2011 Annual Meeting Abstracts

Industrial Oil Products

MONDAY

MORNING

IOP 1: Alternative Fuels

Chair(s): R. Dunn, USDA, ARS, NCAUR, USA; and R.W. Heiden, R.W. Heiden Associates LLC, USA

Will Biodiesel Fuels Derived from Algae Perform? G. Knothe , USDA, ARS, NCAUR, Peoria, IL, USA

The issue of sufficient supply and availability of feedstock is one of the major non-technical issues affecting the widespread commercialization of biodiesel. Another aspect is the food vs fuel issue that biofuels should not be produced from edible feedstocks. In these connections, lipid-producing microorganisms, algae, have found considerable attention recently. Most research has been focused on production-related issues such as growth and harvesting of the algae as well as obtaining the oils. The fatty acid profiles of many algal oils have been reported. However, hardly any reports deal with fuel properties and performance of the corresponding biodiesel fuels. Therefore, the properties and performance must be estimated from the fatty acid profiles. As the fatty acid profiles of many algal oils contain significant amounts of saturated (palmitic acid probably being the most common fatty acid in algal oils) and polyunsaturated fatty acids, biodiesel fuels derived from them likely would exhibit problematic cold flow and oxidative stability behavior. Therefore, it appears advisable that research on algae-derived biodiesel fuels should also focus on producing oils with fatty acid profiles more suitable for this purpose.

The Effects of Minor Constituents on Biodiesel Cold Flow Properties: Differential Scanning Calorimetry (DSC) Analyses. R.O. Dunn, Food & Industrial Oils Research, USDA, ARS, NCAUR, USA

Biodiesel is an alternative diesel fuel made from vegetable oils, animal fats and other lipid feedstocks. Fuel properties and performance of biodiesel during cold weather are influenced by factors related to lipid feedstock as well as small concentrations of monoacylglycerols and other minor constituents. This study applies a thermodynamic model based on the Hildebrand equation to determine the effects of small concentrations of minor constituents on crystallization onset temperature of biodiesel. DSC curves were analyzed to determine melting point (MP) and enthalpy of fusion of various FAME components, monopalmitin, monostearin, monooleate, distearin, tristearin, palmitic acid, stearic acid, glycerol and water in pure form. Data calculated from thermodynamic models were compared with direct experimental measurement of CP of corresponding mixtures of FAME and constituents.

Conversion of Algal Oil to Biodiesel via Heterogeneous Transesterification. D. Sams, Catilin, Inc., Ames, IA USA

Catilin, Inc has developed process technology to convert algal oil to biodiesel via transesterification. The process uses a heterogeneous catalyst and operates at 160F and 1 atm total pressure. The T300 catalyst is a granular solid that is mixed into a continuous stirred tank reactor (CSTR) which allows for catalyst replacement during normal operation to maintain targeted catalyst activity. The algal oil must be partially refined such that the free fatty acid (FFA) level does not exceed 1% vol. The biodiesel is distilled to minimize the monoglyceride level while the glycerin is recovered at 98-99% purity without additional processing. The catalyst does not contain added metals and is non-hazardous and non-toxic.

Characterization of Activated Sludge Oil Lipidic Components. P.J. Pham, R. Hernandez, E. Revellame, W.T. French, A.H. Mondala, R. Callahan, J.D. Cain, Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762 USA

Current petroleum energy issues have evoked the requisite search for alternative sources of energy. In this study, activated sludge oil (ASO) extracted from activated sludges obtained from five wastewater treatment facilities around Mississippi was characterized to provide information for ASO refinement. The refining process and subsequent optimization will improve activated sludge as a feedstock for biodiesel production as well as a source of value-added products. The ASO extracts were fractionated into five ASO solvent fractions. Lipidic profiles for the ASO hexane (HX), chloroform ($CHCl_3$), acetone (ACE), methanol (MeOH) and MeOH/ammonium hydroxide (HPC) fractions for the wastewater treatment facilities were obtained using gas (GC) and liquid (LC) chromatographic techniques. The ASO HX fraction contained mostly hydrocarbons. The ASO $CHCl_3$ fraction consisted of fatty acids, sterols, diglycerides, steryl esters and triglycerides. The ASO ACE and MeOH fractions were analyzed for glycolipids and phospholipids, respectively. Phospholipid profiles were obtained using ^{31} P NMR Spectroscopy. The fatty acid methyl ester (FAME) profiles revealed methyl palmitate and oleate as the major FAMEs present. Employing activated sludge can reduce feedstock cost, however refining requires additional expense. Other components obtained before and through the refining process will thus be essential.

The Use of Free Fatty Acids as Additives for Improving the Efficiency of the Supercritical Synthesis of Ethyl Esters from Vegetable Oils. I. Vieitez, B. Irigaray, P. Casullo, M.A. Grompone, I. Jachmanián, Laboratorio de Grasas y Aceites, Departamento de Ciencia y Tecnología de los Alimentos, Facultad de Química, Universidad de la República, 11800-Montevideo, Uruguay

Previous studies showed that high efficiencies can be achieved performing the catalyst-free transesterification of vegetable oils in supercritical alcohols. However, the main drawback of this method is the occurrence of the decomposition of unsatured fatty acids, due to the high temperatures that must be used. Therefore, temperature appears as the critical parameter to be controlled in order to maximize the efficiency of the process without promoting the decomposition of the lipid raw material. This work studied the effect of adding free fatty acids on soybean, rice and high oleic sunflower oil at different proportions on the efficiency of their

supercritical ethanolysis. Reactions were performed in a continuous tubular reactor of 39mL, at 20MPa, 300 to 350ºC, using a molar ratio oil/ethanol of 1:40 and flow rates from 0.8 to 2.5mL/min. When the continuous reactor was operated at 300ºC without adding FFA to the oil, an ester content of 53% was obtained, while at identical conditions but processing a soybean oil with 10% of FFA, the ester content raised to 91%.Results showed that the addition of free fatty acids is a useful tool for favoring alcoholysis against decomposition, whit the consequence of a substantial increase in process efficiency.

Biodiesel Production by Direct Transesterification of Activated Sludge using Supercritical Methanol. A. Coker[1], R. Hernandez[1], T. French[1], A. Iretski[2], M. White[1], E. Revellame[1], W. Holmes[1], [1]Mississippi State University, USA, [2]Lake Superior State University, USA

Our research group has demonstrated the production of fatty acid methyl esters (biodiesel) using activated sludge generated from a wastewater treatment facility. However, drying of sludge prior to oil extraction is a major operating cost of this process. To address this challenge, we have conducted a study to determine the yield of biodiesel produced from reacting wet sludge using only supercritical methanol. Activated sludge was obtained from a wastewater treatment plant and an approximate composition of 85% water and 15% solids was reacted with methanol using a methanol: solids ratio of 30:1 (mass basis) at 300 °C for 12 -16 hours. Analysis of the product by Gas Chromatography-Mass Spectrometry (GCMS) showed a number of fatty acid methyl esters (biodiesel) such as methyl linoleate and methyl palmitoleate. This work will show the optimization of temperature, reaction time and methanol volume for the production of biodiesel from sludge with high water content. Since sludge has approximately 5% lipids in it and variability in its constituent compounds, the authors also used a model system of oleagineous yeast - Rhodotorula Glutinis to evaluate the production of biodiesel in a system similar to sludge. The kinetics from this system will be presented as well.

ZnO-based Heterogeneous Catalysts for the Second Generation of Biodiesel. S. Yan[1], C. DiMaggio [2], S. Mohan [2], M. Kim [2], H. Wang [2], L. Yang [2], S. Salley [2], K. Ng [2], [1]NextCAT Inc., Detroit, MI, US, [2]Department of Chemical Engineering and Material Science, Wayne State University, Detroit, MI, US

Biodiesel is a domestic, renewable, non-toxic, and biodegradable fuel derived from vegetable oils and animal fats. The ?fuel vs. food? debate has an unfavorable impact on the biodiesel industry, since the majority of biodiesel is currently produced using refined edible oils. Using waste oils is one of the economical sources for biodiesel production. However waste oils generally contain some content of FFA. The current catalytic approach is to use a H2SO4 and NaOH combined process to handle oils with high FFA content. A novel process is developed based on Zn-mixed oxide catalysts, which effectively converted crude soybean oil, crude coconut oil, crude palm oil, crude corn oil from DDGs, crude algae oil, waste cooking oil brown grease, crude algae oil and waste fishing oil into FAME. Under the conditions of 160 g of acidic oil (containing 14.1 % of oleic acid), 36 g of methanol, 1.5 g of catalyst, 200 oC, 280 Psi, 60 min, FAME yield could be as high as 81 %. This series of catalyst also shows a long durability in converting soybean oil into biodiesel. Catalyst structure was characterized and found that the acidic groups on catalyst surface played an important role in esterification reaction; and the base groups catalyze transesterification reaction.

Biodiesel/ULSD Blend Ratios by Analysis of Fuel Properties. Robert Dunn, USDA, ARS, NCAUR, Peoria, IL, USA

Biodiesel is an alternative fuel that is made from vegetable oil or animal fat. Biodiesel is often blended with ultra low sulfur diesel (ULSD; 15 mg/kg maximum sulfur content) in volumetric ratios (VBD) of up to 20 vol% (B20). Government tax credits and other regulatory requirements may depend on accurate verification of biodiesel blend ratio levels (VBD). A survey on biodiesel/petrodiesel blends conducted in Spring 2007 in Michigan reported that 15 of 19 different B20 samples were actually no more than B10 (see Tang et al., Fuel 87, 2951-2955, 2008). Many laboratory instruments capable of accurately determining VBD of biodiesel/ULSD blends are expensive to acquire and maintain. This work explores the use of calibration curves based on more cost-effective analysis of fuel properties that may also be conducted with portable instruments in the field. Curves derived from regression analyses of VBD versus kinematic viscosity, specific gravity (SG), cloud point (CP) and refractive index (RI) were evaluated for methyl esters of soybean oil (SME) and used cooking oil (UCOME) in blends with ULSD. Results showed generally high coefficients of regression (> 0.986) with models based on SG data demonstrating accuracy for determining VBD to within 1.3 vol%.

Interactions of Biodiesel Impurities that Alter the Solubility of Saturated Monoglycerides. Richard W. Heiden[1], Martin Mittelbach[2], [1]R.W. Heiden Associates LLC, Lancaster, PA, USA, [2]Karl Franzens-University Graz, Graz, Austria

Insoluble matter that forms in-situ during biodiesel B100 and blend storage has occasionally lead to rashes of fuel filter blockages, particularly during cold weather at temperatures above the cloud point. Laboratory analyses of materials collected from field failures of filters have implicated mainly steryl glucosides and saturated monoglycerides (SMG). Through a judicious choice of feedstocks and manufacturing process controls, such incidents can be reduced in severity and frequency. How-ever, these actions can increase the cost of production substantially, and firm, feedstock neutral footing that guides manufacturers to prevent such incidents is lacking.To address this need, we have undertaken studies to elucidate the mechanisms of precipitate form-ation, the aggravating and ameliorative factors. In previous presentations the solubility of the SMG as a function of temperature and blend composition was discussed, and data showing a possible inter-action between partial glyceride species that affect-ed the solubility was shown*. Now, we present new data that estimates the magnitude of interactions between the SMGs and several other biodiesel im-purities. The results of these studies and the types of chemical interactions are discussed.*R.W.Heiden, "Solubility Limitations of SMG..During Cold Weather", AOCS Meeting, May 17, 2010.

Panel Discussion.

AFTERNOON

IOP 2: Biobased Lubricants, Plasticizers, and Value-Added Products

Chair(s): D. Kodali, Global Agritech Inc., USA; and H. Ngo, ARS, USDA, ERRC, USA

Novel Soy Based Urethane and Soy Based Thiol Resins. Jon Nietfeld [2], Jennifer Wu[1], Shashi Fernando[1], Bathiya Warnakula [1], Dimuthu Weerasinghearachchilage [1], Jinling Yan [1], Zhigang Chen [1], Dean Webster[1,2], [1]Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, ND, USA, [2]Department of Coatings and Polymeric Materials, North Dakota State University, Fargo, ND, USA

With rising petroleum prices and stricter environmental regulations, there is a great demand for renewable materials that have low VOC content. Our group has been working on soy based functional resins for industrial applications with the objective to expand the portfolio and improve the performance of soy based resins. Two groups of novel soy resins are discussed in this presentation. First, a set of UV-curable soy urethane acrylate monomers and oligomers are synthesized via facile isocyanate-free synthetic routes. The synthetic routes and corresponding characterizations are described along with some improved basic properties of the UV cured materials. Another set of soy based resins are multi-functional soy-thiol oligomers produced via direct, thermal induced free radical thiol-ene reactions. The synthesis and characterizations of these soy-thiol oligomers are presented. The soy-thiol oligomers find potential applications in UV curable materials and thiourethane materials.

Zeolite-Catalyzed Additions of Aromatic Compounds to Oleic Acid. H. Ngo, P. Fox, M.J. Haas, USDA, ARS, ERRC, USA

There is significant research interest in developing new materials from vegetable oils and animal fats. Biobased materials can be more environmentally friendly because they tend to have good biodegradability and are derived from renewable resources. In this talk, efficient approaches for the addition of aromatic compounds to vegetable oil, i.e., oleic acid, at the internal olefinic site using zeolite catalysts will be presented. A number of experimental parameters were examined, including different catalysts, reaction components and their ratios, and reaction conditions (such as time, temp., and pressure). The reactions were typically performed at high temperature (150-280oC) and elevated pressure (

Model Reaction for Vegetable Oil-based Polyurethane by Nonisocyanate Route. Jian Hong, Doo Pyo Hong, Ivan Javni, Zoran S. Petrovic, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS, USA

Polyurethanes can be made from carbonated vegetable oils and diamines. This route eliminates the need for isocyanates, but there are disputes about whether the amine reacts with only the carbonate group or also with ester group in the oil chains. To clarify, we synthesized carbonated methyl oleate and 9-octadecene then reacted with amine or diamine as model reactions. The products were characterized with FT-IR, GC-MS and GPC. FT-IR spectra of products showed absorbance peak of amide group. GC-MS and GPC results showed products contained some from the reaction of amine and ester group. Our results suggest that the amines not only reacted with carbonate group but also with ester group. The effect of hydroxyl groups formed during the

reaction is being studied.

The Effect of Nano and Micro Clay Fillers in Bio-based Thermoplastic Polyurethanes. I. Javni, O. Bilic, D.-P. Hong, Z.S. Petrovic, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS, USA

Thermoplastic polyurethanes (TPU) have a wide range of hardnesses including the elasticity of rubber and the processability and recyclability of thermoplastics. TPUs are formed by reacting polymeric diols and chain extenders with diisocyanates. We synthesized diols by the hydroformylation and polymerization of methyl oleate and prepared TPUs by reaction with diphenylmethane diisocyanate and 1,4-butanediol chain extender. The objective of this study was to examine the effect of nano-clays (surface treated and non-treated montmorilonite) and micro-clay fillers on properties of bio-based segmented polyurethanes. TPUs have segmented structures consisting of soft, elastic segments and hard segments, and fillers can interact with both. Improvement of elastic properties of elastomers would be expected if fillers interact strongly with fatty acid-based polyester soft segments. Interactions of fillers with hard segments could change hard domain crystallization and alter physical properties in a negative way. All fillers increased modulus of elasticity, but decreased tensile strength and elongation. The fillers did not significantly affect the glass transition temperature or thermal stability of the material.

Emerging Sustainable Technology for Biomass-based Plasticizers and Application Perspective. Zheng Guo, Department of Molecular Biology, Aarhus University, Aarhus, Denmark

The chemical industry increasingly looks to sustainable technology in order to reduce environmental impact and minimize footprint of chemical process. This work presented the emerging technologies from academia and industry in the development of alternative plasticizers to phthalates and epoxidized soybean oil (EPSO), and the progress of our group in enzymatic production of new generation of plant oil-based plasticizer. Particular attention will be given to principle and strategy of application of green processes, new media design and application, and effects of medium properties the selectivity and conversion. As a representative of part of the strategy, all about ionic liquid-mediated reactions for production of sustainable plasticizer were intensively presented.

Lipid Storage Compounds in Raw and Enhanced Activated Sludges. E. Revellame, R. Hernandez, W. French, W. Holmes, Mississippi State University, Mississippi State University, MS, USA

Raw activated sludges obtained from wastewater treatment facilities were analyzed for lipid storage compounds. The lipids from the sludges were extracted using Bligh and Dyer extraction protocol. Polyhydroxyalkanoates from the extracts were isolated by precipitation in methanol. Separation of other storage compounds from the PHA-free extract was done by solid phase extraction (SPE) using 1000 mg silica columns. Initial results showed that the extract from raw activated sludges contains (by wt.) PHAs (1.8?4.4 %), triacylglycerides (2.0?3.0 %), sterols (6.2?12.4 %) and sterols and free fatty alcohols from steryl esters and wax esters (1.7?4.9 %). Enhanced activated sludges will be produced by introducing the raw activated sludges to a

medium with high carbon to nitrogen ratio with glucose as carbon source. Lipid enhancement will be done for a period of 10 days after which, cells will be harvested. The lipid storage compounds in the enhanced activated sludge will be analyzed in the same way as the raw activated sludges. The results will be compared to determine if the amount and speciation of storage compounds accumulated by the enhanced activated sludges are source-independent. This will solidify the concept of using waste water treatment facilities as source of oil feedstock for the biofuel industry.

TUESDAY

AFTERNOON

IOP 3: New Glycerol Uses

Chair(s): T. Benson, Lamar University, USA; and D. Brown, HBI USA, USA

Efficient Acrolein Production from Crude Glycerol Using Sub- /Super-critical Water Technology. X. Philip Ye, Leming Cheng, The University of Tennessee, Knoxville, TN, USA

Acrolein currently manufactured via the oxidation of petroleum-based propylene is one of those glycerol derivatives, holding an important status as intermediate for the production of many high-value chemicals, such as acrylic acid, methionine, polyester resin, superabsorbents, polyurethane, etc. To make a new technology for acrolein production commercially viable from crude glycerol, it is important to emphasize sufficient acrolein yield without or with minimum costly refining/purifying processes for crude glycerol. This presentation will show our development of an efficient process for acrolein production directly from industrial crude glycerol with diverse chemical compositions, which were derived from different biodiesel production technologies and various feedstocks like virgin soybean oil and canola oil, waste cooking oil mixture, and chicken fats. Problems such as how to efficiently separate or recover both organic and inorganic impurities in crude glycerol for acrolein production, and what the effects of these impurities on glycerol dehydration may be, were considered in the technological development. High yield of acrolein (as high as 90 mol%) from crude glycerol has been achieved using the developed process. This bio-based route for fine chemical production has the potential to be used in medium-large scale chemical plants, directly utilizing industrial crude glycerol.

Synthesis of Biodiesel Fuel Additives from Glycerol using Green Chemistry and SFs. W.E. Artz[1], E.C. Self[1], C.C. Hurst-Thomas[1], M.L. Kraft[1], R.O. Dunn[2], [1]University of Illinois, Urbana, IL, USA, [2]USDA, ARS, NCAUR, Peoria, IL, USA

For every 3 moles of fatty acid esters produced, 1 mole of glycerol remains, ~11% of the biodiesel volume. One new method of glycerol use could be as a biodiesel fuel additive/extender using eco-friendly heterogeneous catalysts and supercritical fluids (SFs). SFs have advantages such as greater diffusivities, lower viscosities, better catalyst surface ?wetting?, and more rapid transfer to/from catalyst surfaces. Samples were analyzed using GC/MS. Experiments were completed at SF and non-SF conditions with Amberlyst® catalysts. Glycerol ethyl ethers and cyclic compounds (dioxanes and dioxolanes) were formed. For the reactions in glass vials at low

pressures (100C), the yields were ~0.26% to 0.48% (ethers) and ~0.16% to 0.78% (cyclics). At SF conditions (100C and 205 atm) the yields ranged from ~0.28% to 3.84% ethers and ~0.21% to 1.26% cyclics. For the SF experiments at 120C and 205 atm, the glycerol conversion was ~9 to 19% with 94% to 98% ethers and ~2 to 6% cyclics. For experiments completed at 180C and 314 atm, the glycerol conversion rate was ~25.5%, with 55.4% mono-ethyl-, 13.8% di-ethyl-, 0.2% tri-ethyl ether of glycerol, and 30.6% combined cyclic compounds. One investigator used non-SF conditions and non-green methods with better glycerol conversion (32%) (160-200C), but the primary product (90%+) was the mono-ethyl ether, which is not very soluble in biodiesel.

****Cancelled** Potential Oxygenates from Glycerol.** S. Kaul, Indian Institute of Petroleum, India

Considerations on the Mechanism of Self-Condensation of Glycerol to Polyglycerol in Presence of Alkaline Catalysts. Mihail Ionescu, Xianmei Wan, Zoran Petrovic, Pittsburg State University, Kansas Polymer Research Center, Pittsburg, KS, USA

It is well known that glycerol polymerizes in presence of alkaline catalysts (NaOH, KOH, $NaOCH_3$}, $KOCH_3$}, CsOH, $Ca(OH)_2$ etc. at 230-250°C) forming polyglycerol and water as a byproduct. Until now there was no a satisfactory mechanism to explain all the experimental facts of this unusual kind of etherification. We showed that simple primary alcohols do not form ethers in the presence of alkaline catalysts even at higher temperatures and that the formation of ether bonds by glycerol self-condensation follows an unusual etherification mechanism. Based on an old assumption that glycidol is the reactive intermediate in self-condensation of polyglycerol, we proved that the formation of intermediary epoxy groups is characteristic of 1,2 glycols. Thus 1,2,6 hexane triol undergo polycondensation, but triethanolamine and ethoxylated glycerol do not. The presence of glycidol during alkaline polycondensation of glycerol was proved by heating the mono-potassium glycerolate (the active species in glycerol polycondensation) in high vacuum at 250°C. We collected four liquid fractions, each of them containing around 20-26% glycidol. The presence of glycidol as a very reactive intermediate, explains majority of the experimental facts of this unusual polycondensation of glycerol.

Glycerine and Levulinic Acid: Two Valuable Co-products for the Fermentative Synthesis of Poly(hydroxyalkanoate) Biopolymers. R.D. Ashby, D.K.Y. Solaiman, G.D. Strahan, USDA, ARS, ERRC, Wyndmoor, PA, USA

Poly(hydroxyyalkanoates) (PHAs) are biopolyesters derived from bacterial sources. Many of these polymers exhibit properties that approximate petro-based plastics with the advantage of biodegradability. However, widespread use of these biopolymers is limited due to high production costs. To improve the application potential of these biopolymers, glycerine (GLN) and levulinic acid (LEV; co-products from the biodiesel and pulp and paper industries) were used as carbon sources to synthesize poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate (PHB/V), two thermoplastic PHA biopolymers. It was concluded that by utilizing GLN and LEV, either alone or as mixed substrates, the physical properties (*i.e.,* composition, molecular weight) of the polymers could be controlled thus

broadening the range of their material properties. In this presentation, we will discuss our results utilizing GLN and LEV in PHB and PHB/V synthesis, polymer property control and the effect of methanol on property management. It is envisioned that large-scale use of these co-products to produce PHB and PHB/V will help reduce polymer production costs and, simultaneously, improve co-product value thus benefitting the biopolymer as well as the biodiesel and pulp and paper industries.

Production and Purification of Arabitol from Biodiesel Byproduct Glycerol. S. Koganti, A. Loman, L.-K. Ju, The University of Akron, Akron, OH, USA

Glycerol is a major byproduct from biodiesel production. Developing new industrial/commercial uses of biodiesel glycerol is imperative to economics and sustainability of biodiesel industry.We targeted arabitol as the value-added product to be produced from biodiesel glycerol. A Debaryomyces hansenii strain was selected after screening 214 strains from ARS Culture Collection at USDA. The strain was selected for its ability to produce high concentrations of arabitol as the only polyol using glycerol as substrate. This strain was subsequently studied for developing optimal medium composition and culture conditions, such as temperature, pH, dissolved oxygen concentration, nitrogen-to-phosphorus ratio, and glycerol concentration. Optimizing the culture conditions improved arabitol yield to 50-60% and volumetric productivity to 0.35g/L-hr. Maintaining high glycerol concentrations, >30 g/L, was found necessary so far for continual arabitol production. At lower glycerol concentrations, cells tended to consume arabitol. Maintaining high glycerol concentrations for better arabitol productivity, however, complicated the downstream arabitol collection and purification. An effective procedure was therefore developed to separate and purify arabitol from the fermentation broth containing 20-30 g/L glycerol and 40-50 g/L arabitol. Arabitol was successfully collected with 60% yield and 95% purity.

****Cancelled**** **Biodegradable Glycerol Ester Base Stock for Neat Cutting Oils.** S. Kaul, Indian Institute of Petroleum, India

Identifying New Uses for Glycerine - Production of a Renewable Amino Alcohol. Victor M. Arredondo, Mike S. Gibson, Neil T. Fairweather, Patrick J. Corrigan, Debbie J. Back, Angella C. Daniels, David P. Kreuzer, The Procter & Gamble Company, USA

Amino alcohols are bifunctional molecules used in a variety of applications. They are typically derived from petrochemical feedstocks; for example, by the reaction of an epoxide with ammonia; or by the reduction of nitro alcohols produced from the condensation of nitroparaffins with formaldehyde. As the world?s largest producer of USP grade glycerine, a material widely used in many market applications, P&G embarked in research to develop materials with added-value potential from this renewable feedstock. In this paper we will summarize some efforts made in this area and more specifically share our experience developing the two-step process for the catalytic transformation of glycerine to 2-amino-1-propanol (2AP), a renewable-based amino alcohol.

WEDNESDAY

MORNING

IOP 4: Oleochemicals and Polymers

Chair(s): D. Pioch, CIRAD, France; and J.O. Metzger, University of Oldenburg and *abiosus* e.V., Germany

Synthesis of a Phosphorous Derivative of Methyl Oleate. K.M. Doll[1], B.K. Sharma[2], P.A.Z. Suarez[3], [1]BOR-NCAUR, ARS, USDA, Peoria, IL, USA, [2]ISTC- University of Illinois-UC, Champaign, IL, USA, [3]Instituto de Quimica Universidade de Brasilia, Braxilia, DF, Brazil

The development of sulfur free additives that are compatible with bio-based lubrication fluids is an important topic. Utilizing an epoxidation route, this type of additive was made from dialklyphosphates and methyl oleate. The ring opening reaction of epoxidized methyl oleate produces primarily an alkyl dioxaphospholane group in the olechemical. This compound has potential for use in the biobased lubricant industry, as well as coating applications. Yield of this product are ~ 25%, which can be increased slightly with the use of a heterogeneous catalyst. The titanium (IV) / zirconium (IV) system was used with varied molar ratios of the metals. The 50/50 mol % catalyst was the most effective giving a yield of the desired compound of 37%. The trend of a higher surface area with greater reactivity was observed.

Phosphonate Derivatives of Methyl Oleate. G.B. Bantchev, G. Biresaw, S.C. Cermak, USDA, ARS, NCAUR, Peoria, IL, USA

Phosphorus-containing compounds are often incorporated in lubricants and plastic to improve their properties. In lubricants, phosphonates, or diphosphites improve the oxidative stability, anti-wear and extreme pressure properties. In the current work, we describe the synthesis and characterization of derivatives of methyl oleate containing phosphonate groups. Both direct reaction of the methyl oleate with phosphite and indirect, through epoxystearate, are used for the synthesis of the derivatives. The tribological (anti-wear, friction reduction, extreme pressure) and the antioxidant properties of the compounds will be reported.

Maleinized Fatty Compounds as Plasticizers. U. Biermann[1], A. Jungbauer[2], J.O. Metzger[1,3], [1]University of Oldenburg, Oldenburg, Germany, [2]University of Applied Sciences, Emden, Germany, [3]abiosus e.V., Oldenburg, Germany

The synthesis of maleinized fatty compounds was performed on the one hand by solvent-free Diels-Alder reactions using unsaturated fatty acids with a highly reactive hexatriene system such as calendic acid (octadec-8,10-trans-12-cis-trienoic acid) and α-eleostearic acid (9-cis-,11,13-trans-octadecatrienoic acid) as substrates to give highly functionalized cycloaddition products,1,2 and on the other by the thermal ene reaction of e.g. methyl oleate with maleic anhydride.3 Ring opening and esterification of the maleinized products was carried out with different alcohols such as methanol, ethanol, isopropanol, and isobutanol affording the respective tricarboxylic acid esters which showed good properties as plasticizers.1. U. Biermann, W. Butte,

T. Eren, D. Haase, J. O. Metzger, Eur. J. Org. Chem., 2007, 3859?3862. 2. U. Biermann, W. Butte, R. Holtgrefe, W. Feder, J. O. Metzger, Eur. J. Lipid Sci. Technol. 2010, 112, 103?109. 3. J.O. Metzger, U. Biermann, Fat Sci. Technol. 1994, 96, 321-323

Water Soluble Metalworking Fluid from Palm Oil Methyl Ester. S.K. Yeong[1], Hazimah Abu Hassan[1], Jaharah Abdul Ghani[2], [1]Malaysian Palm Oil Board, Bandar Baru Bangi, Selangor, Malaysia, [2]Department of Mechanical and Material Engineering, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

Most of the metalworking fluids in the market have been formulated using mineral oil. The use of mineral oil poses some problems such as waste disposal and operator's health.Vegetable oils are inherently biodegradable and non-toxic, thus could be used to replace mineral oils in the metalworking fluid formulations. Palm-based material, such as palm oil methyl esters, was found to be suitable to replace mineral oil in the formulation of emulsifiable metalworking fluid. The formulation has been formulated using non-ionic emulsifiers replacing the petroleum sulphonate emulsifier commonly used by the industry The formulation showed good properties such as non-corrosive to metals, possessed good lubricity, biodegradable, non-toxic to the aquatic life and did not cause dermal irritation. Efficacy trial was performed using a lathe machine and it was found to perform as well as commercial cutting fluid in turning operation. No adverse deformation on the microstructure of metal or abnormal microhardness changes was observed when palm-based metalworking fluid was used. In terms of tool life, tool life which used palm-based metalworking fluid was shorter than commercial cutting fluid, but gave better surface finish (less rough).

Steel-corrosion Inhibitors Against Sulfate Reducing Bacteria Derived from Soy Oil. R. Dacomba, M. Khawaji, A. Jaros, D. Graiver, K. Berglund , R. Narayan, Michigan State University, East Lansing, MI, USA

We prepared and evaluated derivatives of soybean oil with corrosion inhibiting and biocidal properties against SRB to prevent natural bio-films formation on submerged steel structures in both fresh and saltwater environments. These films contain a consortium of bacteria and fungi generating an anaerobic film directly in contact with the metal surface, which allows Sulfate Reducing Bacteria (SRB) to proliferate on the metal surface and carry out anaerobic corrosion. This corrosion occurs by removing electrons from the iron in the steel through the electron transport chain of the SRB cellular respiration. Annual losses in industry due to Microbially-Induced Corrosion (MIC) have been documented to be in the billions of dollars. Current methods implemented by industry to control MIC include the use of highly toxic compounds such as glutaraldehyde, formaldehyde and chloramines. FTIR and NMR were used to confirm the structures of the soy-based compounds. The corrosion inhibiting properties were evaluated using ASTM G31-72 and the biocidal activity was evaluated using ASTM D4412-84 on Gram-positive SRB, Desulfosporosinus orientis. Results showed that the addition of 500 ppm of these compounds to SRB cultures completely inhibited bacterial growth. Furthermore, 25 ppm of our product yielded satisfactory corrosion inhibition of carbon steel in 2N HCl.

One Step Extraction of Vegetable Oil and Lipase Mediated Synthesis of Commodity Oleochemicals under Critical Fluid Conditions: Case of Fatty Acid Ethyl Esters. M.N. Baig[1,2], R.C.D. Santos[1], S. Bowra[2], D. Pioch[3], [1]University of Birmingham, Birmingham, United

Kingdom, [2]Phytatec, Aberystwyth, United Kingdom, [3]CIRAD, Montpellier, France

Critical fluids offer environmental advantages over chemical solvents, while providing enhanced separation, and chemical selectivity. This work will demonstrate the use of critical fluids for recovering multiple products from biomass and combine this with transformation of selected molecules to add value. To achieve this overall objective we have begun by selecting sunflower oil as a model substrate. As a first step, the conversion of sunflower vegetable oil (Triglycerides) in sub-critical water (SCW) was studied in a continuous flow reactor. In the second step of the process, FFAs were bio-catalytically transformed to fatty acid esters using lipase within supercritical fluid carbon dioxide environment. The response surface equation was used to identify the optimum process conditions which maximised fatty acid ester yield. In summary we will present optimised process conditions for continuous flow SCW hydrolysis of sunflower oil and the subsequent transformation of Fatty acid to ethyl esters. We will also discuss the process advantages of coupling the two steps to one continuous flow unit and the power of RSM modelling in assisting process development.

Latent Heat Characteristics of Biobased Oleochemical Carbonates. J.A. Kenar, USDA. ARS. NCAUR, Peoria, IL, USA

Oleochemical carbonates represent biobased materials that can be readily prepared through a carbonate interchange reaction between renewably available C10-C18 fatty alcohols. Although these carbonates have commercial use in cosmetics and lubricant applications, they have not been examined as phase change materials (PCM) for thermal energy storage (TES) applications to store and release heat to their surroundings. In this work, the latent heats of melting and freezing for a series of oleochemical carbonates were evaluated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to develop a fundamental understanding of the solid-liquid transitions of these materials for utilization in TES applications. Decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl carbonates had peak melting and freezing points of -2.2, 19.3, 33.7, 44.9, 51.6 and -6.3, 14.3, 28.7, 40.3, and 46.9 °C, respectively. These carbonates exhibited sharp phase transitions and good latent heat properties. The latent heats of melting and freezing for decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl carbonates were 144, 200, 227, 219, 223 J/g and 146, 199, 229, 215, and 215 J/g, respectively. Data for eutectic mixtures of these carbonates will also be presented.

Properties of Vegetable Oil-based Casting Compounds Prepared via "Click" Chemistry. Zoran S. Petrovic, Jian Hong, Qiang Luo, Mihail Ionescu , Bipin K. Shah, Pittsburg State University, USA

New monomers were prepared by introducing azide groups in castor, canola, corn, soybean and linseed oils. They were reacted with alkynated soybean oil (ASBO) in the absence of solvents and catalysts to obtain crosslinked elastomeric matrials without by-products. Glass transitions varied from -5°C for canola/ASBO to 16°C for linseed/ASBO. Tensile strengths varied from 0.6 to 3.4 MPa and elongations from 30 to 60%. New all renewable casting compounds are an interesting alternative to the currently used materials in electrical industry.

Synthesis and Properties of UV-curable Soy-based Branched Oligomers. Ren Liu[1,2], Jingling

Yan[1], Sharonie Ariyasivam[1], Xiaoya Liu[2], Zhigang Chen[1], [1]Center for Nanoscale Science and Engineering, North Dakota State University, Fargo, ND, USA, [2]School of Chemical and Material Engineering, Jiangnan University, Wuxi, P.R. China

A new, green approach to improve the performance and biorenewable content of natural plant oil based UV-curable materials is presented. Novel soybean oil (SBO) based UV-curable oligomer SBO-g-CNL (CSO) was synthesized by chemically introducing the cashew nutshell liquid (CNL) onto the epoxidized soybean oil (ESBO) backbone. The epoxidized SBO-g-CNL (ECSO) was used to produce cationic UV-curable coatings with a cycloaliphatic epoxy. Dramatic improvement in compatibility with the photoinitiator and the cycloaliphatic epoxy were discovered as compared to ESBO. ECSO based coatings also had better impact resistance and thermal stability. Acrylated epoxidized SBO-g-CNL (ACSO) with high biorenewable content was also prepared and the properties of UV cured films were studied by evaluating their mechanical properties, thermal stability and glass transition temperatures (Tg). The CNL segment plays an important role on the Tg, and thermal and mechanical behaviors of the ACSO based coating films. Compared to acrylated soybean oil, the Tg of ACSO increased from 9.5 to 23.7°C, and the thermal stability and mechanical properties including hardness, crosshatch adhesion and tensile stress of ACSO film were also improved,. This reported approach provided a new direction to the future development of advanced bio-based UV-curable oligomers from a variety of plant oils.

The Development of Canola Oil Based Bio-resins. X. Kong, T.S. Omonov, G. Liu, E. Kharraz, P. Tiege, J.M. Curtis, Lipid Chemistry Group, Department of Agricultural, Food and Nutritional Sciences, University of Alberta, Edmonton, Alberta, Canada

Thermoset resins are amongst the most commonly used materials in the automotive, construction, and furniture industries where they are used in a wide variety of composites ranging from particleboard to glass fibre panels. At present, thermoset resins are mainly produced from petrochemicals. Furthermore, some of the starting materials which are used in their production, such as formaldehyde, are associated with levels of toxicity and potential environmental, health and safety concerns. Bio-based resins made from vegetable oils offer a sustainable alternative to petroleum-based thermoset resins, with overall lower carbon emissions. Our research is focusing on developing viable routes for their production using cost-effective green technology. Here, we describe the development of thermosetting resin systems from epoxidised canola oil. We have shown that understanding both the production of epoxide intermediates and their further reactions with multifunctional ligands is key to converting oils into thermosets such as epoxy or polyurethane resins. Furthermore, we have demonstrated real potential for the replacement of conventional petroleum-based thermoset resins with products containing a high renewable content.

An Update on the USDA BioPreferred Program. G. Norton, Iowa State University, IA, UA

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. The United States Department of Agriculture manages the BioPreferred program. BioPreferred includes two main components, which are a preferred procurement program for Federal agencies

and their contractors, and a voluntary labeling program for the broad scale consumer. The USDA database on biobased products currently contains about 3100 companies and about 23,500 products. The biobased products catalog that is used by Federal procurement officers currently contains nearly 400 companies and 1700 products in product categories that the USDA has designated as having preferred procurement status for Federal agencies. An overview of the BioPreferred program will be presented, with an emphasis on the voluntary labeling program that was initiated in February, 2011. The USDA BioPreferred labeling program will be compared with the EU Ecolabel program.

AFTERNOON

IOP 5: General Industrial Oil Products

Chair(s): D. Sparks, Mississippi State University, USA; and P. Pham, Mississippi State University, USA

Purification of Pollock Fish Oil using Synthetic Magnesium Silicate. G. Hicks, B. Cooke, Dallas Group of America, Inc., Jeffersonville, IN, USA

Crude fish oil, such as Pollock, contains a wide variety of impurities that must be removed in order to achieve desired specifications. In this study, synthetic magnesium silicate was used to treat a crude Pollock fish oil sample in an attempt to remove these impurities and produce finished oil with high quality. Treatment of the crude Pollock oil with synthetic magnesium silicate resulted in:71% Unsaponifiable matter reduction84% Water reduction91% Acid Value reduction13% Peroxide Value reduction100% Soap reduction97% Color reduction100% Chlorophyll removal149% Improvement in oxidative stability

The Development of Rigid Polyurethane Foam Insulating Panels for the Construction Industry using Low Cost Polyols Derived from Canola Oil. X Kong[1], G Liu[1], Z Zhang[2], T Tekle[2], J.M. Curtis[1], [1]Lipid Chemistry Group, Department of Agricultural, Food and Nutritional Sciences, University of Alberta, Edmonton, Alberta, Canada, [2]TTS Inc., Edmonton, Alberta, Canada

Conventional polyurethane foam is produced from the reaction between petroleum derived polyols and isocyanates with other additives to aid foam formation and reactivity. With the increasing emphasis on issues concerning depletion of non-renewable resources, it would be desirable to replace petroleum-derived ingredients in PU foam formulations. Here, we have used a novel polyol mixture produced from canola oil via epoxidation. Thus, we have been able to replace about half of the material used in the foam panel with polyol from a renewable resource produced by an inexpensive process emphasizing green chemistry. In this work we explore the differences between the reactions that form PU foams from commercial polyol formulations to those using the canola-derived polyols. We also demonstrate how the properties of PU insulating foams incorporating various levels of renewable materials compare with standard formulations in terms of compressive strength, R-value and ease of production. We have found that the overall properties of PU insulation foams prepared from canola-derived polyols are comparable to those

of commercial PU foams.

Optimization of Production of Conjugated Linoleic Acid (CLA) from Corn Oil by Response Surface Methodology and Enrichment by Urea Fractionation Method. S. Karasan, M. Tuter, G. Ustun, Istanbul Technical University, Chemical Engineering Department, Istanbul, Turkey

Conjugated linoleic acid (CLA) refers to positional and geometric conjugated isomers of linoleic acid. Beneficial effects of CLA on human health, such as reduced body fat, enhanced immunity, anticancer, antidiabetic.ie. have been reported.In this study production of CLA from corn oil fatty acids by alkali isomerization with KOH was investigated. Effects of temperature, time and the amount of catalyst on the conversion of linoleic acid to CLA were examined and the reaction conditions were optimized by Response Surface Methodology. Face centered cube experimental design was used for optimization. Optimum conditions were obtained as 143ºC, 4.85 M KOH and 2 h of reaction time. At these optimum conditions, isomerization product was obtained containing 42.3% CLA and the conversion ratio of linoleic acid to CLA was found as 77%. Later this isomerization product was enriched in CLA by urea fractionation method at 4ºC. Experiments were carried out at different urea/fatty acids and ethanol/urea ratios, and crystallization time to optimize conditions. Final product having 62.5% CLA was obtained at optimal enrichment conditions (urea:fatty acid ratio of 1:2.25, ethanol:urea ratio of 1:7 and 2h). This concentrate could be used for food and pharmaceutical purposes.

****Cancelled** Development of Pellet Type of Supported ZrO2 Catalyst for Renewable Diesel Production from Lower Grade Oils.** M. Kim, Wayne State University, USA

Separation of Omega-3/6 Fish Oil from Fish Waste using Pressure Swing Technique of Supercritical Carbon Dioxide. Md. Zaidul Islam Sarker, Sahena Ferdosh, Jinap Selamat, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

The total oil was extracted from the ground skin of Indian mackerel (Rastrelliger kanagurta) using various techniques of supercritical fluid extraction (SFE) at 20Ã¢â?¬â??35 MPa and 45Ã¢â?¬â??75 Ã?Â°C and by the Soxhlet method for comparison. The oil yield increased with pressure and temperature and the highest yields were 24.7, 53.2, 52.8, and 52.3/100 g sample (dry basis) for the continuous, cosolvent, soaking, and pressure swing techniques, respectively, at 35 MPa and 75 Ã?Â°C. The yield from the Soxhlet extraction was 53.6/100 g sample (dry basis). The CO2 consumption was 581.8, 493.6, 484.9 and 290.9 g for the continuous, cosolvent, soaking and pressure swing techniques, respectively, at 35 MPa and 75 Ã?Â°C. The largest recoveries of PUFA, especially the Ã • â?°-3 family, were achieved from the soaking and pressure swing techniques at 35 MPa and 75 Ã?Â°C. Thus, the pressure swing and soaking techniques are the most effective at extracting the oil from fish skin.

****Cancelled** Production of Biodiesel Using Dimethyl Carbonate as the Methylating Agent: A Glycerol-free Biofuel.** M. Miguez, Lamar University, USA

Next Generation Feed Stocks for Bio-based Lubricant and Polymer Manufacture. J. Grushcow[1,2], [1]Linnaeus Plant Sciences Inc., Vancouver, BC, Canada, [2]Industrial Oil Seed Network, Vancouver, BC, Canada

Camelina sativa shows great promise as a potential industrial oil seed crop. It is a short season non-food oilseed that can be grown on marginal land, is drought tolerant and requires minimum inputs. The challenge with this crop is to improve the oilseed profile to remove oxidatively unstable oils. This paper will discuss developments in camelina improvement as well as present data from the field tests of high oleic bio based hydraulic fluids. There will also be a discussion of future directions including the production of Hydroxy Fatty Acids such as Castor oil in transgenic oil seeds.

Enhanced Lipid Accumulation for Biofuels Production by Sewage Anaerobic Sludge Microorganisms via Cultivation in Glucose-fed Aerobic Bioreactors. A. Mondala, R. Hernandez, P. Pham, T. French, L. McFarland, Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS, USA

The potential of utilizing municipal sewage anaerobic sludge microbial communities for the production of lipid biofuel feedstocks was investigated. Previous studies found that aerobically-grown activated sludge lipid contents can be increased by fermentation of high C:N ratio wastewater media supplemented with glucose. As opposed to activated sludge, which contains primarily aerobic microorganisms, anaerobic sludges contain both obligate and facultative anaerobes, the latter of which may be able to grow and accumulate lipids under aerobic conditions. This process could potentially reduce waste sewage sludge outputs and utilize existing wastewater treatment plant infrastructures as biorefineries. Anaerobic sludges were cultivated in batch bioreactors with glucose as the carbon source at various initial C:N ratios to evaluate its biomass and lipid productivity and compared with that of activated sludge. Kinetics of cell growth, lipid accumulation, and sugar consumption were analyzed. The resulting lipid extracts were fractionated, characterized using gas chromatography methods, and evaluated for biofuel application.

Industrial Oil Products Posters

Chair(s): D. Root, Agricultural Utilization Research Institute, USA; and K. Doll, USDA, ARS, NCAUR, USA

The Influence of Oxygen Flow Rate on Oxidation Induction Times (OITs) by High Pressure DSC.
Gabriela Sekosan, Neil Higgins, Tiffanie West, Bunge North America, Bradley, Il, USA

A rapid oxidation bench test that can be used to establish the oxidation stability of engine oils, greases, transmission and hydraulic fluids was used for vegetable oils-the oxidation stability of oils as estimated by high-pressure differential scanning calorimeter (PDSC). A group of

vegetables oils and non food oils were used to establish a relationship between certain standard variables and oxidation induction times (OITs) by High Pressure DSC. The variables studied were gas flow rate, temperature and pressure.

The Acrylation of Glycerol over Solid Bases: a Precursor to Functionalized Lipids.
Michael A. Jackson, Judith A. Blackburn, Steven N. Rheiner, NCAUR/ARS/USDA, Peoria, IL, USA

Heterogeneous basic catalysts were used for the synthesis of didecanoylacryloylglycerol from decanoic and acrylic acids and glycerol. This reaction was carried out in hexane in a closed stainless steel reactor at 200°C for 5h in the presence of K2O, Cs2O, and BaO both as free bases or immobilized on the silicas SBA-15 and HMS as catalysts. The reactants were added in a 1:3:4 glycerol:decanoic acid:acrylic acid molar ratio. The resulting product which was isolated at about 40% yield, was then converted to Heck reaction products. It was reacted with bromobenzene in the presence of tris(o-tolyl)phosphine and PdCl2 to yield didecanoylcinnamoylglycerol in high yield.

Characteristics of Some Algal Oils Useful for Industrial Applications.
I. Javni, D.-P. Hong, Z. S. Petrovic, A. Myers, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas, USA

Algal oils offer significant potential as feedstocks for food, pharmaceuticals, biofuels or other chemical products. In comparison to the terrestrial oil crops (soybean, palm, corn, sunflower, etc.), algae has the advantage of a non-food resource with a greater oil yield per acre. The objective of this work was to provide additional information on algae oil properties needed for their consideration as substrates for industrial products. Four algal strains supplied by AlgaGen were studied: Cyclotella nana, Neochloris oleoabundans, Nannochloropsis oculata and Isochrysis galbana. The characteristics of algal oils were compared with soybean oil that is the dominant natural oil used in the chemical industry. The most significant difference of algal oils to vegetable or animal oils is their low triglyceride content and high free acid and monoglyceride contents. The hydroxyl values for algal oils were in the range 137-208, acid value 109-135 and free fatty acid content (measured by GPC) was in the range 55-80%. Iodine value, as a measure of unsaturation, was higher for algal oils (152-193) than for soybean oil (125), which can be beneficial in many applications. In conclusion, algal oils are interesting chemical substrates, but very different than typical vegetable or animal oils. Chemical conversion methods for the synthesis of industrial products should be accordingly designed.

Characterization of Thermal and Viscoelastic Properties of Hyperbranched Oligo(glycerol-diacid)s Synthesized in Toluene.
V.T. Wyatt, Agricultural Research Service, USDA, ERRC, Wyndmoor, PA, USA

Thermal and viscoelastic properties have been determined for hyperbranched poly(glycerol-diacid)s synthesized by the Lewis acid-catalyzed polyesterification of glycerol with either succinic acid, glutaric acid or azelaic acid. The polyesters were previously characterized by ^{13}C NMR to determine the degree of branching (D.B.%) and by gel permeation chromatography (GPC) to determine molecular weight (M_n), degree of polymerization (D.O.P.) and the

polydispersity index (PDI). In the present study, the effects of those physical properties on the thermal and viscoelastic properties on the polyesters were evaluated by determining their thermal stabilities by thermogravimetric analysis (TGA) and by determining their glass transition temperatures (T_g) and changes in heat capacity (ΔCp) by differential scanning calorimetry (DSC). Dynamic mechanical analysis (DMA) was used to determine viscoelastic properties such as elastic modulus (G'), viscous modulus (G''), and complex viscosity (η^*).

Synthesis and Physical Properties of Polyester Amides Derived from Lipid Based Components.

Jiaqing Zuo, Shaojun Li, Suresh Narine, Trent Biomaterials Research Program, Trent University, Peterborough, Ontario, Canada

Polyester Amides (PEAs) typically demonstrate the biodegradable properties of polyesters, with the thermal and mechanical properties of polyester being enhanced by the introduction of amide linkages into the polymer backbone. Three lipid-based nontoxic PEAs with varying ratios of ester and amide linkages were synthesized. Oleic acid was used as the starting material to produce the intermediates used for polymerization. A relatively simple synthesis procedure was utilized, requiring mild conditions.The intermediates in the synthesis were characterized by Nuclear Magnetic Resonance and Mass Spectroscopy. PEAs were characterized by Fourier-Transform Infrared and their molecular weights were determined by Gel Permeation Chromatography. All three PEAs demonstrated similar number average molecular weights, allowing comparison of their physical properties from a structural perspective. The thermal behaviour of the polymers was assessed by Modulated Differential Scanning Calorimetry and Thermogravimetric Analysis. The mechanical properties were investigated by Dynamic Mechanical Analysis and Tensile Test. The crystallinity of three polymers was studied by wide angle X-ray diffraction. The effects of additional ester linkages on the physical properties of PEAs were therefore determined and will be discussed in context of the structure of the monomers.

Production of Gamma Linolenic Acid (GLA) concentrates from Evening Primrose Oil by Urea Complexation.

L. Kent, G. Ustun, Istanbul Technical University, Istanbul, Turkey

Recently it has been shown that gamma linolenic acid (GLA) supplementation has positive health effects for the certain diseases such as rheumatoid arthritis, diabetic neuropathy, hypertension, asthma, multiple sclerosis, migraine and cancer. In this study, GLA concentrates were obtained from evening primrose (Oenothera bienis L.) oil by urea complexation reaction. Effects of reaction conditions [fatty acid-to-urea (w/w) ratio, urea-to-ethanol (w/v) ratio and time (h)] on the GLA content and yield of product were investigated and reaction conditions were optimized. Evening primrose fatty acids, containing 10.4% GLA were treated with urea in 95% aqueous ethanol at different fatty acid-to-urea (1/2-1/5) and urea-to-ethanol (1/4-1/9) ratios at +4 ºC for 3-24h. The crystals formed were separated from the liquid (nonurea-complexing fraction, NC) by filtration. Fatty acids were recovered from NC fractions and their fatty acid compositions were determined by GC analysis. The optimum conditions for production of GLA concentrate were a reaction time of 8 h, a fatty acid/urea ratio of 1/3.25 and a urea/ethanol ratio of 1/6.5. At these conditions, the concentrate was obtained containing 40.0% GLA with a product yield of

21.8%. This product could be used as GLA supplement for food and pharmaceutical purposes.

Palm Oil Polyols for Polyurethane Applications.
T.I. Tuan Noor Maznee, Malaysian Palm Oil Board, Malaysia

Studies on the Solubility of Steryl Glucosides in Biodiesel and Fossil Diesel.
H. Feichtinger[1], R. Heiden[2], S. Schober[1], M. Mittelbach[1], [1]Institute for Chemistry, Department of Renewable Resources, Karl-Franzens-University Graz, A-8010 Graz, Austria, [2]R.W. Heiden Associates LLC, Lancaster, PA, USA

Steryl glycosides (SG) as well as saturated monoglycerides have been identified for being responsible for filter plugging using biodiesel and biodiesel blends. SG are formed during transesterification of vegetable oils out of acetylated steryl glycosides (ASG) naturally existing in vegetable oils. As SG?s are less soluble in biodiesel than ASG, they can precipitate in biodiesel during longer storage and lead to filter plugging. Within this paper the solubility of a purified SG sample coming from a biodiesel plant in different fossil diesel, biodiesel and blends at different temperatures was studied. Saturated solutions of the SG sample were prepared, using ultrasound at higher temperatures, then the samples were cooled down to the wanted temperature and after filtration the content of SG was analyzed using GC/MS. It could be shown, that the maximum solubility in B100 depends on the temperature, starting from 60 mg/kg at 23°C to 200 mg/kg at 100°C. Surprisingly the solubility in B20 at 23°C was significantly higher ranging up to 800 mg/kg. Also tests with pure fossil diesel samples showed that the solubility in diesel fuels seems to be higher than in biodiesel.

The Use of Municipal Wastewater as a Media for Cultivation and Induction of Lipid Synthesis in the Oleaginous Yeast Rhodotorula glutinis.
M. Hetrick[2], J. I. Hall[1], W.T. French[1], R. Hernandez[1], B. Holmes[3], H. Ryu[4], B. Iker[4], J. Santo-Domingo[4], J. Donaldson[2], [1]Dave C. Swalm School of Chemical Engineering, Mississippi State, MS USA, [2]Department of Biological Sciences, Mississippi State, MS USA, [3]Mississippi State Chemistry Lab, Mississippi State, MS USA, [4]EPA-Cincinnati, Cincinnati, OH USA

Municipal wastewater can be considered as an effective growth medium for the cultivation of microorganisms due to the high content of organic material found in the water. Oleaginous microorganisms produce triacylglycerol (TAG), a metabolic by-product that is synthesized when the organisms are cultivated on media that contains high sugar content, which can be used to generate biodiesel. To determine if R. glutinis could sustain survival and synthesize lipids using municipal wastewater as a cultivation medium, we inoculated R. glutinis into primary effluent wastewater that had been supplemented with glucose. Bligh and Dyer results indicate that lipids were synthesized and this coupled with quantitative polymerase chain reaction (Q-PCR) suggest that R. glutinis was able to successfully compete with the indigenous microbial population in an effort to maintain survival in the municipal wastewater. FAMES generated from lipid extraction further aid in the confirmation that R. glutinis is present and responsible for lipid production.

Oil Production by *Desmodesmus subspicatus* in Tubular Photobiorreator using Alternative

Nutrient.
Pablo Diego Gressler[1], Thiago Rodrigues Bjerk[1], Maiara Priscilla de Souza[1], Ana Beatriz Zappe[1], Rosana de Cassia de Souza Schneider[1], Valeriano Antonio Corbellini[1], Eduardo A. Lobo [1], Carlos Peres Bergman[2], Tânia Basegio[2], [1]Universidade de Santa Cruz do Sul, Santa Cruz do Sul, Rio Grande do Sul, Brazil, [2]Universidade Federal do Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil

Microalgae have been suggested as good candidates for carbon fixation and biofuel production highlighting, among their advantages, a high photosynthetic efficiency, large biomass production and rapid growth compared to other crops for energy purposes. Thus, this study aimed to use commercial NPK (18:6:18) as a nutrient for the culture of the microalgae Desmodesmus subspicatus in tubular photo bioreactor and to evaluate the cell growth and fatty acid profile resulting from this biomass. The illuminance was 3600 lux supplied by eight fluorescent tubes (32W) with air injection to 1600 cm3 min-1 from the diaphragm air pumps. For the analysis of the lipid fraction, gas chromatography coupled with mass spectrometry was used in order to recognize the profile of fatty acids present in oil. The sample of D. subspicatus showed 0.93 ± 0.05 g biomass per liter of cultivation and lipid content of 19.43 ± 4.73% in 14 days of cultivation. Chromatographic analysis of this oil indicated that it presents the greatest amount of oleic acid (C18: 1). CNPQ, AES Uruguaiana, FAP-UNISC and CAPES.

Methods to Improve Oxidative Stability of Biodiesel.
B.R. Moser, USDA, ARS, NCAUR, Peoria, IL, USA

Oxidative degradation during storage is one of the chief technical deficiencies of biodiesel relative to petrodiesel. Traditional methods to mitigate susceptibility to oxidation include employment of synthetic antioxidants, switching to more stable feedstocks, reducing the storage time of the fuel and improving the conditions of storage. The current study explores two additional options: 1. a naturally occurring antioxidant known as gossypol; 2. blending less stable FAME with FAME possessing unusual resistance to oxidation. Meadowfoam (*Limnanthes alba*) oil-based biodiesel exhibits exceptional oxidative stability (IP: 66.2 h by EN 14112) and was therefore selected as a blend component for less oxidatively stable FAME prepared from soybean (SME) and waste cooking (WCME) oils. With regard to natural antioxidants, the results indicated that gossypol improved the oxidative stability of FAME, as determined by Rancimat (EN 14112) and pressurized differential scanning calorimetry (PDSC) methods. Additionally, meadowfoam FAME significantly improved the Rancimat induction periods and PDSC results of SME and WCME with the effect more pronounced at higher blend levels.

Oil Content Among the Diverse Castor Genetic Resources in the U.S. Collection.
J.B. Morris[1], M.L. Wang[1], D.L. Pinnow[1], J. Davis[2], P. Raymer[2], G.A. Pederson[1], [1]USDA, ARS, Plant Genetic Resources Conservation Unit, Griffin, GA, USA, [2]University of Georgia, Griffin, GA, USA

Castor (Ricinus communis L.) contains oil used for medicine, as an ingredient in shampoo, soap, hand lotion, high-speed lubricants, and as a coating material. Due to its high oil content, oil derived from castor seeds is currently proposed to be used as a feedstock for biodiesel production. The USDA, ARS, Plant Genetic Resources Conservation Unit curates 1,033 castor

accessions. The objectives of this study were to evaluate these 1,033 castor accessions for seed weight and oil content using nuclear magnetic resonance. Oil content among all castor accessions ranged from 37.2 to 60.6% with an average of 48.2%. One hundred seed weight ranged from 10.1 to 73.3 g with an average of 28.3 g. These results will be useful for castor breeders to develop improved germplasm as well as cultivars of castor containing high levels of oil for use as biodiesel.

Biodiesel Production from Corn Oil in the Presence of Enzyme Catalyst.
C. Kesgin, D. özçimen, S. Yücel, Yildiz Technical University, Istanbul, Turkey

Biodiesel has become more attractive recently because of its environmental benefits and made from renewable resources. The conventional method (transesterification reaction) for producing biodiesel involves acid and base catalysts to form fatty acid alkyl esters by thermal heating. In this study, microwave energy will be used for heating that is different from conventional production. The microwave energy offers a fast, easy route reaction with the advantages of enhancing the reaction rate and improving the separation process. Additionally in our study, immobilized lipase enzyme will be used as a biological catalyst as distinct from traditional catalysts to occur transesterification reaction. Stability, reusability, continuously operating facilities, better control of the reaction, high purity and high yield conversion are advantages of immobilized lipase enzyme usage. In this study, the enzymatic microwave assisted biodiesel synthesis from corn oil and methanol using immobilized Lipozyme TL IM (Thermomyces lanuginosus) was studied with different process conditions. The investigated variables were oil/methanol molar ratio, reaction temperature, reaction time and enzyme amount. The main purpose of this study was to obtain the optimum reaction conditions for enzymatic biodiesel production by microwave method.

Biodiesel Optimization from the Whole Stillage Extracted Corn Oil.
Savita Kaul, Jyoti Porwal, Mahender Negi, Dinesh Bangwal, Indian Institute of Petroleum, India

In the present work, the synthesis of fatty acid methyl esters from corn stillage oil (CSO) was studied, using a basic catalyst, KOH. The process was developed and optimized by following the factorial design and response surface methodology. This methodology has been applied to obtain the relationship between two variables (i.e., biodiesel purity and yield) and the operating conditions affecting the transesterification process (temperature, initial catalyst concentration and the methanol :CSO molar ratio). In addition , the method was utilized to calculate the optimum values for these operating variables in order to obtain the maximum values for biodiesel purity and yield.

The Effect of Nano and Micro Clay Fillers in Bio-based Thermoplastic Polyurethanes.
I. Javni , O. Bilic, D-P. Hong , Z.S. Petrovic, Kansas Polymer Research Center, Pittsburg State University, Pittsburg, KS, USA

Thermoplastic polyurethanes (TPU) have a wide range of hardnesses including the elasticity of rubber and the processability and recyclability of thermoplastics. TPUs are formed by reacting polymeric diols and chain extenders with diisocyanates. We synthesized diols by the hydroformylation and polymerization of methyl oleate and prepared TPUs by reaction with

diphenylmethane diisocyanate and 1,4-butanediol chain extender. The objective of this study was to examine the effect of nano-clays (surface treated and non-treated montmorilonite) and micro-clay fillers on properties of bio-based segmented polyurethanes. TPUs have segmented structures consisting of soft, elastic segments and hard segments, and fillers can interact with both. Improvement of elastic properties of elastomers would be expected if fillers interact strongly with fatty acid-based polyester soft segments. Interactions of fillers with hard segments could change hard domain crystallization and alter physical properties in a negative way. All fillers increased modulus of elasticity, but decreased tensile strength and elongation. The fillers did not significantly affect the glass transition temperature or thermal stability of the material.

Model Reaction for Vegetable Oil-based Polyurethane by Nonisocyanate Route.
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Polyurethanes can be made from carbonated vegetable oils and diamines. This route eliminates the need for isocyanates, but there are disputes about whether the amine reacts with only the carbonate group or also with ester group in the oil chains. To clarify, we synthesized carbonated methyl oleate and 9-octadecene then reacted with amine or diamine as model reactions. The products were characterized with FT-IR, GC-MS and GPC. FT-IR spectra of products showed absorbance peak of amide group. GC-MS and GPC results showed products contained some from the reaction of amine and ester group. Our results suggest that the amines not only reacted with carbonate group but also with ester group. The effect of hydroxyl groups formed during the reaction is being studied.

Totally Biobased Diisocyanates, Polyols, and Polyurethanes.
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Entirely biobased polyurethanes (PUs) have been prepared using polyols and diisocyanates both derived from vegetable oil. 1,7-Heptamethylene Diisocyanate (HPMDI) and 1,16-Diisocyanatohexadec-8-ene (HDEDI) synthesised from oleic acid have been successfully reacted with polyol produced from canola oil. The physical properties of these novel PUs have been compared to similar PUs made from petroleum-derived diisocyanates, such as 1,6-Hexamethylene Diisocyanate (HDI). The entirely biobased PU made from HPMDI had thermal and mechanical properties comparable to those prepared from HDI. Therefore, these new biobased PU materials have proven to be a potential valuable substitute for existing materials in various applications.Also, 1,18-Octadec-9-endiol (ODEDO) and 1,9-Nonanediol (NDO) have been synthesized from oleic acid. Novel PU has been successfully prepared by reacting ODEDO and NDO with HPMDI. Their physical property and phase behaviour have been compared to PU prepared from these diols (ODEDO and NDO) and HDI. Furthermore, ester group has been introduced into the diol compounds to improve flexibility and elasticity properties of the TPUs. This work represents a determining improvement in our ability to produce totally biobased polyurethanes which can be easily recycled through melting and reprocessing.

A Comprehensive Toolbox to Evaluate the Functional Properties of Waxes.
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The present study offers a comprehensive "toolbox" of physical tests which has been developed to comparatively evaluate the physical properties of commercial waxes. This toolbox allows us to quantify functionality on a wider range of properties than is normally done by the current ASTM standards of the industry. The study was motivated by the growing importance of vegetable-oil derived waxes for varied uses ranging from food applications to industrial, pharmaceutical and cosmetic applications. Currently, the most widespread use of vegetable oils as replacements for waxes has been in the relatively inexpensive paraffin replacements. However, significantly higher margin applications exist but the structure and functionality of the materials required in these applications has not been comprehensively studied. Therefore, the engineering of vegetable oils to function as replacement materials has been limited. The physical properties of a wide range of waxes were examined by XRD, DSC, textural and rheological analysis, and pNMR. Excellent reproducibility was obtained from the tests, which were also found to provide physically meaningful parameters.The physical functionality ranges established on these samples now provide a target for re-engineering of these waxes as vegetable oil-derived wax mimetics.

Effect on Phenolic Compounds and Antioxidant Activity of *Jatropha cordata* and *Jatropha cardiophylla* Seed Cakes by Different Solvent Systems.

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Jatropha cordata (JC) and *Jatropha cardiophylla* (JCph) are species native of Northwestern of Mexico and Southwest of E.E.U.U. adapted to arid and semi-arid conditions. These plants produce seeds with 35% of oil, which have a potential interest as feedstock for biodiesel production, because these oils are not used as food. The residual seed cake from JC and JCph (65%) may be an important source of phenolic compounds. For this reason, the aim of this study was determinate the effect of different solvent systems (methanol 60, 70 and 100%) on the extraction of phenolic compounds of seed cakes from JC and JCph and evaluate their antioxidant capacity by the methods DPPH$^{\bullet}$ ABTS$^{\bullet+}$. The results showed that the 60% methanol extracts exhibited the highest phenolic compounds concentration and the highest antioxidant activity (DPPH$^{\bullet}$ and ABTS$^{\bullet+}$). The highest phenolic compound in JC seed cake was sinapic acid (27.44 ± 2.34 mg/100g), and myricetin (14.9 ± 1.34 mg/100g) the highest in JCph seed cake. The results showed that extracts of JC and JCph seed cakes have a potential as source of natural antioxidants. Is needed to put attention in the studies of these natural antioxidants that could be use to improve the oxidative stability of oils and biodiesel.

Changes in the Quality of Salmon Skin Oil under various Storage Conditions.

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The effects of various storage temperatures and duration on the stability of solvent-extracted salmon skin oil (SSO) were evaluated using both spectrophotometric and titrimetric methods. The stability of SSO was assessed with respect to free fatty acid (FFA) content, peroxide value

(PV), thiobarbituric acid reactive substance (TBARS) as well as changes in the fatty acid (FA) profile after storage at 4oC, 25oC, -18oC and -80oC, and over 45 days.Higher and longer storage temperatures and time resulted in correspondingly higher quantities of oxidative products in SSO. Generally, there were progressive increases in the FFA content, PV and TBARS at all the treatment combinations studied. At storage temperatures 4oC and 25oC, the oil still maintained low levels of oxidative products after 45 days of storage. At day 45 for instance, there were 8.50 and 8.29% FFA, 32.43 and 26.33 µg MDA eq g-1 oil, and 88.19 and 64.53 meq peroxide kg-1 oil at 25 and 4oC, respectively. There were generally no significant differences ($p > 0.05$) within individual FAs of the various treatment combinations.

Fatty Acid Profile as a Basis for Screening Alternative Feedstocks for Biodiesel Production.
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Fatty acid (FA) profile was used as a screening tool for the selection of feedstocks high in monounsaturated content for evaluation as biodiesel. The feedstocks were ailanthus (*Ailanthus altissima*), anise (*Pimpinella anisum*), arugula (*Eruca vesicaria*), camelina (*Camelina sativa*), coriander (*Coriandrum sativum*), cress (*Lepidium sativum*), cumin (*Cuminum cyminum*), field pennycress (*Thlaspi arvense*), hazelnut (genus *Corylus*), Indian cress (*Tropaedum majus*), meadowfoam (*Limnanthes alba*), shepherd's purse (*Capsella bursa-pastoris*), upland cress (*Barbarea verna*), and walnut (genus *Juglans*). FAME were prepared from feedstocks with monounsaturated FA contents in excess of approx 60%. Anise (64.4% monounsaturated FAs), arugula (69.8%), coriander (77.4%), field pennycress (55.6%), meadowfoam (76.7%), upland cress (64.8%), and hazelnut (79.0%) oils were selected based on their FA profiles. Camelina and walnut oils were selected as antagonists to the FA profile tool, as they had polyunsaturated contents of 54.3% and 89.4%. The following properties were measured: oxidative stability, cold flow, viscosity, energy content, specific gravity, iodine value, acid value, glycerol content, cetane number, as well as sulfur and phosphorous content. This work summarizes those results and comments on the utility of FA profile as a screening device for feedstock selection.

Corrosion Inhibition of Mild Steel in Mineral Oil and Acidic Media by Several Alkyl Succinate Derivatives.
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Succinic acid is identified as a potential platform chemical for the production of various high value-added derivatives from renewable resources. It can be used as a precursor of many chemicals, which are used in pharmaceutical products, solvents, biodegradable polymers, surfactants and lubricating additives. In this study, several alkyl succinate derivatives were synthesized through esterification and amidation of alkyl succinic anhydride with fatty alcohol and fatty amine. Synthesized compounds were characterized with FT-IR, 1H-NMR spectra and GC and then their physical properties and their inhibiting action on the corrosion of mild steel in mineral oil and acidic media was investigated. All compounds were tested with steel stripe in paraffinic based mineral oil medium by ASTM D665 method and also some of them were tested with steel in acidic media by gravimetric method and electrochemical techniques. Inhibition efficiencies of all tested inhibitors in oil medium and acidic media depended on the structures and concentration of inhibitors.

Hydroxylated Polyester Resin Synthesizing from Crambe Oil by Mass Polymerization.

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In the present work, a hydroxylated polyester resin was synthesized by the mass polymerization process from the modified crambe oil and after characterized. The prepared resin was classified as medium oil length. The first process was produced the polyol by trans-sterification method with trimethylolpropane. After, the polyol reacted with phthalic anhydride inside the reactor in the temperature close to 220°C to obtain the polyester resin. Various physical chemistry properties of the raw material and resin values such as iodine, acidity, saponification and hydroxyl, as well as specific gravity, viscosity and moisture content were determined. The FTIR spectra present a significant band at 3300 cm-1 to the polyols and the polyester as indicated the formulation. The 1H e 13C NMR confirms the modification of the crambe oil and its polymerization. The thermal stability was studied using different atmospheres (O2 and N2), which showed higher thermal stability of the thin film close to 200 °C. The curing process of the hydroxyl polyester resin formed a film and occurred through thermal oxidation at 120ºC during 24h without catalyst. The film presented chemistry resistance to acids, saline and water solutions.

Selective Heterogeneous Acid Catalyzed Esterification of n-terminal Sulfyhdryl Fatty Acids.

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Mercapto fatty acid esters are useful intermediates en route to thiol containing structured lipids and are more efficient substrates than their corresponding acids when used in nonaqueous, enzymatic transesterification processes. Literature methods to the mercapto acid esters describe the catalysis with strong acids, which catalyze reactions at the N-terminal sulfydryl group. Two mesoporous silicas functionalized with propylsulfonic (SBA-15-PSA) and arenesulfonic (SBA-15-ASA) acid groups, and a highly acidic, functionalized styrene divinylbenzene copolymer ion exchange resin (Amberlyst-15) were examined for their ability to catalyze the ethanolic esterification of the N-terminal sulfydryl fatty acid, 11-mercaptoundecanoic acid (MUA), without catalyzing unwanted side reactions at the sulfhydryl group. The activation energy for the catalytic esterifications were determined from 50 to 75 °C, resulting in apparent E_a of 54, 71, and 59 kJ/mol for SBA-15-PSA, SBA-15-ASA, and Amberlyst-15, respectively. GC-MS analysis determined that all three catalysts produced near quantitative conversion of MUA to its ethyl ester with very little reactivity towards the sulfhydryl group, a marked improvement over sulfuric and p-toluenesulfonic acids which produced thiothers and disulfide side products.