

### AFTERNOON

#### IOP 1: Alternative Fuels I

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Chair(s): J. Van Gerpen, University of Idaho, USA; and G. Chupka, NREL, USA

**Effects of Temperature Cycling on Formation of Solid Deposits in Biodiesel.** R. Dunn, USDA, ARS, NCAUR, Peoria, IL, USA

Biodiesel is produced mainly from transesterification of newly refined vegetable oils or used cooking oils with methanol. Most conversion processes require extensive treatment of product streams to remove co-product glycerol, unreacted alcohol, catalyst and minor constituents. Minor constituents including saturated monoacylglycerols (MAG) and free steryl glucosides (StG) can interfere with biodiesel stability during storage. MAG and StG have very high melting points and when present in small (trace) concentrations, can present problems when the fuel is storage in outside storage tanks during cold weather. If exposed to cold temperatures over a long period of time during storage, minor constituents can precipitate to form solid residues that are resistant to re-melting and dissolving back into solution. Furthermore, fuels stored in outside tanks may experience several warming/cooling cycles as temperatures rise in daytime and decrease at night. This study is designed to determine the effects of repeated temperature cycling between 25°C (room temperature) and 5°C (refrigerator temperature) on the rate of solid residue formation in methyl soyate (SME). Results showed temperature cycling accelerated the rate of solid formation compared to constant cooling of the SME at low temperatures over the same total time period.

**A Survey of Biodiesel Feedstocks under Performance Perspectives.** G. Knothe, U.S. Department of Agriculture, Agricultural Research Service, National Center for Agricultural Utilization Research, Peoria, IL, USA

Biodiesel, defined as the mono-alkyl esters of vegetable oils and animal fats, can be produced from an ever-growing number of feedstocks. The development of the various feedstocks is spurred to a significant extent by the issue of availability as there is no feedstock that can replace significant amounts of petrodiesel. These include classical commodity oils such as soybean, rapeseed (canola), palm and sunflower as well as non-edible, more recently emerging oils such as jatropha. Animal fats and especially used cooking oils have attracted interest as low-cost feedstocks. Castor oil, which contains a hydroxy fatty acid, has also been reported as a feedstock. Algae are currently one of the most researched feedstocks due to the claimed high production potential. Other issues affecting the search for additional feedstocks are the so-called food vs fuel issue and growing requirements of the plants. An issue, however, ultimately affecting the commercialization and use of biodiesel is that of fuel properties as other factors may not matter much if the fuel does not perform. The various feedstocks will be compared here in light of their properties and routes towards improvement of the properties discussed.

**A Direct Method for the Synthesis of Fatty Acid Methyl Ester from Crude Jatropha Oil as Second Generation Feedstock Using Versatile Green Catalysts.** A. Baig, F.T.T. Ng, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

Due to the high cost of edible oils and growing concern of food for oil, the commercial production of biodiesel is in great need of new inexpensive second-generation feed stocks which do not compete with food. Recently, Jatropha oil has been considered as one of the most promising potential feedstock for the production of biodiesel in Asia, Africa, Europe, South America, and now is gaining momentum in North America due to its advantages over edible oils. Currently, most of the fatty acid methyl ester from Jatropha oil produced by using multi-step process using

homogeneous-catalyzed process. Therefore, here we are reporting the synthesis of biodiesel from un-pretreated crude Jatropha oil as second generation feedstock using versatile green heterogeneous catalysts in a single-step. These preliminary results are very promising and suggest the feasibility of using Jatropha oil as low cost non-edible feed stocks with high FFA content for the industrial production of biodiesel using this green heterogeneous single-step process as compared to the current multi-step industrial process. To the best of our knowledge, this is the first report on the development of a single-step heterogeneous-catalyzed process for the production of biodiesel from un-pretreated crude Jatropha oil.

**Sterol Glucoside Identification Using a New MALDI-TOF-MS Technique.** K. Duff, J. Van Gerpen, University of Idaho, Moscow, Idaho, USA

Sterol glucosides (SG) have been identified as one cause of plugged biodiesel fuel filtration systems. These natural products negatively impact the cold flow performance of biodiesel resulting in intermittent fuel filter failures. The current state of the art methods for the evaluation of SG were surveyed and tested, and new analytical procedures and techniques have been developed. A modified high performance liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (HPLC-APCI-MS) method for the resolution of SG and acylated sterol glucosides (ASG) was developed and validated, which produced high populations of stable SG ammonium adducts, appropriate for capture in an ion trap. A novel matrix assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS) method was developed for the detection of SG allowing for direct experimental analysis. A preparative method to separate triglycerides in seed extract from sterol glucosides with size exclusion chromatography (SEC) was also developed and validated. The SEC preparative method and MALDI-TOF-MS method developed were able to identify sitosteryl-glucoside and campesteryl-glucoside with accurate mass in a winter canola seed sample.

**Characterization of Lipids in Five Microalgae Species.** L. Yao, J.A. Gerde, T. Wang, Z. Wen, S-L Lee, Department of Food Science and Human Nutrition, Iowa State University, Ames, IA, USA

Microalgae are one of the promising future sources for biofuels. In order to identify the most suitable algae species for specific applications, such as biofuel, industrial fluids, and nutraceutical applications, and for facilitating the downstream oil extraction, the lipid profiles of five microalgae were characterized, which were *Nannochloropsis spp.*, *Schizochytrium limacinum*, *Scenedesmus spp.*, *Chlamydomonas spp.* (*genetically modified*), and *Chlorella vulgaris*. The lipid class composition was determined by HPLC, <sup>31</sup>P NMR and TLC-GC. The fatty acid composition of total lipid and each lipid class were quantified by GC. Total content of unsaponifiable matters was determined and the profile of unsaponifiables was quantified by GC-MS. The melting and crystallization profile of the total lipid and its methyl and isopropyl esters was analyzed by DSC. The present study provides valuable compositional information to algae growers and downstream processors to select the most profitable candidates for specific applications.

**Carbon Residue Formation of Stressed Biodiesel and Biodiesel Blends.** A. Narani, R. Maglinao, N. Soriano, Montana State University-Northern Bio-Energy Center, Havre, MT, USA

Biodiesel is a renewable and environmental friendly transportation fuel, but unlike petroleum diesel it degrades faster in the presence of oxygen when subjected to high temperatures and pressures especially in the presence of certain metals. The presence of unsaturation in biodiesel makes it more susceptible to thermal oxidation and fuel aging. The products of oxidation are mainly aldehydes, peroxides, hydroperoxides, and acids. During combustion, these compounds lead to the formation of sediments and gums that may accumulate as black deposits causing adverse effects on engine performance. In this study, diesel#2, neat biodiesel and 20% blends were subjected to stress by exposing fuels to air at elevated temperatures. The carbon residues of the control and stressed fuel samples were determined in accordance to ASTM protocols. Compared with diesel#2, oxidized neat biodiesel from camelina, canola and safflower produced 34%, 25% and 10% increase in the carbon residue, respectively. Oxidative degradation of these fuel samples were monitored by FTIR Spectroscopy and products were analyzed and quantified by GC/MS. The results confirmed that stressed biodiesel will have more adverse effect on the fuel systems.

**Esterification and Transesterification of Greases to Fatty Acid Methyl Esters with Highly Active Diphenylammonium Salts.** H. Ngo, H. Vanselow, G. Strahan, M. Haas, USDA, ARS, ERRC, USA

We have conducted an investigation designed to identify alternate catalysts for the production of fatty acid methyl esters (FAME) to be used as biodiesel. Diphenylammonium sulfate (DPAS) and diphenylammonium chloride (DPA-HCl) salts were found to be highly active homogeneous catalysts for the simultaneous esterification and transesterification of waste greases. In this presentation, we will talk about recent results of this effort. In the presence of catalytic amounts of DPAS or DPA-HCl and excess methanol, the free fatty acids, which comprised as much as 90% of the substrate, as well as the glycerides in the greases to an extent, were converted to FAME at 125°C within 1 hour. The yields of the FAME products were as high as 95% depending on the greases used. The diphenylammonium salts are easier to work with when compared to strong liquid acids such as concentrated sulfuric acid and hydrochloric acid. Interestingly, the DPA-HCl salt performed better than the parent liquid hydrochloric acid in FAME synthesis.

### **Blends from Biodiesel, Diesel Fuel and Alcohols to Prevent Chemical Interactions between Fuel Components.**

Jürgen Krahl<sup>1</sup>, Lasse Schmidt<sup>2</sup>, Olaf Schröder<sup>2</sup>, Kevin Schaper<sup>2</sup>, Christoph Pabst<sup>2</sup>, Axeö Munack<sup>1</sup>, <sup>1</sup>Coburg University of Applied Sciences and Arts, Coburg, Germany, <sup>2</sup>Johann Heinrich von Thünen-Institut, Institute of Agricultural Technology and Biosystems Engineering, Braunschweig, Germany

Today most diesel vehicles do not have a release for neat biodiesel (B100) by their manufacturers. Passenger cars with diesel particulate trap should not be fueled with higher blends than B7, in case the engine oil changing interval shall not be reduced. However, blending of fuels can lead to chemical reactions between fuel components and may result in undesired products. In detail, aged biodiesel from unsaturated FAME and fossil diesel fuels can form oligomers and precipitations with a maximum in the range of B10 to B20. Precursors are oligomers that can be separated from the biodiesel or the blends in an amount of up to 20%. These oligomers are soluble in the fuel, but they seem to have potency for chemical reactions with fuel components or the engine oil. To prevent problems the formation of oligomers should be disabled in blends. Alcohols have been proven and tested to dissolve precipitations in the fuel. However, flash point problems occur, in case the alcohols have too low boiling points. Some alcohols could be identified to reach the demands of the specification. Additionally, engine test were carried out to monitor regulated and non-regulated emissions. In the result, some blends from biodiesel, diesel fuel and alcohols tend to be appropriate to suppress chemical reactions in the fuel or the engine oil.

### **Thevetia peruviana juss: Studies to Highlight its Economic Potentials as a Veritable Biodiesel Source. S.A.**

Ibiyemi<sup>1</sup>, C.O. Aboyeji<sup>2</sup>, <sup>1</sup>Landmark University, O, Omu Aran, Kwara, Nigeria, <sup>2</sup>University of Ilorin, Ilorin, Kwara, Nigeria

Preliminary studies of thevetia fruits conducted and still on-going for the next three months reveal that the seeds shall be an efficient feedstock for production of biodiesel. The kernel accounts for about 45% of the seed. The oil content of the kernel is 50-65%. The oil is about 50% oleic acid. The seed coating is about 55% of the seed shall make good particle board or plywood. The succulent outer cover of the fruit is being studied for its sugar for fermentation to ethanol. The defated seed cake is rich in glycosides which are cardiac stimulants. The lethal level of each compound is dangerously too close to the dosage as a drug. We have established an efficient method to detoxify the cake. The extract of detoxification is being studied for its anti termite activities. The cake is a good protein source for formulation of livestock meals. Each component of the fruit could serve as a major revenue earning material thereby ranking the plant most valuable of all oil crops, even palm tree.

**TUESDAY**

**MORNING**

Chair(s): D. Sparks, Mississippi State University, USA; and D. Pioch, CIRAD, France

**How to Select Catalysts for the Production of Sustainable Chemicals from Fats and Oils?** R.D. Seaman<sup>1</sup>, A. Zwijnenburg<sup>3</sup>, <sup>1</sup>Johnson Matthey Catalysts Inc., Chicago, IL, USA, <sup>2</sup>Johnson Matthey Plc, Royston, Herts, UK, <sup>3</sup>Johnson Matthey Chemicals GmbH, Emmerich am Rhein, NRW, Germany

Catalytic processes are key to support the growing demand for sustainable industrial chemicals derived from oils and fats. This contribution focuses on the novel catalysts for both existing and new processes, and highlights the key role of catalysis in the production of sustainable chemicals. In some cases, catalysts consist of metals that are not readily available and are derived from limited resources. Therefore, sustainability of both catalyst manufacture and recycling or reuse are key aspects to be considered. It will be shown how these considerations can be included in catalyst selection. This contribution will conclude by some case studies, highlighting an approach to select the most promising catalysts in for the production of sustainable chemicals based on oils and fats.

**A Novel Green Technology for the Production of Biodiesel from Multi-Feedstocks for Global Applications.** A. Baig, F.T.T. Ng, Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada

Biodiesel is a renewable and biodegradable alternative green fuel for petroleum-based diesel. However, the major obstacles for the production of biodiesel at an industrial scale are the high production cost, expensive feedstocks, complex production processes, and limited local availability. Therefore, we have developed a novel green technology for the production of biodiesel using a simple and environmentally green single-step heterogeneous-catalyzed process to produce high quality biodiesel from multi-feedstocks including yellow grease for global applications. It was found that the FFA present in the yellow grease were converted to biodiesel with a 95% conversion using a heterogeneous catalyst. Furthermore, the yellow grease was successfully transesterified to produce a product with 87.3 mass% ester content. Analysis based on the ASTM D974, and EN14103 standards confirmed the production of high-purity biodiesel from yellow grease with only 3% linolenic ester which is far below the limit of EN14214. The recycling studies shows even after 5 reaction cycles, catalyst activity remains at 97% of the fresh catalyst. Also, major process parameters were investigated including FFA content in the feedstock. This green technology has potential for industrial-scale production of biodiesel from multi-feedstocks for global applications.

**Alkene Metathesis of Camelina FAME with Supercritical Ethylene.** R. Maglinao, A. Narani, N. Soriano, Montana State University-Northern Bio-Energy Center, Havre, MT, USA

Alkene metathesis of unsaturated FAME with ethylene is a powerful synthesis reaction to produce terminal alkenes which can be used for synthesis of polymers and other valuable compounds. Although commercial metathesis catalysts have been proven to be efficient in converting pure FAME, this process has not been used effectively in a mixture of methyl esters like biodiesel. Moreover, there has been no study in the literature that has used supercritical ethylene in alkene metathesis. We anticipate to minimize mass transfer limitations with the use of supercritical ethylene during metathesis with FAME. In this study FAME derived from camelina oil, which contains as much as 90% unsaturated components, was allowed to react with supercritical ethylene at room temperature in the presence of Grubbs catalyst. A high pressure syringe pump is used to deliver 750 psi of ethylene and the reaction is performed in a 500 mL high pressure and high temperature reactor for 4 hours. Different commercial first and second generation Grubbs catalysts were tested. Depending on the nature of the catalyst, self metathesis of FAME, isomerization and cyclization were observed as well at varying degrees as evidenced by GC/MS analyses. Percent conversion of unsaturated FAME as high as 87% was obtained.

**Reactive Extraction for Biodiesel Production using Solid Green Catalyst.** Savita Kaul, Jyoti Porwal, Dinesh Bangwal, Rajaram Bal, Madhukaronkarnath Garg, Indian Institute of Petroleum, Dehradun, Uttarakhand, India

The parametric study of reactive extraction of non edible seeds (Indian origin) using different solid green catalyst

receipes was carried out taking the parameters such as seed size, catalyst concentration and seed/ solvent ratio. The product was purified and analysed by GC. Under the optimized conditions: seed size >2.46 mm, seed/ solvent ratio 1:4 (wt/wt), and catalyst concentration 10%, a conversion >90 % to biodiesel was achieved in 1-2 hrs. The paper presents the details of these studies.

**Catalytic Conversion of Crude Glycerin to Lactic Acid under Mild Reaction Conditions.** X.P. Ye, L. Chen, L. Liu, University of Tennessee, Knoxville, TN, USA

Lactic acid derived from renewable resources as a monomer for poly(lactic acid) plastics and as a precursor of green solvents such as ethyl lactate has attracted increasing interests due to its environmental benefits. The future role of lactic acid will largely depend on its production cost. Recent studies showed that glycerin, as a byproduct in biodiesel industry, can be converted to lactic acid with base catalysts under hydrothermal conditions. Although the chemical catalysis route promises improved process design options, resulting in faster reaction speed, higher productivity, less waste, and reduced costs related to product work-up, the high alkalinity conditions used would cause severe corrosiveness to a stainless steel reactor, hindering practical application of the technology. This presentation will show our development in the conversion of glycerin to high yield of lactic acid under low corrosive conditions with homogeneous and heterogeneous catalysts. Furthermore, the effects of impurities in crude glycerin on the conversion process will be discussed.

**Study of a New Environment Friendly Catalytic System for the Oxidative Scission of Unsaturated Fatty Acids.**

Anais Godard<sup>1,2</sup>, Sophie Thiebaud-Roux<sup>1,2</sup>, Pascale de Caro<sup>1,2</sup>, Emeline Vedrenne<sup>1,2</sup>, Zéphirin Mouloungui<sup>1,2</sup>,  
<sup>1</sup>Université de Toulouse, INPT, LCA (Laboratoire de Chimie Agro-Industrielle), ENSIACET, Toulouse, France,  
<sup>2</sup>INRA, LCA (Laboratoire de Chimie Agro-Industrielle), Toulouse, France

Monounsaturated fatty acids are renewable starting materials that are particularly interesting for the chemical industry to substitute fossil resources. Obtained from vegetable oils, they can produce mono and di-acids by the oxidative scission of their double bonds. These synthesized saturated acids (e.g. pelargonic and azelaic acids) exhibit shorter and odd hydrocarbon chains, rarely present in natural resources, and are very interesting raw materials for the preparation of biobased products such as polymers, plasticizers, lubricants...Hence, we propose to study a new alternative oxidative scission process using a green oxidant and solvent-free system to substitute the non eco-friendly conventional process: ozonolysis. Fatty acids were oxidized in a batch reactor with a biphasic system consisting of H<sub>2</sub>O<sub>2</sub> as an oxidant and a peroxo-tungsten complex Q<sub>3</sub>[PO<sub>4</sub>[WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>] as a phase-transfer catalyst/co-oxidant. Several phase-transfer catalysts were prepared *in situ* from tungstophosphoric acid, H<sub>2</sub>O<sub>2</sub> and quaternary ammonium salts. Various factors such as temperatures, type/amount of catalyst or stirring speed can affect this process. The optimization led to a complete conversion of fatty acids and yields above 80% for each acid. Besides, a new treatment was developed to obtain high quality products and to recover the catalyst without yield loss.

**Proposed Reaction Mechanism and Effect of Water on Esterification of Palmitic Acid Using Zeolite Catalysts.**

Adebola Coker<sup>1</sup>, Rafael Hernandez<sup>1</sup>, Alexei Iretski<sup>1</sup>, Mark White<sup>1</sup>, Todd French<sup>2</sup>, <sup>1</sup>Mississippi State University, USA, <sup>2</sup>Lake Superior State University, USA

Literature has demonstrated that fatty acid methyl esters (biodiesel) can be produced from activated sludge generated at a wastewater treatment plant. One main operating cost of this process is drying of the sludge prior to reaction. Biodiesel can be obtained by converting the lipids to free fatty acids via hydrolysis, followed by esterification to obtain the fatty acid methyl esters (FAME). A study was conducted to determine the maximum concentration of water that the esterification reaction would tolerate using ZSM-5 and Faujasite (Y) zeolite catalysts. Since the silica:alumina (SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub>) ratio of the zeolites affects its acidity and hydrophobicity, the influence of the SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio in these catalysts on the reactions was analyzed. The effect of water on the reaction was examined at volume compositions of 10%, 20%, 50% and 90%. Reactants included 0.5 g fatty acid, 10 ml methanol, and 10 mass % catalyst, temperature of 65°C, and duration of 3 hours. Reaction kinetics and parameters such as rate constants, rates, and activation energy were obtained. Results on the ZSM-5 catalyst with SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio of 30:1 shows the activation energy to be 37.5 KJ/mol. The yield of FAME shows nonlinear dependency on water concentration.

**Standardisation of Vegetable Oils to be Used as Oleochemistry Feedstock through a Selective Hydrogenation Process.** Federica Zaccheria<sup>1</sup>, Paolo Bondioli<sup>2</sup>, Rinaldo Psaro<sup>1</sup>, Nicoletta Ravasio<sup>1</sup>, <sup>1</sup>National Research Council ISTM, Milano, Italy, <sup>2</sup>Stazione Sperimentale Oli e Grassi, Milano, Italy

Selective hydrogenation over pre-reduced 8% Cu/SiO<sub>2</sub> catalysts has been carried out on a series of non-food oils methylesters. The catalyst shows a very high diene: monoene selectivity, thus allowing one to reduce not only the linolenic C18:3 component, but also the linoleic C18:2 one in this way enriching the oil in oleic C18:1 and avoiding a contemporary increase in stearic acid concentration. This treatment improves the oxidation stability of the oil while keeping acceptable viscosity and cold properties due to limited cis/trans and positional isomerization. The treatment also increase the Cetane Number of the methylester, therefore these materials can meet both EU and USA specification for Biodiesel. Moreover the treatment can be used to standardise a wide variety of different available feedstock making them suitable for many different applications, from polyols synthesis to metathesis.

## AFTERNOON

### **IOP 3: New Uses of Glycerin**

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Chair(s): V. Wyatt, USDA, ARS, ERRC, USA; and T. Benson, Lamar University, USA

**Glycerol and its Derivatives as Sustainable Solvents for Organic Synthesis.** A. Wolfson, D. Tavor, Green Processes Center, Chemical Engineering Department, Sami Shamoon College of Engineering, Bialik/Basel Sts. Beer-Sheva, 84100 Israel

**Effects of Swelling on the Viscoelastic Properties of Polyester Films made from Glycerol and Glutaric Acid.** V.T. Wyatt, ERRC, ARS, USDA, Wyndmoor, PA, USA

Developing new outlets for glycerol would have a significant impact on the economics of biodiesel production if value-added products made from glycerol can be identified. Glycerol is the major co-product produced from the process used to make biodiesel. Before the introduction of biodiesel-derived glycerol, the glycerol market was already saturated with uses in the food industry and in many pharmaceutical, chemical, and personal care applications. Therefore, increased production of biodiesel created a need to find new uses for glycerol. In this study, we have shown that polymer films that include glycerol can absorb various amounts of polar solvents. Dependent upon the solvent used, the cured polymers were able to absorb 9.5 percent to 261 percent of its weight after 24h. The effects of the solvent absorption on the viscoelastic properties of the polyester films were evaluated by determining their elastic modulus, viscous modulus, tan delta, and complex viscosity by performing oscillatory frequency sweep experiments. These types of polymers are important to develop for use in areas such as water remediation, filters, and drug delivery. Such applications require films that can to absorb large amounts of solvents while maintaining structural integrity.

**Progress in the Fermentative Synthesis and Characterization of Glycerine/levulinic Acid-based Poly(hydroxyalkanoate) Biopolymers.** R.D. Ashby, D.K.Y. Solaiman, G.D. Strahan, USDA, ARS, ERRC, Wyndmoor, PA, USA

Glycerine and levulinic acid, two natural, inexpensive industrial co-products have been successfully utilized as fermentation substrates in the synthesis of poly(3-hydroxybutyrate), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(3-hydroxyvalerate) biopolymers. By utilizing glycerine and levulinic acid together in different

concentrations, biopolymers were produced with varying 3-hydroxybutyrate and 3-hydroxyvalerate monomeric ratios resulting in an array of material properties. In this presentation, we will discuss our most recent results using 2 distinct bacterial strains in efficiently utilizing glycerine and levulinic acid in biopolymer synthesis and in the characterization of the physical and material properties of the resultant biopolymers. We will further illustrate the effects of methanol on polymer properties and demonstrate means by which glycerine and levulinic acid can be more efficiently utilized resulting in up to a 4-fold increase in polymer yield, making the entire synthetic process economically sound. It is envisioned that complete carbon source utilization, maximum polymer yields and control over the material properties of the polymer products will result in an economically and environmentally attractive alternative to petroleum-based plastics.

**Development of Functional Green Materials Based on Bio-based Glyceric Acid from Raw Glycerol.** T. Fukuoka, H. Habe, S. Sato, D. Kitamoto, K. Sakaki, National Institute of Advanced Industrial Science and Technology (AIST) JAPAN, Tsukuba, Ibaraki, Japan

Recently, we have developed a new and effective technique to biotechnologically produce glyceric acid (GA) from raw crude glycerol. GA is expected to be one of the promising glycerol derivatives, such as a multifunctional compound, a pharmaceutical and cosmetic material. Here, we report the synthesis of GA-based functional materials, such as surfactants and polymers, and their properties. First, we synthesized fatty acyl GAs as a new class of surfactants. The obtained amphiphilic compounds showed excellent surface tension lowering activities. In addition, we synthesized branched-type poly(lactic acid)s by polycondensation of lactide in the presence of GA as an initiator. The resulting branched poly(lactic acid)s had lower crystallinity and glass transition temperatures than those of linear poly(lactic acid). These materials should have potential as an environmental-friendly and functional green materials based on GA.

**Lactate Polyols based on Glycerol.** Mihail Ionescu, Xianmei Wan, Ivan Javni, Nikola Bilic, Zoran Petrovic, Pittsburg State University, Kansas Polymer Research Center, Pittsburg, KS, USA

A new group of 100% renewable polyols for rigid polyurethane foams were synthesized by ring opening polyaddition of L-lactide to glycerol, diglycerol, polyglycerol, and sorbitol-glycerol mixtures in the presence of  $Ti(OiPr)_4$  as a catalyst. The polyols have a high acid value due to the alkyl-oxygen splitting of L-Lactide ring. The acid values were dropped to values lower than 2 mg KOH/g by the addition of propylene oxide or ethylene oxide to the formed carboxylic groups. Similar products are obtained by the condensation of ethyl lactate and lactic acid with the same polyols. The synthesized lactate polyols based on glycerol were characterized by wet methods (OH#, viscosity, acid value, water content etc.), by GPC chromatography and spectroscopic methods (FT-IR,  $^1H$  NMR and  $^{13}C$  NMR). The glycerol lactate polyols were successfully transformed in rigid polyurethane foams and the characteristics of resulted biobased foams were investigated. The work represent a new valorization of glycerol resulted in large quantities in Bio-Diesel production.

### **IOP 3.1: Alternative Fuels II**

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Chair(s): J. Van Gerpen, University of Idaho, USA; and G. Chupka, NREL, USA

**Characterization and Solvent Extraction of Oils from Digested Wastewater Sludge.** Charles J. Coronella<sup>1</sup>, Cody Wagner<sup>1</sup>, Gene DeShazo<sup>2</sup>, <sup>1</sup>University of Nevada, Reno, Reno, NV, USA, <sup>2</sup>Nowa Technology, Inc., Prairie Village, KS, USA

The treatment and disposal of wastewater sludge is an increasingly expensive problem as traditional methods experience higher costs. The extraction of oils from primary, secondary, or digested sludge is a possibility with both environmental and economical potential. Digested sludge was subjected to solvent extraction under a wide range of operating conditions, with solvents including heptane, cyclohexane, isopropanol, and ethyl acetate. The oil extracted has a boiling range similar to that of diesel, contains significant fractions of free fatty acids, and is characterized with a high sulfur concentration. Six factors for these extractions were evaluated for the effect on oil extraction. A maximum

oil yield of 9% was measured. A sample of the oils from the heptane extraction was found to have a combination of organic acids, esters, silicon, and hydrocarbons. A separate set of extractions was performed with ethyl acetate, cyclohexane, and a combination of the two as co-solvents, with improved extraction yields of up to 11.9%. Finally, a study showing the effectiveness of the solvent extractions on wet digested sludge with heptane was performed, with a full mass balance detailing where losses take place in the process.

**Effect of Aerobic and Anoxic Conditions on Biocrude Production by Activated Sludge via Sugar Fermentation.** A. Mondala, R. Hernandez, T. French, M. Green, L. McFarland, Mississippi State University, Mississippi State, MS, USA

Municipal sewage activated sludge present a low cost and abundant source of lipid biofuel feedstock (biocrude). Initial studies found that batch cultivation of activated sludge in a high carbon-to-nitrogen (70:1) ratio wastewater medium with a high sugar load (60 g/L), increased its lipid content by 70% compared with raw activated sludge. Biodiesel yield from the enhanced activated sludge also reached 10% CDW compared to 2.3% in raw sludge. However, the final lipid content and the sugar conversion yield to lipids was relatively lower than those observed in most pure cultures of oleaginous microorganisms; hence, optimization of specific fermentation conditions is needed. In this paper, the effect of aerobic and anoxic fermentation conditions on biocrude yield was investigated. The activated sludge inocula was first grown aerobically up to 48 h of cultivation after which aeration was terminated and the agitation rate was reduced from 500 rpm to 100 rpm such that dissolved oxygen (DO) levels in the fermentation broth will be reduced to less than 10 % saturation. Samples of the culture were then analyzed for cell biomass and lipid yields, residual sugar, and fatty acid profile of the extracted biocrude.

**Solvent Based Fractionation of Alkyl Esters of Animal Fat.** Martin Mittelbach, Sigurd Schober, Katharina Strohmeier, University of Graz, Graz, Austria

There is a strong demand for biodiesel made out of waste oils and animal fat. Methyl esters of animal fat, however, have only a limited utilization as biodiesel because of the high content of saturated fatty acids leading to low cold temperature behaviour. Therefore separation technologies for saturated and unsaturated fatty acids have been studied. The well known separation via complexation with urea did not lead to satisfying results due to the high content of saturated compounds. A new approach using different solvents and fractionated crystallization at low temperatures lead to very promising results. Methyl-, ethyl-, propyl-, isopropyl- and butyl esters were prepared out of animal fat and the products were diluted with different solvents, cooled down and separated by filtration. Under optimum conditions unsaturated fractions with an amount of up to 93 % of unsaturation and saturated fractions with an amount of up to 95 % of saturation were obtained. The unsaturated fractions could be ideally used as alternative fuel, whereas the saturated fractions can be used as oleochemical feedstock.

**Emissions and Health Effects from Combustion of Hydrotreated Vegetable Oil (HVO) and Jatropha Oil Methyl Ester (JME) in a Euro III Heavy Duty Diesel Engine.** A. Munack<sup>1</sup>, J.M. Bünger<sup>2</sup>, G.A. Westphal<sup>2</sup>, N. Rosenkranz<sup>2</sup>, O. Schröder<sup>1</sup>, J. Schaak<sup>1</sup>, C. Pabst<sup>1</sup>, J. Krahl<sup>3</sup>, <sup>1</sup>Johann Heinrich von Thünen Institute (vTI), Institute of Agricultural Technology and Biosystems Engineering, Braunschweig, Germany, <sup>2</sup>University of Bochum, Institute for Prevention and Occupational Medicine of the German Social Accident Insurance (IPA), Bochum, Germany, <sup>3</sup>Coburg University of Applied Sciences and Arts, Coburg, Germany

The newly developed diesel fuels hydrotreated vegetable oil (HVO) and jatropha oil methyl ester (JME) were compared to those of common diesel fuel (DF) and rapeseed oil methyl ester (RME) for their emissions. The exhausts were compared following combustion in a heavy duty diesel engine (Euro III). Beside regulated emissions we analyzed non-regulated exhaust components as well as bacterial mutagenicity. JME and RME yielded lower total particle numbers and a smaller particle mass than DF and HVO, while particle sizes were comparable in all fuels. Particle extraction showed a very small solid fraction (soot) of RME and JME. RME yielded as well the lowest HC and CO emissions, followed by JME, DF, and HVO. HVO yielded the lowest NO<sub>x</sub> levels and lowest PAH emissions, likewise in particle extracts and condensates. All exhausts induced bacterial mutagenicity. Mutagenicity was stronger in the particle extracts compared to the condensates. The strongest mutagenicity was induced by JME and RME. Only weak mutagenicity was seen with HVO. In conclusion HVO is a promising new fuel with significant technical and

toxicological benefits. JME from the inedible jatropha oil seems to be suitable FAME that does not interfere with the food chain.

**Enzymatic Transesterification Process for Biodiesel Production and Beyond.** G. Chou, Sunho Biodiesel Corporation, Taipei, Taiwan, R.O.C.

Though enzymatic biodiesel production is believed to be environmentally friendly, academic media inaccurately relate it to high operating costs. Evidence can be presented to the contrary. The operating cost of the lipase depends on how its operating life is expanded. This presentation will discuss how to prevent decreasing lipase activity by addressing the co-product glycerol, which causes lipase degradation. In a normal operation, lipase activity degrades very slowly and the half-life can even reach more than 60 months. The enzymatic process is preferably applied using fresh or acidized natural oils. It is frequently mentioned that deodorizer distillate, such as palm fatty acid distillate, soybean deodorizer distillate, etc., waste grease or used cooking oil that contain high amounts of free fatty acid are good candidates for the enzymatic process. This presentation will show that this is not the case with these feedstocks. Enzymatic transesterification reaction utilizes different primary or secondary alcohols in a similar way, with a straightforward reaction applicable even to higher alcohols. The difference resides mostly in the reaction rate. A list of different products made with different oil sources and alcohols will be presented.

**Comparative Calorimetric and Viscometric Study of Biodiesel from Various Feedstocks and Blends with Petrodiesel.** L.N. Okoro<sup>1</sup>, R. Ekop<sup>1</sup>, C. Nwaeburu<sup>2</sup>, <sup>1</sup>American University of Nigeria, Yola, Adamawa, Nigeria, <sup>2</sup>University of Technology, Kaiserslautern, Niedersachsen, Germany

Viscosity and heating value are important fuel properties of biodiesel and fossil diesel fuels. Both animal fats and vegetable oils can be used as alternative fuels directly but they have a major drawback because of their high viscosity values, which causes problems in compression ignitions. This work evaluated the influence on viscosity as well as heat value of a mixture of biodiesel fuels and blends at different ratios obtained from various feedstocks locally. Biodiesel was synthesized from groundnut oil at 65°C via base catalyzed transesterification using KOH as the catalyst. The heat content of each blend was measured using a bomb calorimeter. The data obtained was analyzed and was found that the heat content of the blend decreases as the percentage of biodiesel in the blend increases. As well, a mixture of biodiesel fuels obtained from different feedstock did not have a significant effect on the viscosity values. The research also demonstrates that, the energy output of fuels made from blends of petroleum diesel and biodiesel from the various feedstock decreases as the portion of the biodiesel increases.

## WEDNESDAY

## MORNING

### IOP 4: Polymers from Vegetable Oils

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Chair(s): G. Bantchev, USDA, ARS, NCAUR, USA; and P. Pham, Mississippi State University, USA

**Green Routes to Biobased Polyurethanes.** R. Narayan, D. Graiver, Michigan State University, Lansing, MI, USA

Soy meal was used as a starting materials to produce aliphatic poly(ester-urethane)s and poly(amide-urethane)s by an isocyanate-free route. This approach provides a "green" route to a wide variety of biobased polyurethanes suitable as coatings, adhesives, sealants and elastomers (CASE). The manufacturing process is relatively simple and consists of hydrolyzing the proteins followed by reacting the amino acids with cyclic carbonate to yield low molecular weight,

hydroxyl terminated urethane oligomers. Under appropriate catalytic conditions, trans-urethanation (similar to transesterification) takes place (distilling out ethylene glycol) leading to higher molecular weight urethanes. The manufacturing process is relatively simple and does not require any solvent (other than water), specialized process equipment or expensive reagents. The polyols intermediates can be blended with other polyols and processed in current processes to yield polyurethane foams. This approach offers an opportunity to produce an increasingly desired bio-based alternative to environmentally un-friendly and increasingly expensive petroleum-based polyurethanes. It is expected that these polyurethane will exhibit high UV resistance since no aromatic functionality is used in their preparation.

**Novative Macromolecular Architectures from Vegetable Oils.** L. Averous, LIPHT-ECPM University of Strasbourg, Strasbourg, Alsace, France

Nowadays, replacing petroleum-based raw materials with renewable resources from agro-resources is a major concern in terms of both economical and environmental viewpoints. Vegetable oils are expected to be an ideal alternative feedstock, since they have the particularity to contain lots of active chemical sites that can be used for polymerization. Moreover, they are vegetable sources present in abundance throughout the world. Different macromolecular architectures can be elaborated such as thermoplastics (PA, TPU) or thermosets (PUR). For instance, Polyurethanes (PUR) based on vegetable oil were synthesized with castor oil and toluene diisocyanate, isophorone diisocyanate or hexamethylene diisocyanate, using dibutyltin dilaurate as a catalyst. The polymerization kinetics, degree of swelling and mechanical properties were greatly affected by the diisocyanate nature, whereas the rheological properties and thermal stability were found to be similar for all polyurethanes. Others examples are thermoplastics polyamides or TPU elaborated from fatty acids, from triglycerides based on vegetable oils.

**Vegetable-based Building Blocks for the Synthesis of Renewable Polyurethanes.** L. Maisonneuve<sup>1,2</sup>, H. Cramail<sup>1,2</sup>, E. Cloutet<sup>2,1</sup>, B. Gadenne<sup>3</sup>, C. Alfos<sup>3</sup>, <sup>1</sup>Université de Bordeaux, Laboratoire de Chimie des Polymères Organiques, IPB-ENSCBP, 16, Avenue Pey Berland, Pessac Cedex, F-33607, France, <sup>2</sup>CNRS, Laboratoire de Chimie des Polymères Organiques, UMR 5629, Pessac Cedex, F-33607, France, <sup>3</sup>ITERG, Institut des corps gras, 11 rue Gaspard Monge, 33600 Pessac, France

World-wide potential demands for replacing petroleum-derived raw materials with renewable ones are quite significant from the societal and environmental points of view. Among the various polymeric systems derived from renewable resources, polyurethanes are one of the most studied and exploited materials. Vegetable oils have a large potential to substitute currently used petrochemicals, thanks to their availability, sustainability and biodegradability. In this present work, new ester diols and bis-epoxides from ricin and sunflower oils obtained by transesterification, thiol-ene reaction and epoxidation are presented. The starting bio-sourced materials used are methyl undecenoate and oleate, propanediol and isosorbide. The latter two can be obtained from glycerol and starch respectively. A large range of polyurethanes with various thermomechanical properties can be obtained by varying the diol structure. Glass transitions from -27°C to 66°C but also crystallizations were obtained with these linear polyurethanes. The relationship between the diol structure and properties of the so-formed polyurethanes will be discussed in the presentation. One non-isocyanate route to PUs that consists of the reaction between diamines and biscarbonates, obtained by reaction of the fatty ester bis-epoxides, was also explored.[4]

**Polymers from Algae Oil.** Zoran S. Petrovic, Xianmei Wan, Alisa Zlatanic, Jian Hong, Ivan Javni, Mihail Ionescu, Jelena Milic, DooPyo Hong, Pittsburg State University, Pittsburg, KS, USA

Algae oil from *Solix* was analyzed and the presence of different species was determined. Algae oil is high in saturates and free fatty acids, which lower their value for the conversion to polymers. Several chemistries were used to modify the oil: epoxidation, hydroformylation, ozonolysis and cationic polymerization. Algae oil can be epoxidized but the conversion is lower than in vegetable oils. Polyols were prepared from epoxidized oil and tested as urethane cast resins and in flexible foams. Another series of polyols was prepared by hydroformylation/hydrogenation and used to make polyurethanes. Ozonolysis of algae oils to polyols gave polyols with lower OH number and a range of byproducts. Cationic polymerization of algae oil was not successful. The feasibility of using algae oil for different polymeric products is discussed.

**Bio-based Non-Isocyanate Polyurethanes.** I. Javni, O. Bilic, Z.S. Petrovic, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS, USA

Non-isocyanate polyurethanes were synthesized from bio-based cyclic carbonates and amines. The research on polyurethanes by non-isocyanate route consisted in synthesis of different model cyclic carbonates and reacting them with different amines. The effect of carbonate and amine structure on polyurethane properties was studied. Non-isocyanate polyurethanes synthesized from cyclic carbonates and amines are interesting new polymeric materials. Avoiding isocyanates is beneficial to the environment and reduces personal exposure to a health hazard. The benefit of this technology is the utilization of carbon dioxide, an inexpensive and environmentally friendly monomer. New polyurethanes have different properties than those prepared by classical isocyanate route due to the presence of hydroxyl groups in their structure.

**Polymerization of Euphorbia Oil in Carbon Dioxide Media.** Zengshe (Kevin) Liu, NCAUR, ARS, USDA, 1815 N. University Street, Peoria, IL 61604, USA

Boron trifluoride diethyl etherate ( $\text{BF}_3\text{OEt}_2$ ), Lewis acid, catalyzed ring-opening polymerization of euphorbia oil (EO), natural epoxy oil, was conducted in carbon dioxide. The resulting polymers (RPEO) were characterized by FTIR,  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR, solid state  $^{13}\text{C}$ -NMR spectroscopies, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and gel permeation chromatography (GPC). The results indicated that the ring-opening polymerization of EO occurred at mild conditions, such as at room temperature, and a subcritical carbon dioxide ( $\text{CO}_2$ ) pressure of 65.5 bar. The formed RPEO materials were cross-linked polymers. The glass transition temperatures of these polymers ranged from  $-15.0$  to  $-22.7$  °C. TGA results showed that the RPEO polymers were thermally stable at temperatures lower than 220 °C and significant decomposition mainly occurred above 340 °C.

**Synthesis and Properties of Glycidyl Esters of Epoxidized Fatty Acids.** R. Wang, T. Schuman, Chemistry Department, Missouri University of Science and Technology, Rolla, MO, USA

Glycidyl esters of epoxidized fatty acids (EGE) were synthesized from vegetable oils. Mixed free fatty acids (FFA) derived from soybean oil or linseed oil were refined by removing saturated components through low temperature crystallization. The FFAs were epoxidized in situ with hydrogen peroxide and acetic acid, the epoxidized fatty acids reacted further with sodium hydroxide to produce epoxidized soap. The EGE were then obtained from reaction of epoxidized soap with excess epichlorohydrin in the presence of phase transfer catalyst. The EGE showed a higher epoxy content and lower viscosity than the epoxidized soybean oil (ESO) and linseed oil (ELO). The EGE were cross-linked with anhydride, polyamine, and cationic initiation to prepare network polymers. The curing behavior and glass transition temperature ( $T_g$ ) were monitored by differential scanning calorimetry (DSC). The polymer performance was studied by observation of thermal, tensile and flexural properties. The results indicated that EGE resins provide better intermolecular crosslinking and yield polymers of higher  $T_g$  and strength than materials obtained from ESO or ELO. Therefore, EGE may enable renewable fabrication of complex, shaped epoxy composites for structural applications. Other applications include coatings, plasticizers, epoxy reactive diluents, toughening agents, etc.

**Novel High Molecular Weight Polymer and Coatings Derived from Soybean Oil.** Samim Alam, Anurad Jayasooriya, Bret Chisholm, North Dakota State University, Fargo, ND, USA

A process was developed to obtain vinyl ether-functional monomers containing fatty acid pendent groups directly from soybean oil (SBO) using base-catalyzed transesterification. In addition, a carbocationic polymerization process was developed for the vinyl ether monomers that allowed for high molecular weight polymers to be produced without consuming any of the vinyl groups present in the fatty acid portion of the monomers. Compared to SBO, which possesses on average 4.5 vinyl groups per molecule, the polyvinyl ethers based on the soybean oil-derived vinyl ether monomers (polyVESFA) possess tens to thousands of vinyl groups per molecule depending on the polymer molecular weight produced. As a result of this difference, coatings based on polyVESFA were shown to possess much higher crosslink density at a given degree of functional group conversion compared to analogs based on conventional SBO. In addition, the dramatically higher number of functional groups per molecule associated with polyVESFA results in gel-

points being reached at much lower functional group conversion, which was shown to dramatically reduce cure-time compared to SBO-based analogs. Based on the results obtained, it appears that these new renewable materials may have tremendous commercial utility in the coatings industry.

### **Semicrystalline Polyamide Engineering Thermoplastics Based on the Renewable Monomer, 1,9-nonane Diamine.**

Alex Kugel, Jie He, Satyabrata Samanta, James Bahr, Jessica Lattimer, Michael Fuqua, Chad Ulven, Bret Chisholm, North Dakota State University, Fargo, ND, USA

A series of poly(1,9-nonamethylene adipamide-co-1,9-nonamethylene terephthalamide) copolymers were produced using melt polymerization and the thermal properties, crystal structure, and moisture uptake characterized. The results confirmed that the copolymers exhibit isomorphism. As expected, glass transition temperature and the apparent melting temperature increased with increasing terephthalamide content. Using the difference in the apparent melting temperature to the crystallization temperature as a measure of relative crystallization rate, it was observed that crystallization rate decreased as the terephthalamide content of the copolymer was increased from 0 to 50 mole percent but then sharply increased when increased beyond 50 mole percent. This behavior may be the result of extensive inter- and intramolecular interactions in the melt associated with terephthalamide units in the polymer chain that nucleate crystallization upon cooling below the equilibrium melting temperature. Comparing the thermal properties of copolymers possessing an excess of terephthalamide units to the commodity polyamide Nylon 6,6, it is believed that these copolymers may have utility as partially renewable engineering thermoplastics.

### **The Oleic Oils: Analysis from Demand to Supply.** F. Turon, FAT & Associes, France

Global end consumer industries are very interested in oleic oils for health and oxidative stability reasons. Current oleic supply is high oleic and is sunflower, soy and canola are in infancy, but growing quickly in US and Canada. The trans fat replacement in Latin America and Asia Pacific, and the saturated fats reduction in North America and EU27 will drive the future demand of Oleic oils. What segments of application would drive the growth? and how far the oleic oils supply would be able to keep up with the global demand till 2015? A scenario is proposed to answer such a questions.

### **Polyols Production by Chemical Modification of Palm Oil.** Arniza Mohd Zan, Zainab Idris, Tuan Noor Maznee Tuan Ismail, Seng Soi Hoong, Shoot Kian Yeong, Hazimah Abu Hassan, Malaysian Palm Oil Board, Kajang, Selangor, Malaysia

Palm oil is a commercial source of multifunctional monomers and oligomers for polyurethane synthesis. Wide variety of chemical modification of palm oil can be carried out to functionalize its structure with hydroxyl groups. In this study, a series of palm-based polyols, namely POP polyol, TEs polyol and Polymo polyol were prepared via different routes. These polyols have different valuable properties determined by the chemical composition. POP polyol was prepared by epoxidation of palm olein triglyceride and followed by ring opening of epoxidized palm olein triglyceride. The resulting polyol has hydroxyl value of approximately 150 mg KOH/g sample. TEs polyol was synthesized by transesterification of palm olein triglyceride followed by epoxidation and ring opening reaction. The hydroxyl value obtained for TEs polyol is 315 mg KOH/g sample, much higher than the POP polyol. For producing Polymo polyol, esterification of oleic acid was first carried out, followed by epoxidation and ring opening reaction. Polyol having a hydroxyl value of 240 mg KOH/g sample was obtained. Among the three types of polyol, TEs polyol have the highest hydroxyl value where higher hydroxyl value indicates higher functionality of the polyol. The different range of hydroxyl value leads to a variety of polyurethane materials with different industrial specifications.

### **Development of Bio Grease for Girth Gears.** Savita Kaul, Ponnekanti Nagendramma, R.P.S Bisht, M.R. Tyagi, Indian Institute of Petroleum, Dehradun, Uttarakhand, India

High performance lubricating grease resulted from Aluminium isopropoxide with benzoic, stearic and oleic acid complex soap thickener in residual base oils. Synthesized lubricating grease exhibited excellent mechanical stability, good oxidation stability, good extreme pressure and antiwear properties, good water resistance and corrosion inhibiting characteristics. The girth gear lubricating grease can also be used in modern plants having central lubrication system due to the fine spray able nature of grease.

# AFTERNOON

## IOP 5: Oleochemicals

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Chair(s): J. O. Metzger, University of Oldenburg, Germany; and D. Kodali, Global Agritech Inc/University of Minnesota, USA

**Oleochemicals: Challenges, Opportunities and Trends.** Bhima Vijayendran, Battelle Memorial Institute, Columbus, OH 43201, USA

Vegetable oil production for 2010-11 is estimated to be 145 million tons with over 15 million tons consumed in the production of traditional oleochemical industrial applications such as soaps and detergents, personal care and emulsifiers. In the last decade, the oleochemical industry has been growing steadily due to increased global demand for more environmentally friendly products. The presentation will highlight some of the recent developments in the field related to improved catalysts, traditional thermo chemical and emerging biochemical conversion technologies, availability of plant oils with various fatty acid compositions, and ability to use co-products from the crushing of seeds. Both conventional breeding and genetic engineered transgenic oil crops, to a lesser extent, are showing potential with increased yields and oils with tailored fatty acid compositions. These advances have helped oleochemicals to be well positioned for emerging applications such as bioplastics, biopolymers, biolubricants and others. The presentation will review few of the recent developments in bioproducts and their commercial status. Some of the challenges facing the oleochemical industry as well as opportunities will be addressed.

**Thermally Initiated Additions of Thiols to Unsaturated Fatty Compounds and Thiol Catalyzed cis-trans Isomerization of Methyl Oleate without Added Initiator.** U. Biermann, J.O. Metzger, R. Koch, University of Oldenburg, D-26111 Oldenburg, Germany

The radical addition of thiols to alkenes has attracted renewed interest as "thiol-ene click reaction". It has recently been recognized as a valuable tool for the synthesis of dendrimers, polymer modification, and polymerization reactions. The reaction was initiated by either thermal decomposition of azo derivatives or  $\gamma$ -irradiations, or by photochemically generated thiyl radicals. Remarkably, it can be performed thermally also without addition of any special initiator. The solvent-free reaction of thiol and methyl 10-undecenoate gave quantitatively the addition product. Chatgialialoglu showed that thiyl radicals are among the most efficient isomerizing agents, and observed an unknown thermal generation of thiyl radicals which could be of decisive importance in biological systems. We could show by kinetic studies that the thermal thiol catalyzed isomerization of methyl oleate is initiated by the formation of an EDA complex of thiol and alkene in a preequilibrium followed by MAH reaction of EDA complex and thiol to give a sulfuranyl radical being in equilibrium with thiol and thiyl radical. The latter catalyzes the isomerisation of methyl oleate.

**Fatty-Acids as Renewable Feedstocks in the Synthesis of Diols, Hydroxyesters and Polyesters Made Thereof.** Thierry Lebarbe<sup>1,2</sup>, L. Maisonneuve<sup>1,2</sup>, E. Cloutet<sup>1,2</sup>, Benoit Gadenne<sup>3</sup>, Carine Alfos<sup>3</sup>, Henri Cramail<sup>1,2</sup>, <sup>1</sup>Universte de Bordeaux-LCPO, Pessac, France, <sup>2</sup>CNRS - LCPO - UMR5629, Pessac, France, <sup>3</sup>ITERG, Pessac, France

Polyesters derived from renewable resources gained a widespread interest over the last decades since new semi-crystalline thermoplastics are needed. Poly(lactic acid) is commonly considered as one of the best candidates to replace polymers from petroleum. However vegetable oils are also gaining widespread interest thanks to their availability, sustainability and biodegradability. Vegetable oils methyl esters bring different functional groups (ester functions, double bonds, hydroxyl groups) that can be derivatized to design new functional building blocks for the synthesis of

novel polymers. In this present work, monomers with various functionalities were synthesized. Thus new building block diols from ricin and sunflower oils were designed for step-growth polymerization with bio-based diacids or diesters. Hydroxyesters and AB<sub>2</sub> type monomers were also studied in order to vary the macromolecular architecture of the polyesters made thereof. These building-blocks were obtained by transesterification, aminolysis, metathesis, epoxidation and thiol-ene reactions. Depending on the monomer structure, a large range of polyesters with various thermomechanical properties were obtained. The structure-properties relationship of the so-formed polyesters will be discussed in the presentation.

**Bio-renewable Plasticizers Derived from Vegetable Oil.** D.R. Kodali, L. Stolp, M. Bhattacharya, Department of Bioproducts and Biosystems Engineering, 203 Kaufert Lab, University of Minnesota, 2004 Folwell Avenue, St. Paul, MN 55447, USA

Plasticizers are non-volatile organic compounds that impart flexibility to polymers. The majority of plasticizers are used in polyvinylchloride (PVC), one of the oldest and widely used high volume plastics. Petroleum derived phthalates are the dominant class of plasticizers used in plastics industry. Phthalates are known to cause hormonal disruptions in humans and are not considered desirable for use in sensitive applications such as toys, food packaging, medical devices and others. So the plastics industry is actively looking for an alternative non-toxic, cost effective and high performance bio-plasticizers. In this study we present the synthesis and evaluation of a bio-renewable plasticizers from vegetable oils. A series of bio-plasticizers containing estolide ester functionality at the site of unsaturation are synthesized from soybean oil fatty acid esters. The structural variations include the head group and the estolide ester. The estolide esters are compounded with PVC at 20, 40 and 60 phr. The compatibility, glass transition temperatures, volatility and tensile strength of the compounded PVC are evaluated by DSC, TGA and Instron. The results indicate that the experimental materials performed comparable to commercial compounds. The synthesis, characterization, physical properties and functional evaluation of estolide esters will be presented.

**Film-forming Properties of Vegetable Oil-Synthetic Oil Blends in Elastohydrodynamic Conditions.** G.B. Bantchev, G. Biresaw, USDA, ARS, NCAUR, Peoria, IL, USA

There is a need for more environmentally-friendly and renewable lubricants that can be met by formulating lubricating blends with bio-based components. One of the most important properties of lubricants is its ability to form films between moving parts, such as those encountered in gears and bearings. In the presentation we will report the study of the viscosity and elastohydrodynamic (EHD) film thickness properties of binary blends of vegetable oils with synthetic oil. The viscosities of the blends were correlated with the predictions of existing theoretical models. The elastohydrodynamic film thicknesses were used to calculate the pressure-viscosity coefficients (PVC) of the blends. The results for the PVC are compared with the literature data for similar oils. The PVC of soybean and canola oils were close to the estimated ones from a single mixing rule. The film thickness and PVC of the blends containing castor oil displayed complex dependence on the composition of the blends and could not be fully described with the existing simple models.

**Characterization of the Solvent Properties of Oleochemical Carbonates.** T Huynh<sup>1</sup>, K Srinivas<sup>1</sup>, J.A. Kenar<sup>2</sup>, J.W. King<sup>1</sup>, <sup>1</sup>University of Arkansas, Dept. of Chemical Engineering, Fayetteville, AR, 72701, USA, <sup>2</sup>USDA, ARS, NCAUR, Peoria, IL, 61604, USA

Oleophilic carbonates, such as hexadecyl carbonate, can be characterized with respect to their solvent properties using inverse gas chromatography (IGC). Physicochemical properties of these renewable lipid derivatives are of importance for applications such as their use as phase change materials, fuel additives, and as reagents in chemical synthesis. Initial IGC measurements have been conducted using hexadecyl carbonate over the temperature range of 70 – 100 C. The logarithm of the solute specific retention volumes follow a linear trend with respect to the reciprocal of absolute temperature based on the solute's relative volatility or molecular weight. Solute mole fraction activity coefficients in the carbonate stationary phase are positive for four of the classes of solutes consisting of aliphatic hydrocarbons, select ketones, and homologous series of the lower aliphatic alcohols and acids; while negative deviations from Raoult's Law occur for the selected aromatic and chlorinated solutes. Similarly, weight fraction activity coefficients, Henry's Law constants, partition coefficients, and chi solute-solvent interaction parameters have been established for the six solute

classes. Chi interaction parameters support the use of aliphatic-, aromatic- and chlorinated solutes to dissolve in the lipophilic carbonates.

**Performance of Vegetable Oil-based Biolubricants.** J. Nie<sup>1</sup>, J. Shen<sup>2</sup>, Y. Wang<sup>3</sup>, M. Reany<sup>2</sup>, <sup>1</sup>Department of Food and Bioproduct Sciences, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, <sup>2</sup>Department of Plant Sciences, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, <sup>3</sup>Department of Food Sciences and Engineering, Jinan University, Guangzhou, China

Vegetable oils are typically over 95% triacylglyceride (TAG) a potential low-cost feedstock for biolubricant production. Properties of lubricants produced from TAG are strongly influenced by the constituent glycerol and the fatty acid profile. When compared with commercial lubricant oils vegetable oil has poor low-temperature performance and oxidative stability. These properties limit the application of vegetable oil directly as lubricants. In this work, the glycerol backbone of vegetable oil was replaced by trimethylolpropane (TMP), a colorless triol, via a two-step reaction. Optimization of the reaction afforded 100% yield of triester in the crude product. The low-temperature performance of enriched TMP triesters was analyzed by 500 MHz <sup>1</sup>H-NMR and oxidative stability index of the crude mixture was determined. The results suggest that biolubricant with improved low-temperature performance and good oxidative stability may be produced from vegetable oils by synthesis of fatty acid polyesters on alternative polyols.

**Evaluation of the Relative Oxidative Stability of Potential Lubricants Based on Ricinoleic Acid.** J.A.C. da Silva<sup>1,2</sup>, L. Yao<sup>2</sup>, E. Hammond<sup>2</sup>, T. Wang<sup>2</sup>, <sup>1</sup>Petrobras - Research Center - CENPES, Rio de Janeiro, RJ, Brazil, <sup>2</sup>Iowa State University - Department of Food Science and Human Nutrition, Ames, Iowa, USA

Ricinoleate esters have been shown to have desirable properties as biolubricants such as low melting point and ease of purification, but their oxidative stability has been questioned. Surface oxidation on silica gel was used to study the oxidative stability of these esters. Surface oxidation requires a modest amount of sample and gives accelerated oxidation rates because of the transition metal ions typically present in the silica gel, and the tests can be done at relative low temperatures. Methyl ricinoleate and Methyl 12-acetylricinoleate were prepared from castor oil. They were mixed with methyl palmitate, methyl linoleate, and Silica gel H and allowed to oxidize at 60°C. Methyl palmitate was assumed to be unchanged and the relative amount of the other methyl esters was determined. They disappeared, approximately following first order kinetics. The rate of oxidation per day of methyl linoleate was 0.9388, that of methyl ricinoleate was 0.0950, and that of methyl 12-acetyl ricinoleate was 0.0347. Methyl oleate oxidized too slowly to be measured under these conditions, but is regarded as ~ 10 times slower than methyl ricinoleate. The stability of these esters also was determined by the OSI method for comparison.

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## Industrial Oil Products Posters

**Chair(s): N. Soriano, Montana State University, USA**

### **Synthesis and Corrosion Inhibition Behavior of Imidazoline Derivatives Based on Vegetable Oil.**

Young-Wun Kim<sup>1</sup>, Kunwo Chung<sup>1</sup>, Seung-Hyun Yoo<sup>1</sup>, Joon-Seop Kim<sup>2</sup>, <sup>1</sup>Korea Research Institute of Chemical Technology, Daejeon, S. Korea, <sup>2</sup>Chosun University, Gwangju, S. Korea

Bio-diesel-based 1-(2-hydroxyethyl)-2-alkyl-2-imidazolines (HEAIs) were prepared as green corrosion inhibitors to investigate their corrosion inhibition behavior. As control materials, we also prepared the HEAIs using petroleum-based chemical products and measured their corrosion inhibition properties. It was found that when the HEAIs concentration was over 100 ppm, bio-diesel-based HEAIs acted as effective green corrosion inhibitors. It was also observed that the presence of double bonds and functional groups in the HEAI chain and the sufficiently long chain length enhanced the attachments of HEAIs on the metal surface, leading to high inhibition efficiency. Thus, it was suggested that the present work provided very promising results in the preparation of green corrosion inhibitors.

### **Optimization of Transesterification by CCRD.**

A Aryee<sup>1</sup>, P Dutilleul<sup>1</sup>, M Paszti<sup>2</sup>, B Simpson<sup>1</sup>, <sup>1</sup>McGill University, Ste. Anne de Bellevue, Quebec, Canada,

<sup>2</sup>Rothsay Biodiesel, Guelph, Ontario, Canada

Biostatistical approaches to interpolate enzyme-catalyzed reactions, generate models and predict patterns are critically important. In this study, the combination and variation of the magnitude of reaction parameters using statistical and mathematical techniques of response surface methodology (RSM) with central composite rotatable design (CCRD) was successfully applied to improve fatty acid ethyl ester yield of two oils recovered from fishery and animal discards and optimized the production process. The model fitting ability of the design and its capacity to identify significant coefficients and optimum conditions is presented. Optimum conditions were close to the centre point values of temperature, enzyme load, and oil: alcohol molar ratio for the various time studied (50°C, 8U, and 1:2). Response surfaces and contour plots of the determined coefficients are presented. ASTM methods for biodiesel (D6751-11) confirmed the presence of residual tri-, di-, mono-acylglycerol and FFA and also revealed significant proportion of moisture and dissolved glycerol in the transesterified oils. °

### **Biodiesel from Salt-tolerant Seashore Mallow (*Kosteletzkya virginica*).**

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Seashore mallow (*Kosteletzkya virginica*) is a halophytic perennial dicot that produces up to 1500 kg of seeds (22% oil) per hectare and is tolerant of saline soils and brackish water. FAMES were prepared in high yield by transesterification of hexane-extracted seashore mallow seed oil. The crude oil was initially treated with catalytic sulfuric acid and methanol to lower its acid value from 2.72 to 0.08 mg KOH/g, thus rendering it amenable to sodium methoxide-catalyzed methanolysis. The principal components identified in seashore mallow oil methyl esters (SMME) were methyl linoleate (48.9%), methyl palmitate (24.4%) and methyl oleate (18.3%). The fuel properties of SMME were within the specifications listed in ASTM D6751 and EN 14214 with the exception of oxidative stability, which was improved upon addition of 1000 ppm BHT. Of note was the high cetane number (59.9) of SMME along with its low iodine value (111 g I<sub>2</sub>/100 g), which both represent advantages over FAMES prepared from soybean oil. The properties of SMME blended with petrodiesel were within the ranges specified in the petrodiesel standards after the addition of BHT. In summary, seashore mallow is a promising feedstock for coastal areas that are not otherwise suitable for agricultural production.

### **Polyurethane Containing Crambe Oil Modified Polyester and its Clay Nanocomposites.**

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Crambe oil modified with trimethylolpropane synthesized oligomers (MW 1750) was prepared by the transesterification technique. The oligomers reacted with two different PU prepolymer with aromatic (TDI) and aliphatic (HDI) in different proportions (1:1, 1:2, 1:3). However, these obtained films are soft and need to be reinforced. Significant improvement of mechanical and thermal properties was obtained as the result of Laponite RD and Laponite RDS nanoclays addition, from 0.1 to 1%. Reinforced films were prepared by strong mechanical shear force. Studies on the degree of dispersion of nanoclays were performed. The degree of nanoclay dispersion in PU matrix and the resulting nanocomposites morphologies were evaluated using scanning electron microscopy (SEM) and X-ray diffraction. Scanning electron microscopy (SEM) images of the PU matrixes showed well dispersed material containing the intercalated and partially exfoliated nanoparticles. X-ray diffraction confirmed the presence of the silicate contents. The studies revealed well-dispersed, intercalated or partially exfoliated nanocomposites. Mechanical and thermal properties of the nanocomposites were improved as an effect of nanoclay addition. All results show the potentiality of these prepared nanocomposites to be used as an advanced material.

### **A Single Method for the Direct Determination of Total Glycerols in All Biodiesels Using Liquid Chromatography and Charged Aerosol Detection.**

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Biodiesel provides a clean and renewable, liquid fuel that can be used in current diesel engines and oil burners without any or significant modification. Using natural oils as a feedstock, ranging from virgin or waste cooking oils to algal oils, biodiesel is an esterified form of these oils. The simplest reaction uses a basic esterification reaction using methanol, sodium hydroxide and heating. The reaction esterifies the acylglycerols of the oil, producing fatty acid methyl esters (FAMES), which is the biodiesel fuel. Harmful impurities, existing as unreacted acylated and free glycerols must be removed to avoid fuel-system damage. The current ASTM method uses derivatization and gas chromatography, but it cannot be used for the analysis of in-process materials or biodiesel-petroleum blends. Other HPLC methods have separate methods for acylated or free glycerols, and another hydrolyzes the acylated glycerols to free glycerol, which is a loss of information. This normal-phase HPLC method provides a measurement of all acylated and free glycerols with a sample dilution and provides for an underivatized Free and Total Glycerides determination of all in-process, B100, and mixed petroleum blends, and it satisfies the current ASTM requirements.

### **Biocrude Production by Activated Sludge via Fermentation of Bagasse Hydrolyzate.**

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Raw municipal sewage activated sludge present a potential abundant source of lipid biofuel feedstock (biocrude). Previous studies have shown that sludge lipid contents can be enhanced by 70 % via batch cultivation in a high carbon-to-nitrogen (70:1) ratio wastewater medium with a high sugar load (60 g/L). Biodiesel yield from the enhanced activated sludge was also increased to 10 % CDW compared to 2-3 % in raw sludge. Cost analysis of the biocrude and biodiesel obtained from the sludge enhancement process have shown that the cost of the sugar substrate constitutes more than 80 % of the total production costs. Therefore, low-cost alternatives to pure sugars must be investigated as fermentation substrates. In this study, a hydrolyzate liquor obtained from mild acid pretreatment of sugarcane bagasse was tested as the substrate for biocrude production by activated sludge aerobic cultures. The hydrolyzate contains (in % w/v) around 60 % xylose, 10 % sugar dimers, and < 5 % each of glucose, galactose, and arabinose. It also contains the lignocellulose degradation by-products acetate (5 %), and around 2 % each of formic acid and furfural. Samples of the culture were then analyzed for biomass and biocrude yields, and residual sugars and degradation by-products.

### **Production, Recovery and Valorisation of Exotic Butters.**

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Butters are anhydrous and solid fats at room temperature mainly available in tropical countries. The family of the Sapotaceae family is of great interest because of the parenchyma contain articulated latex-bearers. Shea butter is an ancient African commodity, still playing an important role in the village's life. Its history is documented in the western world since the days of Mungo PARK. Shea butter is traditionally and locally used cooking and in cosmetic applications. After the colonial period, works have been done to develop industrial ways of producing shea butter: storage, drying, butter production, quality parameters,.. More recently, researchers have studied a new promising deep fat frying dehydration method of the kernels and the use of enzymes in order to improve the extraction rate. An example of manufacturing a CBE (called BK 778) is given. Other markets for Shea butter exist in the personal care industry due to its therapeutic benefits (ultra violet light protection, anti-inflammatory, moisturizing, regenerative, anti-eczema and anti-wrinkle properties) The unsaponifiable content is a key factor. ITERG worked and patented an interesting method of increasing the unsaponifiable content of Shea butter using cryogenic enrichment by fractionation. The final product can be enriched up to more than 50% of unsaponifiable and shows excellent dermo-cosmetic properties.

### **Vegetable Oils Incorporation in Kaolin and Bentonites.**

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Vegetable oils are important renewable raw materials for industry, and offer the possibility of a large number of uses, for example, in the cosmetic industry. In this work we studied the incorporation of almond oil, castor oil, mineral oil, Avocado oil and olive oil in several types of clays. We used a sample of Brazilian kaolin and 6 samples of Brazilian

bentonites, all in the form of powder. The clay samples were characterized by XRD, thermal analysis, IR, SEM, chemical analysis, cationic exchange capacity and ability of oil absorption. The ability of absorption (g oil/g clay) was determined by adding oil to a certain amount of clay, mixing with spatula and repeating the operation until the formation of a brilliant film that indicates the saturation of clay by oil. The obtained pastes were characterized by XRD and their plastic index was measured. The pastes have high potential for use in cosmetology.

### **Status of the USDA Federal Procurement and Labeling Programs for Biobased Products.**

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The BioPreferred program was created by the Farm Security and Rural Investment Act of 2002 (the 2002 Farm Bill) and expanded by the Food, Conservation, and Energy Act of 2008. BioPreferred includes two main components, which are a preferred procurement program for Federal agencies and their contractors, and a voluntary labeling program (implemented in February 2011) for targeting all consumers. An update on those program components will be presented, with a focus on the voluntary labeling program. Updated statistics on the USDA data base will be provided, along with updated statistics on products in the BioPreferred products catalog. For the labeling program, statistics will be provided on certification turnaround times, the number and types of products receiving the 'Certified Biobased Product' label, and the success rate in achieving product certification. The role of chemical intermediates in the labeling program will also be discussed, and an overview of chemical intermediates being pursued by the BioPreferred program will be summarized.

### **The Solubility of Free glycerin (FG) in Biodiesel (FAME) Products.**

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We report here the results of a study designed to better define the solubility of FG in FAME and commercial biodiesel blends as a function of temperature and fuel composition. FG is one of several impurities, including saturated monoglycerides and steryl glucosides, that can impact fuel operations. FG is routinely removed from FAME blend stocks by various separation processes to help meet engine performance and air pollution standards. Typically, physical processes such as gravity settling, or centrifugation are used to achieve better than 99% removal, taking advantage of its density and limited solubility. A final polishing, usually consisting of water washes or adsorbent based dry processes, is used to drive residuals below 0.02% to help meet fuel specifications. However, residual FG, well above 0.001%, is frequently found in purified commercial FAME biodiesel. Rogue, separated FG phases in the form of macro pools or micro emulsions are particularly onerous in fuel, and can go undetected until process and field performance is compromised. An improved understanding of solubility limits will help guide efforts to improve processing and performance.

### **Characterization of Biodiesel and Bio-oil from *Sterculia striata* Oil.**

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This work aims to evaluate the potential of *Sterculia striata* as source for liquid biofuels productions. Indeed, *Sterculia striata* seed oil was used as raw material to produce bio-oil and biodiesel and the physical/chemical properties of the products were investigated. It was determined that the products contain over 50% of fatty acids that have a cyclopropenoid ring in their structures (7-(2-octylcycloprop-1-en-1-yl)heptanoic acid - Malvalic Acid - and 8-(2-octylcycloprop-1-en-1-yl)octanoic acid - Sterculic Acid). Some of the studied physical/chemical properties of the *Sterculia striata* biodiesel are in acceptable range for use as biodiesel in diesel engines, showing a promising economic exploitation of this raw material in semi-arid regions. It was also observed that the cyclopropenoid ring remains after transesterification and is decomposed during pyrolysis.

### **Castor Oil Derivatives As Precursors For The Synthesis Of Perfumery Chemicals: Heptaldehyde.**

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Heptanal having herbaceous, fatty, fruity odour with sweet, almond taste is obtained with undecylenic acid by pyrolysis of castor oil. Heptanal and its derivatives are widely used in perfumery. The unstability of heptanal (aldehydes) in alkaline conditions produce alterations in odour and discolouration. To preserve the odouriferous character of heptanal, it is converted to its nitrile and other derivatives. In the present work, we converted the heptanal and its derivatives 2-methylidene -1-heptanal, 2-methyl-1-heptanal and few intermediates into respective nitriles; amides; alcohols; methyl, 2-phenoxy ethanol esters and methyl, ethyl, n-propyl acetals. The present paper reports the synthesis and olfactory characteristics of fourteen heptanal based perfumery compounds. We found that, few of the products have interesting olfactory characteristics like woody, ozonic, rosy, etc.; completely different from the parent molecule. Considering simplicity and low cost of materials, these methods seems to be promising one.

### **Preparation and Characterization of Biodiesel from Camel (hachi) Fat.**

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Recently biodiesel has been gaining market share against fossil origin diesel due to perceived ecological benefits and because it can be directly substituted for traditional diesel oils. However, the high cost of the raw materials required to produce the biodiesel make it a more expensive fuel than fossil diesel. Therefore, low-priced raw materials, such as waste cooking oil and animal fats are of interest as they can be used to drive the cost of biodiesel down. In this study, biodiesel was produced from camel fat using a transesterification reaction with methanol in the presence of sodium hydroxide (NaOH) as a catalyst and under standard reaction conditions. These reaction conditions were reaction time 2 h; catalyst addition at 1 wt% of initial fat weight; a molar ratio methanol:fat of 6:1; and a reaction temperature of 65°C. 94% biodiesel yield was thus obtained and analysis by gas chromatography showed that the contribution of saturated fatty acids in the biodiesel camel fat was 51 wt%. The fuel properties of biodiesel such as density, kinematic viscosity, sulfur content, carbon residue, water and sediment, high heating value, refractive index, cloud point, pour point, and distillation characteristics were measured. The properties were compared with EN 14214 and ASTM 6751 biodiesel standards and an acceptable level of agreement was obtained.

### **Mesoporous Basic Catalysts for Etherification of Glycerol.**

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Glycerol is a by-product from transesterification of vegetable oil; it can be used in various manufacturers such as food industry, cosmetic, plastic, drug, and etc. Since the increasing of biodiesel utilization, glycerol is nowadays expected to be oversupplied. This situation brings the price of glycerol to drop dramatically. Hence, it is so attractive to increase the value of glycerol by converting it into more valuable substances such as diglycerol. It can be utilized as a raw material to produce the surfactants in cosmetic area. The objective of this work was the study of glycerol etherification catalyzed by Magnesium Oxide on SBA-15 and Calcium Oxide on SBA-15 with the variation of temperature from 230 to 250 °C in order to produce diglycerol. The results showed that the highest glycerol conversion was observed when using Calcium Oxide on SBA-15 as a catalyst and the temperature was at 250° C. In addition, the catalysts were characterized by several instruments such as BET surface analysis, X-ray Fluorescence, and X-ray Diffractometer (XRD).

### **Life Cycle Assessment of Safflower Originated First and Second Generation Engine Biofuels in Turkey.**

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Biofuels are a clean alternative to the fossil fuels and they are used to partly replace fossil fuels with environmental and economical benefits. They are classified as first, second, third and fourth generation biofuels. First generation diesel engine biofuels cover biodiesel (fatty acid methyl esters) and second generation diesel engine biofuels cover

fatty acid ethyl esters. Higher production costs and biofuel versus food and feed increase the importance of new oil seed resources and safflower is one of the most appropriate feedstock for biodiesel production in Turkey, today. Life cycle analysis, which is called also as "cradle to grave approach" aims to quantify environmental impacts and energy requirements of products over their full lifetime. This study covers a comparison between the life cycle assessment of safflower originated first and second generation biofuels in Turkey. The life cycle assessment of these biofuels are done for the first time in Turkey according to the ISO 14040 series by using SimaPro 7.2 LCA software, Ecoinvent database, real data from safflower and sugar beet originated ethanol suppliers in Turkey and the Eco-indicator 99 methodology. The results of the safflower ethyl esters are given for the first time in the literature and a comparison between these engine biofuels is given.

### **Methyl Ester Production from Hazelnut Oil with Microwave Assisted Method.**

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In this study, transesterification of hazelnut oil was studied by using microwave assisted method to examine reaction factors which affect the yield of the ester product, including the molar ratio of methanol to hazelnut oil, the amount of alkaline catalyst, and the reaction time. Methyl ester from hazelnut oil has not been produced before by using the microwave-assisted method in the literature. Also, Turkey is the first world hazelnut producer and hazelnut oil production is extremely high. So, hazelnut oil can be evaluated in the different areas such as a methyl ester production. The transesterification reactions were carried out by using hazelnut oil, methanol and potassium hydroxide as the catalysts at 64°C. A statistical design technique was applied by the use of a two-level factorial design matrix to interpret the experimental results and analysis of variance is made to analyze data and to check the adequacy and accuracy of the fitted models. Empirical relations between the methyl ester yield and the reaction conditions were developed. The experimental results indicated that microwave assisted transesterification efficiently produced high yield of methyl esters in a short reaction time, showing that this method may be a promising alternative to the conventional method.

### **Citrus Seed Oil: A Novel Source for Biodiesel Production.**

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Response surface methodology (RSM) was appraised for process optimization due to the strong interaction of reaction variables: NaOCH<sub>3</sub> catalyst concentration (0.75-1.50%), methanol/oil molar ratio (3:1-12:1), reaction time (20-90 min) and reaction temperature (35-65°C) for methyl esters production from citrus seed oil. The quadratic polynomial equation was evaluated using RSM for predicting the optimum methyl esters yield. The analysis of variance (ANOVA) indicated significant ( $p < 0.0001$ ) interactions between molar ratio  $\times$  catalyst concentration, molar ratio  $\times$  reaction temperature, catalyst concentration  $\times$  temperature and catalyst concentration  $\times$  time, mostly effect the CSOMEs yield. The optimum CSOMEs yield (88.1%) was obtained at 7.5:1 methanol/oil molar ratio, 1.00% catalyst concentration, 63°C reaction temperature and 75-min reaction time. Based on the residual analysis, the appropriateness of the central composite design was acceptable. The CSOMEs was analyzed by gas chromatography (GC), elucidated five fatty acid methyl esters (linoleic-, palmitic- oleic-, linolenic-, and stearic- acids). The fuel properties of CSOMEs were found to be completely satisfy ASTM D 6751 and EU 14214 specifications.

### **High Quality Biodiesel Production from Waste Acid Oil Using Ion-exchange Resins as Catalysts and Adsorbents.**

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Biodiesel has received much attention as a clean and renewable fuel. However, the refining vegetable oils with low free fatty acid content, <0.5wt%, are mainly used as its feedstocks. This causes increases in not only the production cost of biodiesel but also the price of cooking oils. In this research, an acid oil dumped during the cooking oil processing and consisting of about 95wt% of free fatty acids and 5wt% of triglycerides, was used as a new cheaper

feedstock. The acid oil was efficiently transformed to high quality biodiesel by combining esterification of free fatty acids using the cation-exchange resin catalyst, and transesterification of a trace of triglycerides and adsorption of byproducts, water and glycerin, using the anion-exchange resin catalyst. The experiments of biodiesel production from a rice bran acid oil, donated by the rice bran oil company, were performed. The free fatty acids and triglycerides in the oil could be completely converted to biodiesel at the stoichiometric molar ratio of methanol to fatty acid residue. The dark brown pigment in the oil as well as the byproducts could be removed by adsorption on the resin. The product biodiesel almost met the standards for fuel quality in Japan and the USA.

### **Chemical Composition and Physicochemical Properties of *Acacia senegal* (L.) Willd. Seed Oil.**

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This study was conducted to evaluate the physicochemical properties of oil extracted from *Acacia senegal* (L.) Willd. seeds. The oil content, the moisture and the ash content of the seeds were 9.80%, 6.92% and 3.82%, respectively. Physicochemical properties of the oil included: iodine value 106.56 g/100 g of oil; saponification value, 190.23 mg KOH/g of oil; refractive index (25°C), 1.471; unsaponifiable matter, 0.93 %; acidity, 6.41 % and peroxide value, 5.43 meq. O<sub>2</sub>/kg of oil. The main fatty acids in the oil were oleic acid (43.62%) followed by linoleic acid (30.66 %) and palmitic acid (11.04%). The triacylglycerols (TAGs) with equivalent carbon number (ECN) 44 (34.90%) were dominant, followed by TAGs ECN 46 (28.19%), TAGs ECN 42 (16.48%) and TAGs ECN 48 (11.23%). The thermal stability analysed in a normal oxidizing atmosphere, showed that the oil decomposition began at 268.6°C and ended at 618.5°C, with two stages of decomposition at 401.5°C and 576.3°C. According to these results, *A. senegal* seed oil has chemical composition and physicochemical properties that may be suitable to be used in food and non-food products.

### **Pre-treatment of Acidic Crude Palm Oil Using Strong and Weak Acids.**

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Pre-treatment of acidic oils such as acidic crude palm oil (ACPO) is an essential stage in biodiesel production. This study investigated the effect of using weak acids such as (H<sub>3</sub>PO<sub>4</sub> and CH<sub>2</sub>O<sub>2</sub>) and strong acids such as (HCl, H<sub>2</sub>SO<sub>4</sub> and C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S.H<sub>2</sub>O) in the pre-treatment stage of ACPO. The studied strong acids outperformed weak acids in terms of FFA content reduction. The conversion of FFA to FAME using weak acids was low compared to the corresponding strong acids. Using C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S.H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub>, The FFA content was decreased from 10 to less than 2%. Consequently, this study selected C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S.H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> in the pre-treatment of ACPO and for further optimization of the esterification process. This selection was based on cost effectiveness and catalytic activity of both strong acids.

### **Effect of Beta Hydrogen on Thermal Stability of Biolubricant Esters.**

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The thermal stability of lubricants derived from vegetable oils is an important concern. It has been suggested that the stability of triacylglycerols is lowered by the presence of a hydrogen atom on the β-position of their glycerol and that alcohols without such a hydrogen, e.g. trimethylolpropane, would form esters with greater thermal stability. However, the evidence for this theory is weak. To test this hypothesis, we synthesized triacetate esters of trimethylolpropane and compared its stability with that of commercial glycerol triacetate (triacetin). Thermal gravimetric analysis and differential scanning calorimetry indicated losses for both compounds but it was difficult to distinguish evaporation from decomposition. Reflux heating at 160 to 200°C for several days generated strong odors of acetic acid in both

esters, and gas chromatographic measurement of the original esters showed losses for both. The disappearance of triacetin followed first order kinetics, while trimethylolpropane quickly lost about 20% of its weight and then stabilized. These results do not support the hypothesis that absence of a structure similar to the  $\beta$ -hydrogen of glycerol delivers greater heat stability to esters.

### **Antioxidant Activity of Phenolic Extracts from *Jatropha cordata* and *Jatropha cardiophylla* Seed Cakes in Soybean Biodiesel.**

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*Jatropha cordata* (JC) and *Jatropha cardiophylla* (JCp) are species natives of Northwest of Mexico and Southwest of E.E.U.U. adapted to arid and semi-arid conditions. These plants produce seeds with oil content about 35%. The residual seed cake after oil extraction could be an important source of phenolic compounds. The phenolic compounds of JC and JCp seed cakes were extracted using 60:40 (v/v) methanol/water mixture. The antioxidant activity in soybean biodiesel of these extracts was performed by Rancimat method. The antioxidant activity of the extract was compared with the tertiary butyl hydroquinone (TBHQ) and butylated hydroxyanisole (BHA) activity, at the same concentrations (0.025, 0.05 and 0.1%). The antioxidant activity of the extracts and the synthetic antioxidants on soybean biodiesel increased as increased the concentration. The TBHQ showed a higher activity (8.8 h) followed by BHA (7 h) at 0.1%. No significant differences ( $p > 0.05$ ) were observed on the antioxidant activity of methanolic extracts of JC (6.67 h) and JCp (6.5 h) and synthetic antioxidant BHA, at the same concentration. The methanolic extracts from JC and JCp are a good source of natural antioxidants with antioxidant activity.

### **Methods for Extraction, Isolation, and Quantification of Insoluble Constituents in Canola Biodiesel.**

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Steryl glucosides (SG) and other biodiesel insoluble constituents may cause fuel filter plugging and engine performance issues at low temperatures. Laborious sample extraction and quantification procedures make analysis of minor biodiesel precipitates difficult. While much research has focused on the identification of steryl glucosides and other minor seed constituents from palm, soybean, and European rapeseed feedstocks, little information is available on steryl glucoside content or other insoluble materials associated with North American canola (*Brassica napus*) feedstocks. The objectives of this research is to evaluate HPLC and FTIR spectroscopy as methods for detecting and quantifying insoluble components obtained from canola biodiesel. The relationship of acylated steryl glucosides (ASG) in canola oil with SG in canola biodiesel can also be evaluated during bench scale biodiesel processing. In addition, the validation of these methods is crucial to retain the highest degree of recovery, robustness, and repeatability. These are the defining factors reflected in the results and discussion section when determining the best methods for analysis, extraction, isolation, and purification of insoluble compounds in canola biodiesel.

### **Hydrocracking and Hydroisomerization of Hydrogenated Biodiesel for Producing Bio-jet Fuel over Pt, Ir Supported H-Y Zeolite and ASA Catalysts.**

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Bio-jet fuel is a renewable fuel and an interesting alternative source for aviation fuels in the future. In this research, bifunctional noble catalysts i.e. Pt/H-Y, Ir/H-Y, Pt/ASA and Ir/ASA were studied for their activity in producing bio-jet fuel from hydrogenated biodiesel derived from jatropha oil (C15 to C18 hydrocarbons). The optimum reaction conditions of selected catalysts were elucidated. The catalysts were prepared by incipient wetness impregnation (IWI), characterized by TPR, TPO, TPD and BET and tested in a continuous flow packed-bed reactor at 290 °C to 320 °C, 500 psig to 600 psig, liquid hourly space velocity (LHSV) of 0.5 h<sup>-1</sup> to 2.0 h<sup>-1</sup>, and H<sub>2</sub>/feed molar ratio of 30. The results showed that the major products obtained over Pt/H-Y, Ir/H-Y, Pt/ASA and Ir/ASA were n-pentane (n-C5) to n-nonane (n-C9) which were in the gasoline specification range. H-Y zeolite support was stronger acidity and higher selective for bio-jet fuel than ASA support. Pt/H-Y catalyst gave a jet fraction (23% biojet yield) with a lower gasoline

fraction which could result from the hydrogenation on metal sites.

### **Synthesis and Study of Bioplasticizers Derived from Vegetable Oils used with PLA.**

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Plasticization of polymer is a real challenge. Ideal plasticizers should be compatible with polymers, insensitive to solar radiation, leaching and migration resistant, stable in both low and high temperature environments, inexpensive, health safety and improve the flexibility and processability of resins. Traditional plasticizers as phthalates are generally efficient but the main drawbacks are their toxicity (they are restricted in some applications), their migration out the polymer and they are from petroleum-based raw materials. Legislation, industrial safety, economical and environment aspects play an important role and led to the development of new type of plasticizers from renewable resources. The aim of this research is divided into two parts: first at all, the synthesis of several bioplasticizers from vegetable oils and secondly the study and comparison of their performances into different polymers.

### **Advances in Biodiesel Production and Quality Improvement: The In Situ Transesterification of Corn Germ, and the Removal of Saturated Monoglycerides via Enzyme-Catalyzed Transesterification.**

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The U. S. fuel ethanol industry generates approximately 1 billion gallons of coproduct corn oil annually. There is interest in its development as a biodiesel feedstock. We have explored the application of in situ transesterification, which eliminates the need for oil extraction and degumming, to the production of biodiesel from corn germ generated during ethanol production. Optimal conditions for the conversion of at least 80% of the resident corn oil to FAME will be described. In addition, a process for reduction of the saturated monoglyceride (MAG) content of biodiesel will be described. The last intermediate in the production of biodiesel from triacylglycerols, MAG can persist in finished product biodiesel. Saturated MAG have been implicated in the formation of solids that block fuel delivery systems and jeopardize engine operability. Lipase-catalyzed transesterification has been shown effective in eliminating saturated MAG from biodiesel.

### **Synthesis of Dimer Acid and Esters from Fatty Acid and Fatty Acid Methyl Ester Based on Used Vegetable Oil.**

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Dimer acid derivatives for monomers of eco-friendly polymers were synthesized by Diels-Alder reaction of fatty acid or fatty acid methyl ester prepared from used vegetable oils. C18 fatty acids (or fatty acid methyl esters) with one or more double bonds reacts with each other at temperatures of about 210-250°C in the presence of catalysts forming a complex mixture C36 dimer fatty acid (or methyl esters), C54 trimer fatty acids (or methyl esters), and C18 monomer fatty acids (or methyl esters), respectively. In this study, dimer acid derivatives were prepared through a green two-step to obtain cyclic C36 dimer fatty acid and methyl esters as good yields. The first step was to obtain the conjugated linoleic acid derivatives (CLA) through isomerization from linoleic acid derivatives. The second step was to give dimer acids using CLA and oleic acid derivatives catalyzed by catalysts.

### **Synthesis and Characterization of Polyurethane Coatings with Low Volatile Organic Compounds.**

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Polyurethane (PU) is a versatile polymer, its application in coatings technology is widely used for resin of high-performance. However, the solvents used in this application have are high volatile organic compounds like: toluene, benzene, xylene, etc. In this paper we were synthesized and characterized two PU pre-polymers from: toluene-

diisocyanate (TDI) and hexamethylene-diisocyanate (HDI) with solvents derived from acetate and other green solvents. In addition, we have been interested in using vegetable oils as cheap and bio-renewable raw materials in prepolymer and polyols. The PU coatings were synthesized with prepolymer derived mainly from castor oil, polyols from ricinoleic acid, and crambe oil oligomers at NCO/OH proportions 1:1, 2:1 and 3:1. Curing process of the films were carried out under laboratory atmosphere. The films were analyzed by FTIR, TGA/DTA, dynamic mechanical thermal analysis instruments (DMA) and the coating films on metal and glass surface were characterized by their hardness and adhesion. FTIR data indicated that the prepolymer reacted with oligomers, because of the disappearance of NCO-band at 2270  $\text{cm}^{-1}$ . The films showed good thermal stability ( $> 200^\circ\text{C}$ ) and mechanical properties. Films derived from crambe oil were softer than ricinoleic acid mainly in the pre polymer from HDI.