

**BIO 1.1 / IOP 1: Biorenewable Polymers**

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

**Strategic Planning of Polymeric Materials from Vegetable Oils** Zoran Petrovic\*, *Pittsburg State University, USA*

Plant oils are excellent substrates for new chemistries and design of high value sustainable materials. Designing materials must take into account the structure of lipids. Essential property of materials is the cost which imposes limitation on the number of steps for conversion of oils to products. Ideally a product should be made in a single step. Direct polymerization of oils was used to prepare liquids of different viscosities useful for printing inks, plasticizers for rubber, and modifiers for asphalt etc. For better control of properties functional groups must be introduced.

Functionalization of saturated lipids could be carried out by transesterification or transamidation. Unsaturated fatty acids or triglycerides are functionalized by oxidation, epoxidation, hydroformylation, metathesis, ozonolysis, thio-ene reactions with mercaptans etc. Thermosetting oil-based polymers are useful for foams, coatings, adhesives and as matrix resins for fiber-reinforced composites. They are based on multifunctional triglycerides and multicomponent curing systems. Thermoplastic polymers and elastomers can be made from two-functional fatty acids or their fragments. Excellent biodegradable shape memory materials were made from oil-based monomers. Direct polymerization of epoxidized oils leads to pure oil-based polyether foams. The largest outlet for oil-based polyols is in flexible and rigid polyurethane foams.

**Sequential Liquefaction of Nicotiana Tabacum Stems Biomass by Crude Polyhydric Alcohols for the Production of Polyols and Rigid Polyurethane Foams** Chiragkumar M. Patel\*<sup>1</sup>, Jina R. Patel<sup>2</sup>, Amitkumar A. Barot<sup>2</sup>, and Vijay K. Sinha<sup>1</sup>, <sup>1</sup>*Industrial Chemistry Dept., V. P. & R. P. T. P. Science College, India;* <sup>2</sup>*V. P. & R. P. T. P. Science College, India*

In this work, Nicotiana tabacum stalks and castor oil-based polyol was synthesized via a two-step process. Preliminarily, stalks were liquefied using acid catalyst to procure glycol-glycoside and the optimized conditions for liquefaction of N. tabacum stem's biomass was 150°C temperature for 180 min time using PTSA as catalyst. Progressively, the glycol-glycoside obtained from the former step was further reacted with castor oil in the presence of lithium hydroxide to get dark brown-coloured polyol with hydroxyl value was running in between 200 and 400 IOH. Glycol-glycoside and polyols were characterized by chemical and instrumental methods. Further, by employing open-cup method involving the mixing of polyol and isocyanate adducts, the desired polyurethane rigid foam was obtained. The product was tested for their physical, mechanical, thermal, and morphological characteristics, while the thermal conductivity was in the range of 0.013 to 0.017 kcal/mh AQ1. The performed study may yield high quality rigid or semi-rigid polyurethane.

**The Effect of Monoglyceride Incorporation on the Solvent Absorption and Mechanical Properties of Glycerol-based Polymer Films** Prince G. Boakye\*<sup>1</sup>, Kerby C. Jones<sup>2</sup>, Nicholas P. Latona<sup>2</sup>, Cheng Kung Liu<sup>2</sup>, Samuel A. Besong<sup>3</sup>, Stephen E. Lumor<sup>3</sup>, and Victor T. Wyatt<sup>2</sup>, <sup>1</sup>*Delaware State University, USA;*

<sup>2</sup>USDA, ARS, ERRC, USA; <sup>3</sup>Dept. of Human Ecology, College of Agricultural Sciences, Delaware State University, USA

Monoglycerides (MGs) have been incorporated into the matrix of poly-(glycerol-co-glutaric acid) films to investigate their effect on the thermal, mechanical, and solvent absorption properties of these films. MGs were concentrated using a combination of molecular distillation and solvent extraction, resulting in a concentrate with 99.15% purity. The MG concentrate was predominantly monoolein (92.65%). The films were made by first synthesizing polyester gels from glutaric acid and glycerol with or without the incorporation of MGs. The polymer gels were then cured at 150°C for 24 h, forming clear, solid films with a yellow hue. Solvent absorption studies revealed that poly(glycerol-co-glutaric acid-co-MG) films were able to absorb and resorb solvents better than poly(glycerol-co-glutaric acid) films, albeit they had higher erosion levels. Thermogravimetric Analysis (TGA) showed that the incorporation MGs did not remarkably affect the thermal stability of the glycerol-based films. The MG-incorporated films were qualitatively softer than the poly(glycerol-co-glycerol) films which correlates to the observed 39-fold reduction in Young's Modulus and 17-fold reduction in fracture energy. Mechanical property studies also revealed that the incorporation of MGs increased the elongation and reduced the tensile strength of poly(glycerol-co-glutaric acid) films. Correlation analysis revealed a strong linear relationship between Young's Modulus and fracture energy ( $R^2 = 0.9962$ ), and between Young's Modulus and tensile strength ( $R^2 = 0.9972$ ). Our study proved that MGs can be successfully incorporated in the polymer matrix of poly(glycerol-co-glutaric acid) films to produce softer films with increased elongation and increased solvent absorption capacity.

### **Fluorescence Emission and Catalyst Effect of Precious Metal Nanocomposites Based on Autoxidized Unsaturated Plant Oils/Fatty Acids**

Baki Hazer\*, *Bülent Ecevit University, Turkey*

Unsaturated plant oils/fatty acids (UPOFA) have gained great interest as monomers to produce bio based polymers. UPOFA is prone to react with air oxygen under daylight at room temperature which is called "ecofriendly autoxidation". Eco-friendly autoxidation process creates peroxide linkages in order to obtain unsaturated plant oil/fatty acid polymer that can initiate the free radical copolymerization of some vinyl monomers. Mixture of salt of silver and soybean oil was spread out in a glass container and exposed to air oxygen at room temperature to obtain soybean oil nanocomposite. Similarly, a mixture of salt of gold and soybean oil was spread out in a glass container and exposed to air oxygen at room temperature to obtain soybean oil nanocomposite. Catalyst effect of gold NPs is dramatically decreased the rate of autoxidation. For example the gold catalyzed autoxidized soybean oil polymer was obtained in ten days oxidation period while the autoxidation time takes nearly one month to obtain oxidized soybean oil polymer without Au NPs. In addition, high fluorescent emission of silver/oxidized soybean oil polymer nanocomposite is obtained. The nanocomposite solutions were analyzed by UV-VIS spectrometer in view of the surface plasmon resonance. TEM was used to characterize size and shape of the metal nano particles embedded into the copolymer nano composites.

### **Reactivity and Structure-property Performance of Natural Oil Polyols in Polyurethanes**

Ibrahim Sendijarevic\*, *Troy Polymers, Inc., USA*

The key principle in selection of raw materials in polyurethanes is the understanding of structure-properties relationship, as different building blocks impart different performance characteristics to

polyurethane materials. In addition, raw materials are selected to meet the reactivity requirements of the applications. To meet the performance and processing requirements, in many applications it is common to use a combination of polyols. In some applications, natural oil polyols (NOPs) contribute to the performance of polyurethanes, and NOPs have been used from early days of polyurethanes industry. A perception exists that NOPs with pendant hydroxyl groups in the triglyceride backbone are less reactive compared to the conventional polyether polyols with terminal hydroxyls. However, results of recent kinetic studies demonstrated that the isocyanate reactivity of NOPs requires lower activation energy than polyether polyols, and under certain conditions NOPs are more reactive than polyether polyols. Studies of model systems also showed that the reaction profiles are not significantly affected by drop-in replacement of NOPs in place of polyether polyols in elastomers, energy-absorbing and resilient polyurethane foams. The impact of the NOPs on physico-mechanical properties of polyurethane is more significant. The effect of the NOPs on the hard/soft segment phase separation has been evaluated and correlated with dynamic and mechanical properties of model elastomers, which can be used to guide the selection of NOPs in polyurethane applications. The use of NOPs as performance materials will be demonstrated in energy-absorbing polyurethane foams.

**Free Radical Polymerization of Monomers Based on Plant Oils** Zoriana Demchuk<sup>1</sup>, Kyle Kingsley<sup>1</sup>, Oleh Shevchuk<sup>1</sup>, Ihor Tarnavchik<sup>1</sup>, Vasylyna Kirianchuk<sup>2</sup>, Ananiy Kohut<sup>2</sup>, Stanislav Voronov<sup>2</sup>, and Andriy Voronov\*<sup>1</sup>, <sup>1</sup>North Dakota State University, USA; <sup>2</sup>Lviv Polytechnic National University, Ukraine

Most currently available syntheses of polymers from plant oils are limited to polycondensation and oxypolymerization. This work targets development

of novel waterborne polymeric materials (latexes, dispersions, emulsions etc.) from plant oils for coatings, paints, adhesives etc. Due to highly hydrophobic nature of plant oils (triglycerides), their use for development of such materials has been challenging. To overcome hydrophobicity, converting oils into vinyl monomers to synthesize latexes via classic radical chain polymerization in emulsion was performed. Novel plant oil-based acrylic monomers are synthesized in a one-step direct transesterification (alcoholysis) of oil triglycerides. While the vinyl bond of the monomers is reactive in radical chain polymerization, the double bonds of the fatty acid fragments are unaffected and capable of post-polymerization oxidative reactions. New acrylic monomers are synthesized from soybean, linseed, sunflower and olive oil, possessing remarkably different compositions of fatty acids in triglycerides. While length of fatty acid carbon chains is similar (mostly oleic, linoleic and linolenic acids), average number of double bonds per oil triglyceride (degree of unsaturation) varies significantly. Specifically, degree of unsaturation in fatty acids was utilized as a criterion for understanding fundamental behavior of new monomers in radical chain (co)polymerization. Key questions addressed include understanding of i. how degree of unsaturation impacts new acrylic fatty monomers reactivity in (co)polymerization as well as the resulting latex properties, and ii. do polymer latexes, based on monomers from different plant oils, demonstrate different performance in coatings, paints, adhesives, once they are copolymerized with a variety of petroleum-based counterparts?

**Synthesis of a New Generation Biopolyols from Canola and Other Plant Oils** Jonathan M. Curtis\*<sup>1</sup>, Tolibjon S. Omonov<sup>2</sup>, Ereddad Kharraz<sup>2</sup>, Xiaohua Kong<sup>2</sup>, and M. Hossein Tavassoli-Kafrani<sup>2</sup>, <sup>1</sup>Dept. of

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Recently, various polyols have been developed from soy and other plant oils, primarily to replace petrochemical polyols used polyurethane production. In many cases these biobased polyols retain aspects of the starting triacylglycerol structure, have moderate hydroxyl numbers of 200-250 mg KOH/g and high viscosity that tends to increase significantly with increasing hydroxyl numbers and oligomeric content. Biobased polyols with high hydroxyl numbers and low viscosities are highly desirable since these can be functionally incorporated into rigid materials. In a recent patent application we described the process for the synthesis of a new class of biobased polyols from a range of unsaturated plant oils. This comprises the sequential reaction steps of (a) epoxidation of the unsaturated plant oil; (b) transesterification to produce hydroxyalkyl esters of fatty acid epoxides; and (c) further hydroxylation to obtain polyols. Using this synthetic pathway with canola oil, a polyol with high hydroxyl numbers (i.e. 350-360 mg KOH/g) and with low viscosities (i.e.

#### **Synthesis and Characterization of Fatty Acid Modified Amines with Improved Water Barrier Properties**

John H. Vergara<sup>\*1</sup>, Yunze Tian<sup>1</sup>, John J. La Scala<sup>2</sup>, Joshua M. Sadler<sup>2</sup>, and Giuseppe R. Palmese<sup>1</sup>, <sup>1</sup>Drexel University, USA; <sup>2</sup>Army Research Laboratory, USA

Fundamental studies aimed at elucidating the key contributions to corrosion performance are needed to make progress toward effective and environmentally compliant corrosion control. Epoxy/amine systems are typically employed as barrier coatings for corrosion control, however, the curing agents used for coating applications can be very complex, making fundamental studies of water and oxygen permeability challenging to carry

out. Creating model building blocks for epoxy/amine coatings is the first step in carrying out these studies. This work demonstrates the synthesis and characterization of model amine building blocks from saturated fatty acids and diethylenetriamine (DETA) with tunable hydrophobicity. The glass transition temperature (T<sub>g</sub>) of modified amine samples suffered a 45-50 °C T<sub>g</sub> reduction, which has been attributed to a loss of labile hydrogens available for crosslinking in these samples. It was observed that the fatty acid modified amines exhibited a reduced diffusivity to water of up to 50%. This has been attributed to the increased tortuosity of samples with a pendant aliphatic chain in the network. Samples with modified amines were observed to have lower solubility of water of up to 30%. We propose that the reduction in solubility can be caused by a dilution of oxygen in the polymer network caused by the addition of aliphatic pendant chains.

#### **Microwave-assisted Maleation of Tung Oil for Bio-based Products**

Chengguo Liu<sup>1</sup>, Zengshe Liu<sup>\*2</sup>, Brent H. Tisserat<sup>3</sup>, Rongpeng Wang<sup>4</sup>, Thomas Schuman<sup>5</sup>, Yonghong Zhou<sup>1</sup>, and Lihong Hu<sup>1</sup>, <sup>1</sup>Institute of Chemical Industry of Forestry Products, CAF, China; <sup>2</sup>Food and Industrial Oil Research, NCAUR, ARS/USDA, USA; <sup>3</sup>Function Food Research, NCAUR, ARS/USDA, USA; <sup>4</sup>CVC Thermoset Specialties, USA; <sup>5</sup>Dept. of Chemistry, Missouri University of Science and Technology, USA

A simple, "green" and convenient chemical modification of tung oil for maleinized tung oil (TOMA) was developed via microwave-assisted one-step maleation. This modifying process didn't involve any solvent, catalyst or initiator, but demonstrated the most efficiency of functionalizing plant oils: at a reaction time of 4 min, the yield of purified TOMA target product reached 94.5 wt.%. A mechanism of this microwave-assisted maleation was investigated by

nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Moreover, three oil-based epoxides including epoxidized glycidyl ester (EGS), epoxidized soybean oil (ESO), and epoxidized octyl soyate (EOS) as well as hydroxyl-terminated polydimethylsiloxane (PDMS) were employed to react with the optimized TOMA product. Novel fully oil-based epoxy resins and silicon-containing alkyd resins were prepared. Mechanical, thermal, thermo-mechanical, and hydrophobic properties of the as-prepared epoxy and alkyd resins were evaluated.

**BIO 2.1 / IOP 2: Biofuels**

*Chairs: Adeeb Hayyan, University of Malaya, Malaysia; Lieve Laurens, National Renewable Energy Laboratory, USA; and Jun Ogawa, Kyoto University, Japan*

**Recovery of Fatty Acids from Advanced Biofuels: Improvement in Acid Number and Value** Justice Asomaning\*, and David C. Bressler, *University of Alberta, Canada*

The development of renewable alternatives to fossil derived chemicals and fuels have attracted a significant interest due to socioeconomic and environmental concerns. Advanced biofuels, particularly from lipids that can be used as drop-in fuels, which is directly compatible with current petroleum infrastructure has seen considerable advancements over the last couple of years. One of the major drawbacks of advanced biofuels is the high acid number as a result of residual acids, which necessitates further processing to convert the residual acids hydrocarbons using techniques such as hydrotreating. The aim of the present study was to develop methods for removing and recovering fatty acids from advanced biofuels thereby reducing the acid number to acceptable level. The recovered fatty acids can then be utilized in high value application such as in the cosmetic and pharmaceutical industries. Various methods were used to directly remove the acids from the advanced biofuels. The systems were then tested for their ability to recover the acids and also regenerate the system. Results show that the acids can be successfully removed from advanced biofuels using these methods providing acid numbers below detectable levels. The systems were then used for ten cycles after regeneration without significant loss in acids removal from the advanced biofuel. This study demonstrated the feasibility of improving the quality and value of advanced biofuel through acid number reduction and fatty acids recovery.

**Synthesis and Purification of Polyphenolic Branched-chain Fatty Acids with Natural Monophenols** Helen Ngo Lew\*<sup>1</sup>, Zongcheng Yan<sup>2</sup>, Karen Wagner<sup>1</sup>, and Robert A. Moreau<sup>1</sup>, <sup>1</sup>USDA, ARS, ERRC, USA; <sup>2</sup>South China University of Technology, China

Polyphenolic branched-chain fatty acids (poly-PBC-FAs) are hybrid compounds produced by linking electron-rich aromatic rings such as natural monophenols (i.e., thymol, carvacrol and creosote) with mixed free fatty acids derived from soybean and safflower oils through a process known as arylation. The antimicrobial properties of these poly-PBC-FAs are similar or better than their parent monophenol compounds. This paper will focus on the continuing development of the arylation process using mixed fatty acids coupled individually with thymol, creosote, and carvacrol in the final products to give poly-PBC-FA yields of 72.4%, 77.2%, and 48.8%, respectively. The difference in yields is strongly dependent on the different functional groups on the three phenolic aromatic rings. Water is a co-catalyst in the reaction and the concentration of water has a significant influence on the arylation reaction by depressing the isomerization reaction. Another aspect of this presentation will focus on the development of a highly efficient distillation method to clean up the products achieving up to 97% purity, which is extremely important for evaluating their antimicrobial properties.

**Animal Fatty Wastewater Sludge recovery by Acid-catalyzed Esterification into Fatty Acid Butyl Esters as Potential Biodiesel** Christopher Wallis<sup>1</sup>, Muriel Cerny<sup>1</sup>, Eric Lacroux\*<sup>2</sup>, and Zéphirin Mouloungui<sup>1</sup>, <sup>1</sup>Laboratoire de Chimie Agro-



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Animal Fatty Wastewater Sludge (AFWS) represent a novel source of glyceride and free fatty acids (FFA) material for the future. These lost lipids were studied for potential conversion into biodiesel. Often referred to floatation greases, AFWS were found to be composed of 20-70% of water, demonstrating the variability in composition that one can expect from such slaughterhouse wastes. Generally regarded to be completely hydrolyzed to FFAs, however, as our analysis shows they contain up to 20 % of tri-, di- and mono-glycerides. Whilst current technologies employed for biodiesel production are very effective when applied to clean sources of lipids (transesterification of glycerides; FFAs esterification), they are far less effective when applied to mixtures, or if there is significant amount of water present. Fatty acids esters were synthesized in complex aqueous media. The 4-dodecylbenzenesulfonic acid catalyzed esterification of AFWS with 1-butanol was performed in a novel batch reactor fitted with a drying chimney for “in situ” water removal. Conversion yield was optimized using a Doehlert surface response methodology. Two products that meet the biodiesel standards (Biodiesel European Standard EN14214): First type of product developed with properties similar to diesel, Fatty Acid Butyl Esters (FABEs) were isolated in good yields (analysed on CG-FID: 95 %+). The second original biodiesel developed is a blend of FABEs with 1-butanol (16%). These two potential biofuels were analyzed in comparison with current analogous biofuels (FAME based biodiesel, FABE products from vegetable oils) and were found to exhibit high cetane numbers and flash point values.

**Ionic Liquids Derived from Amino Acids for Catalytic Biodiesel Production** Jingbo Li\* and Zheng Guo, Aarhus University, Denmark

Ionic liquids (ILs) derived from biomolecules have attracted more and more attention due to their generally biodegradable, non-toxic, and more sustainable properties. Amino acids are a group of biomolecules with additional unique property that they are able to be converted into both cations and anions. Herein, we synthesized a series of amino acid-based ionic liquids (AAILs) possess either strong acidic or strong basic properties. Structure evolution strategy was adopted to gain the most promising AAILs for catalyzing biodiesel production. The strong acidic AAILs were used to catalyze esterification reaction to convert free fatty acids into biodiesel while the strong basic AAILs were employed to catalyze transesterification reaction to convert acylglycerides into biodiesel. The catalytic activity of AAILs was strongly correlated to the properties of the side chains of the parental amino acids. [Asp<sup>+</sup>][NO<sub>3</sub><sup>-</sup>] and [Choline<sup>+</sup>][Arg<sup>-</sup>] were the most effective for esterification and transesterification, respectively due to the strong acidity and basicity of the side chains of aspartic acid and arginine. The best catalyst, [Tetrabutylammonium<sup>+</sup>][Arg<sup>-</sup>], was obtained following structure evolution strategy. Esterification efficiency of 97% was achieved within 5 h, at 70°C, with 10% [Asp<sup>+</sup>][NO<sub>3</sub><sup>-</sup>] loading and 7.5:1 methanol to oleic acid ratio. Complete transesterification of triglycerides was achieved within 15 min, at 90°C, with 6% [Tetrabutylammonium<sup>+</sup>][Arg<sup>-</sup>] loading and 9:1 methanol to triglyceride ratio without soap formation. The AAILs directly used as catalysts for both esterification and transesterification reactions may result in greener and sustainable biodiesel production processes in the future, which highlights the importance of the current study.

**Grease Formulation Using Post-consumed Clothes:**

**A Sustainable Approach** Amitkumar A. Barot\*<sup>1</sup>, Chiragkumar M. Patel<sup>2</sup>, Tirth M. Panchal<sup>3</sup>, Jigar V. Patel<sup>3</sup>, and Vijay K. Sinha<sup>2</sup>, <sup>1</sup>V. P. & R. P. T. P. Science College, India; <sup>2</sup>Industrial Chemistry Dept., V. P. & R. P. T. P. Science College, India; <sup>3</sup>Dept. of Industrial Chemistry, Institute of Science and Technology for Advanced Studies and Research, India

Recent scenario demands environmentally adaptable routes for recycling synthetic polymeric waste. Also, the demand of bio-based products is increasing due to strict environmental laws. Finding a suitable way to recycle polyester is a worldwide concern due to its environmental impact and increasing volume of these materials produced in society. In the field of lubricants, much effort has been spent on substitution of petro-based raw materials by natural-based renewable ones. In this frame work, current paper shows the utilization of castor oil as replacement to diols in recycling of polyester waste. This in comparison with diols is renewable, easily available, environmental friendly, economically cheaper and hence sustainable indeed. Glycolized products were then used as base oil in the formulation of grease. Glycolized products were characterized by using various chemical and instrumental methods and prepared greases were evaluated for its tribological properties.

**Enzymatic Catalyzed Fat-splitting as Replacement to Chemical Fat-splitting Process** Anders Rancke-Madsen, Hans Christian Holm, Per Munk Nielsen, and Simon Emil Lausen\*, *Novozymes Denmark*

Conventional chemical fat-splitting processes suffer from environmental problems and equipment corrosion. Enzyme-catalyzed fat-splitting is an attractive alternative and lipases offer many advantages such as low CAPEX, high quality and environmental safety. However,

enzymatic processes are only applied to a limited extent at industrial scale due to low degrees of conversion, typically < 95%, and relatively high costs of current fat-splitting lipases. A protein engineered variant of *Thermomyces lanuginosus* lipase expressed in high yields has been tested at 55oC/131oF in 1L-stirred glass reactor system using castor oil as feed-stock, a two-step reaction set-up, 100% water w/w and 0.6% w/w enzyme solution. The results suggest that the new lipase is superior to traditional lipases and gives both higher degree of conversion and lower costs. Kinetic studies and initial engineering assessments of industrial scale applications suggest that enzymatic catalyzed fat-splitting technology holds a great potential to replace chemical fat-splitting process within a few years.

**Process Development of a Sustainable Aromatic Hydrocarbons Derived from *Camelina sativa***

Randy L. Maglinao\*<sup>1</sup>, Chazley J. Hulett<sup>2</sup>, Eleazer P. Resurreccion<sup>2</sup>, and Alexandra K. Jones<sup>1</sup>, <sup>1</sup>Advanced Fuel Center, Montana State University-Northern, USA; <sup>2</sup>Montana State University Northern, USA

Aromatic compounds in petroleum-based jet fuels are necessary to give the fuel's desirable lubricity and seal swelling properties. Without these compounds in jet fuel, operational problems, such as failure of fuel tank gaskets, could occur and with disastrous consequences. Research on the synthesis of renewable aromatics mostly focused on pyrolysis of lignin coupled with hydrotreating. We report an alternative feedstock and synthesis route for selectively producing renewable aromatic hydrocarbons, which can be used in both as a blend component for jet fuel. Using fatty acid methyl esters derived from camelina, renewable aromatics and straight chain hydrocarbons were produced through a two-step process. Batch reactor systems (20 – 30 mL) were used to convert FAME to hydrocarbons. Results showed that the



polyunsaturated fatty acids in camelina FAME yield renewable aromatics. It is also found that multisubstituted benzenes were produced.

**Novel Building Blocks Designed from Metathesized Vegetable Oils** Frederyk Ngantung\*, Elevance, USA

Elevance produces high-performance, cost-advantaged and bio-based chemicals from metathesized vegetable oils. The processes use a highly efficient, selective catalyst to break down natural oils such as soybean or palm oil and recombine fragments. The resulting products are high-value, difunctional chemicals with superior functional attributes previously unavailable commercially. These chemicals can be used as ingredients and building blocks for detergents, personal care, oil field and agriculture chemicals. In this talk, two industrial examples will be presented to showcase the applicability of Elevance's ingredients and building blocks. Example 1. Hydraulic fracturing chemicals D-limonene when added as fracking fluid additive has been demonstrated to improve production rate of gas in many conventional and unconventional reservoirs and basin. The availability and price of d-limonene, however, have been volatile in the past five-to-six years. Elevance HFS™ is a high-performing, hydraulic fracturing fluid ingredient that can be a cost-effective substitute to d-limonene. In independent laboratory tests where Elevance HFS™ was blended into hydraulic fracturing fluids and compared to d-limonene-based fluid, Elevance HFS™ clearly outperformed the d-limonene-based fluids in enhancing the productivity of oil and gas wells. Example 2. Building blocks for surfactants in laundry detergents A series of methyl ester ethoxylates were prepared from our building block. Their physical properties and efficacy in fabric care were evaluated and compared to incumbents. It was found that the unsaturated methyl ester

ethoxylates derived from Elevance Inherent building blocks exhibited superior cleaning performance, foam control, viscosity control and more compact formulations when compared to standard ethoxylates.

**Sterol Molecular Fingerprinting in Different Algae Provide Options for High-value Co-Product Development in a Conversion Process** Lieve Laurens\*, Oliver Palardy, Keegan Duff, and Stefanie Van Wychen, *National Renewable Energy Laboratory, USA*

Improving biomass production and utilization is imperative for commercializing a future algae-based biorefinery. Sterols are high-value products that can be isolated from algal biomass and have not been studied before in the context of a conversion pathway to biofuels and bioproducts and provide value as either nutraceuticals or as feedstocks for novel surfactant production. Mass spectral analysis indicates that there are 11 sterol compounds in *Chlorella* and 16 in *Scenedesmus*. The compounds we identified fall within two major classes: 28-carbon 4-desmethylsterols and 29-carbon 4-desmethylsterols. Within the 28-carbon group, the spectra either more closely resemble campesterol (MW 472) or ergosterol (MW 468). Within the 29-carbon group, the spectra could be grouped into compounds with a MW of 484 (EG stigmasterol, fucosterol,  $\Delta$ 5-avenasterol) and those with a molecular weight of 486 (sitosterol or  $\Delta$ 7-stigmastenol). The commercially available surfactants (e.g. linear alkyl benzene sulfonates) are often mixtures of compounds. We demonstrate here that the variety of sterols present is greater in *Scenedesmus* than in *Chlorella*, which seems to be almost entirely 28-carbon variants of ergosterol, while the former contains a mixture of both 28 and 29-carbon sterols. We present data on a new method for sterol characterization in algae and highlight the growth phase specific accumulation of

this class of compounds along with preliminary data on conversion of sterols to non-ionic surfactants, and surfactant characterization after esterification with succinic anhydride and polyethylene glycol.

**Determination of Solubility and Kinetic Parameters for Switchable Solvents Using**

**Microfluidics** Ghata M. Nirmal\*<sup>1</sup>, Thomas F. Leary<sup>2</sup>, and Arun Ramchandran<sup>2</sup>, <sup>1</sup>*University of Toronto, St. George, Canada*; <sup>2</sup>*University of Toronto, Canada*

Current separation processes in the industry involve use of specific solvents at every step, which can be material and energy intensive. An alternative, eco-friendly route is utilization of CO<sub>2</sub>-triggered switchable solvents. These solvents are capable of switching properties, such as hydrophilicity, polarity or ionic strength, upon reaction with carbon dioxide. They revert their property when heated, or in the presence of an inert. Application of these solvents in the current industrial setup entails optimization of operational parameters, for which we use microfluidics. The experiments are carried out in the Taylor flow regime, which involves alternating segments of gas and liquid flowing in a straight circular capillary. The advantage of this setup is the availability of high interfacial areas and well-characterized flow profiles. As the mixture flows through the capillary, the gas segments shrink in size. We provide a systematic framework to interpret this data to extract solubility and kinetic parameters (e.g. diffusivity, reaction rates), supported by scaling analysis and simulations. To demonstrate our experimental method and analysis approach, experiments were carried out in circular, silica capillaries of different radii by generating segmented flow of CO<sub>2</sub> in physical solvents such as acetonitrile and propylene carbonate. Our approach can be applied to diverse gas-liquid reaction systems to determine optimum

operational parameters, and thereby moving a step closer towards implementation of green chemistry in the industrial setting.

### IOP 3: Green Chemistry

*Chairs: Long Yu, South China University of Technology, China; and Andrew Myers, USA*

#### **Lipid Profile of Oklahoma Native Microalgae Strains and Chemical Composition of the Bio-oil Produced by Pyrolysis of the Algal Biomass**

Nurhan Dunford\*, *Oklahoma State University, USA*

The objective of this study was to characterize lipid content, fatty acid profile and biomass characteristics of seven algae strains isolated from the same environment and grown in standard media under similar conditions. Proximate composition of the algal biomass was determined using a thermogravimetric analysis method. Algal biomass was used for bio-oil production via microwave assisted pyrolysis, and the effects of final temperature on the product yields and bio-oil composition were evaluated. Average biomass productivities of SP20, SP46 and SP50 were similar and significantly higher than the other strains examined in this study. Green algae strains, SP20 and SP22, accumulated significantly higher amount of lipids than all the cyanobacteria investigated in this study. Saturated fatty acid contents of the algal oils varied between 32.5% and 39.9%. The highest mono and polyunsaturated fatty acid contents were observed in SP46 and SP22, respectively. Total FAME content was highest in SP22 and the second highest in SP20. The bio-oil yield from microwave assisted pyrolysis of algal biomass produced by SP 46 increased from 4.6% to 22.5% with the increasing final temperature from 450 °C to 750 °C. The major compounds in the bio-oil were acids, aliphatic hydrocarbons, aromatic hydrocarbons, phenols, organic nitrogen compounds. Microwave pyrolysis of algal biomass did not produce polycyclic aromatic hydrocarbons at temperatures higher than 450° C.

#### **New Development of Starch-based Materials** Long Yu\*, Xioayan Ge, and Ying Chen, *South China University of Technology, China*

The development and production of biodegradable starch-based materials have been spurred by oil shortages and the growing interest in easing the environmental burden of petrochemically derived polymers. Furthermore, the unique microstructures of different starches and their multiphase transitions during thermal processing can be used as an outstanding model system to illustrate our conceptual approach to understand the structure–processing–property relationships in polymers. Various conventional processing techniques such as extrusion, injection compression molding, and casting, as well as some new techniques such as reactive extrusion, have been adapted for processing starch-based polymers. In order to overcome disadvantages pure starch-based materials have, such as poor mechanical properties found in natural polymers; or the high price of synthetic polymers, various blends and composites have been developed in the last decade. The starch-based materials reinforced with natural fibres and nano-particles have been developed to various environmentally friendly composites. The hydrophilic properties of starch provide the advantage of compatibility with cellulose and nano clay. Compatibilizers and the technology of reactive extrusion have been used to improve the interface between natural and synthetic polymers. Various starch-based products have been developed and commercialized. Examples of commercialized products of starch-based materials.

**Synthesis and Characterization of Cardanol Based Epoxy/Amine System for Corrosion Prevention**

John J. La Scala<sup>1</sup>, Giuseppe R. Palmese<sup>2</sup>, and Emre Kinaci\*<sup>2</sup>, <sup>1</sup>*Army Research Laboratory, USA*; <sup>2</sup>*Drexel University, USA*

In this study, a cardanol based mono-epoxy, cardanol glycidyl ether (CGE) resins (LITE 2513HP, Cardolite®) was epoxidized from the unsaturation sites of the side chain by using hydrogen peroxide and formic acid to achieve a cardanol based side chain epoxidized cardanol glycidyl ether (SCECGE) resin with 2.45 epoxy functionality per molecule. This side chain epoxidized resin was incorporated with the synthetic based phenolic resin (DGEBA) with different ratios (0-100 wt.%) and thermally cured in the presence of a cyclo-aliphatic curing agent (PACM). The thermo-mechanical properties of the fully cured formulations were obtained via DMA and DSC methods and mechanical characterization was achieved via an UTM. Water and vapor sorption studies along with the gravimetric water uptake measurements were also applied to these fully cured formulations to determine the corrosion coating performance of the polymers. Our findings suggest that; despite a significant reduction in the thermo-mechanical properties, addition of cardanol based epoxy resin to epoxy/amine system is significantly improved the hydrophobicity and water barrier properties of the final materials. In addition, the reactivity and the conversion of the secondary epoxies presented on the C15 side chain of the SCECGE resin were also explored and discussed in this study. Cardanol has a growing potential to supply bio-based aromatic building blocks for corrosion prevention and composite applications for over 50 years.

**Integrated Methyl Esters Synthesis Technology for Multiple Feedstock Oils via Hydrodynamic Cavitation Pilot Scale System**

Syed Awais Ali Shah Bokhari\*, Suzana Yusup, and Lai Fatt Chuah, *Universiti Teknologi PETRONAS, Malaysia*

Methyl ester contributes to environmental protection as it is biodegradable, renewable, non-toxic, and produces less sulphur oxides emissions and greenhouse gases. The proposed system is a pilot scale system developed for semi batch process capacity of 50 lit/batch. The present work highlights the potential of hydrodynamic cavitation for the methyl ester production from edible and non-edible oils. The transesterification process was conducted under optimised conditions, i.e. oil to methanol molar ratio of 1:6 in the presence of 1 wt. % potassium hydroxide as alkali catalyst at 60°C. Current innovative method is capable in reducing the acid value of the feedstock oil and increasing the purity of the final product of methyl esters, and able to process blended feedstock oil and/or produce blended methyl esters. Four newly designed orifice plate geometries induced cavities assisted by a double diaphragm pump in a pilot scale hydrodynamic cavitation reactor were investigated. It is shown that the high turbulence generated by the cavitating bubbles were effective in reducing the mass transfer resistance between immiscible reactants during the transesterification reaction due to increased interfacial area. This makes the process more environmentally friendly. In conclusion, methyl ester produced via hydrodynamic cavitation proved to be energy efficiency and time saving. Technology can be suitable with different types of orifice plates to produce cavities by regulating flow rates and adjustable pressure to produce cavities to study its effect on methyl esters conversion. This technology can accommodate various types and blends of oils by varying different catalysts and alcohol types.

**IOP 4: New Uses of Glycerine**

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

**Glycerol: A C3 Bio-based Platform Intermediates for Value-added Products**

Christophe Len\*,  
*Université de Technologie de Compiègne, France*

The design of environmentally friendly methodologies has been the driving force of scientists in recent years. In particular, the use of biomass-derived materials, green solvents and alternatives techniques has been investigated. In this regards, glycerol has the potential to be both an excellent renewable solvent in modern chemical processes and a versatile building block in biorefineries. In this conference, several green chemistry approaches that target advanced synthesis and processes using glycerol will be presented. Few approaches will be described: (i) green synthesis of quinoline and phenanthroline derivatives in sole water using microwave irradiation and high temperature/pressure; [1] (ii) production of oligomer of glycerol for polymerisation. [2] Conception, synthesis and physico-chemical properties will be detailed. [1] (a) H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, *Catal. Commun.* 2014, 44, 15; (b) H. Saggadi, D. Luart, N. Thiebault, I. Polaert, L. Estel, C. Len, *RSC Adv.* 2014, 4, 21456; (c) H. Saggadi, I. Polaert, D. Luart, C. Len, L. Estel. *Catalysis Today* 2015, 255, 66. [2] M. Kumari, M. Billamboz, E. Leonard, C. Len, C. Böttcher, A.K. Prasad, R. Haag, S.K. Sharma. *RSC Adv.* 2015, 5, 48301.

**Overcoming Catalyst Deactivation in Glycerol Dehydration to Enable Sustainable Production of Acrolein and Acrylic Acid**

Shoujie Ren<sup>1</sup>, Bin Zou<sup>1</sup>, and Xiaofei P. Ye\*<sup>2</sup>, <sup>1</sup>*Biosystems Engineering, University of Tennessee, USA;* <sup>2</sup>*University of Tennessee, USA*

Acrolein and acrylic acid are promising derivatives of glycerol holding important status as

versatile intermediate or building block for the production of methionine and plastics and polymers that are environmentally friendly with wide applications in such as superabsorbent polymers, textile treating agents, and adhesives. Despite their industrial values and intensive effort to convert glycerol to acrolein/acrylic acid in recent years, quick catalyst deactivation in the conversion of glycerol remains as a major technical obstacle hindering the commercial production of acrolein and acrylic acid from glycerol. In this study, supercritical carbon dioxide (SC-CO<sub>2</sub>) was used for the first time as reaction medium for the dehydration of glycerol to acrolein catalyzed by solid acids. Unprecedented catalyst stability over 500 hours of time-on-stream was achieved and the rate of coke deposition on the catalysts is the lowest compared to the extensive literature data, showing potential for industrial application. The coking pathways in SC-CO<sub>2</sub> were also elucidated for future development. The results should also have implications for other dehydration reactions catalyzed by solid acids.

**New Catalytic Process for Highly Efficient**

**Conversion of Glycerol to Allyl Alcohol** Yoshihiro Kon<sup>1</sup>, Marcia Araque<sup>2</sup>, Benjamin Katryniok<sup>2</sup>, Takuya Nakashima<sup>1</sup>, Joëlle Thuriot<sup>2</sup>, Sébastien Paul<sup>2</sup>, and Franck Dumeignil\*<sup>3</sup>, <sup>1</sup>*AIST, Japan;* <sup>2</sup>*Unite de Catalyse et Chimie du Solide, Université de Lille, France;* <sup>3</sup>*Université de Lille, France*

Allyl alcohol is known as a valuable starting material for the chemical industry. We have developed a Re-based reusable catalyst, which, in the presence of a sacrificial alcohol, enables a yield of 91 % of allyl alcohol from glycerol. This process could significantly increase the economical viability of the biodiesel value chain by proposing a high

value-added / high volume application for the by-produced glycerol. Moreover, this new methods reduces the environmental impact of allyl alcohol production, currently petro-sourced.

**Reactive Distillation: Exploring Process Intensification Routes for the Oil Products**

**Industry** Tracy Benson\* and Obakore Agbroko,  
*Lamar University, USA*

Combining reaction engineering and distillation into a single unit operation presents some interesting challenges, yet, reduces the operational footprint as well as the operating and capital costs of manufacturing. Operational and design challenges include mismatched temperatures between the separating components and the reacting components, unfavorable volatilities, and slow reaction rates generally due to poor reactant/catalyst/product mass transfer rates. Reactive distillation is a likely pathway towards process intensification to minimize overall energy consumption, particularly since distillation accounts for 20 % of total energy used within the U.S. manufacturing sector. Increased reflux ratios typically yield higher product In this study, Aspen was used to model the conversion of glycerol to 1,3-propanediol and 1,2-propanediol while being separated from methanol, water, and other inorganic components that are commonly found in waste glycerol from biodiesel production processes. Using the Non-Random Two Liquid activity coefficient model, the number of trays, conversion, and product selectivities were estimated. To verify simulation results, laboratory experiments were conducted using a 1-inch ID, 32-tray glass distillation column. Column temperature profiles and reboiler heat duties were determined. The complete reactive distillation analysis will be presented as well as the extension of this technology into other areas of the oil products industry.



**IOP 5: Oleochemicals**

*Chairs: Eric Cochran, Iowa State University, USA; and Guoqin Liu, South China University of Technology, China*

**Oleosomes: Isolation and Commercial Use of Nature's Oil-storage Vesicles** James V. Gruber\*, *Botaneco Inc., USA*

Nature has a way of perfecting the storage of large amounts of important materials into very small spaces. The storage of starch in corn kernels, the storage of DNA in a cell's nucleus, and the storage of triglyceride oils in oleosomes all are elements of Nature's way of perfecting storage of fragile things in unique storage vesicles. Normal commercial oil isolation processes typically squeeze oil from oil body structures or employ harsh organic solvents like hexane to enhance recovery of desired oil. However, under more controlled and unique aqueous isolation conditions, it is possible to commercially recover oil seed oleosomes in their native state. As such, these products do not appear as normal refined oils, but rather as creamy emulsions held intact by the unique emulsifying properties of the non-denatured oleosome surface proteins. Commercial use of oleosomes has expanded significantly in the cosmetic arena where such emulsions are a natural and sustainable substitute for many synthetically-derived emulsifiers. This talk will focus on commercial mechanisms of oleosome isolation including how they differ from standard oil recovery operations. In addition, the talk will focus on current uses of oleosomes based on safflower and almond oil seeds and how they are finding unique spaces in cosmetic ingredients.

**Toughening Thermoset Resins Using Grafted Epoxidized Soybean Oil** Santosh K. Yadav<sup>1</sup>, John J. La Scala<sup>2</sup>, and Giuseppe R. Palmese\*<sup>3</sup>, <sup>1</sup>*Dept. of Chemical Engineering, Drexel University, USA;* <sup>2</sup>*Army Research Laboratory, USA;* <sup>3</sup>*Drexel University, USA*

In this study, fatty acid/fatty anhydride residues

were grafted onto epoxidized soybean oil (ESO) to produce a liquid rubber modifier superior to traditional butadiene-acrylonitrile copolymers for toughening thermosets. FTIR and <sup>1</sup>H NMR were employed to understand the chemical structure of the bio-rubber (BR). The composition of grafted ESO can be tuned to work with the many formulations of available thermoset resins. It was demonstrated that significant improvement in fracture toughness is achieved with a minimal reduction of T<sub>g</sub>. Scanning electron microscopy (SEM) of the fracture surfaces shows the appearance of a discontinuous rubber phase resulting from chemically induced phase separation mechanism. The size of the phase-separated domains can be varied from tens of nm to several μm by changing the composition of the BR and the processing conditions. Particle cavitation along the crack was clearly observed and is believed to account for the greatly enhanced fracture toughness. Dynamic mechanical thermal analysis (DMA) provides additional verification of the existence of a prominent rubbery second phase that does not result in significant loss of T<sub>g</sub>. Moreover, the low viscosity associated with the BR provides ease of processing compared to common liquid and particulate rubber modifiers.

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

Plasticizers, the largest class of plastic additives, 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 and/or head group of soy fatty acid esters have been synthesized and evaluated as plasticizers in poly

vinyl chloride (PVC) applications. Synthetic procedures such as epoxidation, methoxylation, acetylation, thiiration, and aziridination were used for synthesizing multifunctional soy fatty acid esters. Epoxidized soybean oil fatty acid esters served as the key intermediate to incorporate most of the functional groups on the fatty acid backbone. The physical and analytical properties of bioplasticizers such as acid and saponification values are acceptable for plasticizer applications. The high viscosity and darker color of aziridine and thiirane derivatives limit their usefulness, whereas the physical properties of the other derivatives were acceptable for PVC applications. The plasticizer evaluation of epoxy, acetoxo soy fatty acid ester derivatives demonstrated excellent compatibility with PVC, high efficiency (Shore Hardness), thermal stability and gelling properties. The functional properties were comparable to commercial plasticizer, diisononylphthalate (DINP).

**Extraction, Fractionation, and Characterization of Waxes from Sorghum** Megan E. Hums\*<sup>1</sup>, Jonathan L. Hoyt<sup>1</sup>, Michael J. Powell<sup>1</sup>, and Robert A. Moreau<sup>2</sup>, <sup>1</sup>*US Department of Agriculture, USA*; <sup>2</sup>*USDA, ARS, ERRC, USA*

Sorghum has potential as a domestic source of wax for applications in the food and non-food industries. The waxes extracted from sorghum have similar physical properties to those of Carnuba wax, a common imported commercial wax. This work focused on the extraction, fractionation, and characterization of waxes from sorghum kernels and sorghum bran (obtained by abrading the surface layers of the kernel, ~ 10% by mass). Extraction was performed using various types of extractors and solvents, including hexane, ethanol, and methanol. A fractionation technique was developed to separate and quantify waxes from non-waxes. The fractions were then characterized using a reverse phase high

performance liquid chromatography method developed in our laboratory that utilizes an evaporative light-scattering detector for quantification and mass spectrometer for chemical identification. The results showed that the average amount of wax extracted from the surface of intact sorghum kernels was about 0.3% weight percent using hexane at temperatures between 25-120 °C and 1000 psi. The yield of wax varied among common sorghum hybrids and cell lines and ranged from about 0.1 to 0.5 wt %. For sorghum bran, the yield of wax was about 1% and the yield of oil was about 7-10%. For both whole grain sorghum and bran, extraction with more polar solvents resulted in higher yields of extracts, but after fractionation, the weight percent of waxes remained the same.

**Animal Fats as Oleochemicals: Nitrogen Containing Contaminants** Martin Mittelbach\*, Sigurd Schober, and Tamara Ruprecht, *Institute of Chemistry, University of Graz, Austria*

Waste animal fats are an important feedstock for the oleochemical industry. A series of contaminants restrict conventional conversion processes. Impurities like sulfur, phosphorus, calcium as well as polyethylene residues can have a negative impact on the conversion itself, like poisoning heterogeneous catalysts, or remain within the end product leading to quality problems. The composition of these impurities depends on the source of the material and the treatment of animal waste fat during the rendering process. In recent time also nitrogen containing impurities were identified to influence the production of biodiesel, leading to separation problems during the transesterification process or to precipitation in the final product. One compound group could be identified as primary fatty acid amides. Because of the relatively high melting points of those compounds they could separate after longer storage of biodiesel, together with steryl glycosides

or saturated monoglycerides. We want to present an analytical approach for quantitative determination of fatty acid amides in animal fats as well as in biodiesel, based on GC as well as HPLC including SPE for sample treatment. The results based on spiking with synthesized C-19 fatty acid amide as ISTD were compared with the measurement of total nitrogen in the samples. It can be seen that only a part of nitrogen could be assigned to fatty acid amides, the origin of the remaining nitrogen is still unclear. Possible sources of fatty acid amides and other nitrogen containing compounds are discussed.

#### **Application of Low Cost Ionic Liquids Analogues for Removal of Free Fatty Acid from Sludge Palm Oil**

Adeeb Hayyan\*<sup>1</sup>, Shahidah N. Rashid<sup>2</sup>, Maan Hayyan<sup>3</sup>, M. Y. Zulkifli<sup>3</sup>, and Mohd A. Hashim<sup>2</sup>, <sup>1</sup>University of Malaya, Malaysia; <sup>2</sup>University of Malaya Centre for Ionic Liquids (UMCIL), Kuala Lumpur, Malaysia; <sup>3</sup>Institute of Halal Research University of Malaya, Malaysia

Sludge palm oil (SPO) low grade industrial oil generated from oil palm mills. SPO has high free fatty acid and therefore deep eutectic solvents (DES) was used as catalyst for reduction of FFA of SPO. This DES was made from ammonium acetate (AmAc) and toluene-4-sulfonic monohydrate acid (PTSA). Different operating conditions were optimized such as catalyst dosage, molar ratio and reaction temperature. FFA was reduced from 10% to less than 2% under optimum conditions. This study revealed that DES made from AmAc and PTSA has high catalytic activity for FFA removal.

#### **An Investigation to Achieve Physical Consistency of Oleogels During Scale up**

Sai S. Sagiri\*<sup>1</sup>, Malick Samateh<sup>2</sup>, and George John<sup>3</sup>, <sup>1</sup>Center for Discovery and Innovation, Dept. of Chemistry, The City College of New York, USA; <sup>2</sup>The City College of New York & Ph.D. Program in Chemistry at Graduate

Center, City University of New York, USA; <sup>3</sup>The City College of New York, USA

Oleogels are supramolecular soft materials, in which gelator molecules self-assemble to form 3-D network through weak intermolecular forces in vegetable oils. Although an extensive research has been done on oleogels for various applications (pharmaceutical, food, cosmetics, petrochemical, environmental, tissue engineering, and art), their industrial usage is still in the budding stage. One major foreseeable constraint for the industrial application of oleogels is how to maintain consistent physical properties during scale up. It has been discovered in this study that, when different sizes (1g, 5g, 10g, 15g, and 20g) of oleogels were prepared, the minimum gelation concentration of the gelators (sorbitol dioctanoate (S8), mannitol dioctanoate (M8), and 12-hydroxy stearic acid (12-HSA)) varied when tested by the inverted tube method and rheological studies. Efforts to address this problem, including even after maintaining a constant aspect ratio (height: diameter ratio) for all sizes, proved futile. Through a rigorous investigation, it was subsequently found that, when surface area to volume (S/V) ratio of the gels was kept constant, MGC and other physical properties of the gel remained consistent regardless of the sizes of the gel prepared; the other physical properties were solid phase content (SPC), oil binding capacity (OBC), melting temperature (T<sub>m</sub>), melting enthalpy (ΔH<sub>m</sub>), and rheological properties (yield stress, Y<sub>s</sub>). Based on these findings, it could be inferred that S/V ratio of the oleogels seems crucial in understanding and modulating the properties of the oleogels during scale up studies.

## IOP-P: Industrial Oil Products Poster Session

Chair: Tracy Benson, Lamar University, USA

**1. Edible Oleogels: Viable Alternative toward Healthier Solid Fat Food Products** D. Pulido\*<sup>1</sup>, Malick Samateh<sup>2</sup>, Sai S. Sagiri<sup>3</sup>, Nannette Hernandez<sup>1</sup>, Riliwan Sanni<sup>1</sup>, and George John<sup>4</sup>, <sup>1</sup>*Dept. of Chemistry & Center for Discovery and Innovation (CDI), The City College of New York, USA;* <sup>2</sup>*The City College of New York & Ph.D. Program in Chemistry at Graduate Center, City University of New York, USA;* <sup>3</sup>*Center for Discovery and Innovation, Dept. of Chemistry, The City College of New York, USA;* <sup>4</sup>*The City College of New York, USA*

Gelation is a favorable alternative to the current methods of edible oil hardening (structuring): hydrogenation, interesterification, and addition of saturated fat. These traditional hardening methods have been associated with syndromes such as obesity, coronary heart disease, and diabetes. As an alternative, gelation of liquid oils into semisolids (oleogels) is a viable option for the future. Consequently, molecular gels are being explored due to their biodegradability, biocompatibility and verse number and diversity of applications. In this study, low calorific sugars (sorbitol and mannitol) are converted to amphiphilic molecules with gelation ability for edible oil hardening. The gelators were synthesized in a single step from the respective raw materials using and capitalizing on the regiospecificity of lipase enzyme. The gelators were well characterized (TLC, 1H-NMR and 13C-NMR), followed by gelation studies. Minimum gelation concentration (MGC) and gel-to-sol transition temperature (T<sub>g</sub>) studies have confirmed the gelation efficiency of the sugar derivatives towards the oils. In the nearby future, the as-synthesized molecules and structured oils may lead to the

development of eco-friendly food processing technologies.

**2. Starch Derivative to Emulsify Cedarwood Oil and Pressure Treat Wood** Fred J. Eller\*<sup>1</sup>, William Hay<sup>1</sup>, Grant Kirker<sup>2</sup>, and Mark Mankowski<sup>2</sup>, <sup>1</sup>*USDA, ARS, NCAUR, USA;* <sup>2</sup>*USDA, FS, FPL, USA*

Previously, we demonstrated that CO<sub>2</sub>-derived cedarwood oil has a range of bioactivities, including insect repellency and toxicity as well as conferring resistance to termites and wood-rot fungi. In the earlier pressure treatment work, ethanol was used as the diluent/carrier. However, it is preferable to use a water-based carrier for several reasons. Because water and cedarwood are immiscible, an emulsifier was used to prepare a stable mixture of the materials. This research reports the use of a starch derivative to prepare a cedarwood oil-water emulsion and its use for treating wood against termites and wood-rot fungi.

**3. Waste Eggshell Catalyzed Conversion of Jatropha Oil to Biodiesel Under an Ultrasonication** Jitenkumar C. Patel\*, Gaurav K. Patel, and Hasmukh S. Patel, *Dept. of Chemistry, Sardar Patel University, India*

Jatropha oil consisting of saturated and unsaturated fatty acids was extracted from the seeds of *Jatropha curcas* using petroleum ether. The extracted oil was further utilized for transesterification process catalyzed by CaO procured from the waste egg shell leading to biodiesel under ultrasonic irradiation as energy source. The pure CaO was obtained by calcination of egg shell at 900 °C for a period of around 3 hours. The catalyst was characterized by X-ray diffraction, FT-IR and DT-TGA studies. Various parameters like methanol to oil ratio, reaction time and quantity of the catalyst were considered to

obtain biodiesel in high yields. The catalyst was recycled and reused for over 5 reaction cycles. Diverse physical and chemical properties like density, kinematic viscosity, etc. were also studied.

**4. Palm-based Mung Bean Cakes: Production via Blending Three Different Palm Fractions with Soybean Oil** Jun Jin<sup>\*1</sup>, Yin-hui Ma<sup>2</sup>, Li-you Zheng<sup>3</sup>, Cheng Keat Ooi<sup>2</sup>, Xing-guo Wang<sup>1</sup>, and Qing-zhe Jin<sup>1</sup>, <sup>1</sup>Jiangnan University, China; <sup>2</sup>Palm Oil Research and Technical Service Institute of Malaysian Palm Oil Board, China; <sup>3</sup>CAAS, China

Objective: Mung bean cake is one of the most famous soybean oil (SBO)-containing snacks in China. But the short shelf life and high cost dramatically reduce its market competitiveness, which needs to be improved. Methods Used: Super olein (SO), palm olein (PO) and palm stearin (PS) were selected respectively to partially replace the SBO in ratios of 20%, 40%, 60% and 80%. The slip melting points, triacylglycerols and compatibilities of the oil blends were analyzed to determine the best blending ratios and additive amounts of the cake oils. Then the sensory, textural (gumminess, chewiness and resilience) and oxidative stability indexes (OSIs) tests were carried out on the final products: the cakes. Results: No eutectic effects occurred at 0–40 °C when 20%–80% SO, 60%–80% PO and 40%–60% PS were separately blended with SBO. The best conditions for manufacturing the cakes based on the compatibilities of the cake oils as follows: SO-cake, containing 20% cake oil that consisted of 80% SO and 20% SBO; PO-cake, containing 20% cake oil that consisted of 80% PO and 20% SBO; and PS-cake, containing 15% cake oil that consisted of 60% SO and 40% SBO. These cakes demonstrated better quality compared to the soybean-based cake in terms of sensory scores and textural profiles. Furthermore, they showed longer oxidation time (SO- and PO- and PS-cake: 0.66, 0.73 and 0.83 h, respectively) than the soybean-based cake (0.51 h). Conclusions: High-

quality mung bean cakes with higher quality could be produced by partially replacing SBO with palm oil fractions.

**5. New Bis (Alkylthio) Fatty Acid Methyl Esters** Gerhard Knothe<sup>\*</sup>, USDA, ARS, NCAUR, USA

The addition reaction of dimethyl disulfide (DMDS) to mono-unsaturated fatty acid methyl esters is well-known for analytical purposes to determine the position of double bonds by mass spectrometry. In this work, the classical iodine-catalyzed reaction is expanded to other dialkyl disulfides (RSSR), including diethyl disulfide (DEDS), dipropyl disulfide (DPDS), dibutyl disulfide (DBDS), di-iso-propyl disulfide (DiPDS) and di-tert-butyl disulfide (DtBDS). Yields decrease with increasing length or branching of the alkyl moieties in the RSSR. While MS analysis is straightforward for the new derivatives, similar to the derivatization with DMDS, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy is now also extensively applied. The compounds exhibit various interesting effects in NMR, including the possibility to distinguish erythro- and threo diastereomers. Besides this, initial investigations indicate potentially interesting properties of these compounds for a variety of applications.

**6. Studies on Modulating Aesthetic and Mechanical Properties of Molecular Gels** Riliwan Sanni<sup>\*1</sup>, Malick Samateh<sup>2</sup>, Sai S. Sagiri<sup>3</sup>, Raul Rivas<sup>1</sup>, and George John<sup>4</sup>, <sup>1</sup>Dept. of Chemistry & Center for Discovery and Innovation (CDI), The City College of New York, USA; <sup>2</sup>The City College of New York & Ph.D. Program in Chemistry at Graduate Center, City University of New York, USA; <sup>3</sup>Center for Discovery and Innovation, Dept. of Chemistry, The City College of New York, USA; <sup>4</sup>The City College of New York, USA

Molecular gels are being designed as functional soft materials for food and personal care applications. There has been a need to develop them as structured oils that are solid-like as fats



but are healthier than the current solid fats (trans-fat and saturated fat). The mechanistic resemblance of molecular gels to solid fats has made them promising healthier alternatives. In this regard, our research focuses on developing green, sustainable molecular gels. The gels are prepared using low molecular weight gelators (LMWGs) that are derived from abundant, green and inexpensive biomass. The LMWGs are hence rendered renewable, eco-friendly, sustainable, biodegradable and producing less carbon print. From our previous studies, two sugar alcohol based LMWGs, mannitol and sorbitol derivatives, have shown great potential to structure vegetable oils. However, while the gel of sorbitol derivative is translucent, it is weak; on the other hand, while the gel of mannitol derivative is strong, it is opaque. Here we show how a gel with optimal properties could be formulated by using a mixture of the two LMWGs. The results have shown that 2:8 ratio of the mannitol and sorbitol derivatives gave the most efficient (lowest minimum gelation concentration) gel that was most translucent. The results have also indicated a correlation between the composition of gelator-mixture and other properties like microstructure, oil binding capacity, gel-to-sol transition temperature, rheology, opacity and solid fat content. Thus, aesthetic and desirable physical properties of the oleogels may be achieved by a simple physical mixture of the gelators.

**7. High Oleic Algal Oil Polyurethanes** Olivera Bilic\*<sup>1</sup>, Zoran Petrovic<sup>2</sup>, Jian Hong<sup>1</sup>, and Scott Franklin<sup>3</sup>, <sup>1</sup>Kansas Polymer Research Center/PSU, USA; <sup>2</sup>Pittsburg State University, USA; <sup>3</sup>Checkerspot, Inc., USA

Polyurethanes are among the most widely used classes of polymers due to their excellent physical and mechanical properties. Vegetable oil polyols have usually very heterogeneous composition

which may affect the properties of polyurethanes. Algae are a future potential renewable source that can be manipulated by genetic modification to make desired oleochemicals for the use in polyurethanes. New algal oils have been developed with very regular structure which can be used for polyols and polyurethanes with improved properties. Polyols prepared by epoxidation/ring opening and hydroformylation were made from algal oil with structure close to triolein. Novel polyurethanes were tried in foams for surfboards, flotation devices, elastomers for boot soles and adhesives. Mechanical properties of new materials were excellent.

**8. Evaluation of Octane Number Property of Renewable Hydrocarbons Synthesized from *Camelina sativa*** Randy L. Maglinao<sup>1</sup>, Chazley J. Hulett\*<sup>2</sup>, Eleazer P. Resurreccion<sup>2</sup>, and Alexandra K. Jones<sup>1</sup>, <sup>1</sup>Advanced Fuel Center, Montana State University-Northern, USA; <sup>2</sup>Montana State University Northern, USA

Currently, the most widely used piston engine aircraft fuel is 100 low lead aviation gasoline. It contains lead which is used to boost octane number of the fuel. Although, its lead toxicity and contribution to air pollution have been long been realized and finding a replacement is imperative. *Camelina sativa*, a good rotational crop for wheat, can be processed to produce renewable hydrocarbons with desirable octane number rating. The novel conversion technology is a two-step process, wherein the fatty acid moieties are split and refined to renewable hydrocarbons of varying carbon lengths and medium-chain fatty acids. This study evaluates the prospect of utilizing the renewable hydrocarbon fraction derived from camelina processing as a blend component for unleaded aviation gasoline. Results of the study includes detailed hydrocarbon analyses of distillates and combustion and physico-chemical



properties (e.g., distillation, viscosity, acidity, octane number, etc.). The novel and patented process to selectively convert camelina to aviation gasoline is also discussed.

### 9. Starch-lipid Complexes for Aerogel Formation

Jim A. Kenar\*, Fred J. Eller, Frederick C. Felker, George F. Fanta, Michael A. Jackson, and Jeffrey A. Byars, *USDA, ARS, NCAUR, USA*

Recently, we have reported that aqueous slurries of starch can be excess steam jet-cooked and blended with aqueous solutions of fatty acid salts to produce inclusion complexes between amylose and the fatty acid salt. These complexes can be simply prepared on large scale using commercially available steam jet cookers. The physical interaction between the fatty acid salt and the amylose component of the starch confer unique polyelectrolytic and physicochemical properties to the bulk material not inherent to either the native starch or fatty acid salt alone. Aqueous dispersions of inclusion complexes were used to form hydrogels between pH 5.5-6.5. Subsequent, solvent exchange with ethanol followed by supercritical carbon dioxide (SC-CO<sub>2</sub>) drying of these gels preserved the structure of the gels and yielded the corresponding aerogels. This study describes recent results concerning the characterization and properties of these starch-fatty acid salt inclusion complexes and their corresponding aerogels.

### 10. Preparation of 2-Monoacylglycerol Rich in DHA by Enzymatic Ethanolysis and Crystallization

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It has been reported that 2-monoacylglycerol rich in DHA exhibits various biological functions. In this paper, the preparation of 2-monoacylglycerol

(2-MAG) rich in DHA through a three-step process is performed: 1) synthesis of 2-MAG by ethanolysis of tuna oil, 2) 2-MAG purification by liquid-liquid extraction, 3) 2-DHA-MAG purification by low temperature crystallization. The effects of enzyme type, reaction time, reaction temperature, reactant ratio and lipase amount were investigated. Under the optimized conditions (ethanol/tuna oil=4:1 (w/w), 8% Lipozyme 435 from *Candida Antarctica*), there was about 26.5% (area/area) 2-MAG produced in the crude mixture with 78.6% yield in 3 h. Subsequently, 2-MAGs were purified by liquid-liquid extraction. Using hexane and 85% ethanol aqueous solution, there was 95.0% 2-MAG obtained with 87.2% yield. Finally, 2-DHA-MAG was concentrated by low solvent crystallization. Hexane, acetone, ethanol and acetonitrile were used to enrich 2-DHA-MAG. The highest content of 2-DHA-MAG (70.3%) was purified by acetonitrile in -40 °C for 5 h. The remaining MAGs content in the product was 94% and PUFA-MAGs was more than 87%. Compared to previous methods, our method for preparation of 2-DHA-MAG is more economical and easier to scale up. In addition, the method conducted in low temperature is good for stability of PUFA and also avoids acyl migration of 2-MAG. Keywords: 2-monoacylglycerol, DHA, enzymatic ethanolysis, low temperature crystallization

### 11. A Sustainable Process for the Synergy Between Petroleum and Biofuels Industries in Nigeria

Chika S. Ezeanyanaso\*, Gloria N. Elemo, Viola A. Nwachukwu, Segun Munir, and Chima C. Igwe, *Federal Institute of Industrial Research Oshodi, Nigeria*

Fossil fuels are globally consumed commodities and the world is facing acute peaking problems due to the ever increasing demand in the face of dwindling production rate and very serious environmental challenges. In Nigeria, the dependence on imported petroleum products for

meeting local demands coupled with the instabilities in the centers of petroleum production has resulted in fluctuations in oil price and destabilizing the nation economies. Our near total reliance on petroleum to fuel transportation threatens our economy, causes devastating effects of climate change that threatens man's existence, and poses a unique threat to our energy security. Combination of these factors has renewed the interest in finding alternate sustainable fuels such as biofuels to augment energy-security and at the same time maintain food security. Hence, this paper highlights the opportunities and challenges of a synergy between petroleum and biofuels industries in Nigeria for sustainable energy security. In conclusion, the paper recommends efficient policy implementation as a pathway of ensuring a sustainable petroleum and biofuels synergy, especially with large availability of arable land and varieties of bio-resources for biofuel production.

**12. The Benefits, Uses, and Future of Pine Chemistry for Lubricant Applications** Monica A. Ford\*, Eric J. Olivier, Nicholas Kob, and Aaron Engel, *Ingevity, USA*

Tall oil based products have historically been used in the lubricant industry for a wide range of applications, and they are used as additives to boost the performance of many different lubricant systems from metalworking fluid formulations to fuel additives. This variety of applications is made possible by the chemical nature of the products; all tall oils are naturally occurring mixtures of monomer fatty acids and tricyclic diterpene acids. Each grade of tall oil has its own unique mixture of fat and rosin isomers, and the ratio of these molecules dictates the performance of each product. Not all tall oil based products are created equal. Some tall oil based products only provide emulsification, lubrication or corrosion inhibition;

while others provide all three of these benefits and more. The flexibility of tall oil based chemistry allows for a wide range of products providing an array of additive benefits to lubricant manufacturers. This presentation sheds some light on how tall oil is made, the multi-functional nature of tall oil based chemistry, and the unique characteristics that make these additives a good fit for such a wide range of applications.

**13. Synthesis and Characterization of Phosphonates from Methyl Linoleate and Vegetable Oils** Grigor Bantchev\*, *Bio-oils Research Unit, NCAUR, ARS, USDA, USA*

Phosphonates were synthesized at medium scale (~200 g) from three lipids – methyl linoleate (MeLin), high-oleic sunflower oil (HOSO) and soybean oil (SBO), and three dialkyl phosphites – methyl, ethyl and n-butyl, using radical initiator. Staged addition of the lipid and the initiator to the dialkyl phosphite was needed to achieve good yields. Good results were observed with MeLin and HOSO using tert-butyl perbenzoate as initiator. With SBO, benzoyl peroxide was used as initiator, due to its capability to generate radicals at higher rate at slightly lower temperature and thus to shorten the reaction time. The progress of the reaction was monitored with GC-MS. The products were characterized using <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR, IR and gel permeation chromatography. Prolonged reaction led to some transesterification between the carboxylic and dialkyl phosphite ester groups. Higher reaction rate led to formation of more oligomers and benzoate fatty ester byproducts. The benzoate fatty ester byproducts were formed by attack of a benzoate radical on a double bond.

**14. Designing Multifunctional Sugar Alcohol-based Oleogels as Solid Fat Substitutes** Malick Samateh\*<sup>1</sup>, Sai S. Sagiri<sup>2</sup>, and George John<sup>3</sup>, *<sup>1</sup>The City College of New York & Ph.D. Program in Chemistry at Graduate Center, City University of*

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The use of vegetable oils, instead of solid fats, has been receiving special attention due to their nutritional and health benefits associated with unsaturated fatty acids (UFAs). However, efforts to incorporate the oils in food products are challenged by lack of similar organoleptic properties and oxidative stability as those of fat-structured food materials; the oils are prone to oxidation due to the presence of UFAs. The techniques adapted to solve these issues include partial hydrogenation and addition of solid fat and synthetic antioxidants. However, the limitations include, for instance, catalytic hydrogenation leads to trans fats, which are being restricted owing to growing health concerns. To address these challenges, multifunctional low molecular weight gelators (LMWGs) are hereby proposed to impart both mechanical and oxidative stability to oils. Selecting optimal precursors from plant sources and combining the capabilities of biocatalysis in a GRAS protocol, we have successfully designed and demonstrated an array of simple sugar alcohols (mannitol, sorbitol, and xylitol) based LMWGs as multifunctional structuring agents, exploiting their low-/non-caloric and antioxidant properties. Structuring ability was systematically tested in edible oils such as canola, soybean, olive and corn oils, which created excellent oil gels (oleogels) with minimal gelator concentration. The nature and aesthetic value (transparency/opaqueness) of the oleogels can be tuned by gelator concentration, nature of oil, etc. The study also aims at finding the correlation between textural and organoleptic properties against the nanostructure and rheology of the oleogels for future food applications.

#### **15. Analysis of Phorbol Ester of *Jatropha Curcas* L. by HPLC with UV-VIS and ToF-MS Detection**

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The oil of the seeds from *Jatropha curcas* L. is a promising biodiesel feedstock which gets transesterified to obtain biodiesel. The remaining press cake contains proteins and other nutritional compounds which makes it as ideal source for animal feed supply. However, most of the harvested *Jatropha* products are toxic to humans and animals due to the natural ingredients toxalbumin curcin and the group of diterpenester: phorbol esters. These phorbol esters show skin irritant, inflammatory and carcinogenic promotor activity. Analytic procedures were established for the phorbol esters content like HPLC-UV at a wavelength at 280 nm and comparison with phorbol myristat acetate as internal standard. The difference in the fatty acid sidechains leads to different absorption effects at the detected wavelength and cause problems for exact quantitative measurements. Furthermore, the lack of commercial available standards hinders deeper investigations. In this work we want to focus on a fast identification and precise measurement of phorbol ester content. This is performed on an Agilent 6200 Series HPLC-ToF-MS. We use a RP-C18 column to separate the analytes of a methanolic oil extract chromatographically and with the help of the high resolution mass spectrometry focused on the formic-PE analyte adducts the interfering matrix e.g. free fatty acids is reduced. The results were measured by standard addition method with a three step purified PE and PMA as internal standard. The LOQ of the used method was 50 µg PE/ g Oil. Tested *Jatropha* oils had a PE content of approximately 1 mg/g oil coming from different origins.