

## Industrial Oil Products

### BIO 1.1/IOP 1: Biopolymers

*Chairs: Richard Ashby, USDA, ARS, ERRC, USA; and Rongpeng Wang, CVC Thermoset Specialties, USA*

#### **Plant Oil Derived Emulsion Copolymers with Predictable Properties** Meghan E. Lamm\*, Ping Li, and Chuanbing Tang, *University of South Carolina, USA*

Emulsion polymerization is an important industrial synthetic method. Unfortunately, it relies mostly on petroleum-based chemicals. Recent research has focused on incorporating biomass derived chemicals and intermediates, such as plant oil-based monomers. Due to their good hydrophobicity, plant oil monomers can struggle to be incorporated into emulsion polymers to achieve optimal properties. Herein we present an industrially relevant semi-batch method of emulsion polymerization used to prepare copolymers of soybean methacrylate (SBMA), using high oleic soybean oil (HOSO), with various industry co-monomers such as methyl methacrylate, styrene, and butyl acrylate. All polymerizations displayed good control with minimal coagulation and high conversion. Variation in feed ratios (from 0 to 50 wt% of SBMA) offers tunability of thermal and mechanical properties in resulting latex materials. The alkene present on the soybean chains allowed for oxidative crosslinking of latexes films, which resulted in high levels of crosslinking, consistent with SBMA content, and significant enhancement in mechanical properties. Overall, the promising results indicate good potential for replacement of petrochemical methacrylates in commodity thermoplastics and acrylic coatings.

#### **Corn Oil for Highly Flame Retardant Rigid Polyurethane Foams for Industrial Applications**

Camila Zequine, Sanket Bhojate, Brooks Neria, Pawan Kahol, and Ram Gupta\*, *Pittsburg State University, USA*

Vegetable oils are being used as starting

materials for the synthesis of various biopolymers. Polyurethanes are an important class of polymers because of their wide industrial applications in consumer and industrial sectors. The main disadvantage of the polyurethane foams is their high flammability which is due to the predominant presence of carbon and hydrogen in their structure. Highly porous and combustible nature of polyurethane foams further facilitates the flame spread rate. High flammability of polyurethane foams restricts some of its valuable applications. In this work, we have used corn oil as a starting material for the synthesis of polyurethane foams. Corn-oil was converted to polyol for polyurethane foams using “thiol-ene” click chemistry. Flame-retardant polyurethane foams were prepared by addition of different concentrations of dimethyl methyl phosphonate in the final foam composition. The effect of additive flame retardant on the physicochemical and flammability of the polyurethane foams was studied. Additive flame retardant significantly reduced the flammability of the polyurethane foams without affecting their physicochemical properties. The foam containing flame retardant showed over 30 times reduction in the burning time and over 6 times reduction in weight loss during horizontal burning test compared to foam without the flame retardant. In addition to reducing the burning time and weight loss after the addition of the flame retardant, these foams showed a significant reduction in heat release rate and thermal heat release. Our research opened a new pathway to utilize vegetable oils for industrial applications, particularly in the polyurethane industry.

#### **Rapid Conversion of Oils into Various**

**Monomers and Biopolymers** Aman Ullah\*, Muhammad Arshad, Reza Ahmadi, and Liejiang Jin, *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 CO<sub>2</sub> production. Microwaves, being clean, green and environmentally friendly, are emerging as an alternative source for product development. Solvent free conversion of 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 monomers were separated and polymerized into different polymers including biopolyesters, biopolyamides and biopolyolefins. The polymers were characterized in details for their structural, thermal, mechanical and viscoelastic properties. The ability for complete conversion of oils under solvent free conditions and synthesis of different biopolymers is undoubtedly an attractive concept from both an academic and an industrial point of view.

**Cationic Polymerization of Epoxidized Oils to Cast Resins and Foams** Zoran Petrovic\*, and Dragana Radojic, *Pittsburg State University, USA*

Epoxidized oils are an excellent platform

for a range of new products. Here we describe the use of bulk polymerization of epoxidized soybean oil, linseed oil and triolein to obtain resins useful as encapsulants, potting compounds, and foams based upon using different cationic initiators. While super acids and Lewis acids were preferable in making foams because they enhance reaction rates, novel catalysts were used to slow down and control the polymerization rate and obtain solid polymers with unusual properties.

**Synthesis, Properties and Structure Function Correlation of Bioplasticizers in PVC.** Dharma R. Kodali\*, and Lucas J. Stolp, *University of Minnesota, USA*

This presentation provides an overview of the synthesis, properties and functional evaluation of bioplasticizers in polyvinylchloride (PVC) that are derived from vegetable oils. Plasticizers, the largest class of plastic additives, are non-volatile organic liquids that impart flexibility and improve the functionality of plastics. The currently used phthalate plasticizers have EHS concerns. Bioplasticizers with various functional groups such as epoxy, acetoxy, methoxy, thiirane, aziridine on the acyl chain backbone combined with ester group variations of alkyl, mono, di and tri alkoxy or solketal of fatty acid esters have been synthesized and characterized. The bioplasticizers were derived from regular and high oleic soybean, canola and castor oils, and formulated with PVC and evaluated for their functional properties. Epoxysoybean oil fatty acid esters served as the key intermediate to incorporate most of the functional groups on the fatty acid backbone. The ring opening of the epoxy group with acetic acid resulted in cyclic tetrahydrofuran derivatives. The high viscosity and darker color of aziridine and thiirane derivatives limited their usefulness, whereas the other compounds physical and analytical properties such as acid value, color and

viscosity, were acceptable. The plasticizers having epoxy and acetoxy groups demonstrated excellent compatibility in PVC, with high efficiency (Shore Hardness), thermal stability and gelling properties. The structural variations of molecular weight, polarity, and branching of the fatty acid esters and their effect on functionality is examined and rationalized. The functional properties of number of bioplasticizers were comparable to commercial plasticizer, diisononylphthalate (DINP).

**Synthesis and Characterization of Lipid-based Biopolymers and Bionanocomposites from Poultry Industry By-product** Muhammad Safder\*, *University of Alberta, Canada*

Spent hen is a by-product of the poultry industry and has potential as a source of lipids. Lipid-based monomers and corresponding polymers have successfully been synthesized by using free radical polymerizations. The effect of temperature and time on molecular weight of polymer was studied and conditions for obtaining high molecular mass biopolymers were optimized. Furthermore, using optimized conditions, the biopolymers were reinforced with different nanoparticles such as nanoclay, POSS, and monocrySTALLINE cellulose (NCC) using in-situ polymerizations. The monomer, homopolymer and nano-reinforced polymers were characterized by different techniques such as nuclear magnetic resonance (NMR), attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), tensile testing and dynamic mechanical analysis (DMA). The thermal properties of the synthesized materials were evaluated by the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The nanofiller addition into the polymer matrix substantially improved the thermal and mechanical properties of the composites.

**Corn Stover and Levulinic Acid: Two Valuable, Renewable Substrates for Biosynthesis of Unique Polyhydroxyalkanoate Biopolymers**

Richard D. Ashby\*, Daniel K.Y Solaiman, Gary Strahan, and Alberto Nunez, *USDA, ARS, ERRC, USA*

Lignocellulosic materials are abundant and cheap and as such, are being evaluated as feedstocks for bio-based product synthesis. Our laboratory used the hydrolysate from corn stover (CSH) as a base fermentation feedstock for the synthesis of polyhydroxyalkanoate (PHA) biopolymers using *Burkholderia sacchari* DSM 17165 and *Azohydromonas lata* DSM 1122. *B. sacchari* utilized all of the available sugars in the hydrolysate while *A. lata* only used the glucose fraction of the hydrolysate to produce poly(3-hydroxybutyrate) (PHB). Introduction of levulinic acid (another inexpensive bio-based material produced from both C-5 and C-6 sugars) into the media in a co-feeding strategy resulted in block copolymers composed of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV; P3HB-3HV) from *B. sacchari* and terpolyesters composed of 3HB, 3HV, and 4-hydroxyvalerate (4HV) from *A. lata* with varying monomer ratios. This presentation will focus on the specific details of polymer production and characterization protocols involved in the synthesis of these unique PHA biopolymers.

**Microalgae for the Production of Novel Biopolymer Feedstocks** Scott Franklin\*<sup>1</sup>, Zoran Petrovic<sup>2</sup>, Jian Hong<sup>3</sup>, Leon Parker<sup>1</sup>, Lauren Slutzky<sup>1</sup>, Mona Correa<sup>4</sup>, Nina P. Reyes<sup>1</sup>, Constantine Athanasiadis<sup>4</sup>, Jon Wittenberg<sup>1</sup>, Estelle Schaefer<sup>5</sup>, and Kevin Ward<sup>1</sup>, <sup>1</sup>Checkerspot, USA; <sup>2</sup>Pittsburg State University, USA; <sup>3</sup>Kansas Polymer Research Center, Pittsburg State University, USA; <sup>4</sup>Checkerspot; <sup>5</sup>Checkerspot, France

The oleochemicals industry represents an enormous market valued at greater than \$23B

U.S. that is responsible for the production of myriad products, materials and polymers via processing of fats and oils derived from animal and vegetable sources. Surprisingly, this industry relies on just 14 fatty acids to create these chemical building blocks, because these fatty acids are what are readily available at commodity scale and price. On the other hand, plant oilseeds found in nature, most of which will never be cultivated at industrial scale, elaborate an incredible diversity of fatty acid moieties (> 500 species) unavailable in today's oleochemicals industry. The chain lengths, degrees of saturation, functionalities and purity of these fatty acids and their resulting triglycerides offer unique opportunities for the production of polymer feedstocks, particularly with regard to polyols for PU applications.

Microalgae, which elaborate fatty acids and triacylglycerols utilizing cellular machinery homologous to that found in higher plants, have proven to be highly efficient microbial factories for the production of biomass, proteins and oils, and many species appear to be quite amenable to genetic manipulation as well as to standard techniques of microbial strain improvement. Utilizing these tools and combining whole genome and transcriptomic sequencing of unique oilseeds and host microalgae, novel triglycerides can be produced in these single-cell factories at exceptionally high purity and titer, exceeding what is present even in the natural oilseed host. Data gleaned from materials (foams, elastomers and cast urethanes) produced utilizing the above approach will be shown.

**IOP 2: Olechemicals and Green Chemistry**

*Chairs: Darrell Sparks, Mississippi State University, USA; and Zheng Guo, Aarhus University, Denmark*

**Chemistry and Property of pH-responsive Amino Acid-based Amphiphiles** Weiwei Cheng<sup>1</sup>, Sampson Anankanbil<sup>2</sup>, Liu Guoqin<sup>3</sup>, and Zheng Guo\*<sup>4,1</sup>*South China University of Technology, China; <sup>2</sup>Dept. of Engineering, Aarhus University, Denmark; <sup>3</sup>School of Food Science and Engineering, South China University of Technology, China; <sup>4</sup>Aarhus University, Denmark*

Two novel series of lysine-based ampholytic amphiphiles, with alkylsuccinic anhydrides or fatty O-acylated malic anhydrides of varying chain lengths as hydrophobic acylating agents, were synthesized in medium to high yield (50.23%–90.15%) based on a facile, catalyst-free, and highly efficient method in water medium. The structures of the synthesized compounds were confirmed by MS, FTIR, and <sup>1</sup>H/<sup>13</sup>C NMR analysis. The synchronous presence of amino and carboxyl groups in the synthetic amphiphiles results in a pH-regulatable amphiphilic property, represented by pH-dependent change of critical micellar concentration (CMC), surface tension ( $\gamma$ ), and stability of oil-in-water emulsion. Results showed that CMC values decrease,  $\gamma$  value increase, and emulsion stability increase with increasing medium pH, suggesting that the surface activity of synthetic compounds at air/water and oil/water interface under neutral and alkalic conditions was remarkably higher than that under acidic condition. Surprisingly, lauryl O-acylated malic lysine presents excellent foaming ability close to detergent sodium dodecyl sulphate; and dodecyl succinic lysine affords highly stable o/w nanoemulsion. Moreover, lauryl O-acylated malic lysine displays excellent ferrous ion chelating property as good as lysine and DPPH antioxidative capacity as effective as commercial food ingredient DATEM, indicating its multi-faceted

functionalities. In addition, the cytotoxicity study of selected compounds by sulforhodamine B colorimetric assay proved a non-toxic nature; contributing further evidence to potential multi-purpose applications in food, laundry, pharmaceutical, and cosmetic industries.

**Modifying the Double Bond in Fatty Acids for New Materials: Oleo-chemistry versus Linoleo-chemistry** Grigor B. Bantchev\*, and Girma Biresaw, *USDA/ARS/NCAUR, USA*

This presentation will be about some reactions explored in search of novel lipid-based materials, with an emphasis on the differences between the chemistries of oleic and linoleic fatty acids. Thiol-ene, H-phosphonate-ene, and the epoxide-ring opening reactions will be discussed and the differences in the products contrasted. Oleate chain has one double bond, and when it reacts, only two very similar isomers (four isomers, if we account for chirality) are produced. Linoleate chain has two double bonds, which, upon reaction, yields a larger number of isomers, with functional groups in close proximity. In some cases, those functional groups react with each other, leading to a variety of linoleate-based structures that are not predictable from studying the reaction of oleates. Examples of such linoleate-based structures include: tetrahydrofuran, furan, tetrahydrothiophene, 1,2-dithiane and others.

**Membrane-based Oil Washing** Nikolai Kocherginsky\*<sup>1</sup>, Brajendra K. Sharma<sup>2</sup>, and Kishore Rajagopalan<sup>2,1</sup>*Biomime, USA; <sup>2</sup>Illinois Sustainable Technology Center, USA*

Both edible oils and biodiesel are often washed with aqueous alkali solutions to reduce

the fatty acid content – a process called alkali refining. The resulting soap leads to oil losses due to emulsification and typically requires centrifugation to accomplish a clean phase separation. A simple method to wash oils without mixing with water has been patented (US 10,065,132 B2, 2018). Oil flows on one side of a porous membrane with an aqueous phase on the other side. Due to the nature of the membrane, one of the phases is immobilized within the pores, vastly increasing the interfacial area without droplet creation. The extraction of fatty acids and other polar impurities is then accomplished in a facile manner. No transmembrane pressure or additional oil/water separation after washing is necessary. It can be used for example for removal of free fatty acids from high fatty acid feedstocks such as DDG oil, rice bran and conversion of virgin to extra virgin olive oil.

#### **Applicability of Esters from Mono-unsaturated Linear Dicarboxylic Acids for Lubricants**

Svajus J. Asadauskas<sup>\*1</sup>, Asta Griguociene<sup>2</sup>, Linas Labanauskas<sup>2</sup>, Jean-Luc Couturier<sup>3</sup>, and Jean-Luc Dubois<sup>3,1</sup>*FTMC, Lithuania*; <sup>2</sup>*Institute of Chemistry, FTMC, Lithuania*; <sup>3</sup>*Arkema, France*

Good combination of low temperature fluidity, oxidative stability and tribological properties makes esters from vegetable oils a frequent choice as lubricant basestocks, hydraulic fluids in particular. Some mono-unsaturation can be tolerated in lubricant applications as long as the above properties are still acceptable. Trans- double bonds often result in problematic pour points (PP), therefore, lubricant manufacturers strongly prefer cis-unsaturation. In this study predominantly trans- unsaturated linear  $\alpha$ - $\omega$ -C18 diesters were synthesized using various branched C5-C20 alcohols. Unexpectedly favorable PP below -50°C were recorded for trans-unsaturated C18 linear dibasic acid, esterified with C8 - C12 Guerbet and some

other alcohols. PP of their saturated homologues were 40-50°C higher. The diesters also showed outstanding resistance to heat thinning, with viscosity index VI~200. Methyl branching had only medium effect, while ethyl or longer branches improved cold fluidity dramatically without significantly compromising VI. Lubricant properties were compared to those of mineral oil and synthetic hydrocarbons, widespread as basestocks. Tribological performance, non-volatility, additive solvency and other properties were clearly superior. Oxidative stability was much better than that of typical fatty esters used for lubricants. Dioxane and dioxalane esters were also synthesized, but had poorer stability. Remarkably good VI, cold fluidity and other lubricant properties provide excellent opportunities for mono-unsaturated dibasic esters in high performance hydraulic fluids and other lubricants. The project COSMOS has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 645405.

#### **Investigation of a Heterogeneous Chemical Process to Convert Sunflower Oil into a Value Added Branched-Chain Oil**

Helen Ngo Lew<sup>\*1</sup>, Yunzhi Chen<sup>2</sup>, and Robert A. Moreau<sup>1,1</sup>*USDA, ARS, ERRC, USA*; <sup>2</sup>*USDA-Agriculture Research Service, USA*

Vegetable oils (i.e., triglycerides) are currently used in the industry as bio-lubricants. Unfortunately, these oils are not stable at high temperatures and are viscous at low temperatures. Modification of triglycerides (from linear-chain to branched-chain structures) has been found to be one of the most direct and efficient ways to overcome these drawbacks. We found that heterogeneous acid catalysts such as H<sup>+</sup>-BETA zeolite and sulfated zirconia solids work well in catalyzing the sunflower oil to branched oil products. The solids can be easily prepared, handled, and

separated from the oily products. These products are usually a complex mixture of isomers which can be isolated and characterized by various analytical instruments. Such branched-chain oils should exhibit improved low temperature fluidity while maintaining good lubricant properties.

**Feasibility of the novel utilization of modified Azadirachta Indica seed oil as transformer insulating fluid** Chinedu Agu\*<sup>1</sup>, Matthew Menkiti<sup>1</sup>, Albert Agulanna<sup>2</sup>, and Emeka Udokporo<sup>3,1</sup>, *Nnamdi Azikiwe University, Nigeria*; <sup>2</sup>*Project Development Institute, Nigeria*; <sup>3</sup>*University of Nigeria, Enugu Campus, Nigeria*

This work focuses on the solvent extraction and chemical modification of Azadirachta Indica seed oil (AISO) into a novel bio-based transformer insulating fluid. The effects of temperature, time and particle size on the AISO yield were studied. Extraction kinetics and thermodynamics were also investigated. The AISO batch was sequentially subjected to transesterification and epoxidation-esterification treatments to evaluate product quality after each stage. The vital operational characteristics of the modified Azadirachta Indica seed oil (MAISO) were determined. The AISO yield of 54.14 % was obtained at 55 °C, 150 min and 0.5 mm particle size. For the solvent extraction, pseudo-second order, hyperbolic, Elovich's and parabolic diffusion models all described the process kinetics, while Gibbs free energy, entropy and enthalpy values evaluated at 0.5 mm particle size were – 168.63 kJ/mol, 1.82 kJ/mol, and 428.11 kJ/mol, respectively. MAISO characteristics obtained for epoxidation-esterification were better than that of transesterification. The final MAISO characteristics after epoxidation-esterification are: -9 °C, 179 °C, 818 Kg/dm<sup>3</sup>, 1.66 mm<sup>2</sup>/s, 0.25 mgKOH/g, 0.11 mg/Kg and 52.86 KV for pour point, flash point, density, viscosity, acid value, moisture content and dielectric strength,

respectively. The dissolved gas analysis result (in ppm) of the key gases for MAISO obtained after epoxidation-esterification are :

**Coating Performance and Rheological Characteristics of Novel Soybean Oil-based Emulsions** Kangzi Ren<sup>1</sup>, Tao Fei\*<sup>1</sup>, Tong Wang<sup>1</sup>, and Keneth Metzger<sup>2,1</sup>, *Iowa State University, USA*; <sup>2</sup>*Eurica Group LLC., USA*

Aqueous emulsions of soybean oil based coating materials consist of ethylene glycol and propylene glycol mono- and di-esters of stearic acid (EGMD and PGMD, respectively) and compound emulsions (mixtures of EGMD emulsion with four commercial polymer emulsions) were formulated and tested for paperboard coating. Paper coated with the EGMD emulsion alone had low water resistance (5-min Cobb of > 20 gram per square meter) and grease resistance (100% oil penetration). Paper coated with compound emulsions had significantly improved water resistance and grease resistance. With EGMD accounting for as high as 60% of the emulsion's solid content, 5-min Cobb value of about 1.0 gsm was achieved. Increased number of coating drawdown significantly improved water and grease resistance of the coated papers. With three-drawdown and coat weight of 14.93-23.00 gsm, 5-min Cobb value of less than 2 gsm and oil penetration of less than 2% were achieved. Greater heat exposure during drying resulted in better water resistance. Increasing the drying temperature from 100 to 200 °C for 30 s reduced the 5-min Cobb value of papers coated with PGMD compound emulsions from 34.1 to 1.1 gsm. The addition of cross-linking agent, zinc ammonium carbonate (ZAC), in the emulsions improved water repellency but not grease resistance. The yield stress of cetyltrimethylammonium bromide (CTAB) based emulsions (1.61-21.32 Pa) were much higher than those of Tween 80 based emulsions (0.023-0.066 Pa), and they were generally more

viscous than the compound emulsions. The compound emulsions had comparable surface energy but lower gluability than the commercial emulsions.

**Synthesis of Lipid Derived Nanocomposites and Microwave Assisted Copolymers** Aman Ullah, Muhammad Arshad\*, Liliang Huang, and Mahrzadi N. Shahi, *University of Alberta, Canada*

Fatty acid based monomer and corresponding hybrid polymer nanocomposites have successfully been developed by in situ polymerization where nanoclay was used a reinforcement material. Different ratios of nanofiller was used to prepare hybrid materials by free radical homopolymerization of 2-(acryloyloxy)ethyl stearate (AOES) monomer and copolymerization of AOES with styrene. Solvent free synthesis of copolymers from fatty acids epoxides, derived from waste cooking oil and phthalic anhydride was also performed using (salen)Cr(III)Cl as catalyst and n-Bu<sub>4</sub>NCl/DMAP (tetrabutylammonium chloride/4-(dimethylamino)pyridine) as co-catalysts for the first time under microwave irradiation, where reaction time was reduced from a number of hours to minutes. DMAP was found to be more effective even at lower concentration providing higher molecular weight and narrow dispersity values of copolymers as compared to co-catalyst n-Bu<sub>4</sub>NCl. The prepared nanocomposites and copolymers were characterized and analyzed by proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy, transmission electron microscopy, XRD, atomic force microscopy, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, gel permeation chromatography, thermogravimetric analysis (TGA) and differential scanning calorimetric techniques. Moreover, flammability tests of nanocomposites were also performed. Addition of nanofiller into the polymer matrix

substantially improved the thermal properties and fire retardancy of the nanocomposites. While the renewable (waste/recycled cooking oil) based biopolymers with good molecular weight have a great potential to replace petroleum based products in the future. The current studies will contribute greatly in making fatty acids, derived from renewable materials and waste cooking oil useful for the polymer industry.

**Waterborne Glycerol Based Thermoplastic Adhesives for Wood Composites** Eric Cochran\*, Chris Williams, Andrew N. Becker, Nacu B. Hernandez, and Michael J. Forrester, *Iowa State University, USA*

With the rise of biodiesel on a global scale, a large volume of low quality crude glycerol has emerged on the market. Unsuitable for many end-use applications without costly refining, the industry continues to struggle to valorize this important side-stream. At the same time, recent EPA rules strictly limit the use of formaldehyde in the manufacture of wood composite materials, posing challenges to manufacturers in terms of identifying cost-effective substitutes that are compatible with existing process technologies. Addressing these problems, we have developed curable water-soluble adhesives from crude glycerol that provide both cost and performance advantages over other formaldehyde alternatives such as isocyanates. We are currently working with industry partners to produce 3,000 gallons of adhesive for full-scale manufacturing demonstrations. This talk will elucidate the path we followed beginning with the early technical innovations that gave birth to the base material culminating with the development of a minimum viable product at the cusp of successful commercialization.



**Understanding Improvements to Stiff Asphalt Binders Modified with Epoxidized Plant Derived Oil Materials through Analytical Chemistry**

Nacu B. Hernandez<sup>1</sup>, Chris Williams\*<sup>1</sup>, Eric Cochran<sup>1</sup>, Joseph H. Podolsky<sup>2</sup>, Mohamed Elkashef<sup>2</sup>, and Austin D. Hohmann<sup>2</sup>, <sup>1</sup>Iowa State University, USA; <sup>2</sup>Iowa State University, United States

Through recent work at Iowa State University, great potential has been identified using epoxidized plant oil materials as fluxes/rejuvenators in stiff asphalt binders. This work found that improvement in low temperature performance was greater than improvement in high temperature performance for Solvent De-Asphalting (SDA) and Residuum Oil Super critical Extraction (ROSE) unit bottoms when using epoxidized plant oils as compared to results from modified Vacuum Distillation (VD) tower bottoms. Additional research work has been done on recycled asphalt pavement demonstrating the performance and economic opportunity for using the epoxidized plant oils facilitating the increased amount of RAP that can be used in asphalt paving mixtures. Analytical chemistry was done using Fourier Transformed Infrared with Attenuated total reflection (FTIR-ATR) and Ion Mobility Mass Spectrometry equipment on the asphalt binders studied.

**Engineering Green Phase Change Materials: Dibasic or Diol Esters?** Latchmi Raghunanan\*<sup>1</sup>, Laziz Bouzidi<sup>2</sup>, and Suresh Narine<sup>2</sup>, <sup>1</sup>Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Canada; <sup>2</sup>Trent University, Canada

Increasing sustainability in the chemical enterprise continues to be a significant motivator for the use of renewable resources to prepare functional materials that perform similar to or better than commercially existing petro-chemical materials. Already, our group has presented several series of diol-derived

saturated diesters which are commercially promising phase change materials (PCMs). In fact, at least one of these PCM diesters has already been utilized in the food industry for the regulation of beverage temperatures. As part of efforts to widen the range of accessible temperatures and latent heats of these materials, we have studied also the analogous dibasic esters. Preliminary results show, however, that not all diesters are created equally; the dibasic esters of oxalic, malonic and succinic acids consistently melt at ~ 10 °C lower than the analogous diol-derived diesters of ethylene, trimethylene and tetramethylene glycols. Furthermore, the dibasic ester series possess consistently lower energy storage densities (~ 200-240 J/g) compared to the diol-derived diesters (230-260 J/g). We propose that the differences in the thermal performances lie in their packing behaviours. In this work, we will report on the phase trajectories of these materials using X-ray diffraction, Differential Scanning Calorimetry and Polar Light Microscopy experiments. While crystal structure elucidation has traditionally not played a significant role in the characterization of phase change materials, we expect that such insights will lead to a better understanding of the observed thermal properties. This information, in turn, can be used to make informed chemical modifications that improve the performance lipid derived phase change materials for the chemical enterprise.

**New Insights for the Advancement of Bio-based Diamides as Phase Change Materials**

Kosheela D. Poopalam\*<sup>1</sup>, Latchmi Raghunanan<sup>2</sup>, Laziz Bouzidi<sup>1</sup>, Yeong SK<sup>3</sup>, and Suresh Narine<sup>1</sup>, <sup>1</sup>Trent University, Canada; <sup>2</sup>Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Canada; <sup>3</sup>Malaysian Palm Oil Board, Malaysia

The thermal transition properties and the

crystal structure of a series of linear aliphatic diamide phase change materials (PCMs) were investigated. The diamides were prepared from stearic acid (C18) and diamines of varying carbon number (18-n-18, n=2, 4, 6, 8 and 10) via a simple amidation reaction. The <sup>1</sup>H NMR, DSC and XRD results were predictably correlated, and their differences was explained primarily in terms of intermolecular hydrogen bonding ability. These data revealed a peculiar behaviour of 18-2-18 attributed to its unique conformational arrangement influenced by limited degrees of freedom and strong steric hindrance within the ethylene diamine segment. Notably, although all the diamides presented sharp and narrow thermal phase transitions without significant supercooling, those with n≥4 showed a similar thermal storage density of ~220 J/g (160 J/g for 18-2-

18). The uniqueness of 18-2-18 was further highlighted via a singularity observed in the transition temperatures versus n curve. The thermal data were corroborated by the XRD. The diamides with n≥4 crystallized in single high-stability β-phases, whereas the 18-2-18 diamide crystallized in a lesser stable β-phase co-existing with a β'-phase. Experiments conducted at very different cooling rates (20 - 0.1 °C/min) indicated that the thermal transition behaviour and crystal structure were solely dependent on thermodynamics. Overall, the diamides are shown to have energy storage and thermal transition temperatures amongst the highest currently accessible by organic PCMs. The results also show that one can custom engineer the thermal and structural properties of diamide PCMs by fine-tuning the hydrogen bonding and aliphatic chains.

**ANA 3.1 / EAT 3.1 / IOP 3.1: Analysis of Food Applications of Low Saturated Fats/Oils; and PUFA, and Fat-Soluble Vitamins with Emphasis on Nutrition Labeling**

*Chairs: Jillonne Kevala, Food and Drug Administration, USA; and Serpil Metin, Cargill R&D, USA*

**Modernizing the Nutrition Facts and Supplement Facts Labels** Jillonne H. Kevala\*,  
*Food and Drug Administration, USA*

Objective: To modernize the Nutrition Facts and Supplement Facts labels (NFL and SFL) to reflect current scientific information on nutrition and enhance its presentation to consumers. Methods: Review and analysis of information from sources including the U.S. Department of Health and Human Services' and the U.S. Department of Agriculture's, "Dietary Guidelines for Americans 2015–2020"; the Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans (February 2015); The Institute of Medicine, which reviewed several reports on individual nutrients, from 1997 to 2011; consensus statements from the National Institutes of Health; and a Surgeon General report on Bone Health and Osteoporosis (October, 2004). FDA also relied on data from the National Health and Nutrition Examination Survey (2003–2008). Results: FDA's review and analysis of the large body of information described above showed that a significant number of different elements in the NFL and SFL, established in January 1993, were out of date with respect to current nutrition science. Other elements of the label needed updating to present nutrition information in a manner more clear and useful to consumers. Conclusions: FDA made numerous amendments to the requirements for mandatory and voluntary declarations of specific nutrients and amendments addressing different aspects of label formatting and issues related to serving sizes. The final rules published in May of 2016. FDA is drafting numerous guidance documents, in different stages of development, to aid

manufacturers in implementing changes in the NFL and SFL. The presentation will provide an overview of the key changes.

**Low Saturate High Oleic Canola Oil in Health and Nutrition** Xiaolan Luo\*<sup>1</sup>, Nisa Tharayil<sup>1</sup>, and Diliara Iassonova<sup>2</sup>,<sup>1</sup>*Cargill, USA*; <sup>2</sup>*Cargill Inc., USA*

Nutrition research has been focused on specific food ingredients beneficial to nutrition and health as diet has been linked to various diseases such as diabetes, obesity and cardiovascular disease. Fats and oils are one of the most important components of diet as one-fourth of total daily dietary energy is supplied by these fatty acids. Recently, Cargill scientists have developed a low saturate high oleic canola oil with a high level of mono-unsaturated and moderate level of polyunsaturated fatty acids. The new canola oil has the lowest saturated fat content on the market and can offer a 40% reduction in saturated fat from conventional canola oil. Oxidative stability and performance in food applications of the new canola oil was evaluated by analytical tests such as rancimat and schaal oven tests as well as sensory test in comparison with other specialty and commodity oils. The new canola oil demonstrated superior flavor and high oxidative stability. Its OSI slightly decreased from 18.6 to 18 even after storage for over 3 years at 55F. Food fried in low saturate canola oil showed favorable flavor, texture and high overall liking score while containing significantly reduced saturated fat content. The impact of natural antioxidants on oxidative stability of low saturate canola oil was also investigated. With high oxidative and application performance, low saturate high oleic canola oil offers a healthier

choice through reduced saturated fat per serving in labelling of a wide range of foods.

**Validation of a HPLC Method for Analysis of Provitamin A Carotenoids ( $\beta$ -carotene,  $\alpha$ -carotene and  $\beta$ -cryptoxanthin)** Sneh Bhandari\*, and Ming Gao, *Merieux NutriSciences, USA*

The 2016 Nutrition labeling regulation by US FDA (FR 33741) replaced the International unit (IU) for label declaration of vitamin A to mcg Retinol Activity Equivalents (RAE).  $\beta$ -carotene, and  $\alpha$ -carotene, and  $\beta$ -cryptoxanthin have different RAE values. There is a need for an accurate and precise method for analysis of  $\alpha$ -carotene,  $\beta$ -carotene and  $\beta$ -cryptoxanthin in foods for labeling of correct amount of total vitamin A, the current study is an attempt to validate such a method. The carotenoids were extracted using a hot saponification followed by the solvent extraction. The extract was analyzed by a reverse-phase HPLC on a C30 column. The method did provide a good chromatography and response of the carotenoids. The NIST SRM 2383 a baby food and BCR 485 vegetable powder reference material were analyzed by the method and the results of  $\beta$ -carotene,  $\alpha$ -carotene and  $\beta$ -cryptoxanthin as well as trans- $\beta$ -carotene were within the range specified by the respective reference materials for the corresponding carotenoids. The method precision in different food matrices in terms of % RSD values for  $\beta$ -carotene,  $\alpha$ -carotene and  $\beta$ -cryptoxanthin were in the range 1.9-5.4%, 3.1-15.1% and 1.6-7.9% respectively. Spike recovery in different matrices of carotenoids was found to be in the range of 86- 106%. LOD and LOQ of the method in terms of mcg/100g was in the range 1.1-2.2 and 2.1-3.6, respectively. The method was found to be accurate and precise for the analysis of carotenoids in different food matrices. The method can be used for carotenoid analysis for nutrition labeling of vitamin A.

**Rheology and Baking Stability of Water in Oil Emulsion Designed as Low saturated Bakery Shortening** Fernanda Davoli\*<sup>1</sup>, Serpil Metin<sup>2</sup>, and Paul Smith<sup>3</sup>, <sup>1</sup>*Cargill, USA*; <sup>2</sup>*Cargill R&D, USA*; <sup>3</sup>*Cargill Global Foods Research, Belgium*

There is a strong drive for low SAFA shortenings, but development is challenging because of the difficulty in reproducing the “plasticity” of traditional systems with reductions in SAFA. In this study, a two-step approach was taken. First water in oil emulsions were produced and their rheology was manipulated by emulsifier composition (including combinations), in order to find the behavior most resembling a traditional shortening. Then, the water phase was structured as a stable hydrocolloid gel to allow better water management during baking. Emulsion systems (water in oil emulsion) containing 35% saturated fat were prepared using a variety of different emulsifiers and crystallized with careful processing control in a pilot scale SSHE and characterized by rheology and water droplet size. Fat systems with good rheological behavior were selected, then used to further prepare emulsions with alginate to structure the water phase. Application tests were then performed with cookies. Control and manipulation of rheological properties were achieved, showing that the mechanical properties of the emulsion could be manipulated through the choice of emulsifier. Emulsions where the water phase was an alginate gel presented the best application performance in terms of cookie dimensions, suggesting better water control during baking. This research aims to build the foundational knowledge to lead to the development of a low saturated fat system that deliver the expected plasticity of a bakery shortening (responsible for proper dough formation) as well as an emulsion which maintains the final cookie dimensions by managing water loss during the baking process.

**Quantification of Furan Fatty Acids by LC-MS/MS and their Identification in New Zealand Marine Oils**

Matthew R. Miller\*<sup>1</sup>, Donato Romanazzi<sup>2</sup>, Hajime Uchida<sup>3</sup>, Johnathon Puddick<sup>2</sup>, Yutaka Itabashi<sup>3</sup>, Masashi Hosokawa<sup>4</sup>, Toshiyuki Suzuki<sup>3</sup>, and Michael Boundy<sup>2,1</sup>*Cawthron, New Zealand; <sup>2</sup>Cawthron Institute, New Zealand; <sup>3</sup>National Research Institute of Fisheries Science, Japan; <sup>4</sup>Hokkaido University, Japan*

Furan fatty acids (F-acids) are heterocyclic fatty acids with a furan moiety in the acyl chain. They are generally found as minor components in the lipid fraction of marine organisms, plants and mammals. F-acids are potent antioxidants and radical scavengers and are thought to contribute to the health benefits of fish-rich diets. The role and benefits of dietary F acids are yet to be fully understood, however they show promising potential as therapeutic marine drugs for the treatment of inflammatory-disorders. Objectives To develop a rapid quantitative liquid chromatography tandem mass spectrometry (LC-MS/MS) method for unequivocal identification and quantitation of F-acids in marine oils Methods For the past two years, the Cawthron Institute (NZ) has been engaged in an international research collaboration with the Hokkaido University (Japan) and the National Research Institute of Fisheries Science (NRIFS) of Japan to develop novel methods to identify and quantify F-acids. We have developed LC-MS/MS methods that in positive ESI mode, F-acids gave a prominent [M + H] ion, by which individual F-acids could be detected and identified to a level of 5 ng/mL. Results Our LC-MS/MS method provides selective detection of F-acids in marine oils without the need of lengthy sample processing. Through our research we have also identified a new source of F-acids, a unique New Zealand marine oil with surprisingly high levels of these minor fatty acids, offering new research opportunities in this field.

**Physicochemical Properties, Chemical Composition and Risk Assessment of Polycyclic Aromatic Hydrocarbons of Commercial**

**Fragrant Rapeseed Oils** Youfeng Zhang\*, *School of Food Science and Technology, Jiangnan University, People's Republic of China*

Fragrant rapeseed oil is a type of hot-pressed oil in China. In this work, physicochemical properties, chemical composition, presence and risk assessment of (PAHs) polycyclic aromatic hydrocarbons in 38 representative Chinese fragrant rapeseed oil samples were evaluated for the first time. The acid value (0.64-2.68 mg KOH/g), peroxide value (1.58-4.86 mmol/kg) and color value (R=2.6-5.8 Y=35) were all within codex limits. Thirty-two samples whose erucic acid concentrations exceeded 2%. A well negative linear correlation between oleic acid and erucic acid was shown (R<sup>2</sup>=0.876), which suggested to be a potential marker for prediction of adulteration. Benzo[a]pyrene and PAH4 (chrysene, benz[a]anthracene, benzo[b]fluoranthene, and benzo[a]pyrene) were nd-6.93 and nd-30.79 µg/kg, respectively. Monte Carlo simulation was applied to deal with the uncertainties in the dietary exposure and risk estimation. The median dietary exposure of BaP<sub>eq</sub> contents from total PAH4 were found to be 0.0826, 0.0530, 0.3082 and 0.0724 ng·kg<sup>-1</sup>·d<sup>-1</sup> for children, adolescents, adults and seniors of male, respectively, whereas that for the above groups of female were 0.0777, 0.0504, 0.3014 and 0.0659 ng·kg<sup>-1</sup>·d<sup>-1</sup>. Results from health risk estimation indicated high potential carcinogenic risk. Fragrant rapeseed oil is still a product subject to contamination by PAHs. Limits for PAH4 of fragrant rapeseed oil should be included in Chinese regulation to improve the safety.

**The Role of Fat in Determining the Structural and Textural Properties of Semi-sweet Biscuit**

Hasmadi Mamat\*, *Universiti Malaysia Sabah, Malaysia*

Fat plays a unique role in many food products due to its hygroscopic nature. In the area of baked goods, biscuits belong to a group of products that contains considerable fat and the overall quality is largely determined by the type of fat used. In this study, the effect of fat type on dough rheology properties and quality of semi-sweet biscuit (rich tea type) was investigated using various techniques. Four types of fat, namely palm oil, palm olein, palm mid-fraction and butter, which varied in composition and solid fat content, were used to produce semi-sweet biscuits. The role of fat and type of fat were analysed in terms of the texture, appearance and the starch behaviour of the final baked biscuit. Rheological properties of the dough were also compared. Texture profile analysis results showed that the type of oil significantly influenced dough rheological properties. Hardness measurement showed that biscuit produced with higher solid fat oil had higher breaking force, but this was not perceived when tested with a human panel. Gelatinization and pasting results showed that fat type also influenced thermal profiles of starch granules in biscuits with most of the granules retaining their crystallinity. Microscopy observations showed that biscuit produced with palm mid-fraction had an open internal microstructure and heterogeneous air cells as compared to the other samples. As conclusion, fat is an important ingredient in baking products and it plays many roles in providing

desirable textural properties of baking products, particularly biscuit.

**Effect of Tempering Parameters on the Plasticity and Hardness of Puff Pastry**

Margarine Miroslav Buchmet\*, *DuPont Nutrition Bioscience, Denmark*

Puff pastry margarine is one of the most challenging products for the margarine industry. There are many demands to good puff pastry margarine; it must be stable, plastic and non-greasy. Plasticity of margarine is determined by fat base and processing. Usually, fat base consists of palm oil and/or its fractions and some liquid oil. Such blends give good plasticity and workability. But to achieve that, it is necessary to temper margarine at proper temperature right after production and before distribution. Results of this study have proven that tempering conditions have a great influence on the margarine quality. Freshly produced samples of full-fat puff pastry margarine were tempered for one week at temperatures of 10, 20, 30°C, and followed by evaluation after one week's and two months' storage at 20°C. Samples were evaluated by hand for plasticity and workability. Hardness of margarine was measured by means of texture analyzer. The samples demonstrated different plasticity and hardness. Hardest and most plastic were samples tempered at 10°C, followed by samples at 20°C. Samples tempered at 30°C were brittle. Observed behavior can be explained by the polymorphic nature of fat. Data can be used as a guideline during margarine production and troubleshooting.

**BIO 3.1/IOP 3/PRO 3.1: Biofuels**

*Chairs: Frank Dumeignil, Lille University, France; Xiaofei P. Ye, University of Tennessee, USA; and Megan Hums, USDA, ARS, ERRC, USA*

**Synthesis of Thiophene and Thiolane Derivatives Found in Biodiesel Produced from Brown Grease Lipids.** Shehu Isah\*, Delaware State University-USDA, USA

Brown grease lipids (BGL), the primary component of dewatered grease trap waste (GTW) and sewage scum grease (SSG) is a potential low-value feedstock for biodiesel production. Market limitations of these feedstocks for use in biodiesel production include high sulfur (S) content. A combination of analytical techniques including GC-FID, GC-PFPD, and GC-MS have been previously used to elucidate the identity of thiophene derivatives (C<sub>4</sub>H<sub>4</sub>S-X), thiolane derivatives (C<sub>4</sub>H<sub>8</sub>S-X) and other S-bearing compounds in BGL-derived biodiesel. These compounds do not exist in the MS library; therefore, a small degree of uncertainty surrounds their identification. These molecules cannot be isolated from biodiesel because their concentrations are too low. Therefore, this project was designed to synthesize the S-bearing compounds believed to be found in BGL-derived biodiesel in quantities sufficient to characterize them by analytical methods such as NMR. We have developed strategies to synthesize thiophene and thiolane and preliminary results indicate they can be produced in yields sufficient to assist in their characterization in biodiesel. The identification of S-bearing compounds in BGL-derived biodiesel is necessary to devise effective desulfurization protocols needed to reduce the concentration of S-bearing impurities in biodiesel to < 15 ppm, as specified by ASTM.

**Modulating the Solubility of Saturated Monoglycerides (SMG) and Glycerol (GLY) in Blended Biodiesel Fuels** Richard W. Heiden\*<sup>1</sup>, and Martin Mittelbach<sup>2,1</sup>R.W. Heiden

*Associates, LLC, USA; <sup>2</sup>Institute of Chemistry, University of Graz, Austria*

The unexpected in-situ formation of heterophases from residual impurities in biodiesel fuels has deleterious consequences stemming from limited solubility. To get beyond simple expressions of “like dissolves like” requires an understanding of compositional factors which promote or discourage entry of an impurity into the molecular network of the liquid fuel. As such, the liquid composition acts to modulate dissolution and precipitation processes. Diesel fuels are comprised of hundreds to thousands of distinct chemical compounds when mixed together in commercial blends of diesel #2(ULSD)diesel #1(ULS kerosene), renewable diesel (RD) and biodiesel FAME. Together with FAME these compounds create an environment with a defined polarity- a predisposition to modulate solubility that is determined by concentrations of main and minor hydrocarbon components at levels greater than about 0.1%. Despite the complexity in the molecular composition of biodiesel fuels, various international definitions and restrictions greatly narrow the range of possible compositions. However, low concentrations of impurities have intrinsic solubilities complicated by specific interactions\*. We present here a study of possible relationships between the saturation points (SP) of GLY and SMG, fuel composition, and classical markers of solvent polarity, using existing theories to assist in explaining experimentally determined SPs and interactions. The results help establish an improved understanding of the compositional factors defining solubility, the barriers imposed by current fuel definitions, and the magnitude of compositional changes needed to reduce the unwanted effects of impurities.

\*Heiden,Schober, Mittelbach,(2017)JAOCS  
94:285-299.

**Co-production of acrylic acid in a typical biodiesel plant: a techno-economic assessment**

Xiaofei P. Ye\*, *University of Tennessee, USA*

Producing value-added chemicals from glycerol is imperative for a sustainable future of biodiesel. Despite efforts worldwide, the commercial production of acrylic acid from glycerol faces challenges, both technologically and economically. Based on our patented technology using carbon dioxide as reaction medium in a two-step process to catalytically convert glycerol to acrylic acid, we established computer simulation models to analyze the energy efficiency and economics of the process. The analysis was conducted in conjunction with published data of a typical intermediate-sized biodiesel facility, aiming at the possibility of producing acrylic acid on site. Sensitivity analysis in response to the market value of glycerol, the source and cost of carbon dioxide recycling, and the changes in process kinetics will also be presented.

**The Use of Controlled Flow Cavitation to Improve the Performance of Degumming, Refining and Biodiesel Operations** Darren J. Little\*, *Arisdyne Systems, Inc., USA*

An overview of the application of controlled flow cavitation and compression-decompression jet atomization phenomenon for the intensification of chemical processing applications is presented. For vegetable oil acid degumming and/or neutralization reactions, the reasons for enhanced performance of the refining operation, reduced environmental impact, observed reduction in necessary acid and/or caustic addition as well as decrease in oil loss, potential savings in steam consumption and decrease in maintenance opex is discussed and industrial scale examples given. The efficient removal of residual soaps, phosphorus, ffa and metals while minimizing and in some cases even eliminating the need for water washing or silica addition is also described. Finally, the power of controlled flow cavitation to reduce catalyst consumption, increase throughput, and reduce monoglyceride content in finished biodiesel is also described.



**IOP 4 / PRO 4.1: Biorefinery Technology and Catalysis**

*Chairs: Helen Ngo Lew, USDA, ARS, ERRC, USA; and Kris Knudson, Crown Iron Works Co., USA*

**An Efficient Catalytic Approach to the Synthesis of Wax Esters from Fatty Acid Methyl Esters**

Duc Hanh Nguyen<sup>1</sup>, Guillaume Raffa<sup>1</sup>, Yohan Morin<sup>1</sup>, Simon Desset<sup>1</sup>, Frédéric Capet<sup>1</sup>, Véronique Nardello-Rataj<sup>1</sup>, Franck Dumeignil<sup>\*2</sup>, and Régis Gauvin<sup>1</sup>,<sup>1</sup>UCCS, France; <sup>2</sup>Université de Lille, France

**Objective:** Wax esters are commodity materials used as cosmetics, lubricating agents, plasticizers or surface coatings. They are obtained either from specific bioresources, with limited availability, or from non-trivial synthetic processes. In order to circumvent these issues, we propose to develop an efficient access to these compounds using catalytic upgrading of fatty acid methyl esters (FAME). **Methods used:** To achieve this, we reasoned that catalytic dehydrogenative conversion of alcohol into esters and its reverse reaction, ester hydrogenation, can be performed using the same catalytic system, by adjusting operational conditions. Thus, we targeted the one-pot, two-step conversion of fatty acid methyl esters into wax esters using a molecular ruthenium-based catalyst. The first step was performed under hydrogen pressure, affording fatty alcohols, which were then converted into wax esters by H<sub>2</sub> extrusion. **Results:** In the absence of solvent and of base additive, and after optimization, excellent conversion and selectivity were reached, from both methyl oleate and from a commercial FAME mixture. Specific studies were devoted to feed purification, which proved to be the key to achieve full conversion of FAME substrates. Physicochemical investigations revealed that resulting compounds display properties similar to benchmark commercial products such as jojoba oil, of lesser availability compared to the herein considered bioresources. **Conclusions:** This study validates the interest of this simple and

efficient access to specific cosmetic oils. It paves the way for further larger implementation of this catalytic approach, which affords wax esters from readily available bioresources, with applicative properties comparable to those of benchmark products.

**Towards the Biolubricants Endgame: Building Superior Lubricants, One Structural Feature at a Time** Latchmi Raghunanan<sup>\*1</sup>, Laziz Bouzidi<sup>2</sup>, and Suresh Narine<sup>2</sup>,<sup>1</sup>Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Canada; <sup>2</sup>Trent University, Canada

Structure-property relationships are increasingly valued for the identification of specifically engineered materials with properties optimized for targeted application(s). To date, a significant amount of research effort has been exerted globally towards the preparation of bio-derived lubricants with continually improved performance properties, including a large body of work from our own group, the Trent Center for Biomaterials Research. However, while numerous reviews can be found in the recent literature on the synthesis and performance of bio-derived lubricants, those content which review specifically the recent advances in their predictive cold flow properties (i.e., crystallization/melting, viscosity and flow behaviours) are still noticeably absent from the literature. Such studies are important not only for applications including lubricants and biodiesel production which are obviously influenced by fluidity at low temperatures, but also for applications whose properties are in whole or in part dependent upon thermal processing and/or flow. The latter includes materials such as phase change materials for energy storage, and waxes for cosmetic

formulations and as food modifiers. In this contribution, the structure-property relationships of linear and branched esters prepared from lipid-based oleochemicals are reviewed from a fundamental perspective. We will show that ester materials with tunable-on-demand cold flow properties can be custom engineered based on the judicious design of the molecular architecture from a toolbox of sorts comprising of all possible structural elements.

#### **Renewable Diesel from Waste Lipids:**

##### **Challenges and Conversion Impacts**

David Schwalje\*<sup>1</sup>, Larissa Perotta<sup>2</sup>, and Michael Zhao<sup>3,1</sup>,<sup>1</sup>*Axens NA, USA*; <sup>2</sup>*Axens, France*; <sup>3</sup>*Axens, USA*

Renewable diesel production via the hydrogenolysis, saturation, and isomerization of lipid feedstocks is a proven technology solution, with multiple worldwide projects either in operation, construction, or engineering. Recent debates related to land usage and multi-industry demand for traditional vegetable oils coupled with regulatory incentives has resulted in renewable diesel plants increasing the percentage of feedstocks derived from animal fats and wastes such as tall and used cooking oil. This presentation will focus on the catalytic and processing impacts of those feedstocks including: • Tall oil rosin acid conversion and impacts • The effects of organic nitrogen on hydroisomerization activity and the value of reliable feedstock pretreatment • Used cooking oils: contaminants and process impacts • Co-processing alternative feedstocks with petroleum diesel and catalytic challenges associated with alternative feedstocks The topics will be addressed utilizing pilot test results, case studies, and commercial feedback.

#### **Challenges in converting various fats and oils into a high yield of renewable jet fuel**

Asbjørn S. Andersson\*,*Haldor Topsoe A/S, Denmark*

In order to convert fats and oils into

renewable jet fuel the feed stock needs to undergo various types of chemical reactions, like hydrodeoxygenation (HDO), hydrodewaxing (HDW), hydrocracking (HDC) and hydrodearomatization (HDA). Detailed knowledge and control of these reaction mechanisms is key to design a process, that will produce a high yield of renewable jet fuel meeting the ASTM D 7566 specification. The properties of different fats and oils have been analyzed, and the impact of those properties, like fatty acid distribution, contaminants ect. on the design and setup of the conversion process, will be discussed. Especially, the carbon chain length plays a huge role in determining the final jet yield, since alkanes with a carbon number of 18 or higher cannot be included in the jet fuel product, and therefore has to be converted into molecules with lower carbon number, which result in a jet yield loss. Another important step in the process is the isomerization of linear alkanes into branched alkanes, a step that is key to produce a jet fuel meeting the low freezing point requirement. Case studies covering the whole process from fats and oils to renewable jet fuel will be presented.

#### **Effect of Thermal Treatment on Feeding Value of Expeller Soybean Meal in Hexane-free Soybean Processing**

Michal Kaválek\*<sup>1</sup>, and Vladimír Plachý<sup>2,1</sup>,<sup>1</sup>*Farmet a.s., Czech Republic*; <sup>2</sup>*czech, Czech Republic*

Extrusion-expeller processing (EP1) of soybeans is used mainly in local processing and it is suitable for annual capacities up to 400,000 tonnes. The EP1 process is based on separation of oil from seed in a screw press, therefore no chemicals like hexane are used. EP1 products are expeller meal and vegetable crude oil. Expeller meal has about 6-8% of residual oil. Before oil pressing in a screw press, the oilseed is usually conditioned and extruded. Extrusion process is accompanied by flash steam release – a mixture of steam and air under atmospheric

pressure. About 65 kilograms of flash steam per tonne of soybeans is released. Therefore there is a great potential for recuperation of energy and it can be transferred to soybeans in multistep preheating conditioner before soybeans reach the extruder. During the study the amount of recuperated energy and influence of thermal exposition on feeding values has been evaluate (PDI, urease activity, protein fraction according to CNCPS and protein digestibility in chicken balance trials). Experiences have shown that it is possible to recuperate 20 kWh per tonne from this flash steam. Recuperation of heated air from the oil press can save additional 10 kWh per tonne. Energy savings of recuperation amount to about 25%. Optimization of thermal exposure during the EP1 is the key to achieve the best feeding value at lower operating costs. Different thermal exposition of soybeans causes changes in the protein solubility and digestibility, therefore an optimized feed for ruminants and monogastric animals can be produced.

**Maximizing Heat Recovery in Soybean Processing** Mohamed Abid\*, *Solex Thermal Science Inc., Canada*

Soybean processing plants are always evaluating options to maximize operating margins. Conditioning of Soybeans is an energy intensive process and is critical in achieving target efficiency in oil extraction plants. The availability of waste heat sources vary with plant layout, steam sources and meal cooling technology used. However the choice of a heat transfer technology to efficiently recover this low grade energy is critical to finding an efficient and economical solution. Plate Heat exchangers provide high density of heat transfer area within a compact design that allows for an efficient utilization of the recovered energy. The plate channels maintain high velocities which is essential to higher rates of heat transfer. The Bean Heater Modules

allow existing installations to reduce steam consumption, with low capex and minimal shutdown time for installation. These modules can be installed on top of existing bean conditioners, allowing use of waste heat to increase capacity, improve overall conditioning or replace leaking tube sections. The modular design makes installation faster and less expensive. The modules can also be used for new conditioning application using a combination of waste heat and steam sources. The long life of the plates in this abrasive environment reduces maintenance costs associated with frequent replacement of tube sections and required downtime. The external flexible hoses connected to manifolds allow for easy isolation. Any plate can be blocked off without opening the modules. Also each module has an access door that can be used to replace any plate with minimal disruption of production.

**A New Material for Reducing Glycidyl Esters in Edible Oil** Chelsea L. Grimes\*, and Cristian Libanati, *W.R. Grace, USA*

Glycidyl esters (GE) in edible oil are known carcinogenic and mutagenic process contaminants that have recently been subjected to European legislation. In order to reduce glycidol concentrations in one pass RBD oil to proposed regulatory limits, we have studied a material at different temperatures, contact time, dosages, and initial GE concentrations without adversely affecting oil quality. Our presentation will outline properties of this novel material as well as catalytic performance in multiple oil matrices. We will also present a kinetic analysis of this reaction to incorporate this material into existing oil refining technologies and ultimately remove the necessity for secondary refinement.

**A Comparison of Conventional Short Path Distillation to a Proprietary Short Path Stripper**

**in Reducing Glycidyl Fatty Acid Esters ( GEs)  
and 3-MCPD Esters in Refined Edible Oils** Marc  
Koukoulas\*, *Artisan Industries Inc. , USA*

Short Path Distillation has been identified as a potential technology for significantly reducing the concentration of GEs and MCPDs, identified as potential carcinogens, in refined edible oils. The technology, also commonly referred to as “Short Path Evaporation” has been predominantly used in the distillation of high boiling, heat sensitive materials, such as

FAMEs, monoglycerides, tocopherols, and similar products, owing to its ability to operate at extremely low pressures. This presentation compares the viability of applying “Short Path Distillation” in eliminating these heat-induced contaminants to a “Proprietary Short Path Stripper”. An overview of the features of the Short Path Stripper and Short Path Distillation is presented for this “Stripping-only” application.

**IOP-P: Industrial Oil Products Poster Session**

Chair: Jerry King, *Critical Fluid Symposia, USA*

**1. Copolymers from Photochemical Thiol-ene Polycondensation of Fatty Dienes with Alkyl Dithiols.**

Bryan R. Moser\*, *USDA Agricultural Research Service, USDA*

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 °C or greater, crystallization onset temperatures ranged from -15 to 55 °C, glass transitions varied from -26 to 17 °C, and thermal stabilities were greater than 330 °C (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.

**2. Effect of Burgundy Solid Extracted from Eastern Red Cedar on Subterranean Termites and Wood-Decay Fungi.**

Fred J. Eller\*, *USDA, ARS, NCAUR, USA*

Eastern red cedar (ERC) is an abundant resource in the U.S. and has been investigated for the extraction of cedarwood oil (CWO) and CWO bioactivity, particularly its use to protect wood against termites and decay fungi. Methanol extraction of ERC sawdust gives a burgundy oil (BO). This BO contains CWO and a burgundy solid (BS). Evidence indicates the BS itself has inhibitory bioactivity. This study investigated the wood preservation properties of BS alone, in combination with CWO and in conjunction with an amylose inclusion complex (AIC) against termites, brown-rot decay fungi and white-rot decay fungi. Wood was treated by vacuum impregnation and tested for resistance to termites and four species of decay fungi. The AIC made wood less palatable and more toxic to termites but did not inhibit the brown-rot fungi or the white-rot *T. versicolor* but did inhibit the white-rot *I. lacteus*. The CWO led to both lower termite mass loss and higher termite mortality and had an inhibitory effect on the white-rot decay fungi. However, it took a combination of AIC and CWO to have an inhibitory effect on the brown-rot fungi. The BS had a minor inhibitory effect on termites but did not inhibit the brown-rot fungi or the white-rot *I. lacteus*. It did, however, inhibit the white-rot *T. versicolor*. Wood blocks vacuum impregnated with the combination of the AIC, CWO and BS resulted in the highest termite mortality, and the lowest percentage wood mass losses for the termites and all four wood decay fungi species studied.

**3. Synthesis of Thiophene and Thiolane Derivatives Found in Biodiesel Produced from Brown Grease Lipids.**

Shehu Isah\*, *Delaware State University-USDA, USA*

Moved to talk in **BIO 3.1/IOP 3/PRO 3.1: Biofuels**

**4. Proximate Composition, Fatty Acid Profile, Mineral and Tocopherol Contents of Two Industrial Hempseed Varieties in Response to Sowing Dates and Pesticide Treatment.** Peiyi Shen\*<sup>1</sup>, Zili Gao<sup>1</sup>, Hui Li<sup>1</sup>, and Bingcan Chen<sup>2</sup>, <sup>1</sup>*Dept. of Plant Sciences/North Dakota State University;* <sup>2</sup>*North Dakota State University, USA*

With the 2018 Farm bill, industrial hemp will be treated as an emerging crop which is anticipated to encourage rapid growth in the burgeoning U.S. hemp industry. Industrial hempseed contains all the essential amino acids and fatty acids necessary to maintain healthy human life, and could be a new good source of nutrients for both humans and livestock. However, the nutritional quality of industrial hempseed, including the levels of protein and oil, is influenced by numerous factors, such as seed varieties, sowing date, and pesticide treatment, etc. In order to obtain a specific quality of industrial hempseeds suitable for growth in the United States, we investigated the impact of sowing dates and pesticide treatments on the proximate composition, fatty acid profile, mineral and tocopherol contents of two industrial hempseeds varieties (Katani and Delores) grown at the NDSU Langdon Research Extension Center (LREC), Langdon, ND. The results showed that there was an important range of variation for almost all seed composition, and the cultivars × sowing date × pesticide treatments interaction effect was significant for chemical compositions.

**5. Cost-effective Polyurethane Sealants and Adhesives from Soybean Polyols.** Jian Hong\*<sup>1</sup>, Dragana Radojic<sup>2</sup>, Mathew Long<sup>1</sup>, and Zoran Petrovic<sup>2</sup>, <sup>1</sup>*Kansas Polymer Research Center, Pittsburg State University, USA;* <sup>2</sup>*Pittsburg State University, USA*

Cost-effective soybean oil-based polyols were developed by an economical process based on one-pot two stages reaction. By adjusting the

ratio of reactants, the hydroxyl numbers (OH#) of polyols varied from 120-330 mg KOH/g, useful for foams, adhesives, sealants and coatings. Polyols were used to formulate strong and elastic polyurethane sealants and adhesives with glass transitions above room temperature, tensile strengths above 10 MPa and elongations above 100%.

**6. Lipid-Based Sulfones as Next-Generation Organic Phase Change Materials.** Navindra Soodoo\*<sup>1</sup>, Latchmi Raghunanan<sup>2</sup>, Laziz Bouzidi<sup>1</sup>, and Suresh Narine<sup>1</sup>, <sup>1</sup>*Trent University, Canada;* <sup>2</sup>*Trent Centre for Biomaterials Research, Departments of Physics & Astronomy and Chemistry, Trent University, Canada*

Three n-alkyl sulfones (n-SO<sub>2</sub>-n) synthesized from vegetable oil derivatives and representative of an n-SO<sub>2</sub>-n series (n = 10, 12 & 18) were investigated and contrasted with the current lipid-based PCMs found in the literature. The resulting sulfones displayed excellent thermal characteristics suitable for phase change material (PCM) applications. The series were synthesized in high yield and purity via the solvent-free oxidation reaction of the lipid-based n-alkyl sulfides using hydrogen peroxide and acetic acid catalyst. Their molecular structures were confirmed by Fourier Transform Infrared Spectroscopy, Proton Nuclear Magnetic Resonance, and Mass Spectrometry. Their thermal transition and thermal stability properties were studied under an inert environment using Differential Scanning Calorimetry and Thermogravimetric Analysis, respectively. Crystal structures were elucidated by Powder X-Ray Diffraction. The sulfones possessed melting points from 89-109 °C and energy storage densities of 196-266 J/g, and underwent evaporation with an onset which increased with molecular mass. Further, 10-SO<sub>2</sub>-10 crystallized in the energetic  $\gamma$ -polymorphic form, whereas 12-SO<sub>2</sub>-12 and 18-SO<sub>2</sub>-18 crystallized in the thermodynamically

more stable  $\beta'$  +  $\beta$  and  $\beta$ -polymorphs, respectively. Overall, the sulfones possessed higher melting points and enthalpies, and better thermal stability than analogous monofunctional lipid-based counterparts. The superior performance of the sulfones is attributed to the strong intermolecular interactions associated with the highly polar sulfonyl group within the fatty chains. The new knowledge generated on the thermal behavior and crystal structure of these sulfones revealed that they have desirable tunable-on-demand properties to be used as PCMs for thermal energy storage.

#### 7. Soy Oil-Based Non-Isocyanate Polyurethane Resins for Stereolithography.

Ivan Javni\*<sup>1</sup>, Olivera Bilic<sup>2</sup>, Vivek Sharma<sup>1</sup>, Camille Holman<sup>3</sup>, and Xianmei Wan<sup>1</sup>, <sup>1</sup>Pittsburg State University, USA; <sup>2</sup>Kansas Polymer Research Center/PSU, USA; <sup>3</sup>Pittsburg State University - KPRC, USA

Stereolithography (SLA) is a three-dimensional printing method. It is based on photopolymerization of liquid reactive precursor by focused ultraviolet laser beam controlled by specific software. Parts made by SLA have good surface finish, excellent dimensional accuracy and good mechanical properties. Stereolithography can be used to create prototypes, models and fabricate a variety of products. The rapid expansion of stereolithography caused strong demand for novel resins, which are dominantly produced from petrochemicals. Due to the depleting of natural resources and the negative effect of carbon dioxide on the environment, there is a tendency for replacement of petrochemicals with bio-based renewable materials. Natural oils are one of those that have great potential for synthesis of variety of resins for stereolithography. Among them are non-isocyanate polyurethanes (NIPUs), which are synthesized from soy oil based cyclic carbonates

and amines, and without use of hazardous isocyanates. Due to some structural specifics, along with easy variation of their chemical structure and characteristics, soybean oil based NIPUs can be a material of choice for fabrication by SLA of many products, particularly for healthcare industry and for variety of consumer products. We created a range of novel soybean oil based NIPU resins; the effect of their structure on characteristics of SLA printed parts was studied. The experimental results showed that these resins can be used as virgin or blended with commonly used petrochemicals, and, as such, they can be used for preparation of variable products.

#### 8. Renewable Polyols for Polyurethane from Soybean Oil.

Maha L. Shrestha\*<sup>1</sup>, Petar Dvornic<sup>2</sup>, and Mathew Long<sup>1</sup>, <sup>1</sup>Kansas Polymer Research Center, Pittsburg State University, USA; <sup>2</sup>Pittsburg State University, USA

The main objective of the research is to synthesize renewable, bio-based polyols from soybean oil and utilize them in preparation of rigid polyurethane foams and casts. Thiol-ene "Click" Chemistry was employed for synthesis of functionalized polyols from soybean oil derived polymercaptans. The reaction can be initiated with UV light in presence of 2-hydroxy 2-methylpropiophenone as a photoinitiator or via thermal pathway utilizing radical initiator, 2,2'-Azobis(2-methylpropionitrile). The polyurethanes prepared from these polyols possesses good thermal and mechanical properties, which are comparable to the commercially available polyurethanes.

#### 9 Isocyanate-Free Polyurethane Coatings from Soybean Oil.

Olivera Bilic\*<sup>1</sup>, Ivan Javni<sup>2</sup>, Tim Dawsey<sup>3</sup>, Xianmei Wan<sup>2</sup>, and Camille Holman<sup>1</sup>, <sup>1</sup>Kansas Polymer Research Center/Pittsburg State University, USA; <sup>2</sup>Pittsburg State University, USA

Polyurethanes, due to their excellent physical and mechanical properties, find uses in a wide range of applications, such as adhesives, packaging, insulation, bedding, upholstery, footwear, vehicle parts, coatings, etc. Recognized as being among the most versatile families of polymers, polyurethanes are commonly prepared by the reaction of isocyanates with polyols. However, an increasingly strict regulatory environment, within which the industry must operate, is driving strong demand for safer, and renewable, components in polyurethane production. Growing pressure to reduce the use of the highly toxic and hazardous isocyanate starting materials is in addition to ongoing concerns around depletion of petrochemical resources and the negative effects of carbon dioxide on the environment. A promising alternative for the preparation of isocyanate-free polyurethanes, with renewable content, involves the reaction of cyclic carbonates (carbonated soybean oil - CSBO) with multifunctional amines. Using this approach we have developed methods for the production of isocyanate-free soy-based polyurethane coatings. The two-step preparation, reported here, involved synthesis of a soy polyamine non-isocyanate (NIPU) followed by reaction to produce a soy polyamide-polyester NIPU resin with pendant double bonds. The resin was used for thiol-ene photopolymerization. The goal of this work is a cost-competitive route to high modulus, and high abrasion resistant, coatings from safe and renewable feedstocks. Mechanical and thermal properties are reported here on our work to date, along with plans for continued improvement to the process. Promising results indicate that soy-based coatings have comparable, or better, properties than representative commercial coatings.

**10. Feruloylated Vegetable Oils Protect Vitamins C and E from UV Degradation.** David L. Compton\*<sup>1</sup>, Kervin O. Evans<sup>1</sup>, and John R. Goodell<sup>2</sup>, <sup>1</sup>USDA, ARS, NCAUR, USA; <sup>2</sup>Active Naturals, USA

Vitamins C and E and their derivatives are used as antioxidants in topical formulation in cosmetics and personal care products. Vitamin E (100  $\mu$ M) was rendered a poor antioxidant in the 2,2-diphenyl-1-picrylhydrazyl (DPPH\*, 200  $\mu$ M) assays in acetonitrile, scavenging < 50 % of DPPH\* within 30 min, after exposure to (UV) for 4 h. Vitamin C solutions (100  $\mu$ M) were rendered moderate antioxidants, scavenging > 50 % of DPPH\* within 30 min, after exposure to UV radiation for 4 h. Feruloyl soy glycerides (FSG) are UV absorbers synthesized from the biocatalytic conversion of soybean oil and ferulic acid ethyl ester that have a total UV absorbance and photostability comparable to the commercial UV absorber, octinoxate (ONX). FSG (100 – 1000  $\mu$ M) was added to acetonitrile solutions of the vitamins and their derivatives to determine if FSG could photoprotect the vitamins and their derivatives, allowing them to retain their antioxidant efficacy after 4 h of UV irradiation. The addition of FSG, 500 and 1000  $\mu$ M, allowed Vitamin E and most of the antioxidant derivatives to retain rapid antioxidant activity after 4 h UV exposure. Vitamin C retained rapid antioxidant capacity with 100  $\mu$ M FSG after 4 h of UV exposure. FSG performed slightly better than the commercial UV absorber, ONX, in protecting the vitamins' and their derivatives' antioxidant activities from UV degradation. FSG also possessed intrinsic antioxidant capacity that ONX did not, which may have contributed to its better performance when mixed with the vitamin's and their derivatives in the DPPH\* assays.

**11. Development of New Coconut Oil-based Biting Fly Repellents.** Jim A. Kenar\*<sup>1</sup>, Steven C.



Cermak<sup>1</sup>, and Junwei J. Zhu<sup>2</sup>, <sup>1</sup>USDA-ARS-NCAUR-FFR, USA; <sup>2</sup>USDA-ARS-Lincoln, USA  
Many blood-sucking insects such as are capable of transmitting human and animal pathogens worldwide and can be serious pests of humans and animals. For example, stable flies (*Stomoxys calcitrans*) alone can cause over \$2 billion annually in losses to the U.S. cattle industry. Repellents are an important tool for reducing the impact of biting insects on humans and animals and plant- and botanical-based derivatives have been used against insects in agricultural and urban settings for at least two millennia. However, most of plant-based repellents are short-lived in their effectiveness, primarily due to their high volatility. We recently discovered that inexpensive coconut oil-based fatty acids are an excellent insect repellent and active against a broad array of blood-feeding insects. The C8 to C12 medium-chain fatty acids represent >65% of total fatty acids present in coconut oil and were shown to be the predominant repellent compounds. Laboratory bioassays showed these compounds to repel biting flies for two weeks after application with stronger repellency and longer residual activity than that of DEET (N,N-Diethyl-meta-toluamide) the most effective and long-lasting repellent currently available commercially. The coconut fatty acids were also formulated into an aqueous starch formulation that showed up to 96 h protection (which to our knowledge is the longest lasting repellent reported to date) against biting flies for cattle treated with this formulation. These promising results suggest these compounds may be easily adopted for livestock animal producers as well as other public health applications for preventative repellent protection.

**12. Application of Green Technology using Natural Deep Eutectic Solvents (NaDES) for Recovering Canola Seed Phenolics.** Sumudu N. Warnakulasuriya\*<sup>1</sup>, Takuji Tanaka<sup>1</sup>, and Janitha

P.D. Wanasundara<sup>2</sup>, <sup>1</sup>University of Saskatchewan, Canada; <sup>2</sup>Agriculture and Agri-Food Canada, Canada

Application of green technology is becoming a foremost tool in any industries to mitigate harmful results created by environmentally-unfriendly processes and solvents. A new designer solvent, natural deep eutectic solvents (NaDES) is a potential green, bio-based ionic liquids composed of two or more compounds that are generally plant based primary metabolites. NaDES can provide desired extractability for a range of compounds by employing the most suitable solvent composition. This study focused on extraction of phenolic compounds from canola seed and meal using NaDES as a replacement for organic solvents. Eight different NaDES systems were prepared by mixing choline chloride (hydrogen bond acceptor) with different hydrogen bond donor compounds that are found in plant cellular environment. Those solvent combinations were choline chloride: citric acid (1:1, 2:1, 3:1), choline chloride: glucose (1:1, 2:1), choline chloride: sucrose (4:1), choline chloride: maltose (4:1), and choline chloride: raffinose (11:2) with 20% (w/w) water content in each. Defatted samples of canola seed coat, endosperm, ground whole seed, and commercial canola meal [expeller pressed (EP) and desolventized and toasted (DT)] were extracted at 1:30 (solid:solvent, by weight) ratio at 50°C for 1 hr. Direct UV absorbance spectrum of each extract was taken at 200 – 340 nm and compared with sinapic acid standards. The different NaDES showed a wide range of difference in the extractability of sinapic acid and derivatives for different canola substrates. This presentation will discuss the potential of utilizing NaDES on different canola substrates using <sup>1</sup>H- and <sup>13</sup>C-NMR as the tool of confirmation of compound identity.

**13. Extraction, Purification and Characterization of Wax from Sorghum as an Alternative Natural Wax.** Junsi Yang\*, Loren Isom, Felipe Sperotto, Curtis Weller, and Ozan N. Ciftci, *University of Nebraska-Lincoln, USA*

There is a growing demand for alternative natural wax sources due to dwindling wax supply, increasing wax applications and prices. Global wax demand will grow 1.5% annually till 2019, whereas wax supply growth will be only 0.4%. Sorghum is a promising alternative natural wax source. However, there is no specific processing method to obtain high quality sorghum wax that meets natural wax industry specifications. Therefore, the objective of this study was to develop an improved processing method to obtain a high quality wax from sorghum. Sorghum whole kernel, bran, and DDGS were extracted with hexane and supercritical carbon dioxide (SC-CO<sub>2</sub>) and then purified by a simple ethanol washing process. Wax yield from whole kernel was 0.11 wt.% from hexane extraction, whereas it was 0.8 wt.% from SC-CO<sub>2</sub> extraction at 40 MPa/70 °C. Temperature and pressure of SC-CO<sub>2</sub> extraction positively affected wax yield. Following ethanol washing, wax recovery from whole kernel, bran and DDGS extracts was 81, 32.3 and 27.5%, respectively, and the melting point improved to 80, 79, and 78 °C from 77.5, 56.8, and 56.3 °C, respectively. Moreover, the ethanol washing process improved the hardness (needle penetration method) from 40 to 2, which is comparable to Carnauba waxes. Ethanol washing also decreased acid and iodine numbers (USP 401) from 20 to 3.3, and from 59.4 to 23.6, respectively. Sorghum wax is promising natural wax which may reduce U.S. dependence on non-renewable petroleum-derived waxes or natural wax imports. Our process minimizes processing steps and generates superior quality sorghum wax.

**14. Novel Catalyst for Cationic Homopolymerization of Epoxidized Methyl Oleate.** Dragana Radojicic\* and Zoran Petrovic, *Pittsburg State University, USA*

Epoxidized natural oils are very valuable monomers in various polymerization reactions. Various cationic catalysts were used to polymerize epoxidized oils such as superacids and Lewis acids. Here, we report polymerization of epoxidized methyl oleate as a model compound in the presence of the new catalyst (BCF), affording lower reaction rate at very low concentration and higher degree of polymerization. The effect of different catalysts on the polymerization process was investigated.

**15. Filled Epoxy Resins from Natural Oils.** Dragana Radojicic\*, *Pittsburg State University, USA*

Thermosetting cast resins with different SiO<sub>2</sub> filler content were prepared from epoxidized soybean oil (ESO) and epoxidized algal oil (EAO) in order to study matrix-filler interaction. Ring opening polymerization and copolymerization was catalyzed by fluoroboric acid. Effect of filler on thermal and mechanical properties was investigated. Matrix cross-link density was a direct function of epoxy oxygen content in epoxidized oils, being higher for ESO polymer samples. Effect of filler on properties was stronger in composites prepared with lower functional EAO.

**16. Impact of Delivery System Type on Curcumin Bioaccessibility: Comparison of Curcumin-loaded Lipid Nanoparticles with Commercial Curcumin Supplements.** D. Julian J. McClements, Bingjing Zheng\*, Xiaoyun Zhang, and Shengpeng Pen, *University of Massachusetts Amherst, USA*

The bioavailability of curcumin depends on the physical form that it is delivered. In this study, nanoemulsion-based delivery systems fabricated using pH-driven method was

compared with three commercially available curcumin supplements. The pH-driven method involved dissolving curcumin in an alkaline solution (pH 12.5) and then adding this solution to an acidified nanoemulsion (pH 6.0). The three commercial curcumin products were capsules or tablets purchased from an online supplier: Nature Made, Full Spectrum, and CurcuWin. The different curcumin formulations were then subjected to a simulated gastrointestinal tract (GIT) model consisting of the mouth, stomach, and small intestine phases. A comparison of the prepared nanoemulsions and commercial products indicated that the curcumin concentration in the mixed micelles decreased in the following order: CurcuWin  $\approx$  nanoemulsion  $\gg$  Full spectrum  $>$  Nature Made. This study provides valuable information about the impact of the delivery form on the bioavailability of curcumin. It suggests that encapsulating curcumin within small lipid particles may be advantageous for improving its absorption from the GIT.