 carbons such as heptanoic acid, heptanol - and in the other hand methyl undecylenate that leads by successive transformations to 11-aminoundecanoic acid (11 carbons), the PA11 monomer.

Arkema, leading consumer of castor oil, enhances all the co-products of the Rilsan® and Pebax® manufacturing processes. Heptaldehyde and heptanol, 100% linear chain saturated fatty bio-based chemicals, can be used as a synthesis intermediate in fragrance and aroma industries, and as plasticizers for polymers. Heptanoic acid is used primarily in the form of salts for aqueous anticorrosion or in the form of esters for industrial lubricants (aviation, refrigeration, ..), plasticizers and flavors. The properties of methyl undecylenate and undecylenic acid make them interesting molecules that found applications as such or as a precursor for flavors, fragrances, pharmaceuticals, hygiene products and cosmetics. But they can also be used in formulations requiring anti-odor properties. Undecylenic acid is well known for its bioactivity against some fungi and bacteria. Finally, all the methyl esters of linear fatty acid presents in Castor Oil and separated from methyl ricinoleate are gathered in a unique biodegradable product, Esterol A, that has a wide range of applications : solvents, cutting oils, fat liquors for leather treatment, textile oils, mold-release formulations for concrete, anti-foaming agent and all greasing/lubricating formulations.

Actually, every last drop is put to good use, often replacing petrochemical-based products.

Thermoplastic polymers from renewable resources via entirely chemical routes

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Thermoplastic polymers are currently prepared almost exclusively from fossil feedstocks. In view of their limited range, alternative renewable resources are desirable in the long term.

Polyesters are one of the most important classes of organic polymers, and indeed the more recently developed and commercialized biomass-based polymers are thermoplastic polyesters.¹ Their preparation employs a fermentation step, with carbohydrates, most often glucose, as a feedstock. By comparison to routes employing a fermentation step, chemical synthetic routes in which the original molecular structure of the plant biomass employed is substantially retained are attractive as they can be efficient in terms of feedstock utilization and reaction space-time-yields, and provide novel properties. Plant oils are in principle attractive substrates for the preparation of aliphatic polyesters, as the substrate provides relatively long $-(CH_2)_n-$ hydrocarbon segments. Their conversion to linear polyesters employing carbonylation² and other catalytic routes is discussed.

Cellulose is an abundant resource. It possesses excellent mechanical properties. A more widespread application as a material is restricted by its difficult processability. Studies on the direct catalytic conversion of cellulose to a thermoplastic material employing low-cost basic chemicals are presented.

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Well-defined soy-based poly(2-oxazoline)s: More than just Renewable

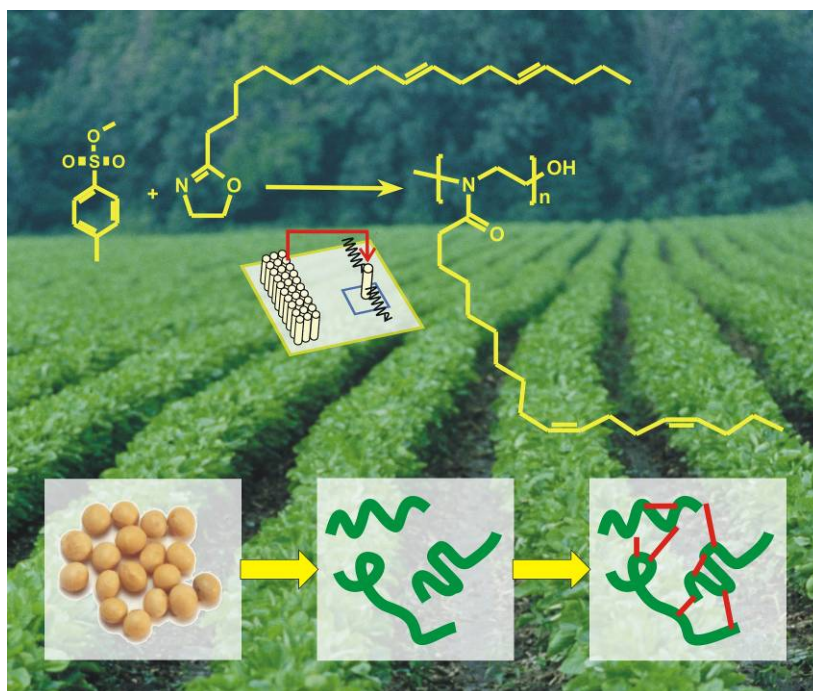
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The use of renewable feedstock is becoming a more and more important issue in chemistry due to the increasing oil-prices and the concerns about future oil-supplies. In polymer chemistry, the use of renewable resources has attracted significant attention in the last couple of years as well.

In this contribution, we discuss the cationic ring-opening polymerization of a 2-oxazoline monomer with soybean fatty acid side chains (SoyOx) under microwave irradiation.¹ Kinetic experiments were performed to investigate the livingness of the polymerization in both acetonitrile and in the absence of solvent. In addition, both block and statistical copolymers were prepared using the SoyOx monomer.² The synthesized (co)polymers were crosslinked under UV-irradiation resulting in insoluble polymeric materials and core-crosslinked micelles.^{1,3}



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Polyurethanes with bio-based and recycled components

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The topic deals with two actual environmental tasks: waste management (especially waste plastic recycling) and utilization of bio-materials (renewable resources) in polymer synthesis. The paper is focused on a preparation and a characterization of polyurethanes (PUR) combining renewable bio-based raw materials and PUR waste. A fish-oil based polyol and a castor oil are used as the bio-based raw materials. The recycled component is in the form of recycled polyols prepared by chemolysis of PUR waste. Based on the properties of the natural and the recycled polyols, final PUR materials were design as rigid PUR foams or cast PUR systems. Processing parameters as well as final thermo-mechanical properties of the prepared PUR materials were evaluated and discussed. The results showed that the PUR system containing the fish-oil based polyols and the recycled polyols are suitable for rigid PUR foam preparation. Usually, the recycled polyols prepared by conventional glycolysis can be only added as a minor part into the PUR system. Surprisingly, a combination of the bio-polyols and the recycled polyols enables to replace a majority of petrochemical polyols in the rigid PUR foam formulation without any inferior effects on final quality of the product.

In the case of the castor oil based polyols, a preparation of cast PUR compact materials seems to be the most suitable application. Due to the high content of secondary hydroxyl groups, the castor oil based polyols are less reactive with isocyanates than the fish oil based polyols. Long aliphatic chains of the castor oil based polyols are advantageously utilized in the formulation of soft PUR floor materials.

Glycerol as a sustainable C3 platform: contribution of 'heterogeneous' catalysis

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During the last decade, glycerol has gained a lot of attention because of the rapid development of the vegetable oil industry especially for the production of biodiesel, lubricants, solvents, among others. Glycerol is the main co-product of the oleochemistry and the growing demand on biodiesel is now creating a significant glut of the glycerol production. In this context, the catalytic conversion of glycerol to higher value added chemicals has become of growing interest.

The recent advances made in the field of heterogeneous catalysis now open very efficient ways to selectively convert glycerol to a wide range of C3-monomers such as acrolein, acrylic and glyceric acids, glycidol, allylic alcohol, acrylonitrile, 1,3-propanediol, propylene glycol, among others. These biomass-based routes offer now suitable alternatives for preparing a diverse array of chemicals with a high content of renewably sourced ingredients. As for propene-based processes, the conversion of glycerol to C3-monomer generally requires harsh conditions such as a high temperature and, in some cases, a high pressure. Moreover, due to the presence of three hydroxyl groups on glycerol, many secondary products can be formed under such reaction conditions. The control of the reaction selectivity determines the viability of these glycerol-based processes. The rapid development of the material chemistry gives now access to a diverse array of sophisticated heterogeneous catalysts which were found particularly efficient for the selective conversion of glycerol.

In this communication, we will present the contribution of heterogeneous catalysis for the conversion of glycerol and glycerin to C-3 chemicals. In particular, we will make a comparative between the existing C-3 propene platform with that of glycerol. Even if it is clear that glycerol will not replace propene in the industrial production of C3-chemicals, we will present successful examples where glycerol has been incorporated into propene-based units.

Glycerol etherification to dimers using basic and acidic catalysts

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Etherification is a promising way for valorization of glycerol. Besides conversion to fuel blending components (e.g. *tert.*-butyl ethers [1]), glycerol etherification to di- and polyglycerols yields attractive products required for manufacturing of biodegradable surfactants, lubricants, cosmetics, food additives and others.

Earth alkaline oxides [2,3] or alkaline modified zeolites and mesoporous materials [4,5] are reported to be promising solid catalysts for glycerol etherification to diglycerol. A theoretical study on the role of surface basicity and Lewis acidity is described in [3].

The current contribution will give an overview on the base- and acid-catalyzed reaction pathways including application of heterogeneous and homogeneous catalysts.

Recently, we have shown [6] that the etherification reaction using Na and Cs modified zeolites X, Y and Beta can favorably be accomplished at 260 °C under atmospheric pressure. Activity (glycerol conversion after 8 h reaction time) was found to be highest on CsX, with 63 % glycerol conversion and selectivity to linear diglycerol of ca. 80 %.

However, XRD and SEM analysis of spent catalysts proved that CsX zeolites suffered a structural collapse during reaction with release of Cs into solution (as confirmed by XRF). This inspired us to look for the role of alkali metal salts that can be considered as homogeneous catalysts because of their facile solubility in glycerol. We studied the reaction using MeHCO_3 (Me = Na, K, Cs) as well as CsAn (An = OH^- , CH_3COO^- , NO_3^-) for clarifying the influence of catalyst basicity on the reaction. Results were compared with Cs ion exchanged zeolites (the zeolite aluminosilicate structure might be viewed as complex inorganic anion).

Whereas the influence of the cations was not significant, the conversion of glycerol decreased using CsOH, CH_3COOCs and CsNO_3 . The highest conversion was observed for CsOH, one of most powerful base in aqueous solution.

Alternatively, an acidic reaction route has been investigated, to avoid the drawback of separating the desired products from solid and dissolved catalyst components. The acid-catalyzed glycerol etherification was carried out in a tube reactor under reflux vacuum conditions at ca. 150-180 °C [7,8] using a super-acidic polymer resin as catalyst. The glycerol had only short contact time with the resin catalyst where the etherification proceeded in a liquid film running across the catalyst foil. The di-/polyglycerol mixture was accumulated at the bottom of the reactor construction. This reaction technology allowed maintaining high selectivity of diglycerol at nearly complete glycerol conversion.

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Oxidative Decarboxylation of Unsaturated Fatty Acids

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There is an increasing demand for fuels and chemicals based on renewable resources. Olefins and hydrocarbons obtained by decarboxylation of fatty acids are expected to have superior fuel properties and are interesting starting compounds for further chemical modification.

In relation to our quest for mild methods for catalytic decarboxylation of fatty acids and their derivatives, we would like to present results on the silver/copper mediated decarboxylation of unsaturated fatty acids with sodium persulfate to give internal olefins.

The products provide good starting materials for e.g. ethenolysis to linear alpha-olefins.

Since the availability of seed oils for biofuels production is limited, we are evaluating the potential of fast growing microalgae as a source for fatty acids.

Abstracts

Part 2: Posters

Being aware of global warming, one result of using fossil resources as raw materials for fuel and industrial applications, environmental considerations become more important and inevitable. Using plant oils as raw materials for the synthesis of polymers is more sustainable, environmentally-friendly, and can also provide economic solutions to the above mentioned problems.[1,2] Especially castor oil is an example of a renewable raw material showing a great number of possibilities to be used as a renewable feedstock for the chemical industry.[3]

Additionally, thiol-ene addition reactions, which are considered to qualify as click chemistry, for monomer synthesis as well as polymerization seem to be an efficient tool for the production of materials offering manifold possibilities to complete our goal.[4,5] Up to now, this efficient reaction was only marginally und unsystematically studied with plant oils.[6,7] Herein, we report the application of thiol-ene coupling reactions as a facile synthetic route to modify 10-undecenoic acid, a castor oil derived platform chemical,[3] in order to synthesize

various monomers. A variety of functional groups, including e.g. –hydroxy and –methyl ester groups, were thus introduced under solvent- and initiator-free conditions in high yields. The prepared monomers were subsequently polymerized yielding hyperbranched as well as linear polyesters in high yields. All materials were fully characterized by GPC, ¹H-NMR and DSC analysis, the results of which will be presented within this contribution.

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Clicking Renewable Resources: Thiol-ene Additions as a Versatile Tool for Terpene Modification

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The utilization of renewable resources for the synthesis of new platform chemicals has been accepted as a great challenge in order to contribute to a sustainable development [1,2]. Terpenes are found in many essential oils and represent a sustainable and versatile chemical feedstock [3]. α - and β -Pinene are the major components of wood turpentine and can be obtained from the resinous sap of pine trees by steam-distillation, whereas limonene can be obtained as a byproduct of the citrus industry. In contrast to many other terpenes, pinenes and limonenes are abundant and inexpensive natural compounds that are real building blocks for the synthesis of new important chemicals [3].

Known chemical transformations of these renewables include, for instance, isomerizations, epoxidations, or hydration reactions in order to obtain products for the fragrance industry. Thiol-ene addition reactions, on the other hand, were not studied in detail with these compounds, even if the first reports date back more than 100 years [4]. Today, thiol-ene addition reactions are considered as click reactions and are versatile tools for the preparation of value added chemical intermediates [5,6]. Here, we report on the addition of thiol compounds to β -pinene and (R)-limonene under solvent free conditions. High conversions and isolated yields of the desired compounds were achieved, confirming that the preparation of renewable monomers and polymers from this feedstock is possible in a sustainable fashion.

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Synthesis of plant oil derivatived polyols via ADMET polymerization

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The utilization of renewable feedstocks is an important issue for a sustainable development due to the depletion of our fossil resources. As important as the feedstocks is the efficiency of the chemical processes in order to avoid or minimize the impact in the environment. For this purpose the development and optimization of the catalytic systems is needed.^{1,2}

Plant oils are one of the most important renewable resources for the chemical industry due to the available amount, its quality and the versatility of their transformations. Moreover, their inherent double-bond functionality offers the possibility of several efficient catalytic transformations, as for instance olefin metathesis.³

Within this contribution we report the synthesis of plant oil derived polyols via metathesis reactions. First, different monomers have been synthesized from undecenoic acid and glycerol derivatives. In a second step, ADMET polymerization has been applied to obtain polyols with different architecture, functionality and molecular weights. These polyols will be tested in the synthesis of polyurethanes.

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P4

Transformation of unsaturated fatty compounds by ene-yne cross-metathesis

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The production of raw materials from natural renewable resources is a topic of current interest as petroleum chemical substitutes and for its contribution to sustainable development. Within this trend the use of unsaturated esters, arising from transesterification of vegetable oils, is attractive.[1] The selective cleavage by cross metathesis of this unsaturated fatty esters, catalyzed by ruthenium-alkylidene complexes, constitutes a potentially useful and powerful transformation. Among metathesis transformations, the ene-yne cross metathesis,[2] represents a novel route to the formation of a conjugated dienes (Figure 1).

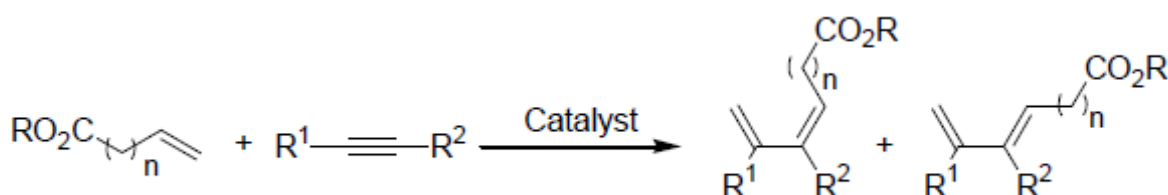


Fig. 1. Ene-yne cross metathesis of fatty unsaturated esters

These new conjugated dienes can be further transformed into added value chemicals by Diels Alder reactions or allylic substitution.

We will present our results concerning the cross metathesis of unsaturated esters with different functionalized alkynes in “one-pot” reactions[3] and their subsequent transformation by Diels-Alder and allylic substitution reactions.

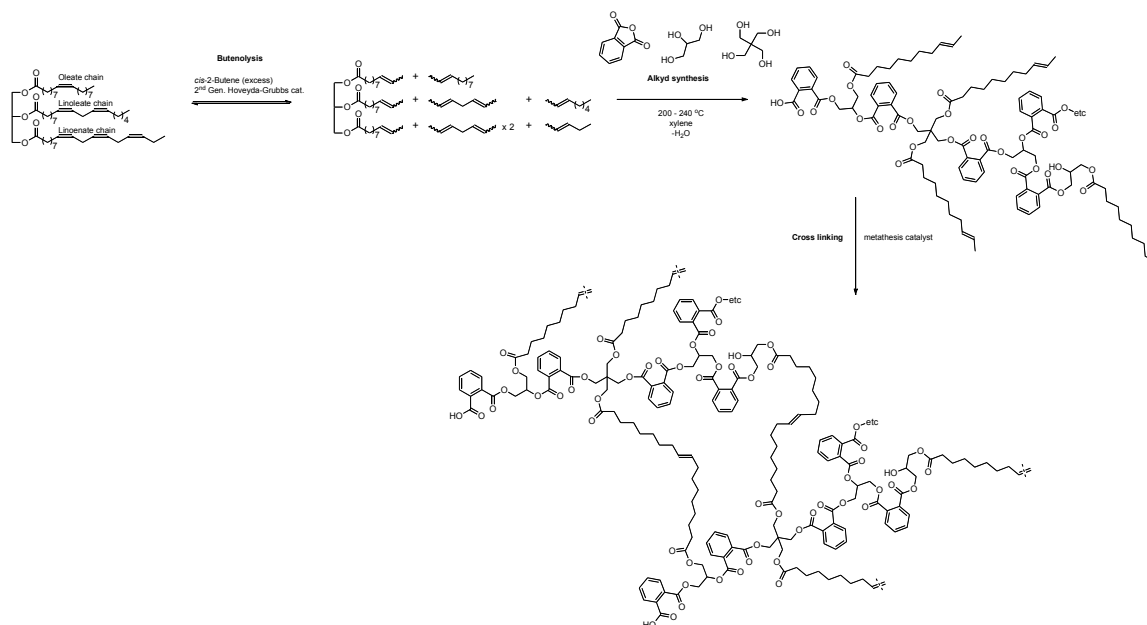
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Environmentally Friendly Surface Coatings from Renewable Fats and Oils.

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Fats and oils have long been used in the surface coating industry. However, problems with extended drying times, large amounts of metals to induce drying, high use of volatile organic solvents and inherent lack of durability leading yellowing and embitterment have reduced their popularity. Over the past 40 years water based acrylate paints have taken over and dominated the market. Now health hazards and environmental concerns regarding the use of acrylates are the subject of increasing legislative pressure. In addition the acrylates are derived from non-renewable feedstocks. This poster summarises the joint efforts of Monash University and the DuluxGroup to produce new improved surface coatings from vegetable oils in an environmentally acceptable manner.



Attention is being focussed on investigating microwave heating as a more efficient means of small scale resin synthesis. Cross-linking of these resins can then be screened under a range of conditions using various metathesis catalysts.

Ring Opening Metathesis Polymerization of Fatty Acid Derived Monomers

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Interest in the synthesis of bio-based polymers, especially derived from vegetable oils, has grown significantly due to rising costs and the environmental impact of petroleum based polymers [1]. Fatty acid derived monomers can be polymerized with various polymerization methods. For instance, ring opening metathesis polymerization (ROMP) employing well defined transition metal alkylidene catalysts was shown to be an efficient method to obtain polymers with controlled molecular weights, narrow polydispersities, and various side chain functionalities [2,3]. In the search for high performance polymer architectures, bicyclo[2.2.1]hept-2-ene (known by its trivial name norbornene) and its derivatives have recently been in the centre of interest due to interesting properties of the thereof derived polymers [4].

Herein, we report two synthetic approaches towards polynorbornenes functionalized with fatty acids varying from 6 to 22 carbons. The first approach involves the esterification of a hydroxy-functional norbornene monomer with fatty acids of different chain lengths and their subsequent living ROMP with “Grubbs” 3rd generation catalyst. In the second approach, ROMP has been used to produce well defined functional group containing polymer backbones. Therefore, a hydroxy-functional monomer was first polymerized to the desired molecular weight. This functional polynorbornene precursor polymer was then reacted with fatty acids methyl esters of different chain lengths in a grafting onto approach. All synthesized polymers were characterized by GPC and NMR. Furthermore, the effects of the fatty acid chain length on the polymerization process, and the thermal and mechanical properties of the resulting polymers have been extensively investigated.

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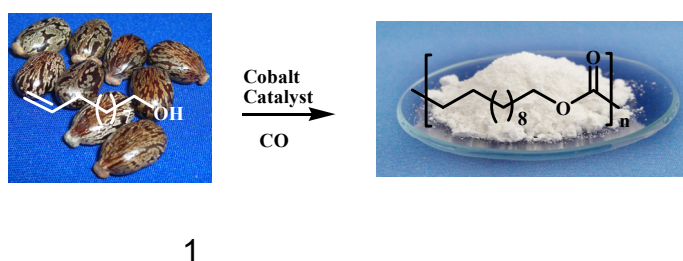
Thermoplastic Polyesters from Plant Oils by Carbonylation Chemistry

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Thermoplastic polyesters are currently prepared almost exclusively from fossil feedstocks. In view of an ever increasing demand for fossil fuels and their limited range a more efficient utilisation of the renewable substrate and the exploitation of other sources is an attractive long term challenge.¹

We report a carbonylation polymerisation route to prepare aliphatic polyester based on castor oil², a readily available plant seed oil.^{3,4} The major component of castor oil is ricinoleic acid, which is converted in two high conversion steps to the ω -unsaturated alcohol undec-10-en-1-ol 1.

Alkoxycarbonylation, resembling an AB step growth polymerisation, was utilised for the synthesis of poly(dodecyloate) 2 by exposing neat 1 to carbon monoxide pressure at elevated temperature in the presence of catalytic amounts of d^8 -metal catalysts. Higher molecular weight semi crystalline polymer with $M_n > 10^4 \text{ g mol}^{-1}$ was obtained. A control of polymer microstructure and thus thermal properties via the catalyst is addressed. In this entirely chemical polyester synthesis, not involving fermentation, the molecular structure of the plant oil feedstock is largely retained in the polyester product.



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Towards Sustainable Polymerization: Biodiesel as a Green Polymerization Solvent

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A number of polymer products have been traditionally made using a solution polymerization technique. However, with increased environmental awareness and thus, concerns over the volatile organic content (VOC) of various polymer processes, industry has been trying to find alternatives to traditional solvents.

In an effort to use cleaner technologies, biodiesel produced from canola oil was used as a polymerization solvent. Biodiesel or fatty acid methyl ester (FAME) is environmentally benign and has a low volatility. Because biodiesel is a high boiling solvent, its use can increase productivity by enabling polymerizations at elevated temperatures. This would result in faster reaction rates and thus, shorter reaction times. Solution polymerizations of four commercially important monomers (i.e., methyl methacrylate (MMA), styrene, butyl acrylate (BA) and vinyl acetate (VAc)) were studied at 60°C and 120°C using biodiesel as a solvent. Reactions were carried out at different solvent concentrations to verify the effect of the biodiesel solvent on the polymerizations. Chain transfer to solvent rate constants were obtained using the Mayo method. These estimated chain transfer to solvent rate constants were employed in a polymerization simulator to predict the polymerization rates and cumulative average molecular weights of the polymer product. Moreover, to study the effect of feedstock a series of homopolymerizations was carried out at different solvent concentrations for two other biodiesel feedstocks: soybean oil and 50%yellow grease - 50%canola oil. Results were compared to FAME produced from canola oil.

The use of FAME or biodiesel as a renewable and cost-effective polymerization solvent with good solubility, low viscosity and high boiling point fulfills the requirements of a solution polymerization solvent in different cases. Therefore, the “environmental friendliness” of FAME, coupled with its effectiveness as a polymerization medium, makes it an attractive alternative to traditional polymerization solvents.

Synthesis of 2-(methacryloyloxy)ethyl palmitate by transesterification of tripalmitin with HEMA

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The vital issue regarding the preservation of natural resources has refurbished the interest in developing novel materials from the use of *renewable* sources, whose ubiquitous character offers civilization valuable elements of sustainability [1]. Vegetable oils, predominantly formed by mixed triglycerides with fatty acid moieties, have become an emergent field of research due to their remarkable potential as starting materials for the production of original polymers. However, the rather low reactivity of the saturated or unsaturated aliphatic chains of fatty acids makes them ineffective monomers for direct polymerization. This drawback can be overcome by functionalizing the fatty acids with polymerizable moieties. The transesterification with monohydric alcohols (mostly methanol) yields fatty acid alkyl esters, which are promising substitutes for diesel fuel [2,3], but which do not acquire the monomer status because the transformation does not incorporate reactive functions.

The present communication reports the synthesis of a fatty acid-based *monomer* bearing acrylic moieties via the transesterification of tripalmitin with 2-hydroxyethyl methacrylate (HEMA). A systematic study was performed in order to optimize reaction conditions, yields and purity of the ensuing monomer. Results related to a preliminary investigation of its polymerization will also be reported.

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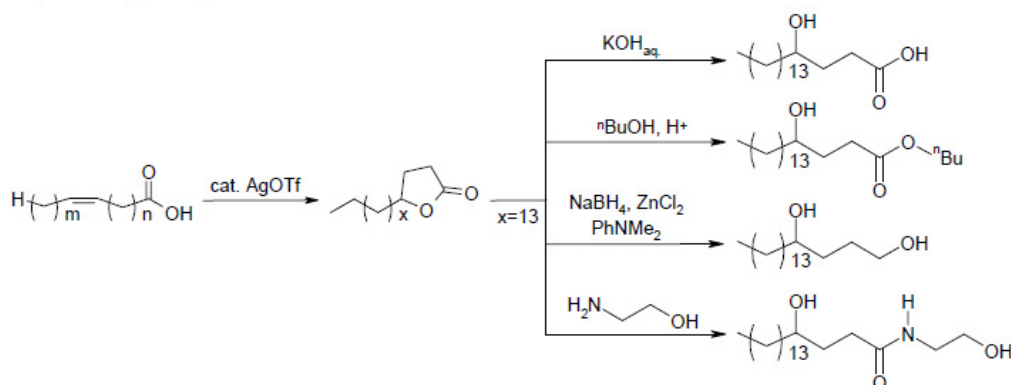
Catalytic Double Bond Isomerization as a New Way to Valuable Products from Fatty Acids

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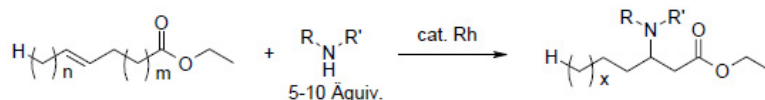
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Fatty acid derivatives provide a useful renewable source for a growing number of functionalized compounds and fine chemicals. Especially the naturally occurring unsaturated fatty acids hold a great potential for functionalization and derivatization.[1] Our goal was to realize a new type of transformation involving a catalytic double bond migration followed by a selective functionalization reaction. A silver(I)-based catalytic system was found to efficiently promote the double-bond isomerization of unsaturated fatty acids and to mediate the intramolecular addition of the carboxylate group to the isomerized double bond under selective formation of five-ring lactones.[2] These products can be further derivatized to materials bearing special properties, e. g. long-chain γ -hydroxycarboxylates, γ -alcohols or γ -amides.



Expanding this concept from free fatty acids to esters, we have developed a protocol for the direct conversion of unsaturated aliphatic esters with N-nucleophiles into β -amino esters. We herein want to introduce our new tandem reaction, which allows the one-step synthesis of β -amino esters *via* double-bond isomerization followed by conjugate addition of amines or amides. The products are valuable intermediates in organic synthesis since they represent direct precursors of β -lactam derivatives.



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Synthesis and Evaluation of Renewable Oil Based Cationic Lipids

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Gene therapy is a modern approach for treatment of diseases of inherited or acquired origin. For the success of gene therapy the delivery of nuclear material to the cells is essential and the most important step. Cationic lipids are important non viral gene delivery systems.¹ These cationic lipids form stable lipoplexes with DNA which are readily taken up by the cell by the phenomenon of endocytosis. Recently we have reported a series of novel gemini pyridinium amphiphiles having good surface properties, DNA binding capability and low cytotoxicity.² In continuation to our research aimed to develop novel non viral gene delivery agents. We, in the present work, report the synthesis of several gemini imidazolium lipids using renewable cardanol oil feed stock. The evaluation surface properties, DNA interaction studies and cytotoxicity of these cationic lipids shall also be presented.

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Soap Stock Separation process

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Soap stock is recovered from alkaline neutralization of the crude soybean oil. Soap stock consists of water, soap, neutral oil, Phosphatides and unsaponifiable matter. Its composition depends on seed quality, oil extraction and refining conditions. Soap stock is the least valuable byproduct from oil processing. This experiment is based on the recovery of Phosphatides, neutral oil, fatty acid, color pigment from soap stock through solvent extraction, precipitation and distillation.

KINETICS MODELING OF FATTY ACID ESTERIFICATION USING ION EXCHANGE RESIN CATALYST IN THE BIODIESEL PRODUCTION

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Fossil-fuels is being depleted to date. Therefore, a global movement toward the generation of renewable energy is in progress to meet energy needs. Among the various alternative energy resources, biodiesel has been receiving increasing attention due to its advantages. Conventionally, biodiesel is produced by transesterification of triglycerides by homogeneous alkaline catalysts. However, such process is not suitable for the feedstocks that contain high amount of free fatty acids (FFAs). FFAs will react with the alkaline catalysts, forming soap by-products and deactivating the catalyst. It accordingly causes problems of product separation and lower the biodiesel yield. To overcome this problem, a 2-steps process involving fatty acid esterification and subsequent alkaline-catalyzed transesterification have been applied.

Esterification by acid catalyzing is a common method of producing biodiesel from high FFA oil. Homogeneous acidic catalysts usually gives high conversion. However, it has drawbacks in terms of selectivity, equipment corrosion, and difficult separation of catalyst from the products. Hence, heterogeneous acid catalysts have been studied as substitutes since it is easy to recover and reuse, and compatible with environmental considerations. One of the solid catalysts is ion-exchange resin, which has good properties and high esterification efficiency. Considering the significance of this esterification step in the biodiesel production process, the kinetics modeling of the heterogeneous esterification of fatty acid over an acidic ion-exchange resin was investigated in this work. The experimental data of the esterification reaction of lactic acid with ethanol was used for validation.

Different kinetics models taking into account both the ideal and the non-ideal solution assumption have been developed to represent the kinetic behaviors of heterogeneous esterification. The models studied in this work were Eley-Rideal (non-ideal-solution assumption), Modified Langmuir-Hinshelwood (ideal and non-ideal-solution assumption), Langmuir-Hinshelwood-Hougen-Watson (ideal and non-ideal-solution assumption) and Quasi-Homogeneous (ideal and non-ideal-solution assumption) Models. For the non-ideal approach, the activity coefficients were obtained based on the UNIFAC model. It was found the Modified Langmuir-Hinshelwood Model taking into account the non-ideal-solution assumption gives the best representation for the kinetic behavior of the lactic acid esterification over acid ion-exchange catalyst. The proposed rate expression was:

$$-r_A = \frac{(2.14 \times 10^{12}) \exp\left(\frac{-8.84 \times 10^4}{RT}\right) \left[a_A a_B - (3.39 \times 10^{-2}) \exp\left(\frac{9.19 \times 10^3}{RT}\right) a_C a_D \right]}{\left[1 + (5.62 \times 10^6 \exp\left(\frac{-4.14 \times 10^4}{RT}\right)) a_D \right]^2}$$

A good agreement between the experimental data and the model has been obtained.

PHENOLIC COMPOUND PRODUCTION FROM LIQUID SMOKE AND ITS POTENCY TO INHIBIT LINOLEIC ACID OXIDATION

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Liquid smoke, which has antioxidant activity, needs to be distilled for reducing benzo[α]pyren and tar. Modification of the liquid smoke distillation equipment by three stage condenser have been conducted to prevent carry over of benzo[α]pyren and tar during the process. Modification of the equipment will influence the characteristic of liquid smoke distillate produced at each condenser. Hence, these research objectives are investigating the rate of phenolic compound production during the process, and examining its potency to inhibit the linoleic acid oxidation. Distillation was conducted by separating the distillate per 10 minute during the process. The distillate was produced from four stage, i.e. pre-condensation stage, 1st stage, 2nd stage, and 3rd stage. The results showed that each condenser produced phenolic compound on different rate. The 1st stage condenser produced phenolic compound with high rate, but the most potential as antioxidant was showed by pre-condensation fraction. The distillates exhibited antioxidant activity tested under linoleic acid; however, the activity was less than BHA on the same concentration.

The dry fractionation of some adulterated vegetable oils

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The paper analyses the results of capitalization (recovery) studies by dry fractionation of some saponifiable vegetable fatty systems (saturated and unsaturated) (mono and/or polyunsaturated) from pumpkin oil processed by cold compressing (*Cucurbita Pepo*, styriaca variety) adulterated with 5 – 10 % sunflower oil (*Helianthus Annus*) with modified the structure of a functional aliment with monitored destination, but precious material wearer of fatty fractions [C12:0, C14:0, C14:1, C16:0, C16:1]. The individual recovery of some superior mono and polyunsaturated acids [C18:1, C18:2, C18:3] with physiological recognized importance, recorded in literature a continuous interest. The main physical - chemical and chemical parameters of oils, individually or in combination [aspect, density, cinematic and dynamic viscosity, refraction index, iodine index (Wijs), acidity, esterification, saponification and chromatography distribution], were determined as work premises, to optimize the monitored efficiency of the superior mono and/or polyunsaturated acid dictated previously.

Fractioned crystallization also dictated the rigorous nominalization of unitary operations in a coherent diagram from which can be collected a defined succession of fatty fluid (liquids) and/or solid fractions, depending on work parameters (temperature gradients, filtration speeds, thermostated centrifugation, etc.). After repeated separations were certificated notable analytical purities of isolated structures. It was conferred attention to environment and/or agropedoclimatic characteristics of mentioned vegetable oils provenience geographic areas by connecting of the two trophic chain major bangles soil (environment) – herb. There were determined the evolution and the weight transfer of heavy metallic cations [Mn, Zn, Cu, Co, Ni, Cr, Pb, Cd] in the track soil – herb – dry fraction. It was used the biologic material afforded by two private agroalimentary farms with integrated vegetable processing from the South – West of Romania (counties Timiș and Caraș – Severin), first one situated in a geographic area without excessive geogenic pollution with heavy metals mentioned cations, with clay soils, such as stagnic albis luviosoil and the second one placed in geographic area more geogenic and antropic polluted with heavy metals cations, situated 3 – 5 km far from a power-station, respectively underground mining.

The balance of heavy metals cations in the analyzed system by their presence under the international accepted limits justifies the researches and encourages their extending in the future.

The dry fractionation of fats from piggish fleshing wastage

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The paper presents the result of recovery researches by dry fractionation of piggish fleshing wastage obtained as waste in pigg buff processing (tanning). Valuable material wearers of fatty fractions [C12:0, C14:0, C14:1, C16:0, C16:1, C18:0, C18:1, C18:2, C18:3, C20:0, C22:0, C24:0], the piggish fleshing wastage can negatively affect, by non-processing, ecological and financial the costs of tanned leather. After raw and fine hot filtration, the individually piggsh fat (saponifiable and unsaponifiable) is crystallized fractionated in the next operating protocol, which permitted the establishing of relationships between physical – chemical major parameters and work parameters. Liquid (fluids) and solid fractions, adequate thermostated centrifugal separated were physical – chemical evaluated (aspect, density, melting range, refraction index, static and dynamic viscosity, acidity index, esterification, iodine, saponification and gas-chromatography distribution) to evaluate and optimize the efficiency of controlled isolation of a superior acid dictated previously. The most reach fatty fraction was multiple fractioned crystallized with gradients, respectively at lower temperature ranges. After repeated separations were registered analytical purities.

It was conferred an important attention to environment and/or agropedoclimatic characteristics of processed piggish fleshing wastage provenience geographic areas by following the trophic chain soil – herb (forage) – animal (pigs). There were determined the evolution and the weight transfer of heavy metallic cations [Mn, Zn, Cu, Co, Ni, Cr, Pb, Cd] in these bangles. The Chromium cation, present mainly in technological processing phase (tanning) got the most attention. It was used the biologic material afforded by two private pigg farms (agro-industrial associations) with integrated processing (growing, sacrifice, classic and unconventional technological processing) from the South – West of Romania (counties Timiș and Caraș – Severin), first one situated in a geographic area without geogenic pollution with heavy metals and the second area more geogenic and antropic polluted with heavy metals cations, situated near a power-station, respectively underground mining. The balance of heavy metals cations in the analyzed system by their presence under the international accepted limits justifies the researches and encourages their extending in the future.

Iron(II)- and Manganese(II)-Induced Oxidation of Limonene by Dioxygen

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Monoterpenes are widely used in flavor and fragrance industry. Among these compounds R-(+)-limonene (D-limonene) is the most abundant, low-priced, naturally occurring product, which is suitable feedstock for production of important compounds.

We have found that labile iron(II), iron(III), and manganese(II) complexes $\{[\text{FeII}(\text{bpy})_2]^{2+}\text{solv}$, $[\text{FeIII}(\text{bpy})_2]^{3+}\text{solv}$, and $[\text{MnII}(\text{bpy})_2]^{2+}\text{MeCN}\}$ in acetonitrile activate dioxygen for the oxidation of limonene to produce mainly carvone, carveol, limonene oxide, and perillaldehyde.

Iron(III) complex is reduced by the substrate to respective iron(II) one, which activates dioxygen. Probably the catalyst interacts with limonene prior to the oxidation process. Perillaldehyde is likely formed directly from oxidation of methyl group (not via alcohol). However, the aldehyde is also reduced to perillyl alcohol by the reduced form of the catalyst.

In the case of manganese(II) used as a catalyst the reaction efficiencies after 24 h reaction time are approximately 5-times higher than those obtained for analogous iron(II) complexes. However, the 5 h long induction period is observed for the common conditions of the reaction. The simultaneous presence of the catalyst, dioxygen and the substrate is necessary for the active species to be formed. When *t*-BuOOH is present in the reaction mixture, the induction period does not appear. In contrast, the replacement of *t*-BuOOH by HOOH completely inhibits the reaction. This is, to our best knowledge, the first case when manganese(II) complex activates dioxygen for oxygenation process. We have proposed a putative mechanism, in which a manganese(IV)-hydroperoxo adduct with incorporated substrate is formed during the induction period and it becomes an active catalyst for limonene oxidation.

Immobilization of bis(2,2' bipyridine) -manganese(II) and -iron(II) complexes using bentonite as a support has led to the loss of their activity but higher selectivity of carvone was observed. Moreover, heterogenization of the homogenous catalyst eliminated the necessity of using solvent in the process. In addition, complexes included in bentonite can be reused at least for three times without a detectable catalyst leaching and a significant loss of their activity.

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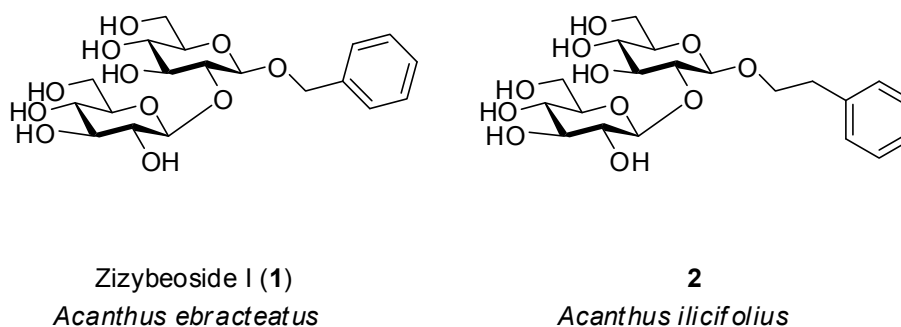
Syntheses of natural products from semi-mangrove plants

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Nature is commonly accepted to be one of the most important resource for new active agents and medicinal products. With an increased understanding of biological processes, research including the search for new target structures has focused on oligosaccharides and glycoconjugates.^[1] Their high functionalisation and complexity have challenged and will challenge synthetic chemists. One simple example is the successful isolation and structure elucidation of sophorose containing glucosides **1+2** from semi-mangrove plants of the genus *Acanthus*, which are used as an anti-inflammatory and antihepatitis agent in traditional Chinese medicine.^[2-4]

Figure 1: Sophorose containing glucosides isolated from *Acanthus* sp.



The current work focuses on the synthesis of natural products Zizybeoside I (**1**) from *A. ebracteatus* and phenylethyl-O- α -D-glucopyranosyl-(1,2)- α -D-glucopyranoside (**2**) from *A. ilicifolius*. To avoid a long synthesis of the expensive sophorose glycon in this work the synthesis starts from fermented sophorose-lipids.

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Used frying oils as a source for supercritical FAME preparation

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Triglycerides of vegetable oils and fats are becoming increasingly important as alternative fuels for diesel engines due to the diminishing petroleum reserves. However, their high viscosities and low volatilities do not permit their direct use or in oil/petrol blends in any engine diesel engine type. Nowadays the main process development to overcome this drawback is the methanolysis transesterification reaction to produce a mixture of FAME (Fatty Acid Methyl Esters) called biodiesel (BDF) which is a biodegradable, non-toxic diesel fuel substitute that can be used in unmodified diesel engines. It has a significant added value compared to petro-diesel because of its higher lubricity, which extends engine life and reduces maintenance costs and environmental benefits as well as contribution to fuel economy.

Although the alkaline catalyst transesterification method with methanol has the benefit of using moderate reaction conditions, several aqueous washings are needed to remove the catalyst after the reaction. Moreover, the oils and fats used, especially the waste ones, may contain water and free fatty acids. The presence of water reduces the catalytic activity, while free fatty acids react with the catalyst to produce saponified products, risking a reduction in the yield of FAME. Therefore, manufacturing biodiesel from waste cooking oils by the alkaline catalyst method is not necessarily easy.

Moreover biodiesel produced by transesterification with alcohols of vegetable oils presents glycerol as the major side-product. Due to the growing production rate of biodiesel, the availability of glycerol has also been rapidly increasing in recent years. Because the high costs due to its purification, glycerol from biodiesel is not economically suitable.

Non-catalytic biodiesel production methods with supercritical fluids have been, therefore, developed in order to resolve these various problems.

The aim of our project is the production of biodiesel using waste frying vegetable oils and different supercritical fluids as methanol, ethanol or carbon dioxide in order to reduce or eliminate the glycerol production.

All experiments were carried out batchwise in a 100 ml supercritical reactor. The sampling system was designed to monitor the reaction at various times. A GC-FID system was used to measure the fatty acid methyl esters composition of the produced biodiesel.

Transesterification of triglycerides applying zeolitic heterogeneous catalysts

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The transesterification of triglycerides is a well-established process due to its relevance in the production of fatty acid methyl esters (biodiesel). Commonly, homogeneous catalysts, e. g. sodium hydroxide and sodium methanolate, are used. The main drawback is that these catalysts necessitate several washing and purification steps. An appropriate solid catalyst would, therefore, reduce the product separation and purification steps. Thus, basic zeolites with faujasite structure and $\text{Si/Al} = 1$ (low silica X zeolites, LSX) have been tested in the transesterification of glycerol trioctanoate with methanol and ethanol, respectively, in a batch set up at ambient pressure and boiling temperature of the corresponding alcohol as well as in an autoclave at elevated temperatures between 100 and 150 °C and 50 bar pressure.

Among these catalysts, the potassium exchanged low silica X zeolite (K-LSX) revealed the highest catalytic activity resulting in the total conversion of glycerol trioctanoate with methanol to octanoic acid methyl ester and glycerol after 1 h reaction time, while in case of ethanol 2 h reaction time were required. Total conversion of glycerol trioctanoate in the autoclave at 100 °C was accomplished after 46 min. Furthermore, catalyst extrudates based on K-LSX were applied as catalysts in the transesterification of glycerol trioctanoate with methanol in a semi-continuously operated trickle bed reactor and exhibited a constant high performance resulting in methyl ester yields over 70 mol% and glycerol yields up to 25 mol%. Beside application of these zeolites as industrial catalysts for biodiesel production, use as catalyst in the production of fine chemicals could benefit to new ecological benign and sustainable processes.

**Novel Cationic Asymmetrical Gemini Surfactants
Based on Tartaric Acid**

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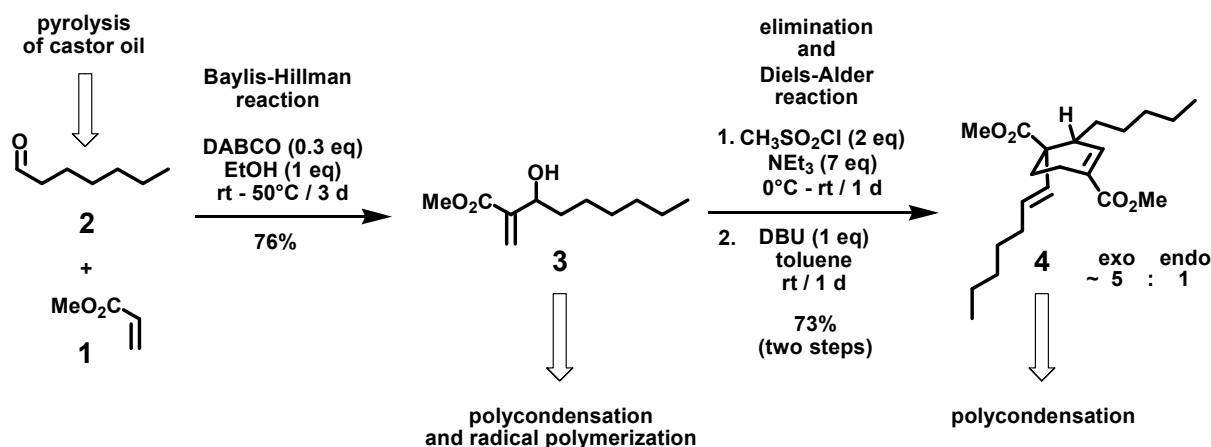
The conversion of fatty acid chlorides with (L)-tartaric acid resulted in the easy formation of acylated tartaric acid anhydrides¹. We have shown that this class of anhydrides provides convenient entry into a variety of gemini surfactants. They readily react with natural or synthetic nucleophiles like alcohols, carbohydrates, amines and amino acids². A series of compounds were synthesized and characterized, their surface and antibacterial properties have been measured.

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New castor oil derived monomers via Baylis Hillman reactions

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The Baylis-Hillman reaction is an organocatalytic and environmentally friendly reaction, in which an activated alkene is coupled with an aldehyde.^[1,2] The sequence of Baylis-Hillman reaction and elimination of the hydroxy group leads to 1,3-dienes, which undergo diastereoselective Diels-Alder reactions (Scheme 1).^[3]



Scheme 1: Sequence of Baylis-Hillman-reaction, elimination and cycloaddition.

The reaction of methyl acrylate **1** with heptaldehyde **2** thus leads to the α,β -unsaturated hydroxycarboxylic acid derivative **3** in a good yield. **3** is a potential monomer for polycondensation reactions and radical polymerizations. The following one pot reaction sequence of mesylation, elimination and Diels-Alder reaction yields cyclohexene derivative **4** with a satisfying diastereoselectivity and good yield. Also **4** is an interesting candidate for polycondensations.

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Adsorbed oils as ABE fermentation substrate

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Bleaching earth is a mineral adsorber which is applied in tremendous amounts for purification of fats and oils. The world market of this adsorber material is estimated to approximately 625,000 tons per year. The bleaching earth is used to remove undesired by-products from the raw material which are concomitantly released from the plant material during the applied disintegration procedures. Such by-products can be summarized as chlorophyll, carotinoides, trace metals, soaps, phospholipids, and corresponding oxidation products. However, after separation of the bleached oil from the bleaching earth the adsorber still contains a great amount of oil, which ranges usually from 20-40 % of the minerals' dry mass. Its utilization as additive for animal feeds, biogas plants or the cement industry was established as well as further extraction to obtain the remaining oil fraction, respectively.

Alternatively, the loaded bleaching earth can be utilized as a fermentation substrate to obtain valuable commodities as such as acetone, butanol or ethanol. Thus, a higher added value of the subsequent adsorber usage is established.

Our research is focused on the recycling of oil loaded bleaching earth, which was previously used within palm oil purification processes. We are interested in the anaerobic fermentation of the remaining palm oil fraction to the corresponding ABE compounds and fatty acids, whereas the latter shall be serve as building blocks for the synthesis of novel polymers. The production process is based on the hydrolysis of the oil to glycerol and fatty acids with subsequent or simultaneous biotransformation of the glycerol to ethanol, butanol and acetone. For this, three approaches will be presented: a) fermentation of the adsorbed oil by lipolytic Clostridia strains, without further treatment of the adsorber, b) pre-treatment of the adsorber with lipases prior to fermentation of the supernatant, and 3) co-fermentation of Clostridia sp. with lipolytic yeast.

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Chemical structure and thermal properties of polyesters based on renewable resources

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The use of biomass based monomers in polymer chemistry is a significant driving force for the development of environmentally friendly technologies. In this area particularly interesting materials are polyesters for coating applications. Various types of polyesters based on renewable resources have been synthesized so far. Examples are polycondensation products of 1,3-propanediol[1] glycerol[2] or succinic acid[3]. Among a wide variety of monomers with natural origin 1,4;3,6-dianhydro-D-glucitol (isosorbide, IS) is a promising substrate for the synthesis of high T_g furnishing biobased polyesters[4]. In the light of the reports concerning biomass based polymers, the scope of our research was the synthesis and molecular characterization of unsaturated polyesters derived from isosorbide, maleic anhydride and succinic acid. The investigated polyesters were obtained via solvent-free bulk polycondensation catalyzed by titanium(IV) n-butoxide. 2D NMR, MALDI-Tof-MS and FT-IR spectroscopy as well as TGA and DSC techniques were used for examination of the structure-properties relationship of the obtained products. Since the thermal properties of the hydroxyl functional polyesters were appropriate for coating applications, the polymers were successfully cross-linked with 2-hydroxyethyl methacrylate, by radical copolymerization. The cross-linking process was studied using FT-IR spectroscopy and by measurements of the soluble part of the cured coatings.

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Continuous deoxygenation of triglycerides on solid catalysts

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In times of declining oil reserves and rising fuel prices research focuses on new processes to produce chemicals and fuels from renewable resources (e.g. triglycerides). Biofuels are an alternative, with biodiesel (fatty acid methyl esters) being used most. Besides its ecological advantages, biodiesel has some drawbacks such as limited durability, corrosion and formation of deposits in car engines, and a lower specific energy content. This is due to the residual oxygen, and removal of oxygen could minimize the above-mentioned disadvantages and allow upgrading of biodiesel. One possible route for deoxygenation of triglycerides is the conversion to alkanes with hydrogen on noble metal catalysts [1]. However, an additional hydrogen supply reduces economical attractiveness of the process. Experiments with autoclaves at LIKAT proved that a partial deoxygenation of triglycerides in the presence of basic oxides is possible. In the presented work, the continuous deoxygenation of sunflower oil in the presence of basic and acidic catalysts was investigated.

The catalysts used are basic and acidic oxides and basic carbonates. By pressing, crushing and sieving a particle size fraction from 400 to 500 μm was obtained, which was tested in a glass tube reactor together with SiO_2 as inert diluent material. The catalyst screening was carried out with nitrogen in feed at 400 $^\circ\text{C}$, a GHSV of 1200 h^{-1} and a test time of 5 hours. In further tests, the influence of temperature, contact time and the time of operation were investigated.

By means of GC-MS analysis mainly hexacosadien, decanoic acid, C17- and C18-hydrocarbons and other by-products were identified. The formation of hexacosadien, decanoic acid and C18-hydrocarbons runs via a radical mechanism [2]. The C17-hydrocarbons were formed per direct deoxygenation. The best results were obtained for K_2CO_3 and Cs_2CO_3 . Applying these catalysts, GC-MS and NMR analyses proved the absence of organic acids and oxygenated compounds in the liquid products. It was found during the study of temperature dependence that the radical mechanism is being suppressed with increasing temperature. At the same time, an increase in the yield of C17-hydrocarbons was observed. A long-term experiment over 24 hours revealed that for catalyst K_2CO_3 no change in product distribution with time and particularly no formation of oxygen-containing molecules occurred.

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Enzymatic synthesis of low molecular weight polyols from methylesters of ricinoleic acid

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In this work the catalytic efficiency of immobilized *Candida antarctica* lipase B (Novozym 435) for the transesterification reaction of methylesters of hydroxyfunctional fatty acids and low molecular weight di- and polyols was studied. The starting raw materials for the preparation of model samples were methylesters of ricinoleic acid and growing centers of 1,3-propanediol, trimethylolpropane and sorbitol. The reaction was catalyzed with 5 and 10 wt. % of the enzyme and carried out at 65°C in bulk and pressure reduced to 250 mbar in order to remove methanol as a side condensation product. The reaction was studied by molecular weight distribution development within 12 h period using gel permeation chromatography. The results showed that Novozyme 435 preferably catalyses condensation of primary hydroxyl groups of low molecular weight di- and polyols while reaction of secondary hydroxyl groups of methylesters of ricinoleic acid is suppressed. The selective catalytic efficiency of Novozyme 435 allowed the synthesis of star branched low molecular weight polyols terminated with secondary hydroxyl groups. This is not possible using conventional condensation catalysts and high reaction temperatures over 200°C leading to production of high molecular weight polyester polyols.

Branched renewable polymers via metathesis and thiol-ene additions

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Highly branched macromolecules, from monodisperse dendrimers to less defined hyperbranched polymers, find multiple applications in different areas of polymer chemistry [1]. Due to the high number of chain ends present within these macromolecules, their properties are highly influenced by the chain-end functionalities. Therefore, hydrophobic branched polymers can, for instance, be rendered water-soluble by introduction of suitable hydrophilic groups at the chain-ends. Polymers with such properties could be able to encapsulate hydrophobic drugs while maintaining their water solubility, being thus potentially useful as drug delivery vehicles. However, this application field requires not only efficient delivery systems, but also ones being biodegradable and biocompatible. In this way, plant oil derived platform chemicals are useful building blocks for the synthesis of branched polymers presenting the promise of biodegradability and biocompatibility. The objective of this work is the synthesis of plant oil based branched macromolecules. For this purpose, olefin metathesis and thiol-ene click chemistry are useful and versatile chemical transformations. Olefin metathesis has developed into one of the most powerful tools for the synthetic chemist [2] and thiol-ene additions, which are undergoing an exciting revival, offer a straightforward way to functionalize alkenes [3]. Therefore, unsaturated fatty acid derivatives are perfect starting materials for such conversions. In this work, two different approaches to branched macromolecules are presented. First, the step-wise synthesis of a fully renewable dendrimer is described by alternating thiol-ene and condensation chemistry. Second, the synthesis of a first generation dendrimer is attempted taking advantage of the selectivity of cross-metathesis between acrylates and terminal olefins.

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Hydrocarbon based raw materials from free fatty acids, lipids and soaps

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Soaps, lipids as well as lipid related compounds such as free fatty acids (FFA) can be converted into hydrocarbons. FFA and soaps are process byproducts of edible oils or plant oils from alkaline transesterification in biodiesel production.

The process is conducted as follows: Substrates are continuously fed into the reactor. Decarboxylation takes place in the presence of sodium at $T = 400\text{ }^{\circ}\text{C}$. Hydrocarbons formed are condensed outside the reactor. By rectification of the raw material 70% hydrocarbon based diesel as well as 20% gasoline and 10% bottom product are collected.

As a result GC-patterns of the products show the homologous series of alkanes and alkenes. The range of hydrocarbons is of interest both for fuels as well as renewable raw materials for anionic detergents. The parameters of the diesel fraction are in accordance with DIN 590. The cold flow plugging point (-18°C) is significantly higher in comparison to biodiesel (app. -2°C) from animal fat. Organic wastes to fuels and renewable raw materials for the chemical industry are of ecological and economical interest.

NEW LINSEED OIL-BASED UV-CURABLE MATERIALS

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Environmental concerns are increasingly present in our society. Industry must adapt to this evolution and find satisfactory solutions to solve the decrease of fossil raw materials while protecting the environment. The elaboration of “ecological” materials using a clean chemistry, i.e. without of volatile organic compound (VOC) emission, and allowing the valorisation of renewable raw materials is of increasing interest. Nowadays, vegetable oils are one of the most important classes of renewable sources. They can be obtained from common plants, such as sunflower, cotton, linseed...

Linseed oil belongs to the family of drying oils. Indeed, once deposited in thin layer, this oil can dry at room temperature according to an oxidative process consisting in reaction of the fatty double bonds with the atmospheric dioxygen. Unfortunately, this drying process is very long (several days). In order to accelerate this reaction, a process of thermal polymerization called stand reaction has been developed. It consists in heating the oil at high temperature ($> 270^{\circ}\text{C}$) in the absence of dioxygen. These "cooked" oils are known as stand oils. The drying of stand oil is then much faster but is again too long (several hours). Another way to “dry” is to use a photochemical process of polymerization. However, since linseed oil triglycerides don't bear any UV reactive groups, a chemical modification of these molecules is necessary to introduce photopolymerizable functions.

Thus, new materials mainly based on linseed oil were performed by means of an easy and ecological synthesis process in three stages: a thermal or stand stage, a chemical modification stage, and at last a photopolymerization stage. According to the properties of the ultimate materials, this new process could be interesting for the elaboration of flexible coatings.

NEW BIOSOURCED POLYAMIDE UV-POWDER COATING

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Powder coatings have been developed since a few years because of their several advantages: easiness of implementation, no material loss, no emission of volatile organic compound (VOC). Moreover, UV powder coatings are of great interest for heat sensitive substrates. Until now, these ones are essentially constituted of (meth)acrylic or unsaturated polyester resins. Polyamide-based UV powder coatings are therefore original in this application field.

In a general way, polyamides are semi-crystalline polymers with high melting points (around 200°C). In order to allow their application on heat sensitive substrates, low melting point copolyamides were synthesized. Nonetheless, it is well known that mechanical properties of the ultimate products are strongly dependent on the polyamide crystallinity. Thus, the crystallinity loss induced by the decrease in T_f was compensated for an additional crosslinking step under UV radiation. In this aim, polyamide chain ends were functionalized by allylic double bonds.

To prevent the decrease of fossil raw materials while protecting the environment, copolyamides were synthesized from biosourced monomers which are derivatives of vegetable oils such as castor oil. Thus, a 6/11/12 α,ω -unsaturated copolyamide was synthesized according to a process in molten state. The properties of the obtained UV-cured coating were then characterized.

Evaluation of Nigerian plant oils for polymer chemistry

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Preliminary studies on *Plukenetia conophora* (PKCO), *Jatropha curcas* (JTCO) and *Telfaira occidentalis* (TOO) oils to reveal their suitability in producing new renewable polymers via acyclic triene metathesis (ATMET) will be presented.[1] Seeds of the three mentioned species were collected in Nigeria, crunched and extracted in order to evaluate these locally growing plants as potential renewable raw materials for the African chemical industry. PKCO had an oil yield of 45% (~ 70% linolenic acid, 17.0% linoleic acid, 11.7% oleic acid and 0.8% stearic acid) while JTCO and TOO gave 32% and 40% oil yields, respectively. The composition of JTCO was (~ 41.2% linoleic acid, 31.4 % oleic acid, 6.8.% stearic and 19.5% palmitic acid) and the composition of TOO was (~ 37.9% oleic acid, 12.3% linoleic acid, 14.1% stearic acid, 24.1% palmitic acid and 11,5% myristic acid). Thus, these three oils have different levels of unsaturation allowing to obtain different molecular weights and degrees of functionalization during ATMET polymerizations with functional group containing chainstoppers. The investigation of the olefin metathesis polymerizations of these oils, the characterization of the thus obtained branched polymers and their use as resins are in progress.

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How 'Green' Is Your Chemistry?

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So, you believe your chemistry is green, only because of using ionic liquids or renewable feedstocks etc.? Of course, at least the latter is a good beginning, but there are also catalysts, auxiliary materials, coupled and by-products etc.. An overall mass balance helps to identify relevant weak points for optimization purposes and to enable a comparison to alternative procedures. Maybe (hopefully) you can (then) prove the advantage of your approach.

Selfmetathesis of ethyloleat – A process engineering approach

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The metathesis reaction of unsaturated fatty acid derivatives [1,2,3,4] is a promising approach leading to long-chained bifunctional compounds that can be used as monomers for polymer synthesis. However, the metathesis reaction is typically associated with a yield limitation caused by the reaction equilibrium. In the investigated metathesis reaction of ethyloleat, the equilibrium composition of the reaction mixture is 25 mol-% based on the target molecule octadec-9-ene-1,18-dicarboxylic acid ethyl ester.

For the future industrial scale application, the purification of the yielded reaction mixtures is a crucial step. Furthermore, removing the low-boiling side-product 9-octadecene should shift the position of the equilibrium towards the product side. A yield of 50 mol% is possible theoretically under ideal conditions, and if the side-product could be removed completely. Our aim was therefore to investigate whether the combination of reaction and separation in a reactive metathesis reaction is able to shift the equilibrium in the desired direction leading to an increase in the yield. We consequently simulated and evaluated the possibility of a reactive distillation process.

Short-path distillation is the method of choice for the separation of high-boiling and thermal instable compounds. Using this technique, it should be possible to remove the low-boiling side-product under gentle conditions without or at most with a barely increased deactivation of the used catalyst.

Therefore, the starting point of this work was to investigate the feasibility of the metathesis reaction under the required working conditions. Afterwards, a modified short-path apparatus was used to investigate the metathesis reaction under the conditions needed for the distillation process. Based on these experiments the requirements for the purification of metathesis product mixtures were determined and verified in initial basic experiments. As a result of our work, we have been able to prove that although the separating capacity of the apparatus we used is not high enough to significantly increase the yield, that the reactive metathesis might still be an interesting approach to improve the performance of the reaction. Based on initial experimental results and process simulation an advanced apparatus consisting of several short-path evaporators and a rectification column to purify and recover the unconverted reactant was designed, and could lead to further improvements of the metathesis reaction.

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The Development of Palm Methyl Ester Sulfonic Acid (MESA) To Increase Oil Well Recovery

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Surfactant plays important role in Enhanced Oil Recovery (EOR) in reducing interfacial tension (IFT) between brine and oil up to 10^{-4} - 10^{-6} dyne/cm. Surfactant structure allows oil and water mixed, so oil which trapped between brine can be produced from well and increase the oil well productivity. Palm Methyl Ester Sulfonic Acid (MESA) is produced from the reaction between palm olein methyl ester and SO_3 gas as reactant in Single Tube Falling Film Reactor (STFR). Methyl Ester Sulfonic Acid (MESA) is an intermediate product of Surfactant Methyl Ester Sulfonate (MES) which have many various application in personal care, toiletries products, and for EOR. Palm oil as the largest vegetable oil produced in world play an important role in human life as a raw material of oleochemical. Palm olein are renewable resources, environmentally friendly, and rich of fatty acid of C16 and C18 which has good detergency. This study was done in three stages which were analysis of palm olein, production and analysis of palm olein methyl ester, and sulfonation process of palm olein methyl ester. MESA is produced by using SO_3 gas in STFR at temperatures of 70, 90, and 110°C and sulfonation time of 30, 60, and 90 minutes. In the interval 30-90 minutes long sulphonated process, the active matter and the acid value of MESA increased linearly with increasing of sulfonation time. In the meantime, IFT between brine and oil decreases with increasing of sulfonation time. MESA can reduce IFT from 30 dyne/cm to 2.99 dyne/cm.

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