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

2nd Workshop on Fats and Oils as Renewable Feedstock for the Chemical Industry

Program
Abstracts
List of Participants

22. - 24. March 2009
Emden, Germany

in Cooperation with:
University of Applied Sciences OOW
German Society for Fat Science (DGF)
Agency of Renewable Resources (FNR)

Deutsche Gesellschaft für Fettwissenschaft e.V.

Scientific and Organizing Committee

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

Michael A. R. Meier, University of Applied Sciences OOW

Acknowledgement

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Content

Program

Lectures and Posters

Sunday, 22. March 2009

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

15:30
Welcome and Opening

Jürgen O. Metzger, abiosus

Uwe Bornscheuer, President of German Society for Fat Science

Manfred Weisensee, Vicepresident of University of Applied Sciences OOW

Norbert Holst, Agency for Renewable Resources (FNR)
Use of renewable raw materials in industry and funding of research and development in this field

16:00 – 18:00
1. Session: Joel Barrault, Chair

16:00 **Vegetable oils as raw materials for industrial applications**
L1 Karlheinz Hill, Cognis, Germany

16:30 **Carbonylation as a route to chemicals from biomass**
L2 David Cole-Hamilton, Cristina Jimenez-Rodriguez, W. Roy Jackson, Yulei Zhu, University of St. Andrews, School of Chemistry, St Andrews, UK

17:00 **Metathesis with oleochemicals: a sustainable match to obtain monomers and polymers from renewable resources**
L3 Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

17:30 **Biocatalysis in the modification of fats and oils for oleochemistry**
L4 Uwe Bornscheuer, Institute of Biochemistry, Greifswald University, Greifswald, Germany

18.00 - 20.00
Poster session and opening mixer
Posters will be displayed until the end of the workshop.

Monday, 23. March 2009

9:00 – 10:30
First Morning Session: George John, Chair

09:00 **Catalytic functionalisation of fatty compounds**
L5 Jessica Pérez Gomes, and Arno Behr, University of Dortmund, Germany

09:30 **Oxidation of tensidic alcohols to their corresponding carboxylic acids via Au- and AuPt-catalysts**
L6 Ulf Prüße, Katharina Heidkamp, Nadine Decker, Kerstin Martens, Klaus-Dieter Vorlop, Oliver Franke, and Achim Stankowiak, Johann Heinrich von Thünen-Institut (vTI), Braunschweig, Germany

09:50 **Plant oils as precursors of N-containing compounds via alkene metathesis**
L7 Christian Bruneau, Pierre H. Dixneuf, Raluca Malacea, Cédric Fischmeister, Xiaowei Miao, Institut Sciences Chimiques de Rennes, University of Rennes 1, Rennes, France

10:10 **Phytomining of plant enzymes for biotechnological use of fats and oils**
L8 Andreas Müller, and Guido Jach, Phytowelt GreenTechnologies GmbH, Nettetal, Germany

10:30 – 11:00 **Coffee break**

11:00 -12:20
Second morning session: Zoran Petrovic, Chair

11:00 **Rational design of solid catalysts for selective glycerol activations**
L9 François Jerome, and Joel Barrault, CNRS/LACCO, Poitiers, France

11:30 **Acid-catalysed rearrangement of fatty epoxides: perspectives in application of acid saponites**
L10 Matteo Guidotti, Nicoletta Ravasio, Rinaldo Psaro, Maila Sgobba, Chiara Bisio, Fabio Carniato, and Leonardo Marchese, CNR-ISTM, Milan, Italy

11:50 **Fatty acids: safe and versatile building blocks for the chemical industry**
L11 Peter Tollington, Croda, Gouda, The Netherlands

12:20 – 13:30 **Lunch break**

13:30 – 14:50
First afternoon session: Selim Küsefoglu, Chair

13:30 **Lipids and Lipases - Combination Products From Renewables**
L12 Manfred P. Schneider, Matthias Berger, Kurt E. Laumen, Guido Machmüller, Stefan Müller, and Claudia Waldinger, University of Wuppertal, Wuppertal, Germany

14:00 **O-Acylated Hydroxy carboxylic acid anhydrides: Novel Building Blocks for Surfactants and Emulsifiers**
L13 Bernd Jakob, Hans-Josef Altenbach, Manfred Schneider, Karsten Lange, Rachid Ihizane, Zeynep Ylmaz, and Sukhendu Nandi, University of Wuppertal, Wuppertal, Germany

14:20 **Biocompatible surfactants from renewable hydrophiles**
L14 Maria Rosa Infante, Lourdes Perez, MCarmen Moran, Ramon Pons, and Aurora Pinazo, IQAC - CSIC, Barcelona, Spain

14:50 – 15:20 **Coffee break**

15:20 – 17:30
Second afternoon session: Marina Galià, Chair

15:20 **Gemini-Tensides and Ion Channels from Fatty acids**
L15 M. Dierker, and Hans J. Schäfer, University of Münster, Münster, Germany

15:50 **Aliphatic ß-Chlorovinylaldehydes as versatile building blocks in syntheses of heterocycles**
L16 Annett Fuchs**,** Dieter Greif, and Melanie Kellermann, University of Applied Sciences, Zittau, Germany

16:10 **Calendula Oil as Paint Additive**
L17 Ursula Biermann (a), Werner Butte (a), Ralf Holtgrefe (b), Willi Feder (b), and Jürgen O. Metzger (a), (a) University of Oldenburg, Oldenburg, Germany, (b) bio pin, Jever, Germany

16:30 **Crops: A Green Approach toward Self-Assembled Soft Materials**
L18 George John, City College of City University of New York, New York, USA

17:00 **Exploiting vegetable oils for the delivery of hydrophilic drugs**
L19 Sarina Grinberg, Charles Linder, and Eliahu Heldman, Ben-Gurion University of the Negev, Beer-Sheva, Israel

19:30 **Conference dinner *Upstalsboom Parkhotel***

Tuesday, 24. March 2009

09:00 – 10:30
First morning session: Maria Rosa Infante, Chair

09:00 **The role of renewable resources for Bayer Material Science**
L20 <u>Ralf Weberskirch</u>, Bayer Materials Science, Leverkusen, Germany

09:30 **Vegetable oil-based triols from hydroformylated fatty acids and polyurethane elastomers**
L21 <u>Zoran Petrovic</u>, Ivana Cvetkovic, DooPyo Hong, Xianmei Wan, Wei Zhang, Timothy Abraham, and Jeffrey Malsam, Pittsburg State University, Kansas Polymer Research Center, Pittsburg, Kansas, USA

10:00 **New approaches to polymers and composites from plant oils**
L22 <u>Selim Küsefoglu</u>, Bogazici University Chemistry Department, Istanbul, Turkey

10:30 – 11:00 **Coffee break**

11:00 -13:15
Second morning session: Michael A.R. Meier, Chair

11:00 **Vegetable-oil based thermosetting polymers**
L23 <u>Marina Galià</u>, Joan Carles Ronda, Gerard Lligadas, Virginia Cádiz, University Rovira i Virgili Tarragona, Spain

11:30 **Chemo-enzymatic synthesis of oil polyols and polyurethanes of them**
L24 <u>Tomas Vlcek</u>, SYNPO, Pardubice, Czech Republic

11:50 **Study of ASA (alkenyl succinic anhydrides) from fatty acid esters of vegetable oils as paper sizing agents**
L25 <u>Laure Candy</u>, Carlos Vaca-Garcia, Elisabeth Borredon, Laboratoire de Chimie AgroIndustrielle; ENSIACET, Toulouse, France

12:10 **Use of vegetable oil based thermosetting resins in compound stone technology**
L26 <u>Stefano Zeggio</u>, Fabio Bassetto, Breton Research Centre, Castello di Godego, Italy

12:30 **Life cycle assessment of high performance polyamides**
L27 Georg Oenbrink, Martin Roos, Franz-Erich Baumann, <u>Harald Häger</u>, Evonik Degussa GmbH, Marl, Germany

13:00 - 13:15 **Best poster award**
Uwe Bornscheuer, European Journal of Lipid Science and Technology, Editor-in-Chief

Closing remarks, Michael A. R. Meier, University of Applied Sciences OOW

Poster

P1 **Catalytic cleavage of methyl oleate or oleic acid**
A. Köckritz[1], M. Blumenstein[2], A. Martin[1]
[1]Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Berlin, Germany
[2]Hobum Oleochemicals GmbH, Hamburg, Germany

P2 **Heterogeneously catalyzed hydrogen-free deoxygenation of saturated C8, C12 and C18 carboxylic acids**
S. Mohite, U. Armbruster, M. Richter, D.L. Hoang, and Andreas Martin, Leibniz-Institut für Katalyse e.V. an der Universitaet Rostock, Berlin, Germany

P3 **Flame retardant polyesters from renewable resources via ADMET**
Lucas Montero de Espinosa, Joan Carles Ronda, Virginia Cádiz, Universitat Rovira i Virgili, Tarragona, Spain, and Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

P4 **Catalytic access to bifunctional products from plant oil derivatives**
Xiaowei Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, Institut Sciences Chimiques de Rennes, Rennes, France

P5 **Synthesis and Characterization of Surfactants from Renewable Resources**
Rachid Ihizane, Bernd Jakob, Karsten Lange, Zeyneb Yilmaz, Sukhendu Nandi, Manfred P. Schneider and Hans. J. Altenbach, Fachbereich C – Mathematik und Naturwissenschaft, Fachgruppe Chemie, Bergische Universität Wuppertal, Wuppertal, Germany

P6 **Synthesis of bifunctional monomers via homometathesis of fatty acid derivatives**
Jürgen Pettrak, Herbert Riepl, Martin Faulstich, and Wolfgang A. Herrmann, TU München, Lehrstuhl für Rohstoff und Energietechnologie, Straubing, Germany

P7 **Synthesis and evaluation of value added products from Glycerol**
Avinash Bhadani, and Sukhprit Singh, Guru Nanak Dev University, Department of Chemistry, Amritsar, India

P8 **New Polymers from Plant Oil Derivatives and Styrene-Maleic Anhydride Copolymers**
Cem Öztürk, and Selim Küsefoğlu, Bogazici University, Chemistry Department, Istanbul, Turkey

P9 **Chain Extension Reactions of Unsaturated Polyesters with Epoxidized Soybean Oil**
Ediz Taylan, and Selim Küsefoglu, Bogazici University, Chemistry Department, Istanbul, Turkey

P10 **Soybean Oil Based Isocyanates: Synthesis, Characterizations and Polymerizations**
Gökhan Çaylı, and Selim Küsefoğlu, Bogazici University, Chemistry Department, Istanbul, Turkey

P11 **Aliphatic ß-chlorovinylaldehydes as versatile building blocks in syntheses of heterocycles**
Annett Fuchs, Dieter Greif, and Melanie Kellermann, University of Applied Siences, Zittau, Germany

P12 **Syntheses and reaction behavior of long-chained alkyl methyl ketones starting from fatty acids, fatty alcohols and fatty nitriles**
Melanie Kellermann, Annett Fuchs, Dieter Greif, University of Applied Sciences, Zittau, Germany

P13 **Hydrophobic modification of Inulin in aqueous media using alkyl epoxides and basic catalysis**
Jordi Morros, Bart Levecke, and Mª Rosa Infante, IQAC - CSIC, Barcelona, Spain

P14 **Short Chain Sugar Amphiphiles: Alternative Oil Structuring Agents**
Swapnil R Jadhav, Praveen Kumar Vemula, and George John, City College of City, University of New York, New York, USA

P15 **Novel enzymes for lipid modification**
H. Brundiek, R. Kourist, M. Bertram, and U. Bornscheuer, University of Greifswald, Germany

P16 **Production of fine and bulk chemicals using silage as a renewable resource**
Tim Sieker, and Roland Ulber, University of Kaiserslautern, Kaiserslautern, Germany

P17 **Enzymatic degradation of pre-treated wood**
Sebastian Poth, Magaly Monzon, Nils Tippkötter, and Roland Ulber, University of Kaiserslautern, Germany

P18 **PA X,20 from renewable resources via metathesis and catalytic amidation**
Hatice Mutlu,and Michael A.R. Meier, University of Applied Sciences OOW, Emden, Germany

P19 **DERIVATIVES OF VEGETABLE OILS AS COMPONENTS OF HYDRAULIC FLUIDS**
Talis Paeglis, Aleksejs Smirnovs, Rasma Serzane, Maija Strele, Mara Jure, Riga Technical University, Riga, Latvia

P20 **ULTRASOUND PROMOTED ETHANOLYSIS OF RAPESEED OIL**
Pavels Karabesko, Maija Strele, Rasma Serzane, Mara Jure, Riga Technical University, Riga, Latvia

P21 **From Glycerine via Acetals to new Amphiphils**
J. Baumgard (a,b) , E. Paetzold (a), and U. Kragl (a,b), (a) Leibniz-Institut für Katalyse an der Universität Rostock e.V., Rostock, b) Institut für Chemie, Universität Rostock e. V., Rostock

P22 **BIOBASED SEGMENTED POLYURETHANES FROM METHYL OLEATE BASED POLYETHER POLYOLS**
Enrique del Río, Virginia Cádiz, Marina Galià, Gerard Lligadas, Joan Carles Ronda, Universitat Rovira i Virgili, Tarragona, Spain

P23 **DETAILED STUDIES OF SELF- AND CROSS-METATHESIS REACTIONS OF FATTY ACID METHYL ESTERS**
Guy B. Djigoue, and Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

P24 **Temperature dependant double bond isomerization side reactions during ADMET polymerizations studied with a monomer from renewable resources**
Patrice Aimé Fokou, and Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

P25 **Reducing the Environmental Impact of Olefin Metathesis Reactions**
Manuela Kniese, Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

P26 **An approach to renewable Nylon-11 and Nylon-12 via olefin cross-metathesis**
Tina Jacobs, Michael A. R. Meier, University of Applied Sciences OOW, Emden, Germany

P27 **Ultrasonic assisted finishing of cellulose fiber by fatty acid amide derivatives**
Mazeyar Parvinzadeh, Mohammad Shaver, and Bashir Katozian, Islamic Azad University, Shahre rey branch, Tehran, Islamic Republic of Iran

P28 **Hydrolysis of nylon 6 with proteolytic enzyme**
Mazeyar Parvinzadeh, Islamic Azad University, Shahre rey branch, Tehran, Islamic Republic of Iran

P29 **Comparing finishing of polyester fibers with micro and nano emulsion silicones**
Mazeyar Parvinzadeh, Islamic Azad University, Shahre rey branch, Tehran, Islamic Republic of Iran

P30 **PIBOLEO project: Eco Innovative process for multi-functional bi-oleothermal teatment for wood preservation and fire proofing**
Sandra Warren, Carine Alfos, and Frédéric Simon, ITERG, Pessac, France

P31 **Cellulases in bi-phasic media**
Nathalie Berezina, Joel Nys, and Laurent Paternostre, Natiss - Materia Nova, 7822 Ghislenghien, Belgium

Abstracts

Part 1: Lectures

L1 Vegetable oils as raw materials for industrial applications

Karlheinz Hill, Cognis, Germany
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Natural fats and oils, carbohydrates and proteins are key raw materials for the chemical industry using renewable resources. Although in general, biomass is available in large amounts (e.g. cellulose), the annual production volumes of selected biobased commodities are still small compared to coal or crude oil.

Annual production of commodities worldwide (2004, million tons)[a]

Wheat	Rice	Starch	Sugar[b]	Fats&Oilsc	Crude Oil	Coal[d]
610	610	40	145	131	3600	3800

a) sources: OilWorld, USDA, Industrieverband Agrar, Wikipedia; b) from beet and cane; c) vegetable and animal based; d) as SKE (1 kg SKE = 0,984 kg bituminous coal)

Until now, availability and use was quite balanced and the quantities could be adjusted according to different demands. For example, in the case of natural oils and fats, the production volume was steadily increased from 30 million tons in 1960 to 131 million tons in 2004. Most of it was used for food (81% in 2004), a minor amount for animal feed (6% in 2004) and chemistry (10% in 2004). However, what we have observed for some time is a shift towards an increasing use of renewable raw materials for bioenergy and biofuels. In the case of natural vegetable oils, the expected share for energy is estimated to grow to 15% (!) of the total annual capacity in 2012 compared to 3% in 2004. This is one consequence of political measures such as the European Biofuel Directive 2003/30/EC. Biodiesel production volumes were expanded significantly in the recent past and this trend is expected to continue in Europe and other regions such as South East Asia, South America and India, with a further increase in production capacities forecasted at least for the next 5-10 years.

When the so-called 2nd generation products, such as sundiesel or biomass-to-liquid fuels, are ready to be launched on the market, the demand on fats and oils for biofuels might decrease again. These new technologies are definitely needed assuming that even with increasing production volumes for fats and oils, the future bioenergy and biofuel demand cannot be satisfied by this source alone.

In the meantime, the high demands for biodiesel, still further stimulated by subsidies, will create strong competition with the established uses for vegetable oils for nutrition and also for the chemical industry (oleochemistry). A very similar situation is being observed in the case of bioethanol from carbohydrates and/or sugar. The competition between the use of agricultural products for nutrition and energy is one of the reasons why market prices of such agricultural commodities are recently subject of extremely high volatility. Other reasons are the increasing demand for food in various regions of the earth, crop yield, and financial speculations by investment funds.

The use of renewable resources is only one important part of the future "green" strategy in industry. What must also be considered are sustainability practices across the entire value chain. This strategy is already applied to palm oil. It is the first time an expert group (The Round Table of Sustainable Palm Oil, RSPO) involving all participants in the industrial agricultural commodity value chain has defined what sustainable agriculture really should mean. The challenging goal to develop, implement and verify credible global standards for sustainable palm oil products has finally been achieved. The principles and criteria for sustainable palm oil are in the implementation process and this year the first products are available according to the standards. Cognis was the first chemical supplier in membership and is until today one of the few. Its expertise in natural raw materials enables Cognis to develop concepts with its customers on how to make renewable raw materials sustainable as almost all of its raw materials from the palm tree are being sourced from RSPO members.

L2

Carbonylation as a route to chemicals from biomass

David Cole-Hamilton, Cristina Jimenez-Rodriguez, W. Roy Jackson, and Yulei Zhu,
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As oil stocks dwindle and become increasingly expensive, it will become essential to develop routes to chemicals starting from feedstocks that can be derived from plant sources. One interesting group of chemicals is the diesters. Especially desirable are the alpha-omega diesters since they are used in a wide variety of polyesters for use in plastic bottles, synthetic carpets and speciality plastics. We have been developing a range of palladium based catalysts that can form alpha-omega diesters from unsaturated esters by methoxycarbonylation reactions. When these catalysts are applied to methyl oleate, dimethyl 1,19-nonadecanedioate is formed in high selectivity. This remarkable reaction involves isomerisation of the double bond to the end of the chain and, only when it is there, is it carbonylated. The same product is formed from methyl linoleate and methyl linolenate. Since shorter chain length diesters are often required, the group of W. R. Jackson in Monash Australia has coupled this isomerisation carbonylation reaction with metathesis of the original oil with butene. The metathesis shortens the chain to give an unsaturated ester which can be isomerised and carbonlyated to give shorter alpha-omega diesters. We shall discuss the nature of the catalysts and the reasons for their very specific actions.

L3

Metathesis with oleochemicals: a sustainable match to obtain monomers and polymers from renewable resources

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In ages of depleting fossil reserves and increasing emission of green house gases it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. Especially plant derived 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 resources in a straightforward fashion taking full advantage of nature's synthetic potential. Here, new approaches for the synthesis of monomers as well as polymers from plant oils as renewable resources[1] via olefin metathesis[2,3] will be discussed. As an example, we recently showed that different chain length α,ω-diester monomers can be obtained from plant oil derived fatty acid esters via olefin cross-metathesis[4] with methyl acrylate taking advantage of natures "synthetic pool" of fatty acids with different chain lengths and positions of double bonds.[5]
Similarly, we could show that the cross-metathesis with allyl chloride and other functional olefins allows for the synthesis of α,ω-difunctional compounds.[6,7] Therefore, this strategy offers the possibility to introduce a variety of different functional groups to the ω -position of fatty acid derivatives, thus providing valuable starting materials for a variety of polyesters and polyamides.
Moreover, acyclic diene metathesis (ADMET), can be used to directly obtain macromolecules from such starting materials. The ADMET polymerization [8] of undecyl undecenoate, for instance, led to high molecular weight polyesters.[9] It was possible to effciently control the molecular weight of these materials and to prepare telechelics via the application of mono-functional chain-stoppers.[9] More interestingly, this approach can also be used to prepare ABA triblock copolymers with control of the degree of polymerization (DP) of the B block in a single reaction step.[9] Furthermore, if tri-functional monomers in combination with chain stoppers are investigated the synthesis of hyperbranched polymer architectures with functional groups in their periphery can be achieved in a single reaction step.[10]

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L4

Biocatalysis in the modification of fats and oils for oleochemistry

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Lipases and related enzymes (esterase, different phospholipases) are currently used as biocatalysts in a broad range of lipid modifications [1]. In this lecture, the identification of novel esterases/lipases from the metagenome will be shown highlighting the discovery of biocatalysts with certain fatty acid chain-length profiles [2]. Furthermore, methods for the identification and immobilization of desired enzymes using a microtiterplate (MTP) based method [3, 4] will be presented. An example for protein engineering deals with a lipase from Rhizopus oryzae (ROL), which was engineered to increase its stability toward lipid oxidation products such as aldehydes with the aim of improving its performance in oleochemical industries. Key to success was the saturation mutagenesis of selected Lys and His residues combined with a MTP-based high-throughput screening of stable variants [5]. Furthermore, the use of ionic liquids as media for the synthesis of sugar fatty acid esters will be covered [6].

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L5

Catalytic Functionalisation of Fatty Compounds

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Every year the chemical industry uses about 250 million tons of resources for the production of organic chemicals. Only 20 millions tons, that means only 8-10 %, are based on renewable resources, especially on fat and oils. This contribution gives a short overview about the numerous possibilities to functionalise fatty compounds via homogeneous transition metal catalysis.

Unsaturated fatty compounds contain one or more C=C-double bonds which can be easily functionalised via coordination to transition metal complexes [1]. Some important examples of these functionalisations are epoxidations, dihydroxylations, oxidative cleavage reactions, hydrosilylations [2-3], hydroformylations [4] and hydroaminomethylations [5]. Thus new carbon-oxygen-, carbon-silicon-, carbon-carbon- and carbon-nitrogen-bonds can be formed yielding a broad spectrum of chemical compounds with new properties and new applications. Further important examples are the rhodium-catalysed cooligomerisations [6-7] or the ruthenium-catalysed metathesis of fatty compounds with alkenes.

If fats and oils are transesterified with methanol **glycerol** is formed as an important by-product in oleochemistry. A great number of applications of glycerol are well known, however, the raising amounts of glycerol because of the enormous production of biodiesel can not be put into the market. Therefore new reactions are needed to transform glycerol into new products with new markets. Once again, homogeneous catalysis offers interesting possibilities [8-9]: Via catalytic oxidations glycerol acid or dihydroxyacetone can be formed. Dehydratisation yields acrolein which is further oxidised to acrylic acid. Further follow-up products of glycerol are for instance propanediols, epichlorohydrine, glycerol dimers or trimers, glycerol carbonate, glycerol acetals or ketals. Another important group of chemicals are the glycerol ethers, for instance the glycerol tertiary butyl ethers [10] or the telomers of glycerol [11-14].

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L6

Oxidation of tensidic alcohols to their corresponding carboxylic acids via Au- and AuPt-catalysts

Ulf Prüße, Katharina Heidkamp, Nadine Decker, Kerstin Martens, Klaus-Dieter Vorlop
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Reducing the use of environmentally hazardous chemicals in industrial processes plays a key role in the science of catalysis. Particularly the liquid-phase oxidation of tensidic alcohols to the corresponding carboxylic acids holds a great potential for improvement towards a “greener” process. Currently ether carboxylic acids are either synthesized via Williamson’s ether-synthesis using chloroacetic acid derivatives. Incomplete conversion and consequential excess use of chloroacetic acid lead to impurities (e.g. educt residues and by-products) which accelerate the deterioration of the acid and impair its solubility. Or they can be produced by oxidising the corresponding alcohol with dioxygen using supported Pt- or Pd- catalysts. However, difficulties such as metal leaching and incomplete conversion may occur during this process. Our research group is first to develop and employ mono- and bimetallic Au-catalysts for the liquid-phase oxidation of fatty alcohol ethoxylates and related model compounds, i.e. alkyl ethoxylates and ethoxylates, to their corresponding carboxylic acid.

Several preparation methods, catalyst supports and Au-Pt-ratios (for bimetallic catalysts) were screened. For all model compounds monometallic Au-catalysts featured a selectivity of 100 % to the carboxylic acid. Maintaining total selectivity, the activity could be increased significantly by using a bimetallic Au-Pt-catalyst with a gold: platinum ratio of 90:10. Thus, for comparable reaction conditions our catalyst was ten times as active as a Pt-catalyst.

The experiments were carried out at elevated pressures (5-30 bar) in thermostatted stainless steel autoclaves at constant pH (9 -11). Variation of reaction parameters and kinetic studies revealed a dependency of the activity on temperature (80 – 130 °C), oxygen pressure, pH-value and educt concentration (5 – 80 %) – all of which do not affect the selectivity.

The reaction mechanism should be identical for all model compounds. However, during the oxidation of certain fatty alcohol ethoxylates with monometallic Au-catalysts intermediate metal leaching occurs. This phenomenon does not arise with the other two model compounds. Preliminary results suggest that metal leaching can be reduced considerably by employing bimetallic catalysts with a proper Au-Pt-ratio.

L7

Plant oils as precursors of N-containing compounds via alkene metathesis

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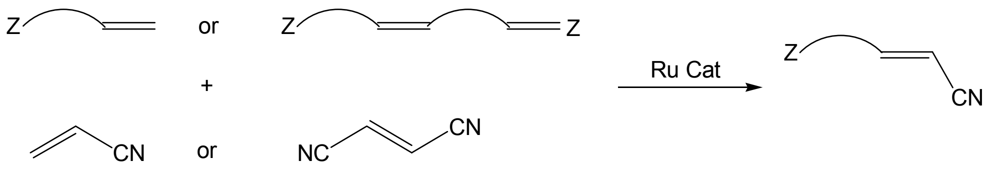
Plant oils, the known precursors of a variety of unsaturated acid derivatives have also the potential to produce, by action of alkene metathesis catalysis, new intermediates useful for chemical industry, from renewable materials.

The cross-metathesis, promoted by selected ruthenium catalysts, of unsaturated esters, acids and other oil derivatives with acrylonitrile and fumaronitrile will be presented [1]



The formed bifunctional compounds are thus the precursors of linear aminoacids and thus polyamides.

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L8

Phytomining of plant enzymes for biotechnological use of fats and oils

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Human history is closely linked to the use of plants as valuable sources for nutrition, commodities and energy as well as a multitude of raw materials, such as fats, oils and natural polymers like cellulose or starch. However, only recently have we come to see plants as a cornerstone of sustainable industry by exploiting lead structures and biosynthetic pathways for the modification of plant derived, renewable resources.

Plant derived fats and oils are already used by the Chemical Industry as renewable feedstock and unsaturated fatty acids, often found in plant oils, represent well suited raw materials for the production of polymers, plasticizer and lubricants. Doubtlessly, the wealth of plant biosynthetic pathways makes plants an attractive source for fascinating new enzymes for fat and oil modification and biotechnological applications. Use of plant enzyme and compounds in industrial biotechnology offers new means to address/reach energy savings and increases of efficiency and sustainability by reducing the number of steps in processing chains, for example.

Phytowelt GreenTechnologies GmbH excels enzyme discovery via phytomining, a combinatory high content approach. Our four step integrative approach aims to increase the efficiency of current production processes, e.g. by complementing microbial production lines with a suitable gene, or implementing completely new and innovative fermentation processes. Phytowelt's approach unlocks the huge potential of plant biodiversity.

Phytowelt's presentation will introduce its phytomining platform and the power of (plant) enzymes. Examples for the application of plant enzymes will be given.

L9

Rational design of solid catalysts for selective glycerol activations

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With the aim of finding solutions to the disappearance of fossil raw materials, scientists focused their attention towards the use of natural products. However, these products are in most cases polyfunctional and their transformations require the close control of the chemio- and/or regio- and/or enantioselectivity of processes. To overcome these problems, catalysis was expected to play a pivotal role by offering to chemists useful tools for performing selective transformations of renewables to high added value chemicals. Recent studies clearly showed that inorganic solid supports can directly and positively impact on the reaction selectivity.

Development of new catalysts with controlled distribution of active sites is probably one of the most fascinating examples. But a control of the hydrophilicity of catalytic surfaces is also an important parameter. Playing with the hydrophilic properties of the catalyst surface, we found that it was possible to limit a lot of secondary reactions allowing us to transform glycerol with yields and selectivities higher than those obtained with homogeneous and usual solid acid or basic catalysts.

L10

Acid-catalysed rearrangement of fatty epoxides: perspectives in application of acid saponites

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The ring opening of epoxidized fatty acid derivatives is a valuable transformation for the production of compounds functionalized on the alkyl chain. Rearranged epoxides could find applications as precursors of biopolymers, lubricants, polyurethane foams and casting resins.

A two-step process, starting from fatty acid methyl esters and based uniquely on heterogeneous and easily recoverable catalysts, is here proposed. The FAME methyl oleate is epoxidized in liquid phase with tert-butylhydroperoxide in batch reactor over Ti-grafted MCM-41. The transformation is optimized and the conversion attains >90% after 24 h, with selectivity >95% to methyl 9,10-epoxystearate. After separation of the organic product from the solid Ti-catalyst, the ring opening of the epoxidized fatty ester is performed in the presence of a protonic acidic saponite clay, obtained by exchanging a synthetic Na+ saponite in aqueous HCl solutions at different concentrations. The catalytic results for the nucleophilic addition of methanol to methyl epoxystearate show the good performance of different acid saponites in terms of activity. The saponite catalysts were also compared with other widely used heterogeneous systems, such as mesoporous ordered aluminosilicate Al-SBA-15 and a protonic Beta zeolite (H-BEA). Protonic saponites showed better results than H_2SO_4 too (0.45 mmol g^{-1}), the typical industrial catalyst for this reaction.

The best result is obtained over the protonic saponite prepared with a mild pretreatment (ion exchange in aq. 0.01 M HCl): with methanol, after 5 min, 90% of the epoxide is readily converted into Me-methoxyhydroxystearate and Me-oxostearate.

L11

Fatty acids: safe and versatile building blocks for the chemical industry

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Fatty acids are basis ingredients for a wide range of consumer and technical products, for which they provide properties and benefits not readily or economically achieved using mineral-derived sources.

They can contribute to the development of a more sustainable, biobased economy –not only through their inherent natural basis, but also through the ability of the fatty acid producers to handle a wide range of technical/non-edible oil and fat sources and to make from them high quality, well-defined materials for value-added onward application. Furthermore, the natural mixtures can be readily purified and separated to yield end products with precise functionality and properties, distinct from those of the parent triglyceride compositions.

This talk will outline the processing and chemistry of fatty acids, and illustrate their versatility as basic building blocks with two contemporary examples ; development of a synthetic oleochemical wax, and (the properties and benefits provided by) polymerised fatty acids in a solvent-free coating.

L12

Lipids and Lipases - Combination Products From Renewables

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Agricultural crops represent a considerable reservoir of useful and low cost raw materials like fats and oils, plant proteins and carbohydrates. By selective combination of their molecular constituents (e.g. fatty acids, glycerol, amino acids, mono- and disaccharides, amino sugars etc.) a wide variety of surface active materials can be prepared, all of them - due to their molecular structures - being potentially highly biodegradable.

Lipases are well established biocatalysts for the selective formation of ester and amide bonds and thus ideally suited for the preparation of combination products with surface active properties such as partial glycerides, N-acylated amino acids and sugar esters. A common problem associated with enzymatic acylations of hydrophilic materials in hydrophobic aprotic organic solvents is the low solubility of the above substrates in such media. Consequently, practical solutions had to be developed in order to obtain acceptable yields. Using a) immobilizations on solid supports, b) supersaturated solutions and c) temporary protection groups acceptable results were achieved in most cases. In the lecture examples for the preparation of the above product lines will be discussed, this also in context with similar activities in other research groups.

L13

O-Acylated Hydroxy carboxylic acid anhydrides: Novel Building Blocks for Surfactants and Emulsifiers

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We recently discovered that hydroxy carboxylic acids like malic, tartaric and citric acid can be converted in one step and quantitatively into the title compounds by reacting them with fatty acid chlorides. The title compounds are excellent electrophiles for ring opening reactions with a broad variety of nucleophiles – also frequently from renewable resources - such as alcohols, carbohydrates, amines, amino acids and amino sugars. This way a wide variety of novel surface active compounds are obtained, many of which turned out to be interesting (useful) surfactants and/or emulsifiers for applications in cosmetics, as food additives and for a variety of industrial processes. In the lecture we describe a) the preparation of these materials, b) their surface active properties c) antimicrobial activities.

L14

Biocompatible surfactants from renewable hydrophiles

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There is today a strong trend to replace conventional surfactants with more environmentally benign compounds. Manufacturers and consumers demand for novel environmentally friendly surfactants from renewable resources produced by clean and sustainable technologies (bio-based surfactants). The challenge is to find molecules which meet mild, biodegradability, as well as performance and cost benefit requirements. The use of hydrophilic renewable raw materials to prepare novel “natural” surfactants is an exciting and attractive research activity to conciliate the sustainable issues with the industrial development. In this talk we will describe significant advances have been made in the field of surfactants derived from hydrophilic sources: lysine and arginine.

L15

Gemini-Tensides and Ion Channels from Fatty acids

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Nature provides in fatty acids a raw material of high synthetic value. Fatty acids are even numbered carboxylic acids with 12 to 24 carbon atoms and an unbranched alkyl chain that bears one to several - mostly *Z*-configurated - double bonds and hydroxy groups in distinct positions.

A variety of efficient synthetic conversions has been reported for fatty acids [1]. These comprise C,C-bond formations and functional group interconversions. There are substitutions of CH-bonds in ω- and ω-1-position, in allylic position or adjacent to a carbonyl group. Described are furthermore electrophilic, radical, nucleophilic additions, cycloadditions, metathesis, formation of triple bonds and their conversion. Carbon atoms adjacent to the carboxyl group can be subjected to radical coupling and addition by way of electrochemical decarboxylation.

Higher value products have been obtained by us by combining the amphiphilic nature of the fatty acid with bioactive groups [2], carbohydrates [3], dyes [4], corrosion inhibitors [4], antioxidants [5] and as organogels [6] or ion channels [7].

Tensides are surface active compounds for which the amphiphilic nature of fatty acids provides excellent preconditions. For applications of domestic oils as tensides the hydrophilic properties of C_{18} to C_{22} fatty acids have to be increased. We report here on Gemini-tensides obtained by attaching two polar groups to the double bond of oleic acid, erucic acid and petroselinic acid [8]. Polar groups are ethoxylates, carbohydrates, sulfates and phosphates.

The tensidic properties of the compounds as water solubility, decrease of the surface tension, critical micelle concentration, interfacial tension and foaming behaviour are reported and compared with these from lauric oils.

The 9,10-bis(methylethyleneglycol) adduct to methyl oleate turned out to be an artificial ion channel. The activity was determined by measurements of the acid induced fluorescence decay in vesicles and ion conductance of single channels in lipid membranes. The ion conductivity is comparable to this of the natural ion channel forming compound: gramicidine. As gramicidine the synthetic channels exhibit an antibiotic acitivtity against Gram-positive and Gram-negative microorganisms.

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L16

Aliphatic ß-Chlorovinylaldehydes as versatile building blocks in syntheses of heterocycles

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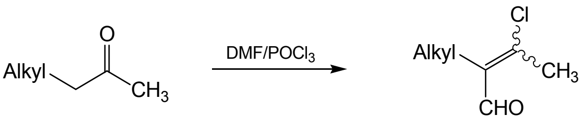
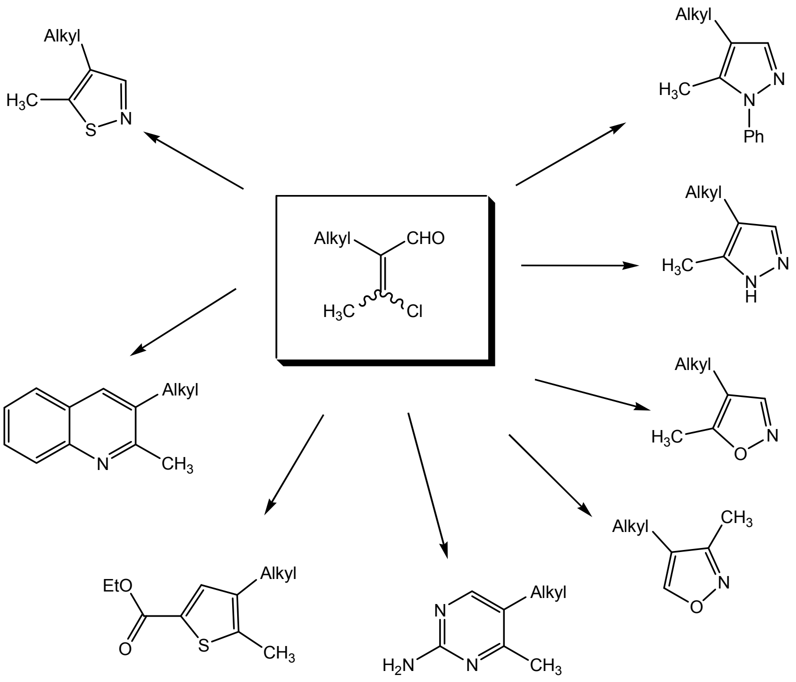
Aliphatic ß-chlorovinylaldehydes are readily prepared from alkyl methyl ketones using Vilsmeier-Haack-Arnold reaction.



A survey of the literature often shows complex reactions by great expending time and resources for getting aliphatic substituted heterocycles. On the other hand such compounds can easily synthesize from ß-chlorovinylaldehydes by reaction with O-, N- and S-nucleophiles. So we synthesized a variety of heterocyclic systems like isothiazoles, pyrazoles, quinolines, isoxazoles, thiophenes and pyrimidines.



A survey of the literature let us expect that these compounds have a broad spectrum of useful biologically activity. With this research we look for new applications of fatty renewable materials in the matter of fine chemicals. It is also of interest that aliphatic ß chlorovinylaldehydes show a different reaction behavior compared with those described in the literature.

L17

Calendula Oil as Paint Additive

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During the last few years modern synthetic methods have been applied extensively to fatty compounds for the selective functionalization of the C,C-double bond of unsaturated fatty compounds and gave a large number of novel fatty compounds from which interesting properties are expected.[1] Presently our interest is focused to plant oils containing unsaturated fatty acids with a highly reactive hexatriene system such as calendula oil and tung oil. The latter – obtained from the nuts of the tung oil tree - is a drying oil and is used for a number of products including varnish, resins, inks, paints and coatings. Similar properties are expected from calendula oil. Octadec-8,10-trans-12-cis-trienoic acid (calendic acid) is the main fatty acid (ca. 60%) in the seed oil of calendula officinalis. We obtained calendic acid esters from the native oil by a simple transesterification method using alcohols, i.e. methanol, ethanol or isopropanol and sodium methoxide as catalyst. The solvent-free Diels-Alder reaction of methyl calendulate and maleic anhydride gave exclusively one highly functionalized cycloaddition product in 78% yield. The endo-8,12-cycloaddition product was formed with high regio- and stereoselectivity.[2] The reaction can be applied to the native oil as well.

In a patent by DSM methyl calendulate is described as a very efficient reactive diluent.[3] In addition to this we obtained even better results for ethyl and isopropyl calendulate as reactive diluent showing low viscosity and good drying properties.

In special applications e.g. in coating material used in the outskirt area the substitution of tung oil should be possible by calendula oil.

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L18

Crops: A Green Approach toward Self-Assembled Soft Materials

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This talk presents novel and emerging concept of generating various forms of soft materials from renewable resources. In future research, developing soft nanomaterials from renewable resources (an alternative feedstock) would be fascinating yet demanding practice, which will have direct impact on industrial applications, and economically viable alternatives. Our continuous efforts in this area led us to develop new glycolipids from industrial byproducts such as cashew-nut-shell-liquid, which upon self-assembly produced soft nanoarchitectures including lipid nanotubes, twisted/helical nanofibers, low-molecular-weight gels and liquid crystals. More recently, we have developed multiple systems based on biobased organic synthesis by chemical/biocatalytic methods for functional applications. We used the 'chiral pool' of carbohydrates using the selectivity of enzyme catalysis yield amphiphilic products from biobased feedstock including amygdalin, trehalose and vitamin-C. Amygdalin amphiphiles showed unique gelation behaviour in a broad range of solvents such as non-polar hexanes to polar aqueous solutions. Importantly, an enzyme triggered drug-delivery model for hydrophobic drugs was demonstrated by using these supramolecularly assembled hydrogels. Intriguingly, by combining biocatalysis, with principles of green and supramolecular chemistry, we developed building blocks-to-assembled materials. Also address the advances that have led to the understanding of chiral behaviour and the subsequent ability to control the structure of glycolipid nanostructures, and the resulting impact of this on future material applications. These results will lead to efficient molecular design of supramolecular architectures and nanomaterials from underutilized plant/crop-based renewable feedstocks.

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L19

Exploiting vegetable oils for the delivery of hydrophilic drugs

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The use of oils and fats as pharmaceuticals dates back to biblical times. Through the ages, the science and technology of fats and oils and their chemical derivatives has progressed from traditional products to high-value applications, including lipid-based drug delivery systems. Lipid-based drug delivery is considered a viable strategy for increasing drug efficacy and reducing drug toxicity. Liposomes are among the lipid-based delivery systems which are extensively studied but targeting them to specific tissues, is still problematic. Toward overcoming the limitations of the classical liposomes (made of phospholipids that form bilayer membrane), we are developing lipid-based monolayer cationic vesicles made of bolaamphiphilic compounds containing two hydrophilic head groups at each end of an alkyl chain. The concept is to mimic the high chemical and physical stability of archaebacteria membranes, which is made from bolaamphiphiles. Since it is hard to isolate bolaamphiphiles from araebacteria and their synthesis is also difficult, we took a different approach - synthesizing novel bolaamphiphiles designed to form stable nano vesicles from functional vegetable oils that are excellent renewable resources for the chemical industry. Vernonia oil, a naturally epoxidized triglyceride obtained from the seeds of Vernonia galamensis, is probably the most promising of these functional oils with respect of a facile synthesis of functionalized bolaamphiphiles. Yet, other natural fatty acids, or oleochemicals derived from them, can also serve as a starting material for the synthesis of such bolaamphiphiles.

Here we describe the synthesis of a series of symmetrical and asymmetrical bola¬amphiphilic compounds that form vesicles with unique properties needed for targeted drug delivery. When the head groups are substrates for an enzyme with high activity at the target tissue, the vesicular structure will be disrupted and the vesicles will release the encapsulated drug primarily there. Conjugates between vernonia moiety and polyethylene glycol (PEG) or chitosan, were also prepared and incorporated into the membrane of the cationic vesicles in order to prolonged the circulatory survival of the vesicles and to increase penetrability through the blood-brain barrier (BBB) and the intestinal wall.

Efficacy of these vesicles as a drug delivery system was demonstrated with encapsulated enkephalin (ENK) that was shown to induce analgesia whereas non-encapsulated ENK did not cause any analgesic effect.

In summary, we have demonstrated that cationic vesicles with monolayer membrane made from novel bolaamphiphiles with head groups that are hydrolyzed by specific enzyme with high activity at the target tissue constitute an efficient targeted drug delivery system.

L20

The role of renewable resources for Bayer Material Science

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The usage of renewable resources has a long tradition in chemical industry. Depletion of fossil resources, climate change and CO2 footprint discussions along with technical breakthroughs in the past decade to convert renewable resources more efficiently have led to many initiatives in industry and academia as well as to further explore opportunities of renewable resources. [1]
In this presentation an overview will be given how BayerMaterialScience approaches the area of renewable resources and two examples will be discussed in more detail relating to the polyurethane industry: (1) The use of vegetable oils for the manufacture of polyether-polyols with a renewable content ranging from 40-70 % by weight and (2) the use of succinic acid in polyester-polyols and as a C4 platform chemical. [2]

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L21

VEGETABLE OIL-BASED TRIOLS FROM HYDROFORMYLATED FATTY ACIDS AND POLYURETHANE ELASTOMERS

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Novel bio-based polyols were prepared from hydroformylated oleic acid (9-hydroxymethyl-octadecanoic acid) methyl esters and trimethylol propane by transesterification. Hydroformylation produces primary hydroxyls, which allow relatively lower transesterification temperatures and better yields than hydroxyfatty acids with secondary OH groups. These non-crystallizing polyols (HFME) have no double bonds and their viscosities are acceptable. Polyurethane elastomers prepared by reacting these polyols with diphenylmethane diisocyanate (MDI) had glass transitions temperatures from -33 to -56 ^{o}C, depending on the molecular weight of the triols. Tensile strength and Shore A hardness were higher and elongation, swelling and sol fraction lower than those of corresponding networks from polyricinoleic polyols. The plasticizing effect of longer dangling chains in HFME-based polyurethanes were matched to a certain degree by the presence of double bonds in the polyricinoleic polyols, effectively resulting in similar glass transitions.

L22

New approaches to polymers and composites from plant oils

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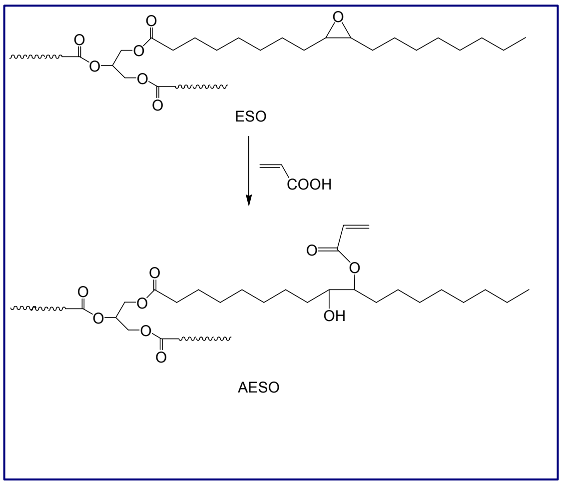
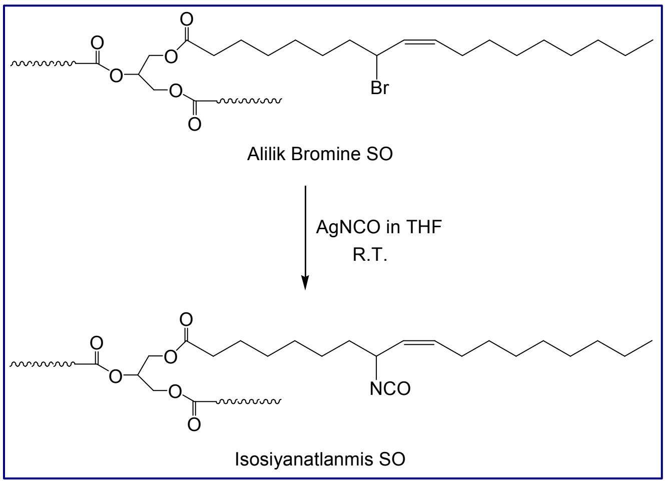
Almost all commercially successful polymers and plastics are now synthesized from petroleum based raw materials. Manufacture of useful polymers from plant oils would present a number of advantages such as the renewability of the raw materials, fast biodegradability of the polymers and cheaper prices. Synthesis of polymers from plant oils is not new: ancient Egyptians used flax oil to protect the wood in their ships. However synthesis of rigid, load bearing polymers that are suitable for fiber reinforcement is a new and very active research field.

When an organic chemist looks at a triglyceride the double bonds, the allylic positions, the carbonyl group and the alfa position to the carbonyl group are noticed as the only useful positions for derivatization. So the task of the polymer chemist is to synthesize new monomers from plant oils using these functional groups. The following are some examples from our efforts in this field.

Epoxidation of the soybean oil double bonds followed by opening of the epoxy ring with acrylic acid gave acrylated epoxidized soybean oil (AESO) which is a plant oil based analog of vinyl ester resins. When this monomer is mixed with styrene reactive diluent, a liquid molding resin is obtained which can be reinforced with glass fiber and can be cured free radically to give laminates with a tensile strength of 450Mpa (1)

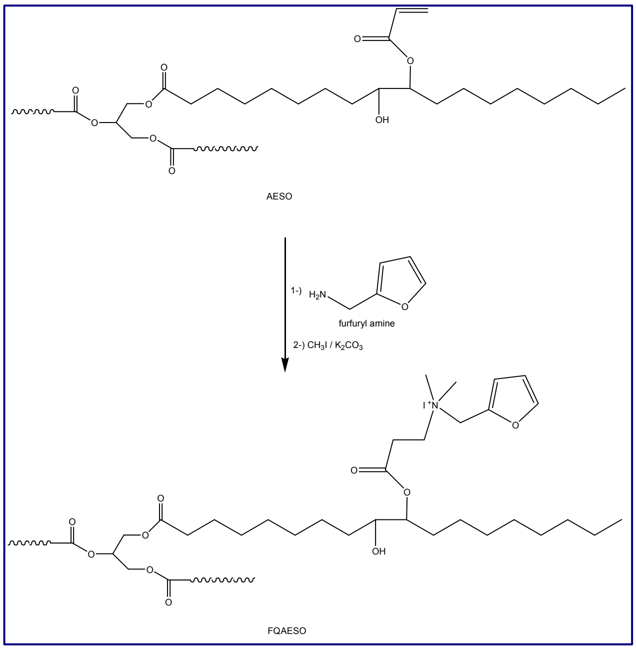




Plant oils can be brominated at the allylic positions easily . Reaction of allylic bromide with silver isocyanate gives the isocyanate substituted triglyceride. This molecule can be easily converted to polyurethanes with various diols and polyols and particularly, with hydroxyl bearing oils such as castor oil. Thus the first example of a polyurethane where both of the monomers are plant oil based are obtained. The polymer is suitable for the production of flexible foams. (2)

Acrylated epoxidized soybean oil can be reacted with furylamine in a Michael reaction. When the amine is the limiting reagent a desired fraction of the acrylate groups can be preserved for future manipulations. The resulting amine can be easily quaternized with methyl iodide and the product turns out to be an excellent exfoliating agent for montmorillonite clay. XRD analysis indicated an increase in intergallery distance from 12

A to 26 A. When a sample of exfoliated clay is mixed with AESO and free radically cured one observes a 30 % increase in modulus with a 2 % clay loading. This constitutes the first nanoclay reinforced material whose matrix polymer and exfoliating agent are plant oil based. (3)



Our work in this exciting field has so far produced approximately 140 new plant oil based polymers among which 12 are promising in terms of mechanical properties and ease of synthesis. Newer strategies wherby the oil based monomer is grafted onto an existing high molecular weight polymer are now being persued with the hope of increasing fracture toughness of the products.

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L23

Vegetable-oil based thermosetting polymers

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In the search for sustainable chemistry, there are increasing demands for replacing petroleum derived raw materials with renewable raw materials in the production of polymers. The importance of natural products for industrial applications becomes very clear from a social, environmental and energy standpoint, with the increasing emphasis on issues concerning waste disposal and depletion of non renewable resources. Vegetable oils are one of the cheapest and most abundant, annually renewable natural resources available in large quantities from various oilseeds and are now being used in an increasing number of industrial applications. In recent years, extensive work has been done to develop polymers from triglycerides of fatty acids as the main component.

The purpose of our research is to develop new biobased thermosetting polymers from vegetable oils as renewable resources. Vegetable oils are triglycerides of different fatty acids with varying degrees of unsaturation. Although they possess double bonds, it is generally considered difficult to polymerise vegetable oils themselves due to its low reactivity. Our research focuses on improving the physical properties of triglyceride based materials, because they demonstrated low molecular weights and light crosslinking, incapable of displaying the necessary rigidity and strength required for structural applications by themselves. In this way, polymers ranging from soft rubbers to hard plastics can be obtained by cationic copolymerisation with styrene and divinylbenzene. Like other organic polymeric materials, the flammability of vegetable oil based materials is a shortcoming in some applications. The concept of sustainable development requires fire retardant technologies to be developed which have minimum impact on health and the environment through the life cycle of the fire-retardant material; that is to say, its synthesis, fabrication, use, recycling and disposal. To further extend the application of renewable resources and to obtain flame retardant polymers, we synthesized polymers from vegetable oils, styrene, divinylbenzene and silicon, phosphorus or boron-containing reactive modifiers.

The presence of double bonds makes possible to attach some functional groups through chemical modification and we described various chemical pathways for functionalising triglycerides and fatty acids. An enone-containing triglyceride was obtained by an environmentally friendly chemical procedure from high oleic sunflower oil that could be an interesting alternative to epoxidized vegetable oils to produce thermosets by crosslinking with conventional aromatic diamines. In a similar way, triglycerides containing secondary allylic alcohols can be obtained, that can be further functionalised with acrylate or phosphorus-containing derivatives to obtain flame retardant themosets. We also obtained organic-inorganic hybrid materials with promising properties for optical applications by the hydrosilylation of alkenyl-terminated fatty acid derivatives and biobased polyhedral oligomeric silsesquioxanes-nanocomposites. Moreover, we described the preparation of a new family of epoxidized methyl oleate-based polyether polyols which were used in the synthesis of polyurethanes with specific applications: silicon-containing polyurethanes with enhanced flame-retardant properties and polyurethane networks with potential applications in biomedicine.

L24

Chemo-enzymatic synthesis of oil polyols and polyurethanes of them

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In this work we have studied possibility to apply chemo-enzymatic catalysis for preparation of new types of oil polyols. Starting raw materials were methylesters of hydroxyfunctionalized fatty acids derived from castor oil, hydroformylated soybean oil, and epoxidized soybean oil ring opened with low molecular weight (poly)alcohols. Reacting these fatty acids with green growing centers such as 1.3-propanediol or glycerol we were able to synthesize 100 % renewable content polyols differing in molecular weight, and hydroxyl group's functionality. We catalyzed the condensation reactions with up to 5 wt. % of immobilized Candida antarctica lipase B (Novozym 435). Setting up the reaction temperature to 70 °C and applying low pressure we allowed easy removal of a side product, methanol. Curing the synthesized oil polyols with aliphatic and aromatic type of isocyanate we prepared model polyurethane cast resins and evaluated physical-mechanical properties of these materials. We will discuss results of our work in our presentation.

L25

Study of ASA (alkenyl succinic anhydrides) from fatty acid esters of vegetable oils as paper sizing agents

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New sizing agents from natural origin were obtained by reaction between maleic anhydride and esters from vegetable oils and mainly alkyl oleates. They belong to the alkenyl succinic anhydrides family (ASA).

Paper hydrophobation, which limits water penetration, relies upon the reaction between the hydroxyl fonctions of cellulose and the anhydride moiety of ASA.

Our vegetable ASA (oleo-ASA) are characterized by a maximum composition in C18:1 and a varying terminal ester moiety. More than thirty oleo-ASA were tested as paper sizing agents at laboratory scale. Among them, three oleo-ASA presented a sizing and an emulsion behaviour equivalent to the one obtained with petrochemical ASA, commonly used in industry. Moreover, their hydrolysis in diacid is two-fold slower and their resistance to stripping phenomenon is ten-fold higher. Their use would then allow longer emulsion storage and fewer deposits in air ducts.

These advantages make them excellent candidates to the substitution of ASA from fossil origin. Once the synthesis and purification of the three preceding molecules optimized, one among them has been successfully tested as sizing agent at a 100 kg paper machine pilot scale.

Acknowledgements: Authors wish to thank ONIDOL and ADEME for their financial support.

L26

Use of vegetable oil based thermosetting resins in compound stone Technology

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Unsaturated orthopthalic polyester resins (hereafter indicated as UP resins), dissolved in styrene, are widely used as binders to aggregate stone and other inorganic raw materials in the production of compound stone slabs using vibratory compaction in a vacuum environment, patented worldwide as Bretonstone Technology.

The use of UP resins involves some technical inconveniences: both resin and styrene monomer are oil-based, hence they come from non-renewable sources and their cost mainly depends on the value of crude oil; due to its high volatility rate, styrene is a dangerous chemical, which involves the designing of complex and expensive intake and burning plants.

Many efforts are dedicated to the development of a new organic binder, having similar properties to those of UP resins, which may solve these difficulties.

We have found that chemically modified vegetable oil could be used as new renewable raw material: the epoxidation of vegetable oils with a high iodine number (such as soybean and linseed oil) forms epoxidated oils which are cured with aliphatic dicarboxilic anhydride, preferably in liquid state. The curing process must be accelerated using a basic catalyst. The new resin contains more than 50% by weight of renewable raw materials and contains no volatile organic components.

The properties of both new thermosetting resin and compound stones produced in this way are even better than traditional ones. In fact, the mechanical properties (such as the flexural strength and the water absorption) and the aesthetic effect (valuated technically by the gloss value) of the industrial slab remain constant, but the resistance to weather conditions (evaluated by QUV panel) is increased. The latter feature permits the use of compound stone in many outdoor applications.

L27

Life cycle assessment of high performance polyamides

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Introduction

Although fossil carbon sources make up less than 10% of all materials utilised, there is currently intensive discussion in the chemical industry on the use of renewable raw materials to produce fine chemicals and also monomers for polymer production.

In Brazil, for instance, Braskem and DOW are planning to produce ethylene and then polyethylene from sugarcane-based ethanol. This is just one example of recent attempts to produce known basic petrochemical materials from renewable raw materials.

The approach is somewhat controversial, however, because the starting compound, sucrose, has a carbon to oxygen ratio of 1:1, while the target polyethylene molecule is a pure hydrocarbon. Even assuming maximum theoretical yields, more than three metric tons of sugar are required to produce one metric ton of polyethylene.

On the other hand, synthetic routes based on renewable raw materials to produce basic chemicals had been used industrially for many years, until such plants became uneconomical with the advent of highly cost-effective cracked products from fossil carbon sources. The research effort required for a return to the earlier approach would therefore be fairly small. The slight technological risk exists, however, that it might not be possible to build up the relevant patent portfolio.

In another approach, “new” monomers are produced from renewable raw materials. An example is provided by DuPont's biotechnologically produced 1,3-propanediol. In polyesters such as Sorona and Hytrel, this diol produces materials with new properties. Patent protection for substances and applications is undoubtedly possible here. However, new materials must be entered in the relevant registers of chemicals and launched on the market.

Application-oriented characterisation and market launch of new materials cannot be delayed until the new biotechnological production methods for the relevant monomers become available. A production plant for these monomers must therefore be built, at least on a pilot scale, which allows their synthesis by "classical" chemical methods.

Polyamides from Renewable Raw Materials

Polyamides are a class of materials of which representatives based on renewable raw materials have been known for at least 50 years. Most of these are based on castor oil and its cracked product ricinoleic acid methyl ester.

Boiling with NaOH produces sebacic acid. According to Arnold and Smolinsky(1), pyrolytic cracking at temperatures above 500°C produces 10-undecylenic acid, which is converted in further reaction steps to 11-amino carboxylic acid and PA11. Other representatives of the class of polyamides based on renewable raw materials are PA610 and PA1010, both of which are based on sebacic acid.

In the above processes, significant amounts of by-products and waste are unavoidably produced.

This is why, in the 1970s, polyamides were developed from petrochemical raw materials, which process generates significantly less waste. PA12 is a typical example of such compounds.

Polyamides from Renewable Raw Materials—Back to the Future?

Following the rapid growth of petrochemical-based polyamides during the final decades of the last century, there has been increased interest over the last few years in sustainable products, resulting in intensified marketing of fatty-acid based polyamides as biopolyamides.

At the K'2007, BASF announced the re-introduction of PA610 and DuPont of PA1010. For the last couple of years, Arkema has been advertising its own PA11 as a biopolyamide.

It must be pointed out, however, that the underlying synthetic methods will continue to be based on the above mentioned chemistry, with high proportions of by-products and waste.

Polyamides from renewable raw materials therefore continue to offer promise for the future: The task that lies ahead is to combine the sustainability of renewable raw materials with the sustainability and selectivity of petrochemical production methods.

In this talk we will discuss and compare the various production methods for polyamides. Property profiles of polyamides from renewable raw materials and of their petrochemical analogues will be discussed. First results from a life cycle assessment of different polyamides will be discussed as well. Finally, suggestions will be proposed as to how the sustainability of the resources can be combined with “green” chemistry.

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Abstracts

Part 2: Posters

P1

Catalytic cleavage of methyl oleate or oleic acid

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Introduction

The cleavage of oleic acid via ozonolysis is the industrially applied process for the synthesis of azelaic acid from renewables. Alternatives are in demand due to safety concerns of ozone handling. Recently the authors reported on the epoxidation of methyl oleate with molecular oxygen in the presence of aldehydes.[1] Now the cleavage of oleic acid or methyl oleate using this system and additionally OsO_4 or potassium osmate as catalysts is presented.

Experimental

In a typical experiment, 2 mmol substrate, 7.5 mmol aldehyde, 0.04 mmol OsO_4 or $K_2OsO_4 \bullet 2H_2O$ and 50 mg azobisisobutyronitrile were placed in a 100 ml Buechi glass autoclave and were dissolved in 20 ml of the appropriate solvent. Then the autoclave was pressurized with 4 bar O_2 and stirred at 70-90°C for 1-4 hours. The progress of the reaction was controlled by GC-MS.

Results

Monomethyl azelate **4** ($R=CH_3$) and pelargonic acid **5** were the main products in the Os-catalyzed oxidation of methyl oleate **1** ($R=CH_3$) with O_2/aldehyde besides varying amounts of the epoxide **2** and the diol **3**, whereas azelaic acid (**4**, R=H) was solely obtained from oleic acid (**1**, R=H). However, a comparative application of RuO_4 or RuO_2 instead of Os-catalysts did not lead to cleavage products.

The simultaneous formation of the cleavage products **4** and **5** as well as of the epoxide **2** and the diol **3** is interpreted mechanistically as parallel reactions (route **A**-**C**), this assumption was supported by monitoring the course of reaction. Epoxide **2** seems to be evolved according both to a radicalic and non-radicalic pathway. The formation of **2** in 42% yield by oxidation of methyl oleate in the presence of 2,6-di-tert.-butyl-4-methyl-phenol argues for a non-radicalic mechanism, probably peracid is generated from the aldehyde via Os-catalysis. A further conversion of **2** under these conditions did not lead to **3** but only to a minor degree to 9- or 10-keto derivatives.

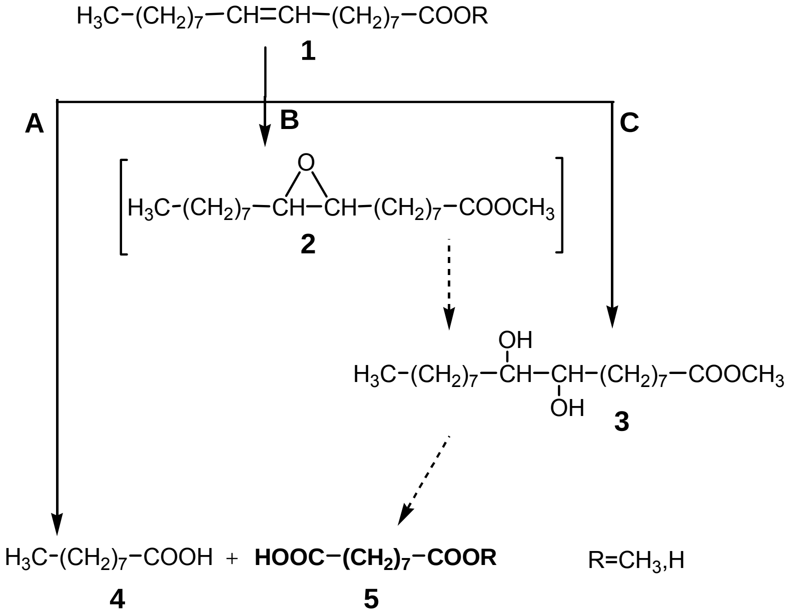

Fig. 1. C=C cleavage of oleic acid or methyl oleate

The diol **3** originated supposably by direct Os-catalyzed dihydroxylation of **1** using in situ-formed peracid. This guess was drawn on the increase in yield of **3**, if the reaction conditions were adapted to known optimal dihydroxylation conditions (e.g. addition of diazabicyclooctane, solvent DMF or MeCN/H_2O/ethyl acetate). A possible acid-catalyzed cleavage of **2** to **3** or of **3** to **4** and **5** was found to a minor degree. The direct cleavage of the double bond of **1** to **4** and **5**, most likely via a glycolate complex, was also presumed to be non-radicalic due to significant amounts of products, even under application of a radical scavenger. Also in that case, the reaction of O_2 with the aldehyde to peracid is likely. On the basis of the experimental results, the reaction pathways **B** and **C** to **4** and **5**, discussed in Figure 1, seem not to be the preferred routes at least. In summary, the obtained yields of **5** (R=CH_3) amounted to 50-70%. Suitable solvents were acetone or dichloromethane, more polar or aqueous-organic mixtures decreased the yield.

If oleic acid was used as substrate under equal reaction conditions, surprisingly only the formation of **4** and **5** in about 50 % yield (non-optimized) was observed.

The authors gratefully acknowledge the Federal Ministry of Education and Research (BMBF) for financial support (FKZ 22003704).

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P2

Heterogeneously catalyzed hydrogen-free deoxygenation of saturated C_8, C_{12} and C_{18} carboxylic acids

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Biodiesel comprises fatty acid methyl esters with various chain lengths. It has clear environmental advantages compared to fossil fuels, nevertheless, some drawbacks rise from its limited shelf life, corrosion in vehicle engines, and lower energy value. These are mainly related to oxygen content of biodiesel, which should be removed. Possible ways for upgrading are pyrolysis [1] or hydrogenation [2,3]. In presence of H_2 and noble metal catalysts (Pd, Ru, Ni) the latter route selectively forms hydrocarbons. Though H_2 addition leads to high yields of desired paraffins, the use of external H_2 sources lowers process economy. A hydrogen-free route may benefit from decomposition of by-product glycerol that generates H_2 in situ. This work focused on model studies to investigate the hydrogen-free deoxygenation of C_8, C_{12}, and C_{18} acids exclusively.

Supported Ni and Pd catalysts (1-10 wt-%) were prepared by impregnation of ZrO_2, active carbon, zeolites, and hydrotalcites. Autoclaves (25 ml) served for catalytic tests. Catalysts were reduced in situ with H_2 (300 °C, 2 h) and the vessel was flushed with N_2. Then, solutions of carboxylic acids in dodecane or tetralin were added and the reaction was started.

Initial catalyst survey was done with lauric acid (C_{12}) at 300 °C. With supported Ni catalysts, highest conversion was found on 10%Ni/ZrO_2 (59 %) and 5%Ni/ZrO_2 (57 %), but alkane selectivity was little. In a second series, Pd catalysts supported on active carbon were tested. The best performing catalyst was 10%Pd/C with 37 % undecane yield at 68 % conversion of lauric acid. Such Pd catalysts then were used for deoxygenation of caprylic acid (C_8) and stearic acid (C_{18}). At similar reaction conditions (300 °C, 6 h), chain length of carboxylic acid has a strong impact on conversion as well as alkane selectivity (caprylic acid: $X = 35$ %, $S = 54$ %; lauric acid: $X = 55$ %, $S = 68$ %, stearic acid: $X = 93$ %, $S = 13$ %). The observed maximum in selectivity may be due to increased cracking as a side reaction, the probability of which increases with number of carbon atoms and bonds. At 300 °C, conversion without H_2 addition may not be favorable for long chain carboxylic acids anymore.

Further work aimed at optimization of reaction conditions with 10%Pd/C catalyst. Raising temperature also was found to have a strong promotional effect on carboxylic acid conversion as well as alkane selectivity. Increasing pressure lowered conversion, but improved selectivity towards alkane. Characterization of spent catalyst 10%Pd/C showed a slight loss in Pd content due to leaching, but no agglomeration of metal particles.

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P3

Flame retardant polyesters from renewable resources via ADMET

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Polyesters are widely used for textile fibers, technical fibers, films, bottles or as a finish on high-quality wood products. The demand of polyesters in 2006 is an estimated 35 million tons and will grow annually by 9%.[1] Due to environmental concerns much work is devoted to the industrial use of products from renewable resources, and for this reason the development of polymeric materials, such as polyesters, from renewable resources has attracted much attention.[2] On the other hand, many kinds of flame retardants (FRs) have been tested to improve the flame retardancy of polyesters and have been applied to commercial products. Among these, phosphorous FR and halogenated FR are the most common. However, many kinds of halogenated FR, especially brominated FR, are restricted in many countries due to the formation of dioxin under combustion. Therefore most of the inherent FR polyesters are now produced using phosphorous FR by blending and/or copolymerizing with flame retardants. However, to obtain efficient flame retardancy by blending, high amounts of the flame retardant agent must be added and usually the polymer properties are affected. Also, when a blended fiber is washed, the blended flame retardants migrate to the fiber surface, leading to decreased flame retardancy and increased danger for the customers. Because of these problems, the copolymerizing method is becoming more common.

Acyclic diene metathesis polymerization (ADMET) has been shown to be an efficient tool for the synthesis of a wide variety of polymers and polymer architectures that are not available using other polymerization methods.[3] Among them, polyesters can be prepared with molecular weights that range between 20.000 and 70.000. In the present work, a renewable phosphorus containing monomer bearing two 10-undecenoic acid moieties has been homopolymerized and copolymerized with a 10-undecenoic acid derived monomer[4] via ADMET using the Grubbs second generation metathesis catalyst. Polymers with Mn up to 65.000 were obtained in absence of solvent. This procedure allowed us to synthesize a variety of polyesters with controlled phosphorus contents which are promising candidates for flame retardant materials.

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P4

Catalytic access to bifunctional products from plant oil derivatives

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Plant oils constitute a class of renewable raw materials which can produce a large variety of chemicals useful for industry. The cross-metathesis of unsaturated fatty esters, derived from seed oils, with functionalized olefins has potential to generate bifunctional compounds, as it has been shown by reactions with acrylates[1]. The objective of our presentation will be to describe, with some practical aspects, the cross-metathesis reactions of both terminal and internal double bond containing esters, arising from seed oils, with acrylonitrile. This metathesis was performed using ruthenium catalysts and led to bifunctional nitrile-esters with high conversions [2]. TON improvement was achieved by slow addition of catalyst.

It will be shown that the metathesis catalyst residue can be used as a hydrogenation catalyst in a sequential cross-metathesis/hydrogenation process leading to saturated nitrile-esters.

The prepared bifunctional nitrile-esters are precursors of amino acid monomers for the production of polyamides from renewable resources.

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P5

Synthesis and Characterization of Surfactants from Renewable Resources

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The conversion of fatty acid with natural hydroxycarboxylic acids, especially malic-, tartaric- and citric acid resulted in the easy formation of acylated hydroxycarboxylic anhydrides. We have shown that this class of anhydrides provides convenient entry into a variety of products. They readily react with natural or synthetic nucleophiles like alcohols, carbohydrates, amines and amino acids. A series of compounds were synthesized and characterized, their surface and antibacterial properties have been measured.

P6

Synthesis of bifunctional monomers via homometathesis of fatty acid Derivatives

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Thermoplastic elastomers consist of two molecular regions, an amorphous region for elastic and a harder crystalline section for thermoplastic properties. Long-chained bifunctional compounds, products of the conversion of fatty acids, can serve as “soft”, amorphous monomer. The synthesis of bifunctional monomers from oleic acid and their derivatives for the production of polymers based on renewable resources is thus useful in the field of thermoplastic elastomers.

Organo-metal-catalyzed metathesis [1] of C18-compounds, based on oleic acid [2], oleic acid esters [3, 4] and other readily available educts from the tenside industry such as oleyl alcohol [5], oleic amide and amines as feedstock can supply the necessary bifunctional monomers for polycondensation. The metathesis of oleic acid provides two olefins, octadec-9-ene and octadec-9-ene-1,18-dicarboxylic acid, both C18 compounds. The homometathesis of oleic acid and derivatives -functionalized fattyω,αtherefore is an interesting way to synthesize acid compounds.

To be applied later in industry, the production of these monomers must be scaled up now. Ruthenium compounds for metathesis belong to a class of extremely efficient catalysts, tolerant to many functional groups. Technical grade educts may provide catalyst poisoning effects. Especially nitrogen-containing compounds present many problems due to their basicity. We report the metathetic synthesis of bifunctional products, based on nitrogen based derivatives. Ruthenium-based homometathesis of oleic acid esters, oleyl alcohol, oleic acid amides and oleyl amines have been conducted. For esters and oleyl alcohol, maximum conversion could be achieved, even with technical grade educts without further pretreatment. Even solvent-free synthesis at low catalyst loadings was possible. The C18-diester was obtained via thin film evaporation, the diol was obtained via precipitation and recrystallization.

Oleyl amine itself could not be converted, but protected amines, like oleyl amides or oleyl n-alkyl-amines can be converted. The metathetical conversion of amides provide a lower yield in bifunctional compounds compared to diester and diol, but is nevertheless interesting, because the diamide precipitates during reaction and is easily isolized via centrifugation and recrystallization.

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P7

Synthesis and evaluation of value added products from Glycerol

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The use of renewable feedstock like Glycerol for producing important industrial chemicals having bulk demand is the priority of 21st century. Glycerol is an important by product of biodiesel manufacturing which is produced by transesterfication during the production of biodiesel fuel. Approximatly 10 kg of glycerol is produced for every 100 kg of oil taken for production of biodiesel. With the total production of biodiesel in thousands of tons, huge amount of glycerol is also produced as a by product. 1 It has been estimated that by 2010 the overall production of glycerol will touch 1.2 million tons. The cost of B100 type biodiesel can be reduced from US$ 0.63 to US$ 0.35 provided the use of glycerol is enhanced for the production of value added products.2 In spite of green origin and over production the scientific community had not been able to fully explore potential usefulness of this naturally occurring molecule for making value added products.
Recently our research group reported synthesis of β-Bromo Glycerol Monoethers directly from α-Olefins by cohalogenation protocol.3 With the continuation of our work we have developed glycerol based pyridinium surfactants and compared its properties with some commercially available surfactants. We found better surface and biological properties such as low cytotoxicity towards animal cell line and better DNA binding capability of new glycerol based cationic surfactants. As the production of cationic surfactants amounts to 350000-500000 tones per annum.4 The replacement of commercially available cationic surfactants with new glycerol based surfactants will check loss of energy and resources due to over production of glycerol.

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P8

New Polymers from Plant Oil Derivatives and Styrene-Maleic Anhydride Copolymers

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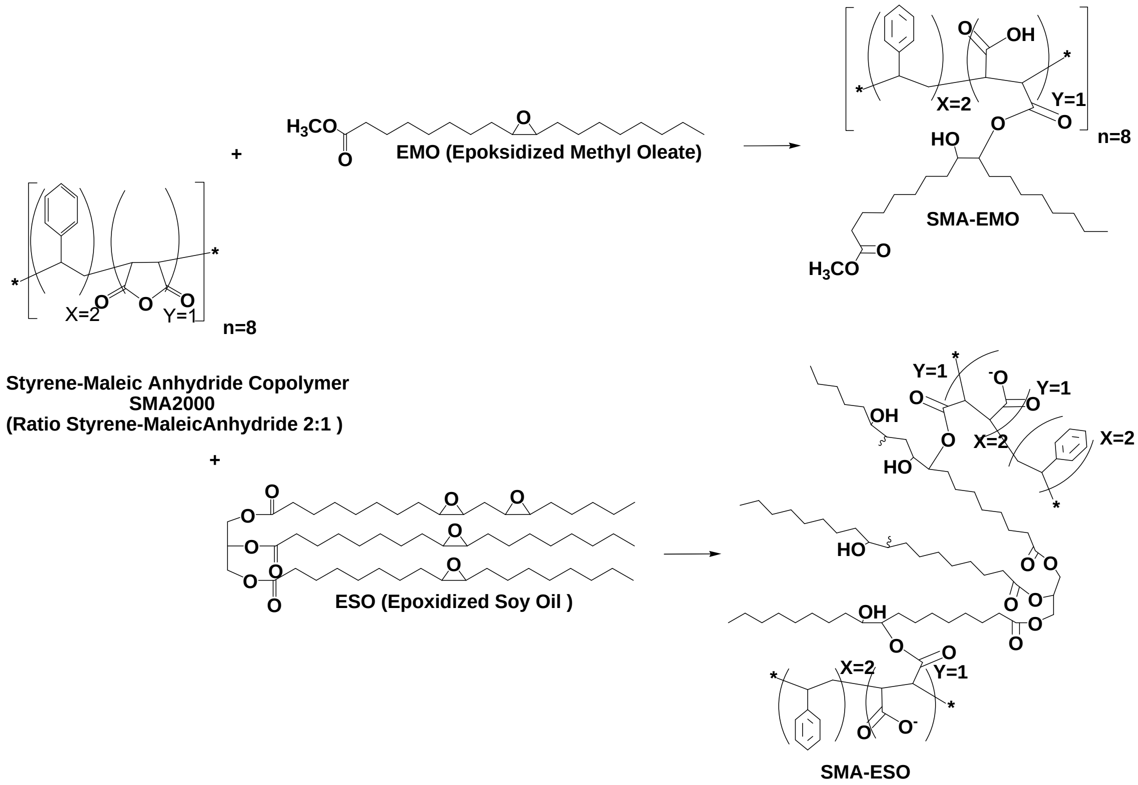

Polymerization of triglycerides is usually carried out by attaching a polymerizable group to the triglyceride [1]. Polymers derived from such monomers have low connectivity and low mechanical properties due to the bulky structure of the monomer. This manifests itself in low fracture toughness of the polymers obtained. In this work we changed our strategy by starting first with a suitably substituted polymer having a reasonable molecular weight and attaching the triglyceride derivative to it. This strategy is bound to provide molecular weights that are higher and provide the entanglement lengths needed for higher fracture toughness.

In this study, styrene maleic anhydride copolymer (SMA2000, Styrene:Maleic Anhydride 2:1) is grafted and/or crosslinked with epoxidized methyl oleate, epoxidized soybean oil, methyl ricinoleate, castor oil and soybean oil diglyceride. Base catalyzed epoxy-anhydride and alcohol-anhydride reactions were carried out by using the anhydride on SMA, the epoxy or secondary alcohol groups on the triglyceride based monomers. The characterizations of the products were done by DMA, TGA and IR spectroscopy. SMA-epoxidized soy oil and SMA-castor oil polymers are crosslinked rigid infusible polymers. SMA-epoxidized soy oil and SMA2000-castor oil showed Tg’s at 70 and 66 ºC respectively. Dynamic moduli of the two polymers were 11.73 and 3.34 Mpa respectively. SMA-epoxidized methyl oleate, SMA-methyl ricinoleate and SMA-soy oil diglyceride polymers were soluble and thermoplastic polymers and were characterized by TGA, GPC, DSC, NMR and IR spectroscopy.

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P9

Chain Extension Reactions of Unsaturated Polyesters with Epoxidized Soybean Oil

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Unsaturated polyesters were chain extended with epoxidized soybean oil. The molecular weight increase was monitored using Gel Permeation Chromatography. The obtained polymer was characterized by FTIR and 1H-NMR, styrene solubility and gel time. The chain extended polyester was then diluted with styrene and cured with a radical initiator and compared to a commercial reference polyester. Thermal and mechanical properties of the cured polyester were characterized by DMA and TGA. The results show that unsaturated polyesters can be chain extended with epoxidized soybean oil which substantially shortens the condensation polymerization during manufacture, without compromising their thermal and mechanical properties.

P10

Soybean Oil Based Isocyanates: Synthesis, Characterizations and Polymerizations

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Isocyanates are valuable compounds that are used widely in many application areas of polymer industry. The most important area of use of isocyanates is to synthesize polyurethanes and polyureas. Important isocyanates, used in the polyurethane manufacturing, are 2, 4-toluene diisocyanate (2,4TDI), 2, 6-toluene diisocyanate (2,6TDI), 4, 4'-diphenyl methane diisocyanate (MDI), 1, 6 hexamethyl diisocyanate (HMDI), xylene diisocyanate (XDI), and isophorone diisocyanate (IPDI), all of which are petroleum derived [1-3].

Isocyanates can be synthesized in many ways. The Curtius, Hoffman and Lossen rearrangements, which may involve nitrene as an intermediate, are not succesful for large scale operations [4].

Literature search reveals a number of bio-based polyurethanes. In almost all of them, castor oil was used as a polyol source and petroleum based isocyanates were used as the isocyanate [5-12]. There are no examples where the isocyanate is bio-based. With the simple synthesis described in this work it is possible to obtain polyurethanes where both the isocyanate and polyol are bio-based.

In the first strategy, soybean oil isocyanates were obtained by substitution reaction between allylically brominated soybean oil and AgNCO [13]. In the second strategy, soybean oil was reacted with iodine isocyanate reagent [14-15]. Addition of iodo isocyanate to plant oils gives valuable intermediates. Similar to thiocyanogen addition, just one mole iodo isocyanate can be added to one mol of polyunsaturated fatty acids. This means that one mole unsaturated plant oil triglyceride can bind around three mol iodo isocyanate easily. Many positional isomers are obtained at the end of the both reaction. The products are valuable intermediates to synthesize poly-urethanes and poly ureas. Synthesized soybean oil isocyanate and iodo isocyanate were polymerized with castor oil and glycerol. Castor oil and glycerol polyurethane of soybean oil iodo isocyanate showed tensile strength of 140 KPa and 270 KPa respectively. On the other side, polyurethanes of soybean oil isocyanate with same triols showed tensile strength of 100 and 125 KPa respectively

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P11

Aliphatic ß-chlorovinylaldehydes as versatile building blocks in syntheses of Heterocycles

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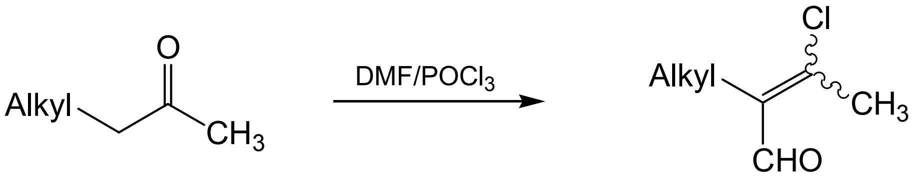
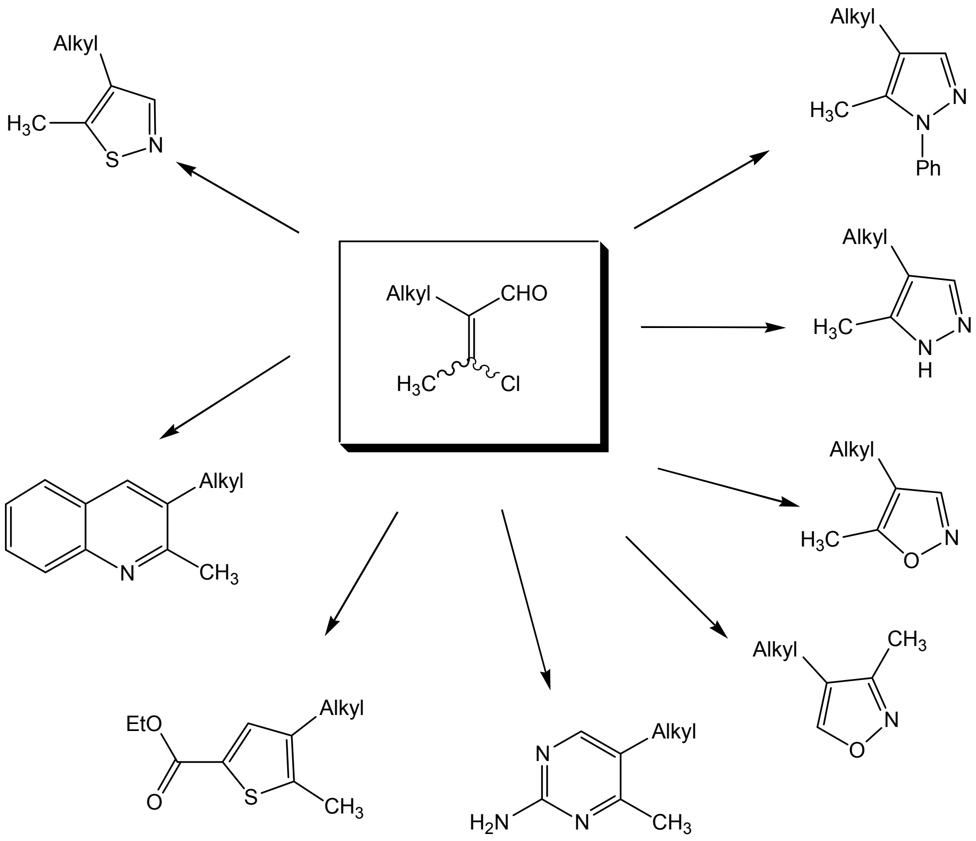
Aliphatic ß-chlorovinylaldehydes are readily prepared from alkyl methyl ketones using Vilsmeier-Haack-Arnold reaction.



A survey of the literature often shows complex reactions by great expending time and resources for getting aliphatic substituted heterocycles. On the other hand such compounds can easily synthesize from ß-chlorovinylaldehydes by reaction with O-, N- and S-nucleophiles. So we synthesized a variety of heterocyclic systems like isothiazoles, pyrazoles, quinolines, isoxazoles, thiophenes and pyrimidines.



A survey of the literature let us expect that these compounds have a broad spectrum of useful biologically activity. It is of interest that aliphatic ß-chlorovinylaldehydes show a different reaction behavior compared with those described in the literature. In this poster we will report experimental details on syntheses and spectroscopic studies of the described compounds.

P12

Syntheses and reaction behavior of long-chained alkyl methyl ketones starting from fatty acids, fatty alcohols and fatty nitriles

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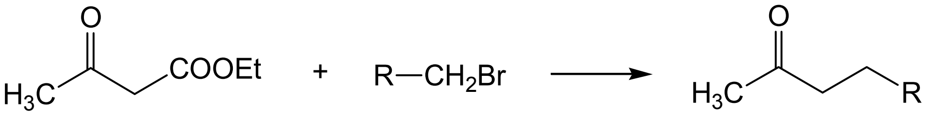
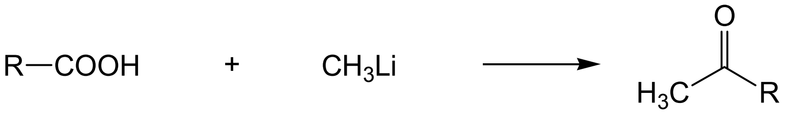
There are well known a lot of methods for preparation of fatty ketones. Long-chained alkyl methyl ketones can also prepared from different fatty compounds using the following reactions.



(A)



(B)

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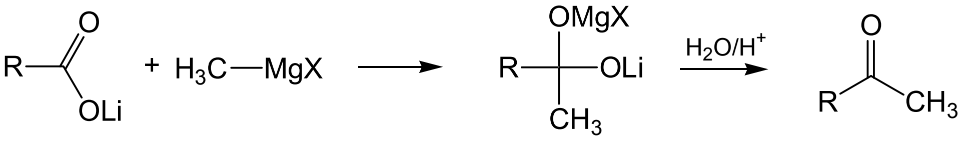

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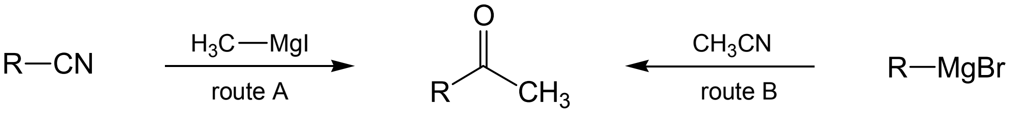
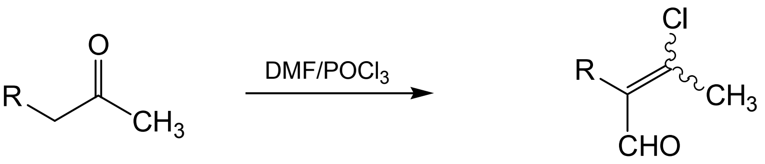


(E)

We investigated the synthesis of long-chained alkyl methyl ketones systematically in order to optimize reaction conditions, yields and purity of the products.

We also report in this poster about new applications of the microwave technology to transform fatty acids derivatives and fatty alcohols into long-chained alkyl methyl ketones. These compounds are versatile building blocks to synthesize long-chained substituted ß-chlorocrotonaldehydes.



P13

Hydrophobic modification of Inulin in aqueous media using alkyl epoxides and basic catalysis

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Inulin, the polydisperse reserve polysaccharide from chicory, has been modified with fatty epoxy derivatives of different chain length in high alkaline aqueous media. Etherification of inulin has been carried out with high efficiency. The influence of several reaction parameters such as amount of organic co-solvent, catalysts, reaction time and temperature has been studied. After purification, emulsion power of the final products was tested, considering these products as promising green polymeric surfactants.

P14

Short Chain Sugar Amphiphiles: Alternative Oil Structuring Agents

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Owing to the need of developing environmentally benign functional materials by adopting green chemistry methods, usage of biorefinery concept for the development of biobased molecular building blocks of such materials has emerged as a prime focus of the current research. The present study focus of developing sugar based low molecular weight gels (a type of functional soft materials) by enzyme catalysis exemplifies the above approach. The underexplored open chain sugars (sugar alcohols) were chosen as hydrophilic moieties to develop low molecular weight gelators (LMWGs). Mannitol, sorbitol and xylitol were selected as representative sugar alcohols (headgroups) and series of amphiphiles were synthesized by attaching hydrophobic carboxylic acids at one-end of the sugar using an enzyme-mediated regioselective transesterification reaction. For control tuning of hydrophobicity various carboxylic acids different chain length were attached (typically (CH2)4-14). The resulting amphiphiles were studied for their self-assembling behavior in organic liquids. Only the amphiphiles with short chains {(CH2)4-8} were found to be efficient organogelators; immobilizing various solvents ranging from crude oil fractions to vegetable oils. In addition, Effect of chiral and structural variations in sugar amphiphiles on microstructure formation (responsible for immobilization of organic liquid) was also investigated in detail. Furthermore, the efficiency of the short chain sugar amphiphiles as a healthy alternative structuring agents for vegetable oils compared to existing oil structuring agents was studied and has been demonstrated in this report.

P15

Novel enzymes for lipid modification

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Enzymes have received considerable and increasing attention in lipid modification over the last few years. In particular, hydrolases have a high potential for applications such as the lipases-catalyzed interestification [1, 2] as an alternative for the hydrogenation of fats or the preparation of designer-fats [3].

Many enzymes, however, do not fulfill all demands of a technical process. Properties such as stability under process conditions or the chemical selectivity leave often much to improve. Together with this growing demand for tailor-made lipases goes the increasing knowledge about the molecular structures. Considerable progress in molecular biology techniques has made the cloning and expression of lipases in bacteria and the subsequent improvement by techniques of state-of-the art protein design [4] possible.

An alternative for the improvement of enzymes by protein design represents the screening for novel enzymes. The limited number of commercially available lipases can be extended by high-throughput screening in enzyme collections. Enzymes from metagenome represent a rich source for this purpose.

Herein we present an outline and the scope of both techniques that can provide novel biocatalysts for new applications in lipid-modification.

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P16

Production of fine and bulk chemicals using silage as a renewable resource

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The presented work aims for the use of silage as a renewable resource for the fermentative production of bulk- and fine chemicals and is a cooperation with the Institute of Thermal Process Engineering at the University of Kaiserslautern and the Institute of Biochemical Engineering at the Saarland University.

In 2006 321,300 ha of farmland were used for the production of grass and clover, yielding 36,268,000 t of harvested grass clip. Thus, grass clip provides an enormous potential as renewable resource in Germany. Since fresh grass clip is available only during summer and it decays if stored inappropriately, it is conserved by ensiling.

In the ensiling process, the water-soluble carbohydrates are fermented to lactic acid, resulting in a pH-shift and thus the conservation of the silage. The processes in development are to use the remaining carbohydrates, including cellulose and hemicellulose, as well as the lactic acid produced during ensiling. Aspired products are ethanol, 1,2-propanediole, itaconic and succinic acid. Remnants and wastes of the processes should be reuseable as animal food or in biogas production, resulting in a complete substantial and energetic utilisation of the silage.

In the presented work two strategies for the utilization of silage are pursued:

First, a silage juice containing the water-soluble carbohydrates and the lactic acid is won directly from the silage by pressing. This silage juice can either be used directly as a cultivation medium or by the isolation of the contained lactic acid, the main product of ensiling, and its further use.

Secondly, the hydrolysis of the celluloses and hemicelluloses contained in the silage is aspired. After the separation of solid and liquid phases the latter, a mixture of organic acids produced during ensiling and pentoses and hexoses released during hydrolysis, is fermented.

Taken together the described work is able to offer an all-season renewable resource for the production of base and fine chemicals and to increase the value of an agricultural product respectively to improve the economics of biogas production.

The Project is funded by the Fachagentur für Nachwachsende Rohstoffe (22025407 (07NR254)).

P17

Enzymatic degradation of pre-treated wood

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The economic dependency on fossil fuels and the changes of climate due to them has led to an intensive search for renewable resources for the production of chemicals and fuels. At present there are several processes established which use sugar cane and corn for the production of bioethanol. As these crops are commonly used as food there is an ethical drive to use alternative resources for industrial processes. Promising feedstock for the chemical and fuel production are in this context the fermentable sugars derived from wooden celluloses and hemicelluloses by enzymatic hydrolysis. The great challenge in this regard is to design new simple and beneficial processes that can compete against conventional petrochemical production processes.

The most important step in these processes is the hydrolysis of the lignocellulosic material into the corresponding sugar monomers, which can be fermented to ethanol for example. The aim of the presented work is to optimize the enzymatic hydrolysis with regard to the used substrates and the usage of hydrolysates for the fermentation of alcohol. The substrates are cellulose and hemicellulose fractions obtained by thermo-chemical pre-treatment of beech wood. This pre-treatment is carried out by our project partner at the Johann Heinrich von Thünen Institute, Hamburg, Germany.

Several commercially available enzymes, even thermo stable ones were tested on their ability to degrade these fractions. In first experiments it could be shown, that the enzymes can hydrolyse up to 40 % of the cellulosic fraction into fermentable sugars within 24 h. The hemicellulosic fraction already contains some monomeric sugars which can be fermented. For this fraction the use of hemicellulases is investigated. All sugar containing hydrolysates and fractions were tested for their suitability as carbon source for a co-fermentation of two different yeasts to produce ethanol. The results showed that the addition of a nitrogen source, vitamins and trace-elements is the only necessary preliminary step for the fermentation. To increase the yield of sugars in the hydrolysates further optimizations were made, e.g. the increase of substrate concentration and the amount of added enzymes was investigated.

P18

PA X,20 from renewable resources via metathesis and catalytic amidation

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Polyamides (PA) are engineering plastics with various commercial applications due to their outstanding properties such as high durability, high hardness and rigidity [1]. Methods for the production of polyamides by polycondensation of aliphatic diamines and dicarboxylic acids or the polyaddition of lactams are often described in the literature. These articles are mostly dedicated to standard polyamides based on depleting fossil resources. However, bio-based polyamides are not yet well developed. The unique example of industrially produced 100% bio-based polyamide is the AB-type polyamide-11 [2]. Synthesis of 100% bio-based AABB type polyamides are not expected because of the non-availability of bio-based diamines. Meanwhile, research on routes to obtain diacids from glucose (adipic acid) or vegetable oils (azelaic acid, sebacic acid) for the production of partially biobased polyamides-6,6, -6,9, and -6,10 are under investigation [3].
Among various polycondensation methods, acyclic diene metathesis (ADMET) polycondensation is useful in the synthesis of a veriety of polymer architecures that would otherwise be difficult to obtain [4]. The main goal of this study is to describe the synthesis of unsaturated polyamides that can be obtained from plant oil derivatives via two different approaches. First, long chain aliphatic α,ω dienes with two symmetrically spaced amide segments were polymerized via ADMET polymerization. Secondly, E-dimethyl-eicos-10-enedioate, a bio-based unsaturated monomer that was obtained via metathesis and other reactions from castor oil, was polymerized with different aliphatic diamines using strong organic bases, such as TBD, as catalysts. Both reaction pathways led to PA X,20 and the two different routes were investigated, optimized and comapred to one another. Moreover, the properties of the resulting polyamides were investigated revealing that these long-chain polyamides are well applicable as engeneering plastics and that their properties depended on the structure of the applied monomers, as expected. Last, but not least our investigations led to new synthetic approaches that allow for the synthesis of ABA type polyamide block-copolymer with interesting application possibilities.

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P19

DERIVATIVES OF VEGETABLE OILS AS COMPONENTS OF HYDRAULIC FLUIDS

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Though not total loss lubricants, hydraulic fluids have been classified as “high risk loss” lubricants - they are used in large volumes in equipment that is susceptible to spills. The hydraulic fluids currently used in Latvia in wood harvesting and other environmentally sensitive areas still are mainly based on mineral oils. Completely different is situation in other EU countries, e.g., in Sweden, where the Swedish standard SS 155434 for biodegradable hydraulic fluids is a legal requirement. There is an obvious need for elaboration of formulations of hydraulic fluids based on renewable natural resources in order to initiate and to promote production of such products in Latvia.

Hydraulic fluids of harvesters should operate at temperature C and under high pressure (180-200 atm) till°C up to 70-100°range -25 change-over after 800-1200 operating hours. The main problems of biodegradable hydraulic fluids based on vegetable oils are their low hydrolytic, thermal and oxidative stability, as well as bad low-temperature fluidity and shear stability.

The biodegradable hydraulic fluids of harvesters available nowadays on market are much more expensive than their mineral oil based analogues and often can not fulfill technical requirements set; due to this, new and cheaper technologies are developed using renewable base stocks. Investigations regarding new base fluids as well as new additives are very topical.

We used rapeseed oil, its methyl- and ethylesters (RME and REE, correspondingly), by-products of biodiesel production - mixture of free fatty acids, mono- and diglycerides - as raw materials for creation of biodegradable hydraulic fluids. Following basic components for hydraulic fluids were synthesized:

- Esters of fatty acids of rapeseed oil and polyols:
  - NPE - esters of neopentyl alcohol,
  - TMPE - esters of trimethylolpropane,
  - PEE - esters of pentaerythritol.
- Estolides of rapeseed oil and their ethylhexylesters.

Several derivatives of glycerol and fatty acids were prepared as potential additives for improvement of technical parameters of new compositions:

- Ethers of glycerol, obtained from:
  - glycerol and epoxydized rapeseed oil,
  - glycerol and mixture of epoxydized rapeseed oil fatty acids and mono-, diglycerides (formed as a by-product in biodiesel production).
- Polyhydroxycompounds, obtained from epoxydized RME.

C, as well as°C and 100°We determined kinematic viscosity at 40 viscosity index, oxidative stability, cold-flow properties, acid value, foaming, air release, flash point of elaborated compositions. The most of tested parameters corresponded to requirements, but low temperature fluidity after 7 days were unsatisfactory – addition of temperature depressants (e.g., Lubrizol 7671A) improved this parameter. We used TBHQ as oxidation inhibitor, Lubrizol 7671A as pour point depressor and polymethylsiloxane as antifoam agent in rapeseed oil based formulations.

P20

ULTRASOUND PROMOTED ETHANOLYSIS OF RAPESEED OIL

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Biodiesel usually is produced by transesterification of various vegetable oils or animal fats with methanol. Unfortunately, methanol is highly toxic and harmful to human health. Application of bioethanol instead of methanol would lead to more environmentally friendly production technology which almost completely would be based on renewable resources. Currently in Europe there are no biodiesel producers using ethanol as a raw material, nevertheless FAEE (Fatty Acid Ethyl Esters) is used as biodiesel in Brazil. Mandate to CEN for standards for FAEE for use in diesel engines and heating fuels (M/393) was set in 2006.

Previously we explored optimization of the synthesis of rapeseed oil ethyl esters (REE) using anhydrous ethanol and dehydrated ester-aldehyde fractions of ethanol rectification [1]. We were interested to study possibilities of biodiesel preparation from locally produced bioethanol. Therefore our aim was to establish optimal conditions for synthesis of rapeseed oil ethyl esters (REE) by transesterification of oil with bioethanol produced by distillery “Jaunpagasts Plus” from the local wheat. Experiments were carried out at room or higher (75-80oC) temperature; duration of reaction and amount of catalyst were varied. The best results were obtained when reaction was run 1 h at room temperature in the presence of 1.3-1.7% KOH catalyst (from oil mass). When reaction was run at room temperature, yield of biodiesel reached just 71-82%. Therefore we repeated the reaction, adding catalyst-alcohol solution in two steps. The best result (yield of reaction 97%) was reached, when total amount of added potassium hydroxide was 1.5%.

Secondly, we have established optimal conditions for production of REE using ultrasonication, as it is well known that ultrasound assisted transesterification of fatty acids proceed more quickly [2] allowing replacement of batch processing with continuous flow processing and reduction of investment and operational costs. Results of our experiments showed that duration of reaction can be reduced to 0.5 h - twice in comparison with classical method.

Traditional workup process of REE with orthophosphoric acid and water lead to hardly separable emulsion. Therefore we applied Magnesol for purification of REE. Biodiesel treated with Magnesol corresponds to requirements of standard LVS EN 14214 and this method is simpler than workup with acid and water.

We managed to prepare REE with 97% yield in two steps reaction of rapeseed oil with bioethanol of local origin. Also we succeeded to reduce a duration of reaction by ultrasonication (24 kHz) from 1 h to 0.5 h. Simplification of REE purification was reached by application of Magnesol. The technical parameters of our REE corresponded to requirements of LVS EN14214 set for biodiesel.

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P21

From Glycerine via Acetals to new Amphiphils

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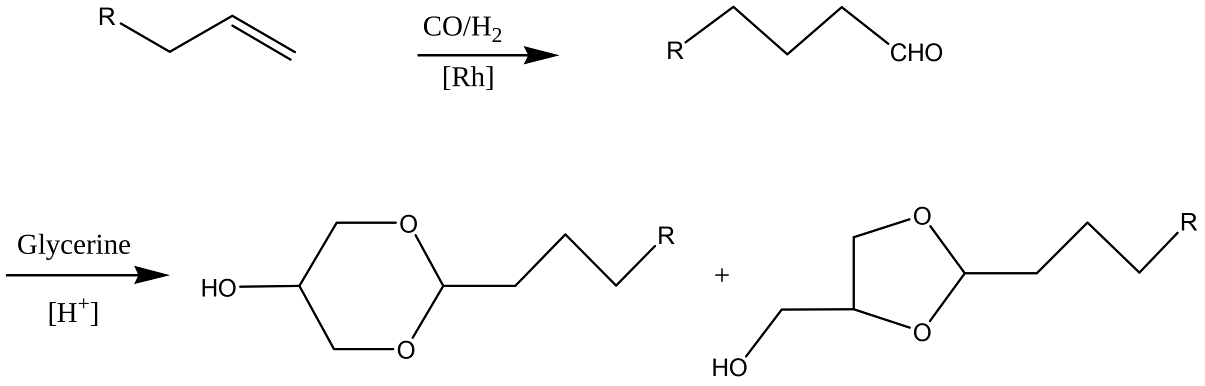
Bis 2010 wird die Herstellung von Biokraftstoffen aus nachwachsenden Rohstoffen weltweit kräftig gesteigert. Natürliche Ole und Fette werden zu Biodiesel umgeestert und bis zu 6 Millionen t Glycerin werden auf dem Weltmarkt zusätzlich erwartet [1]. Die gegenwärtigen Anwendungsgebiete für Glycerin können diese Produktmengen nicht aufnehmen, deshalb werden weltweit neue marktfähige Produkte auf Glycerinbasis gesucht.[2-4]

ZIEL :

Glycerin als ein billiges Massenprodukt muss mittels chemischer Stoffwandlung in verkaufsfähige Produkte gewandelt und auf dem Weltmarkt abgesetzt werden [2 – 4].

Ergebnisse :

Die Hydroformylierung von Olefinen führt zu Aldehyden, Aldehyde reagieren mit Glycrerin zu Acetalen [5] (Gl. 1). Die Acetale enthalten Hydroxylgruppe, die für eine Umsetzung z. B. mit Säure und -derivaten zur Bildung von neuartigen Amphihilen genutzt wird.



Gl. 1

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P22

BIOBASED SEGMENTED POLYURETHANES FROM METHYL OLEATE BASED POLYETHER POLYOLS

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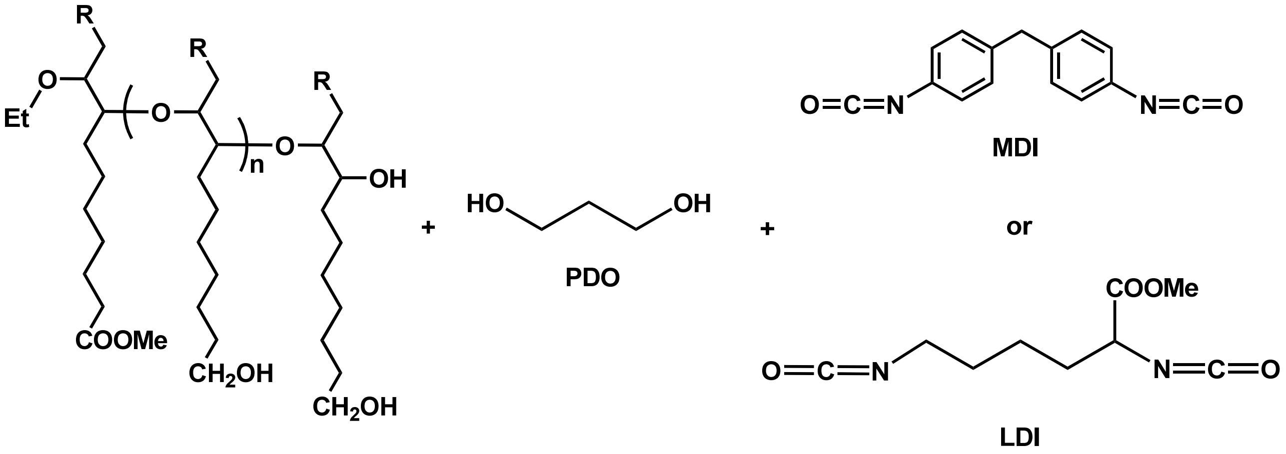
In the polyurethane industry, conventional polyether polyols are mostly produced from petroleum-based alkylene oxides. Due to uncertainty about the future cost of petroleum, as well as the desire to move toward more environmentally friendly feedstocks, many recent efforts have focused on replacing all or part of the conventional petroleum-based polyols with those made from renewable resources such as vegetable oils. In addition, it is a challenge to use diisocyanates derived from aminoacids, making possible to produce polyurethanes completely from renewable resources.[1-3]

In this work we report the synthesis and characterization of polyether polyols from methyl oleate. The coordinative ring opening polymerisation of epoxidized methyl oleate yields a linear polyether with Mn= 6.500 Da. The controlled reduction of the carboxylate groups allows to obtain a set of polyether polyols with different primary hydroxyl contents. Depending on the degree of reduction the polyols can have different properties and, when converted to polyurethanes, may impart different properties to the final product.



These renewable polyols react with 4,4’-methylenebis(phenyl isocyanate) (MDI) or L-lysine diisocyante (LDI) to yield polyurethanes with different crosslinking density. Moreover, we carried out the reaction of the polyetherpolyol with the isocyanates and 1,3-propanediol as chain extender to obtain segmented polyurethanes with different hard segment contains. These materials were characterized by infrared spectroscopy (FTIR/ATR), differential scanning calorimetry (DSC), termogravimetric analysis (TGA) thermodynamomechanical analysis (DMTA), scanning electron microscope (SEM) and X-Ray difraction.

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P23

DETAILED STUDIES OF SELF- AND CROSS-METATHESIS REACTIONS OF FATTY ACID METHYL ESTERS

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Self- and cross-metathesis[1] reactions with oleochemicals offer the potential to obtain value added chemical intermediates from plant oil renewable resources.[2,3] Here, the self-metathesis (SM) of methyl undec-10-enoate (1) as well as its cross-metathesis (CM) with methyl acrylate (MA) was investigated in detail by systematically varying the applied reaction conditions. The thus resulting unsaturated α,ω-diesters with a chainlength of 20 and 11 carbon atoms, respectively, have a large potential from the synthesis of polyesters as well as polyamides from plant oil renewable resources.[4] Hence, four different metathesis catalysts were investigated under solvent-free conditions at catalyst loadings ranging from 0.1 to 1 mol % and at temperatures ranging from 30 to 70 °C. All reactions were followed by GC and/or GC-MS in order to evaluate the conversion as well as the selectivity of the reactions. In the case of the SM reactions good to excellent conversions were obtained with all catalysts, but the second generation metathesis catalysts revealed high amounts of olefin isomerisation side-reactions.[5] In general, these SM reactions were highly reproducible, but at low catalyst loadings and low temperatures sometimes large variations in the observed conversions were obtained. This was not the case for the investigated CM reactions. Here, also good conversions and CM yields were observed, if second generation metathesis catalysts were applied. Quite interestingly, these reactions showed a better reproducibility and the olefin isomerisation of the also observed SM products was almost completely suppressed. Moreover, due to these optimizations we were able to run these CM reactions with a 1:1 ratio of the reactants and low catalysts loadings, which is an improvement over described literature procedures.[3]

Thus, in summary, we report on the detailed investigation of the described SM as well as CM reactions leading to new and optimized reaction conditions for the productions of unsaturated α,ω-diester monomers from renewable raw materials.

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P24

Temperature dependant double bond isomerization side reactions during ADMET polymerizations studied with a monomer from renewable resources

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Acyclic diene metathesis (ADMET) polymerization has developed into a very versatile technique for the preparation of a variety of macromolecular architectures, including linear polymers [1,2], polymers with a defined degree of branching [3], telechelics as well as block-copolymers [4,5]. Recently, the technique was also applied to monomers with a functionality > 2, thus resulting in hyperbranched macromolecules from AB2, AB3, and A3 monomers with B1 chainstoppers, respectively [6,7]. 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 [8].

Within this contribution, the utilization of plant oils as renewable raw materials for monomers and polymers will be discussed. Therefore, the synthesis of a novel and degradable monomer from fatty acid derivatives will be described and its subsequent ADMET polymerization discussed in detail. We will focus our discussions on the investigation of double-bond isomerization side-reactions occurring during these ADMET polymerizations. Therefore, the resulting polyesters were transesterified with methanol in order to investigate the nature and the amount of isomerization side-reactions that occurred during the polymerizations by GC-MS. These investigations revealed that the Grubbs first generation catalyst does hardly show any side reactions up to a polymerization temperature of 90 °C, whereas the second generation catalyst from Grubbs showed up to 75% isomerisation side reactions depending on temperature as well as other polymerization conditions. This study represents the first quantitative study of isomerisation side reactions during ADMET polymerizations and will therefore help to tailor polymeric architectures prepared via this technique.

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P25

Reducing the Environmental Impact of Olefin Metathesis Reactions

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As with most catalytic processes, olefin metathesis was discovered by accident as a result of the study of Ziegler polymerizations with alternate metal systems.[1] The recent development of ruthenium olefin metathesis catalysts with high activity and functional group tolerance has expanded the scope of this reaction to synthesize organic compounds and to form new C-C bonds.[2,3] Many variants of this very useful and versatile reaction have been developed in the meantime including self-metathesis (SM), cross-metathesis (CM), ring-closing metathesis (RCM), ring-opening metathesis (ROM), ROM polymerization (ROMP) as well as acyclic diene metathesis polymerization (ADMET).[2,3] Within this project three reactions were investigated, which were suggested by the Nobel Prize laureate R. H. Grubbs as a useful, general and easily applicable platform for catalyst evaluation: CM of allyl benzene with excess cis-1,4-diacetoxy-2-butene, CM of methyl acrylate with 5 hexenyl acetate and RCM of diethyldiallyl malonate.[4] As also typically described for other olefin metathesis reactions, these reactions were performed in the organic solvent dichloromethane, which is toxic and environmentally unfriendly. Since the aim of this project is to optimize the reaction conditions for these reactions and to avoid the use of toxic solvents, we studied these reactions in detail at different concentrations in two solvents as well as in bulk. Dichloromethane and an environmentally friendly fatty acid derived solvent were used for comparison. Our studies clearly showed that the mentioned reactions can be performed in bulk, thus completely avoiding organic solvents and thus highly reducing the environmental impact of such reactions. As a very positive side effect, the reactions in bulk usually required less catalyst and often provided better conversions than their counterparts in organic solvent, most likely due to the higher concentration of the reactants. Moreover, our studies also revealed that methyl esters of capric and lauric acid are suitable non-toxic and thus environmentally friendly solvents for the investigated olefin metathesis reactions.

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P26

An approach to renewable Nylon-11 and Nylon-12 via olefin cross-metathesis

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In ages of depleting fossil reserves and increasing emission of green house gases it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. Especially plant derived 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 resources in a straightforward fashion taking full advantage of nature's synthetic potential.

Here, new approaches for the synthesis of monomers from plant oils as renewable resources[1] via olefin metathesis[2,3] will be discussed. In particular, the synthesis of α,ω-difunctional chemical intermediates from renewable resources via the cross-metathesis reaction of fatty acid methyl esters with allyl chloride is described.[4] Different ruthenium metathesis catalysts were investigated and the reaction conditions were optimized for high conversions in combination with high cross-metathesis selectivity. New building blocks and chemical intermediates from fatty acid derivates were thus obtained in catalytic reactions with low catalyst loadings under bulk conditions. Therefore, a new potential use of renewable raw materials for the synthesis of intermediates for Nylon-11 and Nylon-12 was demonstrated.

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P27

Ultrasonic assisted finishing of cellulose fiber by fatty acid amide derivatives

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The processing of textiles to achieve a particular handle is one of the most important aspects of finishing technology. Softeners and fatty acids improve soft handle, smoothness, elasticity, hydrophilic, antistatic and soil release properties on textiles. Fatty acid amide derivatives are commercial textile softeners used to improve softness of fibers surface.

In this research, cotton fabric was used as substrate and it was first scoured with nonionic detergent to remove any impurities. The fabric was then treated with anionic, nonionic and cationic fatty acid amide derivative softeners in water including 15 g/l at 30ºC for 30 minutes using ultrasonic energy during treatment. The treated fabrics were then dried/cured at 130ºC for 40 seconds. Some of the physical properties of the fabrics treated under ultrasound and those treated without ultrasonic energy, were compared and discussed.

As the results show, treatment of fabrics with softeners under ultrasound is more effective compared to conventional method.

P28

Hydrolysis of nylon 6 with proteolytic enzyme

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Nowadays, textile processing based on biotechnology has gained importance in view of stringent environmental and industrial safety conditions. The best established application of biotechnology to textiles is the use of enzymes. These vital parts of all living organisms are organic catalysts with specific in the reaction catalyzed and substrates selectivity. Traditional chemical treatments are replaced by enzymes because of their lower product quality, higher manufacturing cost, affecting some favorable bulk properties of textiles, not easily controlling, creating harsh conditions, undesirable side effects and/or waste disposal problems, more waste, high odor process for workers and added energy consumption in textile industry. The main enzymes used in textile processing are amylases, cellulases, proteases, esterases, nitrilases, catalases, peroxidases, laccases and pectin-degrading enzymes.

Nylon 6 fabrics were first treated with different concentrations of subtilisin enzyme in aqueous solutions containing 1, 2, 4 and 6% for 80 min at 30ºC. The dyeing process was then carried out on the treated fabrics with disperse dye. A UV–Vis. spectrophotometer was used for determination of dyebath exhaustion. Disperse dye showed higher exhaustion on the enzyme treated samples. The intensity of major peaks in FTIR spectra of protease treated samples are in favor of chemical changes of the polypeptide fabric. The results of color measurement in the CIELAB system showed that the darkness of the samples increased with an increase in the enzyme percentage in the solution. The wash and light fastness properties of samples were measured according to ISO 105-CO5 and Daylight ISO 105-BO1 and discussed.

P29

Comparing finishing of polyester fibers with micro and nano emulsion silicones

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The processing of textiles to achieve a particular handle is one of the most important aspects of finishing technology. Softeners are one of the main compounds in finishing process and can improve some properties of textiles, depending on the chemical nature, including soft handle, smoothness, elasticity, hydrophilic, antistatic and soil release properties. They are classified according to their ionic character and the main classes are: anionic, cationic, nonionic, amphoteric, reactive and silicone. Macro- and micro-emulsion silicone softeners are commercial classes of softeners but nano-emulsions are new class of softeners in textile industry. The purpose of this research was to study the effect of micro and nano-silicone softeners on different properties of polyester fiber.

Polyester fabrics were first scoured with nonionic detergent and were then treated with three concentrations (10, 20 and 30 gr/lit) of micro and nano-emulsions of silicones. The drape length of treated samples with 10 gr/lit of solution was decreased and more decrease was observed with increase in silicone concentration. Colorimetric properties of softener treated fabrics were evaluated with a reflectance spectrophotometer. Nano-emulsion silicones changed a little the surface reflectance of fibers compared to micro-silicone softener. Increase in weight of all samples was observed which shows the coating of silicones on fiber surface. Nano-emulsion silicones showed better results on samples treated compared to micro-emulsion silicones.

P30

PIBOLEO project: Eco Innovative process for multi-functional bi-oleothermal treatment for wood preservation and fire proofing

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Although they are usually quite effective, typical wood treatments are not necessarily very environment-friendly, in terms of the treatment itself and of the active substances used (flame retardants, biocides). In this day and age, as the ecological aspects are becoming more and more important, many research projects aim at improving wood treatment in an environment-friendly manner.

In France a simple bi-oleothermal© process has been developed by CIRAD and FCBA in order to make the treated wood more stable and less sensitive when used outdoors. The interest of this now well mastered alternative method for wood protection is to allow wood drying as well as wood treatment in a single process. This two stage process operates at atmospheric pressure and uses two hot oil baths. Nevertheless, the formulation of the oils used needs major improvement in order to adapt the performances of the treated wooden material (durability towards wood destroying organisms, fireproofing, etc...) to its end-use. The improvement of this bi-oleothermal wood treatment is the subject of the PIBOLEO project, which is supported by the French National Agency for Research (ANR - ADEME). This project is currently in its early stages and focuses for now on the optimization of the composition of the second bath, which is the one containing the active substances.

The nature of the second bath depends a lot on the active substances used for improving the fire, fungus or insect resistance of the treated wood. If these substances are not miscible with oil but soluble in water, it is then necessary to develop an emulsion containing enough of each of the substances to impart the desired properties to the treated wood. In that case, the use of surfactants is required. Therefore, a major axis of the PIBOLEO has been to optimize the surfactant systems in these water-in-oil (W/O) emulsions. It is quite challenging to design emulsions that can withstand the thermal shocks and the addition of impurities coming from the wood (water, sap, etc.) associated with the treatment without dephasing.

In the case of active substances that are not soluble in oil, chemical modification and grafting of those substances onto oil can be an alternative option. They can then become soluble in oil without losing their properties as fire retardants or biocides. Several synthesis routes are currently under investigation in the PIBOLEO project. In that case or if the active substances are naturally soluble in oil, there is no need to add water in the second bath and a simple formulation of the oil is sufficient. The stability of the bath is then improved (the only concern is the oxidative stability of the oil and the active substances since dephasing is not a possibility).

P31

Cellulases in bi-phasic media

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Nowadays, cellulases are considered with great interest by White Biotechnology industry [1]. Indeed, these enzymes are easy to produce at industrial scale, easy to use and present promising route for second generation biofuels. The catalytic activity of common cellulases is well known i.e. optimal pH, temperature, etc [2]. Many possible substrates were also already tested [3]. However, only little work, at our knowledge, was done on cellulases activity in non-aqueous media [4].

We present here a study of enzymatic activity of three different commercial cellulases from A. niger, Aspergillus sp. and Trichoderma virens in various biphasic, organic solvent / buffer, conditions.

We found that the A. niger cellulases had the best catalytic activity in a biphasic media containing up to 75 % of chloroform phase. In this case up to 40 g/L cellulose contained in buffer phase can be transformed in 4 hours by 10 g/L overall enzyme.

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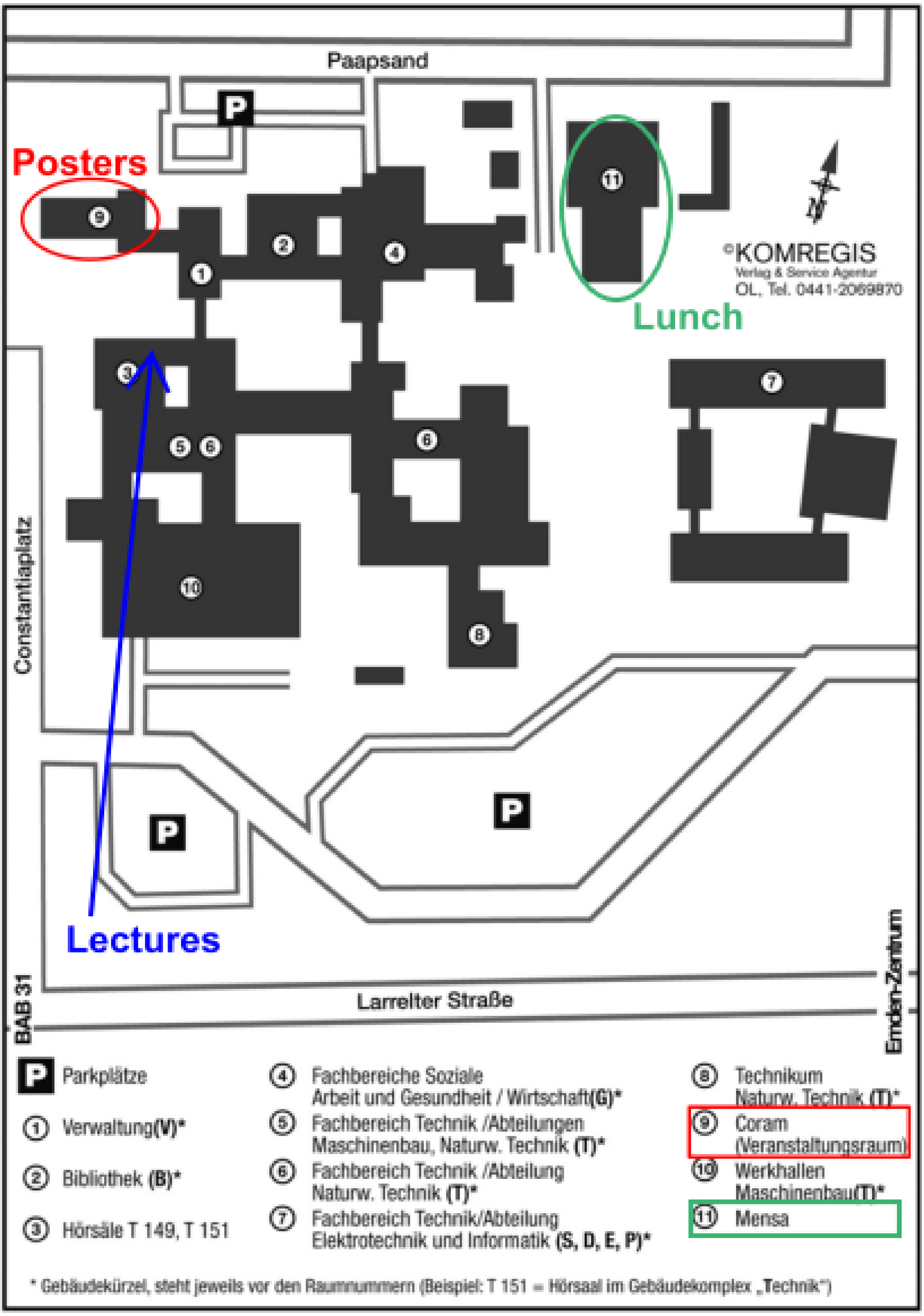
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