2009 Annual Meeting Abstracts

Industrial Oil Products

MONDAY

MORNING

IOP 1: Alternative Fuels

Chair(s): G. Knothe, USDA, ARS, NCAUR, USA; and J. Krahl, Coburg University of Applied Sciences, Germany

Modeling the Crystallization Behavior of Biodiesel at Low Temperatures. R.O. Dunn, Food & Industrial Oils Research, USDA, ARS, MWA, NCAUR, Peoria, IL, USA

The most common form of biodiesel is made by transesterification of vegetable oil or animal fat fatty acids with methanol (FAME). Biodiesel from feedstocks such as palm oil (PME), rapeseed oil (RME), soybean oil (SME) or used cooking oil (UCOME) is susceptible to performance issues during cold weather. The temperature where solid crystals begin to form (onset temperature) depends on composition and melting properties of the individual FAME components in the biodiesel. For example, SME is composed of long-chain esters that are 14-18 wt% saturated (melting point [MP] > 27°C) mixed with unsaturated esters (MP < -20°C). As a result, SME has a cloud point (CP) near 0.5°C. In contrast, PME may contain 32-47.5 % methyl palmitate (MP = 27.79°C) and has CP = 11.7°C. This work utilizes sub-ambient differential scanning calorimetry (DSC) analysis to accurately determine MP and enthalpy of fusion of pure FAME components found in SME, RME, PME and UCOME. DSC data were applied to develop thermodynamic models for calculating onset temperature of FAME mixtures based on composition of the four types of biodiesel (determined by GC analyses). Predicted onset temperatures were comparable to corresponding results from direct measurement of CP.

Evaluation of Acylated Sterols Glucosides (ASG) and Sterol Glycosides (SG) of Oil Seed Crops of the Pacific Northwest. K. Duff, J. Van Gerpen, University of Idaho, USA

Currently, there are limited data on the quality and quantity of phytosterols in oil seed crops. The majority of these data were obtained by multistep extraction, saponification, acidification and derivatization for evaluation with GC-MS. This study evaluates dry land oil seed crops of the Pacific Northwest (Canola, Mustard, Camelina) using an exhaustive extraction, then concentration with solid phase extraction (SPE) and HPLC-APCI evaluation for Acylated Sterols glucosides (ASG) and Sterol Glucosides(SG).

Industrial oil extraction is optimized for maximum oil extraction. The extraction efficiency of trace phytosterols compounds may vary significantly depending on the processes used. Biodiesel produced from minimally processed vegetable oils may be more susceptible to these variations. This study provides a base upper limit for sterol glucosides in these oil seed crops.

Levels of SG below 50 PPM in neat biodiesel have been implicated as possible seed crystals, acting as nucleation sites for additional trace contaminations. These agglomerates and/or crystals cause filter failure without elevating the cloud point or pour point of the biodiesel. The cold soak filtration test in ASTM D6751 has recently been added to evaluate for the presence of any problematic contaminates in the neat biodiesel.

***In situ* Transesterification for Biodiesel Production: Investigating the Suitability of the Spent Meal as a Poultry Feed Component.** M.J. Haas[1], R.L. Stroup[2], D. Latshaw [3], K.M. Scott[1], [1]USDA, ARS, ERRC, Wyndmoor, PA, USA, [2]R.L. Stroup Co., Ltd., Troy, OH, USA, [3]Dept. of Animal Sciences, Ohio State University, Columbus, OH, USA

'*In situ* transesterification' is the term applied to the direct transesterification of the glycerides residing in solid materials, yielding simple alkyl fatty acid esters for use as e.g. biodiesel. Such an approach eliminates lipid isolation as a precursor to transesterification. Thus it can eliminate the use of organic solvents or pressing operations in biodiesel production. The approach can be used to produce fatty acid esters from lipid-bearing industry coproducts such as oilseed presscake and meat and bone meal. In previous work we have shown that this method achieves high degrees of

transesterification and yields a product that meets ASTM biodiesel specifications. The fate and value of the spent meal exiting an oilseed processing operation is vital to the economics of the overall process. Therefore we have investigated the suitability of flaked soybeans that were subjected to *in situ* transesterification as a component of a poultry diet. Results will be compared to those of control diets containing soy flakes delipidated by hexane extraction.

Effect of Metals on Antioxidant Effectiveness in Biodiesel Blends. R. de Guzman, H. Tang, S. Salley, K .Y. S. Ng, Wayne State University, Detroit, MI, USA

Biodiesel oxidation is an established scenario that retards the acceptance of the renewable fuel as the mainstream alternative to fossil fuels. Exposure to several factors such as heat, light, air (oxygen), and metallic contaminants could speed up oxidation degrading the biodiesel properties linked to oxidative stability. Although the effect of the latter three sources of oxidation can be addressed by addition of antioxidants in biodiesel, the metallic contaminantsâ?? bearing should not be undermined since it can significantly reduce induction period by just minute amounts. Due to the possibility that minute amounts metallic contaminants can suppress the antioxidants, a study is of significant importance This study will involve the addition of metallic contaminants to neat biodiesel and biodiesel with antioxidant, the oxidation will be monitored by the rate of production of oxidation products via iodometric method and the induction period using the Rancimat. The study will utilize the ICP to help in determining the residual amount of metallic contaminants permissible to be in a biodiesel system that will not have adverse effects even in the presence of antioxidants. Findings will also be recommended for inclusion in standards in production and handling/storage of biodiesel to properly regulate fuel properties.

Sustainable Biodiesel Production Techniques. Rachel Burton, Piedmont Biofuels Industrial, USA

Piedmont Biofuels is a small producer in the US biodiesel industry with an annual production of one million gallons. One of the core tenets of the operation is to produce quality biodiesel through sustainable production techniques. Since 2003, the focus has been in small reactor design for making fuel out of waste. Our expertise in processing includes batch efficiency, continuous flow, cavitational reaction, and small-scale bio-refining. In 2008, Piedmont commissioned the first biorefinery in North Carolina utilizing its co-products from biodiesel production to achieve greater economic sustainability. Also in 2008, Piedmont became first and only small producer to achieve BQ-9000 accreditation. Dedication to fuel quality is a key piece to a role in sustainable biodiesel production. In an industry where commodity markets dictate flexibility in scale, Piedmont has discovered feedstock anomalies to shelter it from market fluctuations. An essential part of sustainable production in understanding production energy balance, Piedmont began energy balance research on its pilot production in 2004 and again in 2009 on its multi-feedstock commercial production facility. Piedmont Biofuels continues to present an unique small-scale model of biodiesel production for the North American market with its diverse production techniques a part of its success.

Properties of Algae Oil and Algal Oil-based Biodiesel: Effect of Extraction and Reaction Methods. N. Abunasser[1,2], H. Tang[2], M.E.D. Garcia Perez[2], J. Wilson[1], S. Salley[2], K.Y.S. Ng[2], [1]Michigan Economic Development Corporation, Lansing, MI USA, [2]Wayne State University, Detroit, MI USA

While interest in using algal oil as a source for biodiesel has increased in recent years, there are few comprehensive studies of the properties of the biofuels that would be produced from these oils. Dunaliella tertiolecta UTEX LB 999, grown in Erdschreiber's Medium and the Chlorella Minutissma UTEX 2219, grown in Modified 3N Bold Medium at room temperature with a 16-8 light/dark cycle were studied. The algal oil was extracted using several different methods including different solvents and mechanical methods. The amount of oil collected from each strain was noted and compared to published values. The oil was then transesterfied to produce biodiesel. Properties of the oil and resulting biodiesel such as content of mono-, di- and tri-glycerides and fatty acid methyl esters composition along with others were studied.

Soybean Enhancement for Improved Biodiesel Production. B.D. Fallen, V.R. Pantalone, D.A. Kopsell, C.E. Sams, University of Tennessee, Knoxville, TN, USA

As energy prices continue to rise, concern continues to grow about the economy and about petroleum supplies. On

January 1, 2009 The Energy Independence and Security Act of 2007 will take effect. It states 500 million gallons of biomass-based biodiesel must be produced in 2009 and 1 billion gallons in 2012. In the United States 90% of the biodiesel is produced from soybean oil, despite its shortcomings. Research was conducted in 2007-2008 to evaluate six newly developed Roundup Ready® soybean recombinant inbred lines with novel oil profiles, exhibiting enhanced levels of monounsaturated fatty acid typically found in soybean oil for enhanced biodiesel oxidative stability and cold flow performance. These enhanced performances in biodiesel could ultimately impact the economy, the environment and augment energy supplies.Analysis of variance was preformed to test the effects of location, replication and their interactions on the levels of five fatty acids in the soybean seed oil of the six inbred lines and two commercial checks. The six inbred lines averaged 38.1% oleic acid, 4.7% linolenic acid and yielded 3485 kg/ha, while the two commercial checks (AG3906 and AG4103) averaged 23.8% oleic acid, 8.3% linolenic acid and yielded 3614 kg/ha.

Round Robin Comparison of ASTM Methods and Networked NIR Methods for Biodiesel Quality Testing. G. Clapper[1], B. Stefl[2], [1]AOCS, Urbana, IL, USA, [2]Cognis, Cincinnati, OH, USA

A collaborative study was organized to examine the equivalence between several primary chemistry methods, ASTM and CEN, listed in biodiesel fuel specifications, and the secondary technology, QTA, networked NIR. A total of sixteen laboratories, one from Brazil and fifteen from the United States, participated in the study, with eight laboratories reporting results for the primary chemistry, one from Brazil and seven from the US, and eight US biodiesel producers reporting results for the secondary technology, networked NIR. The test parameters included: Karl Fischer Moisture, Acid Value, Cloud Point, Total Glycerin, Free Glycerin, and Methanol Content. Analysts were advised to analyze each sample in duplicate using standard ASTM International or CEN methods for primary chemistry and the QTA system for the secondary technology. Eight bulk samples of B100 were obtained by Cognis Corporation, thoroughly mixed to ensure homogeneity and 500 mL portions were sealed in amber bottles. Bottles were labeled and packed in boxes for shipment to the laboratories. Each laboratory received ten samples, including two blind-duplicates. All 16 laboratories invited to participate in the study returned results within the allotted period for the study. The statistical analyses were performed using a Microsoft Excel software program obtained from AOAC International. Outliers were determined and removed in accordance with the AOAC Collaborative Study Guidelines (JAOAC Intl. Vol. 78, No. 5). The Collaborative Study Report for this round robin has been sent to the Rapid or Non-Destructive Technologies Subcommittee of the AOCS Uniform Methods Committee. Data were also analyzed by ASTM D 6708, Standard Practice for Statistical Assessment and Improvement of Expected Agreement Between Two Test Methods that Purport to Measure the Same Property of a Material. Initial findings from the ASTM 6708 analysis indicate equivalence for Cloud Point, Karl Fischer Moisture, and Methanol Content.

Layered Zinc Carboxylates as Catalysts for Esterification and Transesterification Reactions. L.P. Ramos, C.S. Cordeiro, F. Wypych, Department of Chemistry, Federal University of Paraná, Curitiba, PR, Brazil

Zinc laurate (ZL) was used as a heterogeneous catalyst in the esterification of lauric acid with methanol. Preliminary optimization studies, using a 23 factorial design with three replicates at the center point, indicated that 98% ester yields were achieved after 2h at 140ºC, 10:1 methanol:lauric acid molar ratio and 4% catalyst. X-ray diffraction and FTIR spectroscopy showed that the ZL retains its structure after 10 consecutive recycling stages with little loss in catalytic activity throughout the reaction cycles. In addition, the catalyst was tested in the esterification of oleic acid, stearic acid, a mixture of these with lauric acid and tall oil fatty acids. In all cases, the conversion was above 96% in a single reaction step using 6% catalyst and 10:1 methanol:fatty acid molar ratio at 140ºC for 2h. ZL also catalyzed the transesterification of refined palm oil with methanol and ethanol, giving high conversion yields and producing a raw glycerin layer containing 96% of glycerol.

Use of Animal Fat and Used Cooking Oils for Biodiesel, Electricity, and Steam Production. R. Verhe[1], V. Van Hoed[1], C. Echim[1,2], W. De Greyt[2], [1]Ghent University, Faculty of Bioscience Engineering, Department of Organic Chemistry, Ghent, Belgium, [2]Desmet-Ballestra, Zaventem, Belgium

Animal fat and used cooking oils can be used in the production of biodiesel and energy production such as electricity and steam. Animal fats are used in the production of oleochemicals and animal feed.Animal fat and used cooking oils are converted into biodiesel after a pretreatment and transesterification and a post treatment.Also the conversion of

animal fat into electricity needs a pretreatment involving an acidic degumming, adsorption and a deodorization. The technology to convert animal fat into electricity will be discussed in detail. Steam generation from animal fat is straight forward but precautions have to be taken for emissions of ash.

Genotoxic Effects of Diesel Engine Emissions from Combustion of Diesel, Biodiesel, and Biodiesel Blends. Jürgen Bünger[1], Jürgen Krahl[2], Axel Munack[3], Olaf Schröder[3], Jens Schaak[3], Katharina Schammert[4], Claudia Handrich[4], Ernst Hallier[4], Götz Westphal[1], Thomas Brüning[1], [1]BGFA - Research Institute of Occupational Medicine, German Social Accident Insurance, Ruhr-University Bochum, Bochum, Germany, [2]Coburg University of Applied Sciences, Coburg, Germany, [3]Federal Research Institute for Rural Areas, Forestry and Fisheries (vTI), Braunschweig, Germany, [4]Institute of Occupational and Social Medicine, Georg-August-University of Göttingen, Göttingen, Germany

The replacement of petrol derived fuels by fuels from renewable resources has become of worldwide interest and is scientifically investigated for its environmental costs and benefits. Several governments have defined policies to reduce GHG by blending diesel fuel with up to 20% biodiesel, among others the EU and the USA. To investigate the influence of blends on the regulated and non-regulated emissions and estimate possible health effects, we performed a series of studies with blends of common diesel fuel (DF) and rapeseed methyl esters (RME, biodiesel) measuring regulated and non-regulated exhaust compounds and determining the mutagenic effects of the particulate matter and the gas phase.The emissions of DF, RME, and several blends up to 50% RME content were investigated running the standard European cycles ESC and ETC on three different diesel engines. The particles of DEE were trapped on PTFE-coated glass fiber filters and the gaseous phase was cooled and sampled as condensate according to the VDI-Guideline 3872 part 1. Regulated emissions were measured with standard equipment. The mutagenic effects of the particle extracts and condensates were determined using the Salmonella typhimurium / mammalian microsome assay (OECD guideline 471) with tester strains TA98 and TA100.The regulated emissions of blends showed an approximate linear dependency on the blend composition and did not differ significantly from the neat fuels. However, a negative effect of blends was observed with respect to mutagenicity of the exhaust gas emissions. For the particle extracts a maximum of the mutagenic potency was found in the range of B20 exceeding the mutagenicity when pure DF or RME was combusted. This effect occurred with each of the three engines. However, these unexpected results were not consistently observed in assays with the condensates.In the view of these results, B20 must be considered as a critical blend, at least if DF and biodiesel are used as binary mixtures. It was not possible to predict the higher mutagenicity of the blends from the measurements of regulated emissions. A systematic research on not federally regulated emissions is urgently needed to elucidate the effects of fuel combustion on possible health hazards for exposed humans.

Regulated and Non-regulated Emissions from Bio-based Fuels. Jürgen Krahl[1,2], Jürgen Bünger[3], Axel Munack[2], Olaf Schröder[2], Jens Schaak[2], Lasse Schmidt[2], Yvonne Ruschel[2], [1]Coburg University of Applied Sciences, Coburg, Germany, [2]von Thünen Institute, Braunschweig, Germany, [3]University of Bochum, Bochum, Germany

The blending of 7% biodiesel to fossil diesel fuel is mandatory in Germany since 2009. A quota of hydrotreated vegetable oil (HVO) increases the biogenic amount. However, several engines (passenger cars and heavy duty trucks) run on neat vegetable oil, although most of the OEMs do not cover probable damages by warranty.In an extended set of investigations exemplified at HD engines (Euro III and IV) neat biofuels and blends were tested regarding regulated and non-regulated emissions, such as ultra-fine particles, aldehydes and polycyclic aromatic hydrocarbons. Moreover the mutagenic effects were measured by Ames-tests.The scope was not only to determine the general effects of biofuels or blends. It was the goal to vary the biogenic feedstock. Therefore neat vegetable oils as well as and biodiesels from palm oil, soybean oil, coconut oil, linseed oil and rapeseed oil were used and compared with special interest on the emissions and health effects in dependency on the chemical structure.In the result and in comparison with diesel fuel, all vegetable oils lead to dissatisfying effects on human heath. These negative effects are expressed more clearly when the engines are driven in transient modes.

AFTERNOON
IOP 2: Biolubricants
Chair(s): B.K. Sharma, USDA, ARS, NCAUR, USA; and J.M. Perez, Pennsylvania State University, USA

Reduced Need of Lubricity Additives in Soybean Oil Blends under Boundary Lubrication Conditions. S. Asadauskas[1], T. McClure[2], G. Biresaw[3], [1]Institute of Chemistry, Vilnius, Lithuania, [2]TribSys LLC, Valparaiso, IN, USA, [3]ARS, USDA, Peoria, IL, USA

Vegetable oil lubricants often rely on traditional lubricity additives, designed for mineral oils. In this study boundary lubrication properties of four Extreme Pressure (EP) additive blends in conventional Soy Bean Oil (SBO) and Paraffinic Mineral Oil (PMO) of similar viscosity were screened using Four Ball EP tester (4-ball EP) and Twist Compression Tester (TCT) on steel surfaces. Chlorinated hydrocarbon waxes (CLHW), Zinc di-ethylhexyl dithio phosphate (ZDDP), di t-dodecyl pentasulfide (DTPS) and polymerized saturated fatty esters (PSFE) were evaluated at 3 to 20% concentrations in the two oils, inhibited with antioxidant. Weld points in 4-ball EP and Coefficient of Friction in TCT at 200 MPa or 8 MPa showed that much lower CLHW, ZDDP and DTPS treat levels are needed in SBO to achieve the same performance as PMO blends. PFSE was effective in PMO, but not in SBO. Adding 20% SBO to PMO blends made their boundary lubrication properties similar to those of SBO based blends. CLHW and ZDDP at 5% in SBO produced similar wear as their 20% blends in PMO. Commercial straight oil chlorinated metal forming lubricant showed performance, comparable to that of the best SBO blends. Addition of SBO can greatly reduce the additive treat levels and costs when formulating industrial oils and other lubricants.

Renewably Sourced High Oleic Soybean Oil. S. Knowlton, DuPont Co., Wilmington, DE, USA

Interest in bio-based lubricants and industrial fluids is growing as the need to address environmental concerns, political instability and support for renewable resources becomes critical. Vegetable oils alone, as well as formulated with petroleum based or synthetic materials, offer a range of performance criteria which meet these growing needs. Vegetable oils exhibit a number of functional advantages over petroleum-derived base stocks including high viscosity index and excellent lubricity. However, most vegetable oils are limited by application as a result of oxidative breakdown when used in high temperature applications under oxidative stress. High Oleic Soybean Oil is a new, renewable, domestically-sourced, bio-based oil which has unique potential to provide the functionality needed to meet these requirements. It contains about 80% oleic acid, has about 20% less saturated fat, and is in excess of five fold greater stability compared with commodity soy oil. The oil will find uses in a wide variety of industrial applications based on its stability and as a relatively pure source of oleic acid for oleochemical reactions. Activities and timelines associated with a limited commercial launch of high oleic soybeans will be discussed.

Pennsylvania Grown Canola Oil as a Fuel and a Lubricant Basestock. M.C. Frier, J.M. Perez, The Pennsylvania State University, University Park, PA, USA

Biodiesel production is increasing in Penna., as is the industry demand for vegetable oil feedstock. Canola is an alternative source for making biodiesel with double the oil content of Soybean. Canola oil also has the potential to be a high quality basestock for lubricants. To assess the feasibility as a spring crop in Pennsylvania, some 12 varieties of Canola were tested at small grain areas in three counties, essentially in north, central and southern regions of the state in 2007. The different varieties were evaluated on the basis of their growing conditions and performance. Oil seed yield in the study averaged 1943 kg/ha, similar to those in North Dakota. Some compositional differences, oil yields and quality differences are reported. Mechanically pressed varieties grown in the three growing regions can meet the industry specifications for crude, non-degummed oils. The best oils, in terms of FFA content were those pressed from mature oilseed and grown under the most favorable conditions. Viscosity was typical of canola. Oxidation stability tests conducted using a thin-film oxidation test determined the potential of the different varieties of oil as lubricant basestock. Low and high FFA oils compared with and without additives indicate improved oxidation stability over previous studies with soybean oils.

Lubricant Polyol Derivatives from Epoxidized Vegetable Oils. A. Campanella[1,2], E. Rustoy[3], A. Baldessari[3], M.A. Baltanás[1], [1]Instituto de Desarrollo Tecnológico para la Industria Química, Santa Fe, SF, Argentina, [2]University of Delaware, Newark, DE, USA, [3]Departamento de Química Orgánica y UMYMFOR, Facultad de Ciencias Exactas y Naturales (UBA), Piso 3, Pabellón II, Ciudad Universitaria, C1428EGA, Ciudad Autónoma de Buenos Aires, Argentina

This work reports laboratory results obtained from the production of polyols from epoxidized vegetable oils pertaining to annual, temperate climate crops (soybean, sunflower and high-oleic sunflower oils), focusing on their possible use as components of lubricant base stocks. To this end, two different opening reactions of the epoxide ring were studied. The first one, caused by the attack with glacial acetic acid, (exclusively in a single organic phase,) and the second one using short-chain aliphatic alcohols, methanol and ethanol, in acid media. Both reactions proceed under mild conditions: low synthesis temperature and short reaction times and with conversions above 99%. Spectroscopic (NMR), thermal (DSC) and rheological techniques were used to characterize the oils, their epoxides and polyols, to assess the impact of the nature of the vegetable oil and the chemical modifications introduced, including long-term storage conditions.

Optimized Oil Seed Profiles for Industrial Applications. Jack Grushcow, Linnaeus Plant Sciences Inc., Vancouver BC Canada

Jack Grushcow is the president of Linnaeus Plant Sciences Inc. Linnaeus is actively engineering oil seed profiles designed to replace petroleum for applications such as the manufacture of lubricants and plastics. He will review recent advances in structured TAG designed for base oil formulations as well as discuss a unique bio-refining method which can be used to concentrate valuable methyl esters.

Lubrication Properties of Fatty Acid Derivatives from Oleate and Ricinoleate Esters. Linxing Yao, Earl G. Hammond, Tong Wang, Satyam Bhuyan, Sriram Sundararajan, David Vaknin, Wei Bu, Iowa State University, Ames, IA, USA

Ester of ricinoleate, 12-acylated ricinoleate, and 2,3-butanediol esters were tested for friction and wear in a microtribometer using 10% of the ester in a petroleum-based oil. The petroleum-based oil was used as a control. Friction was determined by resistance to motion. Wear was estimated from the depth of the grove worn in the tribometer plate. Most of the esters showed similar resistance to friction, which was comparable to control. Several of the esters showed significantly lower wear than control. 2,3-Butanediol monoricinoleate exhibited higher wear than 2,3-butanediol monooleate. These esters showed promise for improving the lubricity by reducing wear and energy requirements. To gain insight into the behavior of the esters on polar metal surfaces they were spread as a monomolecular film on water, and their pressure-area isotherms were obtained. The observed molecular area increased with the length of the normal ester and the presence of acyl side chains on methyl ricinoleate. The surface pressure required for dense packing increased for saturated methyl esters compared with unsaturated methyl esters and for compounds having a very polar end group.

BIO 2 / IOP 2.1: Biodiesel
Chair(s): H.C. Holm, Novozymes AS, Denmark; and B. Cooke, Dallas Group, USA

Continual Production of Biodiesel Fuel from Various Oils by Solvent-free Enzymatic System. Yomi Watanabe, Toshihiro Nagao, Yuji Shimada, Osaka Municipal Technical Research Institute, Osaka, Japan

The solvent-free BDF production system using immobilized *Candida antarctica* lipase has been developed. It has the following advantages; 1) high conversion (>95%) can be reached at 30 ^{o} C, 2) the amount of methanol is the smallest among other methods including chemical and supercritical liquid methods, 3) the production cost can be reduced to be competitive to the chemical methods by continuously using the immobilized lipase for over than 3 months, 4) it is free from waste water containing alkali or salts, 5) organic solvent free, and thus 6) pre and post processing can be minimized, 7) glycerol can easily be reused.By stepwise addition of methanol, vegetable oil (from soy bean, rapeseed, and corn), crude oil, used frying oil were converted to >95% FAMEs without any pretreatments. Palm oil was also converted to BDF continually at high degree of conversion. In order to convert materials containing large amount of FFA in addition to acylglycerols, such as acid oil, to FAME, two step conversion system is effective; the first step is the esterification of FFA to FAME and the second step is the transesterification of acylglycerols to FAME. These systems were successfully scaled up to 30 L, and thus were considered to be applicable for industrial production of BDF from various oils.

Present Situation of Biodiesel Research and Development in Brazil. L.P. Ramos, Department of Chemistry, Federal University of Paraná, Curitiba, PR, Brazil

Biodiesel research and development in Brazil has gone a long way ever since the National Program was launched in January 2005. The annual production rose from virtually nothing in the late 90â??s to nearly 500 million liters in January 2008 as a result of a B2 mandate, which was raised to B3 in July 2008 and shall be further increased to B5 in January 2013, according to the current program timeline. These measures represent a biodiesel annual demand of 1.2 billion liters for B3 and more than 2 billion liters for B5 in 2013. To supply the biodiesel required for the B3 mandate, 51 plants of different sizes were built, which corresponded to an annual production capacity of 2.670 MTPY. Hence, it is clear that most of these plants were not in full operation and this was so because lipid sources were either too expensive or scarcely available at this time. Besides, 27 plants were under construction or being commissioned and another 25 plants were on project development stages, coming up to a potential biodiesel annual production capacity of 5.294 MTPY for 2008-2009. Based on these numbers, there are rumors that the Government intends to anticipate the B5 mandate to 2010 but this will depend on the current trends in the international oil market, as well as uncertainties in the raw material supply for the upcoming years.Support: FINEP, MCT, CNPq, FundaÃ§Ã£o AraucÃ¡ria

Enzymatic Production of Biodiesels: A Kinetic Study. Xuebing Xu, Aarhus University, Aarhus C, Denmark

Using enzyme for the biodiesel processing instead of chemical catalysts has raised high interest recently. There are a few heated concerns. One of them is the possibility to use non-edible oils, where they is unlikely easy for chemical catalysts. Using enzymes as catalysts, the reaction has to be conducted in low temperatures such as below 70 °C. Therefore, the reaction system can be complicated with multiple phases and glycerol inhibitions. In this talk, we will present the work focusing on kinetic study. The work will illustrate how the kinetics are related to the overall performance in model reaction systems.

Integrated Production for Biodiesel and PDO with Lipase-catalyzed Transesterification and Fermentation. Dehua Liu, Wei Du, Yan Sun, Department of Chemical Engineering, Tsinghua University, Beijing, China

Lipase-catalyzed transesterification from renewable oils for biodiesel production has some advantages over chemical-catalyzed approaches, such as environmental friendship, lower energy consumption. However, the low stability and the high cost of the lipase had been being regarded as the main hurdle to the industrialization of lipase-catalyzed biodiesel production. Tsinghua University has proposed a novel process, with which the operational life of the immobilized lipase could be improved over 50-fold than traditional enzymatic approaches. After the successful demonstration in a pilot plant with capacity of 200kg/d biodiesel, the first commercial facilities with capacity of 24,000ton/year was constructed in Hunan, China and it was put into operation on Dec. 8, 2006. More and more customers from Germany, Singapore, Korea, Thailand etc, are negotiating for technology license. As a by-product, glycerol will be yielded at about 10% of biodiesel during the process of biodiesel production. How to convert glycerol has become a common problem. It could be a promising way to produce 1,3-propanediol (PDO) from glycerol. PDO is a valuable chemical material and especially it could be copolymerizes with terephthalic acid (or methyl ester) to form polytrimethylene terephthalate (PTT). PTT has excellent properties compared to other polymers such as PET. Tsinghua University has proposed a novel flexible process for PDO production from glycerol or glucose, and the demonstration was finished in pilot plant at the end of 2003. A facility with capacity of 4,000 tons/year1,3-PDO is being run in Hunan Rivers Bioengineering company, China.

Environmental Sustainability Analysis of Biodiesel Production - A Comparative Analysis of Different Production Schemes. I.T. Herrmann, M. Hauschild, Technical University of Denmark, Lyngby, Denmark

Due to their generally positive carbon dioxide balance, biofuels are seen as one of the energy carriers in a more sustainable future transportation energy system, but how good is their environmental sustainability, and where lie the main potentials for improvement of their sustainability? Questions like these require a life cycle perspective on the biofuel - from the cradle (production of the agricultural feedstock) to the grave (use as fuel). An environmental life cycle assessment is performed on biodiesel to compare different production schemes including chemical and enzymatic esterification with the use of methanol or ethanol. The life cycle assessment includes all processes needed for the

production, distribution and use of the biodiesel (the product system), and it includes all relevant environmental impacts from the product system, ranging from global impacts like climate change and loss of non-renewable resources over regional impacts like acidification, eutrophication and photochemical ozone to more local impacts like ecotoxicity and physical impacts like land use, to allow judging on the overall environmental sustainability of the biodiesel and to support identification of the main focus points for improvement of the environmental sustainability

Renewable Petroleum™ Products and Technologies: Production of UltraClean™ Diesel via Fermentation. Wei Huang, LS9, Inc., South San Francisco, CA, USA

The urgent need for renewable alternatives to petroleum has fueled global efforts to commercialize technologies for the conversion of abundant renewable biomass to liquid transportation fuels. In addition to chemical and thermochemical conversion approaches, biocatalytic conversion technologies are being aggressively developed. At LS9, we apply the basic principles of synthetic biology to engineer microbes to efficiently convert renewable carbohydrates directly to diesel and other petroleum derived products. The speaker will discuss the use fatty acid biosynthetic pathway as route to variety of products such as biodiesel. This talk will focus on fermentation and downstream process development and optimization, fuel performance, the underlying economics, GREET analysis, a contrast with alternative routes and technologies.

TUESDAY

AFTERNOON
IOP 3: Oleochemistry
Chair(s): J. Metzger, University of Oldenburg, Germany; and D. Pioch, CIRAD AMIS, France

One Hundred Years of Oleochemistry: 45 Years Done, 55 More to Go. Marcel Lie Ken Jie, University of Hong Kong, Hong Kong

A review of oleochemical work accomplished over the past 45 years with highlights on the synthesis and analysis of unusual fatty acids, exotic fatty acid derivatives and analogues. A look at today's oleochemistry for the purpose of a sustainable development and for renewable raw materials, and a display of bold, imaginative and daring approaches to tomorrow's lipid science through chemical imagineering - 'the next 55 years'.

Metathesis with Oleochemicals: New Approaches for the Synthesis of Monomers and Polymers from Renewable Resources. M.A.R. Meier, University of Applied Sciences OOW, Emden, Germany

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 renewable resources in a straightforward fashion taking full advantage of nature's synthetic potential. Here, new approaches for the synthesis of monomers as well as polymers from plant oils as renewable resources via olefin metathesis will be discussed.As an example, we recently showed that different chain length α-ω-difunctional monomers can be obtained from plant oil derived fatty acid esters via olefin cross-metathesis with methyl acrylate, allyl chloride, and others, taking advantage of natures "synthetic pool" of fatty acids with different chain lengths and positions of double bonds. This strategy offers the possibility to introduce a variety of different functional groups to the ω-position of fatty acid derivatives, thus providing valuable starting materials for a variety of polyesters and polyamides. Moreover, acyclic diene metathesis (ADMET), can be used to directly obtain macromolecules from such starting materials. Examples of renewable polyesters and polyamides using this approach will be discussed in detail within this contribution.

Acyclic Triene Metathesis Polymerization of Oleochemicals: Defined Materials for Coating Applications. U. Biermann[1], M.A.R. Meier[2], J.O. Metzger[1], [1]University of Oldenburg, Oldenburg, Germany, [2]University of Applied Sciences Oldenburg/Ostfriesland/Wilhelmshaven, Emden, Germany

The synthesis of branched macromolecules from renewable raw materials via olefin metathesis should be of

importance because the resulting polymers are expected to show interesting properties e.g. as base materials for coatings. The acyclic diene metathesis (ADMET) polymerization is known to be a versatile technique for the preparation of linear polymers, polymers with a defined degree of branchings, telechelics as well as block-copolymers. Recently, the acyclic triene metathesis (ATMET) polymerization using glyceryl triundec-10-enoate as starting material has been described. In a simple one pot one step procedure using different ratios of the triglyceride and methyl acrylate as chain stopper branched macromolecules of different molecular weights were obtained.1 In all cases mixtures of products were formed containing a lower or higher amount of terminal and/or internal unsaturated functionality depending on the ratio of methyl acrylate and triglyceride, reaction time, and temperature. We have been separating the product mixtures by column chromatography and the products were clearly identified and characterized by 1H, 13C NMR and MS. First experiments showed that the branched polymers can be used in coating applications.1 P. A. Fokou, M. A. R. Meier, Macromol. Rapid Commun. 2008, 29, DOI: 10.1002/marc.200800365.

Potential Biodegradable Lubricant Materials: Saturated Branched-chain Fatty Acid Isomers. T.A. Foglia[1], H.L. Ngo[1], R.O. Dunn[2], B. Sharma[2], W. Yee[1], A. McAloon[1], E. Hoh[1], M.J. Haas[1], [1]USDA, ARS, ERRC, Wyndmoor, PA, USA, [2]USDA, ARS, NCAUR, Peoria, IL, 61604, USA

Sbc-FAs have the potential for being important materials for the production of biodegradable lubricants, emollients and hydraulic fluids. Although there have been previous studies on the isomerization of monounsaturated fatty acids using clay- and zeolite-catalysts, these reactions suffered from low conversions, low selectivity and high amounts of undesired byproducts (10-50%). We recently found that modified Ferrierite zeolites isomerized the unsaturated fatty acids to sbc-FAs at high conversions and selectivity (with only 5-9 wt.% undesired byproducts). Sbc-FAs were characterized by GCXGC-TOF-MS. The physical properties of sbc-FAs as determined by low temperature studies, viscosity-index measurement, oxidative-stability determination, high frequency reciprocating rig test and four ball wear test showed that sbc-FAs are good lubricant candidates for several applications. In particular, the lubricity tests indicate that the synthesized materials are superior to mineral oil (a common petroleum-based material) in several tests. To evaluate the potential of this process for large scale production, we also developed a process model to estimate production costs for preparing sbc-FAs. Based on the analysis model, the process was found to be cost-effective indicating that it can potentially be developed for the large-scale production of useful sbc-FAs.

Investigation, Production and Uses of Novel Hydroxylated Fatty Acids. F.H.M. Graichen, S. Kyi, G. Peeters, M.S. O'Shea, Commonwealth Scientific and Industrial Research Organization (CSIRO), Division of Molecular and Health Technologies, Melbourne, Victoria, Australia

There is significant global momentum around the (re)emergence of bio-derived feedstock for the chemicals and polymer industries. However, current industrial fatty acid options are limited (in broad terms) to palm, soybean, canola and castor sources. While there are many niche oils naturally produced, these are normally unsuitable due to reliability of supply, cost or both. CSIRO′s research in the area of industrial oils is aimed at the production, evaluation and modification of novel oil and fatty acids for a range of industrial applications including: chemical intermediates, oligomers, cross-linkable polymers and bioactive compounds.CSIRO believes that there are significant opportunities in the production of novel hydroxylated oils and fatty acids with novel hydroxy-group positions. We have investigated the production of hydroxylated fatty acids of a range of structures and their utility in the chemicals and polymers industries.For example, alpha-hydroxy fatty acids have a range of interesting properties. Uses for these novel fatty acids include: monomer for use on commodity polymer, modifiers for polyurethanes, polyesters and polyamides, adhesives through to materials to produce optoelectronic devices. This paper will cover synthesis methods for hydroxy fatty acids as well as their applications.

Soy-based Polyols from Oxirane-ring Opening by Alcoholysis Reaction. Zuleica Lozada-Rodriguez, Galen J. Suppes, Fu-Hung Hsieh, Yuan-Chan Tu, Arnold A. Lubguban, University of Missouri-Columbia, Columbia, Missouri, USA

A screening study was conducted to identify a catalyst that promotes epoxy-ring opening of full epoxidized soybean oil (ESBO) avoiding side-reactions at low concentration and temperature. Six catalysts different catalyst: formic acid, phosphoric acid, POLYCAT®5, p-toluenesulfonic acid monohydrate, POLYCAT®SA-1 and DABCO®BL17 were

evaluated in terms of acid number, oxirane oxygen content and color analyses. p-Toluenesulfonic acid shows a particular behavior that promotes the reaction resulting in a maximum oxirane oxygen content reduction; low acid number and color index compare to the others catalyst. To create an alkoxyl hydroxyl ESBO molecule, ESBO was combined with methanol and ethylene glycol using 0.5 % by wt. of p-toluenesulfonic acid at 130, 150 and 170°C for different reaction times. Optimal conditions for oxirane-ring opening by alcoholysis reaction were determined varying temperatures and reaction times. FT-IR spectrum confirmed the emergence of hydroxyl groups in the alkoxyl hydroxyl ESBO polyol sample. The polyol sample G was characterized in terms of its hydroxyl number and its potential of replacing up from 50 to 100% of the petroleum-based polyol in waterborne rigid polyurethane foam applications was evaluated and their thermal conductivity, density, and compressive strength were determined.

New Process for Polymerization of Vegetable Oils. Mihail Ionescu , Zoran S. Petrovic, Pittsburg State University, Kansas Polymer Research Center, Pittsburg, KS USA

It is well known that natural unsaturated vegetable oils were polymerized by oxidative processes (air blown oils), thermal polymerization processes (heat bodied oils) and cationic polymerization catalyzed by BF_{32} or BF_3*Et_2O. We eveloped a new high efficiency proprietary catalyst for the polymerization of unsaturated vegetable oils (soybean oil, corn oil, sunflower oil, canola oil, linseed oil, tung oil etc.) in very high yield, in mild reaction conditions: at 80-100°C and atmospheric pressure. The polymerization process with our catalyst is carried out in bulk and without degradation associated with oxidative and thermal polymerization processes. By polymerization of soybean oil it is possible to obtain highly viscous polymeric oils, soluble solids and crosslinked polymers. The liquid polymers obtained by polymerization of soybean oil have a relatively high iodine value of around 105-110 gI_2/100g (the initial iodine value was 129gI_2/100g). The presence of a high content of high molecular weights oligomers (75-80%) and a broad molecular weight distribution (Mw/Mn=11-12) is observed in the polymeric oil. Polymerized soybean oils, due to the high content in remaining polymerizable double bonds, have potential applications in the area of inks, paints, varnishes or for the chemical transformation to new products by epoxidation, hydroxylation, amidation and transesterification.

Polymers and Composites from Agricultural Oils. M.R. Kessler[1], R. Larock[2], Y. Lu[2], [1]Department of Materials Science and Engineering, Iowa State University, Ames, IA, USA, [2]Department of Chemistry, Iowa State University, Ames, IA, USA

Renewable, bio-based thermosetting copolymer resins, ranging from tough and ductile rubbers to hard and glassy plastics to durable waterborne latex coatings, have been prepared by the polymerization of soybean, corn and linseed oils with various co-monomers. The development of these resin formulations with the right combination of processing viscosity, cure kinetics, and ultimate thermal mechanical properties for various manufacturing processes will be discussed. As expected, the thermal and mechanical properties, as well as the long term environmental durability of the material, are shown to be highly dependent on vegetable-oil composition, processing conditions, and co-monomer chemistry. In addition, the presentation will discuss how these new bioplastic composites are likely to have a tremendous impact economically, environmentally and energy-wise, since the oils are (1) readily available in huge quantities from a renewable natural resource, (2) much cheaper than petroleum-based resins used in many polymers and composites, (3) likely to produce new plastics that more readily biodegrade in landfills than present indestructible, petroleum-based plastics, and (4) able to provide properties not presently available in commercial plastics.

IOP 3.1 / PRO 3: Alternative Feedstocks for Biofuels
Chair(s): B. Moser, USDA, ARS, NCAUR, USA; and N. Dunford, Oklahoma State University, USA

Biodiesel Prepared from Field Pennycress (*Thlaspi arvense* L.) Oil. B.R. Moser, G. Knothe, S.F. Vaughn, T.A. Isbell, USDA, ARS, NCAUR, Peoria, IL, USA

Field pennycress (*Thlaspi arvense* L., FP) is a winter annual species of the mustard family (Brassicaceae) which is widely distributed throughout temperate North America that can serve as a winter rotational crop for conventional crops, thus not displacing farm land or negatively impacting the food supply. FP seed contains 36% oil by weight, which is high in erucic acid, with linoleic, linolenic, oleic, and gondoic acids also present in significant quantities.

Biodiesel prepared from FPO (FPME and FPEE) displays excellent cold flow properties, relatively poor oxidative stability, and relatively high kinematic viscosity versus soybean oil methyl and ethyl esters (SME and SEE). Comparison to ASTM D6751 reveals that FPME and FPEE are satisfactory with respect to all parameters measured here. Viscosity, methyl linolenate content, and oxidative stability do not meet the stated requirements in EN 14214, but blending or treatment with antioxidants are likely to ameliorate these deficiencies. Blends of FPME and FPEE in petrodiesel compared favorably to an analogous set of SME and SEE blends and were satisfactory after comparison to ASTM D975 and ASTM D7467. In conclusion, FPO has excellent potential as an alternative biodiesel feedstock.

Potential of Jatropha and Syringa Oils as Biodiesel Feedstocks as Compared to Canola Oil. N. Dunford[1], A. Su[1], J. Morris[2], [1]Oklahoma State University, Stillwater, OK, USA, [2]Syringa Institute, Centurion, South Africa

Soybean oil has been the preferred feedstock for biodiesel production in USA because of its availability and lower cost. However many European countries limit the use of biodiesel made from highly unsaturated oils because of its lower oxidative stability. Canola oil is known for its higher stability and has a relatively low cloud point. Hence, it is a good feedstock for biodiesel production. The higher oil content of seeds (about 40%, w/w) also makes canola more attractive than soybean (about 20%, w/w oil content) as biofuel feedstock.
Wheat, corn and sorghum have been typical crops grown in the southern Great Plains for many decades. The introduction of winter canola provides a tremendous opportunity as a rotation crop to control weed, insect and disease problems caused by continuous wheat planting. Winter canola is also a good crop as feedstock for biofuel industry. There is great interest in growing canola among farmers in the Great Plains. It is estimated that canola acreages will continue to increase. Currently there are several initiatives involving canola production, oilseed processing and biodiesel production in the region. On-farm or small capacity canola seed crushing and biodiesel production is also expanding in the Great Plains.
Recent price increases in food products including edible oils such as canola and soybean oil has been one of the driving forces for an intensified search for nonfood biofuel feedstocks. Jatropha *Curcas* has a number of agronomic characteristics which make it a good dedicated biofuel feedstock. Jatropha can grow in arid, semiarid and wasteland, requires minimal water and fertilizer and can survive on marginal soils. The oil content of the Jatropha seeds is also high, about 40%.
Syringa tree (*Melia azedarach* L.), also known as Indian or Persian lilac, is an invasive plant in South Africa. The mission of Syringa Bioscience (Pty) Ltd based in South Africa has been finding ways to utilize syringa trees for value-added product development. Since syringa berries contain significant amount of triacylglycerides, conversion of syringa berry oil to biodiesel has been explored.
In this study chemical and physical characteristics of canola, jatropha and syringa berry oil were determined. Oil samples were converted to biodiesel by using the traditional transesterification method. Sodium methoxide in methanol was used as catalyst. Material balances for conversion of oils to biodiesel were calculated. Viscosity, flash point, storage stability, cloud point, free and total glycerol content, differential scanning calorimeter cooling curves, mineral content and calorific value of biodiesel samples were measured. The quality of biodiesel made from jatropha and syringa oil was compared to that of biodiesel from canola oil.

Cuphea Oil as a Potential Source of Biodiesel with Improved Properties. G. Knothe, S. Cermak, R. Evangelista, USDA, ARS, NCAUR, USA

Biodiesel is usually produced from common vegetable oils such as soybean, rapeseed (canola), and palm as well as other feedstocks such as animal fats and used cooking oils. To enhance feedstock supply, other vegetable oils such as jatropha are of increasing interest. However, most of these feedstocks provide fatty acid profiles varying within the range of C16 and C18 fatty acids. To improve fuel properties such as cold flow and oxidative stability, either additives must be used and/or the fatty ester profile modified. The latter approach entails either changing the composition of biodiesel derived from "conventional" feedstocks or utilizing feedstocks with inherently different fatty acid profiles. In this work, a feedstock with a less common fatty acid profile, a variety of cuphea oil (PSR 23; a cross of *Cuphea viscosissima* x *C. lanceolata*) containing about 65% decanoic acid in its fatty acid profile was studied as biodiesel feedstock. Fuel properties such as cetane number, viscosity, oxidative stability and cold flow were investigated. Especially cold flow appears advantageous with the cloud point of cuphea methyl esters determined around -9 to -10°C. Cuphea, although facing technical issues regarding its wide-scale commercialization, is therefore of interest as

biodiesel feedstock and may serve as model for other oils with similar fatty acid profiles.

Preparation of Jojoba Oil Ester Derivatives for Biodiesel Evaluation. Shailesh N. Shah[1], Brajendra K. Sharma[1,2], Bryan R. Moser[1], Sevim Z. Erhan[1], [1]Food and Industrial Oil Research, National Center for Agricultural Utilization Research, Agricultural Research Service, U. S. Department of Agriculture, 1815 N. University St., Peoria, IL 61604, USA, [2]Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA

The jojoba plant (*Simmondsia chinensis* L.) produces seeds that contain around 50 to 60 weight percent of inedible long-chain wax esters that are suitable as a potential feedstock for biodiesel production. Jojoba oil methyl esters (JME) were prepared in an effort to evaluate important fuel properties of jojoba-based biodiesel, such as kinematic viscosity, cloud point, pour point, cold filter plugging point, acid value, oxidative stability, and lubricity. A comparison was made with soybean oil methyl esters (SME) and relevant biodiesel fuel standards such as ASTM D6751 and EN 14214. JME was characterized using FTIR and 1H and 13C NMR. JME displayed superior low temperature properties and inferior kinematic viscosity versus SME. Blends (B5 and B20) of JME in ultra low sulfur diesel fuel (ULSD) were also evaluated for the aforementioned fuel properties and compared to an analogous set of blends of SME in ULSD and relevant petrodiesel fuel standards such as ASTM D975 and D7467. JME blends in ULSD displayed improved low temperature properties in comparison to neat ULSD and blends of SME in ULSD. In summary, jojoba oil has potential as an alternative, non-food feedstock for biodiesel production.

Review of Pretreatment Procedures for Animal Fats as Feedstock for Biodiesel Production. James Willits, Desmet Ballestra North America, Marietta, GA, USA

In todays economic market, it is critical to be able to utilize the most cost effective feedstock for a biodiesel production plant. In almost all cases animal fats require pre-treatment before entering the biodiesel process. This presentation will cover a range of animal fats with discussion of their quality ranges and the corresponding process systems required to deal those that will adversly effect the finished biodiesel quality.

Agro-Industrial Residues as Low-Price Feedstock for Diesel-like Fuel Production by Thermal Cracking. A.L. Santos, D.U. Martins, O.K. Iha, R.A.M. Ribeiro, R.L. Quirino, J.C. Rubim, P.A.Z. Suarez, LMC-IQ-UnB, Brasilia, DF, Brazil

Pyrolysis of industrial fatty wastes (soybean soapstock, beef tallow, poultry industry waste) was carried out in absence of catalysts. In all cases, an organic mixture of hydrocarbons and oxygenated compounds was obtained. These mixtures were distillated and diesel like fractions were isolated and characterized by GC-FID, GC-MS and FTIR, showing the formation of olefins, paraffins, and some oxygenated compounds such as carboxylic acids and esters. The main physical-chemical properties of those isolated diesel-like fuels (density, viscosity, distillation curve, carbon residue, copper corrosion test, cetane index, cold finger plugging point, acid index and heating value) where determined using ASTM standard methods and matched Brazilian specification for diesel fuel.CNPq, FINEP, MCT, MDA, FBB, FINATEC, CAPES

Alternative Crops for Biodiesel Production in Brazil: Potential in Semi-Arid Regions. S.M.P. Meneghetti, UFAL, Maceió, Alagoas, Brazil

Since the biodiesel program has been started in Brazil, the investigation of alternative sources of triacylglycerides from species adapted at semi-arid lands became a very important task for Brazilian researchers. Thus, we initiated studies with various alternative crops with the aim to evaluated some properties and chemical composition of the oil, as well any potential application in biodiesel production.

Safflower as an Alternative Feedstock for Biodiesel Production in Turkey. Asli Isler, Filiz Karaosmanoglu, Istanbul Technical University, Maslak, Istanbul, Turkey

Biofuels are one of the biobased industrial products of the biorefinery technology. Production and use of biofuels have a lot of advantages on local, state and national levels. Biofuels are classified into four classes as first, second, third and

fourth generation biofuels. Biodiesel as one of the most common first generation biofuels uses as feedstock vegetable oils, animal fats and wastes. In the aspect of higher production costs and biofuel versus food-feed new oil seed resources are gaining importance, today. Although Turkey has appropriate lands for oil seeds plant production, production does not meet the consumption and oil seeds and vegetable oils are imported in large quantities.So production of oil seeds must be supported along well with the agriculture policies and appropriate energy agriculture plans. Safflower, which can be used for the production of biodiesel as a feedstock is one of the perfect candidates for Turkey. Since 1980′s use of new seeds was one of the research subjects in Turkey. In this study, safflower is introduced with its history, properties and use in the world and in Turkey, safflower-biodiesel relationship is investigated according to the real data from 2007-2008 harvest season safflower agriculture in Turkey and safflower is presented as an alternative feedstock candidate for biodiesel production.

Low Cost Photobioreactors for Algal Biofuel Production and Carbon Capture. J. Butler, Solix Biofuels, Inc., Fort Collins, Colorado, USA

Photobioreactors facilitate the cultivation of specific strains of algae and allow optimal growth conditions to be maintained. To date, however, the high capital and operating costs of photobioreactors have prohibited their use for "low-valued" products such as biofuels. Recent efforts at Solix Biofuels have focused on the development of photobioreactor technology with high productivity, low capital cost, low operating cost, and low energy utilization. Efforts are now being expanded to develop the downstream production processes necessary to process the algae biomass into fuel and commercially viable co-products. The Solix system is applicable to a wide range of algae species. This presentation will provide details on the Solix photobioreactor technology, control and operational strategy, and downstream processes. Current and projected performance metrics are presented for the system operating with the eustigmatophyte *Nannochloropsis oculata*.

WEDNESDAY

MORNING
IOP 4: Green Chemistry
Chair(s): D. Sparks, Mississippi State University, USA; and T. Benson, Mississippi State University, USA

Integration of Sub- and Supercritical Fluids for the "Green" Processing of Biorenewable Products. J.W. King, University of Arkansas, Department of Chemical Engineering, Fayetteville, AR 72701, USA

Extraction and reaction chemistries performed in critical fluids have been largely dominated by the use of supercritical carbon dioxide (SCCO2), particularly in the field of lipids and fats/oils. The use of mixed fluids either in tandem unit operations, sequentially using SFE and consecutive reactions, and as mixed sub- and super-critical fluid media offer an expansion of the pressurized fluid processing platform. This presentation will describe research on the use of SCCO2 coupled with hot pressurized water, i.e., subcritical water (sub-H2O) to affect extraction-fractionation-reaction chemistry for producing industrially useful oil-based products for fuel, food, and chemical use. Treatment of mixed biomass substrates consisting of lipid-carbohydrate-protein with sub-H20 provides an array of products ranging from industrially useful hydrolyzates, monomers, and fuels, depending on the severity and time of the extraction-reaction conditions. The enhancement of extraction and reaction chemistry by dissolving SCCO2 in pressurized water will be demonstrated via its effect on extraction selectivity as well as an alternative ?green? catalytic medium for use in bioethanol and biodiesel production. Justification, choice, and optimization for using such mixed media will be characterized by using the Hansen 3- dimensional solubility parameter theory and solvation spheres. Our predictive methods coupled with recent extraction and reaction data from our laboratory will illustrate the possibilities offered for ?green? processing of biorenewable substrates using SCCO2, sub-H2O, and subcritical alcohols (methanol and ethanol) as neat salvation media and gas-expanded solvents.

Fatty Acid Ethyl Esters (FAEE) - The "Green-Green" Biofuel of the Future?. P.M. Nielsen, H.C. Holm, J. Brask, M.L. Damstrup, Novozymes, Bagsvaerd, Denmark

Substituting methanol with bioethanol in production of biodiesel will allow for a totally renewable "green-green" fuel with a very low carbon footprint. Fatty acid ethyl ester (FAEE) has similar fuel properties compared to FAME, including somewhat improved low-temperature properties. Our research indicates that enzymatic synthesis of FAEE can be based on 96% ethanol, which is less expensive to obtain and recycle compared to absolute ethanol, which is required for traditional alkaline catalyzed processes. Further, the higher molecular weight of ethanol results in a higher mass yield of FAEE, which more than balances an added cost of ethanol compared to methanol. Hence, in this paper we argue that enzymatically produced FAEE could be the future's sustainable biodiesel.

Imidazolium-based Ionic Liquids for the Separation and Extraction of Unsaturated Fatty Acid Methyl Esters and Related Components. P.J. Pham, M. Li, C.U. Pittman Jr., T. Li, Department of Chemistry Mississippi State University, Mississippi State, MS 30759, USA

Room temperature ionic liquids (RTILs) have recently been used as an alternative for traditional organic solvents. The advantages of RTILs over organic solvents include negligible vapor pressures and their unique adjustable properties that make them useful for a multitude of chemical processes. In addition, they have also been used as solvents for the extraction of a variety of substances. Thus, we explored RTILs as a possible extraction medium. Different immidazolium-based RTIL?s were synthesized,explored in our research group. An initial attempt on the separation of fatty acid methyl esters with varying degrees of unsaturation was done using liquid/liquid biphasic separation. However, emulsion formation has prompted the search for other extraction alternatives. Solid phase extractions using silica gel and mesoporous silica (SBA-15) functionalized with imidazolium-based ionic liquid precursors[1] and complexed with silver salts were employed for the separation of a variety of fat and oil unsaturated components. These include vitamin E (tocopherol)[2] , fatty acid methyl esters (FAME)[3] , triacylglycerols (TAG) and free fatty acids (FFA)[4] . Separations involving natural systems (i.e. fish, vegetable oils and soy-based biodiesel) were also carried out.

Lipid Accumulation in Municipal Sewage Sludge Microorganisms Growing On a Synthetic Wastewater Medium with Glucose as the Carbon Source. A. Mondala, R. Hernandez, T. French, E. Alley, L. McFarland, M. Paraschivescu, Mississippi State University, Mississippi State, MS, USA

The potential for accumulating lipids in municipal wastewater microorganisms contained in activated sludge was investigated using batch experiments in a laboratory-scale fermenter. These lipids could be used as potential feedstocks for the production of renewable fuels such as biodiesel and green diesel. Kinetic analysis of cell biomass growth, lipid accumulation, and substrate utilization was conducted at carbon to nitrogen ratios (C:N) ranging from 11.7 ? 101.5 using the Logistic and Luedeking-Piret models. The maximum specific growth rate and yield coefficient for biomass were found to decrease with increasing C:N, which is evidence of the diversion of greater amounts of the substrate into the production of storage lipids by the microbial cells due to nitrogen limitation. Analysis of the fatty acid composition of the lipid extracts showed a significant increase in the fraction of saponifiable lipids and unsaturated fatty acids (mainly oleic acid) within the first 72 hours of cultivation. Optimization of the media composition in terms of glucose and ammonium sulfate concentrations was accomplished by response surface analysis using a small composite design to develop a polynomial model describing the linear, quadratic, and interaction effects of the two factors on cell biomass and lipid yields.

Enzymatic Processing of Vegetable Oil Refining Byproducts. M. Dasari, M. Abdullah, Feed Energy Company, Des Moines, IA, USA

Gums and soapstock are by products of chemical refining process vegetable oil. These products are further chemically processed to recover the fatty materials that can be used as animal feed ingredients. In some cases these byproducts are further refined to use in food industry. The fatty materials are recovered by hydrolyzing these products in presence of an strong inorganic acid at very low pH and temperatures close to boiling point of water. These severe processing conditions results in several reaction by products reducing the overall yield of the process. Moreover, these processes produce acid waste water that is very difficult to dispose due to its extremely high dissolved organic content. The overall objective of this research is to use enzymes to process these byproducts, as an environmentally friendly, green technology alternative to the traditional acid hydrolysis process. This paper will summarize our experiences in using several commercially available enzymes to process these byproducts.

IOP 4.1: New Uses of Glycerol
Chair(s): M. Dasari, Feed Energy Co., USA and V. Wyatt, USDA, ARS, ERRC, USA

Synthesis of Nanoscale, Monodisperse, Functionalized, Hyperbranched Oligomers Based on Glycerol and Fatty Acids. J.A. Zerkowski, A. Nunez, D.K.Y. Solaiman, USDA, ARS, ERRC, Wyndmoor, PA USA

Polyesters derived from biorenewables are attractive synthetic targets and are receiving attention for uses such as controlled-release gel matrices. One drawback to these polymers, however, is that they are generally prepared in an ? all-at-once? manner that yields a distribution of products, both in terms of size and architecture (degree of branching). A more significant limitation is that this method also precludes the selective incorporation of functional groups at a given site, such as the core or the periphery, or at some desired ratio. By contrast, a stepwise, iterative approach permits unambiguous construction of oligo/polyesters of defined shape and size. This talk will present our results on the stepwise construction of hyperbranched oligomers from glycerol, dicarboxylic acids, and other functionalized building blocks using esterification reagents and, to assemble the final oligomer, the azide-alkyne click reaction. An azido fatty acid that we have prepared is employed in this step. The oligomers are in the size range of 5-10 nm (depending on the building blocks) and 10 kDa and can exhibit upwards of 20 functional groups at their periphery. Alternatively, the synthesis can be designed so that one single reactive functional group can be localized at the surface of the oligomers.

Glycerin-based Polyols of High Biobased Content for Polyurethane Foams. Z. Petrovic, I. Javni, M. Ionescu, D.-P. Hong, Pittsburg State University, Pittsburg, KS, USA

Utilization of glycerin for polyols for polyurethane industry became interesting as a result of availability from biodiesel production. However, polyols for polyurethane foams have to satisfy a range of requirements in order to be accepted by industry such as clarity (single phase), acceptable viscosity < 10 Pa.s, right OH number (100-600 mg KOH/g), good color (not too dark);functionality: 2-10;acid value bellow 2, miscible with organic solvents (1:1) and water (10%), high glycerin content >50% and high bio-based content >80%. We have developed a family of polyols by modifying polyglycerin to control OH number, viscosity, functionality and solubility, and tested them in rigid foams. Properties of polyols and foams are discussed.

Conversion of Glycerol to Lipids via Oleaginous Microorganisms. J. M. Thomas, R. Hernandez, T. French, W. Holmes, E. Alley, Mississippi State University

The growing popularity of biodiesel as an alternative to petroleum-derived diesel fuel has created a dramatic increase in the production of crude glycerol. Currently crude glycerol has a low market value and many biodiesel producers are treating the crude glycerol as a waste product. If biodiesel is to succeed as an alternative to petroleum-based fuels, it is essential that the crude glycerol produced is processed/refined cost effectively into a value-added product. Oleaginous microorganisms have the ability to use many different types of carbon sources and convert them into oils that can then be used for the production of fuels. The purpose of this study is to investigate the feasibility of oleaginous microorganisms to utilize glycerol as a carbon source for the production of oils. The study will focus on the oleaginous yeast species *Rhodotorula glutinis*. The study will investigate the growth and lipid production kinetics of *R. glutinis* grown on pure glycerol as the sole carbon source.

CANCELED - A Metabolic Approach for Increasing Lipid Storage in *Y. Lipolytica* Grown on Glycerol. C.E. Hodgman, B.Y. Tao, Purdue University, West Lafayette, IN, USA

By 2022, biodiesel is mandated to reach 1 billion gallons of annual production. Biodiesel is made from the lipids of any biological material. To make biodiesel, 90% of the lipids are converted to biodiesel while 10% is leftover as industrial glycerol. The success of the biodiesel industry depends on: 1) finding additional sources of oil and 2) a profitable use for industrial glycerol. Through fermentation, glycerol can be used as a feed stock for the oleaginous yeast, *Y. lipolytica*, and converted back into oil for additional biodiesel production. *Y. lipolytica* is known to grow well on industrial glycerol, store large amounts of lipids, and is relatively easy to genetically manipulate. We are looking to increase the rate of glycerol consumption in the cell to increase the rate of lipid storage. This is accomplished by

overexpressing glycerol 3-phosphate dehydrogenase, a key enzyme in glycerol metabolism. The yeast is grown aerobically in a continuous bioreactor with excess glycerol under nitrogen limiting conditions to induce lipid storage. Preliminary results with the native strain yield 14 g dry biomass/L and 4 g lipids/L (30% total mass) at steady state. The genetically modified strain is compared to the wild type strain in terms of total dry mass, percent and composition of lipids, and rate of glycerol consumption.

AFTERNOON

IOP 5: Conversion Technologies: Catalysts

Chair(s): K.Y.S. Ng, Wayne State University, USA; and R. Hernandez, Mississippi State University, USA

Heterogeneous Catalysis for the Transesterification of Vegetable Oils. V. Lecocq, D. Bazer-Bachi, N. Bats, V. Coupard, IFP, Lyon, France

Today, biofuels are front-page news. Environmental constraints and political determination to promote the emergence of alternative energy resources are just two of the factors that have brought them back into the limelight. Biodiesel, consisting of monoalkyls esters, is a fuel obtained from renewable biomass feedstocks. Most of the commercial biodiesel is produced using homogenous basic catalysts. This process has the drawbacks to produce high amounts of wastewaters and low-quality glycerine. These problems can be overcome with the use of an heterogeneous catalyst. Thus the Axens process Esterfip-H, based on a zinc aluminate catalyst, allows the production of monoalkyls esters from vegetable oils and methanol, with high purity glycerine in a continuous mode. In order to bring some ameliorations to the industrial process, some studies have been made on potential future catalysts. Two types of solids will be presented here. The first one is a Metal Organic Framework, for which lab synthesis, upscaling, characterization and catalytic tests for the transesterification of vegetable oils on a batch reactor and a continuous flow reactor will be presented. The second one is an inorganic oxide, for which the same approach has been used. Finally, the pros and cons of these catalysts, for an industrial apllication, will be discussed.

Simultaneous Transesterification and Esterification to Biodiesel Using Zinc-based Catalyst. Shuli Yan, Manhoe Kim, Steven Salley, John Wilson, Simon Ng, Department of Chemical Engineering and Material Science, Wayne State University, 5050 Anthony Wayne Drive, Detroit, MI, USA

Biodiesel is a mixture of fatty acid esters which can be produced from vegetable oils or animal fats with methanol. Recently, many researchers focus on using waste or unrefined oils as feedstock to decrease the production cost of biodiesel. A two-step method was reported, which firstly esterified free fatty acids (FFA) with methanol in the presence of H_2SO_4, then transesterified oil with methanol in the presence of NaOH. This production process is long and highly corrosive. In this study, a single-step method was developed for biodiesel production using waste or unrefined oils as feedstock based on a series of heterogeneous zinc and lanthanum mixed oxides. Oil transesterification and FFA esterification reactions simultaneously took place in one step. In this study, effects of catalyst structure, metal oxide molar ratio, FFA and water contents in feedstock, reaction temperature and oil concentration on the yield of biodiesel were investigated. The zinc and lanthanum catalysts were prepared by a homogeneous coprecipitation method using urea as precipitant, and characterized by XRD, XPS and EDS measurements. Results indicated that there was a strong interaction between Zn and La species which varied with the molar ratio of Zn to La. At a high ratio of Zn to La, La acted as a diluent of the matrix, promoting ZnO particle distribution, increasing the surface basic and acid sites, and enhancing activity of transesterification and esterification. At a low ratio of Zn to La, destruction of ZnO crystal structure by La species was observed and the catalytic activity was decreased. A reaction temperature window was found in 170 ~ 220°C for biodiesel formation. At the optimal reaction conditions, 42:1 molar ratio of methanol to oil, 2.3 (wt) % catalyst and an agitation rate of 400 rpm, a high yield (95 %) of biodiesel was obtained within 3 hours using some kinds of waste or unrefined oils as feedstock. This class of zinc and lanthanum mixed oxides catalysts are very promising to lower the overall production cost of biodiesel.

Esterification of Free Fatty Acids Contained in Vegetable Oils with Cation-exchange Resin for Biodiesel Production. Katsuyoshi Ohara, Hidenori Futakuchi, Toshio Yajima, Masanori Komatsu, Katsuhiro Maeno, Lion Corporation, Tokyo, Japan

Biodiesel fuel is a commercially produced fuel through transesterification of vegetable oils, with methanol, using alkali catalysts. Vegetable oils contain free fatty acids (FFA) which react with alkali catalysts, consuming them and forming soaps which do not allow efficient glycerol separation. During research, esterification of FFA in crude palm oil, with methanol, using cation-exchange resins as a catalyst has been studied. Catalyst activities of gel-type resins and high porous MR-type resins were examined in a batch reactor and in a fixed-bed reactor. Conversion of FFA to their methyl esters increased with a decreasing cross-linking degree of gel-type resin in both reactors. Activity of MR-type resin was lower than that of 4% cross-linked gel-type resin in a batch reactor, but was higher in the fixed-bed reactor. This result suggested that pressure in a fixed-bed reactor promotes the diffusion of reactants into macropores and the use of active sites on the MR-type resin surface. It was found that optimum resin selection was needed in the different reactors. In addition, the influences of the molar ratio of methanol to FFA and the liquid hourly space velocity and the amounts of FFA on conversion were also examined in the fixed-bed reactor.

Methanolysis of Vegetable Oils in the Presence of Tin (IV) Catalyst: Influence of Temperature and Reaction Conditions on the Catalyst Activity. D.R. Mendonça, J.P.V. da Silva, R.M. de Almeida, M.R. Meneghetti, S.M.P. Meneghetti, UFAL, Maceió, Alagoas, Brazil

The use of vegetable oils and their derivatives as a source of energy, replacing mainly fossil fuel, brings forth not only a new element to the energetic matrix of a nation, but also new tendencies on economical, social, and environmental issues. The catalyst dibutyltin dilaurate were used in the methanolysis of soybean oil and the castor oil, with different temperatures and conditions (under reflux and in a pressurized container). The catalytic system was active for methanolysis of soybean oil and castor oil, and an increment of the temperature corresponded to an augmentation of the reaction yield, measured in terms of % FAMEs formed and this fact can be related to enhancement of the reactivity of the involved species. The reactions conduced in pressurized container show better results and this observation can be associated to a favorable change in phase equilibrium, with consequent increase in the concentration of methanol in the liquid phase. The lower yields of FAME obtained following catalysed conversion of castor oil compared with soybean oil may be the result of the atypical chemical composition of castor oil. The hydroxyl group at C-12 of ricinoleic acid can be interact with Lewis acid catalytic site diminishing the reaction yield.

Transesterification of Soybean Oil with Methanol/Ethanol over CaO Based Heterogeneous Catalysts. M. Kim[1], S. Yan[1], S. Salley[2,1], K. Ng[2,1], [1]National Biofuels Energy Laboratory / Next Energy, Detroit, MI, USA, [2]Wayne State University, Detroit, MI, USA

Methyl- and ethylesters of fatty acids were synthesized using both CH3ONa homogeneous and CaO-La2O3 heterogeneous catalysts. With a homogeneous catalyst (0.3% CH3ONa) the yields of methylesters and ethylesters were similar to each other when methanol and ethanol were used in separate batches. However, when the transesterification of soybean oil was carried out with an equimolar methanol/ethanol mixture, selectivities of methylesters to ethylesters at the first 30 min were 2.6 for the homogeneous catalyst (0.3% CH3ONa), 3.4 for unsupported CaO-La2O3, and 4.3 for supported CaO-La2O3/CeO2, respectively. These higher selectivities can be attributed both to higher competitive reactivity of methoxide, and an additional steric hindrance effect of ethoxide bonded on the catalyst surface. Transesterification from methylesters to ethylesters was observed when methanol/ethanol mixture was used. In addition, a synergistic effect in the yield of methylesters was observed when methanol/ethanol mixture was used. The synergy effect on the yield was, not only as a result of the increased solubility but also due to the interaction between alchoxide-alcohol.

Enzymatic Esterification of Fatty Acid Distillates - A Plug-in Alternative to Sulfuric Acid Catalysis. J. Brask[1], P.M. Nielsen[1], M.L. Damstrup[1], J. Maes[2], W. De Greyt[2], [1]Novozymes, Bagsvaerd, Denmark, [2]Desmet Ballestra, Zaventem, Belgium

In today's biodiesel production units oil feedstocks are typicaly deodorized to lower the FFA content to avoid soap-formation in the alkaline catalyzed transesterification reaction. The fatty acid distillate (FAD) is typically converted to FAME with sulfuric acid catalysis, a process with many disadvantages. In this paper we present our work on an enzymatic process to convert FAD to FAME. With FAME being lowered to less than 5%, the deacidified FAD stream

can be joined with the deodorized oil stream to enter conventional alkaline transesterification. The enzymatic unit is hence a plug-in solution for biodiesel producers looking for an alternative to the sulfuric acid process, requiring only few changes in the production units.

Synthesis Gas Conversion to Hydrocarbon Liquids. M.G. White, S. Liu, Mississippi State University, Mississippi State, MS, USA

The catalytic conversion is reported for synthesis gas to hydrocarbon liquids in one step in a fixed bed reactor. This reaction proceeds through oxygenated intermediates to include higher alcohols such as ethanol and propanol. We discuss the catalyst preparation and characterion in addition to representative yields.

The Future of Hydrogenation. X. Dupain[1], R.Z. Lee[2], R.D. Seaman[3], A. Zwijnenburg[1], [1]Johnson Matthey, Emmerich am Rhein, NRW, Germany, [2]Johnson Matthey, West Deptford, NJ, USA, [3]Johnson Matthey, Oakbrook Terrace, IL, USA

Over the past century, catalytic hydrogenation has seen and brought about significant changes in processing. Although there is a decline in partial hydrogenation, some exciting new processes are emerging to face the new challenges. Soaring energy prices and new raw materials have led to the development of new robust catalysts that can handle less purified feedstocks. Furthermore, some new opportunities have emerged in the oleochemical area. Examples of these new applications – in existing equipment – will be given.

Heterogeneous Catalytic Cracking of Phospholipids to Renewable Fuels Using Co-Mo and Ni-Mo γ Al2O3 Catalysts. T. Benson[1], A. Forks[1], M. White[1], E. Alley[2], R. Hernandez[1], [1]Mississippi State University, Mississippi State, MS 39762, USA, [2]Mississippi State Chemical Laboratory, Mississippi State, MS 39762, USA

Recent research has identified the use of lipids for the production of green fuels via heterogeneous catalytic cracking. These green fuels, which are comprised of the same types of compounds as petroleum-based fuels, could be produced from a wide variety of plant, animal, and microbial lipid sources and could replace significant amounts of petroleum fuels. The lipid feedstocks would be comprised mainly of free fatty acids, acylglycerols, and phospholipids. Inasmuch, traditional petroleum refining using hydrotreating with transition metals embedded on Al2O3 catalysts have had difficulties in cracking compounds which contain inorganic species, such as phosphorus. However, combinations of Ni-Mo have shown to have better success over Co-Mo in terms of poisoning of the catalyst. This study focuses on the cracking of phospholipid model compounds, namely phosphatidylglycerol and phosphatic acid, on petroleum-type catalysts. A pulsed-type micro-reactor was used to investigate reaction products and reactant/surface interactions during the production of renewable fuels. The catalysts used in this study were Co-Mo and Ni-Mo on Al2O3 solid acid catalysts that had been sulfided for increased heteroatom removal. Reaction products and pathways will be shown, along with catalyst characterization pre and post reaction.

Enzymatic Transesterification of Rapeseed Oil Using Methyl Acetate. Frank Pudel, Fleck Gunther, Pilot Pflanzenöltechnologie Magdeburg e.V., Magdeburg, Germany

There is a growing number of papers available dealing with the use of lipases for the biodiesel production. Enzymatic processes can have some advantages in comparison to chemical ones. In laboratory scale the reaction conditions of the lipase catalyzed transesterification of rapeseed oil with methyl acetate were investigated. The results will be presented and discussed.

Industrial Oil Products Posters

Chair(s): J.A. Kenar, USDA, NCAUR, ARS, USA.

Microbial Conversion of Seafood Processing Waste into Triglycerides a Biodiesel Feedstock.

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Biodiesel is a displacement fuel for traditional petroleum-derived diesel. Unfortunately biodiesel is an expensive fuel due in large part to the high cost of feedstocks. Oils derived from byproducts with no value could potentially be a cheap source of biodiesel. The byproducts from shrimp processing are heads and shells which contain a wealth of carbon and could be converted into oils via microorganisms. The objective of this investigation is to determine the feasibility of using oleaginous microorganisms to convert the shrimp byproducts into oil. Initial screening experiments were conducted among R. glutinis, R. opacus, C. curvatus,etc, which have been shown by MSU and others to accumulate greater than 50% of its dry weight as oil. These experiments were initially conducted using n-acetyl glucosamine, which is the major sugar product from the hydrolysis of Seafood Processing Waste, at a concentration of 50 g/L. Results suggested that oleaginous yeast Cryptococcus curvatus was the optimal tested microorganism for the production of microbial oil from n-acetyl glucosamine. Cell mass of C. curvatus increased continuously within 97.3 hours to 20.99 g/l under the increase of pH. The oil content in C. curvatus was accumulated from 4.71% at 10.5 hours to 16.99% at 97.37 hours.

IBIOLAB project: Improvement of Biolubricant Manufacturing and Development Thanks to the Obtaining of EcoLABels in a Wide Range of Industrial Sectors.

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In Europe, the inland consumption of lubricants has been estimated to 5 million tonnes in 2001. More than 95% of the market is dominated by the mineral oils based lubricants, which are contaminating the environment but have a very low price and high availability. As 30% of lubricant used in the industry ends up it the ecosystem, it is very easy to understand why some countries are more and more attracted by the bio-lubricant alternative. Vegetable oils have a number of inherent qualities that give them advantages over petroleum oils as the feedstock for lubricants, but up to now there is low experience in their use and some limitations have to be overcomed.Therefore, the IBIOLAB project intends to address several needs to enhance the market share of the bio-lubricants, and thus reinforcing the competitiveness of SMEs:1 Need to improve and better understand the manufacturing processes (immature technologies) in order to decrease the overall cost and improve the properties of bio-lubricants.2 Need to help the SMEs for the awarding of their products with eco-labels.3 Need to provide the SMEs knowledge on best practices in lubricant bases, bio-additives and formulation issues.4 Need for an efficient & widely spread campaign of communication gathering all the actors and potential end users.

Photobioreactor Design and Operation: Effect of Light Intensity and Flow Rate on Algal Growth Rate.

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The rising cost of traditional feedstock for the biofuels industry has led to an increasing interest in algae as a possible supplemental if not replacement feedstock. One of the main hurdles of this becoming a reality is the costs associated with growing, harvesting and extracting oil and carbohydrates from the algae. Here the cost of growing and harvesting the algae is addressed with a novel external loop airlift reactor. A reactor was designed to maximize the light penetration into the interior of the reactor in order to operate at the optimal optical density for the algal growth. This design includes the use of various submersible lights to maintain the required optical density. The flow characteristics in the reactor were also studied and modified to reduce the shear stress effects on algal death. The operation of the reactor is automatically controlled to maintain not only the appropriate optical density, but also the dissolved CO_2 and dissolved O_2 concentrations, pH and temperature for the algal strain being grown.

Characterization of the Corn Oil Deposit Extracted From Condensed Corn Distillers Grains with Solubles (CCDS).

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Oil extracted from condensed corn distillers solubles (CCDS) contains lipid deposit that is solid at ambient temperatures and settle at the bottom of container. CCDS are mixed with distillers grains (DG) to make dried distillers

grains with solubles (DDGS). DDGS are a major coproduct of ethanol production and primarily used as a livestock feed. The objective of the research was to evaluate the physical and chemical properties of the oil deposit and to also determine if valuable phytochemicals found in corn fiber oil such as free phytosterols, ferrulate phytosterol esters, tocopherols were present in the corn oil deposit. The free fatty acid content was high, 35.7 ± 0.1% and the fatty acid composition of the free fatty acid fraction was predominantly palmitic acid: 74.6 ± 0.3 %, stearic, oleic and linoleic acid were 7.0 ± 0.1%, 5.6 ± 0.3%, 12.8 ± 0.1% respectively. The total unsaponifiable fraction was 20mg/g of oil deposit.

Mineral Catalysed Decarboxylation of Fatty Acids.
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Biofuels are an emerging alternative sustainable fuel source to traditional crude oil based fuels. Fuels derived from the lipid fraction of biomass have recently received much attention for carbon neutral substitution of fossil fuels for transport use. Producing fuels which are chemically similar (although they contain less impurity sulphur) to their fossil counterparts means that they are amenable to production using existing petrochemical refining infrastructure. Biofuels can extend the reserves of fossil oil as well as providing the possibility of a direct replacement for them in the future. In this work novel routes to catalytic upgrading of biomass derived fatty acids are explored. Chemical upgrading of the model lipid profiles are performed via decarboxylation, which leads to deoxygenated Green Diesel (not to be confused with Biodiesel), which is chemically identical to compounds found in the fossil diesel fraction. The homogeneous catalysts employed are based on minerals, typically MgO and mixed metal oxides, leading to conversion of the fatty acid into alkanes at constant pressure and temperature in an autoclave batch reactor. Quantitative analysis of the reaction is performed via gas chromatography with high selectivity towards the desired deoxygenated product.

Preparation, Characterization, and Thermal Properties of Starch Microencapsulated Fatty Acids as Phase Change Materials for Thermal Energy Storage Applications.
J.A. Kenar, NCAUR, ARS, USDA, Peoria, IL, USA

Stable starch-oil composites can be prepared from renewable resources by excess steam jet-cooking aqueous slurries of starch and vegetable oils or other hydrophobic materials. Fatty acids such as stearic acid are promising phase change materials (PCMs) for latent heat thermal energy storage applications. However, for use in applications they require special containers since they change from solid to liquid during the energy storage period. We report the microencapsulation of fatty acids and commercial waxes into starch utilizing excess steam jet-cooking. The resulting dried starch-PCM composite powders were found to contain 1 to 10 μm droplets of PCMs and the properties such as the encapsulation ratio of PCM to starch for these starch-fatty acid composites were examined. Thermal characteristics such as melting and freezing temperatures and latent heats were examined by differential scanning calorimetry (DSC) and the results of these experiments and a discussion of the use of starch to encapsulate the PCMs will be presented.

Short Chain Sugar Amphiphiles: Ambient Oil Structuring Agents.
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The present research exemplifies the utilization of biobased resources, and converts them into value-added products using eco-friendly routes such as biocatalysis and green chemistry methods. Mannitol, sorbitol and xylitol were selected as representative sugar alcohols (headgroups) and series of amphiphiles have been synthesized by attaching hydrophobic carboxylic acids at one-end of the sugar using an enzyme-mediated regioselective transesterification reaction. The resulting amphiphiles were studied for their self-assembling behavior in organic liquids and were found to be efficient organogelators; immobilizing various solvents ranging from crude oil fractions to vegetable oils. Effect of chiral and structural variations in sugar amphiphiles on microstructure formation was investigated in detail. In addition, these amphiphiles were demonstrated as healthy alternative structuring agents of vegetable oils compared to the existing oil structuring additives and chemicals.

Synthesis and Physical Properties of Coriander Estolide 2-ethylhexyl Esters.
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Coriander (*Coriandrum sativum* L.) is new crop that is currently being investigated for cultivation in Central Illinois by USDA-NCAUR. Coriander is an annual herb belonging to the Apiaceae (Umbelliferae) family and indigenous to the Mediterranean basin areas and the Near East. Coriander seed oil is rich in an unusual fatty acid, the petroselinic acid (C18:1, n-12), which composes as much as 85% of the total fatty acid. The fresh green leaves of coriander, commonly known as cilantro are widely featured on the menu around the world. The development of a new crop often depends on the synthesis of novel compounds. Estolides are one such derivative of new crop oils which show promise in industrial applications. Estolides are formed when the carboxylic acid functionality of one fatty acid links to the site of unsaturation of another fatty acid to form esters. Estolides were derived from coriander fatty acids and various other fatty acids in the presence of an acid catalyst at 60^{o}C followed by esterification to the 2-EH ester under standard conditions.These new estolide esters were converted to their corresponding hydroxy fatty acid and the degrees of polymerization were determined. Physical properties of the coriander estolide esters were compared to previously synthesized estolides, which have current industrial applications as a cheap alternative bio-based material.

Reaction Kinetics for the Homogeneous Catalytic Cracking of a Saturated Triglyceride.

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Heterogeneous catalytic cracking of lipid feedstocks into transportation fuels could help to displace petroleum-based fuels. Production of these fuels would ensue from hydrotreating/ hydrocracking processes similar to those used in the current petroleum industry. In an attempt to understand the deoxygenation pathways, a homogeneous superacid was used for catalytic cracking of a model lipid compound with the objective of discerning between decarbonylation and decarboxylation. Tripalmitin, a saturated triglyceride, was used to investigate the reaction products and mechanism from cracking associated near the glycerol backbone. Kinetic experiments were conducted using trifluoromethanesulfonic acid as a Bronsted superacid catalyst. Results indicated that reactions occurred through acyl oxygen cleavage, yielding the formation of a free fatty acid and a diglyceride. Subsequent reactions to the acylglyceride yielded two and three free fatty acids which were cleaved from the glycerol backbone. Kinetic results indicated that the reaction was first order with respect to tripalmitin and follows an Arrhenius response in regards to activation energy. These results infer that under heterogeneous conditions, decarbonylation is the primary step towards deoxygenation of lipid molecules.

Effect of Minor Components on Antioxidant Effectiveness in Biodiesel.

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A significant problem associated with the commercial acceptance of biodiesel is poor oxidative stability. Understanding the mechanism of antioxidant to improve the oxidative stability to different types of biodiesel is important.Our study investigated the effectiveness of antioxidants on the oxidative stability of different feedstocks of undistilled and distilled biodiesel. Moreover, this study will develop a robust analytical method to determine nature antioxidant content in biodiesel, and investigate the effect of composition and minor components, such as sterols, nature antioxidant, glycerins, on the effectiveness of synthetic antioxidant to biodiesel. We found that all of synthetic antioxidants enhanced the oxidative stability of different types of biodiesel, while adding α-T had no noticeable effect. The IP increased as a function of the antioxidant concentration over the range of 250 -1000 ppm. Moreover, the effect of each antioxidant on biodiesel stability was different depending on the feedstocks. Moreover, the effect of different antioxidants on distilled SBO-based biodiesel is similar to the original biodiesel. However, for PF-based biodiesel, the antioxidants in DPF-based biodiesel are much more effective than in untreated PF-based biodiesel.

Small-Chain Fatty Acid Solubility in Supercritical Carbon Dioxide.

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Currently, lipids derived from plants, animals, and microorganisms are being considered as promising renewable feedstocks to synthesize a wide range of fuels and chemicals. In fact, biodiesel, a renewable alternative to petroleum diesel, is produced primarily from soybean lipids in the United States. In terms of chemical production, individual lipid

components must be considered. For example, many lipid sources contain unsaturated fatty acids, which can be oxidized to form a variety of products such as diacids and epoxides. These chemicals are valuable intermediates for the formulation of pharmaceuticals, herbicides, detergents, plasticizers, lubricants, paints, and other useful products. The use of supercritical fluids, such as carbon dioxide, in processing lipid components is being heavily researched; however, experimental solubility data primarily exists for lipids composed of higher molecular weight fatty acids such as oleic acid. In this research, the solubility of small-chain fatty acids in supercritical carbon dioxide has been determined at (313.15, 323.15, and 333.15) K over a pressure range of (10 to 30) MPa. The compounds considered include heptanoic, octanoic, nonanoic, and decanoic acids.

Biodiesel from *Crambe abyssinica*: An Alternative Crop for Brazilian Production.

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In this work, seeds from crambe (Crambe abyssinica) obtained from Mato Grosso State, Brazil, were evaluated for biodiesel production. Physical and chemical characteristics of crambe oil extracted by screw press were investigated. The fatty acid composition presented 60.20% of erucic acid as a major component, iodine value 82.92cgI/g, 5.62% of free fatty acid and 1.2meq of peroxide value. Transformation of crude crambe oil to obtain biodiesel by means of transesterification was made with methanol and sodium methylate solution as catalyst. Crambe methyl esters were characterized to their quality properties as fuel for diesel engines. Sulfur content obtained was 35 mg/kg because the raw material is a member of the Brassicaceae family, and oxidative stability was 16.4h without antioxidant addition, although its high unsaturated fatty acid content could affect negatively its resistance to the oxidative processes. Results showed that crambe biodiesel obtained under these conditions is an excellent substitute for fossil fuels.

Biodiesel Production from Crude Coconut Oil Using Ca-based Catalysts.

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Biodiesel, a mixture of fatty acid esters, is obtained from natural oil resources. As it is nontoxic, renewable and beneficial for environmental protection, it is considered as an alternative fuel to traditional petroleum-based fuels. A major barrier to the commercialization of biodiesel is its high production cost, which is primarily related the cost of well refined vegetable oils as raw material. Using unrefined oils is potentially a more economical source for biodiesel production. However unrefined oils generally contain significant free fatty acids (FFA), and the current approach is unable to directly utilized unrefined oils. In this study crude coconut oil (CNO) was investigated and a one-step process was developed to convert CNO into biodiesel based on Ca-based catalysts. The catalysts with different basic properties, specific surface area and surface contents were investigated. It was found that both basic and acid groups played an important role in biodiesel formation reactions. At 65°C, 0.8 mass ratio of methanol to CNO and 5% of catalyst dosage, FAME content can reach 91% within 60 minutes.

Physicochemical Study of Glycerol - Solvent Systems by Inverse Gas Chromatography.

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Glycerol, a polyhdyroxylic functional alcohol, has utility as reactive monomer in polymeric coatings systems and as a sustainable - green solvent. Glycerol is a by-product of biodiesel production which has lead to over capacity in the market place, hence new applications for this chemical are critically needed. This research involves the use of inverse gas chromatography (IGC) to characterize the solute-solvent interactions between glycerol and a homologous series of aliphatic alcohols, where the latter components are at infinite dilution in the glycerol which is distributed within a packed GC column. The derived IGC data ? solute activity coefficients, Henry?s Law constants, and thermodynamic functions of solution can be used to characterize the solvent properties of glycerol as an absorptive solvent as well as to provide data for the removal of the alcoholic solutes from glycerol. IGC experiments conducted between 55 -130 C for the n-alkanols ranging from methanol to butanol exhibited positive deviations from Raoult?s Law resulting in mole-fraction based-activity coefficients ranging from 2.75 ? 17.7 as a function of temperature and n-alkanol carbon number. The very linear plots of log of the specific retention volume vs. 1/T for each alkanol permits interpolation-extrapolation for the determination of mole fraction activity coefficient data as a function of temperature, while the

resultant slopes of these plots for each solute suggest a similar heat of solution for each of the solute-glycerol binaries. This coupled with the relative small variance of the activity coefficient with temperature (small to zero excess heats of solution) suggest that the escaping tendency of the solutes is due to the enthalpy of vaporization and limited interaction with the glycerol solvent. The implications of these results in terms of the removal of the alcoholic solutes from glycerol, and conversely the use of glycerol as a solvent will be discussed.

Strategies for Development of Value-Added Polyols and Derivatives from Vegetable Oils.
Vijay Mannari, Senthilkumar Rengasamy, Reshuk Dawra, Eastern Michigan University, Ypsilanti, MI, USA

Polyols are indispensible components of polyurethane based materials that are finding increasingly important applications in such diverse products as, plastics, foams, coatings, composites, adhesives, among others. Bio-based materials are increasingly used in meeting the present-day demands of developing sustainable products and processes. Vegetable oil is an excellent agro-based resource for development of polyols for aforesaid applications. Depending upon their end-use applications, polyols are required to meet such demanding requirements as functionality, reactivity, compatibility, hydrolytic stability, rheology, to name a few.Epoxidized Vegetable Oils (EVO), a commercial product, offers unique chemistry that allows design and development of a wide range of polyols. This poster highlights our research on development of a wide range of polyols useful for coatings and allied applications. Different types of EVOs and their derivatives have been used as starting materials. Synthetic routes to derive a range of polyols with controlled chemical structures, types and number of functional groups, hydroxy equivalent weight, viscosity and their potential applications will be presented.

Polyurethanes from Soy Oil-based Cyclic Carbonates.
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The synthesis of soy oil-based polyurethanes by non-isocyanate route consists in reacting carbonated soybean oil (CSBO) with amines. This technology has several benefits such as utilization of bio-based resources and carbon dioxide, an inexpensive and environmentally friendly monomer and production of biodegradable polyurethanes. The effect of different catalysts, amines and the reaction conditions on polyurethane properties was studied.

Synthesis and Applications of Novel 2-hydroxy Diyne Acids.
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The topochemical polymerisation of conjugated diacetylenes in the solid state to form polydiacetylenes (PDA′s) has been the subject of intense study since it was first reported by Wegner in 1969. PDA′s form when condensed diacetylene monomers containing appropriate pendant side groups align in a particular orientation and are then subjected to ultraviolet light, gamma radiation or heat. To date, PDA′s have been incorporated into a wide variety of chemical systems, including silica nanocomposites, silver-coated vesicles, liposomes biosensors, picosecond photoswitches, micropatterning and strain sensors. This ubiquity owes itself to a plethora of features exhibited by PDA′s including conductivity, fluorescence, photoluminescence, mechanochromism, chemochromism and thermochromism. The properties and applications of PDA′s have been reviewed, but unsurprisingly, much of the more recent application chemistry is being reported in the patent literature. In the pursuit of new and versatile PDA′s, some novel approaches to the preorganisation of the monomers have been produced. As a part of ongoing studies into the chemistry and applications of diyne containing molecules we recognised a hitherto unreported new class of 2-hydroxy-diyne acids and derivatives. Herein, we describe an efficient synthesis of novel 2-hydroxy diyne acid, ester and amide derivatives.

Determination of Free and Acylated Glycerols in Biodiesel by High Pressure Liquid Chromatography and Charged Aerosol Detection.
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Some of the significant impurities in biodiesel include the mono-, di-, and tri-acylated glycerols, as well as free glycerol. These impurities interfere with the combustion system by clogging fuel injectors and filters. Currently, these

impurities are quantified using the high temperature gas chromatography method, ASTM D6584. This method of analysis also requires derivitization. HPLC analyses have been cited as generally faster and cheaper to use than GC methods,[1] but have remained elusive for this application. We have developed a normal phase HPLC method, based on earlier work conducted at the USDA,[2] using the Corona® CAD® on an SGE 250 x 4.0 mm cyanopropyl HPLC column that can quantify these four glycerol impurities with external standardization, sample dilution, and quantitation. With an 880 µg load of biodiesel, LOQ values are 0.006% (50 ng) for glycerol, and 0.002% (15 ng) each for the three acylated glycerols, mono-oleyl glycerol, 1,3-diolein, and triolein.[1]Knothe, G.. 2001. Analytical Methods Used in the Production and Fuel Quality Assessment of Biodiesel. Transactions of the ASAE. 44(2): 193-200.[2]Foglia, T.A., and Jones, K.C. 1997. Quantitation of neutral lipid mixtures using high performace liquid chromatography with light scattering detection. J. Liq. Chrom. Rel. Tech. 20(12): 1829-1838.

Purifying Fish Oil: Bleaching and Molecular Distillation.
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Bleaching has been a common process for edible oils and is much wider in scope than just removal of color. In some cases, the main purpose is to remove other unwanted components such as products of oxidation, sterol, pollutants and pro-oxidant metals. Special bleaching methods are required for fish oils of low quality. For example, we found that some tuna oil products were especially difficult to refine, some of them were very dark in color and others had elevated pAV and peroxide values. Those oils can only be refined by special treatments. Effects of bleaching methods on fish oil quality were evaluated and different bleaching agents were tested for selective removal of impurities. There are many bleaching agents commercially available, we found some of them were significantly more efficient in certain applications. With the improvement of the technology and equipments, molecular distillation has become more and more popular in edible oil operations. It can be a major technique in the fish oil process to remove volatiles such as free fatty acids and PCBs, but damage to the treated oil has to be avoided. We have evaluated the impact of molecular distillation on the fish oil quality. As a major Omega-3 producer, Ocean Nutrition Canada Ltd. has developed several refining processes to improve the product quality.

Physical, Oxidative and Lubricant Properties of Cold Pressed Cruciferae Oils.
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Cruciferae oils are suggested to possess lubricant properties which may be advantageous in the formulation of an automotive lubricant from renewable sources. Oilseeds from different species within the Cruciferae family were pressed using a Komet Press (Model: CA 59G3). Cold pressed oil samples derived from Brassica juncea, Brassica napus, Sinapis alba and Linum usitatissimum as well as corresponding methyl esters were analyzed for the physical, oxidative and lubricant qualities. Physical properties examined include density, cloud point, pour point, refractive index and viscosity. Viscosities and densities of both oil and methyl esters were also measured on a temperature gradient. Oxidative stability of the samples was measured using an Oxidative Stability Instrument (OSI, Omnion, Inc. Model OSI-24). Lubricity of each sample was determined as a wear scar area produced by a Munson-Roller On Cylinder Lubricity Evaluator (M-ROCLE). The observed physical, oxidative and lubricant properties demonstrate that Cruciferae oils are ideal candidates for the formulation of a plant-based automotive lubricant.

Biodiesel from Activated Sludge *via in situ* Transesterification.
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Waste activated sludge from municipal wastewater treatment plants is a good source of microorganisms with potential use as biodiesel feedstock. In this study, the production of biodiesel from activated sludge via acid-catalyzed *in situ* transesterification was optimized. Freeze-dried sludge was subjected to varying process conditions which include reaction temperature (50-70^{o}C), sludge to methanol ratio (1:5-1:25 w/v) and sulfuric acid concentration (0.1-0.6M) for 24 hours. The yield is expected to increase with temperature and with sludge to methanol ratio. Higher concentration of sulfuric acid is expected to affect the yield positively, however too high concentration might cause some side

reactions to occur because of harsh condition. The optimum condition will be decided based on the yield of fatty acid methyl esters (FAMEs).

Continuous Production of Biodiesel from Soybean and Crude Coconut Oils over La2O3-based Catalysts.
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Biodiesel is a mixture of fatty acid esters and is usually produced from well refined vegetable oils. Recently, many efforts have been made on various ways to lower the production cost, like setting up a continuous reaction system to reduce the operation cost, using waste or unrefined oils to reduce the feedstock cost, etc. In our previous studies, we have developed a class of lanthanum-based catalysts which is highly active in changing well-refined and unrefined oils into fatty acid methyl esters in batch reactors. In this study, we set up a continuous reaction system based on these lanthanum-based catalysts and tested the reaction efficiencies of food-grade soybean oil and crude coconut oil (CNO). Experiments were performed at 200°C and 100 ~ 400 Psi, with a soybean oil/methanol ratio of 1:42. Soybean methyl ester content in the range of 72% ~ 92% has been maintained for 32 days at a flow rate of 0.3 ml/min. The reaction efficiency of crude coconut oil (CNO) was investigated from the 32nd day to 33rd day. Coconut methyl ester content was maintained 82% ~ 91%. Total acid number (TAN) of original CNO was 8.54 mgKOH/g and after reaction it decreased to 0.34mgKOH/g. Thus, it suggests that using CNO oil transesterification and FFA esterification simultaneously took place in one step. This class of lanthanum?based catalyst shows a long catalyst life in biodiesel production, and it is very promising to lower the overall production cost of biodiesel.

Production of Fatty Acid Methyl Esters via the In Situ Transesterification of Soybean Oil in Carbon Dioxide-Expanded Methanol.
Victor Wyatt, Michael J. Haas, USDA, ARS, ERRC, USA

Feedstock prices contribute up to 80% of the total costs associated with the production of fatty acid methyl esters (FAME). In attempts to lower the impact of these feedstock costs, in situ transesterification methods have been employed to synthesize FAME directly from lipid-bearing materials. However, in situ transesterification reactions of oil-borne solid starting materials require as much as a 560-fold molar excess of methanol relative to the amount of triacylglycerol, compared to a 6-fold molar excess of methanol for the conventional transesterification of refined or partially refined oils. To lower the methanol requirement for in situ transesterification reactions, we have performed transesterification in reduced volumes of methanol that had been expanded with CO_2. The results of our study with alkaline- and acid-catalyzed systems will be discussed.

Non-Catalytic Polymerization of Ethylene Glycol and Epoxy Molecules for Rigid Polyurethane Foam Applications.
Arnold Lubguban, Yuan-Chan Tu, Zuleica Lozada, Fu-Hung Hsieh, Galen Suppes, University of Missouri, Columbia, MO, USA

The study investigated an approach to incorporate modified epoxidized soy-based vegetable oil polyol as a replacement for petroleum-based polyether polyol and to substantially reduce the isocyanate loading in the rigid foam formulation. Non-catalytic polymerization of epoxidized bodied soybean oil and ethylene glycol was carried out in a closed batch reaction. Cleavage of the oxirane rings and hydroxyl group attachment at optimum conditions provided the desired polyol products. The polyols were characterized based on its hydroxyl numbers, acidity, viscosity, iodine number and Gardner color index for quality purposes. Reactions of oxirane ring and ethylene glycol were verified by spectroscopic FTIR. Crosslinking performance was evaluated by extractability analysis on the polyurethane elastomer wafers. Rigid foaming performed at 50% and 75% petroleum-based polyether polyol replacements have shown excellent thermoinsulating and mechanical properties compared to epoxidized soybean oil alone or petroleum-based polyether polyol alone. A reduction of up to 8% of the polymeric diphenylmethane diisocyanate was achieved using the synthesized epoxidized soybean oil-ethylene glycol-based polyols. A higher average functionality polyol is key component to the reduction of isocyanate in polyurethane synthesis.

Reaction Engineering of Synthesis of Biodiesel from Refinery Byproducts and Waste Cooking Oil.

Mahendra Bari, Kalpana Shimpi, Ravindra Kulkarni, North Maharashtra University, Jalgaon, Maharashtra, India

Biodiesel is currently manufactured by base catalyzed transesterification of refined oils. However such feedstocks are expensive and in absence of incentives, biodiesel can't compete commercially with diesel. Hence the use of refinery byproducts and waste cooking oil (WCO) has been explored as feedstock for synthesis of biodiesel. Soapstock and spent earth obtained from 5 vegetable oil refineries were analyzed as per AOCS methods while WCO gathered from 6 restaurants were analyzed for AV, IV, SV and polymer content. Three stage saponification permitting upgradation of feedstock followed by suplhonic acid catalysed esterification were established as route for synthesis of biodiesel. FTIR spectrophotometer, GC and HPLC were used to monitor the synthesis. Around 93-97%, 69-81% and 57-84% biodiesel yield were reported within 60 min for soapstock, spent earth and WCO, respectively. Use of sonication further reduced the reaction time for same yield to 15-20, 28-35, 25-45 min, respectively. The mathematical correlations between biodiesel yield and physico-chemical parameters of industrial by products and WCO were established. The data on estimated availability of soapstock, spent earth and WCO in India has been presented. The commercial viability of biodiesel production by sequential saponification and esterification has been discussed.

Recovery and Purification of Fat from Food Processing Wastewater for Use as Biofuel or High-Grade Biodiesel Blendstock.

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Waste fat, oil and grease (FOG) are major components of many food processing wastewater streams, especially animal slaughter and further processing operations. In Georgia, poultry processors are one of the state?s leading producers of these high FOG wastewaters. In 2007, Georgia poultry processors slaughtered over 1.3 billion broilers (14.8% of U.S. production) and generated approximately 9 billion gallons of highly concentrated FOG wastewater in the process (USDA, 2008). Presently, most waste fat from poultry processing plants is sold to rendering facilities at relatively low prices. This current method provides a proven method of handling the disposal of waste FOG, but does not take advantage of the fact that poultry fat can be a more valuable by-product of the processing industry and has great potential as a source of alternative fuel. The current system also does not capture the FOG currently lost to the effluent wastewater stream. This study sought to capture these waste FOG streams using low input methods. The resulting material was then used as a Biofuel in two separate demonstrations; a boiler fuel application using unmodified FOG and a biodiesel application where FOG was used as a blendstock to produce Biodiesel fuel.

Characterization and Detection of Used Frying Oils as Raw Material in Biodiesel Production.

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Used frying fats and oils with highly variable and uncontrolled quality are used for biodiesel production. Thus, the characterization and detection of compounds giving information on the use of used frying oils as raw material in the production of biodiesel is of interest to guarantee the quality of the product.The objective of this study was to define the analytical methods useful to have information on the quality of the used frying oils as raw material for biodiesels as well as for characterization of the biodiesels obtained from them. The most characteristics groups of compounds formed after used frying oil transesterification were analysed by means of the standard technique using gas chromatography at high temperature (EN 14105). Dimeric fatty acid methyl esters (dimeric FAME) is the most important group to be considered as they are present in significant amounts after used frying oil transesterification and absent in the bleached oils used for biodiesel production. The concentration of the dimeric FAME in the polar fraction of the biodiesel, easily obtained by adsorption chromatography, allowed detection of this group of compounds even at very low concentration.

Dependence of Cao Catalyst Performance on Coupled Metal-Oxides and Preparation Methods.

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CaO-La2O3 catalysts were loaded on the various supporters such as lanthanum oxide, cerium oxide, zirconium oxide, titanium oxide, alumina, and ZSM-5 via the impregnation method. Metal compositions and properties in the supported catalysts were measured with SEM-EDS, XRD and pH indicators. Catalytic activities of the supported catalysts were

measured by transesterification reaction of soybean oil with methanol. Even though similar amounts of CaO-La2O3 were loaded on the supports, the catalytic activities of the supported CaO-La2O3 catalysts were very highly dependent on chemical property of the supports. CaO is regarded as main active site due to its basicity. The measured basicity values of the supported catalysts had following order: CaO-La2O3/La2O3 > CaO-La2O3 /CeO2 > CaO-La2O3/Al2O3 > CaO-La2O3/ZrO2 > CaO-La2O3/ZSM-5 > CaO-La2O3/TiO2. Supported base catalysts can be neutralized on acidic support and the basicity of base catalyst can be elevated by the basic support. Strong interaction between CaO-La2O3 and acidic supports was observed. Inversely, base catalyst was loosely loaded on the basic supports and relatively easily dissolved into reaction medium and contributed as homogeneous catalysts. Keywords: Biodiesel; transesterification, , CaO catalyst

Biodiesel from Jojoba and Safflower Oils: Transesterification with Methanol.

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Due to the interest about renewable fuel, various biodiesel production processes have been studied extensively. Besides, the use of oil crop produced in arid lands as a source for biodiesel had increased in recent years. For these reasons, the aim of this study was evaluate the potential of jojoba and safflower oils as material of biodiesel. These oils were subjected to the transesterification reaction with methanol and sodium hydroxide as catalyst at 70°C. Biodiesel from jojoba oil at room temperature (28°C) formed a gel with an acidity of 0.125±0.04 mg KOH/g. Biodiesel from safflower oil showed an acidity of 0.376±0.04 mg KOH/g, a viscosity of 4.55 mm^2/s at 40°C and a density of 0.89 g/cm^3), these values are in accordance with the ASTM biodiesel standards. The results showed that is feasible to produce methyl esters from jojoba and safflower oils with the potential to be used as biodiesel.

Surface Tension Measurements of Chemically Modified Oleochemicals.

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Surface tension is an important physical property of a substance, which plays a part in a variety of physical phenomenon relevant to many industrial processes. For example, the efficiency of the atomization of a fuel has been shown to be effected dramatically by surface tension and viscosity. Because we have synthesized a variety of different materials based on soybean oil, and they have potential use in both the fuel and lubrication industries, we decided a surface tension study was needed. A variety of alkyl esters, with varied functional groups in their fatty chains, were systematically studied. The surface tensions measured for each of the compounds ranged from 25.9 mN m-1 to 30.2 mN m-1, showing that we have reduced the surface tension from the typical triacylglyceride value of ~35 mN m-1. Generally, we observed that addition of an alky ester to the middle of the fatty chains decreases surface tension, where as epoxidation increases it slightly. Finally, mixtures of these compounds with diesel fuels have surface tensions which can be roughly estimated from the surface tensions of the components

Long-term Tests with Palm Biodiesel in a Public Service Fleet.

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It was designed a long-term test (100.000 km) for evaluating the performance of 5 diesel-biodiesel blends (B5, B10, B20, B30 and B50) under normal operating conditions of articulated buses of the mass transportation system in Bogota City at 2600 masl. The trial consisted of four activities: design and construction of the facilities required for the storage and blending of fuels, monitoring the quality of the fuels that were used during the test to guarantee that they meet the required specifications, following the performance of the blends during the operation of the vehicles and finally the assessment of emissions of polluting gases. The results obtained showed that all blends of diesel-palm biodiesel met international quality standard for diesel fuel, improving some of its characteristics and presenting a good performance on the engine of the vehicles. In addition, this blends showed environmental benefits such a reduction on

opacity, particulate matter and CO2 emissions.

Heterogeneous Catalysts for Biodiesel Production via Esterification/Transesterification.

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Commercial processes for the production of biodiesel or Fatty acid methyl ester (FAME) involve transesterification of mono- and/or di- and/or triglyceride feedstocks derived from fats/oils of plant or animal origin with methanol in the presence of a homogeneous alkaline catalyst (i.e., sodium methoxide), with glycerin being the by-product. Such processes are limited to the use of feedstocks having very low free fatty acid (FFA) content due to soap formation associated with the FFAs which causes phase separation problems and hence lower FAME yields. Normally FFAs are stripped away in the oil purification step performed prior to transesterification. To enable the processing of higher FFA-containing feedstocks, the use of a homogeneous acid catalyst (like sulfuric acid) to convert the FFAs to FAME via esterification is also sometimes practiced.Heterogeneous catalysts provide process advantages in terms of avoiding the costly separation step associated with homogeneous catalytic processes. These also enable continuous operation that can lead to a more cost-efficient biodiesel manufacturing process. In this paper, we present novel regenerable catalyst systems for esterification and transesterification reactions. Such catalyst systems can enhance the flexibility for a biodiesel producer to use a variety of feedstocks including those containing high levels of FFAs. We also present transesterification catalysts that can show high FAME yields (>90%) even with significant FFA content.Depending on the amounts of FFA in the feedstock conversion rates of > 90% to FAME can be achieved for the esterification catalyst system.

Assessing Microbial Spoilage of Biodiesel Blends Under Aerobic and Anaerobic Conditions.

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Micro organisms are known to grow in fuel tanks where they may affect both fuel quality and the integrity of storage facilities. Mixing with sustainable, biomass-derived fuel (biodiesel) is suspected to increase these problems, but the underlying, microbiological mechanisms remain poorly understood. In this study, five different mixtures (0, 2, 5, 10, and 20% biodiesel mixed with petrochemical diesel) were incubated with microbially contaminated water under anaerobic and aerobic conditions for 51 and 29 days, respectively, and changes in chemical properties of the fuel as well as in the microbial communities were monitored. The results indicate that rapid microbial growth occurred in all mixtures. Anaerobic mixtures contained mainly fermentative bacteria, and methane-producers were less abundant (< 1% of the population). This is significant since methanogens are thought to increase rates of corrosion in oil installations by maintaining a low hydrogen concentration. Aerobic mixtures contained large amounts of fungi, and both growth and diversity of bacteria was limited, possibly as a consequence of bacteriocides excreted by the fungi or competition for organic substrates. Several conclusions may be drawn from this study: (i) in spite of significant microbial growth, the chemical properties of the fuel was not significantly altered, (ii) the groups of bacteria and fungi identified in this study should be employed in future evaluation of biocidal fuel additives rather than the standard laboratory strains, and (iii) a better understanding of the implication of fungi and fermentative bacteria in biofilm formation and MIC is urgently needed.

Lipid Content and Fatty Acid Composition of "Açai" from Different Euterpe Species.

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"Açai" is a beverage widely consumed in northern Brazil, and its popularity as a health food and a dietary component for athletes is increasing. It is prepared as an emulsion made with water and fruit pulp of palm species of the genus Euterpe, rich in lipids and anthocyanin pigments. The objective of this work was to determine the lipid content and fatty acid composition (Gas chromatography) of "Açai" from different species of Euterpe grown in northern and southern Brazil. Twenty-two samples of Euterpe edulis, E. precatoria and E. oleracea were analyzed (11 pasteurized and 11 unpasteurized). Total lipid content was 34 and 40% (dry matter) in southern and northern samples,

respectively. The main fatty acids were oleic, palmitic, and linoleic, with average values of 47, 24, and 22% for E. edulis, and 58, 24, and 10% for E. precatoria and E. oleracea. The content of oleic and linoleic fatty acids presented significant differences related to local climate, as well as the temperature at time of fruit harvest. Higher content of linoleic acid was observed in samples from southern Brazil (16-21 °C average temperature), and lower content in samples from northern Brazil (26-27 °C).

Biofuels from Castor Oil.
George Tamas, Tina Thomas, Trevor Walker, David M. Birney , Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409, USA

This study seeks to develop second-generation renewable fuels from vegetable oils using chemical methods that minimize the use of toxic reagents and the formation of wasteful and toxic byproducts. Castor oil was chosen for this because it castor beans are a non-food crop that can be grown on marginal land and has a high oil content. Its composition is unusual: eighty-seven percent is ricinoleic acid. The first part of the work consists of optimizing methodologies for the synthesis of biodiesel ethyl ester. Two possibilities were explored: base and acid catalyzed transesterification of triglycerides. The base catalyzed transesterification in the presence of a catalytic amount of potassium ethoxide proved to be a remarkably efficient process. The acid catalyzed transesterification converts the triglyceride into ethyl esters and also converts free fatty acids pre-existing in castor oil, eliminating the formation of soap as by-product.The second part of this work explores the possibility of reducing the viscosity of castor biodiesel through olefin metathesis of methylricinoleate with ethylene, catalyzed by Grubbâ??s catalyst, commonly referred to as ethenolysis.

Preparation of Soypolymers by Ring-opening Polymerization of Epoxidixed Soybean Oil.
Zengshe (Kevin) Liu, Sevim Erhan, NCAUR, ARS, USDA, 1815 N. University Street, Peoria, IL 61604, USA

Ring opening polymerization of epoxidized soybean oil (ESO) initiated by boron trifluoride diethyl etherate in methylene chloride was conducted in an effort to develop useful biodegradable polymers. The resulting polymers (PESO) were characterized using Infrared (IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), ^{1}H NMR, ^{13}C NMR, solid state ^{13}C NMR and gel permeation chromatography (GPC). The results indicate that PESO materials are highly crosslinked polymers. They have glass transition temperatures ranging from -16°C to -48°C. TGA results shows the PESO polymers are thermally stable at temperatures up to 220°C. Decomposition temperature is found mainly after 340°C.

Development of High-throughput Measurement of Canola Biodiesel Cold Flow Properties.
D. Haagenson, R. Brudvik, L. Hongjian, D. Wiesenborn, North Dakota State University, Fargo, ND, USA

Efforts are underway to evaluate the impact of canola germplasm source on biodiesel quality, especially cold-weather performance. *In situ* transesterification is a method of producing fatty acid methyl esters (FAME) directly from seed, where conventional transesterification reactions require that oil is first extracted and refined. Establishing a canola *in situ* transesterification protocol may provide a rapid screening tool for assessing elite germplasm biodiesel quality parameters. In this study, *in situ* reaction parameters were evaluated and a molar ratio of 330:1:1.2 for methanol, acylglycerides, and KOH provided >95% theoretical yields of canola FAME. FAME produced by alkaline *in situ* transesterification of canola seed and by alkaline transesterification of screw-pressed, degummed oil were analyzed for kinematic viscosity, total glycerol, acid number, moisture content, cloud point, and oxidative stability index (OSI). Cloud point, cold soak filtration test, OSI, and several other biodiesel quality parameters were also determined from FAME prepared from two North Dakota growing locations using *in situ* and conventional transesterification methods. The challenges of incorporating a high throughput screening protocol for evaluating canola biodiesel quality will be discussed.

Conversion of Wastewater Treatment Facilities into Biorefineries.
J.I. Hall, W.T. French, R. Hernandez, E. Alley, M. White, B. Holmes, A. Brown, A. Mondala, Mississippi State University, Mississippi State, MS USA

Oleaginous yeasts are a type of microorganism that can produce up to 70 percent of their body weight in oil. In biofuel production, these microorganisms are limited by the availability of cost effective carbon. A growth medium that has not been introduced for cultivating oleaginous microorganisms is wastewater. This study is designed to compare the oleaginous microorganism consortium growth on wastewater to the growth on synthetic wastewater to produce an abundant amount of oil while treating this water to Environmental Protection Agency (EPA) required treatment levels. The growth rate, oil percentage, and oil yield are measured using well-established techniques such Bligh& Dyer and transesterification. In addition, water quality is measured by determining the biochemical oxygen demand (BOD), the chemical oxygen demand (COD), and the amount of nitrates in the wastewater after the yeast growth stabilizes. These quantities will determine the efficacy of the oleaginous microorganisms assist in removing wastewater contaminants. Preliminary results show that the microorganisms are reaching oil accumulation stage within 48 hours. The use of wastewater as a growth medium did not inhibit the growth of the yeast. These results also show a maximum COD reduction of 92% after 96 hours of cultivation. This modification could potentially generate billions of gallons of oil for producing biofuels.

Alcoholysis Reaction of Epoxidized Soybean Oil.

Zuleica Lozada-Rodriguez, Galen J. Suppes, University of Missouri-Columbia, Columbia, MO, USA

Industrial products derived from vegetable oils are gaining wide popularity in many industrial applications like adhesives, coatings, plastics and urethane products. Polyols are one of the predominant reactants in the polyurethane synthesis. Soy-based polyols are potentially low-cost materials and reduced impact on the environment. In addition, the introduction of natural oils into the polyurethane products can provide an opportunity for suppliers and customers to reduce their dependence on crude oil from petroleum. The soybean oil consists primarily of triglycerides with long chain saturated and unsaturated fatty acids. The presence of this unsaturated fatty acids results in poor oxidative stability and reactive sties. This enhanced reactivity also allows for chemical modifications of the soybean oil by adding new functionalities. In this study, epoxidized soybean oil was combined with ethylene glycol and methanol to produce a molecule that contains one epoxy moiety for every two alcohol moieties at low temperature using catalyst to promote the reaction. The purpose for this study were identifying a catalyst that promotes the epoxy-ring opening reaction avoiding side reactions, kinetics study of the alcoholysis reaction of ESBO, follows by polyol production of a preferred reaction condition to use in the water-blown rigid polyurethane foam formulation study.

Selected Castorbean Genotypes Evaluated for Morphological Traits, Seed Yield, Fatty Acids, and Oil Content.

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Castorbean, *Ricinus communis* L. contains oil used in pharmaceutics, cosmetics, soap, shampoo, and as a lubricant. Castorbean is becoming a biodiesel crop because of its high oil content ranging between 30 and 60% depending upon extraction proceedures. Two hundred and three castorbean accessions are curated at the USDA, ARS, Plant Genetic Resources Conservation Unit, Griffin, GA. The objectives of this study are to determine castorbean phenotypes which can be mechanically harvested, seed numbers and weight, fatty acid analysis and oil content from 4 selected genotypes. Morphological data were recorded from field plants and seeds harvested. Gas chromatography (GC) will be used to analyze fatty acid composition and oil content was determined using nuclear magnetic resonance (NMR) from castorbean seeds. The accession, PI 265504 reached 200 cm tall and 166 cm wide as well as producing the most seeds (6514), highest seed weight (1977 g) and most oil (53 %). Fatty acid analysis will be determined. High oil producing and appropriate plant size for harvesting castorbean genotypes were produced and will offer breeders and geneticists valuable germplasm for cultivar development.

Nitrogen Derivatives of Soybean Oil and Fatty Acid Methyl Esters.

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Vegetable oil based products are eco-friendly and non-toxic in nature, which is increasing their utilization in lot of

applications. The presence of double bonds in some of the fatty acids, are attractive sites for functionalization. In this study we have used these sites for functionalization using nitrogen containing compounds and have shown the use of soybean oil, fatty acid esters, and methyl soyate as a renewable feedstock to produce a range of different materials that contain nitrogen. In the past most efforts have been concentrated on converting triglycerides to fatty amines and amides. Indeed, many industrially significant fatty amines and amides are known and widely used. More recently, we have developed novel approaches to functionalize the fatty acid chain structures to produce novel compounds, surfactants, and even polymers that contain nitrogen. Some of the approaches may have industrial relevance.