



107th AOCS Annual Meeting & Expo

May 1–4, 2016 | Salt Palace Convention Center | Salt Lake City, Utah, USA

Industrial Oil Products Interest Area Technical Program Abstracts

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The presenter is the first author or otherwise indicated with an asterisk ().
Abstract content is printed as submitted.*

IOP 1/BIO 1.1/SCC 1: Biorenewable Polymers

This session developed in conjunction with the Biotechnology Division and the Society of Cosmetic Chemists.

This session is sponsored in part by Soy 20/20.

Chairs: R.D. Ashby, USDA, ARS, ERRC, USA; R. Wang, CVC Thermoset Specialties-Emerald Performance Materials, USA; and T. O'Lenick, Society of Cosmetic Chemists/Surfatech Corp., USA

Novel Plant Oil-based Polymers: An Overview. D.J. Kalita¹, I. Tarnavchyk¹, S. Samanta¹, O. Shafranska¹, J. Bahr², A. Popadyuk¹, A. Voronov¹, D. Bajwa³, A. Bezbaruah⁴, M. Sibi⁵, and B.J. Chisholm^{*1,6}, ¹Dept. of Coatings & Polymeric Materials, North Dakota State University, USA, ²Research & Creative Activities, North Dakota State University, USA, ³Dept. of Mechanical Engineering, North Dakota State University, USA, ⁴Dept. of Civil Engineering, North Dakota State University, USA, ⁵Dept. of Chemistry & Biochemistry, North Dakota State University, USA, ⁶Materials & Nanotechnology Program, North Dakota State University, USA.

A wide variety of homopolymers and copolymers were produced from novel plant oil-based vinyl ether monomers. The monomers were produced by base-catalyzed transesterification of 2-(vinyl)oxyethanol with either a plant oil triglyceride or plant oil-derived methyl esters. By proper choice of the polymerization system, linear polymers were produced that retained the unsaturation derived from the plant oil. By preserving side-chain unsaturation, crosslinked networks were achieved either directly through autoxidation or by post-polymerization modification of the double bonds to other reactive functional groups. Select homopolymers and copolymers were found to have utility for a variety of applications including paints and coatings, shampoos, rubber compounds, and environmental remediation. The results obtained clearly show that this monomer and polymer technology provides new opportunities for the use of plant oils in industrial applications. The general concept has also been used to produce novel monomers and polymers from other renewable resources including cashew nut liquid, terpenes, and lignin.

Sucrose Octaesters as Reactive Diluents for Alkyd Coatings.

A. Popadyuk¹, A. Breuer¹, J. Bahr², I. Tarnavchyk³, A. Voronov³, and B.J. Chisholm^{*1,3}, ¹Renuvix LLC, USA, ²Research & Creative Activities, North Dakota State University, USA, ³Dept. of Coatings & Polymeric Materials, North Dakota State University, USA.

Sucrose octaesters, which are 100% biobased, have been proposed as effective reactive diluents for the production of high-solids alkyd coatings. A series of five different sucrose octaesters (SOEs) derived from soybean oil methyl esters, linseed oil methyl esters, and mixtures of soybean oil and linseed oil methyl esters were synthesized and characterized. The drying-time and cured film properties of the different SOEs produced with the same drier package were determined. In general, increasing the concentration of linseed oil methyl esters used to produce the SOEs decreased

drying-time, decreased viscosity, increased hardness, and decreased impact strength. The SOEs were also blended with commercial alkyd resins to produce high-solids alkyd coatings and the drying time and coating properties determined.

Agricultural Waste and Non-traditional Oil in Polyol

Synthesis. C.M. Patel, A. Barot, and V. Sinha, V.P. & R.P.T.P. Science College, India.

Biomass including agricultural residues are promising alternatives to petroleum in the production of value-added products. Polyols were synthesized using a two-step process featuring polyhydric alcohols in the presence of various acid catalysts. The steps involved liquefaction of agricultural wastes followed by optimization of process parameters. Polyols were developed using different non-traditional oils to modify the liquefied products. Each polyol was characterized using both chemical and instrumental methods. Results showed that 93% of the solid raw material was converted into polyols in a PEG/Glycerin-based liquefaction system using a solid/solvent ratio of 0.25 in 60-80 minutes at 160°C. The liquefied product showed an I_{OH} of 200 to 400mg KOH/g and a viscosity of 0.93Pas. The developed polyols can be used for development of foams, adhesives, and paints. In the present study, high quality rigid polyurethane foams, commonly used as insulation materials, were developed from bio based polyols. The present work focuses on formulations, applications and property analyses of these polyols.

Shape Memory Polyurethane Elastomers from Vegetable

Oils. Z.S. Petrovic and J. Milic, Pittsburg State University, USA.

A shape-memory material "remembers" its original shape and returns to its pre-deformed shape when heated. This material is an alternative to conventional actuators with applications in biomedical and other industries. Novel shape memory polyurethanes were prepared from polyols made by polymerization of hydroxynonanoic acid methyl esters generated by ozonolysis of vegetable oils. Segmented polyurethanes consisted of hard segments from MDI and butane diol and highly crystallizable soft segments of polyhydroxynonanoic acid. The materials behaved as elastomers above melting point of the soft segment and hard plastic below. Melting pointes were tunable between 40 and 60°C. The materials displayed complete recovery of shape and length when heated above the transition point.

Catalytic Copolymerization of Methyl 9,10-epoxystearate and Cyclic Anhydrides. U. Biermann¹, A. Sehlinger³, M.A.R. Meier³, and J.O. Metzger^{1,2}, ¹University of Oldenburg, Germany, ²abiosus e.V., Germany, ³Karlsruhe Inst. of Technology, Germany.

Plant oil derived compounds are attractive as raw material for the production of environmentally friendly and in many cases biodegradable consumer products. A great challenge is the production of polymers based on renewable feedstock. We have reported the alternating ring-opening copolymerization of methyl 9,10-epoxystearate with various cyclic acid anhydrides such as phthalic anhydride, succinic anhydride, and maleic anhydride to afford polyesters of narrow molecular weight distributions using a (salen)Cr^(III)Cl catalyst in the presence of *n*-Bu₄NCl [1].

In this way, polyesters (M_n=2000-10000g/mol) with low glass transition temperatures were formed. The reaction is characterized by sustainable aspects, for instance, the use of starting materials derived from renewable resources (> 60%), low catalyst loadings, and no added solvent. The pending long chain alkyl groups introduced in the polyesters by the fat derived substrates attribute amorphous properties to the polymers. Various fatty epoxides are easily available and open up the possibility for the synthesis of new highly branched polyesters.

[1] U. Biermann, A. Sehlinger, M. A.R. Meier, J.O. Metzger, *Eur. J. Lipid Sci. Technol.*, DOI: 10.1002/ejlt.201400631

The Development of Polyols and Polyurethane Spray Foam from Canola and Other Prairie Oilseed Crops. J.M. Curtis¹, E. Kharraz¹, X. Kong¹, T.S. Omonov¹, Y.Y. Zhao¹, D. Treleaven², M. Kennedy³, and D. Kennedy⁴, ¹Lipid Chemistry Group, Dept. AFNS, University of Alberta, Canada, ²Meadow Polymers & Consolidated Coatings, Canada, ³Green Analytics Corp., Canada, ⁴Mod Panel Inc., Canada.

The use of lipid feedstocks in chemical manufacturing is well established and these are sustainable alternatives to petrochemicals. Polyols are one such class of compounds, already commercially produced from vegetable oils. Polyols that incorporate lipids range from intact natural polyols, like castor oil, to polyols that retain certain structural elements of natural lipids, such as the triacylglyceride skeleton, and ultimately to complex polyols that little resemble the starting oil. Here we describe our development of such a range of lipid-based polyol structures with possible applications.

As an example, we have developed a polyol from canola oil, now produced at pilot scale with production facility underway. It has low viscosity and high reactivity so is suitable for use in polyurethane (PU) spray foam for building insulation. Renewable, lipid based components like this can improve the overall environmental impact over the life cycle of PU spray foam. We have developed a PU spray foam formulation with comparable properties to current commercial products, e.g. cream time, rising time, curing

time, and viscosity, and so can be a direct substitute. Finally, the closed-cell content, density, mechanical properties, water absorption, and aging properties of the partly biobased foam matches existing petrochemical products.

Recent Applications of Biobased Polymer Chemistry Platforms for the Development of Novel Personal Care Ingredients. M.J. Fevola¹, F.C. Sun¹, and S.E. York², ¹Johnson & Johnson Consumer Inc., USA, ²University of Oregon, USA.

Polymeric ingredients are preferred for personal care formulations due to their extraordinary combination of functionality, efficiency, and safety. As manufacturers seek to improve the sustainability of personal care products, they increasingly seek “greener” chemistry platforms for ingredients that will increase the renewable and biodegradable content in their formulations without sacrificing performance. Starch and polyglycerol (PG) are examples of versatile platforms that enable development of a broad range of functional ingredients. This presentation will discuss recent advances in the application of these chemistries for designing new amphiphilic molecules with utility as surfactants, conditioners, and thickeners. A 90% biobased, readily biodegradable polymeric surfactant was developed using alkenylsuccinate modified potato starch. This high foaming, ultra-mild cleansing agent was obtained by precisely controlling the starch molecular weight and degree of hydrophobic substitution. Modification of PG with either hydrophobic or combinations of hydrophilic and hydrophobic quaternary ammonium groups enabled the synthesis of novel compounds useful as skin and hair conditioners due to their substantivity and humectancy. PG-modified hydrophobic esters of methyl glucoside or sorbitan, e.g. dioleates, demonstrated the ability to thicken detergents surfactant systems.

Composite Feed Stocks and Imaging with Fluorescence Lifetime Microcopy. J.W. Woodcock¹, D.M. Fox^{1,3}, I.A. Sacui^{1,2}, C.S. Davis¹, and J.W. Gilman¹, ¹National Inst. of Standards & Technology, USA, ²Georgetown University, USA, ³American University, USA.

Design of bio-based composites is best accomplished by taking inspiration from nature. Natural composites are inherently multifunctional; often exhibiting attributes such as: strength (toughness), resilience, sensing, self-healing, light weight, degradability, and optical (camouflage, fluorescence). Designing tough composites is both important and difficult, but in natural systems it is accomplished by incorporating both intrinsic and extrinsic toughening mechanisms over multiple length scales. Molecularly flexible biopolymer matrices are often combined with nano- and micro-scale reinforcing particles or fibers. The rich functionality of bio-based components enables exquisite control of the interactions between the two phases, and allows the reinforcing phase to provide the stiffness and the matrix to provide the flexibility. Here we present examples of semi-

crystalline materials that have large potential in conventional composite applications using common thermoset and thermoplastic matrices. We show the use of basic chemistry enables modification of surface chemical potentials to improve composite interactions. In addition, with easily accessible chemistry, metrologies such as fluorescence lifetime microscopy via stimuli responsive molecular probes that were employed to monitor the stress transfer processes at the composite interphase.

Moisture Resistant Coating for Packaging Paper from Silylated Soybean Oil. C. Tambe, D. Graiver*, and R. Narayan, Michigan State University, USA.

A novel approach of silylating internal double bonds of long chain fatty acids is introduced. Hydrosilylation is so far the most popular and commercially employed way for synthesizing organosilicon compounds by grafting silanes on

organic compounds by formation of Si-C bonds. Unfortunately, hydrosilylation is most effective with alkenes containing terminal double bonds. In this study, we have introduced a solvent free one step silylation process for the preparation of moisture curable silylated soybean oil. The product was characterized qualitatively by ¹H-NMR and ATR-FTIR, while quantified by TGA.

The moisture cure of silylated oil was studied as a function of catalyst concentration, water content, and the temperature of cure. Kraft paper, most widely used in paper packaging, was successfully coated with roll coater. It was followed by a pilot scale up of paper coating process using industrial gravure roll coaters, where more than 50,000 sq. ft. of paper was coated. Coated paper demonstrated up to 50% decrease in Cobb values and a significant decrease in the WVTR values.

IOP 2a: New Uses of Glycerin

Chairs: F. Dumeignil, University of Lille, France; and X.R. Ye, University of Tennessee, USA

Synthesis of α -Linolenic Acid-enriched Triacylglycerol Using a Newly Prepared Immobilized Lipase under Vacuum.

H. Kim^{1,2}, T. Kim^{1,2}, and I.H. Kim^{1,2}, ¹Dept. of Food & Nutrition, Korea University, Republic of Korea, ²Dept. of Health Science, Graduate School, Korea University, Republic of Korea.

α -Linolenic acid (ALA)-enriched triacylglycerol (TAG) was synthesized with ALA rich fatty acid from perilla oil and glycerol using a newly prepared immobilized lipase under vacuum. The ALA rich fatty acid (purity, >90%) was obtained by urea complexation from perilla oil fatty acid. Liquid type lipase from *Thermomyces lanuginosa* (TL) was employed for immobilization. Nine different hydrophilic and hydrophobic carriers for immobilization were used and Duolite A568, a hydrophilic resin, was selected as the best carrier. Optimum pH and protein concentration of enzyme solution for immobilization were pH 7 and 16.89mg mL⁻¹. With this immobilized lipase, TAG was synthesized by direct esterification under vacuum. Parameters investigated were temperature, enzyme loading, and vacuum. The optimum conditions were a temperature of 60°C, enzyme loading of 20% (based on the total weight of the substrate) and pressure of 0.7kPa, respectively. Consequently, the maximum TAG yield of ca. 94.36% was obtained after 9 hour at the optimum conditions.

Glycerol: A Solvent and Building Block of Choice for Alternative Technologies.

C. Len, Université de Technologie de Compiègne, Sorbonne Universités, France.

The design of environmentally friendly methodologies has been the driving force of scientists in recent years. In particular, the use of biomass-derived materials, green solvents, and alternatives techniques has been investigated. In this regard, glycerol has the potential to be both an excellent renewable solvent in modern chemical processes and a versatile building block in biorefineries.

In this conference, several green chemistry approaches that target advanced synthesis and processes using glycerol will be presented. These approaches include: (i) green synthesis of quinoline and phenanthroline derivatives in sole water using microwave irradiation and high temperature/pressure^[1]; (ii) production of oligomer of glycerol for polymerisation.^[2]

Conception, synthesis, and physico-chemical properties will be detailed.

References: ^[1] (a) H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, *Catal. Commun.* 2014, 44, 15; (b) H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, *RSC Adv.* 2014, 4, 21456; (c) H. Saggadi, I. Polaert, D. Luart, C. Len, L. Estel, *Catalysis Today* 2015, 255, 66.

^[2] M. Kumari, M. Billamboz, E. Leonard, C. Len, C. Böttcher, A.K. Prasad, R. Haag, S.K. Sharma. *RSC Adv.* 2015, 5, 48301.

Novel Reaction of Glycerol Direct Amination Over Heteropolyacid-based Catalysts.

F. Dumeignil^{1,2}, M. Safariamin^{1,3}, S. Paul^{1,3}, K. Moonen⁴, D. Ulrichs⁴, and B. Katryniok^{1,3}, ¹Unité de Catalyse et Chimie du Solide (UCCS), Université de Lille, France, ²Inst. Universitaire de France, France, ³Cité Scientifique (CS), Ecole Centrale de Lille, France, ⁴TAMINCO bvba, a Subsidiary of Eastman Chemical Co., Belgium.

The direct amination of glycerol with dimethylamine (DMA) was studied over catalysts based on salts of heteropoly acids. The highest yield to (dimethylamino) acetone (33%) was observed over a catalyst containing 50wt% of Cs_{2.5}H_{0.5}PMo₁₂O₄₀ supported on a mesoporous silica. Over this solid, strong-medium acid sites coexist with weak acid sites due to the presence of two types of Keggin units exposed to the surface. While the strong-medium acidity of stacked Keggin units is preserved, the Keggin units directly in interaction with the SiO₂ surface are stabilized, with the consequence of decreasing their acidity to a weak strength. The first step of the glycerol direct amination reaction consists in the dehydration of a glycerol molecule, which needs a free acid site on the solid. Due to its basicity, DMA extensively covers the strong-medium acid sites, only leaving free a fraction of the weak sites, which explains the need for cooperation between weak and medium-strong acid sites to realize the reaction.

Acknowledgements: The authors warmly thank TAMINCO bvba for financial support. Furthermore, we thank G. Cambien and J.C. Morin for the nitrogen physisorption experiments and technical assistance during IR-RAMAN analysis, respectively. We further thank Fuji Silysia for kindly supplying CARiACT Q-10 silica.

Catalytic Synthesis of Amphiphilic Long Chain Alkylglyceryl Ethers.

F. Jérôme¹, K. De Oliveira Vigier¹, N. Sayoud¹, A. Karam¹, J. Lai^{*2}, and A. Liebens², ¹CNRS/IC2MP, France, ²CNRS/SOLVAY, France.

The catalytic production of downstream products from renewable polyols has become of growing interest. Notably, the catalytic oligomerization of glycerol is a valuable reaction yielding hydrophilic molecules that are useful for the production of biosurfactants.^{1,2} Unfortunately, catalytic processes suffer from poor energy efficiency and a lack of selectivity.

Here, we will first explore the versatility of various homogeneous acid catalysts in such reaction and we will show how their acid strength directly impacts the selectivity of this reaction, the oligomerization degree of glycerol (typically, 3.4 for the best systems), and the regioselectivity (linear isomers vs branched and cyclic products).³ Having identified the most promising catalysts, we will discuss on their heterogeneization and we will highlight perfluorinated

sulfonated polymer as a highly productive, recyclable, and selective (90% selectivity at 90% conversion) acid solid catalyst. Comparison of perfluorinated sulfonated polymer with common solid catalysts will be also discussed to highlight the great potential of this newly commercialized

acid catalyst. Furthermore, owing to its amphiphilicity, we will show that this strong acid solid catalyst is also capable of enabling the tandem oligomerization/etherification of glycerol in the presence of fatty alcohols, thus providing an access to amphiphilic dodecylpolyglyceryl ethers.

IOP 2b/EAT 2.2: Waxes and Phase Change Materials

This session developed in conjunction with the Edible Applications Technology Division.

Chairs: J.F. Toro-Vazquez, Universidad of Autónoma de San Luis Potosí, Mexico; and S.S. Narine, Trent University, Canada

Designing Superior Phase Change Materials from Lipids.

M.C. Floros, Trent University, Canada.

Recently, renewable energy such as wind and solar power has gained economic viability for heating and power generation. However, renewable energy is intermittent in nature; the wind does not always blow nor the sun always shine. This necessitates the need for storage solutions for the excess energy during peak times for off peak use. We have prepared a series of renewable diesters from saturated vegetable oils using cheap facile chemistry and have shown that they melt and crystallize sharply (between 39 and 77°C) and possess high enthalpies of melt, making them ideal green phase change materials for thermal energy storage. All of these diesters have enthalpies of melt and crystallization values in excess of 230 J/g – significantly higher than commercial paraffin wax phase change materials currently on the market. The phase change temperatures of the materials can be predictively varied, while maintaining similar latent heat values, as a function of the length of the fatty acid and/or short chain dialcohols. In addition to applications including thermal energy storage for building heating and power generation, this temperature range is also congruent with hot food and beverage consumption temperatures, allowing foods and beverages to be precisely heated or cooled to a desired temperature.

Controlling the Crystallization and Melting Behavior of Self-metathesized Vegetable Oil Waxes. L. Bouzidi and S.S. Narine, Trent Centre for Biomaterials Research, Dept. of Physics & Astronomy/Dept. of Chemistry, Trent University, Canada.

Oligomers of triacylglycerols (TAGs) derived from the self-metathesis of vegetable oils were used to produce functional non-toxic waxes. A significant understanding, not present before, of the structure and waxy functionality of TAG oligomers was achieved. The TAG-oligomers were shown to present an architecture that deliver performance waxes that are tunable with respect to crystallization and melting ranges. The effectiveness of this architecture relates to the balance between amorphous and crystalline phases, which are functions of chain length, van der Waals additive attractive forces and steric hindrances due to symmetry and unsaturation. Although the effect of saturation on the phase behavior was the most dramatic, with differences in crystallization temperature up to 62°C, isomerism and molecular mass were shown to affect crystallization significantly, leading to differences of up to 30°C. The unveiled predictive trends indicate that the thermal parameters can be adjusted in a very broad range by saturation, isomerism, and size, making the development of a large variety of lipid sourced high-value waxes possible.

Biorefinery Technology: New, High-performance Renewable Approaches in Performance Waxes. J.A. Brekan, G. Zopp, and R. Littich, Elevance Renewable Sciences, USA.

The demand for increased sustainability has expanded the use and research activity of synthetic and bio-derived performance waxes. Waxes such as montan and carnuba are highly desired in many applications including plastics additives, personal care, polishes and adhesives. They contain significant amounts of long chain (>C22) fatty esters, and in the case of montan, the natural wax is commonly oxidized to fatty mono and di-acids and esterified with ethylene glycol (EG) to generate a montan ester derivative (Montan E). These long chain structures impart desirable properties such as hardness, high melt point (>70°C) and high thermal stability.

The ERS C18+ fatty acid methyl ester (FAME) stream also provides a mixture of mono- and di-acids (C18-24) and may provide a feedstock to generate derivatives for use in similar applications. This presentation will focus on the ester wax work targeting this biorefinery stream. This presentation will review the development and design of a number of new, synthetic waxes obtained through either direct functionalization or through esterification reactions of these biorefinery outputs.

Ethylcellulose Oleogels in Cream Cheese. R. Nicholson, A.G. Marangoni, and S. Barbut, University of Guelph, Canada.

A direct reduction of milk fat in cheese is detrimental to various qualities desired by consumers. Recently, new strategies have evolved to gel vegetable oils with ethylcellulose (EC) in combination with fatty acid/fatty alcohol mixtures. Substituting these oleogels for milk fat reduces levels of saturated fat while maintaining the textural properties of the full-fat variety. Mechanical tests have been used to evaluate the effects of incorporating EC oleogels into low-fat cream cheese. Certain formulations of canola oil with an EC and fatty acid/fatty alcohol combination produced samples comparable to those containing identical proportions of added milk fat. Back extrusion results showed hardness values of approximately 18N for samples made with these oleogels. Only slightly less than the 20N value obtained from samples containing milk fat, but significantly greater than the 7N value produced with canola oil. Additionally, cream cheese products containing EC and fatty acid/fatty alcohol oleogels were similar in appearance to those with only milk fat, as demonstrated by lightness (L*) values of 93.89 and 95.35 respectively. This work has the potential to produce low-saturated fat cream cheese alternatives without compromising the appearance or textural attributes and should help expand the use of EC in dairy systems.

Low Saturated Functional Fat systems Structured by MAGs and Waxes.

F. Davoli¹, S. Metin¹, D. Karleskind², and P. Smith³, ¹Cargill Inc., USA, ²Cargill Malt, Belgium, ³Cargill R&D Centre Europe, Belgium.

The reduction of saturated fat while keeping the functional performance of traditional shortenings has been a challenge faced by industry. In general, low saturated fat systems lack performance mainly because of the weak structure. Vegetable waxes and monoglycerides have been studied as structuring agents for oleogels. They are also known for their properties as fat crystallization nucleators. This study also showed their properties as crystal habit modifiers. This study aimed to develop robust fat systems

targeting low saturated fat content. Structuring, nucleation and habit modifier properties of monoglycerides and waxes were studied in a fat system containing canola oil and palm stearin. The structures of the experimental compositions were compared to commercial low saturated shortening by analysing rheology, thermal profile and microstructure. The experimental fat systems studied were submitted to different processing conditions using a pilot-scale scraped surface heat exchanger (SSHE). A combination of controlled crystallization process and composition resulted in promising results so that the obtained fat structures were comparable or even (in some cases) showed improvements to the performance of commercial shortenings.

IOP 3/BIO 3.1: Biofuels I

This session developed in conjunction with the Biotechnology Division.

Chairs: H.C. Holm, Novozymes A/S, Denmark; and G. Knothe, USDA, ARS, NCAUR, USA

Diesel R33. J. Krahl^{1,2}, K. Götz¹, B. Fey³, and J. Bünge^{4,2},
¹Technology Transfer Center Automotive of Coburg University (TAC), Germany, ²Fuels Joint Research Group, Germany, ³Thünen-Inst., Germany, ⁴Research Inst. for Prevention & Occupational Medicine of the German Social Accident Insurance, Ruhr University Bochum (IPA), Germany.

Greenhouse gas (GHG) reduction is a key driver for new technologies in the European Union but also in other countries of the world. Drop-in biofuels can contribute to that goal. The new developed biofuel Diesel R33 enables sustainable mobility fulfilling the European diesel fuel specification.

Diesel R33 is made from 7% used cooking oil methyl ester, 26% hydrotreated vegetable oil (HVO), and 67% high quality diesel fuel. HVO was produced from rapeseed and palm oil.

Diesel R33 was tested in a fleet of 280 vehicles (passenger cars, light duty vehicles, and buses) covering all emission classes. The impact of the new fuel on vehicles, emissions, and the engine oils was investigated.

At the example of five passenger cars (Euro 3, 5, and 6) regulated and non-regulated exhaust emissions were determined.

All vehicles fulfilled the exhaust regulations for both fuels. Except NO_x, Diesel R33 showed a positive impact on regulated and non-regulated emissions, such as carbonyls and polycyclic aromatic hydrocarbons (PAH). Moreover, the mutagenic effects of the exhaust gases were measured. At Euro 5 and 6 passenger cars, PAH and mutagenicity were hardly detectable for both fuels. The positive effects were expressed more clearly at older engine technology. Most relevant is the GHG reduction of 17% versus fossil diesel fuel.

In addition, two vehicles were successfully powered by Diesel R33 based on algae and yeast oil.

In all, 1.900.000 liter Diesel R33 were used without any problems.

Unique Lipids from a Common Algae: Investigating the Biofuel Potential of Commercial *Isochrysis*. G.W. O'Neil¹, G. Knothe², and C.R. Reddy³, ¹Western Washington University, USA, ²USDA, ARS, USA, ³Woods Hole Oceanographic Institution, USA.

Isochrysis is one of a select number of algae currently grown industrially, harvested for purposes of mariculture, and available in multi-kilogram quantities from several suppliers worldwide. It is also one of only a few taxonomically restricted algae that in addition to traditional fatty acids, biosynthesize significant quantities of a unique suite of lipids known as polyunsaturated long-chain alkenones. Results from the parallel production of two liquid fuel streams utilizing

both fatty acids and alkenones from commercial *Isochrysis* are presented. These materials were produced on sufficient scale to allow for comprehensive testing according to ASTM standards. The isolation of other valuable coproducts such as medicinal carotenoids to potentially offset biofuel production costs is also described.

Low-temperature Phase Behavior of Fatty Acid Methyl Esters by Differential Scanning Calorimetry (DSC). R.O. Dunn, USDA, ARS, NCAUR, USA.

Fatty acid methyl ester (FAME) mixtures have many uses including biodiesel, lubricants, metal-working fluids, surfactants, polymers, coatings, green solvents, and phase-change materials. The physical properties of a FAME mixture depend on the fatty acid concentration (FAC) profile. Some products have high concentrations of saturated FAME and other components with high melting points that can crystallize at moderate temperatures. Liquid-solid (L-S) phase transitions, both melting and crystallization, can be efficiently analyzed by differential scanning calorimetry (DSC). This paper evaluates the use of DSC to measure onset, peak maximum and offset temperatures, and enthalpies of fusion of pure FAME. Furthermore, the subsequent use of the DSC data in thermodynamic models to determine crystallization onset and other phase transition temperatures that take place in FAME mixtures is discussed. Finally, the limitations of DSC analysis of FAME mixtures, such as supercooling and polymorphism, are explored.

An Overview of the Properties of Fatty Acid Alkyl Esters. G. Knothe, USDA, ARS, NCAUR, USA.

Fatty acid alkyl esters of plant oils, especially in form of methyl esters, have numerous applications with fuel use having received the most attention in recent times due to the potential high volume. Various properties imparted by neat fatty acid alkyl esters have been shown to influence fuel use, including not only cetane number and other combustion-related aspects, but also kinematic viscosity, melting point, oxidative stability, lubricity, and density. These properties, however, are of significance also for other applications of fatty acid alkyl esters, for example, lubricants and solvents. An overview of these properties will be given in relation not only to fuel use but also in relation to other applications.

Bias and Imprecision in the Determination of Free Glycerine (FG) in B100 Biodiesel: Unexpected Formation of Glycerine Heterophases with Limited Solubility at 23°C. R.W. Heiden¹ and M. Mittelbach², ¹R.W. Heiden Associates LLC, USA, ²University of Graz, Austria.

Residual free glycerin (FG) is a critical marker of biodiesel (B100) quality because of well-known deleterious effects of

excessive concentrations. Yet, routine determinations by standard methods are well known to display considerable imprecision, which undermines the value of the data. We present the results of a systematic investigation of day to day variations in FG determinations of 13 B100 samples.

Elevations caused by vigorous agitation in certain samples indicate the existence of heterophases with limited solubility, and represent a potential source of imprecision and severe sampling bias, previously undocumented. Moreover, bias is observed at levels of FG initially near or below 0.02% in polished B100 samples. We find the solubility of FG in dry soy biodiesel is much lower than expected based upon earlier studies, which helps explain the results. Further, our data indicate that dissolved moisture residuals can interact, sharply reducing the solubility of FG to levels below internationally recognized limits.

Both the magnitude of imprecision and bias are greatly improved by a promising sample pretreatment which is both readily implemented and compatible with standard GC silyl methods. These results and their implications relative to the fate of FG residuals in B100 parcels are discussed.

Enzymatic Conversion of Brown Grease to Biodiesel Fuel.

S. Basheer, TransBiodiesel Ltd., Israel.

The use of lipases as an alternative for conventional chemical catalysts has been intensively evaluated for the esterification/transesterification of oils and fats with methanol for the production of fatty acid methyl esters to be used as biodiesel fuel. Different lipases either in their native or immobilized forms have been tested, including those derived from *Candida antarctica B*, *Alcaligenes sp.*, *Pseudomonas cepacia*, *Thermomyces lanuginose*, and *Candida rugosa*. Reported results showed that most lipases used so far have been inhibited by the different components present in the reaction medium, e.g. methanol, FFA's, and water and glycerol produced as byproducts of the esterification/transesterification reactions. This work will show for the first time the use of a new immobilized lipase for the conversion of low-quality feedstocks, such as brown grease to biodiesel complying with the ASTM spec. The tolerance degree of the immobilized lipase to methanol, water and glycerol, will also be demonstrated in this work. Other parameters of potential effect on the conversion rates, such as temperature, FFAs content, and amount of biocatalyst will also be presented.

New Enzymatic Concept in Crude Oil Transesterification.

P.M. Nielsen, Novozymes A/S, Denmark.

A large volume of biodiesel production is based on crude oil for instance soybean oil or canola oil. Before the oil is reacted in the sodium methoxide catalyzed transesterification it is refined to eliminate FFA and phospholipids. Standard procedure for the refining step is a caustic washing step followed by separation. This refining step leads to significant yield loss dependent on the amount of FFA and phospholipids in the crude oil. One way of reducing yield loss is enzymatic degumming either using a phospholipase C or phospholipase A. But even with this improvement there will still be some yield loss in the separation step and due to the content of FFA.

We have found that it is possible to decrease the yield loss significantly in the biodiesel process if the enzymatic degumming process is merged with enzymatic transesterification and carried out simultaneously. The separation step is eliminated and the FFA in the crude oil as well as FFA and glycerides produced from the phospholipase reaction will be esterified in the enzymatic process. This leads to a significant overall total yield increase. The data from the optimized process will be discussed to document the new combined degumming-transesterification process.

Enzymatic Biodiesel—Single Time Use of Enzyme and One Pot Polishing Solution.

A.R Madsen, P.M Nieslen, H.C. Holm,

T. Balle, and M.K Bollinger, Novozymes A/S, Denmark.

The use of liquid enzymes in biodiesel production has been a break-through as liquid enzymes can handle feedstocks with any content of free fatty acids at low economical risks. However, complexity of re-using the enzyme and lack of robust polishing technologies has been major challenges.

A next version liquid enzymatic biodiesel process is based on a new more stable variant of the *Thermomyces lanuginosus* lipase, single time use of the enzyme, and a polishing neutralization step called "the one pot process". The new process has been tested in both lab scale and large scale and has proven superior to the current process due to simplicity, lower process variations, and excellent separation performance. Reaction conditions are 2-3kg enzyme/ton oil, 1-2% water, 1.4-1.8 equivalents of methanol and 24-36 hours of reaction time at 95-113°F/35-45°C. After reaction, dilute caustic is mixed in to the reaction mixture at 130°F/60°C for 30 minutes. After a few hours of settling time, the FAME phase is separated from the heavy phase, washed with 2% water and dried. The FAME yield is 96% and the glycerol heavy phase has low salt content. A few options for optimizing the yield closer to 100% will be discussed.

IOP 4/BIO 4.2: Biofuels II

This session developed in conjunction with the Biotechnology Division.

Chairs: T. Aki, Hiroshima University, Japan; and R.M. Burton, Novozymes, USA

Influence of Corn Oil Recovery on Life-cycle Greenhouse Gas Emissions of Corn Ethanol and Corn Oil Biodiesel. Z. Wang¹, J.B. Dunn², J. Han², and M.Q. Wang², ¹EcoEngineers LLC, USA, ²Systems Assessment Group, Energy System Div., Argonne National Lab., USA.

Corn oil recovery and conversion to biodiesel has been widely adopted at corn ethanol plants recently. The US EPA has projected 2.6 billion liters of biodiesel will be produced from corn oil in 2022. Corn oil biodiesel may qualify for federal renewable identification number (RIN) credits under the Renewable Fuel Standard, as well as for low greenhouse gas (GHG) emission intensity credits under California's Low Carbon Fuel Standard (LCFS). Because multiple products [ethanol, biodiesel, and distiller's grain with solubles (DGS)] are produced from one feedstock (corn), however, a careful co-product treatment approach is required to accurately estimate GHG intensities of both ethanol and corn oil biodiesel and to avoid double counting of benefits associated with corn oil biodiesel production.

This study develops four co-product treatment methods: (1) displacement, (2) marginal, (3) hybrid allocation, and (4) process-level energy allocation. Life-cycle GHG emissions for corn oil biodiesel were more sensitive to the choice of co-product allocation method because significantly less corn oil biodiesel is produced than corn ethanol at a dry mill. Corn ethanol life-cycle GHG emissions with the displacement, marginal, and hybrid allocation approaches are similar (61, 62, and 59g CO₂e/MJ, respectively). With the process-level allocation approach, ethanol's life-cycle GHG emissions are lower at 46g CO₂e/MJ. Corn oil biodiesel life-cycle GHG emissions from the marginal, hybrid allocation, and process-level energy allocation methods were 14, 59, and 45g CO₂e/MJ, respectively. Sensitivity analyses were conducted to investigate the influence corn oil yield, soy biodiesel, and defatted DGS displacement credits, and energy consumption for corn oil production and corn oil biodiesel production. This study's results demonstrate that co-product treatment methodology strongly influences corn oil biodiesel life-cycle GHG emissions and can affect how this fuel is treated under the Renewable Fuel Standard and Low Carbon Fuel Standard.

Novel Alpha-amylase Technology for Enhanced Fermentation Efficiency and Corn Oil Recovery in Industrial Biofuel Production. P. Mandulak, R.M. Burton*, J. Matthews, and K. Bertz, Novozymes North America, USA.

In commercial dry grind corn ethanol production, over 75% of ethanol production plants employ corn oil recovery systems. Corn oil extraction has become an essential income stream which yields a valuable corn oil by-product for animal feed or biodiesel production. Corn used for industrial ethanol production contains approximately four percent fat content

by weight. Extracting the full percentage of these lipid materials is a challenge for production facilities and requires surfactant chemistries to enhance mechanical extraction. A new approach to significantly increase oil extraction rates is the utilization of novel alpha-amylases enzyme package developed to enhance the oil yields in biofuel plants. This research will review commercial use of these enzymes in dry-grind corn processing including how these combinations can reduce chemical inputs of nitrogen in feedstreams, increase production yield, and enhance the volume of corn oil extraction.

Maximizing Oil Recovery from Corn-soy Slurry After Fermentation with *Saccharomyces cerevisiae*. J.K. Sekhon^{1,2}, K.A. Rosentrater^{2,3}, and S. Jung⁴, ¹Dept. of Food Science & Human Nutrition, Iowa State University, USA, ²Center for Crops Utilization Research, USA, ³Dept. of Agricultural & Biosystems Engineering, Iowa State University, USA, ⁴Dept. of Food Science & Nutrition, California Polytechnic State University, USA.

Utilizing co-products of enzyme assisted aqueous extraction process of soybeans in corn fermentation has shown promising results with significant increase in ethanol yield (20%) and decrease in fermentation time (44 h) compared to corn only fermentation. However, to maximize economic returns oil can be recovered from the slurry after fermentation. Removal of oil from the fermented slurry also leads to production of high quality DDGS (dried distillers grains with solubles) used for animal feed. Efficient sustainable methods are required to maximize oil recovery. In the present study, soy skim (protein rich) and insoluble fiber (IF; carbohydrate rich), co-products of EAEP, were utilized in dry-grind corn fermentation. The effect of 1) fiber hydrolyzing enzymes, 2) proteases, and 3) surfactants alone or in combination on oil recovery from [corn only], [corn + skim], [corn + insoluble fiber], [corn + (skim + insoluble fiber)] slurries were investigated. The process was optimized for type, concentration, and point of addition of enzymes and surfactants. Maximum oil recovery was achieved from [corn only] and [corn + insoluble fiber] slurries when pectinase, cellulase and Fermgen protease were added to corn-soy slurry during fermentation and when Tween80 was used as a surfactant or demulsifier.

Keynote Presentation: Fuels from Oils and Fats: Recent Developments and Perspectives. M. Mittelbach, Inst. of Chemistry, University of Graz, Austria.

The future of fuels made out of fats and oil is evaluated and discussed. Fats and oils today represent the main source for alternative transport fuels, especially for FAME (biodiesel) and HVO (hydrotreated vegetable oils). Recent developments in FAME and HVO production and utilization are highlighted, including microbial oils as potential feedstocks. The use of new heterogeneous catalysts as well as promising reactor designs for FAME production is discussed as well as biocatalytic approaches. Since HVO production technology is based mainly on current mineral oil industry processing methods, the scientific literature is not as extensive as that of FAME production. The main reaction routes of HVO are a combination of hydrogenation, decarboxylation, decarbonylation, hydroisomerization, and cracking under high pressure and temperatures, using supported and unsupported heterogeneous metal catalysts. Own experiments using non food feedstocks as starting material like waste animal fat or tall oil under heterogeneous catalysis are presented. The hype concerning the use of algae based material has been cooled down when comparing different production routes for cultivation at different locations including the production costs. Industrial significant progress has not occurred so far, leading to some disillusionment with this approach. Therefore, a clear strategy should be developed for upstream and downstream processes with parallel evaluation of life cycle assessment (LCA). In addition, energy intensive steps of biomass drying and solvent extraction should be avoided by using intelligent technologies, such as in situ processing of wet biomass.

Production of Biomethane and Functional Lipids from Marine Macroalgae. T. Aki^{1,2}, K.H.V. Arafiles^{1,2}, K. Watanabe^{1,2}, Y. Okamura^{1,2}, T. Tajima^{1,2}, Y. Nakashimada^{1,2}, and Y. Matsumura^{1,2}, ¹Hiroshima University, Japan, ²JST-CREST, Japan.

Marine biomass has attracted great attention in the fields of renewable bioenergy and value-added industrial and biological materials production due to the promised sustainability of its use. We have succeeded at using macroalgae (1) to produce biomethane using marine sediment-derived culture, and (2) to produce functional lipids such as polyunsaturated fatty acids (PUFA), xanthophylls, and terpenoids by using the marine protists, the thraustochytrids. Biomethane was produced through a fed-batch methane fermentation method that used a marine sediment-derived microbial consortium acclimated to high salinity. The consortium was able to degrade algal polysaccharides and assimilate the resulting organic acids to produce biomethane.

In addition to this, a number of bacteria and fungi that can degrade and convert algal saccharides into suitable substrates for thraustochytrid were obtained to serve as intermediate biocatalysts for a composite culture system that ultimately produces PUFA, xanthophylls and terpenoids. Hydrothermal treatment of algal mass and recovery of residual metals for complete utilization of marine macroalgae were also introduced.

Impact of Biochemical Composition on Susceptibility of Algal Biomass to Acid-catalyzed Pretreatment for Sugar and Lipid Recovery. T. Dong, N.J. Nagle, P.T. Pienkos, and L.M.L. Laurens*, National Renewable Energy Lab., USA.

One of the major challenges associated with algal biofuels production in a biorefinery-type setting is improving biomass utilization in its entirety, increasing the process energetic yields and providing economically viable and scalable co-product concepts. Here we focus on the impact of compositional characteristics of biomass on the susceptibility to pretreatment in a biorefinery-type setting. The release of monomeric carbohydrates in the aqueous phase and extractability of the lipid fraction was measured based a response surface methodology, allowing for the analysis of interaction effects for three algal strains; *C. vulgaris* and *S. acutus* and *N. granulata* representing three different nutritional metabolic phases. We identified distinct patterns of acid and temperature combinations on the yield of released monomeric carbohydrates and lipid extractability. Four cultivation conditions of high potential value for a combined sugar- and lipid-based biofuels process were identified, and are based on experimental results obtained from pretreatment and lipid extraction. The results indicate that acid pretreatment has potential to be applicable for a vast range of biomass samples to obtain high energy yields, but that the exact conditions and optima are dependent on the strain and likely the starting composition of the biomass.

Confocal Raman Microscopy for Quantitative Analysis of Microalgal Lipid Contents: An Integrative Workflow for Rapid *in situ* Analysis. S.K. Sharma¹, D.R. Nelson², R. Abdrabu², B. Khraiwesh², K. Jijakli², M.J. O'Connor³, T. Bahmani², H. Cai², S. Khapli^{*1}, R. Jagannathan¹, and K. Salehi-Ashtiani², ¹Div. of Engineering, New York University Abu Dhabi, United Arab Emirates, ²Lab. of Algal, Systems, & Synthetic Biology, Div. of Science & Math, Center for Genomics & Systems Biology (CGSB), New York University Abu Dhabi, United Arab Emirates, ³Core Technology Platform, New York University Abu Dhabi, United Arab Emirates.

Algal biofuels have received worldwide attention as sustainable resources to substitute fossil fuels. The economical feasibility of industrial production of algal

biofuels with desired molecular characteristics is likely to require the discovery and isolation of new algal species and subsequent strain optimization. There is a need to develop analytical techniques for rapid screening of cells for the desired lipid molecular characteristics. Here we describe an integrated workflow for *in situ* analysis of algal lipids through Raman microscopy, a technique that enables *in vivo* monitoring of lipid contents in a rapid, quantitative, and label-free, manner. To establish the workflow, we refined existing Raman analysis techniques to obtain better discrimination in chain-length and saturation of lipids. We performed characterization of lipid content of novel aquatic and soil microalgal isolates as well as lipid-expressing cells obtained in a mutagenesis screen. The workflow enabled quantitative analysis of the different saturation states among the isolates. Cell-to-cell variations among mutagenized *C.reinhardtii* cells grown under identical conditions were also observed. Our results validate the utility of Raman analysis in determination of the key parameters for the selection and engineering of microalgae necessary for optimal production of biofuels.

Integration of Experimental Systems with Engineering Process Modeling for Sustainability Assessment of Microalgal Biofuel Systems. J.C. Quinn, Mechanical & Aerospace Engineering, Utah State University, USA.

Globally, we face an energy crisis due to an increase in

energy consumption combined with the negative effects associated with traditional fossil energy sources. A variety of green technologies coming together to address environmental concerns, while meeting global increases in energy demand, is likely to be a critical component of the solution. This seminar presents the integration of experimental systems with engineering process modeling for sustainability assessment applied to microalgal biofuel systems. Sustainability modeling includes techno-economic assessments, life cycle assessments, and scalability assessment through resource availability. Data feedback from sustainability modeling is used to highlight areas for focused research and development on the metrics of economic viability and environmental impact. Further, engineering process modeling is used to identify knowledge gaps for experimental work. The integration of sustainability modeling with experimental systems is a valuable tool that can decrease experimental design space and focus research in areas that can accelerate commercialization. Experimental research spans the value chain of a microalgal biorefinery system with the focus on the generation of data for system model validation. System models are leveraged for sustainability assessments with data feedback to experimental work for focused research and development. Results show microalgae systems have the potential to be economically competitive with traditional fuels while providing a valuable environmental service.

IOP 5: Oleochemicals

Chairs: D. Graiver, Michigan State University, USA; and G. Liu, South China University of Technology, China

Bio-lubricants from Chemical Modification of Vegetable Oils.

D.D. Chauhan, T.M. Panchal, A.V. Patel, M. Thomas, and J.V. Patel, Inst. of Science & Technology for Advanced Studies & Research, India.

Increased awareness among the community of environmental pollution by petroleum-based oils for use as lubricants cause the switch to vegetable oil which is environmentally friendly. The search for using alternative sources in the preparation of lubricants has begun to actively investigate. Lubricants based on vegetable oils shows excellent tribological properties, high viscosity indices, and flash points. To compete with mineral-oil-based lubricants, some of their drawbacks are to be overcome, such as poor oxidation and low-temperature stability. 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. In present work estolide esters of vegetable oil with oleic acid were developed. Estolides are a class of esters based on vegetable oils that form 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 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 GC-MS. The results were compared with traditional petroleum based lubricants.

Moisture Activate, One Component Protective Coatings Derived from Vegetable Oils. D. Graiver, Dept. of Chemical Engineering & Materials Science, Michigan State University, USA.

Grafting reactive silanes onto unsaturated fatty acids of vegetable oils provided a simple, one component method to cure common vegetable oils by atmospheric moisture. It is well known that highly unsaturated oils (like Linseed oil) have been used for centuries in the paint industry to cure into alkyd resins. These paints cure by oxidation of the double bonds in the unsaturated fatty acid residues and yield relatively hard, brittle coatings. However, the number of unsaturated bonds in soybean oil and similar vegetable oils is not sufficient to cure the oil by this oxidation process. Instead, grafting reactive silanes onto soybean oil produced a one-component, low viscosity oil that cures to yield protective coatings by conventional brushing, dip-coating or spraying techniques with no need for a solvent or a diluent. The silylation reaction of the unsaturated fatty acids was successfully accomplished using the 'Ene' reaction route, which is a subset of the famous Diels Alder reaction. The effect of temperature and silane concentration on the yield and the kinetics of the grafting reaction were studied as well

as the properties of the coatings.

Synthesis of Renewable 1,4-Cyclohexadiene from *Camelina sativa* Through Olefin Metathesis. R.L. Maglinao, C. Hulett, and E.P. Resurreccion, Montana State University-Northern, USA.

Olefin metathesis of unsaturated fatty acid alkyl esters (FAAE) presents a convenient route in producing renewable chemicals such as polymer precursors, functionalized alkenes, and fuels. One particular product of interest is 1,4-cyclohexadiene (1,4-CHD), an organic compound utilized in polymer preparation. The metathesis of polyunsaturated FAAE have been previously researched to produce 1,4-CHD. There are a number of oilseed types suitable as feedstock in the synthesis of 1,4-CHD, one of which is *Camelina sativa* (camelina). Camelina contains about 50% by weight of polyunsaturated fatty acid components with almost equal levels of linoleic and linolenic acids. Olefin metathesis of camelina is anticipated to generate high yields of 1,4-CHD. This study aimed at investigating the production yields of 1,4-CHD through olefin metathesis of fatty acid methyl esters (FAME) derived from camelina. The experiment was allowed to proceed using a closed batch-type reactor. Various reactants (i.e., methyl linolenate, methyl linoleate, and camelina FAME) and a second-generation Grubbs catalyst were used in the metathesis reactions. Results indicated that plants oils with higher amounts of polyunsaturated components, specifically methyl linolenate, yielded more of 1,4-CHD. It was also evident that the separation of 1,4-CHD from other products can be achieved through simple vacuum distillation.

Synthesis and Characterization of Palm Oil Based Polyols and Polyurethanes. S.S. Hoong, T.N.M.T. Ismail, M.N. Sattar, K.D.P. Palam, N.A. Hanzah, N.M. Noor, S. Adnan, A.M. Zan, Z.A. Bakar, S.K. Yeong, and H.A. Hassan, Malaysian Palm Oil Board, Malaysia.

This presentation highlights the synthesis of palm based polyols through different methods that yielded few types of polyols, which eventually were used to make a variety of polyurethane products. Hydroxy groups were introduced to palm oil derivatives structures through chemical manipulation of alkene and ester groups to yield polyols. One of the methods employed was Prilezhaev epoxidation of alkene group followed by epoxide ring opening with ethylene glycol. This method generated palm based polyol with hydroxyl value between 110-130mgKOH/g that can be used as drop-in replacement for conventional petrochemical based polyols in the production of viscoelastic polyurethane foams. Another synthetic approach involved esterification of oleic acid with glycerol to yield monoglyceride and diglycerides that were later epoxidized and subsequently ring opened

with ethylene glycol to yield a polyol with relatively high hydroxyl value of 200mgKOH/g. The high hydroxy content of this polyol enables it to be used in the production of rigid polyurethane foam products such as decorative panels. Furthermore, copolymers of tetrahydrofuran and epoxidized palm oil derivatives were produced through ring opening polymerization. These copolymers have hydroxy groups that were reacted with diisocyanate to make elastomeric polyurethane products.

New Process and Products for Glycerine in Biodiesel

Production? S.S. Awbrey¹, T. Alexander¹, and E.M. Hernandez*², ¹Envirosource, Inc., USA, ²Advanced Lipid Consultants, USA.

The US produced over 1.27 billion gallons of biodiesel in 2014. Biodiesel is made mostly from soybean oil, yellow grease, corn, canola, palm and other vegetable oils. One important byproduct resulting from biodiesel manufacturing is glycerine, or glycerol, approximately ten percent of the starting material. It is generally recognized that due to the rapid worldwide expansion in biodiesel production there is a global oversupply of waste glycerol and outlets for its usage are needed. Glycerol can be purified for food, cosmetic and pharmaceutical applications. However purification steps are costly and therefore the majority of waste glycerol is used in low profit applications. This presentation will include a new low cost method for processing waste glycerol as well as some new patented industrial applications. The basic process starts with an emulsion composed of a glycerol-rich portion and a fatty acids-rich portion. The glycerol-rich portion was first filtered to remove residual solids and reacted with an oxidant and a catalyst which resulted in blends comprising of glyceric acid, oxalic acid, glycolic acid, formic acid and other organic acids. This modified glycerol, in combination with deswelling clays, were used to produce effective, low polluting, drilling and fracking products. Other applications included the production of corrosion removal products and hydrate prevention in oil drilling operations.

Conversion of Lipids into Various Chemicals/Monomers.

A. Ullah and M. Arshad, University of Alberta, Canada.

The use of renewable resources in supplementing and/or replacing traditional petrochemical products, through green chemistry, is becoming the focus of research. The utilization of oils can play a primitive role towards sustainable development due to their large scale availability, built-in-functionality, biodegradability, and no net CO₂ production. Microwaves, being clean, green, and environmentally friendly, are emerging as an alternative source for product development. Solvent free conversion of canola oil and fatty acid methyl esters (FAME's) derived from canola oil and waste cooking oil under microwave irradiation demonstrated dramatically enhanced rates. The microwave-assisted reactions lead to the most valuable terminal olefins with enhanced yields, purities and dramatic shortening of reaction

times. Various monomers/chemicals were prepared in high yield in very short time. The complete conversions were observed at temperatures as low as 40°C within less than five minutes. The products were characterized by GC-MS, GC-FID and NMR. The ability for complete conversion of oils in just few minutes under solvent free conditions is undoubtedly an attractive concept from both an academic and an industrial point of view.

Superior Flexible and Rigid Polyurethane Foams from Metathesized Palm Oil. P.S. Pillai and S.S. Narine, Trent University, Canada.

Palm Oil, because of its high content of saturated fatty acids, is a generally poor substrate for the preparation of functional polyols for use in polyurethane foam manufacture. This talk discloses the use of 1-butene cross metathesized palm oil (PMTAG) as a feedstock for preparation of highly functional polyols which can be used to prepare industry-leading rigid and flexible polyurethane foams. Polyols prepared from PMTAG were demonstrated to result in rigid foams with a compressive strength approximately three times higher than that of rigid foams from palm and soybean oil polyols. Furthermore, strength of the foams were further improved through dry fractionation of the PMTAG, resulting in high quality rigid foams with 1.5 times improved compressive strength. An optimized, cost effective, green, solvent free synthetic strategy for the polyols will be presented, which allows the facile control of hydroxyl numbers. These polyols also provided flexible foams with low compressive strengths and high recovery post compression.

Effect of Roasting on Antioxidant Capacity and Physico-chemical Properties of Wheat Germ Oil. Y. Zou, Y. Gao, and T.K. Yang, Wilmar (Shanghai) Biotechnology Research & Development Center Co., Ltd., China.

Wheat germ oil (WGO) is a good source of highly concentrated nutrients, especially for Vitamin E. In this study, changes in oxidative stability, bioactive components, volatile compounds, and antioxidant activities of WGO extracted from wheat germ roasted at 180°C for 0-20min were investigated. Antioxidant activities and oxidative stability of WGO increased with roasting. Compared to oil from unroasted wheat germ, oils from wheat germ roasted for 20min demonstrated the highest total phenolics, but a slight reduction in total tocopherols and β-carotene content. Fatty acids profile was not affected, whereas hydroxymethylfurfural (HMF) content increased significantly, suggested the extent of Maillard reaction increased significantly with roasting. Among volatiles, esters such as n-butyl acrylate, and acids, such as hexanoic acid, prevailed in WGO from unroasted wheat germ. However, after roasting, these compounds decreased or disappeared and furfurans, pyrazines, and pyranes with high odor activity became the most abundant.

Self-condensed Polyols. M. Ionescu, X. Wan, V. Jaso, and Z.S. Petrovic, Kansas Polymer Research Center, Pittsburg State University, USA.

Vegetable oil polyols (e.g. castor oil, polyols obtained by ring opening of epoxidized oils with alcohols, hydroformylation polyols) have in the same structure ester bonds and hydroxyl groups. By heating of a vegetable oil polyol in the presence of a transesterification catalyst (sodium methoxide, potassium methoxide, stannous octoate,

dibutyl tin dilaurate, titanium isopropoxide, and others) between the ester bonds and hydroxyl groups is established a transesterification equilibrium with the formation of oligomers, monoglycerides, diglycerides, and glycerol. By high vacuum distillation of glycerol from the reaction system the equilibrium is shifted to the formation of high molecular weight biobased polyols suitable for preparation of elastic polyurethanes (flexible and semiflexible foams, cast elastomers, coatings, adhesives).

IOP-P: Industrial Oil Products Poster Session

Chairs: B.R. Moser, USDA, ARS, USA; and D. Pioch, CIRAD, France

1. Bifunctional Fatty Acid Esters as High Performance Bioplasticizers. D.R. Kodali and L.J. Stolp, University of Minnesota, USA.

Plasticizers are high-boiling organic liquids that impart flexibility to polymers. The plasticizers are useful mainly in PVC the third largest commercial plastic. Recently, the use of phthalates in products such as medical plastics, food contact materials, and children's toys has come under intense scrutiny as they have been shown to cause many ailments including hormonal disruptions, cancer and other harmful effects. The high oleic oils are particularly suitable raw materials for developing new plasticizers due to greater homogeneity (>80% oleic acid). Various functional groups were introduced at the ester head group and the fatty acid backbone of oleic acid esters to create polar branches that enhanced the PVC compatibility. The TAGs were converted to fatty acid esters by transesterification with various alcohols. The double bonds present on the backbone and/or at the headgroup were converted to epoxy function. The epoxy groups were ring opened with acids or alcohols to form the esters, ethers and free hydroxyls. The free hydroxyls were acetylated to give the final products. The resulting bifunctional fatty acid esters showed excellent physical and plasticizer properties. They have low color, viscosities, and acid values. The plasticizers compounded with PVC gave low gelation times and temperatures with high thermal stability.

2. Development of Food-grade Filled Hydrogels for Oral Delivery of Lipophilic Active Ingredients: PH-triggered Release. Z.P. Zhang¹, R.J. Zhang¹, and D.J. McClements^{1,2}, ¹Dept. of Food Science, University of Massachusetts Amherst, USA, ²Dept. of Biochemistry, King Abdulaziz University, Saudi Arabia.

For certain applications in the food, personal care, and pharmaceutical industries there is a need for oral delivery systems for lipophilic active agents, such as oil-soluble flavors, antimicrobials, or drugs. Hydrogel particles fabricated from food-grade biopolymers can be used to develop this type of oral delivery system. In this study, hydrogel particles were fabricated by electrostatic complexation of a protein (casein) and an anionic polysaccharide (alginate). Relatively small hydrogel particles were formed at pH values just above the isoelectric point of the protein (where both biopolymers are negative) using 1% fat, 0.33% casein, and 1.33% alginate, which was attributed to electrostatic attraction between anionic groups on alginate and cationic groups on casein. The hydrogel particles remained intact from pH 4 to 5 but aggregated or dissociated at lower or higher pH values. Light scattering and confocal fluorescence microscopy indicated that lipid droplets encapsulated within the hydrogel particles were released under simulated oral conditions, which was triggered by a pH change. Our results suggest that hydrogel

particles based on electrostatic complexation of casein and alginate may be useful for oral delivery of lipophilic active agents.

3. Enhancing Nutraceutical Bioavailability from Raw and Cooked Using Excipient Emulsions: Influence of Lipid Type on Carotenoid Bioaccessibility from Carrots. R.J. Zhang¹, Z.P. Zhang¹, L.Q. Zou¹, H. Xiao¹, G.D. Zhang¹, E.A. Decker^{1,2}, and D.J. McClements^{1,2}, ¹Dept. of Food Science, University of Massachusetts Amherst, USA, ²Dept. of Biochemistry, King Abdulaziz University, Saudi Arabia.

The influence of lipid type on the ability of excipient emulsions to increase carotenoid bioaccessibility from raw and cooked carrots was investigated using a gastrointestinal tract (GIT) model. Excipient emulsions were fabricated using whey protein as an emulsifier and medium chain triglycerides (MCT), fish oil, or corn oil as the oil phase. Changes in particle size, charge, and microstructure were measured as the carrot-emulsion mixtures were passed through simulated mouth, stomach, and small intestine regions. Carotenoid bioaccessibility depended on the type of lipids used to form the excipient emulsions (corn oil>fish oil>>MCT), which was attributed to differences in the solubilization capacity of mixed micelles formed from different lipid digestion products. The bioaccessibility of the carotenoids was higher from boiled than raw carrots, which was attributed to greater disruption of the plant tissue facilitating carotenoid release. In conclusion, excipient emulsions are highly effective at increasing carotenoid bioaccessibility from carrots, but lipid type must be optimized to ensure high efficacy.

7. Fatty Acid Profile of 25 Plant Oils and Implications for Industrial Applications. B.R. Moser, USDA, ARS, NCAUR, Bio-Oils Research Unit, USA.

The fatty acid (FA) profiles of plant oils extracted from twenty-five alternative feedstocks were determined. This information was utilized to determine what industrial application(s) each oil is best suited for. The basis for the selection was the premise that FA composition influences properties of industrial products and fuels produced from plant oils. For instance, saturated FAs have high oxidative stability but poor low temperature properties and lack a double bond to perform chemical modification on. Polyunsaturated FAs exhibit the opposite behavior. Monounsaturated FAs strike a balance between oxidative stability, cold flow properties and chemical functionality. For example, paints, varnishes and coatings are prepared by chemically modifying vegetable oils enriched in polyunsaturated FAs whereas those containing high amounts of saturated FAs find applications in soaps, cosmetics and detergents. Biodiesel, lubricants and plasticizers are typically prepared from vegetable oils containing a high percentage of

monounsaturated FAs. A selection matrix based on FA composition is proposed that aids in the determination of industrial and/or fuel applications of vegetable oils. Some of the feedstocks investigated include camelina, field pennycress, Moringa, Osage orange, and seashore mallow seed oils, among others.

8. Conversion of Crude Glycerol to Value-added Chemicals in Alcohol. S. Ren and X.R. Ye*, University of Tennessee, USA.

To increase the efficiency of biodiesel production and minimize the generation of waste, this study aimed at directly using the residual mixture of glycerol and methanol/ethanol from the biodiesel production for value-added chemical production. Catalytic conversion of refined glycerol to lactic acid (LA) and propylene glycol (PG) using mixed solid catalysts of CaO and CuO in methanol medium was first investigated. At the optimum condition, the yields of LA and PG achieved were 46mol% and 35mol%, respectively. For recycling the catalysts, a combined process of glycerol conversion to alkyl lactate was further investigated. Using this combined process, 45mol% methyl lactate yield and 28mol% PG yield were achieved in methanol medium, and 45mol% ethyl lactate and 18mol% PG yield were achieved in ethanol medium. Test for crude glycerol conversion showed that the impurities had slightly negative effects on glycerol conversion and product yield in methanol medium but no obvious effect in ethanol medium because of the higher reaction temperature use. Similar glycerol conversion and product yield were obtained when the mixture of glycerol, methanol, and CaO from biodiesel production were directly used as starting material. This result suggests that the residual mixture from biodiesel production can be directly used to produce valued-added chemicals such as methyl lactate and PG.

9. A Novel Cardanol-based Antioxidant and Its Application in Vegetable Oils and Biodiesel. Z. Liu¹, J. Chen², G. Knothe¹, X. Nie², and J. Jiang², ¹USDA, ARS, NCAUR, USA, ²ICIFP, CAF, China.

A novel antioxidant, epoxidized cardanol (ECD), derived from cardanol has been synthesized and characterized by FT-IR, ¹H-NMR, and ¹³C-NMR. Oxidative stability of ECD in vegetable oils and biodiesel were evaluated by the pressurized differential scanning calorimetry (PDSC) and Rancimat method, respectively. The results indicated that ECD exhibited antioxidative activity in soybean oil and increased its onset temperature (OT) by nearly 10°C with 0.7wt% ECD. It was also observed that other vegetable oils showed significantly improved oxidative stability with the addition of 0.7wt% ECD. Olive oil showed the highest increased OT by 19.5°C. Furthermore, the ECD has superior antioxidant activity compared to the synthetic antioxidant butylated hydroxytoluene (BHT), and thus could be used as an optimized primary antioxidant for biodiesel. ECD could be a new bio-based antioxidant with better thermal stability.

10. Synthesis and Characterization of Estolides Containing Epoxy and Cyclic Carbonate Groups. J.A. Kenar, S.C. Cermak, K.M. Doll, and T.A. Isbell, USDA, ARS, NCAUR, USA.

The unsaturated sites in 2-ethylhexyl estolides were converted into 5-membered cyclic carbonate groups utilizing a two-step process. First, epoxidation of the alkene bonds was accomplished using formic acid and hydrogen peroxide. The epoxidized estolide material was then reacted with supercritical carbon dioxide in the presence of tetrabutylammonium bromide catalyst to produce the cyclic carbonate moiety. The epoxidized intermediate and the carbonated estolides were characterized by FTIR and both ¹H and ¹³C NMR spectroscopies. The signals at 1807cm⁻¹ and δ 82ppm in the FTIR and ¹³C NMR spectra, respectively, confirmed the desired cyclic carbonate was produced. The carbonated estolide exhibited a dynamic viscosity at 25°C of 172mPa•s as compared to 155mPa•s for the estolide starting material.

11. Synthesis of Phenolic Branched-chain Fatty Acids.

Z. Yan^{1,2}, K. Wagner¹, X. Fan¹, A. Nuñez¹, R.A. Moreau¹, and H. Ngo¹, ¹USDA, ERRC, USA, ²School of Chemistry & Chemical Engineering, South China University of Technology, China.

Microbial food safety continues to be a major health concern despite recent advances. Natural monoterpene phenols are derivatives from bio-resources and exhibit significant biological activities including anticancer, antibacterial and antioxidant activities. Phenolic lipids synthesized from monoterpene phenol are a class of natural products composed of hydrophobic aliphatic long chains and hydrophilic phenolic regions. It occurred to us that designing highly stable fatty acids with natural monophenol branched chains might enhance the original biological activities of parent natural phenolic monoterpene. The synthesis of these kinds of phenolic branched-chain fatty acids is interesting as the raw materials are totally natural and renewable. In this presentation, phenolic branched-chain fatty acids prepared by treating unsaturated linear-chain fatty acids (derived from renewable vegetable oils) and excess monoterpene phenol with catalytic amounts of solid catalysts will be discussed. Preliminary investigations of the antimicrobial properties of these phenolic branched-chain fatty acids will also be presented. These novel compounds promise to have a potential to be used to improve microbial safety of food.

13. The Industrial Application of Modified Fatty Acid Oligomer in Lubricating Oil. J.W. Chu, W.C. Jeong, and Y.G. Choi, Ohsung Chemistry Co., Republic of Korea.

Recently, in order to reduce the use of petroleum products, pro-environmental lubricating oil and lubricant additives are widely studied which was obtained from plant oils or esters. Especially, ricinoleic acid based estolide has been applied for lubricity improver or emulsifying agent for cutting fluid. However, ricinoleic acid derived from castor oil is very expensive and which varies severely depending on the

crop situations. Thus, we have studied on the alternative oligomers and successfully synthesized the oleic acid based oligomer that performs great for cutting fluid. The condensation compound we have synthesized is like the intermolecular esterification of several oleic acid and the -OH group appeared was obtained through the epoxy, ring opening reaction by oleic acid and hydrogen peroxide under the catalyst of formic acid. This modified oleic acid oligomer has a uniform degree of polymerization and good lubrication performance. Compared to the ricinoleic acid molecular, manufacturing unit price of our synthesized oligomer is lower and if our product is used in making cutting fluid, it has better lubricity. In addition, our product is not only applied in cutting fluid, but also used in rolling fluids, metal forming fluids and other industrial lubricants.

14. Biodiesel Production from Oil Extracted from Roselle (*Hibiscus sabdariffa*) Seeds Using Alkaline Transesterification Reaction. A. Hayyan^{1,2}, ¹Dept. of Chemical Engineering, University of Malaya, Malaysia, ²University of Malaya Centre for Ionic Liquids (UMCiL), Malaysia.

Roselle is plant available in West African and Middle East and may be known as carcade. In this study, oil of Roselle (*Hibiscus sabdariffa*) seeds was converted to biodiesel fuel. The seeds were obtained from Sultanate of Oman and the oil was extracted using n-Hexane. The fatty acid composition of the extracted oil was investigated. The extracted oil was further transesterified using methanol in presence of potassium hydroxide. The effects of different operating conditions such as catalyst dosage, reaction time, molar ratio, and reaction temperature were optimized. The produced biodiesel met the EN-14214 international biodiesel standard specifications. This study revealed that oil extracted from Roselle seeds is potential to be used in many applications such as biodiesel and bio-lubricant.

15. Production of Biodiesel from Acidic Crude Palm Oil using 1-butyl-3-methylimidazolium Hydrogensulfate Ionic Liquid as a Catalyst. A. Hayyan^{1,2}, B.E.A. Alweish^{1,2}, M. Hayyan^{2,3}, and M.A. Hashim^{1,2}, ¹Dept. of Chemical Engineering, University of Malaya, Malaysia, ²University of Malaya Centre for Ionic Liquids (UMCiL), University of Malaya, Malaysia, ³Dept. of Civil Engineering, University of Malaya, Malaysia.

In this study, acidic crude palm oil was proposed as a potential raw material for biodiesel production. Ionic liquid (IL) such as 1-butyl-3-methylimidazolium hydrogensulfate was used as catalyst for esterification of free fatty acid (FFA). The effect of operating parameters such as IL dosage, molar ratio, reaction temperature, and reaction time on FFA conversion was reported in this study. Single factor optimization was employed for laboratory scale batch esterification reaction. The optimum conditions reduced the FFA content from 10% to less than 2%. 1-butyl-3-methylimidazolium hydrogensulfate was successfully recycled four times. The

biodiesel produced from ACPO met the specifications in the EN 14214 and ASTM D6751 standards.

16. Supercritical Fluid Extraction and Bioactivity of Cedarwood Oil. F.J. Eller¹, L.B. Flor-Weiler², and R.W. Behle², ¹USDA, NCAUR, ARS, FFR, USA, ²USDA, NCAUR, ARS, CPR, USA.

Supercritical carbon dioxide (70°C, 4,000psi) was used to extract cedarwood oil from Eastern redcedar, *Juniperus virginiana* L. The CO₂-derived oil was tested for biological against several species of arthropods, including mosquitos, ticks, houseflies and ants. The cedarwood oil was found be toxic to all species tested and lethal concentrations were determined. The cedarwood oil was also found to be repellent to ants in a field trial. Cedarwood oil is Generally Recognized as Safe (GRAS) and has potential for use as a natural pest management tool.

17. Biodiesel Production from Acidic Soybean Oil Using Solid Mixtures of Li₂SiO₃ and Zeolite ABW as Heterogeneous Catalysts. Y.J. Chen, D.Y. Lin, and B.H. Chen*, National Cheng Kung University, Taiwan.

Biodiesel is successfully produced via the catalyzed transesterification of acidic soybean oils (acid value=0.75mg KOH/g oil) at 60°C with an initial loading of oil/methanol/cat =1/20/1 (by mas). The heterogeneous catalysts used in this work are the solid mixtures of lithium metasilicate and zeolite ABW prepared hydrothermally from diatomite and alumina using lithium hydroxide as the alkali. Various instruments such as XRD, SEM, FTIR and TPD are employed to characterize these catalysts. Process variables such as catalyst-to-oil, methanol-to-oil ratio, operation temperature are studied in order to optimize the reaction conditions.

The conversion of soybean oil to biodiesel could reach ca. 90% after 3h of transesterification reaction. In general, the durability test of the catalysts indicates that a conversion efficiency near 80% could still be achieved after 5 consecutive runs. With an acid value increased to about 20mg KOH/g oil by spiking 10wt% oleic acid into the soybean oil, a conversion efficiency near 90% could still be attained after 3 hours of transesterification. However, the catalysts are quickly deactivated after the first two runs. The two-stage strategy is proposed to extend the durability of the catalyst.

19. Biodiesel from Microalgae Oil via Ultrasound-assisted *in situ* Alkaline Transesterification: (I). Effect of Co-solvent. N. Martinez¹, N. Callejas¹, E. Morais², J. Costa², I. Jachmanián¹, and I. Vieitez*¹, ¹Facultad de Química, Universidad de la República, Uruguay, ²Escuela de Química y Alimentos, Universidad Federal de Rio Grande, Brazil.

Microalgae oil has been gained interest as a new feedstock for biodiesel. However, oil extraction from biomass involves complex procedures. Thus, *in situ* transesterification, involving reaction directly on dry algae biomass, through a one step process, has shown several advantages over

conventional process.

Efficiency of direct alkaline methanolysis of dry biomass from *Spirulina sp.* (7.0% lipid content), assisted by ultrasound radiation (at 80W and 40KHz) was studied.

Transesterification was performed in batch reactors using a biomass/methanol ratio of 1:2 (wt/v) and 2% of KOH as catalyst. Under these conditions the weight yield obtained after 2 hours of reaction was 0.9%, with an ester content of 63.6%. When reaction was performed with application of ultrasound radiation, although did not affect the yield, the ester content increased to 97.6%.

Weight yield increased to 3.0% when chloroform was used as co-solvent at a ratio 2:1 (v/v to methanol), but the ester content decreased to 64.1%. However, with hexane, ester content decreased only to 92.8%, but weight yield obtained was 1.0%.

Ester content of direct transesterification of microalgae biomass can be enhanced by assisting process with ultrasound radiation. Although using co-solvents could improve weight yield, a negative effect on conversion must be considered.

20. Biodiesel from Microalgae Oil via Ultrasound-assisted *in situ* Alkaline Transesterification: II. Effect of Ultrasound Power. N. Martinez¹, N. Callejas¹, E. Morais², J. Costa², I. Jachmanián¹, and I. Vieitez*¹, ¹Facultad de Química, Universidad de la República, Uruguay, ²Escuela de Química y Alimentos, Universidad Federal de Rio Grande, Brazil.

Microalgae oil has been gained interest as a new feedstock for biodiesel. One single process combining extraction/conversion of oil from microalgae biomass emerges as one of the key parameters in producing biodiesel from microalgae, to improve the profitability of the process. The *in situ* transesterification of microalgae biomass was studied in our previous work, focused on the effect of co-solvent on process efficiency. In this work, effect of the ultrasound power used was studied. Powers of 108, 144 and 180W were applied at a frequency of 37kHz for different reaction times under the same conditions described previously: alkaline methanolysis of dry biomass from *Spirulina sp.* (7.0% lipid content) in batch reactors using a biomass/methanol ratio of 1:2 (wt/v) and 2% of KOH as catalyst.

Weight yields of 1.5% were achieved after 30 minutes of reaction, and it were not affected by the power of ultrasound radiation. However, ester content increased from 73.3% to 95.2%, by increasing the power from 108W to 180W. When the reaction was performed during 120 minutes at 180W, a weight yield of 1.8% was achieved and an ester content of 95.5% was obtained. Results showed that ester content achieved depend of the ultrasound power applied.

21. Crop Production of Acetyl-triacylglycerols as a New Source of Emulsifiers, Plasticizers, Biolubricants, and Reduced Calorie Oil. J.B. Ohlrogge^{1,2}, J. Liu^{1,2}, and T.P. Durrett³, ¹Dept. of Plant Biology, Michigan State University, USA, ²Great Lakes Bioenergy Research Center, USA, ³Dept. of Biochemistry & Molecular Biophysics, Kansas State University, USA.

We have engineered *Camelina* to produce acetyl-triacylglycerols (acetyl-TAG) at high levels in seeds. Structures similar to acetyl-TAG (e.g. acetylated mono- and diglycerides, ACETEM) have GRAS status and are currently used in the food industry as emulsifiers and as plasticizers for food packaging. Compared to conventional vegetable oils, their lower viscosity and freezing point may provide advantages as biodegradable lubricants, coatings, hydraulic fluids, transformer oils or fuels. Field production has provided over 50 gallons of oil and several varieties with medium chain and other fatty acid compositions are under development. Information on the thermal and physical properties of the oil will be presented. Samples are available to researchers and companies interested in testing or collaborating on applications of the oil.

22. Evaluation of Techniques for Reducing Sulfur Content of Biodiesel Produced from Grease Trap Waste and Sewage Scum Grease. R.A. Cairncross^{1,2}, M.E. Hums^{1,2}, and S. Spataro^{1,2}, ¹Chemical & Biological Engineering Dept., Drexel University, USA, ²Civil, Architectural, & Environmental Engineering Dept., Drexel University, USA.

A major challenge to producing biofuels from waste materials is elimination of sulfur contaminants to meet regulated fuel specifications. There are a variety of wastes that are currently underutilized and are being explored for their conversion to biofuels including Fats, Oils, and Greases (FOG) from wastewater. Processing wastes to biofuels requires additional purification steps, with sulfur removal identified as a critical challenge. Research has demonstrated that acid-catalyzed esterification of wastewater FOG combined with stripping and vacuum distillation converts some chemically-bound sulfur groups and removes both light and heavy sulfur species. Our research has shown this process to be effective at reducing sulfur from 300-550PPM in brown grease lipids to 10-50PPM in the biofuel product. The presentation evaluates the potential of several process modifications to reduce sulfur content. Development of an efficient sulfur-reduction technology is necessary to produce economically-competitive and environmentally-benign drop-in fuels from waste greases.

23. Synthesis of Soybean Oil-based Epoxide with a Terminal Epoxy Group for Developing New Polycarbonate Polymers via the Copolymerization with Carbon Dioxide. X. Luo, C. Chang, Y. Qin, and Y.B. Li, Dept. of Food, Agricultural, & Biological Engineering, Ohio State University,, USA.

Aliphatic polycarbonates that are readily accessible by

the copolymerization of epoxides with carbon dioxide (CO₂), have recently attracted considerable interests on their development and applications in plastics industry. In this study, soybean oil-based epoxy monomers with a terminal epoxy group were synthesized by the saponification of soybean oil followed by epoxidation. Three processes for the production of soap from soybean oil were compared. Epoxidation reaction parameters, including the molar ratio of epichlorohydrin (EPCH) to soap, phase transfer catalyst (cetyltrimethylammonium bromide, CTAB) loading, and reaction time, were optimized based on the response surface methodology via a Box-Behnken experimental design. The soybean oil-based epoxy monomers synthesized under the optimal reaction condition was further copolymerized with CO₂ for the production of polycarbonate polymers. The structures of the epoxy monomers and their derived polycarbonates were characterized by ¹H-NMR and FT-IR. The polycarbonate properties were also evaluated using GPC, DSC, and TGA. This study demonstrated great potential in the development of bio-based polymers from soybean oil and CO₂, which reduced the dependence on petroleum resources and CO₂ emissions.

24. A Camelina Oil Polyol That Can Be an Alternative to Castor Oil in Polymer Formulations. T.S. Omonov¹, E. Kharraz¹, J. Grushcow², R. Bergstra², and J.M. Curtis*¹, ¹Lipid Chemistry Group, Dept. AFNS, University of Alberta, Canada, ²Linnaeus Plant Sciences Inc., Canada.

Castor oil is a natural polyol widely used in polyurethanes, lubricants, surfactants and many oleochemical products. Although a renewable biobased product, its production is geographically limited resulting in fluctuations in supply and price. We have developed camelina oil polyols with properties similar to those of castor oil which could be drop-in replacements in various applications. The patent pending derivitization process both preserves the triacylglyceride structure and results in a similar amount of hydroxylation and viscosity to that found in castor oil. The reaction of castor oil and camelina polyols with p-MDI to produce polyurethanes was studied via their rheological behavior during curing, which established their relative reactivities. The thermo-mechanical properties of the PU

produced using both polyols were evaluated by DSC and DMA. Results indicate that in PU applications, the reactivity of camelina polyols can be readily adjusted to match that of castor oil. However, the thermo-mechanical properties (e.g. Tg) of cured polyurethanes from camelina polyol significantly exceed those made using castor oil. Overall, this study demonstrates that polyols from non-food camelina oil can be produced with a range of viscosities, hydroxyl functionalities and overall reactivities. The ability to adjust these parameters offers a significant advantage over castor oil.

25. Techno-economic and Lifecycle Assessment of the Conversion of Microalgae to Liquid Fuels and Intermediate Value Products. C. DeMill², R.W. Davis¹, A. George¹, R.C. Pate¹, B.C. Wu¹, and W. Wu¹, ¹Sandia National Lab., USA, ²Utah State University, USA.

The production of alternative transportation fuels is imperative to meet energy demands without contributing to climate change. Advances in alternative processing techniques that have emerged due to interest in microalgae as a feedstock have led to a variety of potential pathways for the production of bio based fuels.

Comparison of alternative processing pathways on the metrics of environmental impact and economic feasibility has been limited due to inconsistencies in systems boundaries, lack of sub-process fidelity, and unrealistic scaling assumptions. Sub-process modeling combined with life cycle assessment (LCA) and techno-economics (TEA) facilitates the evaluation of various bio refinery processing technologies for the purpose of directly comparing and quantifying environmental impact and economic viability of alternate pathways. Since each pathway can be composed of different processes with varying conditions this model consists of modules that analyze specific portions of each process. One such example compares a base-line scenario cost comparison of a whole algae HTL against a tandem biochemical + HTL processing of residue which indicated a minimum fuel selling cost of \$6.27/GGE and \$6.56/GGE respectively.

Understanding and comparing various processing technologies will enable higher resolution assessments and focus future research and development.