2013 Annual Meeting Abstracts

Industrial Oil Products

MONDAY

AFTERNOON

IOP 1: Alternative Fuels
Chair(s): G. Knothe, USDA, ARS, NCAUR, USA; L. Yao, Iowa State University, USA

Emissions and health effects of biofuel blends used in engines with SCR catalyst

J. Krahl[(1)], C. Pabst[(2)], A. Munack[(3)], B. Fey[(4)], O. Schröder[(5)], K. Schaper[(6)], J. Bünger[(7)]
[(1)]Coburg University of Applied Sciences and Arts, Germany [(2)]Thuenen-Institute; German Federal Research Institute for Rural Areas,, Germany [(3)]Thuenen-Institute; German Federal Research Institute for Rural Areas, Germany [(4)]Thuenen-Institute; German Federal Research Institute for Rural Areas, Germany [(5)]Coburg University of Applied Sciences and Arts, Germany [(6)]Thuenen-Institute; German Federal Research Institute for Rural Areas, Germany [(7)]Institute for Prevention and Occupational Medicine of the German Socia, Germany

The influences of fuel mixtures that were composed of diesel fuel, rapeseed oil methyl ester and hydrotreated vegetable oil on the emissions of a heavy duty engine with SCR catalyst were studied during the present project. The regulated emissions as well as the polycyclic aromatic hydrocarbons and the mutagenicity of the exhaust gas were analysed both in the raw and treated exhaust. In the area of regulated emissions, nitrogen oxides which should be reduced by the SCR catalytic converter are of major interest. The admixture of HVO leads to a reduction of the NOx emissions compared to reference diesel fuel. With the increase in the proportion of RME a clear increase of nitrogen oxides occurs. Therefore an increase in dosage of the added agent ?AdBlue? would be necessary that would allow a reduction of increasing NOx emissions. With respect to the particle mass emissions both RME and HVO show a significant emission reduction potential as admixing components compared to DF. By the use of the SCR catalyst, a very high reduction of the mutagenicity can be achieved. In both the particle fraction and the condensate of the exhaust gas a significantly reduced number of mutations in the Ames test is observed. This positive effect can be explained by the fact that the exhaust gas components, such as PAH and mutagenic nitro-PAH as well as the hydrocarbons are oxidized by the catalyst to a large extent. All these components are belonging to the soluble organic fraction which is reduced by the catalyst.

Thermochemical Properties of Lipids Used for Biofuels

J. Van Gerpen[(1)]
[(1)]University of Idaho, United States of America

Because vegetable oils and animal fats are traditionally used in food products, most of the property data available for these products is limited to that needed for extraction and refining. As lipid compounds have become increasingly used as renewable fuels or feedstocks for renewable fuels, thermochemical property data such as higher and lower heating values and enthalpies of vaporization and formation are important. Measured values of these properties for lipid compounds are limited, and in some cases, nonexistent in the literature. This paper provides estimated values of these

properties using a group additivity method and compares the estimated values to the available experimental data. Comparisons for the heating value indicate that the estimated values are generally within 0.3% of the measured values where data are available and this strongly suggests that the estimates for compounds not currently found in the literature are also of equivalent accuracy.

Cetane Numbers of Biodiesel and its Components

G. Knothe[(1)]
[(1)]USDA / ARS / NCAUR, United States of America

The cetane number is one of the prime fuel quality indicators of a petrodiesel or biodiesel fuel as it relates to the tendency of the fuel to ignite in the combustion chamber. It has been established that compound structure, including chain length, branching and presence of double bonds, is a major factor influencing the cetane number. With more potential feedstocks for biodiesel such as inedible oils and algae receiving increasing interest, fatty acid profiles hitherto unknown in biodiesel affect its properties, including the cetane number. In light of these developments, the cetane numbers of some neat fatty acid methyl esters, for example highly polyunsaturated fatty acid methyl esters (C20:4 and C22:6) and esters with varying double bond positions, found in these biodiesel fuels were determined. They can be evaluated in conjunction with previous results on more common esters which is a focus of this presentation

Effects of Monoacylglycerols on Low-Temperature Viscosity and Cold Filter Plugging Point of Biodiesel

R. Dunn[(1)]
[(1)]USDA-ARS-NCAUR, United States of America

Biodiesel is composed of mono-alkyl fatty acid esters made from the transesterification of vegetable oil or animal fat with methanol or ethanol. Biodiesel must meet rigorous fuel standard specifications (ASTM D 6751; CEN EN 14214) to be classified as an alternative fuel. Nevertheless, biodiesel that is within specification may contain trace concentrations of unconverted monoacylglycerols (MAG). The relatively low solubility of MAG in biodiesel may cause them to form solid residues when the fuel is stored at low temperatures. The present study is an evaluation of how MAG and affect the kinematic viscosity (Visc) and cold filter plugging point (CFPP) of fatty acid methyl esters (FAME) from soybean, canola, and palm oils. Results demonstrated good correlations for both Visc and CFPP-time to filter (TTF) with respect to decreasing temperature. Mixing the FAME with added MAG had an effect on both parameters, especially with respect to TTF. Very sharp increases in TTF were noted at higher temperatures as the added MAG concentration increased in the mixtures. These effects were in contrast to less pronounced effects on Visc. Finally, correlations established between TTF and Visc were found to be disrupted by sharp increases in TTF caused by the presence of added MAG in the mixtures. Results from this study suggest that biodiesel should be periodically tested for CFPP and the TTF recorded when stored during cold weather.

Adsorptive Drying of Oil-solvent Miscella by 4a Molecular Sieves for the Preparation of High-purity Methyl Esters

S. Tabtabaei[(1)], D. Boocock[(2)], L. Diosady[(3)]
[(1)]University of Toronto, Canada [(2)]University of Toronto, Canada [(3)]University of Toronto, Canada

The single- and multiple-stage treatments with cyclic ethers including tetrahydrofuran (THF) and 1,4-dioxane of stable oil-in-water emulsions produced during non-enzymatic aqueous processing of dehulled yellow mustard flour destabilized the emulsions resulting in the formation of low-phosphorous and low-free fatty acid (FFA) oil-solvent-water miscella phases containing between 1 to 7% water. The high water content prevented the direct conversion of the system to fatty acid methyl esters (FAME) through a single-phase base-catalyzed transmethylation process. Dehydration of these miscella phases by adsorption on 4A molecular sieves using both batch and column systems successfully reduced the water content to 0.3-2%. The kinetics and equilibrium of dehydration of oil-solvent-water miscella phases on 4A molecular sieves were studied in detail. The amount of the oil lost during the adsorption process was insignificant. The dehydrated miscella phases were reacted with methanol in a single-phase base-catalyzed transmethylation process with high yields (99.4 wt%) to FAME. The resulting FAME satisfied the international standards for use as biodiesel fuel.

Optimization of Conversion Efficiency of Algal Biomass to Soluble Sugars and Extractable Lipids

L. Laurens[(1)], N. Nagle[(2)], P. Pienkos[(3)]
[(1)]National Renewable Energy Laboratory, United States of America [(2)]National Renewable Energy Laboratory, United States of America
[(3)]National Renewable Energy Laboratory, United States of America

Algae form an excellent basis to develop raw biofuel feedstocks, thanks to the abundance of lipids and carbohydrates in the biomass. One of the main challenges associated with algal biofuels production is improving the lipid extraction and residual biomass conversion efficiency. Process yields are highly dependent on the efficiency of conversion of the individual components and subsequent upgrading or fermentation to fuels. We have developed a novel technology, involving moderate temperatures and low pH to convert algal biomass to soluble sugars, while making the lipids more accessible for downstream extraction. We have explored optimum conversion conditions with regards to release of sugars and extractability of the lipids utilizing an experimental design approach. Two algal strains were used for this work; Chlorella sp. and Scenedesmus sp., each grown to contain over 30% carbohydrates and 40% total lipids. At the ideal conversion conditions we have measured the release > 90% of the available glucose in the treatment liquors and over 85% of the fatty acids can be recovered and extracted. This process yields three components; i) solubilized sugars, ii) pure lipids and iii) protein-enriched residual biomass. We have characterized this process with regards to detailed fingerprinting of the lipids throughout the process, temporal quantification of the release of carbohydrates. In addition, we are using microscopy to provide also visual information on the spatial, temporal and morphological changes during the conversion process. The combined bioethanol and fatty acid conversion makes our process particularly valuable compared with an extraction-only process.

Extraction of algal lipids with surface crosslinked micellar materials

L. Yao[(1)], T. Wang[(2)], X. Li[(3)], Y. Zhao[(4)]
[(1)]Iowa State Universityi, United States of America [(2)]Iowa State University, United States of America [(3)]Iowa State University, United States of America [(4)]Iowa State University, United States of America

A novel extraction method using surface crosslinked micellar materials (SCMM) to extract algal lipids was investigated. SCMM that have high internal capacity to sequester polar lipids from aqueous system were synthesized from tung oil via a simultaneous free-radical polymerization of both the surface and internal functional groups. The extraction performance of SCMM was evaluated by the change of turbidity of the lipid-water emulsion and chlorophyll content. SCMM are efficient in the recovery of residual algal lipids in an aqueous solution. The oil trapping capacity of SCMM was about 1 mg oil per mg of SCMM. SCMM are rigid materials and can be regenerated after the lipids are removed and reused.

An Economic Model to Estimate the Cost of Biodiesel Production by in situ Transesterification

M. Haas[(1)], A. McAloon[(2)], W. Yee[(3)], R. Stroup[(4)], K. Wagner[(5)]

[(1)]Eastern Regional Research Center, Ag. Research Service, U.S.D.A., United States of America [(2)]Eastern Regional Research Center, U.S. Dept. of Agriculture, United States of America [(3)]Eastern Regional Research Center, U.S. Dept. of Agriculture, United States of America [(4)]R.L. Stroup Co., United States of America [(5)]Eastern Regional Research Center, U.S. Dept. of Agriculture, United States of America

The term ?in situ? transesterification (IST) describes the production of simple alkyl fatty acid esters for use as biodiesel by direct transesterification of the acylglycerol-linked fatty acids residing in a solid material. Multiple publications from several labs have shown this method of fatty acid ester production to be generally applicable across a wide variety of substrates and capable of virtually quantitative transesterification of the acylglycerides resident in the feedstock. Since IST avoids the isolation and refining of the feedstock lipid before its conversion to biodiesel it would seem to offer economic advantages over conventional methods of biodiesel production. To investigate this possibility we have constructed a technoeconomic model to estimate the capital investment required and the per gallon process costs for the production of 10 million gallons per year of biodiesel by the in situ transesterification of soybeans. The model begins with intact soybeans and ends with biodiesel, soybean meal, and coproduct glycerol. For comparison purposes we have also constructed a comparable model for biodiesel production by conventional methods, i.e. involving the isolation and refining of feedstock soybean oil and its subsequent alkali-catalyzed transesterification. The estimated capital and process costs from these two models will be examined and compared.

Momordica Charantia Seed oil Methyl Esters: Kinetic Study and Fuel Properties Momordica Charantia Seed oil Methyl Esters: Kinetic Study and Fuel Properties

U. Rashid[(1)], J. Ahmad[(2)], R. Yunus[(3)], H. Masood[(4)], A. Azhari[(5)], A. Al-Muhtaseb[(6)]

[(1)]Universiti Putra Malaysia, Malaysia [(2)]Universiti Teknologi PETRONAS, Malaysia [(3)]Universiti Putra Malaysia, Malaysia [(4)]Universiti Putra Malaysia, Malaysia [(5)]Universiti Putra Malaysia, Malaysia [(6)]Sultan Qaboos University, Oman

Due to concerns such as increasing energy demand and the environmental problems caused by consumption of fossil energy, it is needed to conduct researches on non-food feedstock for biodiesel production. In the present research work, Momordica charantia (M. charantia) seed oil was appraised for the first time as a possible non-food feedstock for synthesis of biodiesel. M. charantia has oil content (36.10 ± 4.50%), high acid value (0.42 mg g-1) and its oil enable base-catalyzed transesterified for biodiesel production after acid pre-treatment. It was transesterified under standard conditions at 6:1 molar ratio of methanol to oil; 1.00% wt sodium methoxide as a catalyst; 60 ? reaction temperature and 90 min of reaction time. A biodiesel conversion of 99.8% was acquired with a yield of 93.2%. The reaction followed first order kinetics. The activation energy (EA) was 254.5 kcal mol-1 and the rate constant values were 1.19 x10-4 to 1.30 x 10-4 min-1. Gas chromatography investigation of M. charantia seed oil methyl esters (MSOMEs) depicted that the fatty acid composition includes a high percentage of monounsaturated fatty acids (64.11±5.02%). MSOMEs were also characterized using Fourier Transform Infrared Spectroscopy (FTIR) and 1H Nuclear Magnetic Resonance (NMR). The tested fuel properties of the MSOMEs, except oxidative stability, were conformed to EN 14214 and ASTM D6751 standards. The low value oxidative stability of MSOMEs can be solved by adding antioxidants additives. In summary, M. charantia oil has potential as non-food raw material for biodiesel production.

TUESDAY

MORNING

IOP 2: Catalysis
Chair(s): D. Pioch, CIRAD, France; A. Nickel, Materia, USA

Achieving Commercial Viability: The Evolution of Natural Oil Processing via Olefin Metathesis

D. Allen[(1)]
[(1)]Materia Inc., United States of America

Olefin metathesis is a powerful reaction for the interconversion of carbon-carbon double bonds that has broad potential for a variety of industrial applications. This presentation will focus on the development of an olefin metathesis process that transforms renewable seed oil based feedstocks into higher value products employing the Grubbs catalyst technology developed at Caltech. This process has led to the construction of a bio-refinery plant in Surabaya, Indonesia with the capability to process over 400 million pounds of seed oils annually. A discussion of a R&D project geared towards the development of a supported heterogeneous catalyst system for the continuous-flow processing of natural seed oil feedstocks will also be discussed.

Examining the Functionality of Self-Metathesized Vegetable Oil and Controlling the Products by Manipulating Reaction Conditions

S. Li[(1)], L. Bouzidi[(2)], S. Narine[(3)]
[(1)]Trent Centre for Biomaterials Research, Trent University, Canada [(2)]Trent University, Canada [(3)]Trent University, Canada

Metathesis reaction of vegetable oil and fats is becoming an important chemical route to produce safer, less toxic fine chemicals. The metathesis reaction produces a complex mixture containing oligomers, cyclic compounds, as well as cis/trans- configurations. The understanding of the composition - reaction conditions dependence would enable the control of the reaction conditions and the production of customized mixtures. Furthermore, detailed structure ? function relationships of components, individually and in combination would enable tailor-engineering of materials with specific/desired properties. In this talk, we will present the metathesis of a model material, namely Triolein, under varying concentrations and a careful study of the constituting oligomers (from dimer to octamer). These model oligomers were carefully synthesized in purities > 99% and fully characterized. The physical properties (crystallization, melting and flow characteristics) of the oligomers are shown to scale very well with molecular mass and to depend strongly on the relative number of double bonds in the trans- configuration. The findings highlighted the competition between the trans- character and size of the molecules as key in determining the functionality of these molecules. Overall, all the investigated proprieties plateaued at the hexamer, suggesting that no further marginal utility can be obtained with larger oligomers.

Biocatalytic Synthesis of Low-molecular Weight Oil-thickening Amphiphiles From Renewable Feedstocks.

J. Silverman[(1)], G. John[(2)]
[(1)]City University of New York, United States of America [(2)]City University of New York, United States of America

The systematic shift from synthetic petroleum based materials to natural and renewable bio-based products has changed the way we look at oil and oil-derived molecules. Using fatty acids, sugars, and glycosides as building blocks

to synthesize functional low molecular weight gelator amphiphiles is an environmentally benign and sustainable method for the creation of novel oil thickeners. From food application to cosmetics and cleaning products, using minute amounts (<5 %wt) of a gelator enables the solidification of liquid substances at ambient temperatures without chemical modification. Bio-based low molecular weight amphiphiles prove to afford practical functional soft materials application to many real world situations.

Effects of Non-thermal Plasma in Glycerol Dehydration to Acrolein Catalyzed by Solid Acids

X. Ye[(1)], L. Liu[(2)], A. Wang[(3)]
[(1)]University of Tennessee, United States of America [(2)]University of Tennessee, United States of America [(3)]University of Tennessee, United States of America

Acrolein is an important intermediate chemical that can be produced from glycerol, leading to an array of high-value products such as acrylic acid, methionine, superabsorbents, and polyester resin. Despite extensive research on the promising gas-phase glycerol dehydration using solid acids to make acrolein, coke formation resulting in fast catalyst deactivation remains a significant challenge to industrial application. Non-thermal plasma (NTP) was integrated in gas-phase glycerol dehydration with argon as the carrier and discharge gas. Heteropoly acid supported on silica or alumina was used as solid acids. Various reaction temperatures and NTP discharge field strengths were studied for the individual and interactive effects regarding the glycerol conversion, product selectivities, and coke formation. Results showed that the presence of NTP always improved glycerol conversion, and NTP increased acrolein selectivity if properly conditioned. Under the experimental conditions, the optimal NTP field strength was 3.78 kV/cm for alumina supported solid acid, and 4.58 kV/cm for silica supported solid acid. Application of the optimized NTP improved acrolein yield by ~10mol% on average when the reaction was operated at 275°C. Such catalytic performance remained stable for >20 hours time-on-stream without showing deactivation, achieving >94mol% glycerol conversion and >85mol% selectivity to acrolein.

Sn (iv)complexes for Fatty Acid Methyl Esters Production

S. Meneghetti[(1)], M. Meneghetti[(2)], J. da Silva[(3)]
[(1)]Federal University of Alagoas - UFAL, Brazil [(2)]Federal University of Alagoas - UFAL, Brazil [(3)]Federal University of Alagoas - UFAL, Brazil

Sn(IV) complexes, like dimetyldineodecanoatetin, dibutyldineodecanoatetin, dioctyldineodecanoatetin, dimetyldiundec-10-enoatetin, dibutyldiundec-10-enoatetin and tributylundec-10-enoatetin, were tested as catalysts for esterification and transesterification reaction in the presence of methanol or ethanol as alcoholysis agents, in order to investigate the effect of different ligands coordinated to the metal center. Two different types of reactors have been employed on transesterification: an open glass reactor, equipped with a reflux condenser (RVCR), and a closed steel reactor (RP). Parameters like reaction time, temperature, and catalyst amount were systematically evaluated. The reaction products were characterized by gas chromatography. Results point out that the use of the closed steel reactor is advantageous, since higher yields are obtained in shorter reaction times. All complexes were active at relative high reaction temperatures and the results can be related to the steric effects of different ligands bearing Sn(IV). The results obtained and discussed in this work can help the development of new catalytic systems to biodiesel production from oils with very high acid content.

Biodiesel production from crude palm oil using CaO and CaO/Al2O3 as heterogenous catalyst

(1) *(2)*

S. Rakshit , W. Chaiwong
(1)Lakehead University, Canada (2)Asian Institute of Technology, Thailand

Thailand has developed a road map for alternative energy in order to reduce the import bill of transportation fuels. The production of biodiesel from renewable vegetable oils is one of the options being put in place. In this study the advantages of using heterogenous catalysts for the production of biodiesel from crude palm oil was explored, Calcium oxide and calcium oxide anchored on ?-alumina were used as the heterogenous catalysts for the transesterification reaction and the conditions optimized for the highest conversion and for the best quality and quantity of methyl ester and glycerol production. This was compared to homogeneous catalyzed reaction by conventional process for FAME formation using palm oil. The properties of obtained biodiesel as also compared to the specification required by the Department of Energy Business (DOEB), Thailand. The optimum conditions of methanolysis of RBD palm oil using CaO and CaO/Al2O3 were slightly different. The parameters studied were the amount of catalyst, the methanol to oil ratio, reaction time and temperature. The purity of biodiesel was higher than the minimum required for use in motor vehicles (96.5% FAME) while the and glycerol purity was higher than that obtained using a homogenous catalyst making it a better by-product for subsequent use. Most of the tested properties of biodiesel produced meet the required specifications for use as a transportation fuel.

Soy Biodiesel Production Over Mg-zn Mixed Oxide Catalysts

F. Ng(1), N. Pasupulety(2), G. Rempel(3)
(1)University of Waterloo, Canada (2)University of Waterloo, Canada (3)University of Waterloo, Canada

Recently, interest in biodiesel use in the Canada and U.S. has been growing due to: 1) its potential to reduce dependence on imported petroleum [1], 2) its potential to help mitigate possible negative impacts of global climate change by lowering net CO and CO2 emissions from the transportation sector, 3) no engine modifications are required and biodiesel blends easily with petroleum diesel. In the present work we focused on development of efficient solid Mg-Zn mixed oxide catalyst for the production of soy biodiesel under mild reaction conditions, so that the optimized process can be developed using catalytic distillation (CD). Transesterifcation of soy oil was carried out on magnesium zinc mixed oxides are synthesized by CO2-ethanol precipitation method. Formation of fatty acid methyl esters (FAME) in this study was influenced by Mg to Zn molar ratio. The results revealed that Mg3Zn1 exhibited maximum catalytic activity for soy FAME of 90 mass % under mild reaction conditions. The catalytic activity of Mg-Zn mixed oxides for FAME formation as follows; ZnO< Mg1Zn1 < Mg5Zn1 < MgO < Mg3Zn1. The contribution towards the greater biodiesel yield is mainly due to generated surface basic sites (M-OH) and also due to newly existed basic sites anticipated from ZnMgO lattice. Reference: [1] Energy Policy Act of 2005 (Public Law 109-58).

Development of a Lewis-based Catalytic System for Biodiesel Production: From a Batch Laboratory Scale to a Continuous Pilot Plant

P. Suarez(1), F. Silva(2)
(1)University of Brasilia, Brazil (2)University of Brasilia, Brazil

We prepared different mixed oxides of the type (Al2O3)0.8(SnO)0.2-x(ZnO)x (0.2 ? x ? 0), from the co-precipitation of aluminum, tin and zinc hydroxides followed by calcinations and extruded them into pellets. The pellets were placed into the tubular reactor as a 30 cm long column (2.65 kg). The reactor was flowed with soybean oil (168 g h-1) and methanol or ethanol (89 g h-1) with the temperature fixed at 100 ?C. It was possible to transesterify soybean oil in up to 80 % yield when using methanol and 40 % when using ethanol. Increasing the temperature to 180 ?C, it was possible to ethanolise soybean oil with yields up to 90 %. It is important to note that after a steady state is achieved the

conversions remained constant with time. It is also worth to mention that the fixed bed remained active for more than 200 h, showing no catalyst leaching or deactivation, and so far was not possible to determine its overall productivity.

AFTERNOON

IOP 3: New Uses of Glycerine
Chair(s): R. Burton, Marc-IV, USA; P. Ye, University of Tennessee, USA

ACI/NBB Glycerine Innovation Award Lecture

Glycerol valorization for sustainable chemical production

A. Martin[(1)]
[(1)]Leibniz-Institute for Catalysis, Germany

The tremendous increase in worldwide biodiesel production from vegetable oil leads to a similar development in availability of glycerol, roughly 10 wt% of such oils is glycerol. Glycerol production in Europe has been tripled within the last ten years to 700-900 kt in 2008-2010, because its production strictly follows the fatty acid methyl ester manufacture. Unfortunately, the present industrial demand is limited due to glycerol application in cosmetics, pharmaceuticals and some fine chemical applications. Thus, the availability of large amounts of cheap glycerol is the driving force to develop new processes. Finding value-added alternatives to glycerol incineration or feeding would improve economic viability of biodiesel manufacture and the biofuel supply chain. The contribution focuses on general trends in valorization of glycerol. A first industrial plant for the manufacture of epichlorohydrine from glycerol by Epicerol® process (Solvay S.A.) was launched in 2007. Other applications may follow such as the synthesis of glycerol tert.-butyl ether by glycerol etherification with isobutene or the manufacture of propanediols by hydrogenolysis. The contribution will give some details from own research on selected reactions, in particular acrolein manufacture by dehydration over supported and alkali cation modified heteropolyacids (HPA). Alkaline metals such as lithium, potassium and cesium were added to HPAs to modify catalyst Brønsted acidity. Furthermore, selective diglycerol syntheses by dimerisation using basic and acidic catalysts were studied. Application of strong acidic Nafion® resin as catalyst foil in a reaction regime of low temperature and reduced pressure showed high diglycerol yields at nearly complete conversion.

Production of Racemic Lactic Acid From Glycerol Using Solid Base Catalyst

X. Ye[(1)], L. Chen[(2)], L. Liu[(3)]
[(1)]University of Tennessee, United States of America [(2)]University of Tennessee, United States of America [(3)]University of Tennessee, United States of America

Lactic acid is one of the value-added chemical that can be produced from glycerol having wide applications in food and chemical industries. Although glycerol can be converted to lactic acid with an alkali as homogeneous catalyst at high glycerol conversion and lactic acid yield, the high alkalinity would cause severe corrosiveness, restricting productivity of the homogeneous process. Conversion of glycerol to racemic lactic acid was performed using low-cost

calcium oxide as solid base catalyst. Different factors, including reaction time and temperature, molar ratio of CaO to glycerol, and water content in glycerol were studied. The highest yield of lactic acid obtained was 40.8 mol%. Calcium oxide maintained its original activity in three cycles of regeneration and reuse. The utilization of CaO in conversion of crude glycerol was also investigated, showing no significant influence of impurities in crude glycerol on CaO catalytic activity when water content in crude glycerol was low. Also, study on the feasibility of CaO used as catalyst for both biodiesel production and following crude glycerol conversion was conducted. Two biodiesel production methods with CaO as catalyst were tested, and lactic acid was successfully produced from crude glycerol.

New Catalyst and New Reactor for Glycerol Conversion to Acrolein

F. Dumeignil[(1)], B. Katryniok[(2)], R. Melendez[(3)], M. Capron[(4)], S. Paul[(5)], N. Fatah[(6)], P. Rey[(7)], S. Pariente[(8)], V. Bellière-Baca[(9)]
[(1)]UCCS, France [(2)]UCCS, France [(3)]UCCS, France [(4)]UCCS, France [(5)]UCCS, France [(6)]UCCS, France [(7)]Adisseo, France [(8)]Rhodia, France [(9)]Rhodia, France

The catalysts used for glycerol dehydration to acrolein suffer from deactivation by coking. We studied the regeneration of spent catalysts based on Keggin-type silicotungstic acid (STA). A 20 wt.% STA sample supported on bare SBA-15, and a specifically developed 20 wt.% STA sample supported on SBA-15 containing 20 wt.% of ZrO2 nanoparticles were prepared. Their performances were determined at 275 °C in a fixed bed reactor. STA/ZrO2/SBA-15 showed significantly increased long-term performances (69 % vs. 24 % acrolein yield after 24 h), which was explained by a decrease in the acid strength of the STA due to a modified active phase/support electronic interaction, which further increased its thermal stability and prevented STA decomposition during one-shot regeneration of the catalyst by coke burning under air. Over the ZrO2-free catalyst, the regeneration step led to a significant loss in acrolein yield (30 %) due to thermal destruction of STA. As this decomposition proceeds via the loss of constitutional water from the Keggin-structure, addition of water in the regeneration feed enabled recovering a slightly higher yield in acrolein (42 %), due to equilibrium displacement. Finally, cyclic regeneration of the catalyst was performed using iso-chronical cycles of 10 min for reaction and coke burning. STA/ZrO2/SBA-15 exhibited poor performances (35 % yield in acrolein) due to the longer activation period needed for this catalyst. The ZrO2-free catalyst exhibited stable performances (74 % acrolein yield) without STA destruction. We then patented an integrated process for simultaneous reaction and regeneration, based on a Two-Zone Fluidized Bed Reactor.

CANCELLED-Advanced bioprocessing to upgrade crude glycerol into high value oils

L. Dyson[(1)]
[(1)]Kiverdi, Inc., United States of America

Thermal, Mechanical and Absorbent Properties of Glycerol-based Polymer Films Infused with Plant Cell Wall Polysaccharides

V. Wyatt[(1)], M. Yadav[(2)], N. Latona[(3)], C. Liu[(4)], M. Haas[(5)]
[(1)]USDA - Agricultural Research Service, United States of America [(2)]USDA - Agricultural Research Service, United States of America [(3)]USDA - Agricultural Research Service, United States of America [(4)]USDA - Agricultural Research Service, United States of America [(5)]USDA - Agricultural Research Service, United States of America

Glycerol and glutaric acid have been reacted to form a poly(glutaric acid-co-glycerol) gel. Polymer composite films were then produced by curing mixtures of the polymer gel and plant wall polysaccharides (sugarcane bagasse, corn fiber gum, pectin, or microcrystalline cellulose) at 135 degrees C for 12 h. Films without any additives and films infused with iminodiacetic acid and higher concentrations of glycerol were also synthesized for comparison. The films were evaluated by FTIR to determine the extent of reaction. Thermal stability was determined by TGA and DSC. The mechanical strength for each polymer composite film was evaluated by determining values for thickness, tensile strength, elongation at break, Young?s modulus, and fracture energy. Solvent absorption studies were performed by incubating the films in various solvents for 24 h. The amount of solvent that absorbed into each film was monitored and recorded at predetermined time intervals. The films were subsequently evaluated for erosion and re-absorption.

Bio-plastics (mcl-PHAs) production from commercial biodiesel-based glycerine (glycerol) by two newly isolated pseudomonas putida species

N. Cicek[(1)], F. Jilagamazhi[(2)], U. Sharma[(3)], P. Sharma[(4)], D. Levin[(5)], R. Sparling[(6)]
[(1)]University of Manitoba, Canada [(2)]University of Manitoba, Canada [(3)]University of Manitoba, Canada [(4)]University of Manitoba, Canada
[(5)]University of Manitoba, Canada [(6)]University of Manitoba, Canada

Production of medium chain-length polyhydroxyalkanoates (mcl-PHAs) from agro-industrial wastes such as glycerine (or glycerol) helps to reduce the current high product cost of this kind of renewable and biodegradable biopolymer. Two pseudomonas putida strains (LS46 and MO2) have been isolated and identified in our lab. Both of them have shown the ability to effectively produce mcl-PHAs from commercial biodiesel-based glycerol (obtained from a full-scale biodiesel production plant in Danville, IL) in minimal culture medium. In this work, Ramsay?s medium with 1g/L of nitrogen source plus 2 v/v% of glycerol was used. Under this condition, the P.putida strains LS46 and MO2 produced 2.71 g/L and 3.32 g/L of biomass with a dry weight content of 10.18 wt% and 13.52 wt% of mcl-PHAs within 48 hours, respectively. The mcl-PHAs content increased to about 30 wt% after 120 hours with both strains. Further comparison of mcl-PHAs production between 10g/L chemical grade pure glycerol and 10 g/L of commercial glycerol revealed comparable results after 72 hours cultivation: 2.13 g/L of biomass and 17.32 wt% of mcl-PHAs from pure glycerol vs. 2.78 g/L of biomass with 13.04 wt% of mcl-PHAs with biodiesel-based glycerol. It was shown that mcl-PHAs production from glycerol was triggered by nitrogen limitations, with little (about 2 %) mcl-PHAs content detected under nitrogen excess conditions (4g/L ammonia sulfate). These preliminary results on mcl-PHAs production show that there is significant potential of using biodiesel-based glycerol as a cost-effective feedstock for bio-plastics production by these newly isolated pseudomonas putida species.

Cancelled-Preparation of Propylene Glycol from Glycerol through Hydro-Thermochemical Process

R. Maglinao[(1)]
[(1)]Montana State University-Northern, United States of America

WEDNESDAY

MORNING

IOP 4: Biobased Polymers and Lubricants
Chair(s): S. Narine, Trent University, Canada; H. Ngo, USDA, ARS, ERRC, USA

Plant oils: The perfect renewable resource for polymer science?!

M. Meier[(1)]
[(1)]Karlsruhe Institute of Technology (KIT), Germany

In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. Especially plant oils bear a large potential for the substitution of currently used petrochemicals, since a variety of value added chemical intermediates can be derived from these resources in a straightforward fashion taking full advantage of nature?s synthetic potential. Here, new approaches for the synthesis of monomers and polymers from plant oils will be discussed. For instance, we could show that different chain length ?,?-diester monomers can be obtained from fatty acid esters via olefin taking advantage of natures "synthetic pool" of fatty acids with different chain lengths and positions of the double bonds. Moreover, thiol-ene click chemistry offers a complementary approach for the introduction of different functional groups to fatty acids in a straightforward and efficient manner. Furthermore, palladium catalysed C-H activation was used to obtain acetoxy ester functionalized fatty acid methyl esters. Most recently, we introduced the first catalytic variant of the well-known Lossen rearrangement, which turned out to be an efficient and sustainable tool for the synthesis of renewable nitrogen containing monomers. The thus obtained renewable platform chemicals are valuable starting materials for a variety of polyesters, polyurethanes and polyamides. In summary, we will thus demonstrate the versatility of plant-oil derived platform chemicals for the synthesis of a large variety of renewable monomers and also discuss some of the thereof derived polymers.

Biopolyester from Ricinoleic Acid: Synthesis, Characterization and Its Use as Biopolymeric Matrix for Magnetic Nanocomposites

P. Suarez[(1)], E. Péres[(2)], F. Machado[(3)], J. Chaker[(4)], F. de Souza Jr[(5)]
[(1)]University of Brasilia, Brazil [(2)]University of Brasília, Brazil [(3)]University of Brasília, Brazil [(4)]University of Brasilia, Brazil [(5)]Federal University of Rio de Janeiro, Brazil

This work presents a study on the production of ricinoleic acid-based biopolyester derived from castor (Ricinus communis) oil with and without in situ insertion of magnetic Fe3O4 nanoparticles with their surface modified by ricinoleic acid. Self-catalyzed reactions, due to H+ from ricinoleic acid, which behaves as a Brønsted-Lowry acid, were performed in a batch bulk polymerization process and some kinetic studies were carried out. It was also observed that the magnetic Fe3O4 nanoparticles act as Lewis acid catalysts during the polymerization. The ester formations were followed by acid value and FTIR spectra and it was observed that the reactions without magnetic nanoparticles (only Bronsted self-catalyzed reaction) reached a steady-state after 14 h of reaction. For the reactions with surface-modified magnetic Fe3O4 nanoparticles the steady-state rate was reached in 6 h of reaction. In the absence of the magnetic nanoparticles, it was observed at 190 ?C that the consumption of the ricinoleic acid follows a second order behavior and increasing 20 ºC the reaction rate was 15 % faster. The polymeric materials have been characterized in order to provide information on their structural and thermal features. It was verified that the thermal stability of the product is significantly increased with the reaction conversion. Magnetic measurements were and have shown that the material exhibited a superparamagnetic behavior when using magnetic Fe3O4 nanoparticles.

Thermoplastic Polyurethane Elastomers With Fatty Acid Soft Segments

Z. Petrovic[(1)], I. Javni[(2)], J. Milic[(3)]
[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America

Polyester diols of molecular weight 2000 were synthesized from hydroformylated oleic acid and used to prepare two thermoplastic polyurethane (TPU) elastomers of different hardness. The elastomers are segmented polymers consisting of soft and hard segments. Soft phase content varied from 50% in the hard TPU to 70% in the soft TPU. Hard segments were based on diphenylmethane diisocyanate and butane diol. Good separation between phases and high molecular weights of the polymers was reflected in high tensile strengths, elongation and elastic recovery. It was demonstrated that fatty acids are viable monomers for polymers with excellent elastic properties.

Glyco-lipids as a Source of Polyols for the Design of Original Linear and Cross-linked Polyurethanes

H. CRAMAIL[(1)]
[(1)]Université de Bordeaux, France

Two novel sugar-based fatty ester polyols were synthesized by selective transesterification of epoxidized methyl or ethyl oleate with unprotected methyl ?-D-glucopyranoside and sucrose respectively, followed by hydrolysis of the epoxide moiety. The so-formed polyols were then used as polyurethane (PU) precursors in the polyaddition with isophorone diisocyanate (IPDI) in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst. Interestingly, the reactivity of the hydroxyl functions attached to the sugar and to the fatty ester chain moieties respectively could be discriminated with respect to the solvent used, enabling the synthesis of either linear or cross-linked PUs. The linear PUs were studied by means of FTIR, 1H NMR spectroscopy and size exclusion chromatography, SEC. The thermo-mechanical properties of these original PUs bearing pendant or intramolecular sugar units were also analyzed by differential scanning calorimetry, DSC

Novel High Molecular Weight Plant oil Copolymers

B. Chisholm[(1)], S. Alam[(2)], H. Kalita[(3)], S. Fernando[(4)], A. Jayasooriyamu[(5)], S. Samanta[(6)], A. Popadyuk[(7)], J. Bahr[(8)], A. Voronov[(9)], A. Bezbaruah[(10)]
[(1)]North Dakota State University, United States of America [(2)]North Dakota State University, United States of America [(3)]North Dakota State University, United States of America [(4)]North Dakota State University, United States of America [(5)]North Dakota State University, United States of America [(6)]North Dakota State University, United States of America [(7)]North Dakota State University, United States of America [(8)]North Dakota State University, United States of America [(9)]North Dakota State University, United States of America [(10)]North Dakota State University, United States of America

A novel polymer platform technology was developed that involves the conversion of a plant oil to a mixture of vinyl ether monomers in which each monomer molecule contains a fatty acid ester group derived from the parent plant oil. The cationic polymerization system developed allows for living polymerization of the monomers exclusively through the vinyl ether groups. This characteristic enables double bonds present in the unsaturated pendent groups to be utilized for the production of thermosets either directly or by derivatization to other functional groups including epoxy, hydroxy, and acrylate groups. In addition to homopolymerization, the monomers have been copolymerized with other monomers to create a wide variety of functionalized polymers expected to have utility for a number of markets including coatings, composites, rubber compounds, and personnel-care products. An overview of the synthesis, characterization, and properties of key polymers will be presented along with the properties of various formulated materials.

Synthesis of Biobased Poly(amide-urethane)s by Isocyanate-free Chemistry

D. Graiver[(1)], E. Hablot[(2)], R. Narayan[(3)]
[(1)]Michigan State University, United States of America [(2)]Michigan State University, United States of America [(3)]Michigan State University, United States of America

Biobased plastics and polymers based on renewable feedstock offer an intrinsic value proposition of a reduced carbon footprint. Such materials are in complete harmony with the rates and the timescale of the natural biological carbon cycle. Furthermore, the synthesis of polyurethanes using no isocyanates offers a safe and environmentally responsible synthetic strategy with a dramatically improved LCA profile. In this paper we wish to report the results of our solvent free synthesis poly(amide-urethane)s from plant oils. This one-pot synthesis comprises three steps; (1) plant oil dimer fatty acids are condensed with ethylene diamine to produce amine terminated oligomers intermediates; (2) These intermediates are reacted with ethylene carbonate to yield hydroxyl terminated di-urethanes prepolymers; (3) The prepolymers are subjected to a urethane-exchange polycondensation reaction to yield the desired polyurethanes. The structure and properties of the intermediates and the products were characterized by FTIR, 1H-NMR and GPC as well as hydroxyl value, acid value and amine value titrations. Typical polymers had a glass transition around -10 °C and a melting point around 73 °C and were stable up to 230 °C. The biobased carbon-content of these polymers increases to 88% as ethylene glycol is removed by the urethane exchange polycondensation reaction. Based on this study, we envision using these new biobased poly(amide-urethane)s as new building blocks for coatings, sealants, adhesives and elastomers in various industrial and consumer application.

Investigating Structure-Property Relationships in Lipid derived Thermoplastic Polymers

J. Jose[(1)], S. Narine[(2)]
[(1)]Trent Universiry, Canada [(2)]Trent university, Canada

Vegetable oil derived polymers are mostly thermosets, which are not reprocessable. Lipid derived thermoplastics are melt processable, and their properties are governed by the interplay between various intermolecular forces as determined by their structure. Design and control of lipid derived thermoplastic polymers for targeted applications therefore necessitates an understanding of their structure-property relationships. This presentation will summarize some five studies, using varying methylene [-(CH2)-] chain lengths (n) of the monomer as a tool, which investigated the structure-property relationships for a group of novel lipid-derived thermoplastic esters, amides and urethanes. Suitable monomers with controlled chain lengths were first obtained by functionalization reactions on vegetable oil, and, were subsequently polymerized to yield similar molecular weight thermoplastics. The crystalline structure, thermal, viscoelastic and mechanical characteristics of polymers were investigated using WAXD, DSC, TGA, DMA, tensile analysis. For thermoplastic polyesters as well as poly(ester-urethane)s, with increasing methylene chain lengths, the increased van der Waals forces favoured crystallization into orthorhombic polyethylene-like packing. Interestingly, for a sufficiently long methylene chain length (n=17), the biodegradable thermoplastic polyester exhibited thermal and mechanical properties comparable to polyethylene. For poly(ester-urethane)s with short methylene chains, as well as for thermoplastic poly(ester-amide)s, the H-bonding interactions favoured polymorphism, resulting in melting characteristics, glass transition and mechanical properties being tuneable as a function of H- bond densities.

Use of Vegetable Oil Derived Branched Linear Monoesters and Diesters as Superior Lubricants

L. Bouzidi[(1)], L. Singh[(2)], S. Li[(3)], S. Narine[(4)]
[(1)]Trent University, Canada [(2)]Trent University, Canada [(3)]Trent University, Canada [(4)]Trent University, Canada

Increasing environmental and sustainability concerns are driving research efforts towards the development of high - performance non-toxic biodegradable lubricants, waxes and gels from renewable sources. In this regard, the Trent Centre for Biomaterials Research is investigating a series of novel materials sourced from renewable feedstock such as vegetable oils and their derivatives to enable custom engineering and delivering optimal physical properties. The present study focuses on jojoba wax ester analogues, more than 46 model systems never investigated before, particularly suitable for use in high-grade lubricating oil formulations and additives as well as for a variety of other high-end wax and gel applications such as cosmetic and medical formulations, and foods. We have examined the structure - function relationships of linear mono- and di-esters and their branched derivatives produced from inexpensive renewable resources, i.e., fatty acids. A wealth of information have been gained on the influence of chain length, branching, symmetry, and functional groups on the physical properties such as crystallization, melt, polymorphism, solid fat content and flow behavior. The findings highlight relatively simple, inexpensive lipid-derived molecules with astonishingly low onsets of crystallization, and predictive structure ? property relationships which are very promising in the formulation of renewable superior lubricants.

Investigating the Thermal Stability of Linear Diesters Derived from Vegetable Oils: Dependence of Thermal Stability on the ?-Hydrogen and its Environment.

Diesters derived from vegetable oils may be used in oleochemical syntheses, polymer syntheses, or lubricant formulations. Thermal stability is one of many physical properties which influence its suitability for an application. Herein, a novel series of linear symmetric diesters have been investigated to determine the effect of structure on thermal stability. FTIR and 1H-NMR have been used to show that ester groups in close proximity to each other result in a weakening of the C-O-C bonds and an increasing lability of the ?- and ?- hydrogens. These results imply that diesters whose ester groups are located closest to each other are the most destabilized. This was further supported by TGA studies which showed decreasing onset of decomposition temperatures with decreasing distances between ester groups. The most stable diesters were obtained when the ester groups were furthest apart; no substantial increase in stability was observed past a distance of six-carbon atoms between the ester groups. TGA kinetic studies using the Friedman isoconversional method supported a preferred ?-elimination thermal decomposition mechanism as long as ?-hydrogens were present. In conclusion, diesters with varying levels of thermal stability may be prepared by manipulating the environment in which the ?-hydrogens exist.

Branched-chain Fatty Acid Isomers as Potential Biolubricants

H. Ngo[(1)], R. Dunn[(2)], E. Hoh[(3)]

[(1)]USDA-ARS-ERRC, United States of America [(2)]USDA-ARS-NCAUR, United States of America [(3)]San Diego State University, United States of America

There is a strong demand for high performance biolubricants because of the increasing costs and negative environmental impacts of petroleum-based oils. Biolubricants are advantageous over petroleum oils because of their ability to degrade into non-toxic components in the environment. Branched-chain fatty acid isomers (i.e., isostearic acid and iso-oleic acid) are well-established biolubricants, but they are not cost-competitive as a result of their inefficient manufacturing processes. They exhibit better oxidative stability than unsaturated fatty acids and typically have lower melting points than their linear saturated fatty acid counterparts. In this presentation, I will talk about highly efficient methods we have developed for the synthesis of branched-chain fatty acids. I will also discuss the detailed characterization and selected physical and lubricity properties of these materials.

Synthesis and Molecular Weight Control of Entirely Lipid Derived Aliphatic Polyester Diols

S. Narine[(1)], S. Merchant[(2)], S. Li[(3)], J. Jose[(4)], A. Vreugdenhil[(5)]
[(1)]Trent University, Canada [(2)]Trent University, Canada [(3)]Trent University, Canada [(4)]Trent University, Canada [(5)]Trent University, Canada

Degradation susceptible aliphatic polyesters from entirely renewable sources synthesized by solvent free melt condensation forms a sustainable and cost effective alternative to fossil fuel derivatives. Aliphatic Polyester Diols (APED)s from vegetable oil suitable as monomers for thermoplastic poly(ester-urethane) synthesis have been prepared by melt condensation of oleic acid derived Azelaic acid and 1,9 Nonanediol, using two methods viz. monomer ratio variation and reaction time. APEDs prepared by introduction of additional diol at varying reaction times have been found to be comparable with APEDs synthesized by monomer ratio variation. Structure has been confirmed by 1HNMR and FTIR. APEDs have been characterized for their molecular weight and its distribution by Gel Permeation Chromatography. Separation of APEDs has been achieved by column chromatography and fractional precipitation. APEDs with desired molecular weights and similar PDI (Polydispersity Index) have been separated by varying solvent ratios using fractional precipitation. Solvent use has been minimized by this method. Thermal stability of APEDs prepared by both methods is comparable as analyzed by Thermogravimetric Analysis and Differential Scanning Calorimetry.

AFTERNOON

IOP 5: Oleochemicals
Chair(s): P. Amora, Stepan, USA; J.O. Metzger, University of Oldenburg, Germany

Synthesis of Fatty Ethers: Catalytic Reduction of Fatty Acid Esters

U. Biermann[(1)], J. Metzger[(2)]
[(1)]University of Oldenburg, Germany [(2)]University of Oldenburg and abiosus e.V., Germany

Ethers, especially ethers of polyols such as glycerol are obtained by reduction of the respective esters by a simple methode. ?High oleic? sunflower oil, tributyryne and methyl oleate were catalytically converted to the respective ethers using silanes as reducing agent in a solvent-free reaction. The reduction could be carried out at room temperature using stoichometric amounts of reductive agent. After a reaction time of only 2 h the conversion of the starting material was 100 %. The product was separated by distillation.

New Polyols for Polyurethanes Based on Cashewnut Shell Liquid.

M. Ionescu[(1)], D. Hong[(2)], X. Wan[(3)], I. Javni[(4)], N. Bilic[(5)], Z. Petrovic[(6)]
[(1)]Pittsburg State University, Kansas Polymer Research Center, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America [(4)]Pittsburg State University, United States of America [(5)]Pittsburg State University, United States of America [(6)]Pittsburg State University, United States of America

The cashew tree, Anacardium occidentale, has a fruit with a very interesting structure, a nut is attached to a cashew apple. The nut has two shells one hard inner and another outer shell. In between these two shells, in a honeycomb structure, is an oil called cashew nut shell liquid(CNSL). The main component of CNSL is anacardic acid (90%)

which by decarboxylation leads to Cardanol, a natural phenol substituted in meta position with a chain of 15 carbon atoms with one double bond (25-30%), two double bonds (16-22%) and three double bonds (30-41%). By using classical reactions of phenols and of double bonds we developed new methods for transformation of CNSL in polyols for rigid polyurethane foams. The reactions used were: Mannich reaction, hydroformylation reactions, epoxydation of double bonds and ring opening of epoxy groups with alcohols and alkoxylation reactions. The synthesized hybrid aromatic-aliphatic polyols were characterized by wet methods (Hydroxyl number, viscosity, acid value, etc.), by Gel Permeation Chromatography and by Spectroscopic methods (FT-IR and 1H NMR). The polyols were transformed successfully in rigid polyurethane foams with good physical mechanical, thermal and fire proofing properties suitable for all specific applications of rigid polyurethane foams, especially for thermal insulation of freezers, buildings, pipes, storage tanks etc.

Rigid Polyurethane Foams and Cast Resins From glycerin-based Polyether Polyols

I. Javni[(1)], O. Bilic[(2)], N. Bilic[(3)], Z. Petrovic[(4)]
[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America [(4)]Pittsburg State University, United States of America

I. Javni[(1)], O. Bilic[(2)], N. Bilic[(3)], Z. Petrovic[(4)]
[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America [(4)]Pittsburg State University, United States of America

One of the requirements for polyols used in polyurethanes, particularly in rigid polyurethane foams is good hydrolytic stability. We successfully chemically converted glycerin, a by-product of the bio-diesel process, to hydrolytically stable, high bio-content polyether polyols that can be used in rigid polyurethane foams, cast resins, coatings, etc. Derived polyols were clear yellow liquids with good hydrolytic stability, OH-number from 400 to 500, viscosity bellow 10 Pa.s, and other characteristics suitable for application in polyurethanes. Rigid polyurethane foams and thermoset resins were prepared by reacting polyols with isocyanates and other ingredients. Prepared low density polyurethane foams had very nice and uniform cell morphology, high compression strength and other characteristics that met the requirements for heat insulating foams. Thermoset resins were hard and very strong materials with tensile strength around 100 MPa and glass transition temperature, Tg, around 100 oC. They can be considered as very good raw materials for composites, cast resins, coatings, etc.

Functionalizing Fatty Acids Through an Alpha-methylene Group

J. Zerkowski[(1)], D. Solaiman[(2)]
[(1)]Agricultural Research Service, United States of America [(2)]Agricultural Research Service, United States of America

Research into the selective functionalization of fatty acids is an area of ongoing interest due to the push for utilizing these bioderived materials in diverse applications. One attractive target for modification is the alpha carbon, and while chemistry for derivatizing that site has been known for many years, aggressive conditions such as strong base or non-selective reagents are usually required. In this presentation we will report on our use of mild conditions and Mannich-type chemistry to elongate fatty acids and introduce a methylene group at the alpha position. This unit is susceptible to nucleophilic attack in a Michael fashion. In particular, the so-called thiol-ene click reaction can be performed, opening the door to inclusion of a wide range of functionality adjacent to the carboxy terminus. We have also used nitrogen nucleophiles to perform the addition. The new fatty acid derivatives should find use in areas such as surfactants, lipid constituents, and polymers.

The Complexity of Interfacial Processes Between Metallic Surface and Free Fatty Acids / Esters

I. Liascukiene[(1)], J. Landoulsi[(2)], N. Aissaoui[(3)], J. Lambert[(4)], S. Asadauskas[(5)]
[(1)]State research institute Center for Physical Sciences and Technology , Lithuania [(2)]Université Pierre et Marie Curie-Paris VI, France [(3)]Université Pierre et Marie Curie-Paris VI, France [(4)]Université Pierre et Marie Curie-Paris VI, France [(5)]State research institute Center for Physical Sciences and Technology , Lithuania

Interfacial processes between metal surfaces and fatty acids or their esters has attracted a broad interest not only from the fundamental point of view, but also due to the importance in many technological applications such as lubrication, water/oil repellency, or corrosion inhibition. Nanostructurization mechanisms between metal and lipids at nano levels were studied by investigating self-assembly of FA and FAME on Al oxides/hydroxides. Thin film infrared spectroscopy (PM-IRRAS), water contact angle (WCA) and atomic force microscopy (AFM) were employed to demonstrate rapid chemical transformations and buildup of organized structures. The study was extended to a thin film test, which was employed for investigation of late stages of FAME degradation. Sample oils were applied in a form of homogeneous film (500?m) on metal coupons under controlled humidity and temperature. Compared to bulk liquids, chemical processes are much more intensive at the interface between fuel, metal and air. Polar compounds, formed after different duration of heating were analyzed by spectroscopic methods. The observations showed that hydrolytic, autoxidative and even electrochemical processes take place concurrently in FAME layers on metals, which can have a major impact on many industrial applications.

Density and Viscosity of Lipids Under Pressure

G. Bantchev[(1)], G. Biresaw[(2)]
[(1)]USDA-ARS-NCAUR, United States of America [(2)]USDA-ARS-NCAUR, United States of America

There is a lack of data for the viscosity of lipids under pressure. The current report is a part of the effort to fill this gap. The viscosity, density, and elastohydrodynamic film thicknesses of vegetable oil (HOSuO) were investigated. Pressure? viscosity coefficients (PVC) of HOSuO at different temperatures were calculated from measured film thickness data using the Hamrock- Dowson method and compared to values estimated from literature data. Literature pressure-density and viscosity-temperature data for oils with high-oleic acid group content were analyzed using the Tait and Casalini et al. models. The available viscosity data was presented as a function of a single scaling variable: (T*V**3.2), where T is the absolute temperature, and V is the molecular volume of the oil. The PVC values calculated from the literature data using the scaling model showed a reasonable agreement with that from film thickness data from this work.

The Effects of Plastics on Rendered Fat Quality

M. Paszti[(1)]
[(1)]Rothsay, a Division of Maple Leaf Foods, Canada

Animal fat produced from the rendering of animal by-products can easily become contaminated by plastic. This research investigates the impact that various types of plastics have on fat quality, including clarity, and unsaponifiable content. Given the variety of plastics used in packaging and the growing number of bio-based, compostable plastics available, the common thinking that all types of plastic contamination are equally harmful is no longer valid. Some plastics, such as polyethylene, have a very deleterious effect on fat quality. Other plastics including bio-plastics, however, have lower solubility in fat, and as such do not impact quality to the same degree. Plastic contamination in

fat (or any triglyceride oil) degrades its clarity, usefulness and selling price. The plastic originates from packaging material such as plastic wrap and containers present within the animal by-products collected from butcher shops, slaughterhouses, and meat processing plants. It is well known in rendering that polyethylene contamination will cause a fat (in liquid state) to have a cloudy appearance and cause substantial downstream processing problems with biodiesel and other oleochemical processes. Blocked piping, fouled heat exchangers and off-specification product are well known impacts. Even levels as low as 100ppm can have severe cumulative effects on processes. By substituting more rendering-friendly packaging, a marked financial benefit to renderers and users of animal fats is possible because costly mitigation measures such as complex filtration can be avoided. The findings are transferable to triglycerides besides animal fats, such as seed oils.

Novel Soybean Oil-derived Acrylates for Uv-curable Coatings

B. Chisholm[(1)], H. Kalita[(2)], S. Alam[(3)], S. Fernando[(4)], J. Bahr[(5)]

[(1)]North Dakota State University, United States of America [(2)]North Dakota State University, United States of America [(3)]North Dakota State University, United States of America [(4)]North Dakota State University, United States of America [(5)]North Dakota State University, United States of America

Acrylate-functional soybean oil (A-SBO) has been commercialized and used for producing UV-curable coatings. Two major drawbacks of A-SBO is its relatively high viscosity (10,600 cP at 25 °C) and relatively high equivalent weight (284 g/mole). The high viscosity of A-SBO typically requires the use of a reactive diluent, which is undesirable since it lowers the renewable content of the coating. The relatively high equivalent weight of A-SBO also typically necessitates the use of a reactive diluent to enable coatings with a high enough crosslink density to provide coatings with acceptable hardness and chemical resistance. The authors have recently developed two new soy-based acrylates that possess dramatically lower viscosity and lower equivalent weight. The viscosity and equivalent weight of one of the soy-based acrylates is 40 cP and 181 g/mole, respectively; while the viscosity and equivalent weight of the other soy-based acrylate is 350 cP and 233 g/mole, respectively. These novel soy-based acrylates were used to produce UV-curable coatings and coating properties characterized. The results obtained indicate that coatings with high renewable content can be produced with these novel acrylates that are competitive with coatings based on traditional petrochemical-based acrylates.

Industrial Oil Products Poster Session

Chair(s): B. Dunn, USDA, ARS, NCAUR, USA

Evaluation of Macauba oil (acrocomia Aculeata) as raw Material for the Supercritical Methanolysis and Ethanolysis

I. Vieitez[(1)], H. Navarro-Díaz[(2)], S. Gonzalez[(3)], N. Callejas[(4)], M. Saibene[(5)], B. Irigaray[(6)], I. Jachmanián[(7)], J. Vladimir de Oliveira[(8)]

[(1)]Facultad de Química (UDELAR), Uruguay [(2)]Universidade Federal de Santa Catarina, Brazil [(3)]Universidade Federal de Santa Catarina, Brazil [(4)]Facultad de Química (UDELAR), Uruguay [(5)]Facultad de Química (UDELAR), Uruguay [(6)]Facultad de Química (UDELAR), Uruguay [(7)]Facultad de Química (UDELAR), Uruguay [(8)]Universidade Federal de Santa Catarina, Brazil

Use of cheaper raw materials for biodiesel production is a key point towards economic competitiveness of this biofuel. Macauba is a palm species native of tropical areas of South-America. It has, after palm oil, the second largest oil productivity (1500-5000 kg-oil/hectare/year). Although Macauba oil is cheap, non-edible and attractive as an alternative feedstock to produce biodiesel, few studies have been made on its characterization. The aim of this work was the characterization of two samples of Brazilian macauba oils obtained by pressing, one from whole fruit (FO)

and the other solely from the pulp (PO). Additionally, efficiency of the transesterification using a catalyst-free supercritical continuous process was studied. Oleic acid was the major fatty acid found in both oils (54.9% in PO and 49.6% in FO), which showed an extremely high amount of FFA (59 and 45%, respectively). Water content was 1.0% (Karl-Fisher). TAG, DAG and MAG concentration were around 7.4, 14.9 and 3.4%, respectively. The high percentages of FFA and the low concentrations of TAG determine that oils could not be efficiently converted using a conventional transesterification method. Thus oils were destined to supercritical transesterification, performed from 300 to 375ºC and from 10 to 20MPa. Ethanol or methanol was used at molar ratios to oil from 1:20 to 1:40, and water addition to alcohol from 5 to 10wt%. The highest yield achieved were 78.4% with ethanol and 69.6% with methanol. Esterification occurring simultaneously to the transesterification permitting the achievement of relatively high ester yields converting macauba oil to biodiesel.

Limitation of Zeolite Type Catalyst in the Alcoholysis of Fats and Oils.

P. Suarez[(1)], A. Filho[(2)], K. Di Ferreira[(3)], G. Martins[(4)], G. Martins[(5)], P. Lima[(6)]

[(1)]University of Brasilia, Brazil [(2)]UnB, Brazil [(3)]UnB, Brazil [(4)]UnB, Brazil [(5)]UnB, Brazil [(6)]UnB, Brazil

Different papers have already published in the literature using zeolite type catalyst for transesterfication of fats and oils. Despite its high acidity, zeolites were described to behave a low activity to produce fatty acids methyl acids and the authors usually assumed that difficulties in the accessibility of triacylglycerides in the catalytic sites that are inside their structure are responsible for the low reaction yields. In this work we prepared zeolite type catalyst with the structure modified in order to expose the acid sites allowing the contact with the triacylglycerides and evaluated their performance in the methanolysis of soybean oil. The solids presented nanosized structure, with their acidity similar to regular zeolites. However, the reaction yields in methyl esters were still very low and comparable to those obtained using commercial zeolites. Studying the solids by TPD (Temperature Programmed Desorption) it was observed that the reaction of the acid sites with alcohol leads to an irreversible coordination of alcoxy groups, blocking the strong active sites. This is probably the reason for the low activity of these solids. CNPq, RHODIA, FAPDF, INCT-CATÁLISE

Does the ?Rancimat Method? Really Measure the Oxidative Stability of Biodiesel?

R. Dunn[(1)]

[(1)]USDA-ARS-NCAUR, United States of America

Biodiesel is composed of a mixture of saturated and unsaturated mono-alkyl esters of fatty acids derived from vegetable oil or animal fat. While the saturated esters are relatively stable, the monounsaturated and especially polyunsaturated esters are susceptible to oxidative degradation. If biodiesel is contacted with air during storage, then oxidation of the unsaturated esters may lead to increases in kinematic viscosity and acid value and affect other important fuel properties. Maintaining good fuel quality during storage is of utmost concern to fuel producers. Therefore, biodiesel fuel standards such as ASTM D 6751 and CEN EN 14214 require it to pass an oxidation induction period (IP) test The test (EN 15751), often referred to as the ?Rancimat method,? measures the IP under accelerated conditions by bubbling air through the oil sample and heating it at 110 °C. The experimental conditions necessary to initiate oxidation in method EN 15751 and provide a timely result are known to promote reaction pathways that differ from those experienced by the same fatty oil sample at lower temperatures. The present study is an investigation into the reaction kinetics of oxidation at different temperatures. Biodiesel made from soybean, canola, and palm oils as well as pure methyl oleate and linoleate were analyzed with a pressurized-differential scanning calorimeter (P-DSC) and a Rancimat instrument. Results suggested that moderate to very high levels of degradation were necessary to achieve the measured IP, suggesting that running the Rancimat instrument at 110 °C may overestimate the actual IP of biodiesel.

Synthesis and Stabilization of Gold Nanoparticles in Castor Oil

M. Meneghetti[(1)]

[(1)]Federal University of Alagoas - UFAL, Brazil

We have prepared different colloids based on gold nanoparticles stabilized and dispersed in castor oil. The colloids are preparing mixing specific amounts of castor oil, ethanol, an aqueous solution of HAuCl4.3H2O, and an aqueous solution of KOH at 80 °C for 24 hours. The oil phase was separated, dried, and depending of the ratio Au/KOH ratio different colloids, with different colors and particle sizes, were obtained. During the study, we verified that the free

fatty acid content in the oil is an important variable that must be controlled for the syntheses of the colloids, since the feature of the colloids are different if the acidity of the oil employed changes, even if the other variables are keeping in constant. The stability of the colloids was evaluated in respect to time, and to the addition of different organic solvents. The colloids were characterized by UV-Vis Spectroscopy, and their gold content was quantified by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP- AES). The size and shape of the AuNP produced were characterized by Transmission Electron Microscopy (TEM).

Highlights on a By-product of Specialty Seed oil of Annona Squamosa as Promising Safe Termite Control Agents

T. DJENONTIN[(1)], N. Amusant[(2)], T. Ruiz[(3)], P. Ducrot[(4)], D. Sohounhloué[(5)], D. Pioch[(6)]

[(1)]University of Abomey-Calavi, Benin [(2)]CIRAD, Guyana [(3)]University Montpellier II France, France [(4)]Institut Jean-Pierre Bourgin - INRA, France [(5)]University of Abomey-Calavi, Benin [(6)]CIRAD, France

We report here on the chemical composition of seed oil, cake of Annona squamosa L. and the investigation of the influence of ethanol/water mixtures as safe extraction media, in batch mode at 20 °C, regarding extract yield and termiticidal activity and also in terms of molecular interaction and of mass transfer. Oil and cake were analyzed by standard analytical procedures. The fractions derived from the cake were also investigated for elucidation of active compounds by detection with Kedde reagents A and B, elemental analysis C, H, O; HPLC/MS and proton NMR. Fruits separated manually give scales (57wt-%), pulp (30wt-%), almonds (8wt-%) and hulls (5wt-%). The oil (33.7wt-% almonds) is of non-drying type according to iodine value (92) and shows linoleic (25.4%) and oleic (47.4%) acids as main unsaturated fatty acids. ?-sitosterol (68.7wt-%) and the tocols (143ppm) with ?- and ?-tocopherol as major components (26.5 and 73.5wt-%) in the unsaponifiable matters (1.0wt-%). The cake is rich in proteins (25.5g/100g) and fibers (NDL 60.1%, ADF 34.7% and ADL 7.4%). The bioethanol/water extract (80/20, v/v; 15.5wt-%) on cake has shown a significant termiticidal activity above 1.2 mg/cm² through the standard procedure EN 118 (2005), with a rating 0 (no attack). Acetogenin type squamocin is the main component of the most active fraction (100% mortality within 3 days, 2 mg/cm²) and the termiticidal activity was also confirmed by EN 118 (no attack).

Harnessing Hansen Solubility Parameters to Predict Organogel Formation

S. Wu[(1)], J. Gao[(2)], M. Rogers[(3)]

[(1)]Rutgers, The State University of New Jersey, United States of America [(2)]Rutgers, The State University of New Jersey, United States of America [(3)]Rutgers, The State University of New Jersey, United States of America

Hansen solubility parameters predict the capacity of molecular gels to form in a vast array of organic solvents. The prediction ability for 12-hydroxystearic acid is closely associated with the hydrogen-bonding Hansen solubility parameter (dh). Solvents with a hydrogen-bonding Hansen solubility parameter less than 4.7 MPa1/2 produce clear organogels, opaque organogel formed between 4.7 < dh < 5.1 MPa1/2 and solutions remained when the hydrogen-bonding Hansen solubility parameter is greater than 5.1 MPa1/2. Furthermore, the critical gelator concentration is linearly correlated with the hydrogen-bonding Hansen solubility parameter. Solvents with the same functional group, which varied only by chain length, have correlations between the static relative permittivity, Hansen solubility parameter, dispersive HSP, polar HSP and hydrogen-bonding HSP and the critical gelator concentration.

Phytochemical Screening and Physicochemical Analysis of Gingerbread Plum (parinari Macrophylla) Seed Oil.

A. Ahmad Warra[(1)]

[(1)]Kebbi State University of Science and Technology, Aliero, Nigeria., Nigeria

This work was carried out to determine the potential applications of gingerbread plum seed oil by investigating its phytoconstituents and physicochemical characteristics. The underutilize oil seed from gingerbread plum tree growing in abundance in Niger Republic was exploited. Phytochemical analysis of the seed oil extracted using soxhlet apparatus with n-hexane revealed the presence of saponins, alkaloids, flavonoids, steroids, terpenoids, and tannins and absence of glycosides and phlobatannins . The physicochemical analysis of gingerbread plum (parinari macrophylla) seed oil was carried out and the following results were obtained; Acid value 12.97? 0.01mgKOH/g, Saponification value 153.30 ? 0.10 , Iodine value 32.07 ?0.01 I2/100g, Free fatty acid 15.10?0.10 (% Oleic), Peroxide value (meq

H2O2) 45.48 ? 0.02. The % yield was 49.3, Color was golden yellow, odour was agreeable, and the oil was liquid at room temperature. Justification of the use of the seed oil for food, medicinal and cosmetics was expatiated.

Bio-based Non-isocyanate Thermoplastic Polyurethanes

I. Javni[(1)], O. Bilic[(2)], Z. Petrovic[(3)]

[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America

Thermoplastic polyurethanes (TPU) are synthesized from isocyanates, polyols and chain extenders. They consists of linear segmented block copolymers composed of hard and soft segments with many useful properties, including elasticity, transparency, and resistance to oil, grease and abrasion. Synthesis of thermoplastic polyurethanes without isocyanates is beneficial to the environment and reduces health hazards. One of possible routes is reaction of cyclic carbonates and amines. The reaction product is polyurethane with different properties than those prepared from isocyanates due to the presence of hydroxyl groups in their structure. We synthesized bio-based non-isocyanate polyurethanes from cyclic carbonate compounds derived from derivatives of soybean oil and diacids. A series of bi-cyclocarbonates of different chain length was prepared and reacted with 1,4-diaminobuthane, isophoronediamine, p-xylylenediamine producing linear (thermoplastic) non-isocyanate polyurethanes. The products were soft or hard solids. The effect of cyclic carbonate and diamine structure on polyurethane properties was studied.

CANCELLED-Biofuels: the Promising Substitute Fuel Over Conventional Fossil Fuel

K. BERA[(1)]

[(1)]INSTITUTE OF GENETIC ENGINEERING, BADU, KOLKATA-128, INDIA, India

Assessment of Flocculation as an Efficient and low Cost Concentration Method for Harvesting Microalgae for Bulk Biomass Production

I. Foubert[(1)], D. Vandamme[(2)], K. Muylaert[(3)]

[(1)]KU Leuven University Kulak, Belgium [(2)]KU Leuven University Kulak, Belgium [(3)]KU Leuven University Kulak, Belgium

The transition of a fossil fuel to a biobased economy in combination with the prospected increase in the world?s population will lead to a growing demand for additional sources of biomass that can complement traditional agricultural biomass production. Microalgae are unicellar aquatic organisms that receive much interest as a promising source of biofuels or bulk protein. But today, the cost and energy demand for production of microalgae using the currently best available technologies is still too high for bulk biomass production. The introduction of a flocculation pre-concentration can be an interesting improvement to existing harvesting processes and reduce significantly overall production costs. The usage of aluminum sulphate; electro-coagulation-flocculation; biopolymers such as chitosan and cationic starch; and flocculation induced by high pH was studied in detail for both freshwater and marine species. Influence of the presence of algal organic matter (AOM) was investigated for all modes of flocculation and related to the flocculation efficiency, the flocculation mechanism and the floc characteristics (floc size, aggregated volumetric index, sedimentation velocity). Our study showed that pH induced flocculation is a promising and cost competitive alternative harvesting technique (US $ 20 ton-1 biomass). Other parameters, such as interference of AOM, medium recyclability and contamination risk are included in the overall assessment of flocculation based harvesting methods.

Rigid Polyurethane Foams and Cast Resins From glycerin-based Polyether Polyols

I. Javni[(1)], O. Bilic[(2)], N. Bilic[(3)], Z. Petrovic[(4)]

[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America [(4)]Pittsburg State University, United States of America I. Javni[(1)], O. Bilic[(2)], N. Bilic[(3)], Z. Petrovic[(4)]

[(1)]Pittsburg State University, United States of America [(2)]Pittsburg State University, United States of America [(3)]Pittsburg State University, United States of America [(4)]Pittsburg State University, United States of America

One of the requirements for polyols used in polyurethanes, particularly in rigid polyurethane foams is good hydrolytic

stability. We successfully chemically converted glycerin, a by-product of the bio-diesel process, to hydrolytically stable, high bio-content polyether polyols that can be used in rigid polyurethane foams, cast resins, coatings, etc. Derived polyols were clear yellow liquids with good hydrolytic stability, OH-number from 400 to 500, viscosity bellow 10 Pa.s, and other characteristics suitable for application in polyurethanes. Rigid polyurethane foams and thermoset resins were prepared by reacting polyols with isocyanates and other ingredients. Prepared low density polyurethane foams had very nice and uniform cell morphology, high compression strength and other characteristics that met the requirements for heat insulating foams. Thermoset resins were hard and very strong materials with tensile strength around 100 MPa and glass transition temperature, Tg, around 100 oC. They can be considered as very good raw materials for composites, cast resins, coatings, etc.

CANCELLED-Application of Castor oil Derived Polyol for Elastomer Synthesis

T. da Silva[(1)], R. Barbosa[(2)], L. Ramos[(3)], S. Zawadzki[(4)]

[(1)]Federal University of Parana, Brazil [(2)]Federal University of Parana, Brazil [(3)]Federal University of Parana, Brazil [(4)]Federal University of Parana, Brazil

Determination of Silicone Oils by Hplc and Corona Charged Aerosol Detector

M. Plante[(1)], D. Thomas[(2)], B. Bailey[(3)], I. Acworth[(4)]

[(1)]Thermo Fisher Scientific, United States of America [(2)]Thermo Fisher Scientific, United States of America [(3)]Thermo Fisher Scientific, United States of America [(4)]Thermo Fisher Scientific, United States of America

Silicone oil is unique in that it can occur in a wide variety of forms that are engineered for specific uses. These materials can be modified so as to differ in hydrophobicity, lubricity, boiling points, and molecular weights. Furthermore, changes in numerous carbon moieties can be used to enhance material properties. Silicone oils are used as lubricants, as hydraulic fluid, as heating oil, and are also used in over-the-counter and pharmaceutical products. Characterization of silicone oils can be problematic: they show a wide distribution of molecular weights, different solubilities in typical HPLC solvents, and varying degrees of hydrophobicity. These properties and the lack of a chromophore, make it difficult to develop HPLC methods for characterization and determination of these materials. HPLC with charged aerosol detection overcomes many of these issues. This approach only requires that the analyte be semi-volatile, or ideally, non-volatile. It does not require that the molecule possess a chromophore or ionize in order to be detected. The charged aerosol detector is fully compatible with reversed phase and normal phase chemistries, and response is independent of chemical structure. With sensitivities in the low nanogram range and excellent precision, this detector is ideal for the analysis of silicone oils. Two methods will be presented for the analysis of silicone oils that use the same column and similar mobile phases. One method provides sample characterization, and the second method provides quantitation of a sample.

Synthesis and characterization of acetylated and stearylyzed soy wax

L. Yao[(1)], T. Wang[(2)]

[(1)]Iowa State University, United States of America [(2)]Iowa State University, United States of America

A solvent-free synthesis method was developed for incorporating acetyl and hydroxy groups and long-chain fatty alcohol in fully hydrogenated soybean oil (FHSO) to produce a wax to be used as beeswax or paraffin substitutes in packaging and coatings. FHSO was reacted with stearyl alcohol and triacetin at 140-150°C for 2 h and the reaction was catalyzed by 0.018 weight % sodium methoxide. The addition of alcohol increased the reaction yield and the melting point of the final wax by 9 and 25% compared to the wax produced from the reaction of FHSO and triacetin alone. Effects of the ratio of stearyl alcohol and triacetin to FHSO on the physical and textural properties of the modified soy wax were examined. The reaction of FHSO: stearyl alcohol: triacetin at a molar ratio of 9:7:15 produced a wax that had 40% acetylation and was 1.2 and 2.4 times harder than beeswax and FHSO, respectively, but 1.7 times softer than a commercial grade paraffin wax. This modified soy wax comprised 75% acetylated glycerol esters including diacetylmonoacylglycerides (31%), monoacetylmono- (12%) and diacylglycerides (32%), and 25% non-acetylated molecules including wax ester (14%), and acylglycerides (11%). The acetylated soy wax had high cohesiveness and did not break under compression.

Optimization of Biodiesel Production via Hydro-esterification Using Heterogeneous Catalysis

P. Suarez[(1)], C. Rodriguez[(2)], H. Lira[(3)]

[(1)]University of Brasilia, United States of America [(2)]University of Brasiliz, Brazil [(3)]University of Brasilia, Brazil

Biodiesel have been pointed out as a good alternative to fossil fuel in terms of environmental quality, safety and economy. Hydro-esterification has been pointed out as an interesting technological approach to produce biodiesel because it enhances the economy of the process since it is possible to use low-grade raw materials and because of the higher pureness of the glycerin produced. In this work, we investigated the physicochemical parameters on hydrolysis of soybean oil and soybean fatty acid esterification; varying the temperature, molar ratio (water on hydrolysis and methanol / ethanol on esterification), percentage of catalyst and reaction time. We have determined reaction yields, achieving up to 90 % in both cases, and other physic-chemical properties during the process, such as viscosity, density and acidity index. CNPq, MCT, FAPDF

Polyamides Based on the Renewable Monomer, 1,13-tridecane Diamine: Nylon 13,t and Nylon 13,6.

B. Chisholm[(1)], S. Samanta[(2)], J. He[(3)], S. Sermadurai[(4)], J. Lattimer[(5)], C. Ulven[(6)], M. Sibi[(7)], J. Bahr[(8)]

[(1)]North Dakota State University, United States of America [(2)]North Dakota State University, United States of America [(3)]North Dakota State University, United States of America [(4)]North Dakota State University, United States of America [(5)]North Dakota State University, United States of America [(6)]North Dakota State University, United States of America [(7)]North Dakota State University, United States of America [(8)]North Dakota State University, United States of America

Erucic acid is a major fatty acid obtained from crambe and rapeseed oil. Oxidation of erucic acid yields the long-chain dicarboxylic acid, brassylic acid (i.e. 1,13-tridecanedioic acid). From brassylic acid, 1,13-tridecane diamine can be produced. Other than nylon 13,13 and nylon 13, very few reports exist on the synthesis and properties of other polyamides based on brassylic acid or 1,13-tridecane diamine. The authors have synthesized and characterized two polyamides based on 1,13-tridecane diamine, namely, nylon 13,T and nylon 13,6. The equilibrium melting temperature, crystallization kinetics, thermal stability, crystal structure, and moisture uptake for these two polyamides were determined and compared to the commodity polyamides, nylon 6 and nylon 6,6. Compared to nylon 6,6, nylon 13,T was found to possess a similar melting point but a significantly higher glass transition temperature (i.e. 90 oC), and very fast crystallization. In addition, the thermal stability was determined to be adequate enough to enable melt processing without significant thermal degradation. Due to the much lower amide content of nylon 13,T, water absorption was found to be dramatically lower than the industrially important nylons, nylon 6 and nylon 6,6. Nylon 13,6 was shown to possess a melting temperature of 206 oC and slower crystallization than nylon 13,T. Similar to nylon 13,T, the moisture uptake of nylon 13,6 was very low.

Cancelled-Papaya Seed Oil from two Malaysian Varieties: Comparison of Solvent Extraction and Ultrasound Technique

H. Mirhosseini[(1)]

[(1)]University Putra malaysia, Malaysia H. Mirhosseini[(1)], S. Samaram[(2)], t. chin ping[(3)], H. Ghazali[(4)]

[(1)]University Putra malaysia, Malaysia [(2)]University Putra malaysia, Malaysia [(3)]University Putra malaysia, Malaysia [(4)]University Putra malaysia, Malaysia

Synthesis of Trimethylolpropane Fatty Acid Triester by Transesterification of Waste Cooking Oil-Based Methyl Esters with Trimethylolpropane

Y. Wang[(1)], E. Wang[(2)], M. Reaney[(3)]

[(1)]Jinan University, China [(2)]Jinan University, United States of America [(3)]University of Saskatchewan, United States of America

Trimethylolpropane fatty acid triester (TMPFATE), which was used as a base oil for biolubricants, was synthesized by transesterification of waste cooking oil fatty acid methyl esters(FAME) with trimethylolpropane. The reaction parameters and oxidative stability of TMPFATE were studied. Under the selected conditions (potassium hydroxide as

the catalyst, a mole ratio of catalyst to trimethylolpropane of 0.25, a mole ratio of FAME to trimethylolpropane of 4:1, pressure at 200 Pa,reaction temperature at 118 ºC, and the reaction time at 1.5 h) a high selectivity for TMPFATE (85.71wt%) was obtained. After purification by molecular distillation at 120 ºC, the content of TMPFATE in the product was 99.59 wt%. The addition of ?-tocopherol, BHA, TBHQ enhanced oxidative stability, as indicated by the induction period of TMPFATE under the Rancimat conditions, while DTBHQ and rosemary extract R40 did not improve oxidative stability. BHA had a positive synergistic effect when used with ?-tocopherol.

Using CLICK Chemistry to Produce Green Monomers and Polymers from Vegetable Oils

M. Floros[(1)]

[(1)]Trent University, Canada

The development of new methods to modify vegetable oils into functional consumer products is an exciting area of green chemistry. Creating plastics from biologically derived, renewable resources has a number of advantages, including reducing reliance on petrochemicals and potential for integration into the human body without toxic effects. Recently, application of azide-alkyne click chemistry based modifications on vegetable oil feedstock's has produced new monomers suitable for the synthesis of unique, green polymers. Modifying four fatty acid derived esters of different chain lengths each containing two unsaturated positions with azide groups at the unsaturated position creates monomers which may be formed into linear polymers when reacted with dialkynes synthesized from esterification of plant derived diacids. The mechanisms of this reaction may also allow polymerization to occur at room temperature in a reaction which consumes all of the starting materials, creating a coating that is free of bubbles and may be applied directly to a surface where it polymerizes in situ. This reaction connects monomers together with a 1,2,3-triazole ring - a structure which may bestow inherent antimicrobial activity on the polymer, opening up a wide range of potential applications.

Investigating the Thermal Stability of Linear Diesters Derived from Vegetable Oils: Dependence of Thermal Stability on the ?-Hydrogen and its Environment

Diesters derived from vegetable oils may be used in oleochemical syntheses, polymer syntheses, or lubricant formulations. Thermal stability is one of many physical properties which influence its suitability for an application. Herein, a novel series of linear symmetric diesters have been investigated to determine the effect of structure on thermal stability. Cursory analytical tools ? FTIR and 1H-NMR ? have been used to show that ester groups in close proximity to each other result in a weakening of the C-O-C bonds and an increasing lability of the ?- and ?-hydrogens. These results imply that diesters whose ester groups are located closest to each other are the most destabilized. This was further supported by TGA studies which showed decreasing onset of decomposition temperatures with decreasing distances between ester groups. The most stable diesters were obtained when the ester groups were furthest apart; no substantial increase in stability was observed past a distance of six-carbon atoms between the ester groups. TGA kinetic studies using the Friedman isoconversional method supported a preferred ?-elimination thermal decomposition mechanism as long as ?-hydrogens were present. In conclusion, diesters with varying levels of thermal stability may be prepared by manipulating the environment in which the ?-hydrogens exist.

Synthesis and molecular weight control of entirely lipid derived aliphatic polyester diols.

S. Merchant[(1)], S. Narine[(2)]

[(1)]Trent Center for Biomaterials Research- Trent University, Canada [(2)]Trent Center for Biomaterials Research- Trent University, Canada

Degradation susceptible aliphatic polyesters from entirely renewable sources synthesized by solvent free melt condensation forms a sustainable and cost effective alternative to fossil fuel derivatives. Aliphatic Polyester Diols (APED)s from vegetable oil suitable as monomers for thermoplastic poly(ester-urethane) synthesis have been prepared by melt condensation of oleic acid derived Azelaic acid and 1,9 Nonanediol, using two methods viz. monomer ratio variation and reaction time. APEDs prepared by introduction of additional diol at varying reaction times have been found to be comparable with APEDs synthesized by monomer ratio variation. Structure has been confirmed by 1HNMR and FTIR. APEDs have been characterized for their molecular weight and its distribution by Gel Permeation Chromatography. Separation of APEDs has been achieved by column chromatography and fractional precipitation.

APEDs with desired molecular weights and similar Polydispersity Index (PDI) have been separated by varying solvent ratios using fractional precipitation. Solvent use has been minimized by this method. Thermal stability of APEDs prepared by both methods is comparable as analyzed by Thermogravimetric Analysis and Differential Scanning Calorimetry. Effectively, synthesis and molecular weight control of entirely lipid derived aliphatic polyester diols has been optimized by introduction of additional diol at predetermined reaction times with subsequent extraction of their desired molecular weights , employing optimized fractional precipitation.

Cedarwood Oil: Cross-Over Pressure Research

F. Eller[(1)], J. Teel[(2)]

[(1)]USDA-ARS, United States of America [(2)]USDA-ARS, United States of America

A series of experiments were conducted to determine the cross-over pressure for cedarwood oil in carbon dioxide. A closed stirrer reactor with an in-line loop connected to the injector of a GC was used to measure the concentration of cedarwood oil in the carbon dioxide. Both neat cedarwood oil as well as cedarwood chips were placed inside the stirrer reactor. All possible combinations of 4 temperatures (i.e., 25, 45, 65, or 85°C) in conjunction with nine pressures (i.e., 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, or 5000 psi) were tested. The solubility of cedarwood oil was determined from the FID counts from the GC analysis. In addition, changes in the composition were also monitored. Although at pressures below ca. 3000 psi the solubility of cedarwood oil was higher in liquid carbon dioxide than supercritical carbon dioxide and solubility isotherms appeared similar to those for triglycerides in carbon dioxide. However, at higher pressures, the similarity was absent. Instead of the solubility of cedarwood oil increasing exponentially with pressure as seen for triglycerides, the solubility leveled off. There were also significant differences between the measured solubility when the reactor was filled with neat cedarwood oil and when it was filled with chips.

Petroleum-Free Structured Emulsion for Cosmetic Applications

F. Wang[(1)], A. Marangoni[(2)]

[(1)]University of Gueloh, Canada [(2)]University of Guelph, Canada

There is increasing consumer concerns regarding the use of potentially toxic petroleum-based chemicals in cosmetic products. This has created a sizeable opportunity for manufacturers of green cosmetics. These cosmetics have to be made from ?natural? ?green? or ?nature-identical? materials such as vegetable oils, polysaccharides, emulsifiers and proteins. The challenge is that natural materials are not as stable as petroleum-based ingredients thus do not have a long shelf life. Current research in our group has focused on the development of a structured monoglyceride (MG) emulsion that is suitable for the formulation of cosmetic lotions and creams. The challenge facing commercialization of such product is that the stability of the emulsion is short. The structured MG gel has initially a homogeneous structure; however, after six weeks, the emulsion starts destabilizing and exudes water, i.e., it undergoes syneresis. During the destabilization process, the MG-gel undergoes a phase transition from the ?-gel phase to the coagel phase. In the ?-gel phase, the monoglyceride binds water and has a pleasant and fresh creamy texture. However, the ?-gel is only metastable in that it is not thermodynamically stable. The ?-gel phase transforms to a coagel phase spontaneously, changing in appearance and texture and causing the release of water from the cream. The primary research objective is to understand the dynamics of the monoglyceride phase behaviour and emulsion stability to enable its stabilization. This will allow for the eventual commercialization of a novel, patented green cosmetic lotion (cream).

Ultrasonic transesterification of microalgae oil (Chlorella protothecoides) to biodiesel

D. Özçimen[(1)], M. Gülyurt[(2)]

[(1)]Yildiz technical university, Turkey [(2)]Uskudar University, Turkey

In this study, micro algal oil was transesterified for fatty acid methyl ester production by using ultrasonic assisted method. The study was focused on the effect of reaction parameters (reaction time, ratios of alcohol and catalyst to algal oil) on biodiesel yield. Microalgal oil, from the type of microalgae species produced in the way of heterotropic cultivation, was used for this study. As an algae source, Chlorella Protothecoides was selected because of its higher oil ratio and faster doubling time compared to other types of algae. The transesterification was carried by using methanol and potassium hydroxide as a catalyst. The ultrasonic probe was used at 20 kHz and 200W with autogenous

temperature. The study showed the relation of biodiesel yield with respect to various reaction conditions. Ultrasonic assisted transesterification of oil presents some advantages compared to conventional stirring methods. Ultrasonic assisted method produces a higher grade of biodiesel and require shorter reaction time. Ultrasonics can be a very useful method for producing biodiesel from microalgae oil, since this method does not require elevated temperatures, speeds up transesterification and so it lowers the cost of processing. So, this method can be an alternative for conventional method for biodiesel production from microalgae.

Effect of self-anticorrosion performance of dimer acid-based polyol microcapsule containing isosorbide-oleic (SAIO) corrosion inhibitor.

E. Koh[(1)]

[(1)]Korea Research Institute of Chemical Technology, Korea, Republic of

Bio-based polyurethane from a waste vegetable oil-based dimer acid polyol was synthesised to affect the structure of microcapsule shell wall, and isosorbide-oleic (SAIO) derivatives corrosion inhibitors were synthesised as core material. Corrosion inhibitors for self-protective composites were encapsulated via a combination of interfacial ultrasonic polymerization. Designed microcapsules were produced by controlling the agitation rates and core-shell materials ratio; these conditions decided the physical properties of microcapsules, microcapsule size, wall thickness and even core content. The self-corrosion protective properties was demonstrated using a paint system, after scratching that microcapsules showed excellent self-corrosion inhibitor efficiency. The mean diameter of the microcapsules was ranged from 1 to 50 ? under ultrasound-trigged. According to the capsules size scale, core contents measured between 50-70 wt%. The effect of the poloy on the chemical properties and structure, core materials and dimer acid-based prepolymer were evaluated by different analytical techniques such as FT-IT, GPC, HPLC, DSC and TGA. And microcapsules integrity was demonstrated using scanning electron microscopy.

Synthesis and Characterization of Polyesters from Glycerol and Succinic acid

T. Horvath[(1)], O. Valerio[(2)], A. Mohanty[(3)], M. Misra[(4)]

[(1)]University of Guelph, Canada [(2)]University of Guelph, Canada [(3)]University of Guelph, Canada [(4)]University of Guelph, Canada

In recent years both glycerol and succinic acid production methods have become available from renewable biosources, succinic acid from the fermentation of glucose by bacteria and glycerol can be purified from crude glycerol a by-product of the biodiesel industry. In order to take advantage of these new resources we looked at synthesising polyesters from pure glycerol and succinic acid. The aim of this work is to study: polyester synthesis under different conditions and characterize the resulting polyesters. Polyesters were synthesised via polycondensation reactions using pure glycerol and succinic acid, without solvents or catalysts. Different molar ratios of the monomers made were 1.3, 0.6 and 0.3 of glycerol to succinic acid. Evolution of the reaction was followed using acid group conversion, measured by acid value determination. The polymers were then analysed using Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). Using FTIR to analyze the reaction showed that esterification occurred and reaction kinetics showed that high conversion of carboxyl groups was reached. TGA showed a degradation temperature of approximately 180°C for all three formulations. The newly engineered polyesters are expected to be biodegradable (compostable) and can find applications in disposable green packaging.

Fabrication and properties of biorenewable epoxy-montmorillonite clay nanocomposites

R. Wang[(1)], T. Schuman[(2)]

[(1)]Missouri University of Science and Technology, United States of America [(2)]Missouri University of Science and Technology, United States of America

Epoxy-clay nanocomposites derived from renewable soybean oils and industrially available, organically modified, montmorillonite clay were prepared. Low viscosity, epoxidized glycidyl esters of soybean oil (EGS) were used as epoxy monomer. The material 4-methyl-1,2-cyclohexanedicarboxylic anhydride (MHHPA) was used as a comonomer with 2-ethyl-4-methylimidazole (EMI) as catalyst. The probable miscibility of the monomers and clay was assessed by solubility parameters. Three types of dispersion technique, mechanical stirring, high speed shearing, and ultrasonication, were carried out to disperse the clay into epoxy or anhydride portion of the thermoset system. Dispersion of clay particles into resin were assessed and measured by means of optical and scanning electron

microscopies. The extent of nanocomposite dispersion was further confirmed by small angle X-ray scattering and transmission electron microscopy. The nanocomposites' morphology showed a mix of intercalated and exfoliated structures dependent on the dispersion technique. Tensile modulus was increased with clay loading. The tensile strength of nanocomposites was affected by clay concentration and dispersion morphologies as were glass transition temperature and composite thermal stability.

Program