

IOP 1: Catalysis

Chairs: A. Zwijnenburg, Johnson Matthey, Germany; and J.L. Dubois, Arkema, France

Design of Zeolite Catalysts for Branched-chain Fatty Acid Synthesis. H.L. Ngo*, USDA, ARS, ERRC, Wyndmoor, PA, USA.

Our research on modified aluminosilicate H-Ferrierite zeolites has shown that they can be highly effective catalysts for converting common linear-chain fatty acids to branched-chain fatty acids (bc-FAs). In this presentation, two heterogeneous zeolitic processes will be presented. First, H-Ferrierite zeolites, whose surface Brønsted acid sites have been deactivated with sterically hindered Lewis bases, were used as catalysts for the synthesis of methyl-bc-FAs (i.e., isostearic acid). The reactions gave >85% yield of the isostearic acid. The H-Ferrierite catalysts displayed excellent reusability for up to 20 cycles. Second, the H-Ferrierite zeolites were highly efficient in producing aromatic-branched-chain fatty acid compounds. These aromatic products have promising applications as lipophilic antimicrobials and antioxidants. The developed zeolite processes represent important new routes for adding value to fatty acid materials.

The Influence of Ligands Cl and CH₃ Bearing Tin(IV) Catalysts into Conversion of Triacylglycerides into Biodiesel. S.M.P. Meneghetti*, M.R. Meneghetti, M.A. Silva, J.H. Bortoluzzi, D.A. Ferreira, and T.V. Santos, UFAL, Maceió, Alagoas, Brazil.

The catalysts dimethyl bis (2,4-pentanedionate) tin (IV) - CH₃-Sn and dichloro complex bis (2,4-pentanedionate) tin (IV) - Sn-Cl were tested in methanolysis of soybean oil in order to obtain fatty acid methyl esters (FAMEs %). It is observed that the CH₃-Sn exhibited a higher catalytic activity, mainly at the kinetic control, as compared to Sn-Cl. In order to confirm this behavior, chemical computational studies were carried out. From the point of view of a possible steric impediment, the chloro atom obviously occupies a smaller space as compared to the alkyl ligands and consequently, this effect does not justify the difference in reactivity observed in transesterification that appears in the contrary sense of steric hindrance. Concerning to electronic effects, organotin compounds containing chloro directly coordinated to tin atom exhibits a higher electron density, since this ligand acts as a p-donor system, electronically assisting the metal center through its nonbonding electrons and, therefore, reducing the Lewis acidity of the metal, compared to alkyl ligands.

So, this observation can be explaining the behavior observed, in terms of reactivity.

Continuous Production of Fatty Acid Ethyl Ester from Crude *Jatropha* Oil Using Ion-exchange Resin Catalysts and Evaluation of Fuel Quality. N.

Shibasaki-Kitakawa*, T. Oyanagi, S. Borjigin, K. Nakashima, and T. Yonemoto, Department of Chemical Engineering, Tohoku University, Sendai, Miyagi, Japan.

Fatty acid ethyl ester, FAEE has received much attention as more environmentally preferable biodiesel than fatty acid methyl ester, FAME, because the second reactant, ethanol is readily available from fermentative processes using biomass. FAEE is also expected to have better fuel properties, such as cetane number and fluidizability at low temperature, than FAME. However, it is difficult to produce high quality FAEE by the conventional method using homogeneous alkali catalysts. This is because ethanol has higher water absorbency than methanol and the catalytic activity decreased by small amounts of water. We proposed a novel method using ion-exchange resin catalysts without the effect of water and constructed a pilot scale production apparatus, which consisted of columns packed with cation-exchange resin for esterification of free fatty acid, FFA and those packed with anion-exchange resin for transesterification of triglyceride in series. FAEE was continuously produced from crude *Jatropha* oil with high FFA content. The feed solution at the stoichiometric molar ratio was supplied to the bottom of the first column and the effluent from the final column was analyzed to check the quality of biodiesel such as international standards and engine performance.

Hydroesterification of Triacylglycerides (TAGs) a Strategy to the Preparation of Fatty Acid Methyl Esters (FAMEs). M.R. Meneghetti*, E.C. Silva, D.M.A. Frago, P.R. Mendes, C.S.T. Santana, J.P.V. Silva, Y.C. Brito, and S.M.P. Meneghetti, UFAL, Maceió, Alagoas, Brazil.

Recently we have observed that *n*-butyl stannic acid, (*n*-Bu)SnO(OH) (BTA), is able catalyze esterification and simultaneous transesterification/esterification reactions in high yields. This is an important result, but other possible approach to

biodiesel production from oils and fats containing high content of free fatty acids (FFA) is based on hydroesterification of TAGs, i.e. hydrolysis followed by esterification. This study presents a comparison of simultaneous transesterification/esterification, and hydroesterification of TAGs with high content of FFA, both approaches catalyzed in the presence of BTA. Pure or mixed soybean oil with FFA was hydrolyzed in the presence of BTA at different temperatures, reaction time, and content of water. In all tests BTA was able to catalyze hydrolysis. High conversions, ca. 96%, can be achieved with TGA/FA mixture of 50/50, at 160°C, after 10 hours. It is worth mentioning that methanolysis of this rich mixture can reach high yields of FAMES just after 2 hours of reaction.

Sustainable Castor Oil Based Production Through Reactive Seed Crushing. J.L. Dubois^{*1}, A. Piccirilli², and J. Magne², ¹Arkema France, Colombes, France, ²Valagro, Poitiers, France.

Castor is known to be non-edible since the seeds contain several toxic materials. However the oil has a growing interest in the production of high value polymers. Arkema has been producing Polyamide-11, a technical polymer used in several industrial applications, for more than 50 years, and through acquisition became a major producer of sebacic acid from castor oil.

In order to promote Sustainable Castor production a new process called "Reactive Seed Crushing" has been developed. Castor seeds are directly reacted with methanol, which is also used as an extraction solvent, in the presence of a catalyst. Through this process, a high quality methyl ester is produced, together with glycerine and a detoxified seed meal. The methyl ester quality is equivalent to the ester that can be obtained through the conventional process of castor oil transesterification.

The Castor meal detoxification has been assessed by Ricin quantification, and animal testing, but also by allergenicity testing.

This new technology requires much less equipment, does not need to refine the oil (since the chemistry is done directly on the seeds), and should enable the processing of seeds from a smaller footprint, allowing to start production from new cultivation areas.

A variation of this technology has also been developed on Jatropha, another non-edible crop.

Oleochemistry at KU Leuven: A Catalytic View. J. Van Aelst^{*}, A. Philippaerts, P. Jacobs, and B. Sels, University of Leuven, Leuven, Belgium.

Vegetable oils are used for various applications, both in food and industrial products. Although different vegetable oils with various chemical compositions are available in nature, catalytic modification is necessary to enlarge their usage possibilities and to anticipate on the fluctuating oil production numbers and oil prices. With the use of a selective heterogeneous catalyst and the appropriate process conditions, the chemical and physical properties of vegetable oils can be tuned to ensure a constant supply of a large range of different oil and fat based products for various uses.

This contribution concentrates on recent catalytic advances realized in our centre, concerning the conjugation of linoleic acid and vegetable oils^{[1][2]}, the isomerization of terpenes^[2], the partial hydrogenation of vegetable oils^[3], and the synthesis of wax esters from oleochemicals. Emphasis will be on the influence of the catalyst properties on the obtained product distribution. It will be illustrated that by means of accurate catalyst design, the selectivity of the reaction can be tuned towards the intended products.

[1] (a) Philippaerts *et al.*, WO2012/068645 A2; (b) Philippaerts *et al.*, ChemSusChem 2011, 4, 684 – 702

[2] Van Aelst *et al.*, submitted.

[3] Philippaerts *et al.*, Angew. Chem. Int. Ed. 2011, 50, 3947 –3949

Microwave Assisted FAME Production – On Large Scale. R. Morschhaeuser^{*} and H.J. Scholz, WeylChem Wiesbaden, Frankfurt, Hesse, Germany.

For more than 10 years efforts have been taken to transfer MW-assisted organic reactions into a commercially relevant scale. Apart from missing technological concepts, the relatively low efficiency in terms of energy conversion from MW radiation into heat was a major hurdle which has so far prevented up-scaling of this promising technology. In many publications over the last two decades attractive features of microwave-assisted organic synthesis such as speed of conversion, minimizing side product formation and clean processing have been demonstrated.

By utilizing a newly designed continuous operating system, we are able to demonstrate the high capabilities of microwave assisted processing at high temperature and pressure. Even in the absence of a "specific microwave effect", the potential of volumetric heating is significant and becomes even

more visible with increasing scale. The possibility of performing chemical reactions close to "borderline" conditions for most transformations opens up a new window for chemical processing

On the example of FAME we will highlight the potential for large scale microwave processing in continuous mode for chemical reactions – in several tons/day scale.

IOP 2/PRO 2: Alternative Fuels

Chairs: G. Knothe, USDA, ARS, NCAUR, USA; and D. Litle, GEA Mechanical Equipment, USA

Lowering of the Boiling Curve of Biodiesel by

Metathesis. J. Krahl¹, A. Munack², C. Pabst², K.

Schaper², L. Schmidt², M.A.R. Meier⁴, R.

Montenegro⁴, A. Mäder¹, M. Kaack³, P. Eilts³, and J.

Büniger⁵, ¹Coburg University of Technology Transfer

Center Automotive of Applied Sciences and Arts,

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Braunschweig, Braunschweig, Germany, ⁴Karlsruhe

Institute of Technology, Braunschweig, Germany,

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Environmental Measurement Technology, Coburg,

Germany.

Rapeseed oil methyl ester (RME) was adapted to match the properties of diesel fuel (DF) by a metathesis reaction. In particular, this adaptation concerned the boiling property. The resultant fuel was very similar to the diesel fuel with respect to its boiling curve. However, the metathesis fuels still contained the ester groups that are already present in biodiesel. In the course of the project, twelve different metathesis products were produced and examined with respect to their properties and the exhaust emissions resulting from engine combustion.

As a design instrument for the adjustment of the boiling curve of a fuel, the alteration of biodiesel molecules by metathesis proved to be extremely effective. Beginning with rapeseed oil methyl ester, which predominantly comprises oleic, linoleic and linolenic acids, a variation in the chain length, which substantially influenced the boiling curve of the fuel produced, was achieved through the implementation of catalysts with the help of the metathesis reaction and the use of 1-hexene. In this way, it was possible to approximate the boiling behaviour of the RME to that of the DF over a wide range. Very different products could be created through variation of the catalysts and the ratio of biodiesel to 1-hexene. As a 20% blend with diesel fuel some of these could hardly be differentiated from DK, based on the boiling curve.

Predicting Various Biodiesel Fuel Properties.

G. Knothe, National Center for Agricultural Utilization Research, US Dept. of Agriculture, Peoria, IL, USA.

Several essential fuel properties of biodiesel are largely determined by the properties of the fatty esters which are its main components. These include cetane number, kinematic viscosity, oxidative stability and cold flow which are contained in almost all biodiesel standards but also other properties. Several properties can be easily predicted by adding the contributions the individual esters. These properties include cetane number and kinematic viscosity. Other properties, such as oxidative stability and cold flow, cannot be predicted in this fashion, rather they are influenced strongly by even relatively small amounts of components with less favorable properties. Besides the major fatty ester components, minor constituents can influence biodiesel fuel properties. It appears that these minor constituents have their greatest effect on those properties that are also most sensitive towards effects of less favorable properties of minor fatty ester components.

Improving the Cold Flow Properties of Biodiesel by Skeletal Isomerization of Fatty Acid Chains.

R.O. Dunn¹, H.L. Ngo², and M. Haas², ¹USDA, ARS, NCAUR, Peoria, IL, USA, ²USDA, ARS, ERRC, Wyndmoor, PA, USA.

Biodiesel is defined as the mono-alkyl fatty acid esters made from vegetable oils or animal fat lipids. Despite its many advantages, has generally poor cold flow properties. The present study evaluates the fuel related properties of branched-chain fatty acid methyl esters (BC-FAME) as potential additives or diluents in admixtures with biodiesel from conventional feedstocks. These esters were synthesized by skeletal isomerization of oleic acid using a zeolite catalyst followed by methylation to yield BC-FAME isomer mixtures. Both saturated and unsaturated BC-FAME were tested in mixtures with biodiesel from soybean, canola, and palm oils (SME, CaME, PME). Cold flow property results for saturated

and unsaturated BC-FAME isomers (iso-stearates and iso-oleates) indicated cloud point (CP) = -13.9°C and pour point (PP) = -25°C with moderately high kinematic viscosities (ν) = 5.6-6.0 mm²/s at 40°C. The CP, PP, and ν of FAME mixtures with BC-FAME concentrations at both additive (= 1 mass%) and diluent (2-50 mass%) scales were also measured. Mixtures with higher concentrations of BC-FAME were more effective in decreasing CP and PP without compromising ν . Furthermore, it was observed that the iso-stearate isomers were more effective than the iso-oleate isomers under certain conditions.

Biodiesel and Industrial Chemicals from Renewable, Non-food Feedstocks. W. Summers, Benefuel Inc., Irving, TX, USA.

Recent advances in heterogeneous catalysis enable simple, commercial scale conversion of triglycerides into useful industrial products. This novel, proprietary refining process combines esterification and transesterification into a single step, while using a broad range of different alcohols. This novel, fully continuous and integrated process affords new platforms for large scale, direct production of biodiesel fuels, bio-based lubricants, fuel additives and a host of glycerin derivatives, using inedible, lower priced, renewable feedstocks. Each of these downstream markets will be well served by the catalytic system, which will result in cleaner processes, more environmentally benign products and attractive project returns. This paper will describe the core chemistry and plant design for the patented process.

Refining of Animal Fats/Fuel for Electrical Power Generation and Feedstock for Biodiesel Production. B. Harten, GEA Westfalia Separator GmbH, Oelde, Germany.

First this work analyses the characteristic of different kind of animal fats. The requirements regarding quality are very much depending on the usage of the final product; the fuel specifications of different user are checked. Compared to the requirement of the edible oil industry, the use of animal fat for power generation or as feedstock for the biodiesel industry is more focused on minor components like sodium, nitrogen, sulfur. As a first approach to achieve the fuel specifications traditional degumming processes developed for edible seed oils are used with limited success. But with this knowledge it was possible to develop a new degumming process specialized on animal fats with

promising results. Depending on the final oil specification the additional use of the bleaching and in some cases even full refining can be necessary. This works shows the quality of the animal fat after all this process stages.

Enzymatic Hydrolysis of Acylated Steryl Glycosides and Method for Treating Biofuel. L.H. Munger and L. Nystrom, Institute of Food, Nutrition and Health, ETH Zurich, Zurich.

Acylated steryl glycosides (ASG) are known to occur in the raw material for biodiesel production (e.g. soy). During the transesterification step of biodiesel production, ASG are converted into steryl glycosides (SG) by the loss of the fatty acid chain. Due to the insolubility of SG in biodiesel severe filter clogging may be caused. As it was observed priorly, SG can be hydrolyzed into free sterols and the sugar moiety incubated in a water-based system using glycosylases (EC 3.2). The aim of this study was to demonstrate that also ASG are hydrolyzed by several glycosylases. Enzymatic hydrolysis was tested on a commercially available pure ASG mixture and ASG extracts from soy. The products of the hydrolysis, free sterols, were detected in all of the incubated samples demonstrating the capability of glycosylases to cleave the glycosidic bond in ASG. The reduction in ASG ranged from 50-56%. These results demonstrate the high potential of enzymatic hydrolysis to be used prior to the transesterification step preferably in combination with a degumming step. Not only ASG but also SG from the raw material will be removed resulting in higher quality of biofuel.

FOG to Biodiesel. R. Parnas^{1,2} and R. Madrak¹, ¹RPM Sustainable Technologies, Tolland, CT, USA, ²University of Connecticut, Storrs, CT, USA.

RPM Sustainable Technologies has placed reactor systems in Connecticut and in France to demonstrate the conversion of brown grease, yellow grease, and canola oil to ASTM/EN specification biodiesel fuel. The brown grease plant is located at a wastewater treatment facility to demonstrate systems integration with the wastewater treatment plant. Dewatered FOG (50% water) is transferred to the RPM plant and converted to biodiesel in a patented, continuous and automated system contained in two shipping containers. Results will be presented on the ASTM testing results.

Various catalysts were investigated for sulfur reduction, and results will be presented illustrating the reduction of sulfur to levels below 10 ppm for

ASTM/EN standards. A baseline process was developed to produce biodiesel at a sulfur level of 30 ppm without any catalytic sulfur reduction, thus minimizing the load on the sulfur reduction process. More advanced catalysts for esterification and transesterification are also in development, and laboratory results will be presented to illustrate the RPM technology pipeline. These catalysts have surface areas up to 400 m²/g, with ordered mesopores in the range of 10–20 nm diameter. Several other features of the catalysts provide activity comparable to sulfuric acid for esterification and potassium hydroxide for transesterification.

Glycerolysis of High FFA Oils and Its Application in Biodiesel Industry. Q. Tu and M. Lu, University of Cincinnati, Cincinnati, OH, USA.

Losing margin in the glycerol market and difficulty in utilizing feedstock oils with high free fatty acid (FFA) concentration have been two major issues for the current biodiesel producers. To address these issues, applying glycerolysis as the high FFA oil pretreatment step by using crude glycerol from biodiesel production process has been investigated in this study. Several key parameters are identified: the initial FFA concentration in the oil, concentrations of residual catalyst and soap in crude glycerol, glycerol-FFA molar ratio, temperature and duration for the reaction. A 2⁶ full factorial study is performed to investigate the influence of each individual parameter and their interactions on the glycerolysis process. Based on the results from parametric study, an analysis is conducted for energy consumption and cost of the process. The scope of the analysis is focused on the glycerolysis reaction between high FFA oil and crude glycerol while still incorporates certain sub-systems, such as material production (e.g. glycerol production). Both

direct and indirect energy inputs and costs are investigated. In addition, the same approach is applied to the quantification of energy consumption and cost of the acidic esterification as the baseline scenario for comparison.

Preparation and Characterization of IPA Extracted Mustard Oil for Biodiesel Production. S. Sinichi and L. Diosady, University of Toronto, Toronto, ON, Canada.

Fossil fuels represent a significant source of worldwide energy consumption. The search for alternative sources of energy is a necessity. Canada is the world's largest exporter of mustard seed. While mustard hulls are useful food ingredients, mustard seed oil contains erucic acid which is responsible for its high lubricity, a positive property of bio-fuels. The most commonly used solvent for oil extraction is hexane. Elimination of hexane is desirable due to its fluctuating prices and health and environmental concerns over its use. Extraction of mustard oil is a good model for testing alternative extraction systems. Investigation of oil recovery from de-hulled yellow mustard flour using isopropyl alcohol (IPA) resulted in 99.7 % oil extractability with 4-stage extraction 2:1 IPA: flour (v: w) ratio. After oil extraction, the IPA-oil miscella and oil has been characterized. The IPA, oil and water content of the final miscella collected and combined were 9.0±0.6%, 85.0±1.1 and 2.1±0.09% respectively. The free fatty acid and phospholipids content of the oil were 3.5±0.18% and 2.6±0.33% respectively. Transesterification of IPA extracted mustard oil was then performed using potassium hydroxide as base catalyst and resulted in an ester conversion of 12.7%.

IOP 3: New Uses of Glycerin

Chairs: X.P. Ye, University of Tennessee, USA; and T.J. Benson, Lamar University, USA

Synergistic Functions of Solid Catalysts in the Simultaneous Production of Lactic Acid and Propylene Glycol from Glycerol. X.P. Ye*, S. Ren, and L. Liu, University of Tennessee, Knoxville, TN, USA.

Development of value-added chemicals from glycerol, the co-product with biodiesel, is imperative to sustain the biodiesel industry. A solid catalyst

system was developed that provides a heterogeneous catalytic pathway to convert glycerol to racemic lactic acid (LA). During the glycerol-to-lactic acid conversion, hydrogen was formed, which could be used *in situ* to generate propylene glycol (PG), another high-value chemical from glycerol. Experimental results will be discussed in the context of roles of reaction media, catalysis, reaction

mechanisms and kinetics, product separation, and process efficiency. The simultaneous yields of LA and PG were achieved in the range of 50-70 mol% and 17-38 mol%, respectively, with corresponding glycerol conversion of 87-98 mol%. The developed method also showed robustness in direct conversion of crude glycerol to LA and PG. This method achieves higher productivity while eases corrosion problems normally associated with lactic acid production from glycerol via chemical route catalyzed by a strong base, and is independent of external hydrogen supply which is required in glycerol hydrogenolysis to produce propylene glycol.

Overview: What's Around the Corner for the Glycerol Market? T.J. Benson* and M. R. Islam, Lamar University, Beaumont, TX, USA.

In recent years, as the global biodiesel production has skyrocketed, the market has been, and will continue to be, flooded with excessive low-value crude glycerol, a major by-product of biodiesel. For small or medium biorefineries, it is expensive to refine crude glycerol above 99% purity for its use in food/fuel additives, chemicals, pharmaceuticals, and cosmetic industries. Therefore, it is of great importance to find new economical applications for crude and refined glycerol. The utilization of crude glycerol may be carried out by feedstock converting into energy carriers such as hydrogen, syngas, and methane or it can be converted into other value-added chemicals (e.g. acrolein, epichlorohydrin, ethers, esters, and alcohols). As hydrogen is a clean energy carrier, the conversion of glycerol into hydrogen is one of the best uses. Among the various chemicals from glycerol, production of methanol, ethanol and butanol are the most promising. Methanol can be recycled by being redirected into the process of creating the biodiesel, whereas ethanol and butanol can be blended with gasoline. In the future, glycerol can be expected to become a substitute for many of the petrochemicals on the market or it may become the next biofuel.

Glycerol Conversion to Acrylonitrile. B. Katryniok^{1,4}, C. Liebig³, C. Guillon^{1,4}, S. Paul^{1,4}, W.F. Hoelderich³, and F. Dumeignil*^{1,2}, ¹Unite de Catalyse et de Chimie du Solide, UMR CNRS 8181, USTL, Villeneuve d Ascq, France, ²Institut Universitaire de France, Maison des Universites, Paris, France, ³Department of Chemical Technology and Heterogeneous Catalysis, RWTH Aachen University, Aachen, Germany, ⁴Ecole

Centrale de Lille, ECLille, Villeneuve d Ascq, France.

The synthesis of acrylonitrile is entirely based on non-renewable feedstock, namely propylene.¹ We propose two alternative pathways for a sustainable route to acrylonitrile from glycerol. The first route involves a dehydration of acrolein in the first step followed by ammoxidation in the second step, while the second route proceeds through the intermediate formation of allyl alcohol:

Route 1. We used a previously optimized WO₃/TiO₂ catalyst for the first step of glycerol dehydration to acrolein. Sb-Fe-O catalysts were then found highly selective for the second step. The reaction conditions were optimized for the catalyst with an Sb/Fe molar ratio of 0.6. A maximum yield in acrylonitrile of 40 % (based on glycerol) could be achieved.

Route 2. According to the literature, allyl alcohol can be obtained from glycerol.^{3,4} We then studied ammoxidation of allyl alcohol as a new alternative. Efficient ammoxidation of allyl alcohol was demonstrated over optimized antimony-iron mixed oxide catalysts with Sb/Fe ratios of 0.6 and 1. Both catalysts showed a high acrylonitrile yield (ca. 84%) at the steady state.

Sustainable Glycerine Dehydration to Acrolein and Acrylic Acid. J.L. Dubois*, ARKEMA, Colombes, France.

Glycerine is a coproduct of the Oleochemistry, and over the last 10 years has been increasingly coproduced with Biodiesel. Glycerine dehydration leads to the production of Acrolein. Acrolein is currently produced by oxidation of propylene in multitubular fixed bed reactors. Its uses include conversion to Acrylic Acid (used to make paints and superabsorbants) where it is usually not isolated, and to Methionine (an essential amino acid). Other much smaller applications include production of pyridine, glutaraldehyde but also Flavors and Fragrances, and pharmaceuticals. Acrolein is a key platform chemical compound, which is more and more difficult to transport and store. Glycerol dehydration offers an opportunity to rely on an ubiquitous raw material to design small plants for production and consumption on-site and on-demand, thereby avoiding all risks linked with transportation and storage. Acrolein production becomes then more sustainable not only because the raw material is renewable, but also because the production process is environmentally safer. This new process offers new opportunities for the fine

chemistry and pharmaceutical industry to design new direct routes for key ingredients.

The key features of the process will be explained during the presentation.

Preparation of Propylene Glycol from Glycerol Through Continuous Hydro-Thermochemical

Process. R.L. Maglinao*, Montana State University-Northern, Havre, MT USA.

Glycerol's increasing surplus from the current biodiesel industry prompts the study to discover alternative ways of converting crude glycerol from biodiesel production to value-added chemicals. Propylene glycol is one of the valuable chemicals that had been successfully produced from glycerol through hydro-thermochemical process using a batch pressure reactor. This study aimed to investigate the process using a continuous flow reactor system for maximizing the productivity of propylene glycol through hydro-thermochemical conversion of glycerol. To achieve this, a high pressure and high temperature tubular PARR reactor was used. The reaction temperature and reactor's pressure were varied from 210 to 250°C and 50 to 300 psi of nitrogen, respectively. A water-to-glycerol mass ratio (WGMR) of 1:1 was fed to the reactor at LHSV (liquid hourly space velocity) range between 0.6 and 3 h⁻¹. The presence of 1-hydroxy-2-propanone, an intermediate compound of the conversion glycerol to propylene glycol, was found in the product. Results showed that propylene glycol was produced continuously in the absence of hydrogen. It is also concluded that further decomposition of propylene glycol to other product can be reduced at lower temperatures.

Catalytic Tri-reforming of Glycerol for Hydrogen

Production. M. Ashwani Kumar, C. Venumadhav, N. Lingaiah, K.S. Rama Rao, and P.S. Sai Prasad*, Indian Institute of Chemical Technology, Hyderabad, AP, India.

The ever increasing production of biodiesel, has laid more emphasis on value-addition of the byproduct glycerol to improve the economics of the process. Hydrogen production from glycerol is a better method, as it has the dual advantages of using a renewable raw material and simultaneous mitigation of global warming. Catalytic steam reforming is largely reported for hydrogen generation. However, it necessitates external heat input, as the reaction is endothermic. In order to make the process thermo-neutral the novel tri-reforming, originally proposed for methane, is ideal. Tri-reforming is a judicious combination of steam reforming, dry reforming and partial oxidation and it has not been reported so far for the conversion of glycerol into hydrogen. The present report highlights our attempts to solve the problem in two ways: i) studying the thermodynamic feasibility and identification of the optimum operating parameters and ii) the development of efficient heterogeneous catalysts that offer maximum hydrogen yield. The theoretical analysis has established the feasibility of the process. Mixed oxide supported Ni catalysts have been found to be very active, offering a hydrogen yield of 95% of the thermodynamically predicted value making the process highly promising. The possibilities of improving the hydrogen yield are also discussed.

IOP 4: Polymers and Additives

Chairs: Z.S. Petrovic, Pittsburg State University, USA; and Z. Liu, USDA, ARS, NCAUR, USA

Novel Alkyd-Type Coating Resins Produced Using Cationic Polymerization.

H. Kalita, S. Alam, A. Jayasooriyamu, S. Fernando, S. Samanta, J. Bahr, S. Selvakumar, M. Sibi, J. Vold, C. Ulven, and B. Chisholm*, North Dakota State University, Fargo, ND, USA.

Novel bio-based poly(vinyl ether) copolymers derived from soybean oil and a cycloaliphatic vinyl ether were produced by cationic polymerization and investigated for application as alkyd-type surface coatings. Compared to conventional alkyd resins,

which are produced by high temperature melt condensation polymerization, the poly(vinyl ether)s were thought to provide several advantages. These advantages include milder, more energy efficient polymer synthesis, elimination of issues associated with gelation during polymer synthesis, production of polymers with well-defined composition and relatively narrow molecular weight distribution, and elimination of film formation and physical property issues associated with entrained monomers, dimers, trimers, etc. As expected, incorporation of

cycloaliphatic groups into the poly(vinyl ether) polymer backbone significantly increased the glass transition temperature and mechanical properties of crosslinked networks produced by autoxidation. Overall, the results of the study suggest a good potential for these novel copolymers to be used for alkyd-type coatings.

New Biobased Monomers from Limonene by Thiol-Ene Reactions. M. Ionescu*, R. Gupta, D. Radojicic, X. Wan, and Z.S. Petrovic, Pittsburg State University, Kansas Polymer Research Center, Pittsburg, KS, USA.

The syntheses of new biobased monomers starting from limonene with hydroxyl, amine, epoxy and isocyanate functionalities were studied. Limonene is a monoterpene containing two double bonds, existing in high concentration (90%) in the oil extracted from orange peel. For functionalization of limonene were used thiol ene additions of various allyl compounds with hydroxyl, amine, epoxy and isocyanate functionalities to thiol groups of limonene dimercaptan prepared by the addition of hydrogen sulfide to the double bonds of limonene. The synthesized new monomers were incorporated in new polymers such as: polyurethanes, polyurea, crosslinked epoxy resins. The synthesized polymers were characterized by standard methods. The synthesized new monomers based on limonene represents a superior valorization of a waste from citrus industry.

Antimicrobial Properties of a Lipid Derived Thermoplastic Polytriazole. M. Floros* and S. Narine, Trent University, Peterborough, ON, Canada.

Concerns over antibiotic resistance is growing. As current generation antibiotics are rendered ineffective by resistances, the search is ongoing for alternatives. One approach is based on reducing the transmission in high-risk areas, such as dental implants and hospitals. This is generally accomplished with frequent sterilization and cleaning, however, it is not always effective. Engineered materials from plant lipids may provide a solution to some of these issues. Lipid derived materials have been previously demonstrated to be biocompatible with the human body.¹ Using a solvent and catalyst free synthesis, polytriazoles were created without residual solvent or catalyst contamination. This functional group has been previously demonstrated to have antimicrobial activity.² Furthermore, when lipid-derived polytriazoles are synthesized in a catalyst and

solvent free process, the polymers have broad-spectrum contact antibiotic and antimicrobial properties. The benefits of a catalyst and solvent free synthesis, the use of renewable feedstock's and the advantageous antimicrobial properties of these materials make them an exciting development in the battle against proliferating drug resistances and implant associated infections.

Thermosets of Epoxy Monomer from Tung Oil Fatty Acids Cured in Two Synergistic Ways. K. Huang¹, Z. Liu^{*2}, J. Zhang³, S. Li¹, M. Li¹, J. Xia¹, and Y. Zhou¹, ¹Institute of Chemical Industry of Forestry Products, CAF, Nanjing, Jiansu, China, ²NCAUR, ARS, USDA, Peoria, IL, USA, ³Composite Materials and Engineering Center, Washington State University, Pullman, WA, USA.

A new epoxy monomer from tung oil fatty acids, glycidyl ester of eleostearic acid (GEEA) was synthesized and characterized by ¹H-NMR and ¹³C-NMR. Differential scanning calorimeter analysis (DSC) and FT-IR were utilized to investigate the curing process of GEEA cured by both dienophiles and anhydrides. DSC indicated that GEEA could crosslink with both dienophiles and anhydrides through Diels-Alder reaction and epoxy/anhydride ring-opening reaction. It is noticed that the Diels-Alder crosslink is much more active than the ring-opening of epoxy and anhydride in the curing process. FT-IR also revealed that GEEA successively reacted with dienophiles and anhydrides in these two crosslinking ways. Dynamic mechanical analysis (DMA) and tensile test were applied to investigate the thermal and mechanical properties of GEEA cured by maleic anhydride, nadic methyle anhydride and 1,1'-(methylenedi-4,1-phenylene)bismaleimide, respectively. Due to the independence between the curing agents, dienophile and anhydride, a series of thermosetting polymers with various properties could be obtained by adjusting the composition of these two kinds of curing agents.

'Green' Route to Poly(amide-urethane)s from Plant Oil Dimer Acids. D. Graiver*, E. Hablot, and R. Narayan, Michigan State University, East Lansing, MI, USA.

Hydroxyl terminated poly(amide-urethane)s were prepared from plant oil dimer acids by a solvent-free process and without the use of isocyanates. This one-pot synthesis is comprised of three continuous steps: (1) Dimer fatty acids are condensed with ethylene diamine to produce amine

terminated intermediates; (2) These intermediates are reacted with ethylene carbonate to yield hydroxyl terminated di-urethanes; (3) The di-urethanes are subjected to a urethane-exchange reaction to increase the molecular weight as ethylene glycol is removed. The biobased carbon-content of these poly(amide-urethane)s is inversely proportional to the molecular weight and approaches 88%. ¹H NMR, FITR and GPC as well as hydroxyl value, acid value and amine value were used to elucidate the the structure and properties of all intermediates and products. Typical glass transition and melting point were in the rang og - 10°C and 73°C, respectively. TGA results indicated that these poly(amide-urethane)s were stable up to 230°C.

On the Reaction of Internal Epoxy Groups with Amines. Z.S. Petrovic*, M. Ionescu, and D. Radojic, Pittsburg State University, Pittsburg, KS, USA.

Often epoxidized vegetable oils are “cured” with amines by analogy with curing of epoxy resins with terminal epoxy groups. However, amines may react with ester groups and enter complex reaction schemes. In order to analyze the reaction of internal epoxies with amines without catalysts, 9-epoxyoctadecene, a model compound with epoxy groups as the only reactive species, was prepared and treated at 100 and 170 °C with primary amines and the products analyzed by a range of analytical techniques. Low or no reactivity was found except when ethanolamine was used.

Autoxidation, Vaporization and Residue Formation of FAME in Thin Films. S.J. Asadauskas*, I. Liascukiene, and A. Stoncius, Institute of Chemistry, Center for Physical Sciences and Technology, Vilnius, Lithuania.

Broader application of biodiesel is often accompanied by reports of residues, varnish and other solid deposits in engines. A thin film test was employed to investigate late stages of biodiesel degradation. Films (25-500 μm on steel) of rapeseed and palm Fatty Acid Methyl Esters (FAME) were exposed to 50°C and 90°C ageing on steel at 20% rel. humidity for up to 2000 hrs. Material vaporization was monitored gravimetrically and by FTIR, while formation of insoluble residues was evaluated in various solvents. Volatilization rates showed that rapid oxidative decomposition began within several hours. Depending on the film thickness, more than 80% of liquid could be vaporized, while the

remainder oxidized into solid residues. Acetone, tetrahydrofuran and isopropanol dissolved most residues, aged for nearly 1000 hrs. Heptane could not dissolve liquid degradation products formed after as little as 50 hrs ageing and fresh FAME performed only slightly better as a solvent. Evidently, conventional fuels and oils are not sufficiently compatible with FAME ageing products. Fuel film formation should be avoided when designing engines for FAME-type fuels. Thin film testing can be much more effective in studying late stages of ageing compared to conventional bulk liquid oxidation tests.

Soy-based Functional Building Blocks for Sustainable and Advanced Coatings. V. Mannari*, C. Patel, C.H. Chen, B. Ahmadi, and W. Li, Eastern Michigan University, Ypsilanti, MI, USA.

In the past few decades while there has been significant advancement in polymeric materials for coatings to improved performance and environmental quality, their dependence on petrochemical resources make them unsustainable for future development. Bio-renewable materials, such as plant oils, are important alternate resources that can be exploited as alternative to petroleum resources. Our research group has developed a platform of functional soy-based building blocks designed and customized for their use in such advanced coatings as water-borne, high-solids and UV-curable coatings.

A broad range of hyperbranched soy-polyols having different chemical structure, morphology and functionality has been developed using principles of green chemistry and engineering. A range of acrylic-functional soy derivatives, both oligomeric and monomeric, have been prepared for UV-cure coating and adhesives applications. Both ambient-cure type (PUDs) and UV-cure type (UV-PUDs) have also been prepared. These value-added functional soy-materials have successfully been used to demonstrate their suitability and applications in “green” and sustainable coatings. The study shows that these bio-renewable soy-based building blocks have tremendous potential for commercial applications for coatings with reduced carbon footprint.

Developing Soybean Oil-based Plastic Fat as Substitute for Paraffin and Beeswax. T. Wang*^{1,2} and L. Yao^{1,2}, ¹Iowa State University, Ames, IA, USA, ²Center for Crops Utilization Research, Ames, IA, USA.

Fully hydrogenated soybean oil (FHSO) was chemically modified to improve its functionality to be used as a substitute for paraffin and beeswax. A solvent-free synthesis method was developed to incorporate acetyl and hydroxy groups to FHSO to increase the cohesiveness of the fat. Stearyl alcohol and straight chain diols were reacted with FHSO to increase the melting point and hardness of the fat. By varying the reactant ratio, waxes having different physical and textural properties were obtained, offering a wide range of applications including candles, packaging, coating, sizing agent, birdseed binding, and encaustic painting medium. Performance tests on the suitability of the modified soy wax for cardboard coating and encaustic painting were conducted. The wax synthesis procedure has a great potential to be adopted commercially as a green processing technology to produce high performance, eco-friendly, and non-toxic based wax materials for various applications.

Development of High Performance Bioplasticizers from Vegetable Oils. D.R. Kodali* and L.J. Stolp, University of Minnesota, St. Paul, MN, USA.

Plasticizers impart flexibility to polymers and thereby increase their usefulness in variety of applications. Polyvinyl chloride (PVC) due to low cost and high performance is one of the largest polymers produced globally (>36MMT/year). Plasticizers are the largest plastic additives (>\$ 10 billion/year) used in PVC applications. The currently used phthalate esters cause health problems like endocrine disruption and other ailments. So an opportunity exists to develop new bioplasticizers from renewable materials. We successfully developed two generations of bioplasticizers from vegetable oils. The fatty acid esters are converted to estolides and epoxy estolides. The structural features such as molecular size, branching and polarity necessary for PVC compatibility will be presented. The new bioplasticizers are compounded at different levels and their functionality in plastisol and dry-blend

applications are evaluated. The physical properties of the new compounds such as acid value, color, viscosity, volatility and functional characteristics in PVC such as gelation, viscosity, efficiency, extractability and thermal stability will be presented and compared to commercial products. In summary, the performance of the new bioplasticizers is comparable to the commercial plasticizers. The commercial opportunity for the new bioplasticizers technology in replacing the phthalates, beyond EHS benefits in terms of higher performance and cost will be presented.

An Unique Industrial Oil. V. Patel*^{1,2}, ¹Gujarat University, Bhadran, Gujarat, India, ²Sardar Patel University, Vidyanagar, Gujarat, India, ³Troy University, Troy, AL, USA.

Worldwide, total trade value of castor oil was about 700 million USD in 2012 and expected to increase because of its unique chemical structure. Castor oil has about 90% Ricinoleic Acid in their fatty acid composition, and castor bean is the one and only one natural source of this fatty acid. Castor oil's triglyceride allows us to modify its structure into various products which have unique applications. Chemical modifications like dehydration, hydrogenation, esterification, saponification, hydrolysis onto this oil converts into strategic products which can be used in various industries while substituting petroleum based products. Processing of castor bean and refining of this oil is pretty much same as traditional vegetable oils instead of few changes. The extraction process, expelling of beans, can extract some solid and soluble proteins into crude castor oil so it needs to be removed prior to go for further refining processes. Physical and caustic refining is difficult due to presence of hydroxyl group and higher viscosity. Furthermore, hydrogenation of castor oil is an exothermic reaction and generates solid-brittle wax like product. 12-Hydroxy Stearic Acid is stage-II derivative where there will be two consecutive chemical reactions, saponification and hydrolysis, on HCO which converts hydrogenated oil into its soap and then splitting it into its fatty acid (12-HSA).

IOP 5: Oleochemicals

Chairs: J.A. Kenar, USDA, ARS, USA; and S.S. Narine, Trent University, Canada

The Lipid Biorefinery: Lubricants, Waxes, Fine Chemicals, Polymers, and More. S.S. Narine, Trent University, Peterborough, ON, Canada.

(abstract not available)

Influence of Structure on Melting Points of Linear Aliphatic Bio-Based Diesters. L.C. Raghunanan* and S.S. Narine, Trent University, Peterborough, ON, Canada.

The effect of varying total chain length, diol chain-length, fatty acid chain-length, and asymmetry on the melting point properties of linear aliphatic diol-derived diesters were systematically investigated using Differential Scanning Calorimetry (DSC).

It was found that varying the positions of the ester groups along the linear backbone resulted in quantifiable changes to low temperature properties. Melting points increased linearly as the tail lengths increased. This increase was greater when the two fatty acid tails on each diester were of equal lengths. Melting points also increased linearly when the lengths of the diol chain segments were increased, but less so than when the acid tail lengths were increased. Subsequent increases in diol chain length past nine methylene units resulted in sharper increases in melting points which were similar to those observed in analogous wax monoesters. These results are the first to quantify systematically the response in the melting points of linear diesters to structural modifications. These results allow predictive control of melting temperatures of waxy and oily esters for use in a variety of applications such as food, fuel, and lubrication.

Software Tools for Improved Understanding of Lipid Crystallization. M.J. Tessier*, M. Baker, S. Joseph, S. McConnell, L. Bouzidi, and S.S. Narine, Trent University, Peterborough, ON, Canada.

The crystallization data being generated by lipid scientists is quite complex, so to help scientists more efficiently analyze their data the Trent Center for Biomaterials Research (TCBR) has developed dedicated software tools. By employing software tools analysis time can be drastically reduced and new insights into the physics of lipid crystallization can be learned. Here, three programs developed at the TCBR will be presented. A relational database was developed that links lipid structure to

functionality and includes processing conditions. The database was designed based on the structural hierarchy of lipid systems. The database allows queries of physical parameters given user constraints and can therefore be used to reveal hidden trends in existing data. The Markov Chain Monte Carlo approach was used for the development of two programs. The first models the liquidus line in the thermal phase diagrams of binary lipid systems and automatically detects its singularities. The other fits crystallization data to the Modified Avrami Model and determines the growth modes and their respective Avrami parameters, and can detect situations where multiple growth modes are occurring simultaneously. All the programs were adapted into automated practical professional software packages which provide impressive results for lipid studies data.

Kinetic Study on the Isothermal and Non-isothermal Crystallization of Monoglyceride Organogels. Z. Meng*, X. Wang, Q. Jin, and Y. Liu, School of Food Science and Technology, Jiangnan University, Wuxi, Jiangsu Province, China.

The isothermal and non-isothermal crystallization kinetics of monoglyceride (MAG) organogels were studied by *p*NMR and DSC, respectively. The Avrami equation was used to describe the isothermal crystallization kinetics. Results showed that the crystal growth of MAG organogels was a rod-like growth of instantaneous nuclei at higher degrees of supercooling and a plate-like form with high nucleation rate at lower degrees of supercooling. The exothermic peak in non-isothermal DSC curves for the MAG organogels became wider and shifted to lower temperature when the cooling rate increased, and which was analyzed by Mo equation. Results indicated that at the same crystallization time, to get a higher degree of relative crystallinity, a higher cooling rate was necessary. The activation energy of non-isothermal crystallization was calculated as 739.59 kJ/mol according to the Kissinger method. Therefore, as the results of the isothermal and non-isothermal crystallization kinetics for the MAG organogels obtained, the crystallization rate, crystal nucleation and growth during the crystallization process could be preliminary monitored through temperature and cooling rate regulation, which laid the foundation for

the real industrial manufacture and application of the MAG organogels.

Synthesis of bis-phosphono Stearates from Methyl Linoleate and Dialkyl Phosphites. G.B. Bantchev* and G. Biresaw, USDA, ARS, NCAUR, Peoria, IL, USA.

The linoleic acid is the major component of soybean, corn, sunflower, and other commodity oils. This makes methyl linoleate is a better than methyl oleate model compound for investigation the chemical modification of vegetable oils for industrial purposes. In the current work, we report of the reaction of radical addition of dialkyl (methyl, ethyl, n-butyl) phosphites to the double bonds in methyl linoleate. The high temperature, needed for some of the radical initiators, caused also a transesterification between the ester groups. An optimization of the conditions (temperature, initiator, etc.) was done. The MS spectra of the products is reported.

Starch-lipid Complexes: Interesting Material and Applications from Amylose-fatty Acid Salt Inclusion Complexes. J.A. Kenar*, F.C. Felker, G.F. Fanta, and J.A. Byars, NCAUR, ARS, USDA, Peoria, IL, USA.

Aqueous slurries of high amylose starch can be steam jet cooked and blended with aqueous solutions of fatty acid salts to generate materials that contain inclusion complexes between amylose and the fatty acid salt. These complexes are simply prepared on large scale using commercially available steam jet cookers. The physical interaction between the fatty acid salt and the amylose component of the starch confer unique polyelectrolytic, water dispersibility, pH responsiveness, and gelling characteristics to the bulk material not available to either the native starch or fatty acid salt alone. At low starch concentrations (3.7-6.0 % solids), low-viscosity liquids are obtained while thicker gels result at concentration above *ca.* 6.64 % solids. The low solid dispersions were found to be pH dependent and became quite viscous upon lowering the solution pH. Here we describe the characterization of these materials starch-fatty acid salt, examine the properties of aqueous dispersions, and describe some potential applications such as starch-based aerogels, thickeners, and emulsifiers.

Anaerobic Digestion of Waste Products into Fuels and Chemicals. E. Revellame*¹, W. Holmes¹, R. Hernandez^{1,2}, D. Fortella², and M. Zappi¹, ¹UL Energy Institute, University of Louisiana, Lafayette, LA, USA; ²Department of Chemical Engineering, University of Louisiana, Lafayette, LA, USA.

Digestion is a technology in which microorganisms are used to anaerobically degrade organic waste constituents into methane and carbon dioxide. The produced methane can then be fed into a genset for on-site production of electrical power and/or used to replace/displace natural gas as a fuel burned on-site. In this study, shrimp processing wastewater was used to produce methane in laboratory scale. The effect of initial pH and seed concentration (digester sludge) on biogas production were determined. The laboratory data were then used to predict the behavior of a pilot scale digester with respect to biogas production. Laboratory results also indicated that the process can be directed to production of bio-hydrogen and volatile fatty acids (VFAs) instead of methane and carbon dioxide. The VFAs were then utilized for production of lipid-rich microbial culture.

Environmentally Benign Dialkyl Carbonates in Non-Catalytic Supercritical Method for Production of Biodiesel and Useful Chemicals. Z. Ilham*^{1,2} and S. Saka¹, ¹Graduate School of Energy Science, Kyoto University, Kyoto, Japan, ²Institute of Biological Science, University of Malaya, Kuala Lumpur, Malaysia.

With increasing concern towards the environment, the industry must come out with cleaner chemical processes particularly in utilizing environmentally benign chemicals or “green reagents”. Green reagents must be produced from an environmentally-friendly process, avoid waste, avoid the use and production of toxic and dangerous chemicals, biodegradable and energy-savvy. Among all, dialkyl carbonates, a neutral and versatile organic compound with interesting chemistry, possess a huge potential as a green reagent. Recently, low molecular weight short-chain aliphatic carbonates such as dimethyl carbonate and diethyl carbonate have been used widely either as fuel additives and as reagents for biodiesel production. Mid-chain dialkyl carbonates, containing alkyl chains between three and eight carbon atoms also represent newer class of interesting fuel and lubricants and functional fluids with improved seal compatibility and toxicology. In this study, existing technologies

related to the production of biodiesel and useful chemicals from dialkyl carbonates will be discussed with a special highlight on the non-catalytic supercritical technology pioneered in our laboratory, discussing its advantages and drawbacks.

IOP-P: Industrial Oil Products Poster Session

Chair: R. Wang, Missouri University of Science and Technology, USA

1. Synthesis and Physical Properties of New Estolide Esters. S.C. Cermak^{*1}, J.W. Bredsguard², T.A. Isbell¹, and R. Murray¹, ¹USDA, ARS, National Center for Agricultural Utilization Research, Bio-Oils Research Unit, Peoria, IL, USA, ²Biosynthetic Technologies, Irvine, CA, USA.

Estolides are a class of esters based on vegetable oils that in this case are formed when the carboxylic acid functionality of one fatty acid reacts at the site of unsaturation of another fatty acid to form an ester linkage. The objective of this preliminary study was to synthesize new esters of estolides from either branch or linear chained alcohols and evaluate the physical properties: viscosity, acid value (AV), Gardner color, pour points (PP), and cloud points (CP). The oleic free acid estolide that were esterified with branched alcohols had the best low temperature physical properties, PP and CP. The best PP performers from the branched series were 2-hexyldecanol, a 16 carbon chained branched material, and 2-octylododecanol, a 20 carbon branched material, with a PP at -39°C. The best CP performers from the same series were 2-octylododecanol, with a CP lower than -50°C, followed by the 2-hexyldecanol at -42°C. In general, the branched alcohols produced materials with better cold temperature properties than current commercially available materials. The viscosities and VIs were as expected in terms of trends and ranges. The iso-stearyl alcohol had the most interesting viscosity at 40°C of 209.3 cSt which was higher than all other materials tested in this study. These new oleic estolide esters showed great potential as commercial lubricants.

3. Strategies for the Conversion of De-oiled Algae Cake into Fuels and Chemicals. E. Revellame^{*1}, W. Holmes¹, R. Hernandez², D. Fortella², and M. Zappi¹, ¹UL Energy Institute, University of Louisiana, Lafayette, LA, USA, ²Department of Chemical Engineering, University of Louisiana, Lafayette, LA, USA.

Algal biomass contains three main components: carbohydrates, proteins and lipids. After lipid extraction, the remaining cake could be a good source of nutrients for humans and animals. With the tremendous interests in growing algae for its lipid content, there is a good possibility that the de-oiled algae cake will pose some issues, much like glycerol in biodiesel technology. This study presents alternative ways of utilizing the de-oiled cake for fuels and chemicals.

4. Synthesis of Tri-aldehyde and Tri-amine from Triolein and Their Characterization. J. Yang¹, J. Yue^{*1}, Y. Deng¹, and Y. Zhao^{1,2}, ¹Department of Food Science & Technology, School of Agriculture and Biology, Shanghai Jiao Tong University, Shanghai, China, ²Department of Food Science & Technology, Department of Food Science & Technology, Corvallis, OR, USA.

Due to limited fossil resources and concerns on environmental pollution, more studies have been focused on the synthesis of green polymers from renewable resources. Polyamine is an essential monomer for the production of polyurea, polyamide, and other polymers. The current polyamines supplied for polymer industry are all derived from petroleum chemicals, which are non-degradable and

lack of varieties in the structure. In this study, a novel tri-amine monomer was synthesized from vegetable oil based triolein via a tri-aldehyde intermediate. Specifically, triolein was ozonized at -78°C followed by treatment of sodium borohydride (NaBH₄). The produced triol was purified by flash chromatography and then oxidized by 2-iodoxybenzoic acid to transfer into tri-aldehyde, which contained three terminal aldehyde groups. After purification, tri-aldehyde was reacted with benzylamine, reduced by sodium triacetoxymethylborohydride, and then went through hydrogenation to yield the tri-amine that contained three primary amine groups. The novel tri-aldehyde and tri-amine compounds were further characterized by ¹H-NMR, ¹³C-NMR, FT-IR and Mass spectrometry. The developed triamine monomer can be utilized to synthesize a hyperbranched polyurea. And the synthetic methodology developed in this study may also be performed on rapeseed oil, tung oil and other vegetable oils.

5. Kinetic Analysis of Esterification Using Liquid Lipase. M.F. Mohd Yusoff^{*1,2}, G. Zheng¹, and S. Fedosov¹, ¹Dept. of Engineering, Aarhus University, Aarhus, Denmark, ²Pusat Pengajian Sains Kimia dan Teknologi Makanan, Universiti Kebangsaan Malaysia, Selangor, Malaysia, ³Dept. of Engineering, Aarhus University, Aarhus, Denmark.

Enzymatic transesterification for biodiesel production recently became feasible because of decreasing prices on lipases. Computer modeling allows fast simulation of different scenarios and facilitates optimization of the process. The process was divided into several individual blocks to aid the modelling. This work presents analysis of esterification and hydrolysis. Catalytic features of the liquid lipase Callera Trans L (TLL) were investigated and compared to the results obtained with the immobilized enzyme Novozym 435 (N435). The corresponding rate constants were evaluated. The most interesting observation concerned difference in the apparent equilibrium constants ($K_{eqTLL} > K_{eqN435}$), which apparently contradicts the laws of thermodynamic. We explain this effect by different chemical activities of micellar water in these two systems. Water phase under the reaction with liquid TLL is apparently dispersed to a lower grade if compared to the reaction with Nvz435. Transitions between different physical forms of water showed that the balance of TLL system is shifted to large water droplets if using agitation

similar to that of N435 system. Substitution of a N435 by TLL will not cause a dramatic accumulation of fatty acid. Dependencies of the reaction velocity on the liquid enzyme concentration appears as hyperbolic function as compared to solid enzyme.

6. Physicochemical and Structural Properties of Glycerin Gel Prepared by Glycyrrhizic Acid Diethyl Ester. K. Koga^{*1}, T. Kimura¹, K. Sakai², H. Kushida³, and N. Yoshikawa³, ¹Hokuriku University, Kanazawa, Ishikawa, Japan, ²Tokyo University of Science, Noda, Chiba, Japan, ³Cokey Systems Co Ltd, Matsusaka, Mie, Japan.

Glycyrrhizic acid diethyl ester (GZ-DE) is a prodrug of glycyrrhizic acid (GZ), a hepatitis therapeutic drug, developed for the purpose of absorption improvement from gastrointestinal tract of GZ. We found accidentally that GZ-DE gelled with glycerin selectively in the experiments of the solvent which dissolved GZ-DE. Based on this gelation's phenomenon, we investigated the preparation method, rheology, DSC, capillary electrophoresis (CEP), NMR and SAXS as physicochemical and structural properties of glycerin gel.

The results from the investigation by glycerin gel containing 2.4% w/w GZ-DE were as following: 1) The glycerin gel accepted a creep phenomenon in constant stress less than 5Pa, but was fragile gel indicating the Newton flow in 10Pa. 2) From the dynamic viscoelastic measurement, the elastic clause (G') exceeded a viscous clause (G''), indicating that glycerin gel was a solid-like property. 3) In the DSC assay, a meaningful difference was observed to a glass transition temperature of glycerin and the glycerin gel. 4) In the CEP assay, new compound was not detected in the glycerin gel. This result supported that glycerin gel was physical gel. 5) In SAXS measurement, it was revealed that the glycerin gel has oval-shaped basic frame (longer axis 118nm, minor axis 65nm).

7. Biodiesel Production with *Jatropha (Jatropha curcas)* and Palm Oil (*Elaeis guineensis*) Catalyzed by *Candida antarctica* and *Thermomyces lanuginosus* Lipases. L. Moreno, F. Bueso^{*}, and R. Pineda, EAP Zamorano University, Tegucigalpa, Francisco Morazan, Honduras.

This study evaluated yield and quality of biodiesel produced from *Jatropha (Jatropha curcas)* and palm oil (*Elaeis guineensis*) using free

Thermomyces lanuginosus (TL) and immobilized *Candida antarctica* (CA) lipases vs. a basic catalyst (sodium hydroxide). Manufacturer recommended reaction conditions were used for each lipase. A completely randomized design was used to evaluate a 2 × 3 factorial arrangement, with three replicates. Biodiesel % Yield (g biodiesel/100g oil), % moisture, % free fatty acids (FFA), peroxide value, oxidative stability index (OSI), color, cetane number and FAME profile were measured according to ASTM D6751. TL lipase yielded 83.4% biodiesel from *Jatropha curcas* oil, statistically similar ($P=0.87$) to CA lipase (82.8%) and higher ($P<0.05$) than NaOH (74.7%). Biodiesel from palm oil using CA lipase showed a 75.3% yield statistically similar ($P=0.52$) to TL lipase (72.7%) and to NaOH (72.6%). Quality was similar for biodiesel produced by basic and enzymatic catalysis according to ASTM D6751 standard. Biodiesel production by enzymatic catalysis with free and immobilized lipases were comparable in yield and quality to basic catalysis for *Jatropha* and palm oil.

8. Phorbol Ester Quantitation in Dehulled Seed Structural Parts of Eight Accessions of *Jatropha curcas* from Latin America. R. Chun and F. Bueso*, EAP Zamorano University, Tegucigalpa, Francisco Morazan, Honduras.

Phorbol esters (PE) present in *Jatropha curcas* seed are heat stable toxic compounds causing activation of promoter's kinase C and cancer. The objective of this study was to quantify and compare the amount (mg/g) of PE in structural parts (cotyledons, tegument and embryo) of eight accessions from Mexico, El Salvador, Brasil and Honduras. PE were extracted and quantified by high pressure liquid chromatography. A split plot design was used where the main plots were the accessions and the subplots were the structural parts of the seed. An LSMeans mean separation test was performed to determine significant differences ($P<0.05$) between accessions and structural parts. All accessions were toxic because they exceeded the value considered non-toxic (PE 0.10 mg/g of dry seed). Accessions with the highest content of PE were Mexican and India Salvadoreña with 7.56 ± 0.36 and 7.36 ± 0.16 mg/g seed respectively and the lowest was Puebla (3.15 ± 0.10 mg/g seed). The cotyledons had significantly higher values of PE (6 mg/g) than tegument (0.9 mg/g) and embryo (0.7 mg/g). The higher concentration of PE in the cotyledons may discard the possibility of reducing toxicity of *Jatropha* seed oil and meal by mechanical

removal of the tegument as previously suggested.

9. Thermal Behavior of Lipid Systems Containing Palm Mid Fraction and Dipalmitin. T.L. Teodoro daSilva*, M.A. Fontenele Domingues, C.C. Ming, and L. Aparecida Guaraldo Gonçalves, State University of Campinas, Campinas, São Paulo, Brazil.

This study aimed to investigate the effects of the addition of dipalmitin (PP) in Palm Mid Fraction (PMF) observing the thermal behavior. The lipid systems were prepared with PMF and two level of PP; 0.5 and 1.0% (w/w). The samples were characterized through minor lipids by High Pressure Size Exclusion Chromatography (HPSEC) and the thermal behavior was evaluated by Differential Scanning Calorimetric analysis (DSC) at the zero time and after 1 day at 25°C. The samples of PMF, PMF with 0.5%PP and PMF with 1.0%PP presented diacylglycerol level of 6.00, 6.47 and 7.08%, respectively. DSC results at time zero, for crystallization events demonstrated acceleration on the 1st peak for samples with PP. In the melting events, all samples presented a single peak with polymorphic transition. Samples with PP had a decrease in the intensity of polymorphic transition. And the enthalpy variation (ΔH) of samples added with PP were lower. After one day, the melting events presented two peaks. The intensity of the 2nd peak increased proportionally with the addition of PP. These results indicated a possible influence of PP in the formation of more stable polymorphic forms in the PMF.

10. Wear Prevention Advantages of Palm Oil-based TMP (trimethylolpropane) Ester Compared with Conventional TMP-C₈₋₁₀. P. Jicheng*, K. Lingjie, Z. Jie, L. Shichun, and Y. Jun, PetroChina, Dalian Lube Oil R&D Institute, Dalian, Liaoning, China.

TMP esters commonly present as base fluid and additive which are biodegradable and have high lubricity properties such as higher flash point temperature and VI (viscosity index). Two different TMP esters are synthesized through esterification and transesterification reactions who are palm oil-based TMP ester (POTE) and Conventional TMP-C₈₋₁₀ ester (CTE) respectively. High-Frequency Reciprocating Rig (HFRR) SRV and four-ball test were used to evaluate wear prevention characteristics. It is found that 3% addition of POTE in ordinary lubricant decreases the maximum amount of WSD (wear scar diameter) and reduces more coefficient of friction compared with CTE. SEM images show

POTE resulted in a smooth surface but the surface of CTE was covered by some fine pits. The lubricity enhancing properties of ester are mainly determined by the cohesive energy of adsorbed films formed on iron surface. Quartz crystal microbalance (QCM) shows that the addition of POTE is necessary to have positive contribution thanks to it has a good adsorption ability compared with CTE.

11. Characterization of Enzymatically Prepared Sugar Medium-chain Fatty Acid Monoesters
Characterization of Enzymatically Prepared Sugar Medium-chain Fatty Acid Monoesters. X. Zhang¹, W. Wei¹, X. Cao¹, H. Zhang¹, and F. Feng^{*1,2}, ¹Institution of Food Science and Biotechnology, Zhejiang University, Hangzhou, Zhejiang Province, China, ²Fuli Institution of Food Science, Zhejiang University, Hangzhou, Zhejiang Province, China.

Various sugar medium-chain fatty monoesters were prepared enzymatically using Lipozyme TLIM in organic solvent. The properties such as surface tension, antimicrobial activity, and ability to foam, emulsify, and stabilize emulsions at room temperature were evaluated to conduct systematic studies on the structure–function relationships of these compounds. Results showed that all monoesters displayed good surface-activity properties. In particular, sucrose monolaurate was the most excellent surfactant among 12 monoesters. The sugar monoesters containing C₈ to C₁₂ alkyl chains showed a broad spectrum of increasing antimicrobial activity. All tested monoesters were more effective against *Staphylococcus aureus* (Gram-positive bacterium) than *Escherichia coli O157:H7* (Gram-negative bacterium). Methyl α-D-glycoside monoesters were the most effective, whereas raffinose monoesters possessed poor antimicrobial activity. Generally, the surface-active properties and antimicrobial activities of sugar fatty acid monoesters were influenced by the carbon chain length and type of saccharide group.

12. Lipid Accumulation of Rhodotorula Glutinis Grown in Waste Paper Hydrolysate. B. Sukhbaatar*, M. Green, L. McFarland, and T. French, Mississippi State University, Mississippi State, MS, USA.

Conversion of lignocellulosic sugars present in waste paper hydrolysate to triacylglycerols using the oleaginous yeast *Rhodotorula glutinis* was investigated in this study. Hydrolysis of the paper was approached by optimizing (1) concentration of sulfuric acid in decrystallization step; (2) ratio of

pure sulfuric acid to cellulose in biomass; and (3) duration of oligo-sugars hydrolysis to monomers after dilution with water. Optimum concentration of sulfuric acid for decrystallization of cellulosic structure was 65% for 1 hour at 30°C. Ratio of pure sulfuric acid to cellulose was 1.01:1. The length of hydrolyzation time of oligo-sugars to monomers was optimum at 15 min using a temperature of 121°C. The resulting sugar stream containing 38 g/L of glucose and 16 g/L xylose used for lipid accumulation by *R. glutinis*. Cells from the treatment were harvested daily and lipids were extracted from total dry cell using a modified Bligh and Dyer method. *R. glutinis* accumulated 24% of cell dry weight as lipid after 5 days of growth in paper hydrolysate media. The fatty acid produced mainly comprised of palmitic (18%), stearic (5%), oleic (41%), and linoleic (31%) acids.

13. Soybean Oil Based Epoxy/Glass Fiber Composites for Structural Application. R. Wang*, T. Schuman, R. Vuppapapati, and K. Chandrashekhara, Missouri University of Science and Technology, Rolla, MO, USA.

High performance bio-based composites were manufactured and that showed mechanical properties comparable to that of the petroleum based counterparts. Pure glycidyl esters of epoxidized fatty acids derived from soybean oil (EGS), blends of diglycidyl ether of bisphenol A (DGEBA) with EGS, and pure DGEBA were copolymerized with anhydride to yield polymer matrix. Glass fiber reinforced composites were fabricated from the matrices via vacuum assisted resin transfer molding (VARTM). The results indicated that EGS is curing compatible with DGEBA and form single phased structure. EGS significantly reduced viscosity of DGEBA and facilitated fabrication of composites through VARTM at room temperature. Mechanical tests showed that EGS composites possessed comparable properties such as flexure and impact strength compared to DGEBA based counterparts. The glass transition temperature, flexural strength and modulus of EGS composite were as high as 110°C, 490 MPa and 22.5 GPa, respectively. This high performance bio-based composite has potential to replace petroleum-based epoxy resin as value-added product from vegetable oils.

14. Continuous Biodiesel Production Using a Fixed-bed Lewis-based Catalytic System. F.M. da Silva,

D.M.M. Pinho, G.P. Houg, I.B.A. Reis, and P.A.Z. Suarez*, Universidade de Brasília, Brasília, DF, Brazil.

It was developed a fixed bed tubular continuous reactor to produce biodiesel, using pellets of aluminum oxide doped with zinc oxide. The pellets were placed into a tubular reactor as a 30 cm long column (2.65 kg). The reactor was feed with soybean oil (168 g h⁻¹) and methanol or ethanol (89 g h⁻¹) with the temperature fixed at 100 °C. Under these conditions it was possible to convert soybean oil into biodiesel in up to 75 % yield in the case of methanol and 35 % for ethanol. Increasing the temperature to 180 °C, it was possible to ethanolise soybean oil with yields up to 78 %. It is important to note that after a steady state is achieved the conversions remained approximately constant with time. It is also worth to mention that the fixed bed remained active for more than 120 h, showing no catalyst leaching or deactivation, and so far it was not possible to determine its overall productivity.

15. Poly-β-Hydroxybutyrate (PHB) Extraction and Purification. T. Fei*, Iowa State University, Ames, IA, USA.

Some bacteria are capable of accumulating poly-β-hydroxybutyrate (PHB) as well as neutral lipids under nutrient limitation condition. One key step of the making the PHB and neutral lipids harvesting profitable is the extraction, separation and purification process. Scientists have tested different solvent and non-solvent systems for the production of these biopolymers. Technically, an ideal method should be capable of achieving high recovery level and purity at low cost, but in this paper, environmental concerns are also taken into consideration. Three extraction methods (solvent extraction, digestion of non-PHB materials using enzymes and application of supercritical solvent) are reviewed and compared. Solvents such as acetone and methylene chloride which are less toxic than chloroform will be tested. Chen et al. (2001) mentioned that hot acetone can be used to extract PHB, and cool water can be used as an antisolvent to precipitate PHB. However, they did not practically apply this method, and no data was reported. In this study, the extraction results (recovery level and purity) as well as costs of using different methods will be compared, and a cost effective and relatively "green" extraction and purification method will be determined. Methods to further separate PHB and neutral lipids will also be studied.

16. Standard Biodiesel from Mustard Emulsion by a Combined Solvent Extraction/Adsorption Process.

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The destabilization of stable oil-in-water emulsion produced during aqueous processing of yellow mustard flour through three-stage treatment with tetrahydrofuran (THF) resulted in the formation of low-phosphorous and low-free fatty acid oil-THF-water miscella phases containing 1 to 2% water. Dehydration of these miscella phases by adsorption on 4A molecular sieves using both batch and fixed-bed systems reduced the water content to the quality standards for biodiesel feedstock (0.3%). Batch method was used to investigate the dominant parameters affecting the uptake of water from miscella phases including adsorbent dose, contact time, initial water content and miscella oil concentrations. The adsorption of the water was strongly dependent on adsorbent dose and miscella oil concentrations. The regeneration of molecular sieves in a nitrogen-filled vacuum oven for 6 h at 275 °C indicated complete desorption of miscella components. The adsorption breakthrough curves in the molecular sieve packed columns with respect to different flow rates, initial water and oil miscella concentrations were determined. The dehydrated miscella phases were reacted with methanol in a single-phase base-catalyzed transesterification process with high yields (99.4 wt%) to FAME that satisfied the international standards for use as biodiesel fuel.

17. Phase Separation of Free Glycerin (FG) in Finished Biodiesel Fuels—Bulk Composition. R.W. Heiden¹ and M. Mittelbach²; ¹R W Heiden Associates LLC, USA, ²KF University of Graz, Austria.

Unexpected separation of heterogeneous phases from diesel fuels remains a concern, particularly at low temperatures above the cloud point. The limited solubility of FG is used routinely to separate and capture over 99% from transesterification reaction products, detectable residues of FG above 10 ppm often remain in biodiesel. When formed, FG phases can inhibit flow through filters or encourage microbial growth. Solubility represents a classical boundary condition, but its role in determining the magnitude of FG phase "fallout" is largely ignored. GC and GC MS are used here to measure the solubility of FG in: dry, distilled B100, B20 and B0 in the range of 2-60C;

different commercial B100's from a variety of sources, and; in various hydrocarbons simulating diesel fuel. Among results, when cooled, solubility in the benchmark B100 drops below the internationally recognized limit of 200 ppm, far lower than reported earlier. Solubilities in different commercial B100's, determined with a precision of less than 5%, vary considerably above and below the benchmark, implicating a role for changing levels of impurities. Dilution by blending is examined from the perspective of solvent strength and actual solubility measurements. The magnitude of changes in formulation needed to improve solubility performance is also discussed.