

BIO 1.1/IOP 1: Biorenewable Polymers

Chairs: Richard D. Ashby, USDA, ARS, ERRC, USA; and Baki Hazer, Kapadokya University and Bülent Ecevit University, Turkey

Synthesis of Resinic Acid and Lignin Derivative Dimers for Copolymerization with Vegetable Oil-based Monomers Audrey Llevot*, *LCPO, France*

The awareness of environmental deterioration and our dependency on depleting fossil feedstocks force research to find innovative solutions in order to design a more sustainable future. With a worldwide plastic production of over 300 million metric tons per year, polymer science represents a very active field in the use of renewable feedstocks. Among the available bioresources, vegetable oils lead to a large platform of aliphatic molecules and to a wide range of thermoplastic and thermoset polymers after modifications. In order to broaden the palette of renewable polymers, other molecules need to be investigated and used to tune the thermomechanical properties of the vegetable oil-based aliphatic polymers. Cycloaliphatic and aromatic compounds are two categories of molecules which enable the synthesis of polymers with high thermal stability and rigidity. In our work, a polycyclic biobased molecule, i.e., resinic acids, and phenolic compounds potentially derived from lignin were studied as comonomers for vegetable oil-based polymers. Both classes of substrates were dimerized in order to get difunctional symmetric synthons. On the one hand, abietic acid dimers synthesized via a cationic mechanism were esterified with undecenol and copolymerized with undecenyl undecenoate by ADMET methodology. On the other hand, we developed a “green” process to dimerize phenolic compounds derived from lignin

in large quantity and high yield via enzymatic catalysis using a laccase. After chemical modifications, the obtained dimers were tested in copolymerization with different fatty acid derivatives. The thermomechanical properties of the polymers will be discussed, as well as the sustainability of their synthesis.

Dual Cure Alkyds Mark D. Soucek*, *University of Akron, USA*

A number of different approaches have been used to speed the curing/drying process: 1) reactive diluents, allyl ether; 2) change catalyst Fe based; 3) change curing mechanism, moisture, UV or Visible light. Light curable alkyds were synthesized by functionalizing hydroxyl terminated medium and long linseed oil alkyds with methacryloyl chloride or acryloyl chloride. Two glycerol based reactive diluents were prepared by reacting glycerol with methacryloyl chloride or acryloyl chloride. Real time FTIR, photo-DSC and UV-Rheometer were used to study the curing kinetics of UV curable alkyd with 0–30 wt% of reactive diluent. The conversion of methacrylic and acrylic double bonds are above 80% within 10s of radiation at wavelength ranging from 320nm to 500nm. The polymerization rate increases with the addition of reactive diluent, however the final conversion slightly decreases with increasing percentage of reactive diluent due to the formation of crosslinking between UV curable alkyd and reactive diluent limiting the mobility of the reactive double bonds. DMA was utilized to

determine the T_g and crosslink density of each system. With the increase of reactive diluent percentage, initial elastic modulus and crosslink density will also increase.

Reflection of Structural features of oils on properties of polymeric materials

Zoran Petrovic*, *Pittsburg State University, USA*

Oils are present in all living organisms as an important energy source. They are triglycerides of widely varying composition. Natural oils as a platform for new oleochemicals have several features which make them attractive for a range of new products. They are generally very heterogeneous in structure, length of fatty acids, number of double bonds, with or without functional groups and varying their positions in the fatty acid chains. Generally, oil-based materials are softer than corresponding products from petrochemical sources but structural peculiarities can be beneficial or detrimental depending on application. Effects of specific features of oils on properties will be discussed.

Bio-based Oil Potential in Additive

Manufacturing. Ivan Javni¹, Olivera Bilic², Jian Hong², Vivek Sharma¹, Xianmei Wan¹, and Jamie M. Messman⁴, ¹*Pittsburg State University, USA*; ²*Kansas Polymer Research Center, Pittsburg State University, USA*; ³*Dept. of Energy's National Security Campus, managed by Honeywell FMT, LLC, USA*

Additive Manufacturing (AM), or 3D printing is a rising technology that is breaking existing product design and manufacturing methods. This technology is advancing very strongly in capability of making complex elements in low volumes in a rapid and cost-effective way. This technology involves very different processes, such as Fused Deposition Modeling (FDM),

Stereolithography (SLA), Selective Laser Melting (SLM), Selective Laser Sintering (SLS), etc. The progress in production systems and machinery is followed by strong demand for new materials that can meet the specific requirements of new technology. Plastics produced from petrochemicals are common materials in this area. Due to the depleting natural resources and negative effect of carbon dioxide on the environment, there is a strong demand for replacement of petrochemicals with bio-based renewable resources. Bio-based plastics can be made from a variety of natural resources, including oils. Bio-oils are emerging and are promising raw materials for synthesis of a variety of polymers and plastics, including those that can be used in additive manufacturing. Natural oil based non-isocyanate polyurethanes (NIPUs) synthesized from cyclic carbonates and amines are promising new materials for this application. There are some structural specifics of NIPUs which give them excellent adhesive properties. We used soybean oil based NIPUs for improvement of interlayer adhesion of polylactic acid filaments used in AM. The effect of natural oil-based NIPUs on physical and mechanical properties of filaments was evaluated. The experimental results corroborated the presumed NIPUs structure and their effect on filament preparation and 3D printing.

Multifunctional Fatty Acid Macroperoxide Initiators Obtained by the Autoxidation. Synthesis of Block/Graft Copolymers via Free Radical and Ring Opening Polymerization Baki Hazer^{1,2}, Melike Eren¹, Elif Ayyıldız², Faruk Bahadır¹, ¹Bülent Ecevit University Faculty of Arts and Sciences, Dept. of Chemistry; Faculty of Engineering, Departments of Metallurgical and Materials Engineering, Turkey; ² Bülent Ecevit

University Faculty of Arts and Sciences, Nano Technology Engineering, Turkey

Unsaturated plant oils/fatty acids (UPOFA) can undergo autoxidation under atmospheric conditions to produce macroperoxide initiators. Pure unsaturated fatty acids such as linolenic, linoleic and oleic acid were exposed to air oxygen under daylight at room temperature which is called “ecofriendly autoxidation”. Eco-friendly autoxidation process creates peroxide linkages in order to obtain fatty acid oligomer that is called macroperoxide initiator. Oleic acid macroperoxide initiator was used in the free radical polymerization of styrene in order to evaluate the polymerization kinetics. Because of different functional groups, the macroperoxide initiators were used in the synthesis of block/graft copolymers. Polystyrene-poly oleic acid-polycaprolactone, polystyrene-poly oleic acid-polyethylene glycol, poly N-isopropyl acryl amide-poly oleic acid-polyethylene glycol block/graft copolymers were obtained. Structural and physicochemical characterization of the products was done. Lower critical solution temperature of the thermo responsive double hydrophilic copolymer, poly N-isopropyl acryl amide-poly oleic acid-polyethylene glycol was found to be 36 oC.

Super Palm Stearin from Enzymatic Directed Interesterification of Palm Oil

Noor Lida Habi Mat Dian*¹, Miskandar Mat Sahri¹, Tan Chin Ping², and Lai Oi Ming², ¹Malaysian Palm Oil Board, Malaysia; ²Universiti Putra Malaysia, Malaysia

Enzymatic directed interesterification (EDIE) of palm oil (PO) resulted in an increase in the

amount of trisaturated triacylglycerols from about 4.2% to about 28.5%, 6.8 times higher than the initial amount found in the mother oil. The high melting fraction which concentrated with the trisaturated triacylglycerols is well separated from the low melting fraction (shown by the differential scanning calorimetry melting profile), indicating easy of fractionation. Fractionation of the EDIE PO produced palm stearin (POs) with an iodine value of less than 10. The POs crystallized rapidly and stabilized in mixtures of β and β' crystals. The POs as it is, blended or restructured with vegetable oil via interesterification, and texturized, produced a trans-free hardstock with excellent oil binding capacity, and able to perform effectively as structural fat in the formulation of trans free reduced saturated solid fat products.

Unexpected Selectivity in the Functionalization of Neat Castor Oil Under Benign Catalyst-free Conditions Latchmi Raghunanan*¹, and José M. Franco², ¹Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Canada; ²Pro2TecS-Chemical Product and Process Technology Research Centre. Departamento de Ingeniería Química, Facultad de Ciencias Experimentales, Universidad, Spain

Abstract Pending

IOP 2: Biofuels

Chairs: Lieve Laurens, National Renewable Energy Laboratory, USA; and Steve Howell, M4 Consulting, Inc., USA

Technical Needs for Biodiesel Blends Over B20

Steve Howell*, *M4 Consulting, Inc., USA*

Over the past 20 years, most technical efforts in the United States have focused on use of blends of up to 20% biodiesel with conventional petroleum-based diesel fuel (petrodiesel). The choice of B20 and lower was primarily based on a combination of factors which include cold flow properties, emissions benefits, compatibility with existing engines and infrastructure, and other societal benefits. Recent natural disasters have spurred on renewed interest in climate change, especially on the East and West Coasts. Goals to reduce carbon emissions by 80% by 2050 are being seriously considered and use of biodiesel in higher blends up to B100 is one potential option. This presentation will review the technical needs and challenges for use of blends over B20 and provide an update of current and planned industry technical efforts in targeted markets to address them.

The Equilibrium Solubility Behavior of Glycerol in Biodiesel Fuels at Reduced Temperatures

Richard W. Heiden*¹, and Martin Mittelbach²,
¹*R.W. Heiden Associates, LLC, USA;* ²*Institute of Chemistry, University of Graz, Austria*

Low level free glycerin (FG) residuals in B100 are limited to 200ppm by internationally recognized specifications dating back to the mid 1990's. FG easily escapes detection because of

interferences from diesel fuel hydrocarbons while using standard analysis methodology, such as ASTM D6584 or EN14105 without suitable procedural and methodology adjustments, or GCMS. Similar interferences thwart routine checks of FG in biodiesel blends by such methods, and can destroy the validity of an analysis of fuel, such as B99. We reported at various earlier AOCS meetings (1) that the solubility of glycerol in polished biodiesel is much lower than previously thought, and can cause a variety of unexpected effects due to its density, high viscosity and biodegradability (2). In addition to temperature, several compositional entities can potentially influence the solubility of glycerol. Data from more recent studies of blend strength and the aromatic content of hydrocarbon diesels at different temperatures using model solutions is presented along with comparisons to our earlier solubility data for saturated monoglycerides. Results show that in addition to temperature and interacting impurities, such as moisture (2), blend composition looms as an important modulator of solubility. However, the anticipated gradual increases in solubility due to increasing FAME%, are surprisingly small in blends below about 50%, and are further attenuated by declining temperatures. This indicates formation of heterophases can be induced by blending.

(1) Heiden and Mittelbach, 105th AOCS National Meeting, 2014. (2) Heiden, Schober, Mittelbach, JAOCS, 2017.

Green Diesel by Hydrotreatment of Vegetable Oils: Effect of Oil Quality on Hydrocarbon Yield and Composition

Elisa Volonterio, Juan Bussi, Jorge Castiglioni, Ignacio Vieitez, and Iván Jachmanián*, *Facultad de Química, Universidad de la República, Uruguay*

The effect of the degree of oxidation of a vegetable oil on the efficiency of its conversion to green diesel by an hydrotreating process was studied. Refined rice bran oil (RBO) was used, which was oxidized for different periods by heating at 180 °C inside an open vessel provided with a magnetic stirrer. Hydrotreatment was performed using 100 g of oil in a high pressure/high temperature Parr reactor (4570 HP/HT, 250 mL) at 350°C and 100 bar of H₂. Samples from the reaction mixture were collected at different reaction periods and analyzed by gas chromatography. When a sample of RBO oxidized after 4.5 h (containing 19.5% of total polar compounds and 4.3% of polymers) was hydrotreated using 0.5% PtO₂ (Sigma Aldrich) as catalyst, a product containing 73.4% hydrocarbons was obtained after 4hs reaction. As TAG disappeared after 30 min of reaction, FFA were rapidly generated and their concentration raised to 88%. From then on, FFA concentration gradually diminished and hydrocarbons started to be accumulated in the system. After 4h reaction FFA concentration was 10,2% and hydrocarbons concentration was 73.4%. Although a similar behaviour of the system was observed when the process was performed at identical conditions using the refined oil, a product with 4.3% FFA and 93.4% hydrocarbons was achieved. Products showed different ratios heptadecane/ octadecane, suggesting that although always hydrodeoxygenation and decarbonylation + decarboxylation occurred,

they had different degree of participation in the global process.

Extractability and Quality of Lipids in Algae, a Study of Species-specific Lipase Activation
Ryan A. Herold and Lieve Laurens*, *National Renewable Energy Laboratory, USA*

Algae form an excellent basis to develop raw biofuel feedstocks, thanks to the abundance of lipids and carbohydrates in the biomass. One of the main challenges associated with algal biofuels production is improving the lipid extraction and conversion efficiency. Process yields are highly dependent on the efficiency of extraction and ultimately conversion of the individual lipid components. This study utilized different storage conditions of mid-stage harvested microalgal biomass from at least six different species to affect lipid extractability and quality and selectively induce lipase activity. All six species that were tested showed a significant increase in lipid extractability, some more than two-fold compared to control samples, following storage for 24 hours at 37°C as a wet paste. It was also shown that storage of *C. vulgaris* as a wet paste for 24 hours at 37°C can induce the upregulation of free fatty acids (FFA), whereas other species appear to exhibit a more constitutive high lipase activity or much more rapid initiation of lipolysis to FFA, since high levels of FFA were detected at all time points and storage conditions. Since many industrial-scale models for algal biofuel production include short term storage of wet algal biomass, it is important to understand any physiological changes induced by storage conditions that might affect fuel quality and/or lipid extractability. Furthermore, if algal lipids can be extracted more easily simply by manipulating short term storage conditions, this may be a

viable way to reduce chemical and energy consumption during lipid extraction, while maintaining yields.

Correlating the Cold Flow and Melting Properties of Fatty Acid Methyl Ester (FAME) Mixtures Robert O. Dunn*, *USDA, ARS, NCAUR, USA*

Fatty acid methyl ester (FAME) mixtures derived from plant oils or animal fats are used to make biodiesel, lubricants, surfactants, plasticizers, ink solvents, paint strippers and many other products. Processing requires a precise knowledge of the physico-chemical properties of mixtures with diverse and changing fatty acid concentration profiles. FAME mixtures may become problematic if ambient temperatures cause them to gel or solidify during processing. This work examines mathematical correlation models for calculating the cloud point (CP) and cold filter plugging point (CFPP) of multicomponent FAME mixtures (biodiesel) based on composition and the melting properties of the FAME species present. To obtain a diverse set of measured property data, binary admixtures were prepared made with biodiesel fuels made from canola, palm and soybean oils and yellow grease. Two models were developed in the present study. The solid-liquid equilibrium (SLE) model correlated CP and CFPP to the SLE temperatures of admixtures calculated from freezing point depression theory. This model yielded close to a 1:1 correlation between calculated and measured cold flow properties for the admixtures. The MODified Empirical Correlation (MODEC) model was developed by correlating the inverse of CP or CFPP ($1/T$) to the natural log of the total methyl palmitate concentration in the FAME mixtures. This model

performed nearly as well as the SLE model despite the presence of small concentrations of other saturated-FAME in the admixtures.

Hydroprocessing Algal Lipids to Renewable Diesel Blend Stock. Jake Kruger, Earl Christensen, Tao Dong, Gina Fioroni, Robert McCormick, and Philip Pienkos, *National Renewable Energy Laboratory, USA*

Objective There has been increasing interest in converting algal lipid feedstocks to a drop-in hydrocarbon diesel fuel via deoxygenation (DO) and hydroisomerization (HI) reactions. A significant body of work exists on the DO step, but the HI step has been less explored. In particular we were motivated to investigate the effect of impurities in the lipid feed on the upgrading catalysts both in two-step DO-HI, and combined, single-step DO-HI.

Methods Used We have performed continuous-flow reactions for DO of crude, hexane-extracted algal lipids and two bleached samples over a commercial Pd/C catalyst, followed by HI of the resulting n-alkane stream over a custom Pt/SAPO-11 catalyst. We have also performed one-step DO-HI of crude, hexane-extracted algal lipids over a Pt/SAPO-11 catalyst.

Results Both two-step and one-step DO-HI are effective for converting algal lipids into green diesel fuel through 10 h time-on-stream, yielding a liquid alkane product with cloud point < 0 °C. The Pt-SAPO-11 catalyst is susceptible to deactivation in one-step DO-HI, however, with cloud points increasing to ~ 10 °C after 24 h time-on-stream.

Conclusions Crude algal lipids can be hydrotreated to green diesel fuel in either two-step or one-step DO-HI reactions, though further process development is necessary, especially for one-step DO-HI.

IOP 3: Green Chemistry

Chairs: Nurhan T. Dunford, Oklahoma State University, USA; Dharma Kodali, University of Minnesota, USA; and Jerry W. King, Critical Fluid Symposia, USA

Oil and Oilseed Processing with Sustainability in Mind Nurhan T. Dunford*, *Oklahoma State University, USA*

The focus of this presentation will be on specialty oils that are used as ingredients in foods, cosmetics and pharmaceuticals. These types of oils are available in relatively small quantities because of the limited feedstock supply and/or challenges involved in feedstock handling and storage. Commonly specialty oils are processed to retain the distinctive qualities naturally associated with the oil. Color, flavor, nutrient content and functionality are some of the important attributes that distinguish specialty oils from commodity products such as cooking oils. Although specialty oils receive a premium price, economic feasibility of producing high quality specialty oils might not be easy to achieve. Typically consumers of the specialty oils tend to be “natural minded” and environment and health conscious individuals who favor products that do not contain chemical residues and are produced by environmentally benign processing techniques and following sustainable practices. The presentation will emphasize sustainable approaches to wheat germ, rice bran, corn fiber and Daphne (*Laurus nobilis* L.) seed oil processing. Challenges involved in feedstock supply and quality, selection of oil extraction and refining processes and the ways to meet consumer expectations while achieving economic feasibility will be discussed. Pros and cons of supercritical fluid technology, aqueous and

mechanical extraction and enzyme aided oil and oilseed processing will be reviewed. Application of biorefinery approach to specialty oil production will also be highlighted in this presentation.

Biobased Surfactants: A Useful Biorefinery Product That Can be Prepared Using Green Manufacturing Douglas G. Hayes*, *University of Tennessee, USA*

Biobased surfactants, readily prepared from common biorefinery process streams and commonly employed as emulsifiers, wetting agents, plasticizers, and agents for lowering surface and interfacial tension, are becoming increasingly popular for use in foods, cosmetics, pharmaceuticals, and other industries. This trend is driven by the enhanced environmental sustainability provided through use of renewable resources, increased abundance of biobased feedstocks resulting from development of biorefineries, and concerns for the increase of cost for petroleum in the future. Although most biobased surfactants are manufactured by chemical means, their preparation via bioprocessing is very attractive for future employment due to further enhancement of sustainability and potential savings in energy, downstream purification, and disposal costs. This presentation provides an overview of current research and development to prepare biobased surfactants via conventional and green manufacturing approaches, including enzymatic processes.

Eastern Red Cedar: Critical Fluid Extraction and Bioactivity of Extracts Fred J. Eller*, *USDA, ARS, NCAUR, USA*

Eastern red cedar is an abundant natural resource in the United States. It is valuable for its lumber and cedarwood oil derived from the wood. Cedarwood is generally obtained by steam distillation; however, this process has several disadvantages, including relatively low yields and altered oil characteristics. Our laboratory has been investigating several alternative methods for extracting cedarwood oil from Eastern red cedar, including liquid and supercritical fluid carbon dioxide and pressurized solvent extraction. Carbon dioxide extractions have been demonstrated to give high yields of high quality oil. Pressurized hexane also gave high yields of cedarwood oil and pressurized polar solvents like ethanol and methanol gave high yields of polar compounds not extracted by CO₂ or hexane as well high yields of flavonoids. The CO₂-derived extracts have been tested for a variety of bioactivities. The extracts have been found to impart resistance to wood-decay and termites when they are impregnated into otherwise susceptible wood. The cedarwood oil has also been shown to be repellent to several species of ants, including red imported fire ants and little fire ants. The cedarwood oil is toxic to black-legged ticks, brown dog ticks, lone star ticks, houseflies and several species of mosquitoes. Interestingly, polar solvent extracts contain compounds that induce egg-laying by ladybird beetles. Cedarwood oil is a very safe material towards humans but has great potential for managing a wide range of economically important pests

Synthesis of Biobased Building Blocks from Cashew Nutshell Liquid: A Chemical Platform Approach for Polymer Synthesis Sylvain Caillol*, *Institut Charles Gerhardt, France*

We propose a platform approach for the synthesis of various building blocks from cardanol in one or two-steps syntheses. Cardanol, which is a natural phenolic oil, is issued from Cashew Nutshell Liquid (CNSL), a non-edible renewable resource, co-produced from cashew industry in large commercial volumes (1Mt p.a.). Cardanol is non-toxic and particularly suitable for the addition of aromatic renewable resources in polymers and materials. Various routes were used for the synthesis of di- and poly-functional building blocks used thereafter in polymer syntheses. Phenolation was used to dimerize/oligomerize cardanol to propose increase functionality of cardanol. Thio-ene was used to synthesize new reactive amines. Epoxidation and (meth)acrylation were also used to insert oxirane or (meth)acrylate groups in order to synthesize polymers and materials. Finally, we also synthesized a new radically polymerizable monomer from cardanol. Hence we synthesized cardanol-based aromatic latex by water emulsion radical polymerization for styrene-free coating applications.

Feruloylated Soy Glycerides: UV Absorbance Capacity and Photostability David L. Compton*¹, John R. Goodell², and Kervin O. Evans¹, ¹*USDA, ARS, NCAUR, USA*; ²*iActive Naturals, USA*

Feruloylated soy glycerides (FSG) are plant-based, naturally derived compounds with antioxidant and ultraviolet (UV) absorbing properties. FSG is synthesized by the transesterification of soybean oil with ethyl ferulate in a continuous, enzymatic, packed-bed bioreactor. A small, limited, independent

laboratory clinical trial determined that FSG has an empirical benefit as an emulsifier and moisturizer in anti-wrinkling applications, thus FSG is beginning to be used in formulations in the personal care and health and beauty industries. The antioxidant capacity of FSG has been well documented in the literature; however, the UV absorbing efficacy of FSG has not been investigated. The total absorbance capacity, photostability, and broad UV spectrum absorbance capacity of FSG (λ_{max} of 328 nm) were determined and compared to commercially used, non-naturally derived UV absorbing ingredients Octinoxate (ONX, λ_{max} 310 nm) and Avobenzone (AVO, λ_{max} 356 nm). FSG was tested as a fungible replacement for ONX in equimolar mixtures with AVO and was found to provide the same or superior UV absorbance capacity, photostability, and broad spectrum coverage.

Subcritical Water Hydrolysis of Hemp Seed Oil in a Continuous Flow Coil Reactor

Andres F. Aldana Rico*¹, Ruben O. Morawicki², Jerry W. King³, Marco E. Sanjuan Mejia⁴, and Antonio J. Bula Silvera¹, ¹*Universidad del Norte, Colombia*; ²*University of Arkansas, USA*; ³*Critical Fluid Symposia, USA*; ⁴*msanjuan@uninorte.edu.co, Colombia*

When water is heated to the subcritical region, changes in the dielectric constant and ionic product, make water capable of intervening in acid- or base-like catalytic reactions, such as hydrolysis. The objective of this research was to study the hydrolysis of hemp seed oil using subcritical water in a continuous flow reactor. The reaction was followed by analyzing the evolution of free fatty acids and the composition of their mixtures. The experimental equipment consisted of two syringe pumps that delivered

degassed water and hemp seed oil through a stainless-steel tubing maintained at the desired temperatures inside a temperature-controlled oven and kept pressurized with a backpressure regulator. An ice bath was used to cool the oil/water effluent from the reactor. Collected hydrolysates were centrifuged and the oil samples were used for analytical tests. Hydrolysis yield was measured by the ASTM-D5555 method, and fatty acid identification was done by gas chromatography with FID detection and mass spectrometry. Process conditions were defined by a central composite rotatable experimental design with three factors and five levels. Factors and levels were temperature (150–275°C), reaction time (40–120 min), and oil/water ratio (0.125–0.250). The free fatty acid yield ranged between 20 and 91% (w/w). The highest degree of hydrolysis took place at temperatures above 200°C and retention times over 60 minutes. Similar fatty acid profiles were observed in the unhydrolyzed and hydrolyzed oils, which indicates minimal or no fatty acid degradation. Linoleic acid (C18:2) was the predominant fatty acid.

Green Chemistry in Cannabis “Oils” Extraction, Processing and Derived Products

Jerry W. King*, *Critical Fluid Symposia, USA*

The dynamic growth of the cannabis industry—both for traditional Cannabis as well *Cannabis sativa* L. (hemp)—is well documented and for hemp-derived-CBD (cannabidiol is projected to be \$1.65 billion by 2021. Production of cannabis-derived “oils” differs chemically from traditional-derived lipophilic oils, although the presence of the latter in cannabis extracts requires both their inclusion and/or removal depending on the desired end product. Although the use of “green”

processing technology is inherent in commercial practice and imperative for consumer safety, quantitative evaluation of such chemical choices and procedures is lacking and will be reported here. “Cannabis derived-oils” are used particularly in infused products and inhalable-delivery systems and can be obtained by hydrocarbon extraction, varying formats of CO₂ extraction, the use of ethanol for extraction and purification, and other processing agents. Here the relative “greenness” of such processes and derived products is assessed with the aid of the “reduced” solubility parameter concept for the major cannabinoid constituents found in extracts, their inclusive “entourage” terpene components,

as well as the inclusion-exclusion of lipophilic co-extractives, i.e., triglycerides, waxes and plant pigments. Particular note will be paid to the use of CO₂ in its dry ice, subcritical, and supercritical states for comminution, terpene isolation, and the extraction of specific ratios of cannabinoids. An assessment of low temperature (<–60°C) and pressure (~300 psi) ethanol for extraction and refining will be provided. Finally, the reduced solubility parameter concept will be shown to be applicable to final product content including desired and unwanted contaminants such as pesticides, solvent residuals, and lipophilic co-extractives.

IOP 4: Oleochemicals

Chairs: Xiaofei P. Ye, University of Tennessee, USA; and Franck Dumeignil, Université de Lille, France

The Global Challenges in Chemicals and Energy

Mischa Schneider*, *Chemspeed Technologies AG, Switzerland*

Standardization and acceleration of R+D within the oil and gas industries are vital for coping with all the dynamically increasing challenges in their broadest sense. Many industry leaders have recognized the need to act and successfully boosted their R+D outputs. The global challenges in chemicals and energy comprise:

- Increasing constraints in energy supply from fossils and recently nuclear power
- Increasing constraints by regulations (CO₂ emission, global warming, ...)
- Increasing energy demand e.g. spurred by the dynamic growths in the BRIC countries
- e.g., by 2020 China is projected to consume more than 50% of the global energy.

Effective Magnesium Oxide-Zeolite Catalysts to Produce Iso-Oleic Acid, Precursor of Isostearic Acid

Helen Ngo Lew, Jianwei Zhang, and Robert A. Moreau, *USDA, ARS, Eastern Regional Research Center, USA*

A family of magnesium oxide (MgO)-zeolite catalysts has been thoroughly investigated to produce iso-oleic acid followed by hydrogenation to give the isostearic acid. Isostearic acid, a type of methyl branched-chain fatty acid, is a unique commercial product that is an important component in the formulation of bio-lubricants including cosmetics and personal care products. In this investigation, three types of zeolites (i.e., H⁺-ZSM5, H⁺-BETA and H⁺-Ferrierite) were

efficiently impregnated with the magnesium nitrate salt and used in the isomerization of oleic acid to produce iso-oleic acid (precursor of isostearic acid). The catalyst surface areas, acid sites, crystallinity, thermal property, morphology and elemental compositions were investigated before and after modifications. When the catalysts were used in the isomerization reactions, various factors were studied including magnesium nitrate loading amounts, zeolite types, reaction times and temperatures, and amounts of catalyst loadings. For instance, when comparing the non-salt H⁺-ZSM5 to the salt version of 5wt%MgO-H⁺-ZSM5 catalyst, with the salt version the amount of undesirable byproduct (i.e., dimer acid) was reduced by 50%, accompanied by a high yield of iso-oleic acid (79%) and a high reaction conversion of oleic acid (98%). Most significantly, these magnesium salts are similar to the zeolite solids since both are not soluble in the oil products and therefore could potentially be a new environmentally friendly catalyst system for producing commercial isostearic acid.

A Soybean Oil-based Adhesive and its

Application for Birdseed Binding Tao Fei*, Melissa Slagle, Darren H. Jarboe, and Tong Wang, *Iowa State University, USA*

A soybean oil-based adhesive was synthesized and tested for birdseed binding. The effects of the quantity of saturated fatty acylglycerols (i.e., fully hydrogenated soybean oil, FHSO) introduced into epoxidized soybean oil (ESO) and a phosphoric acid (H₃PO₄) crosslinker

on product characteristics were investigated. Increasing the quantity of FHSO improved hardness and adhesiveness while further increasing the quantity led to various degrees of phase separation in the binder. Increasing the quantity of H₃PO₄ also improved hardness and adhesiveness of the binder. A binder-MDAG (a mixture of mono and diacylglycerols at about a 1:1 ratio) mixture (BMD) having an average hardness and adhesiveness of 4,024 and 1,197 g, respectively, was selected for seed binding. Curing of BMD in open air led to increased hardness, adhesiveness, and melting point. Seed cakes bound with 15 wt% BMD were about twice as hard as gelatin-bound seed cakes. Curing seed cakes in open air significantly increased their hardness and temperature tolerance. Seed cakes bound with BMD also presented much better water resistance. It is possible and feasible to use a minimally modified soybean oil as bird seed binder.

Bioplasticizers Derived from Regular and High Oleic Soybean Oil Lucas J. Stolp* and Dharma R. Kodali, *University of Minnesota, USA*

Plasticizers are organic liquids added to polymeric materials to improve their flexibility. The majority of plasticizers are used to enhance the polyvinylchloride (PVC) functionality in applications such as flooring, wire and cable coatings, and medical tubing. Currently used petroleum derived phthalate esters have come under scrutiny due to health and safety concerns. Fatty acid esters derived from regular soybean oil (RSBO) and high oleic soybean oil (HSBO) can be further chemically modified to produce plasticizers that can replace phthalates in PVC applications. The ideal plasticizers should possess low volatility, color and viscosity with a moderate molecular weight of about 350 Daltons and

excellent plasticizer functional properties. Two classes of compounds, alkyl and diacetyl glyceryl fatty acid esters from these two oils were synthesized by transesterification with alkanol or triacetin respectively. The unsaturation on the fatty acid backbone was converted to epoxy function by reacting with hydrogen peroxide and acetic acid. The final plasticizer compounds, epoxy estolide fatty acid esters, were synthesized by partial ring opening of epoxide and acetylation. These two classes of compounds derived from two different oils were evaluated for their plasticizer functionality by compounding with PVC. The plasticizers derived from these two structurally different oils showed excellent compatibility, gelation temperatures, cold flexibility, and efficiency. The plasticizers derived from HSBO had greater structural homogeneity resulting in better functional properties. The chemical modifications of the fatty acid esters and the detailed structural differences of the resulting plasticizers and their functionality based on the starting oil composition will be presented.

Innovations in Biodiesel Production Value Chain Toward Circular Economy Xiaofei P. Ye*, *University of Tennessee, USA*

Current biodiesel production fits into a linear economy, which is a take-make-dispose model. For a sustainable future of biofuels, it is imperative to move away from a linear economy toward a circular economy with key elements of prioritizing regenerative resources, using waste as a resource, designing for the future, preserving and extending what is already made, and collaborating to create joint value. In the biodiesel production, considerable amount of methanol remains with crude glycerol and catalyst after separating the produced biodiesel. The separation of methanol and catalyst, and the

purification of crude glycerol are costly. We demonstrated that it is feasible to directly use the mixture of crude glycerol, methanol, and catalyst from biodiesel production for chemical production. This presentation showcases our efforts integrating the production of value-added oleochemicals in the biodiesel production value chain considering the above key elements toward a circular economy.

Improved Synthesis and Cost Estimates for the Production of Saturated Branched-Chain Fatty Acids from Vegetable Oils Jianwei Zhang, Winnie Yee, Robert A. Moreau, and Helen Ngo Lew, *USDA, ARS, Eastern Regional Research Center, USA*

Saturated branched-chain fatty acids, such as isostearic acids, are one of the most important oleochemical ingredients used in bio-lubricants including cosmetics and personal care products. They are produced as coproducts during the dimerization of tall oil fatty acids with clays as catalysts. More recently, research has shown that they can also be produced in high yields from refined fatty acids with zeolite solid catalysts. Both technologies however have their drawbacks in terms of costs and yields. In this poster, discussions on our research efforts to efficiently improve the production of isostearic acids will be presented. Topics will be specifically focused on various types of modified solid catalysts investigated for the synthesis of saturated branched-chain fatty acids from mixed fatty acids derived from vegetable oils. Reaction conditions and detailed characterizations on both solid catalysts and oil products will be presented. Finally, the practicality of the overall processing cost for converting mixed fatty acids to isostearic acids will be discussed.

Laser-assisted Catalytic Oxidation of Glycerol over Gold Supported Catalysts Zeinab Chehadi¹, Jean-Sébastien Girardon², Mickaël Capron³, Franck Dumeignil*⁴, and Safi Jradi¹, ¹*Laboratoire de Nanotechnologie et d'Instrumentation Optique, Institut Charles Delaunay, UMR 6281 CNRS, Université de Technologie de Troyes, France;* ²*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide;* ³*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, France;* ⁴*Université de Lille, France*

We studied the feasibility of new efficient catalytic process by laser excitation in the reaction of oxidation of glycerol over catalysts based on supported gold nanoparticles. We showed that this catalytic oxidation reaction can efficiently proceed via laser excitation of surface plasmon resonance of gold nanoparticles inducing local thermal heating. While the reaction did not occur in the absence of any external heat source, with this original approach, 88% of glycerol was converted after 2 h, leading to the formation of glyceric acid and tartronic acid as primary main products. The photonic activation led to a 2.5 times more efficient conversion than an equivalent thermal activation using a conventional heating source. Investigations of the laser power and the nature of support catalyst revealed a significant contribution of electron transfer from plasmonic nanoparticles to TiO₂ in the oxidation reaction. This work paves the way to a rethinking of the design of industrial processes for glycerol oxidation in the liquid phase, using laser activation.

The Effect of Plant Oil-Based Monomer Structure on Properties of Latex Synthesized in Miniemulsion Polymerization

Zoriana Demchuk*¹, Ananiy Kohut², Ihor Tarnavchyk¹, Stanislav Voronov², and Andriy Voronov¹, ¹*North Dakota State University, USA*; ²*Lviv Polytechnic National University, Ukraine*

Recently, library of plant oil-based acrylic monomers (POM's) was synthesized in one-step direct transesterification of vegetable oils (olive, sunflower, soybean, and linseed) with N-hydroxyethyl acrylamide. Based on kinetic study, POM's behave as conventional vinyl monomers in free radical polymerization and copolymerization. In this study, stable latexes from olive, soybean and linseed oil-based monomers copolymerized with styrene were synthesized using miniemulsion which provides an opportunity to polymerize highly hydrophobic monomers. Using ¹H NMR spectroscopy it was determined that double bonds of fatty acid fragments remain mostly unaffected during the polymerization and can be further used for post-polymerization reactions (e.g., crosslinking). The latex free films were formed by curing at elevated temperature and tested using DMA, DSC and tensile techniques. It was observed that the amount of unsaturation in POM's impacts mechanical properties of the resulting latex films. To investigate the effect of POM unsaturation amount in monomer feed on the mechanical properties of latex films, new mostly saturated monomer from hydrogenated soybean oil (H-SBM) was synthesized. As a result, crosslink density of the polymer network, measured by DMA, can be varied by integration of hydrogenated soybean oil-based monomer (H-SBM) into the polymer backbone. Based on the linear dependence of the crosslink density on

monomer feed unsaturation, it can be concluded that the latex network formation and thermomechanical properties can be adjusted by simply combining various plant oil-based monomers at certain ratios in the reaction feed. The incorporation of POM's fragments into copolymer have a plasticization effect, increases the toughness of latex films and converts brittle polymers into flexible film-forming materials.

Preparation of Mango Kernel Fat Stearin using 2-methylpentane and its Application in Heat-resistant Chocolate Fats

Jun Jin*, Qingzhe Jin, and Xingguo Wang, *Jiangnan University, China*

Objective Mango kernel fat (MKF) is an untapped resource and contains more than 30% of 1,3-distearoyl-2-oleoyl-glycerol (StOSt). The StOSt-rich fat in natural form is difficult to obtain and enjoyed in producing heat-resistant chocolate fats. The present study is focused on preparing StOSt-rich fat from MKF and further making hard chocolate fats. Methods Used StOSt-rich fat (mango kernel fat stearin, MKFS) was produced by three-stage selective fractionation using 2-methylpentane (a new processing solvent). Heat-resistant chocolate fats were then prepared by mixing MKFS, cocoa butter (CB) and palm mid-fraction (PMF, if necessary). Fat and triacylglycerol (including isomers) compositions, compatibilities, solid fat contents, melting and crystallization behaviors, polymorphic forms and hardness were analyzed to select the ideal mixing ratios. Results The new solvent, 2-methylpentane, showed lower toxicity than acetone and higher polarity than hexane, and successfully enriched StOSt into MKFS (44.0%→69.2%) by removing other undesired compounds (e.g., diacylglycerol and di-unsaturated triacylglycerols). However, for

binary blends of MKFS and CB, eutectic effects were observed at 18–32°C. Therefore, PMF (1,3-dipalmitoyl-2-oleoyl-glycerol (POP), 70.2%) was involved to improve the miscibility. Accepted compatibilities were found in the ternary blends consisting 10% PMF, 10%-45% MKFS and 45%-80% CB. The POP-rich fat is help to make the mixtures transfer into β structure and three-pack layer, and contribute to improving their thermal properties and hardness. Conclusions Addition of 10% PMF could improve the miscibility of MKFS and CB mixtures, and further make the fat blends more suitable to be as heat-resistant chocolate fats.

Producing Fully Renewable Medium Chain Alpha Olefins via an Integrated Biorefinery Process

Tao Dong*, Wei Xiong, Jianping Yu, and Philip Pienkos, *National Renewable Energy Laboratory, USA*

Medium chain-length linear alpha-olefins (mcl-LAO) are versatile precursors to produce many commodity chemicals, such as synthetic lubricants and biodegradable detergents. mcl-LAO have been traditionally produced from ethylene oligomerization and Fischer-Tropsch synthesis. Recently it has been reported that polyhydroxybutyric acid (PHB) can be converted into propylene via an intramolecular β -elimination and decarboxylation. Our hypothesis is that mcl-polyhydroxyalkanoic acid (mcl-PHA) might be used as a feedstock to produce mcl-LAO

through a hydrothermal liquefaction (HTL), and the presence of mcl-PHA can also improve the yield and quality of bio-oil. In this study, *Pseudomonas putida* biomass rich in mcl-PHA was used in HTL at 300°C for 30 min. It was found that up to 65mol% of the mcl-LAO was produced from mcl-PHA via the HTL. The yield and quality of obtained HTL bio-oil was remarkably improved with the presence of mcl-PHA in the biomass. Experiments with extracted mcl-PHA revealed the fates of mcl-PHA in HTL. Overall, this work demonstrates a sustainable process to produce mcl-LAO and bio-oil from renewable biomass via an integrated green chemical approach.

High Linoleic Soybean Oil a New Feedstock for Industry: Alkyd Resin and Paint Example

Rick Heggs*, *Oilseed Innovation Partners, Canada*

Oilseed Innovation Partners (formerly Soy 2020) in conjunction with the University of Guelph in Canada has developed a new non-GMO soybean variety that has a unique fatty acid profile with about 70% linoleic acid. The additional unsaturation of this oil has been found to be very useful in producing alkyd resins that are faster drying than conventional soybean oil alkyds and result in paints with surprisingly good corrosion resistance. Other industrial applications that may benefit from this oil include plasticizers, polyols and inks.

EAT 5/IOP 5: Waxes and Phase Change Materials

Chairs: Nuria Acevedo, Iowa State University, USA; and Chelsey Castrodale, Clasen Quality Chocolate, USA

Multiple β Forms of Tripalmitin in Different Crystallization Pathway Seiya Takeguchi*¹, Hironori Hondoh², Hidetaka Uehara³, and Satoru Ueno², ¹The Nisshin OilliO Group, Ltd./Hiroshima University, JAPAN; ²Graduate School of Biosphere Science, Hiroshima University, Japan; ³The Nisshin OilliO Group, Ltd., Japan

Polymorphic transformation of fat crystals, such as fat bloom in chocolate, will be a cause of deterioration of foods. Therefore, it is important to understand polymorphic behavior of fat crystals. Tri-saturated triacylglycerol is known to have three polymorphs, α , β' and β . In addition, some researchers suggested the existence of extra structures. However, the details remain unidentified. Here we report that tripalmitin (PPP) shows different β forms depending on their crystallization history. PPP was crystallized in α or β' forms from melt, and then they were transformed into β forms (β_4 from α , and β_2 from β') by solid-solid phase transition by gradually increasing temperature. Additional heat treatment was applied for further phase transformation to β_3 and β_1 . The following results were obtained. 1) From the polarized microscopy, the β_2 changed its morphology during transformation from β' , while β_4 kept the same morphology as α form. 2) From the X-ray diffraction measurement, we confirmed the β_4 transformed into β_3 (α route) and β_2 transformed into β_1 (β' route) because β_4 (β_2) and β_3 (β_1) had different short spacing. 3) From the differential scanning calorimetry measurements, the order of melting points were $\beta_4 < \beta_3 < \beta_2 < \beta_1$. These results indicated that

PPP have four different polymorphs, β_4 and β_3 , which were transformed from α form, and β_2 and β_1 , which were transformed from β' form.

The Effect of Processing on Hybrid Shortenings Containing Diacylglycerols Iris Tavernier¹, Tom Rimaux², Koen Dewettinck³, and Ian T. Norton⁴, ¹Ghent University, Belgium; ²Vandemoortele R&D Centre, Belgium; ³University of Gent, Belgium; ⁴Chemical Engineering, University of Birmingham, UK

Oleogelation has attracted a lot of attention as possible alternative for saturated and trans-fat structuring of food products. Despite the development of numerous food-grade oleogels, they are still under-appreciated in the food industry. This reluctance to move from fundamental research to actual product development is related to the unknown effect of actual processing conditions on these newly developed products. Oil structuring using solely diacylglycerols (DAGs) have received little attention so far. However, they are known to form crystallite networks in a relatively similar way as TAGs. Furthermore, at concentrations of over 40%, 1,3-DAGs possess nutritional benefits compared to TAGs. In the current research, palm oil DAGs were combined with palm oil TAGs in various ratios, forming hybrid systems. Samples were prepared both statically, without shear or rapid cooling, and dynamically, in a bench-top scraped surface heat exchanger. Results demonstrate the drastic effect of processing on the texture of the final products, which could be related to the different amount of crystalline

matter (DSC) and the different crystalline microstructure (PLM). The functionality of the statically crystallized samples could not predict the behavior of dynamically crystallized samples. Furthermore, post-crystallization effects were more pronounced for the samples with a high concentration of DAGs, which is relevant in terms of further product development. This research clearly demonstrates that a thorough understanding of the processing parameters is essential for efficient product and process development. Furthermore, it is also shown that only realistic processing conditions allow the assessment of the true potential of alternative structuring techniques.

Engineering Lipid Properties Through

Glycerolysis Reed A. Nicholson* and Alejandro G. Marangoni, *University of Guelph, Canada*

Partial glycerols are commonly used as food ingredients because of their emulsification properties. Additionally, monoacylglycerols (MAGs) and diacylglycerols (DAGs) can be found at varying concentrations in some types of edible oils, the most famous being palm oil, which is known to contain DAGs at concentrations of 5–8%. The presence of these molecules alters the crystallization behaviour of palm oil and is thought to contribute to its unique characteristics. The purpose of this research is to investigate the effect that partial glycerols have on the crystallization and melting properties of various edible oils. Glycerolysis reactions were performed at 65°C for various lengths of time in the presence of an excess of glycerol using *Candida antarctica* lipase B as the catalyst. Differential scanning calorimetry (DSC) demonstrated changes in crystallization behaviour of peanut, cottonseed, and soybean

oils, caused by the presence of partial glycerols. The onset of crystallization for peanut oil increased from 2°C to 21°C. For cottonseed oil, this temperature increased from –3°C to 21°C, and for soybean oil the onset was raised from –6°C to 10°C. Furthermore, pulsed nuclear magnetic resonance was used to investigate the melting profile of these modified oils. Solid fat content measurements demonstrated differences in the melting profiles of these modified oils, confirming the earlier onset of crystallization and delay in melting observed through DSC. This research will help to provide a better understanding of how partial glycerols can be used to tailor the physical properties of oils for their use in food applications.

Developing Vegetable Oil Based Wax Coating Alternatives Tong Wang* and Tao Fei, *Iowa State University, USA*

The demand from industry for “green” coating materials has been increasing in recent years due to the environmental concerns as well as the availability and supply fluctuation of imported specialty natural waxes. We have explored minimal and feasible modification methods to make vegetable hardstock have the performance of paraffin and carnauba waxes. Structure-function relationships are studied and established to provide direction for desirable and tunable properties. The effect of hydrocarbon chain length, pendent and terminal hydroxyl group, and type of linkage of the liner chain on physical properties of the bulk materials are demonstrated. These properties and laboratory-scale coating performance are compared to the benchmark commercial products. Hardness, cohesiveness, melting profile and water resistance of the alternative coating compare

well to paraffin wax (hardness of 1.40 mm vs. 1.85 mm penetration, cohesiveness of 1300 g.mm vs. 1500 g.mm, melting point of 67°C vs. 65°C, and water repellency of 90° vs. 100° surface contact angle). Our carnauba-like material has similar hardness (0.10 mm vs. 0.10 mm), much higher melting point (145°C vs. 82°C) and better water repellency (65° vs. 45°) compared to carnauba wax. Working with commercial partners, we expect to have these technologies adopted by the various industries that use waxes in their product formulations.

An Emerging Natural Wax: Sorghum Wax from Bioethanol Production

Jeffrey T. Cafmeyer*, *Battelle, USA*

Wax from grain sorghum has long been suggested as a potential alternative to high-melting, high-hardness natural waxes such as carnauba. However, the uses and potential of sorghum wax have remained largely unexplored due to the lack of a readily available source and process. Recently the bioethanol industry has begun to diversify its feedstocks and in turn has increased its use of grain sorghum. This has created opportunities to collect the sorghum wax resulting from bioethanol production resulting in several millions of pounds potentially available for use. Efficient wax isolation methods that can be performed without affecting ethanol production are under development. Significant sorghum wax quantities are now accessible for sampling to industrial evaluators with the goal of identifying uses for a domestic natural wax product that increases the value of grain sorghum for both the bioethanol producers and sorghum farmers.

Role of Rice Bran Wax on Crystallization and Rheological Properties of Oleogels from Rice Bran Oil Khakhanang Wijarnprecha*¹, Pravit Santiwattana², Sopark Sonwai³, and Dérick Rousseau⁴, ¹*Department of Food Technology, Silpakorn University, Thailand*; ²*Thai Edible Oil Co., Ltd., Thailand*; ³*Silpakorn University, Thailand*; ⁴*Ryerson University, Canada*

The crystallization and rheological properties of oleogels consisting of 0.5–25 wt% rice bran wax (RBX) in rice bran oil (RBO) were explored. RBX was an efficient, thermoreversible oleogelator capable of structuring RBO at concentrations as low as 0.5 wt% RBX. A qualitative temperature-composition phase diagram showed that oleogels containing higher concentrations of RBX were the most resistant to melting. Polarized light microscopy revealed the presence of a network of interlinked, long aspect ratio wax crystal needles up to 50 μm in length in oleogels at higher RBX concentrations. Upon heating, RBX crystals did not undergo any polymorphic transition, based on the short spacings at ~ 4.16 and ~ 3.73 Å, indicative of an orthorhombic subcell, and d001 long spacing at 74–76 Å that persisted until RBX fusion. This long spacing was ascribed to the presence of wax esters consisting of long chain saturated fatty acids (C24 and C22) esterified to C28–C34 saturated fatty alcohols. During cooling from 90 to 20°C, the increase in oleogel viscosity resulting from the RBX liquid-solid phase transition was corroborated by the DSC-based crystallization onset and enthalpy data. Similarly, elastic moduli and hardness both rose with increasing RBX concentration. This study, which demonstrated that RBX can structure RBO with distinct concentration-dependent properties, serves as the foundation for the development of oleogel-

based approaches to saturated and trans fats replacement in processed foods.

Phase Change Analysis of Waxes and Wax Blends by Thermal Microstructure Evolution

Analysis Matt Vanden Eynden*¹, Roland Ramsch², Giovanni Brambilla², Pascal Bru², and Gerard Meunier², ¹*Formulaction, Inc., USA*; ²*Formulaction, France*

Different raw wax materials clearly have different melting and crystallization profiles which can make the formulation of wax blends difficult in regards to achieving a homogeneous crystal structure. In addition to the raw content, heating and cooling types and rates will also have an influence of the resulting mixture. To analyze this, an accurate, reproducible method must be employed to effectively measure the T50 profiles

of these mixtures. Here, we propose using Multi-Speckle Diffusing Wave Spectroscopy (MS-DWS) as a method to monitor the phase change profiles of these mixtures during heating and cooling ramps. This technology utilizes a light scattering method on bulk samples in order to monitor the microstructure evolution of the crystal structures within the wax formulations. This is accomplished by correlating Brownian motion of particles during a phase change event to crystal structure evolution. Specifically, varying cooling profiles of select Beeswax and Candelilla blends will be shown as they are monitored for variances in crystallization structure profiles. This will allow for facile analysis of wax blending formulations as well as to assess the raw material quality of the waxes.

IOP-P: Industrial Oil Products Poster Session

Chair: Jerry W. King, Critical Fluid Symposia, USA

1. Polyol and Polyurethane Prepared from Rubber Seed Oil by Hydroformylation.

Jian Hong¹, Xiao-Qin Yang², Xianmei Wan³, Zhifeng Zheng², and Zoran Petrovic³, ¹*Kansas Polymer Research Center, Pittsburg State University, USA*; ²*Southwest Forestry University, China*; ³*Pittsburg State University, USA*

Renewable raw materials are being increasingly used to satisfy the quest for sustainability and environmental concerns. In the search for new vegetable oils as platform for new polymers, rubber seed oil (RSO) was relatively little investigated. High free fatty acid content of 13% in crude RSO is impediment for many applications including biodiesel, but can be beneficial when strong bonding with substrate is desired. RSO was used to prepare a polyol via hydroformylation/hydrogenation. The polyol had hydroxyl number 244 mg KOH/g and acid number of 21 mg KOH/g. The polyurethane prepared from this polyol and diphenylmethane diisocyanate was highly crosslinked with gel content of 98.1% and 50% swelling degree of toluene. It was a tough plastics at room temperature (T_g: 44°C) with tensile strength of 25.4 MPa, and elongation 16.7%. When used as wood adhesive, it displayed extraordinary shear strength characterized by substrate wood failure at 7.3 MPa rather than the adhesive bond.

2. An Emerging Natural Wax: Sorghum Wax from Bioethanol Production.

Jeffrey T. Cafmeyer, *Battelle, USA*

Wax from grain sorghum has long been suggested as a potential alternative to high-melting, high-hardness natural waxes such as carnauba. However, the uses and potential of sorghum wax have remained largely unexplored due to the lack of a readily available source and process. Recently the bioethanol industry has begun to diversify its feedstocks and in turn has increased its use of grain sorghum. This has created opportunities to collect the sorghum wax resulting from bioethanol production resulting in several millions of pounds potentially available for use. Efficient wax isolation methods that can be performed without affecting ethanol production are under development. Significant sorghum wax quantities are now accessible for sampling to industrial evaluators with the goal of identifying uses for a domestic natural wax product that increases the value of grain sorghum for both the bioethanol producers and sorghum farmers.

3. Soy-based Polyester Polyols for Flexible Polyurethane Foams and Elastomers. Dragana Radojic and Mihail Ionescu, *Pittsburg State University, USA*

The objective of this work was synthesis of new polyols with high renewable content suitable for preparation of elastic polyurethanes (flexible foams and cast elastomers). Most

commonly, polyester polyols for flexible polyurethanes are prepared by polyesterification of diacids with diols using trimethylpropane as starter. A new family of polyester polyols from soybean oil is described, synthesized by polyesterification of hydroxyacids, or of diacids with glycols, initiated by soy polyols; or by ring opening addition of cyclic esters to the hydroxyl groups of soybean polyols. Two different soy based polyols were used as starters: hydroformylated soybean oil, having all primary hydroxyl groups and hydroxyl number of around 220 mg KOH/g; and soybean oil polyol synthesized from epoxidized soybean oil by ring opening of epoxy groups with methanol, having all secondary hydroxyl groups and hydroxyl number of around 170 mg KOH/g. Polyesterification was performed with petrochemical monomers: adipic acid and diethylene glycol, as well as with ricinoleic acid, a bio-based hydroxy acid. ϵ -Caprolacton was used as ring opening polymerization monomer. Final polyester polyols having hydroxyl numbers from 45 to 75 mg KOH/g, by reaction with commercial diphenylmethane diisocyanate, were transformed to cast polyurethane elastomers and flexible polyurethane foams with physical-mechanical properties comparable to the petroleum-based reference.

4. Algal Oil Derived Polyurethane Foams.

Olivera Bilic¹, Zoran Petrovic², Ivan Javni², Milica Lovric², and Scott Franklin³, ¹*Kansas Polymer Research Center/PSU, USA*; ²*Pittsburg State University, USA*; ³*Checkerspot, Inc., USA*

As pressure continues to mount for materials that reduce environmental impact, while retaining performance properties, intensive research efforts have focused on the

development of polyols derived from renewable resources. These intermediates can then be used for the production of a broad range of polymers. Polyurethanes are of particular interest because of their wide use and excellent physical and mechanical properties. One potential drawback for vegetable oil-based polyols, when substituted for petroleum-based polyols, is their naturally heterogeneous composition which greatly impacts the properties of the resulting polyurethanes. Algae, as a promising renewable source, can be manipulated by both classical and genetic means to provide oleochemicals with narrowly defined compositions and, hence, facilitate the production of polymers with highly predictable structures and performance. The primary objective of this work is to develop algal oil-based polyurethane foams with compression strengths comparable to current petroleum-based materials. For the work reported here, our efforts have focused on exploring the preparation of both low and high density polyurethane foams from algal oil-based polyols.

5. Study of Physical and Tribology Properties of Soybean Oil-based Grease Formulated with Polysoap. Zengshe Liu¹, Girma Biresaw¹, Atanu Biswas¹, and H.N. Cheng², ¹*Food and Industrial Oil Research, NCAUR, ARS/USDA, USA*; ²*SRRC/ARS/USDA, USA*

Soybean oil-based grease formulated with polysoaps, which was synthesized from polymeric epoxidized soybean oil, were investigated. Greases were prepared using a mixture of lithium soap and triethanolammonium polysoap. Grease properties investigated were: hardness, using cone penetration procedure (ASTM D217); oxidation stability, using the pressurized

differential scanning calorimetry (PDSC) method (ASTM D-5483); friction and wear, using 4-ball tribometer (ASTM D-2266). Penetration data showed that grease formulated in the presence of polysoap was harder than that without polysoap, and this was attributed to the cross-linking in the polysoap structure which was expected to provide higher resistance to deformation. PDSC results indicated that the onset temperature of grease formulated with 3.8 wt% and 7.3 wt% polysoap increased by 8°C and 12°C, respectively, compared to grease without polysoap. The coefficient of friction of grease formulated with polysoap was much lower (0.015) than grease without polysoap (0.034).

6. Copolymers from Photochemical Thiol-ene Polycondensation of Fatty Dienes with Alkyl Dithiols. Bryan R. Moser, *USDA Agricultural Research Service, USA*

Photochemical thiol-ene polycondensation of unsaturated monomers based on renewable 9-decenoic acid with various alkyl dithiols readily afforded copolymers in high yield. Monomers were prepared by acid-catalyzed condensation of 9-decenoic acid with diols such as ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,4-cyclohexanedimethanol, 9-decenol, and 2-allyloxyethanol to give fatty dienoic esters. These dienes were then polymerized with 1,2-ethanedithiol, 1,3-propanedithiol and 1,4-butanedithiol in the presence of catalytic 2,2-dimethoxy-2-phenylacetophenone as photoinitiator to afford a family twelve novel linear copolymers. Physical properties such as molecular weight, polydispersity index, degree of polymerization, glass transition temperature, melting point, crystallization onset temperature,

and thermal stability were measured. Number average molecular weights ranged from 11–45 kDa, melting points were 25 Celsius or greater, crystallization onset temperatures ranged from –15 to 55 Celsius, glass transitions varied from –26 to 17 Celsius, and thermal stabilities were greater than 330 Celsius (temperature corresponding to 10% mass loss by DSC). Determination of mechanical properties such as tensile strength and Young's modulus are planned for future studies. In summary, thiol-ene chemistry is a useful tool for rapid production of renewable polymers utilizing mild, solventless reaction conditions.

7. Chemometric Comparison of Neutral Lipids in Camellia Oil with Other Cooking oils. Ling Peng, Chi Chen, and Yiwei Ma, *University of Minnesota, USA*

Camellia oil, or tea seed oil, is widely used in Asian countries as a cooking oil due to its high flash point and its favorable properties in color, odor, and flavor. It has also been used in dietary supplement and skin care products for its diverse bioactive components. The fatty acid profile of hydrolyzed Camellia oil has been examined in previous studies, but the composition of intact lipids in Camellia oil has not been reported. In this study, the profile of triacylglycerols (TAG) in Camellia oil was compared with other common cooking oils, including olive, safflower, peanut, canola, soybean, corn, grapeseed, palm and coconut oils, through the liquid chromatography-mass spectrometry (LC-MS) analysis and multivariate modeling. The distribution of all examined oils in the principal components analysis (PCA) model suggested that the composition of neutral lipids in Camellia oil is much more similar to olive oil than other cooking

oils. However, subtle differences in TAG profile exist between Camellia oil and olive oil. Camellia oil has more TAG(18:1/18:1/18:1) (triolein), while olive oil has more saturated fatty acid-containing TAG species, including TAG(16:0/18:1/18:1), TAG(16:0/18:0/18:1), and TAG(18:0/18:1/18:1). The ratio between these two groups of TAG species could be used as an indicator to distinguish Camellia oil and olive oil.

8. Two-Step Temperature Extraction for the Separation of Waxes and Oil in Sorghum Bran.

Robert A. Moreau and Megan E. Hums*, *USDA, ARS, ERRC, USA*

Grain sorghum is primarily used for animal feed and ethanol production but has the potential of providing value-added co-products such as waxes and oil. The surface of sorghum contains 0.1–0.4% w/w wax; however, extraction of wax prior to fermentation may not be economical. An alternative method for wax and oil extraction could occur through decortication, abrasion of the surface to remove bran (pericarp and germ). Decortication can increase the starch content of decorticated sorghum, thereby improving ethanol yields, while concentrating wax and oil to the separated bran. Typically oil and waxes are extracted from bran in a single extraction and then waxes are separated from oil via winterization. The aim of this research was to compare the traditional fractionation to a two-step, dual-temperature extraction for the fractionation of oil (triacylglycerols) and waxes by first extracting oil at room temperature and then waxes with a second higher temperature extraction. Extractions were performed using an accelerated solvent extractor at 1000 psi using hexane or ethanol as a solvent. Ethanol extraction resulted in higher yields (~15% w/w

fresh bran) compared to those of hexane (~11%) because additional materials were extracted. For both solvents, the traditional single-step extraction resulted in a mixture of ~80% oil and ~14% waxes. The two-step, dual-temperature fractionation resulted in predominantly oils in the first pass (~95%) for both solvents. For hexane, primarily waxes (~67%) were extracted in the second pass. For ethanol, the second pass resulted in a mixture of oils (46%), waxes (37%), and other unidentified materials (17%).

9. Free Fatty Acid Generation during Dry-grind Corn Ethanol Fermentation.

Brett Brothers, Tong Wang, and Hui Wang, *Iowa State University, USA*

The fermentation of corn into ethanol is a major usage of the American-grown corn crop. During the process of corn to ethanol, corn lipid class composition changes. The formation of free fatty acid (FFA) from triacylglycerol is commonly observed. Increased free fatty acid fermentation byproducts results in troublesome processing to remove excess FFA. The objective of this work was to determine where in the process of corn to ethanol FFA is generated using both industrial and laboratory-scale approaches. Specific commercial and conditions steps in the process of corn to ethanol were tested to determine their role in the generation of FFA. Thin-layer chromatography (TLC) and gas chromatography was used to quantify FFA in extracted total lipids. FFA assay by titration was also used for quantification to compare to TLC-based methods. Results indicate generation may be due to incremental increases at each step in the process, not due to one specific processing step. Furthermore, laboratory-based fermentations indicate the possible oxidation of linoleic acid, particularly in the FFA fraction, in corn may

increase% FFA determined using titration based methods. Overall FFA generation is seen throughout the entire process of corn to ethanol, and this trend also agrees with the increased FFA levels in industrial samples observed in multiple ethanol plants and studies.

10. Extraction and Characterization of Passion Fruit and Guava Oils from Industrial Residual Seeds and Their Application as Biofuels. Paulo A.Z. Suarez, *University of Brazil, Brazil*

A great diversity of fruits is used in the food industry to obtain different products such as juices, sauces, and foods. However, the food industry produces high amounts of residues. Passion fruit and guava are worldwide known fruits and very used by the food industry and generate tons of seed as residue. This work aims to study the extraction of oils from passion fruit and guava juice industries residues, their characterization and potential application as raw materials to obtain biodiesel and bio-oil. The passion fruit and guava seed oils content were 25% and 9%, respectively. In both oils, polyunsaturated fatty acids are predominant. Biodiesel obtained by esterification/ transesterification of both seed oils match most of the parameters specified for biodiesel in Brazil. Bio-oils obtained by thermal cracking of the seed oils were mainly composed by hydrocarbons similar to those observed in petroleum diesel.

11. Glycerolysis Reaction Under Ultrasound.

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Triglyceride transesterification reaction by small alcohol such as glycerol is used to illustrate the significance of cavitation in ultrasound assisted reactions. When a large negative pressure gradient is applied to the liquid, the

distance between the molecules stretches beyond the critical molecular distance, which is necessary to hold the liquid intact, the liquid will be broken down and voids (cavities) will be created, which is known as cavitation bubbles. It shows that the initial conversion rate is about 50 times higher under ultrasounds than in the purely catalytic system whether or not solvent was added. Performing this reaction under ultrasounds will therefore have important consequences for future developments of this industrial process.