



106th AOCS Annual Meeting and Industry Showcases

Industrial Oil Products Division Technical Program Abstracts

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The presenter is the first author or otherwise indicated with an asterisk ().*

IOP 1a: New Uses of Glycerin

Chairs: X.P. Ye, University of Tennessee, USA; and D. Pioch, CIRAD, France

Heterogeneous Catalysis for Liquid Phase Upgrading of Glycerol: Tackling Two Main Issues Towards Industrialization.

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The production of a large variety of chemicals from glycerol is well documented. However, the industrialization of heterogeneously catalyzed liquid phase partial oxidation processes still needs some R&D:

1- Robust continuous operation must be achieved. To this purpose, we stabilized Au-Pd nanoparticles in an ion-exchange resin, which was used as a catalyst in a fixed bed flow type reactor for glycerol oxidation with oxygen. This system was stable over 4000min, with 50% of conversion and selectivities to glyceric and tartronic acids of 60% and 30%, respectively.

2- Crude glycerol must be used to hope economical viability. We compared the tolerance of alumina-supported Ag, Au, Pd and Pt catalysts to the various impurities we identified in crude glycerol fractions. As a result, we can propose guidelines to efficiently cope with crude glycerol fractions.

Bioconversion into Oil from Glycerol by Oleaginous Yeast.

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Glycerol is a byproduct of biodiesel production. To develop uses for such byproducts, we explored the optimal culture conditions and media for the oleaginous yeast strain *Lipomyces starkeyi* CBS 1807, which grows vigorously on glycerol to produce triacylglycerol (TG).

We found that high nitrogen content in the culture medium enhanced yeast growth, while nitrogen deficiency enhanced TG accumulation. Nitrogen content in the culture medium was

controlled by adding NH₃ and then NaOH throughout the incubation period. We also optimized the glycerol concentration, temperature, and pH to achieve a TG yield of 59.9g/L. The fatty acid composition of TG produced by *L. starkeyi* complied with biodiesel standards, including acid value and iodine value. These results suggest that the *Lipomyces* yeast strain is a superb choice for producing TG suitable for biodiesel production from a glycerol substrate. This study was supported by the Adaptable and Seamless Technology Transfer Program through target-driven R&D (JST), Japan.

Industrial Pathway to Bio-based MPG: The BASF Glycerol to 1,2-Propanediol Process.

M. Paul¹, A. Thornton², and B. Houston², ¹BASF SE, Germany, ²BASF Corp., USA.

Diminishing petroleum reserves and increasing environmental concerns have led to a growing interest in alternative fuels. Processes for producing fuels from biogenic fat- or oil-containing starting mixtures have been known for some time. For example, it is known that triglycerides present in biogenic oil and fat (fatty acid esters of glycerol) can be converted to fatty acid monoalkyl esters, especially methyl or ethyl esters, known widely as biodiesel.

In the biodiesel production process glycerol is also obtained as a by-product (~10%). Due to the increasing use of biodiesel, glycerol is now widely available. Utilizing this glycerol represents a significant opportunity for biodiesel producers to access potentially valuable markets. Therefore, creating an effective and economically viable process which enables the utilization of the glycerol is of paramount importance.

The presented paper introduces a process for the valorization of glycerol on an industrial scale. The process, and a proprietary catalyst, was invented by BASF and leads to high quality 1,2-propanediol (MPG) with high conversion and selectivity. The authors will show a first commercial reference and discuss challenges and advantages of this new process.

IOP 1b: Lubricants, Polymers, and Additives

Chairs: Z.S. Liu, USDA, ARS, NCAUR, USA; and Z.S. Petrovic, Pittsburg State University, USA

Biobased Interpenetrating Polymer Networks (IPN) Derived from Silylated Soybean Oil and Polysiloxane.

D. Graiver, S. Dewasthale, and R. Narayan, Michigan State University, USA.

Soybean oil was grafted with reactive silanes via the 'Ene Reaction' and was then used together with polysiloxanes to prepare several series of Interpenetrating Polymer Networks (IPN). One series of IPNs was prepared via the emulsion route, another via the solvent route and another series was prepared from a water soluble polysiloxane with emulsions of soybean oil. Upon casting films and evaporation of the water (or the solvent) phase, permanent crosslinking were obtained between the soybean oil and the polysiloxane oil that produced entangled networks of these two immiscible components. Additional crosslinks and further reinforcement of the networks could be achieved by adding fine particles silica to these soy/silicone mixtures. The morphology and properties of these IPNs were found to depend on the method of preparation and the composition of the networks. However, in all cases intimate mixing of these two immiscible components was observed with no gross phase separation. The mechanical properties were primarily a function of the ratio of the soft, flexible silicone phase and the more rigid and brittle crosslinked silylated soy phase. These IPNs can be used as high release liners, low friction materials or as a general protective coating.

A Self-crosslinking Thermosetting Monomer with Both Epoxy and Anhydride Groups Derived from Tung Oil Fatty Acids: Synthesis and Properties.

K. Huang¹, Z.S. Liu*², J.W. Zhang³, S.H. Li¹, M. Li¹, J.L. Xia¹, and Y.H. Zhou¹, ¹Chinese Academy of Forestry, China, ²USDA, ARS, NCAUR, USA, ³Washington State University, USA.

A self-crosslinking compound with epoxy group and anhydride groups (GEMA) has been successfully synthesized from tung oil fatty acid by reacting with maleic anhydride via Diels-Alder reaction. GEMA has very good storage stability and could be cured with trace amounts of tertiary amine. This advantage avoided the nonuniformity, bubbles and insolubility during the mixing procedure of the epoxy resins and curing agents. Compared to commercial bisphenol A epoxy resins, GEMA has relatively lower mechanical properties and thermal properties. However, in view

of its renewable properties, GEMA still is a very promising bio-based epoxy which may replace bisphenol A epoxy resins in some applications.

High Functionality Biobased Polyols for Rigid Polyurethane Foams.

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Castor oil, this natural biobased polyol, has a too low functionality (of around 2.7 OH groups/mol) and too low hydroxyl number (of around 160-162mg KOH/g) to be used as sole polyol for rigid polyurethane foams of acceptable physical mechanical properties. We synthesized new polyols of increased functionality and hydroxyl numbers by using thiol-ene reactions of castor oil double bonds with hydroxyalkyl mercaptans (2-mercaptoethanol and 1-thio-glycerol). Thiol-ene additions of hydroxyalkyl mercaptans to the double bonds of castor oil, initiated photochemically or thermally with radical initiators, were carried out in high yield, practically quantitative. Were obtained new polyols of high functionalities of 6-8 hydroxyl groups/mol and of higher hydroxyl numbers than those of castor oil of 250-400mg KOH/g. The synthesized polyols were used as sole polyols to obtain rigid polyurethane foams with excellent physical-mechanical properties. The new high functionality synthesized polyols derived from castor oil are suitable for preparation of rigid polyurethane foams for all known practical applications such as: thermoinsulation of freezers, of pipes, of storage tanks for chemical and food industry and of buildings, as wood substitutes and for packaging.

Structure and Properties of Vegetable Oil Polyols for Polyurethanes.

Z.S. Petrovic, Pittsburg State University, USA.

Structure of polyols from vegetable oils and fatty acids is determined by the way of synthesis. Structure design is influenced by the requirements for their applications but also economics. This presentation reviews different methods of polyol synthesis and their effect on structure and properties as well as some issues when triglyceride polyols are used in polyurethanes.

Non-traditional Vegetable Oil: A Potential Source for Green Lubricants. T.M. Panchal, A.V. Patel, M. Thomas, and J.V. Patel, Institute of Science and Technology for Advanced Studies and Research, India.

In recent times, the emphasis on environmental friendly lubricants is largely due to the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use. Vegetable oils are recognized as rapidly biodegradable and are thus promising candidates as base fluids in environment friendly lubricants. Lubricants based on vegetable oils display excellent tribological properties, high viscosity indices and flash points. To compete with mineral-oil-based lubricants, some of their inherent disadvantages, such as poor oxidation and low-

temperature stability, must be corrected. One way to address these problems is chemical modification of vegetable oils at the sites of unsaturation. This paper presents use of non-traditional vegetable oil and its chemical modifications to make it a compatible lubricating oil. Here, we report the epoxidation of non-edible vegetable oils and their esterification with phthalic anhydride. The products obtained were tested for various performance properties viz. pour point, flash and fire point, viscosity index and carbon residue. The chemical modification compounds were characterized by IR and GC-MS. The results revealed that lubricants from renewable resources exhibits comparable performance with traditional petroleum based lubricants.

IOP 2/BIO 2.1/PRO 2: Alternative Fuels and Enzymatic Biodiesel

Chairs: G. Knothe, USDA, ARS, NCAUR, USA; H.C. Holm, Novozymes A/S, Denmark; R.M. Burton, MARC-IV Consulting, Inc., USA; and S. Lewis, Solenis, USA

Development of Enzymatic Catalyzed Fat-splitting Processes. A. Rancke-Madsen, P.M. Nielsen, and H.C. Holm, Novozymes A/S, Denmark.

Conventional thermal fat-splitting processes suffer from expensive and complex equipment, high energy consumption, product quality problems like *trans* fats and color formation and hazardous work environment. Enzymatic catalyzed fat-splitting processes are attractive potential alternatives but enzymatic processes still only have very limited industrial uses, mainly due to insufficient temperature stability and relatively high cost of current enzymes like *Candida rugosa lipase*.

Thermostable lipases expressed in high yields by industrially relevant host systems have been tested at 55°C/131°F in 100ml shaking glass reactor system using a wide range of feed-stocks, including tallow and acid oil waste materials, 30% water w/w and 0.1-1.0% w/w enzyme solution.

The results suggest new lipases have been identified which are superior to traditional fat-splitting lipases, due to better thermostability, lower cost and high reaction rates. Kinetic studies and initial engineering assessments suggest enzymatic catalyzed fat-splitting technology will become successful in the industries within a few years.

Evaluation of Glycerol Carbonate Production and Its Cosynthesis in Enzymatic Biodiesel Production. R.M. Burton¹ and J. Greenstein², ¹ MARC-IV Consulting, Inc., USA, ²North Carolina State University, USA.

Glycerol is a byproduct of biodiesel production. In large centralized biodiesel production facilities, glycerol may be refined to a high purity product. Yet for many biodiesel plants crude biodiesel glycerin is still a waste concern. Glycerol (1,2,3-propane triol) is a trifunctional molecule that can be modified to produce a wide range of products. Glycerol carbonate (GC) and glycidol (2,3-epoxy-1-propanol) are key intermediates in the production of many of these products. GC is a “platform chemical” which can help substitute bio-based feedstocks for the current petroleum derived sources. Recently, researchers have begun investigating the use of enzymes to convert glycerol to glycerol carbonate. In addition, biodiesel production using enzymatic catalysis has also moved from the research phase to the

commercial arena. When enzymatic catalysis is employed for biodiesel production, there is an opportunity to obtain a higher quality of glycerol co-product. This higher glycerol quality may allow an easier processing to new biobased materials. Here, we will evaluate both the enzymatic conversion of glycerol to glycerol carbonate as well as the enzymatic co-synthesis pathway of biodiesel and glycerol carbonate together.

New Developments in Enzymatic Catalyzed Biodiesel Improve the Process Significantly. P.M. Nielsen, A. Rancke-Madsen, T. Balle, B. Knuthsen, and H.C. Holm, Novozymes, Denmark.

The enzymatic catalyzed biodiesel has been in large scale production for more than two years most of the time in a test period in a few plants, but now it also available for all biodiesel producers. During that period a lot have been learned and the process has been improved.

The technical improvements in the process and lower enzyme costs open the possibility of using the enzyme for one batch only. This has some big impacts on how the process can be designed. In the presentation we will discuss the implications of one time use of liquid lipase including: the reaction can be operated at higher temperature and methanol concentrations leading to shorter reaction time and easier separation of heavy phase after the reaction. The downstream process for enzyme recovery can be omitted, and it opens for the possibility of continuous reaction system.

Continuous Enzymatic Biodiesel Processing. B. Chrabas, Viesel Fuel, LLC, USA.

Feedstock costs are recognized as the highest variable cost in the production of biodiesel accounting for up to 80% of the material costs associated with making a gallon of biodiesel. The Enzymatic Biodiesel Pathway allows for the use of feedstocks which are lower in cost by comparison and have limited use in conventional biodiesel processes.

The ability to optimize process inputs in a continuous system lead to the development of the Continuous Enzymatic Biodiesel Process. Working in collaboration with Novozyme, Tactical Fabrication, and PuroLite, the Skunkworks Team is pioneering the

use of enzymes in their Continuous Enzymatic Biodiesel Process.

The Continuous Enzymatic Biodiesel Process being demonstrated by Viesel Skunk Works, LLC at its World Headquarters in Stuart, FL has been used as a test-bed for the scalable process.

The basic tools required for an enzymatic biodiesel laboratory and how they aid in determining the suitability of various lower cost feedstocks will be outlined in this presentation accompanied by production data taken from the Continuous Enzymatic Biodiesel Processor.

Cold Flow Properties of Fatty Acid Methyl Esters: Additives versus Diluents. R.O. Dunn, USDA, ARS, NCAUR, USA.

Biodiesel is typically composed of fatty acid methyl esters (FAME) converted from agricultural lipids. Common feedstocks include soybean, canola, rapeseed, sunflower and palm oils. Recent debate on the conversion of edible oils into non-food products has created opportunities to develop alternative non-edible feedstocks such as jatropha and used cooking oils, waste grease and animal fat. The cold flow properties of biodiesel are poor compared to conventional diesel fuel (petrodiesel). Vehicles fueled by biodiesel/petrodiesel blends may experience start-up and operability problems if exposed to overnight temperatures below the cloud point (CP). Performance issues are exacerbated when the biodiesel is made from high-saturated fatty acid feedstocks including palm oil and many of the aforementioned non-edible oils. Technical strategies have been devised to improve the cold flow properties of biodiesel. Although cold flow improver (CFI) additives can decrease pour point (PP) and cold flow plugging point (CFPP), these additives do not significantly improve the CP when employed at low concentrations (< 1%) in biodiesel and biodiesel/petrodiesel blends. However, increasing the concentration of some additives (diluents) was more effective. This report provides an updated perspective on the development of new CFI additives and diluents for biodiesel.

Fuel Quality Sensors for Characterization of Biofuels and Determination of Their Aging Degree. J. Krahl, M. Eskiner, and Z. Fan, Coburg University of Applied Sciences and Arts, Germany.

A fuel sensor should prevent engines from damages in the fuel line or the combustion chamber

or the exhaust gas treatment system. Two sensor principles are introduced to control the quality and the age of biofuels: Dielectric relaxation and fluorescence spectroscopy.

The detection principle of the newly designed dielectric sensors for determining the aging degree is based on dielectric relaxation spectroscopy. The sensor is characterized by its simplicity, its small size and low price. A possible future use could be the installation in fuel tanks to control the oligomer concentration.

By measuring the real and imaginary part of permittivity in a broad frequency range, it is possible to observe relaxation processes, because of a lag in response of high-molecular and polar oxidation products from biodiesel in the alternating electric field.

Time resolved laser induced spectroscopy (TRLFS) allows identification and quantification of diesel fuel without sample preparation. Applying a mathematical principal component analysis allows the determination of FAME from different feedstocks in diesel fuel. In a further development step a miniaturization of fluorescence sensor was achieved. This LFS-prototype provides approximately similar features as the TRLFS, but without time resolution.

Three Approaches to Fuels from Fatty Compounds. G. Knothe, K.M. Doll, B.R. Moser, and R.E. Murray, USDA, ARS, NCAUR, USA.

Biodiesel, the alkyl esters, usually methyl esters, of vegetable oils, animal fats or other triacylglycerol-containing materials, are the most common approach to producing a fuel from the mentioned materials. This fuel is obtained by transesterifying the oil or fat with an alcohol, usually methanol, in presence of a catalyst such as alkoxide or hydroxide. In more recent years, a fuel probably best termed renewable diesel has been developed which simulates the composition of conventional diesel fuel. This fuel is obtained by hydrotreatment of the triacylglycerol-containing materials. Even more recently, a decarboxylation process of fatty acids was reported which provides a mixture of long-chain alkene isomers and other products with potential fuel properties. The three materials are compared regarding their production, composition and properties.

IOP 3/ANA 3.1: Algal and Other Non-traditional Oils Characterization

Chairs: B.W.K. Diehl, Spectral Service AG, Germany; and L.M.L. Laurens, National Renewable Energy Laboratory, USA

Radiant Energy vs. Organic Carbon: Algal Lipid Profile Diversity in Relation to Cultivation and Conversion Parameters. B.A. Black¹, E. Christensen¹, T. Dong¹, T. Schaub², and L.M.L. Laurens¹, ¹National Renewable Energy Laboratory, USA, ²New Mexico State University, USA.

On an areal-basis, microalgal lipid yield exceeds that of any terrestrial source and lipid composition can be readily influenced by cultivation methods, which increases the suitability of algal lipids for both commercial products and biofuel production. All microalgae are photosynthetic and use light energy to assimilate atmospheric carbon dioxide to form biomass as autotrophic growth. Some organisms are capable of fermentation of organic carbon, often in the form of sugars. By replacing atmospheric carbon assimilation with an organic source in the absence of light, heterotrophic growth and alternative lipid accumulation pathways are initiated. Advantages of each cultivation method exist for the production of lipids; however, profound distinctions are found in the lipid profile of algal strains grown under different carbon utilization scenarios. We present a comparative lipid analysis for oils derived from algal biomass using a combination of FT-ICR and time-of-flight mass spectrometry for comprehensive characterization. Validation of lipid annotation and functional group identification was compared with traditional quantitative chromatographic methods. We show variation of lipid composition and characteristics that relate to cultivation and conversion scenarios and can predict the utilization of these oils for biofuel and bioproduct synthesis.

Analysis of Marine Dietary Supplement Using NMR Spectroscopy. E. Hatzakis, Pennsylvania State University, USA.

A commercial fish oil supplement is expected to be a mixture of several unsaturated (*n*-3, *n*-6, *n*-9) and saturated fatty acids (SFA) in the form of triacylglycerols (TAG) and diacylglycerols (DAG). The determination of the composition of these compounds and the evaluation of other important parameters, such as the positional distribution of fatty acid chains on the glycerol skeleton and the determination of the *n*-6/*n*-3 ratio by using NMR spectroscopy, rely on the correct assignment of the 1D ¹H and ¹³C NMR spectra. By employing

sophisticated 2D NMR experiments, such as HSQC-TOCSY, band selective HSQC and semi-selective constant time HMBC we performed a systematic two-dimensional analysis of the various components in fish oil. This analysis offered solid proof and confirmation of earlier assignments based on model compounds and revealed the presence of *n*-1 acyl chains and *trans* fatty acids in remarkable concentrations. In addition, we present for the first time the application of ³¹P NMR in the analysis of micro-constituents in fish oil supplements, which allows the fast and easy determination of additional minor compounds in fish oils. Quantitative results of various compounds in the supplements, was achieved by integrating the appropriate NMR signals in the spectra.

NMR Spectroscopy, a Rapid Method for Any Lipid Analysis. B.W.K. Diehl, Spectral Service AG, Germany.

NMR as an absolute analytical method is the preferred tool to characterize any source of lipid, rare edible oils for cosmetics or bulk ware for biodiesel and the finished biodiesel, too.

Nondestructive methods as well as measurements after specific derivatisation allow the origin test and the determination of any important parameter in lipid composition and quality. A series of single cell oils and rare edible oils are presented in detail.

Complex Mixture Analysis by FT-ICR Mass Spectrometry for Microalgal Biofuel Applications. T. Schaub¹, N. Sudasinghe¹, J. Jarvis¹, A. Nag², L.M.L. Laurens², E. Christensen², and K. Dadamudi¹, ¹New Mexico State University, USA, ²National Renewable Energy Laboratory, USA.

Variable biochemical composition of algal biomass from different species and cultivation practices has significant impact on production economics, yield and affects downstream catalytic processing. In particular, the distribution of component lipids, determined at the level of individual molecular distributions, is important to determine downstream processing methodology and identify valuable co-product streams. Ultrahigh-resolution mass spectrometry, such as that offered by FT-ICR MS, provides a means to identify the

molecular profile of lipids in algal biomass and fractions generated by processes developed at NREL. Furthermore, novel molecules discovered by this approach, with multivariate data reduction algorithms, provide additional opportunity for economic improvement. We present a novel elemental composition determination procedure based on the application of iterative atomic constraint scenarios to ultrahigh resolution FT-ICR MS data of microalgal lipid extracts. Constraint conditions are derived from elemental composition of known lipids in the Nature Lipidomics Gateway database and facilitate accurate, rapid and direct elemental composition assignment for several thousand lipids per lipid extract. Elemental composition-to-lipid molecule matching provides an unprecedented view of microalgal lipid composition.

A Simple Method for the Isolation of Fucoxanthin from Brown Algae and Its Antioxidant Activity in 5% Fish Oil-in-Water Emulsion. S.F. Koduvayur Habeebullah¹, S. Alagarsamy², and C. Jacobsen*¹,
¹National Food Institute (DTU FOOD), Denmark,
²Fisheries College and Research Institute, India.

Fucoxanthin, a non provitamin A carotenoid is a yellowish brown pigment found abundantly in brown algae. Along with chlorophyll a it is bound to some proteins and act as a light harvesting and transferring pigment. Fucoxanthin has attracted considerable interest in recent years because of its potent bioactivities. The occurrence of carotenoids and chlorophylls in photosynthetic tissues complicates the isolation of pure fucoxanthin and the current available methods for the isolation of fucoxanthin are tedious with use of many solvents. The present study deals with a simple method for the isolation of fucoxanthin and testing their antioxidant activity both in in vitro assays and in 5% oil-in-water emulsion. The yield of fucoxanthin in this method ranges from 0.1% -0.5% depending on the species and is comparable to other methods. Fucoxanthin showed good DPPH radical scavenging and iron chelating property. However, it showed low reducing power and was poor in inhibition of lipid oxidation in liposome model system. When tested in 5% fish oil in water emulsion in the presence of iron, it showed a pro-oxidative behavior in PV and volatile data but showed a low tocopherol loss compared to control and BHT.

Aggregation Characteristics of Rhamnolipid Biosurfactants and Their Synthetic Variants. R.J. Eismín, R. Palos-Pacheco, C.S. Coss, R. Polt, R.M. Maier, and J.E. Pemberton, University of Arizona, USA.

Rhamnolipids are of current interest as greener alternatives to common synthetic surfactants. However, little is known about the fundamental aggregation properties of these surfactants. To better understand these aggregation properties, surface tensiometry, dynamic light scattering, and static and time-resolved fluorescence spectroscopy were applied to aggregates formed from the native monorhamnolipid mixture produced by *Pseudomonas aeruginosa* ATCC 9027 and to aggregates formed from four diastereoisomers (R-,R; R-,S-; S-,R-; and S-,S-) of the most common, naturally-occurring monorhamnolipid congener, Rha-C10-C10, produced by chemical synthesis. For concentrations above the CMC of ~180 μ M at pH 8, globular micelles of ~2-3nm predominate along with two minor aggregates with dimensions of ~12 and ~80nm. Monorhamnolipid micelles were further probed in fluorescence quenching studies to determine average aggregation number of these aggregates. Micelles from these monorhamnolipids have aggregation numbers of ~25-30 molecules/micelle.

On the Use of Microfluidics to Study the Early Formation and Subsequent Stability of Emulsion Droplets. C.C. Berton-Carabin, K. Muijlwijk, and K. Schroën, Wageningen University, The Netherlands.

To control the end-properties of food emulsions, it is necessary to characterize the parameters that affect their early formation and ageing. Emulsions can be prepared using various instruments, for example high pressure homogenizers. Such devices typically induce the break-up of emulsion droplets in the millisecond range. However, most instruments available to study the formation of oil-water interfaces, and notably the adsorption of emulsifiers, hardly give information on the mechanisms occurring at sub-second timescales.

Our work describes the use of microfluidic devices to measure the dynamic interfacial tension between oil and water at the millisecond scale. Using a Y-shaped junction, the mechanism of oil droplet formation was described by relating the shear forces exerted by the aqueous phase, and the oil-water interfacial tension, to the droplet size. A range of static interfacial tensions and shear rates

were used to build a model, which was subsequently applied to estimate the dynamic interfacial tension of droplets formed with different types and concentrations of emulsifiers. We also used

microfluidic devices to study the coalescence of emulsion droplets, and identified a range of conditions under which coalescence is favored.

IOP 4: Catalysis

Chairs: A. Zwijnenburg, Johnson Matthey, Germany; and T.J. Benson, Lamar University, USA

Sustainable Diesters from Methyl 10-Undecenoate—Hydroesterification Catalyst Recycling in Thermomorphic Solvent Systems (TMS).

T. Gaide, A. Behr, and A.J. Vorholt, Technische Universität Dortmund, Germany.

The implementation of renewable feedstocks in industrial chemistry is of great interest due to the shortage of fossil fuels.

Therefore the SFB-project InPrompt (TRR 63) designed a reaction system for hydroesterification of methyl 10-undecenoate, enabling an easy catalyst recycling via phase separation after reaction in thermomorphic solvent systems (TMS).

The hydroesterification of methyl 10-undecenoate offers an easy access to linear C-12 diesters, which can be applied in polymer synthesis. The yield of the product is 86% using a catalyst system which consists of Pd₂(dba)₃, 1,2-DTBPMB as ligand and methanesulfonic acid.

In homogeneous catalysis the catalyst recovery often is a great challenge.

This presentation will highlight the concept of TMS for catalyst recycling.

This technique exploits the temperature dependency of the miscibility gap of two solvents: methanol as polar, catalyst containing solvent and dodecane as apolar solvent for product extraction. This system is biphasic at room temperature and leads to one single-phase if it is heated up.

The amount of catalyst in the product phase after reaction is low (6ppm Pd; 3ppm P) allowing an efficient catalyst recycling.

Combination of Homo- and Heterogeneous Catalysis in Miniplant Scale: New Process for Synthesis of Saturated Branched Oleo Derivatives.

J. Haßelberg, A. Behr, C. Weiser, and J.B. Bially, Technische Universität Dortmund, Germany.

A new process for synthesis of saturated branched oleo derivatives from renewable raw materials was developed.

Starting from methyl linoleate or linolenic acid with a tandem reaction consisting of isomerization and co-oligomerization with ethene branched derivatives were formed with a yield up to 92% using a homogeneous RhCl₃·3H₂O precursor [1].

Hydrogenation of the product is required to recycle the catalyst because after co-oligomerization, the catalyst coordinates to the

double bonds of the oleo compounds.

From saturated branched oleo derivatives rhodium was extracted leaving an amount of 2ppm (0.2%).

Hydrogenation was tested in a miniplant including a trickle bed reactor. The iodine value was optimized to 4.5 using Pd/C as heterogeneous catalyst.

Adsorption of the homogeneous rhodium catalyst by the heterogeneous one appears to be an obstacle but was dramatically reduced from 76.3% to 9.6% by revealing unique correlation of the adsorption behaviour to the reaction conditions.

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

[1] A. Behr, H. Witte, A. Kämper, J. Haßelberg, M. Nickel, *Chem. Ing. Tech.* 2014, 86, No. 4, 458–466

Formation of Furan Fatty Alkyl Esters from Their Bis-epoxide Fatty Esters. G.B. Bantchev, K. Doll, G. Biresaw, and K. Vermillion, USDA, NCAUR, USA.

Reactions of epoxidized alkyl soyate with four different alcohols: ethanol, isopropyl alcohol, 2-ethylhexanol, and benzyl alcohol were investigated in the presence of Bronsted acid catalyst. Products, not reported in prior studies of similar reactions, were found. These were furan fatty acid alkyl esters (FFE, mixture of alkyl 8-(5-hexyl-2-furyl) octanoate and alkyl 9-(5-pentyl-2-furyl) nonanoate) which were unambiguously identified by means of GC-MS and two-dimensional NMR. Evidence suggests that the FFE are formed by an acid-catalyzed rearrangement of the epoxidized linoleates. The FFE were formed in presence of all four alcohols tested and in the presence of either sulfuric acid or Amberlyst 15 catalyst. Yields of up to 13%, as quantified by GC and NMR spectroscopies, were observed. A mechanism for the formation of the FFE is offered on the basis of kinetics studies.

Kinetic Modeling of Single-cell Oil Production Using Pulp and Paper Wastewater Under Substrate Inhibition Condition for Biodiesel Production.

M. AmirSadeghi¹, S. Shields-Menard¹, T. French¹, R. Hernandez², M. Green¹, and B. Sukhbaatar¹,
¹Mississippi State University, USA, ²University of Louisiana at Lafayette, USA.

Microbial lipophilic compounds, referred to as single-cell oils (SCO), are of potential industrial interest due to their triacylglycerol structure, which can be used as biodiesel feedstock. The utilization of pulp and paper wastewater as fermentation media for cultivation of oleaginous yeast *Rhodotorula glutinis* for the production of single-cell oil has been investigated in aerobic batch bioreactor. Glucose was used as a substrate for lipid accumulation by *Rhodotorula glutinis* in pulp and paper wastewater for the purpose of biodiesel feedstock production. Glucose concentrations in the range of (60-100g/L) and nitrogen concentration of (0.6-1.2) led to various C/N ratios of (147-183) was investigated. Lipid production ranged between 6.5 to 8.9g/L, corresponded to lipid content of 40 to 49%. A Haldane kinetic model was applied to describe the cell biomass, lipid accumulation, and substrate utilization in oleaginous yeast. The kinetic parameters were estimated. The model could be applied for similar systems for lipid production and used as a useful implement for designing bioreactors for large-scale biodiesel production.

Influence of Thermal and Enzymatic Treatments of Rapeseed Meal on Canolol Production and Its Conversion into Potential Polymer Precursors.

E.C. Zago¹, C. Aouf², F. Fine³, P. Carré³, J. Lecomte¹, and P. Villeneuve¹,
¹CIRAD, UMR IATE, France, ²INRA, UMR SPO, France, ³CETIOM, France.

Canolol constitutes a potential platform molecule for the synthesis of polymers or fine chemicals. It can be obtained from sinapine, the major phenolic of rapeseed, after hydrolysis of the latter into sinapic acid and its subsequent thermal decarboxylation. As known, the treatment used for rapeseed de-oiling, and especially the applied temperature, has an influence on canolol and total phenolic contents in rapeseed meal.

The first objective of this work was to determine the influence of processing conditions of rapeseed meal on the total phenolics and canolol yields. The parameters studied were the time of hydrolysis induced by endogenous enzymes and different thermal treatments including microwave and superheated steam. Among all factors, temperature

was the most effective to increase canolol content in rapeseed meal.

The second objective was to study the conversion of bio-sourced phenolic molecules such as canolol, 4-vinylguaicol and eugenol, into polymer precursors in order to replace or reduce the use of bisphenol-A or its diglycidyl ether. The various implemented processes allowed the synthesis of molecules similar to bisphenol-A diglycidyl ether, providing new molecules with an interest in the sphere of green chemistry and material science

Synthesis of Novel Bicyclic Ethers from Castor Oil Catalysed by Lewis Acids.

P. Korlipara, N. Narra, and P. Rachapudi, Indian Institute of Chemical Technology, India.

Novel bicyclic ethers were synthesised starting from methyl ricinoleate. Methyl ricinoleate was acylated with dimethyl carbonate followed by epoxidation using performic acid method to get methyl 8-(3-(2-(methoxy carbonyloxy)octyl)oxiran-2-yl)octanoate. This product on treatment with Lewis acids namely, aluminum chloride and boron trifluoride etherate formed methyl 8-(3-hexyl-2,7,8-trioxa-bicyclo(3,2,1)octan-6-yl) octanoate (MHTOBO), a bicyclic ether by intra molecular rearrangement. Similarly methyl 8-(1-ethoxy-3-hexyl-2,7,8-trioxa-bicyclo(3,2,1)octan-6-yl) octanoate (MEHTOBO), was also prepared starting with diethyl carbonate. These methyl ricinoleate bicyclic ethers were isolated in 85-90% yields after purification by column chromatography. The purified compounds were characterised by FT-IR, ESI-MS, HR-ESI/MS, ¹H NMR, ¹³C NMR and 2D- (DQFCOSY, ¹³C-¹H HSQC, and ¹³C-¹H HMBC) NMR spectroscopy. These long chain fatty ester bicyclic heterocycles may have interesting industrial applications, and may also be used as intermediates to derive new oleochemicals with interesting properties not easily obtainable by other methods.

Modified Natural Oils with New Fatty Acid Traits for Industrial Lubricant Applications.

J. Cafmeyer and D. Garbark, Battelle Memorial Institute, USA.

The wide use of natural oil triglycerides as feedstocks for lubricants is often limited by low thermo-oxidative stability and poor low-temperature flow behavior. The emergence of new oil varieties (e.g., high oleic soybean oil and "high stability high oleic" algae oil) addresses these fundamental issues through compositional changes in the fatty acid profile. Functionalization of the unsaturation of the fatty acids can further enhance the thermo-oxidative

stability of the oil and also has implications for other important lubricant properties such as viscosity index and pour point. The fatty acid composition is key to expanding and improving the properties of these modified oils as high performance lubricant base fluids. A series of lubricant candidates using triglyceride oils of varying compositional traits (e.g., high oleic, low polyunsaturated and low saturate) have been examined in which the fatty acid unsaturation has been converted into di-ester derivatives. The effect on viscosity and pour point has been shown to be lower with reduced polyunsaturates and lower saturate levels, respectively.

Conversion of Acid Oils to Biodiesel Using Immobilized Lipases. S. Basheer and U. Mohsen, TransBiodiesel Ltd., Israel.

Lipases possess the capability of catalyzing esterification of free fatty acids and a short-chain alcohol, as well as transesterification of glycerides (mono-, di- and tri-glycerides) and a short-chain alcohol, to form fatty acid short-chain alkyl esters typically used as biodiesel, and water and glycerol as byproducts of both reactions, respectively. Inhibition of the catalytic activity of lipases caused by short-chain alcohols, typically methanol, and the severe mass transfer constraints imposed by the reactants and products under both reactions conditions have restricted the use of lipases for the production of biodiesel at commercial scales.

This work will present a new developed immobilized lipase preparation possessing the capability of catalyzing the esterification as well as transesterification reactions, separately and simultaneously. The biocatalyst has been designed to enable its use in batch as well as in continuous reactors for the production of fatty acid methyl/ethyl esters using low quality feedstocks of FFA's in the range of 0-100%. The formed crude biodiesel has been post-treated by applying different methods in order to comply with the ASTM and EN specs. Based on the developed enzymatic process different pilot units have been designed and built for the production of biodiesel using high FFA's multiple feedstocks.

The Enzymatic Synthesis of Water-soluble Esters Made from Analogues of Iminodiacetic Acid and Solketal. V. Wyatt and K. Jones, USDA, USA.

Most polyesters produced from glycerol are soluble in polar organic solvent. However, esterifications between iminodiacetic acid (IDA) and its methyl and ethyl derivatives with glycerol or solketal result in water soluble polyesters. Such molecules could be used as model compounds to facilitate the production of more water soluble polyesters and polyesters with tunable water solubility. We have previously reported the successes and failures of making water soluble polyesters from glycerol or solketal, a protected glycerol, and either IDA, dimethyl iminodiacetic acid, or diethyl iminodiacetic acid that primarily produce solketal derivatives of the polyesters. This presentation will focus on some of the challenges encountered when attempting to deprotect the solketal unit and a description of some useful methods for the analytical characterization of the water soluble polyesters.

Next Generation Vegetable Oil Structuring Agents: A Nanotechnology Approach in Food

Materials/Processing. G. John and J. Silverman, City College of New York, USA.

Vegetable oils are frequently structured to enhance their organoleptic and mechanical properties. This is usually achieved by increasing the net amount of saturated and/or *trans* fatty acids in the oil. Prolonged consumption of high calorific and fatty (saturated/*trans* fatty acids) products has been shown to elevate risk of metabolic syndromes such as obesity, coronary heart disease and diabetes. In order to mitigate the generally negative impact of lipid-rich products, several health organizations have called for improving the lipid profile of foods, i.e., reduction in saturated and elimination of *trans* fatty acids. In this context, the medium chain dialkanoates of low calorie sugars (sugar alcohol esters) are investigated as a healthy alternative structuring agent. A new family of sugar-based gelator capable of structuring vegetable oil via self-assembly process were developed *at low concentrations (~50 mM)*. The structuring efficiency of sugar amphiphiles was computed in terms of mechanical, thermal and structural properties and found to be a function of its type and concentration. The gelators potentially offer a mode to transform oil in to fat-like materials without the aid of saturated-/*trans*-fatty acids.

IOP 5: Oleochemicals and Biorefineries

Chairs: D. Root, AURI, USA; and S. Ren, University of Tennessee, USA

Novel Biobased Poly(vinyl ether)s for Coating

Applications. H. Kalita, S. Alam, D. Kalita, A. Chernykh, I. Tarnavchik, S. Samanta, A. Jayasooriyamu, S. Fernando, J. Bahr, S. Selvakumar, M. Sibi, A. Popadyuk, A. Voronov, and B.J. Chisholm*, North Dakota State University, USA.

Carbocationic polymerization was successfully used to produce novel biobased poly(vinyl ether)s possessing unsaturated groups in their side-chains. Linear vinyl ether polymers with narrow molecular weight distributions were obtained from novel vinyl ether monomers derived from a variety of renewable resources including plant oils, eugenol, and cardanol. By appropriate choice of the polymerization system, living polymerization was achieved and unsaturation derived from the renewable resource was preserved in the polymer. By preserving side-chain unsaturation, crosslinked networks were achieved through an oxidative mechanism. Compared to drying oil-based coatings and alkyd coatings, coatings based on these biobased poly(vinyl ether)s offer several advantages including fast drying/curing, tailoring of properties through copolymerization, low color, and synthesis using mild conditions. A number of coating systems were prepared and characterized that utilized different renewable-based monomers and comonomers that provided increases in thermal and mechanical properties. In addition, a hydrophilic comonomer was utilized that enabled water-dispersibility without the need for surfactants.

Recovery of Fatty Acids from Methanotrophic Bacteria via an Efficient Pretreatment Approach. T. Dong, L.M.L. Laurens, and P. Pienkos, National Renewable Energy Laboratory, USA.

The objective of this study is to tailor an efficient and scalable approach to recover fatty acids from methanotrophic biomass in an aqueous environment. As a CH₄-converting biocatalyst, *methylomicrobium buryatense* 5GB1 is capable of converting methane (CH₄) into membrane phospholipids, which could be extracted and upgraded to renewable fuel. The technical hurdles associated with lipid extraction from *M. buryatense* biomass are membrane rupture and significant emulsification of the extraction solvent with the wet biomass due to the amphiphilic nature of the lipids and membrane-protein fraction, which hinders the

separation from aqueous phase. We will present data on pretreatment methods and different solvent extraction systems and a down-selected technology to yield free fatty acids instead of intact lipids. A highly efficient fatty acid extraction approach involving a chemical *in situ* biomass and lipid hydrolysis step followed by solvent extraction of fuel-relevant lipids was developed. Fatty acid recovery of over 90% was achieved in a pure crude extracted oil fraction. Emulsification, which could complicate an extraction process, has been remarkably suppressed by the pretreatment and thus this process has great potential to reduce the cost of lipid extraction by applying a continuous fatty acid recovery process.

Novel Eutectic Solvents for Generation of Multiple Products from Low-grade Palm Oil. A. Hayyan¹, M.A. Hashim¹, M. Hayyan¹, and M.E.S. Mirghani², ¹University of Malaya, Malaysia, ²International Islamic University Malaysia, Malaysia.

This study introduces new raw materials for biodiesel production, namely acidic crude palm oil and mixed industrial palm oil. Characterization of these raw materials showed that they are non-edible oils. Esterification reaction is necessary to convert the free fatty acid (FFA) into fatty acid methyl ester (FAME) before proceeding with biodiesel production. Conversion of hygroscopic organic acids such as *p*-toluenesulfonic acid monohydrate (PTSA) into deep eutectic solvent (DES) provides opportunity in the improvement of the esterification reaction, whereby a DES is synthesized by simply mixing a hydrogen bond donor with a salt. Four DESs based on PTSA using ammonium and phosphonium salts were investigated, and it was found that the ammonium-based DES has a higher catalytic activity. The hygroscopicity and the recyclability of DESs were improved, hence indicating their superiority over the heterogeneous acids. Glycerol and bio-lubricant can be produced after transesterification of treated oil using DES. This study introduced new type of fuel obtained after esterification reaction which can be used for boiler fuel, fuel for stationary engines. The produced biodiesel met the EN 14214 and ASTM D6751 standards. These discoveries open up opportunity for a new processing route for cleaner production of biofuel and other useful products.

Composition and Fuel Properties of Hydrocarbons Prepared via Tandem Isomerization-decarboxylation of Oleic Acid. B.R. Moser, K.M. Doll, G. Knothe, and R.E. Murray, USDA, ARS, NCAUR, USA.

Hydrocarbons were prepared via tandem isomerization-decarboxylation of oleic acid using catalytic triruthenium dodecacarbonyl [Ru₃(CO)₁₂]. Chromatographic and spectroscopic characterization of the isolated mixture indicated that it consisted of 77.6% linear internal isomers of heptadecene, 18.0% heptadecane, and 4.4% aromatics. Fuel properties such as acid value, cold flow, density, derived cetane number, energy content, viscosity, lubricity, moisture content, oxidative stability, specific gravity, sulfur content, and surface tension were measured and compared against the petrodiesel standards ASTM D975 and EN 590. Also of interest was a comparison with ultra-low sulfur (<15ppm S) diesel (ULSD) fuel along with the properties of a 5 vol% blend in ULSD. The hydrocarbons yielded higher energy content (47.08MJ/kg), derived cetane number (86.9), and sulfur content (not detected) than ULSD but inferior low temperature behavior (cloud point -1°C), density (791kg/m³), and oxidative stability (3.4h; EN 15751). All other fuel properties were similar and within the ranges specified in the petrodiesel standards. In conclusion, renewable hydrocarbons were readily prepared from oleic acid that yielded fuel properties amenable to their use as an alternative diesel fuel or as a blend component for diesel fuel.

Differentiation Between the Bio and Fossil Component in Hydrogenated Vegetable Oil Using Direct Liquid Scintillation Counting Method. H. Aromaa, T. Riekkola, and T. Laurila*, Neste Oil Corp., Finland.

A novel direct liquid scintillation counting (LSC) method has been applied to the differentiation of the bio and fossil component in hydrogenated vegetable oil (HVO). In currently used LSC methods used for determining the amount of bio component in oils the carbon contained in the sample is first converted into carbon dioxide (CO₂) by combustion. The resulting CO₂ can either be trapped and mixed with a liquid scintillation cocktail followed by an LSC analysis or benzene can be synthesized from the CO₂ and analysed with an LSC instrument. Here we present the results obtained by directly mixing HVO samples with the liquid scintillation cocktail and then analyzing the mixture for the carbon-14 isotopes by using a state-of-the-art LSC analyser. The results will be compared with reference results obtained with accelerator mass spectrometer (AMS) method. The advantages of the direct LSC method include minimal sample pretreatment and straightforward analytical procedure.

Industrial Production of Camelina Sativa in the Canadian Prairies: Technoeconomic and Carbon Footprint Analysis of Biodiesel, Hydroprocessed Bio-jet Fuel, and Biorefinery Co-Products. E.K. Mupondwa, X. Li, and J.P.D. Wanasundara, Agriculture and Agri-Food Canada, Canada.

This study provides a technoeconomic and carbon footprint analysis of the industrial production and biorefinery processing of Camelina sativa in the Canadian Prairies for bio-jet fuel, biodiesel, and other co-product applications. The study provides the following: a) technoeconomic evaluation of the optimization process for the production of biodiesel and hydroprocessed renewable jet fuel, including valuable co-product streams. b) carbon footprint and sustainability analysis of large-scale production of Camelina-derived biodiesel, bio-jet fuel, and coproducts in major value chains.

IOP-P: Industrial Oil Products Poster Session

Chair: R. Wang, CVC Thermoset Specialties-Emerald Performance Materials, USA

1. Synthesis and Physical Properties of New Coco-oleic Dimer and Trimer Plus Estolide Branched Esters.

S.C. Cermak¹, J.W. Bredsguard², T.A. Isbell¹, and R.E. Murray¹, ¹USDA, ARS, NCAUR, USA, ²BioSynthetic Technologies, USA.

Estolides are a class of esters based on vegetable oils that are formed when the carboxylic acid functionality of one fatty acid reacts at the site of unsaturation of another fatty acid to form an ester linkage. The objective of this preliminary study was to separate coco-oleic estolide into two components based on the extent of oligomerization: coco-oleic dimer estolide and coco-oleic trimer plus estolide and evaluate their physical properties as branched esters: viscosities, acid values, Gardner colors, pour points (PP), and cloud points (CP). The coco-oleic dimer estolide esters had the lowest PP at 45°C with the 2-hexyldecanol and PP of -39°C with the 2-octyldecanol. The best CP performer from the same series was 2-octyldecanol, CP of -37°C. The coco-oleic trimer plus estolide esters had slightly higher PPs (-24 to -39°C) with the same alcohols. The viscosities and viscosity indexes were as expected in terms of trends. The coco-oleic dimer estolide esters ranged 27.5-51.7 cSt @ 40°C and 3.0-9.5 cSt @ 100°C, whereas the coco-oleic trimer plus estolide esters ranged 120.8-227.7 cSt @ 40°C and 17.9-29.4 cSt @ 100°C for the same series as the dimer esters. Outside the series tested, iso-stearyl trimer plus ester had the highest reported viscosity of 417.3 cSt @ 40°C and 38.9 cSt @ 100°C. These new oleic estolide esters showed great potential as commercial lubricants.

2. On the Properties of Biofuels Derived from Different Oils Synthesized with Various Alcohols.

C.C. Cardoso¹, V.G. Celante², E.V.R. Castro³, and V.M.D. Pasa⁴, ¹Universidade Federal Rural de Pernambuco, Brazil, ²Ciência e Tecnologia do Espírito Santo, Brazil, ³Universidade Federal do Espírito Santo, Brazil, ⁴Universidade Federal de Minas Gerais, Brazil.

Biodiesel has emerged as one of the promising alternative fuels for diesel engines that can be produced from renewable resources. The properties of biodiesel are determined by its oleaginous composition and the alcohol used in the transesterification reaction. This study seeks to investigate the combination of both that in the

transesterification process and its influence in terms of thermal stability, cold properties, density, and viscosity of the resulting biofuel. Specifically, this study involves the use of palm oil and its crystallization fractions, olein and stearin oils, with methyl, ethyl, isopropyl and benzyl alcohols as reactants. Product characterization was accomplished using ¹H NMR and HPLC analyses. Results showed that the prior process of crystallization of palm oil is justified in order to improve the cold properties of these biofuel. Otherwise, the choice of the isopropyl alcohol showed a stronger influence on it. Hence the ester of palm synthesized with isopropyl alcohol presented the lowest values of cold filter plugging point (0.3°C). However, all isopropyl esters studied showed kinematic viscosity above the limit of the European specification. Benzyl esters present the highest thermal stability but are inadequate as biodiesel due to their high viscosity and density.

3. Making Biodiesel from Waste Feedstocks. M. Lu, Q. Tu, and J.Y. Liu, University of Cincinnati, USA.

Utilizing waste materials as feedstock is expected to improve sustainability and economic aspects of biodiesel production. This poster presents the R&D work for two types of waste materials, spent coffee grounds (SCGs), fats, oils, and greases (FOG) including trap grease and sewer grease. Sewer grease refers to FOG obtained from the sewer system, while trap grease usually comes from grease trap/interceptors of restaurants and food processing facilities. These FOG feedstocks are low cost (or no cost), but are high in impurities. Research focused on oil extraction from these lower grade feedstocks that are lower cost and more environmentally friendly than the transitional solvent extraction approach. Results showed that SCGs contained approximately 10 wt. % coffee oil which can be extracted and converted into biodiesel. The fatty acid profile of the resultant SCG biodiesel contained mostly C16:0 and C18:2. In addition, the residue after coffee oil extraction can be made into activated carbon or biochar. Current research projects on FOGs include: (1) an innovative and low cost extraction technology; (2) the glycerolysis process using raw glycerine from transesterification process, and (3) tracking sulfur balance in the FOG to biodiesel process.

4. Methyl Lactate Production from Glycerol with Methanol and Carbon Dioxide Using Solid Base Catalysts. S. Ren and X.P. Ye, University of Tennessee Knoxville, USA.

Recently, catalytic conversion of glycerol to lactic acid using base catalysts been studied and promising yield was obtained. However, large amount gypsums generated, severe corrosion to reactor, tedious purification, and the difficulty of catalyst recycling lead to the process unattractive. In this study we investigated methyl lactate production from glycerol by an integrated process using solid catalysts (CaO and CuO) with CO₂ and methanol with the aim to reduce the generation of gypsums and recycle catalysts. Process conditions such as reaction temperature and time, catalyst and methanol/ethanol loading were systematically studied. At the optimum condition, methyl lactate were yielded about 57.2 mol% with the glycerol conversion of 93.8 mol% when using refined glycerol. Similar glycerol conversion but slight reduced methyl lactate yield which was 52mol% were obtained using crude glycerol. The analysis for regenerated catalysts showed about 85-90% CaO was recycled and regenerated. About 10-15% CaO was remained in the product in the form of calcium lactate. The examination of regenerated catalysts for glycerol conversion indicates that regenerated catalysts in reused two times had no negative effects on glycerol conversion but slightly decreased methyl lactate production in 2nd time reuse due to the loss of CaO.

5. Production of Acrolein and Acrylic Acid from Glycerol in Carbon Dioxide Media. X.P. Ye, B. Zou, and S. Ren, University of Tennessee, USA.

Acrolein and acrylic acid are promising derivatives of glycerol holding important status as versatile intermediate or building block for the production of methionine and plastics and polymers that are environmentally friendly with wide applications in such as superabsorbent polymers, textile treating agents, and adhesives. Despite their industrial values and intensive effort to convert glycerol to acrolein/acrylic acid in recent years, quick catalyst deactivation in the conversion of glycerol and the use of crude glycerol as feedstock remain as two major technical obstacles hindering the commercial production of acrolein and acrylic acid from glycerol. In this study, we demonstrate a novel method to produce acrolein and acrylic acid from glycerol using carbon dioxide as reaction media that enables long-time activity and stability of catalysts.

We also further examined the effects of impurities in crude glycerol on the catalytic conversions, concluding that new paradigm of catalytic biomass conversion should pay attention to the biogenic impurities.

6. Thermal Processing of Soybean Oil to Obtain Bio-based Polymers and Bio-oil. V.M. Mello, M.A. Montenegro, G.B.C. Martins, and P.A.Z. Suarez, University of Brasilia, Brazil.

The use of triacylglycerides to produce bio-based resins and bio-oils suitable to be used, respectively, as a binder in printing inks (offset) and as diesel-like fuel was evaluated. Soybean oil was kept under temperatures ranging from 260°C to 370°C for 12h in the presence or absence of a nickel catalyst. Using ATR-FT-IR analysis, it was observed that the reaction occurs in two steps. In the first one the consumption of the double bonds via Diels-Alder to form a polymer occurs. The second step consists in the decomposition via pyrolysis of ester groups and the alkyd chains to form light hydrocarbons. A dramatic effect of the temperature on the selectivity of the products was also observed. Indeed, for lower temperatures it was produced predominantly a polymer and for higher ones it was formed preferentially light hydrocarbons. When using Ni⁺², it was observed a catalytic activity in both polymerization and pyrolysis. Comparing the polymerization and pyrolysis in the presence and absence of Ni⁺², under similar conditions, it was observed that by using the catalyst, the polymers presented up to 35 % higher viscosity and the time to completed pyrolysis was reduced 75%.

7. Kinetics of Epoxidation: Canola Oil and Its Derivatives. T.S. Omonov, E. Kharraz, and J.M. Curtis, University of Alberta, Canada.

The objective of this work is to compare the epoxidation kinetics of canola oil (CO), canola oil fatty acid methyl esters (COFAME) and canola oil free fatty acids (COFFA) using *in-situ* generated performic acid. Epoxidation reactions were performed under identical conditions at atmospheric pressure, without any organic solvents or other catalysts, at temperatures of 40, 50 and 60°C. The kinetics of epoxidation reactions were studied, including both the formation of oxiranes and their subsequent loss due to acid catalyzed epoxy ring opening reactions that yield hydroxyl groups and oligomers. These epoxidation products were systematically analyzed using chromatographic

methods (SEC-RI and GC-FID) and ATR-FTIR spectroscopy.

The kinetic and thermodynamic parameters for the epoxidation of CO, COFAME and COFFA were calculated. It was found that the trends for epoxidation of CO and COFAME were similar. Near complete epoxidation of CO and COFAME can be accomplished with negligible oxirane cleavage within 24 hours at optimum temperatures. The epoxidation behavior of COFFA was completely different: the carboxylic acid groups result in extensive oxirane cleavage and the formation of oligomeric units (estolides or similar). These results have significance in the production of epoxides from CO containing FFA and other derivatives.

8. Effects of Various Metathesized Biodiesels on the Crystallization of Palm Oil Biodiesel. N.

Quezada, I. Zambrano, S. Morales, F. Toro, and J. Chavez, La Fabril, Ecuador.

Various methods have been used to improve the cold flow properties of biodiesel. Previous studies have shown that the use of dimers may delay nucleation and inhibit crystal growth of saturated methyl esters. Biodiesels rich in unsaturated methyl esters may be good sources of dimers following a metathesis reaction. The objective of this research was to study the effects of three metathesized biodiesels with respect to crystallization behavior of palm oil biodiesel.

Metathesized high-oleic sunflower oil, soybean oil and passion fruit seed oil biodiesels were obtained using a 2nd generation Hoveyda-Grubbs type catalyst at 60°C for 2 hours at a 0.1% molar catalyst/substrate ratio. The metathesized biodiesels were analyzed by GC-MS and FT-IR. Mixtures of palm oil biodiesel and 1, 3, and 5% of metathesized biodiesels were prepared. The crystallization behavior of these mixtures was monitored by Differential Scanning Calorimetry (DSC), Polarized Light Microscopy (PLM) and Nuclear Magnetic Resonance (NMR) and compared to mixtures with the corresponding unmetathesized biodiesels. Metathesized passion fruit seed oil biodiesel at 5% exhibited the greatest influence on crystallization behavior of palm oil biodiesel. Structural changes indicating a decrease in crystallization rate were also evident based on PLM images and NMR results.

9. **Physical and Chemical Characterization of 1,8-Cineole for Use as a Fuel in Compression Ignition Engines.** R.L. Maglinao, K. Richardson, and J. Windy Boy, Montana State University–Northern, USA.

Recent discovery of a fungus, capable of producing 1,8-cineole from biomass, could potentially lead to a practical and sustainable production of biofuels. A few studies have showed 1,8-cineole's capability to reduce hydrocarbon exhaust emissions for single cylinder diesel engines when blended with diesel. However, these limited studies only give a diminutive picture of the compound's potential as a biofuel. A comprehensive study on this compound as a fuel in terms of ASTM fuel performance characterization is necessary to provide enough evidence of its viability as a biofuel.

Four blends of 1,8-cineole and diesel, including neat 1,8-cineole, were prepared and its physical and chemical properties determined. Comprehensive crystallization studies of 1,8-cineole and its blends showed the compound's ability to suppress crystal growth in the fuel under extreme cold temperatures. Fuel characterization results also showed that blending 1,8-cineole with diesel improved both cetane number and oxidative stability.

10. Polyepoxide Cardanol Glycidyl Ether Used as Reactive Diluent for Epoxy Resin.

J. Chen¹, X. Nie¹, Z.S. Liu², Z. Mi¹, and Y. Zhou¹, ¹Chinese Academy of Forestry, China, ²USDA, ARS, NCAUR, USA.

A novel cardanol derivative, polyepoxide cardanol glycidyl ether (PECGE), was synthesized and used as reactive diluent for epoxy resin. The synthetic condition was optimized, and the resultant PECGE diluent was characterized using FT-IR, ¹H NMR and ¹³C NMR. The influence of addition of this diluent on the viscosity of the epoxy resin was studied. Mechanical and heat-resistant properties of the cured epoxy resin containing PECGE were especially evaluated. By the addition of PECGE into the epoxy resin, the viscosity of the obtained epoxy resin was reduced. The tensile strength, elongation at break, and heat-resistant property of the resin were all improved, while the flexural and compressive strengths of the resin only slightly decreased, implying the potential of PECGE as a very promising biobased reactive diluent for epoxy resin.

11. Poly-β-hydroxybutyrate (PHB) Extraction and Recovery: A New Non-toxic and Environment Friendly Solvent System.

T. Fei, T. Wang, S. Cazeneuve, and Z. Wen, Iowa State University, USA.

Six different biodegradable solvent systems were tested to extract polyhydroxybutyrates (PHB) from *Ralstonia eutrophus*. A new solvent system which can work on both dry and wet biomass was developed. The effect of extraction conditions on

extraction yield and effect of anti-solvent on PHB recovery efficiency were tested. On defatted dry biomass (DDB), PHB recovery yield of 85% and purity of 92% was obtained. On non-defatted wet biomass (NDWB), PHB recovery yield of 83% and purity of 90% was achieved. Water and hexane were tested as anti-solvents. By adding hexane to the extract solution, recovery and purity of PHB were increased to 92% and 93%, respectively. Larger scale extraction reactor has also been built and tested.

12. Synthetic Lubricant Basestocks from Guerbet Alcohols, Dicarboxylic Acids, and Unsaturated Fatty Acids. C.S. Waykole and A.P. Pratap, Institute of Chemical Technology, India.

Guerbet (β -branched) alcohols of varying chain length were synthesized by using mixed fatty alcohols (linear) ranging from 1-heptanol to 1-decanol. In the present research work, Guerbet alcohols were synthesized at relatively lower temperature by use of heptaldehyde as intermediates and does not includes any expensive hydrogen transfer metal catalyst. Relative fatty alcohol and guerbet alcohol compositions of guerbet reaction products were determined by gas chromatography. The pure guerbet alcohols from the reaction products were separated by reduced pressure fractional distillation. These guerbet alcohols were found to be useful in lubricating oils because of their liquidity at subzero temperatures, resistance to oxidation and minimal variation in viscosity with respect to temperature. Synthetic base stocks were prepared by reacting commonly available unsaturated fatty acids (oleic and erucic) and dicarboxylic acids (adipic and sebacic) with guerbet alcohols using p-Toluenesulphonic Acid (p-TSA) as a catalyst. The guerbet esters were analyzed

by means of ¹H-NMR and FT-IR spectroscopy. These base oils were characterized by physical and tribological properties and compared with commercially available 150N and 500N base oils.

13. Extraction of Oil and Terpenes from Guayule Biomass (*Parthenium argentatum*) Under Supercritical Conditions. T. Punvichai^{1,2}, E. Tardan¹, S. Palu¹, and D. Pioch¹, ¹CIRAD, France, ²Prince of Songkla University, Thailand.

Guayule, a perennial shrub adapted to semi-arid climate, that synthesizes lipids, terpenes, polyisoprene (PI), is suitable for multiple-products biorefinery. Previous R&D work aimed at extracting rubber. We are looking for a “green” process for recovering other products from the left bagasse making ~90% dry weight (dw) of harvested biomass after water-based PI extraction as latex (for allergy-free gloves).

The influence of operating parameters on extraction of lipids and terpenics (yield, selectivity) is investigated under supercritical CO₂. SC-CO₂ shows a higher efficiency compared to acetone alone used as reference (ASE method). As co-solvent with SC-CO₂, ethanol brings better extraction yields (12%) compared to acetone (7%). Temperature has little effect on yield with acetone, while showing a maximum at suitably low setting with ethanol (60°C, 250bar, 1h). Also ethanol increases the selectivity for sesquiterpenes known to be active against termites. Further processing of extract yields fatty (C14-C22) and p-anisic acids as potential industrial feedstock. In addition to PI, extracting resins will bring economic viability.

From this work SC-CO₂+ethanol is a suitable green solvent for an advanced extraction process for Guayule biomass, an underused oleaginous.