



UND SUNRISE REU-2009. Potential Research Projects and Faculty Mentors

Chemistry of Polymer Formation during Vegetable Oil Cracking – Mentors: E. Kozliak and A. Kubatova (Chem.) and W. Seames (Chem. E.)

Future reliance solely on petroleum-based sources is a concern because of the finite supply of this raw material, increasing dependence on foreign oil imports, and the contributions from petroleum-based fuel combustion to the increase in CO₂ concentration in the atmosphere. Thermal cracking in an oxygen-free environment is attractive because it models the natural conversion of TGs to petroleum, only conducted on a much shorter timescale. The proposed research is aimed to gain insights into the chemistry of vegetable oils cracking, focusing on the mechanism of formation and structure of polymers formed as by-products of crop oil cracking. The presence of this large viscous (partly solid) and poorly identified fraction is one of the major setbacks for the process' commercialization. Capitalizing on the use of analytical techniques developed in prior research, the reaction pathways will be evaluated using an on-line GC-FID/MS pyrolysis unit based on quantification of the decay of initial compounds, e.g., pure individual TGs of varied chemical structure, combined with the identification and quantification of products. The mechanism of polymer formation will be elucidated.

Accurate Aldehyde Extraction from Coal-Derived Particulate Matter – Mentors: A. Kubatova and E. Kozliak (Chem.)

Aldehydes are significant components of atmospheric aerosols including particulate matter generated upon coal and other fuel combustion. Although numerous methods have been developed for their analysis, little attention has been given to initial sample preparation including extraction. The problem is that aldehydes undergo reversible condensation (e.g., aldol condensation) resulting in the formation of various oligomers. The project tackles developing accurate methods of solvent extraction of monomer aldehydes and studying their reactions during extraction using the novel methods of accurate aldehyde analysis developed in prior research.

Modeling Atmospheric Aerosols from Sustainable Combustion Sources - Mentor: Frank Bowman (Chem. E.)

Particulate pollution from combustion sources typically contains a large number of semivolatile organic compounds that partition between the gas and aerosol phases. Computer models that describe air pollution health effects, visibility, cloud formation, and global climate all require efficient methods for calculating the aerosol phase activity coefficients that govern gas-particle equilibrium. The UNIFAC group contribution method is commonly used for organic aerosol activity coefficient calculations, but computational demands prohibit its use in large scale models. In this project, the REU student will develop computationally efficient parameterizations of the UNIFAC model for calculating organic aerosol activity coefficients.

Transformations of Trace Elements in Coal-Biomass Combustion - Mentors: Frank Bowman, Michael Mann, and Steve Benson (Chem. E.)

Combustion of biomass together with coal has the potential to reduce the carbon footprint of coal-fired electricity generation. The chemical composition of biomass used can influence the volatility and particle

size distribution of trace elements, such as Se, As, and Sb, that are released during coal combustion, leading to changes in particulate and trace element emissions to the atmosphere. In this project, the REU student will help run experiments with a 19 kW downflow combustor fed by a mixture of biomass and coal. Aerosol samples from the exhaust gas will be collected and analyzed to determine trace element concentrations and size distributions.

Modeling Trace Elements Atomization in Coal Combustion Furnaces Using a Graphite Furnace Atomic Absorption Spectrometer – Mentors: E. Kozliak and D. Pierce (Chem.) and W. Seames (Chem. E.)

The physical property data necessary to model the vapor-liquid equilibrium of TEs (e.g. As, Se, Sb) over Si, Si-Al, and Fe melts at localized combustion conditions at the micro-environmental conditions of the burning char particles are currently not available (temperatures >2400K are required, which create unsurmountable problems with accurate sampling). Our proposed innovation involves the use of AA/GFAA as an extremely high-temperature *in-situ* burning char simulator/sample collector/analytical platform (all at the same time). Currently, a robust and reliable method has been developed to determine the Arrhenius activation parameters for any target analyte. The spin-off undergraduate project will be on applying this method to TEs embedded in matrices, i.e., determining the activation parameters for TE atomization over Fe, Si, and Si-Al melts at 1900 to 2400 K. To model separately the matrix effects in the organic fraction of coal and inorganic inclusions, experiments will be conducted *with and without* carbon (using plain and metal-lined AA furnace).

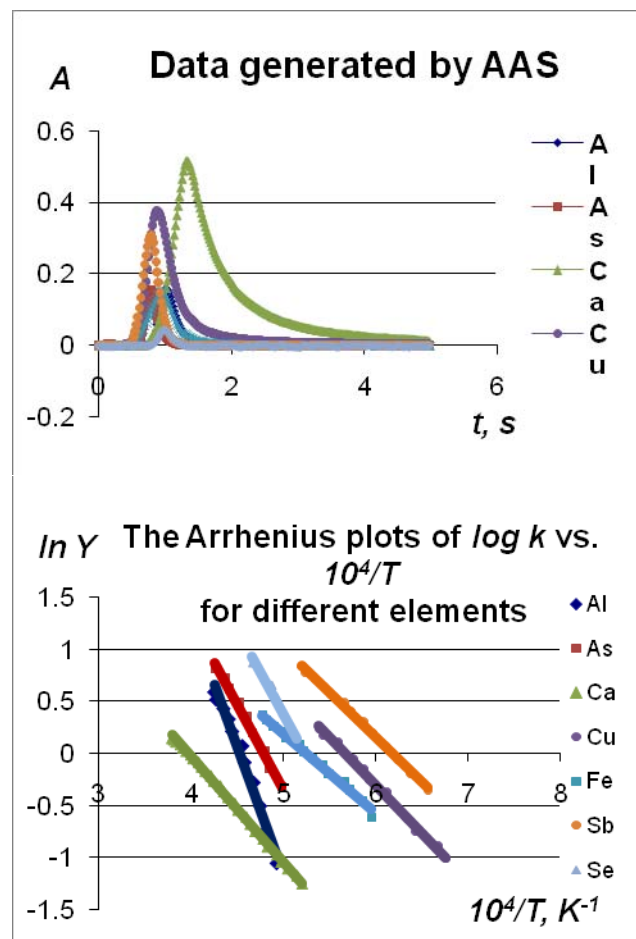
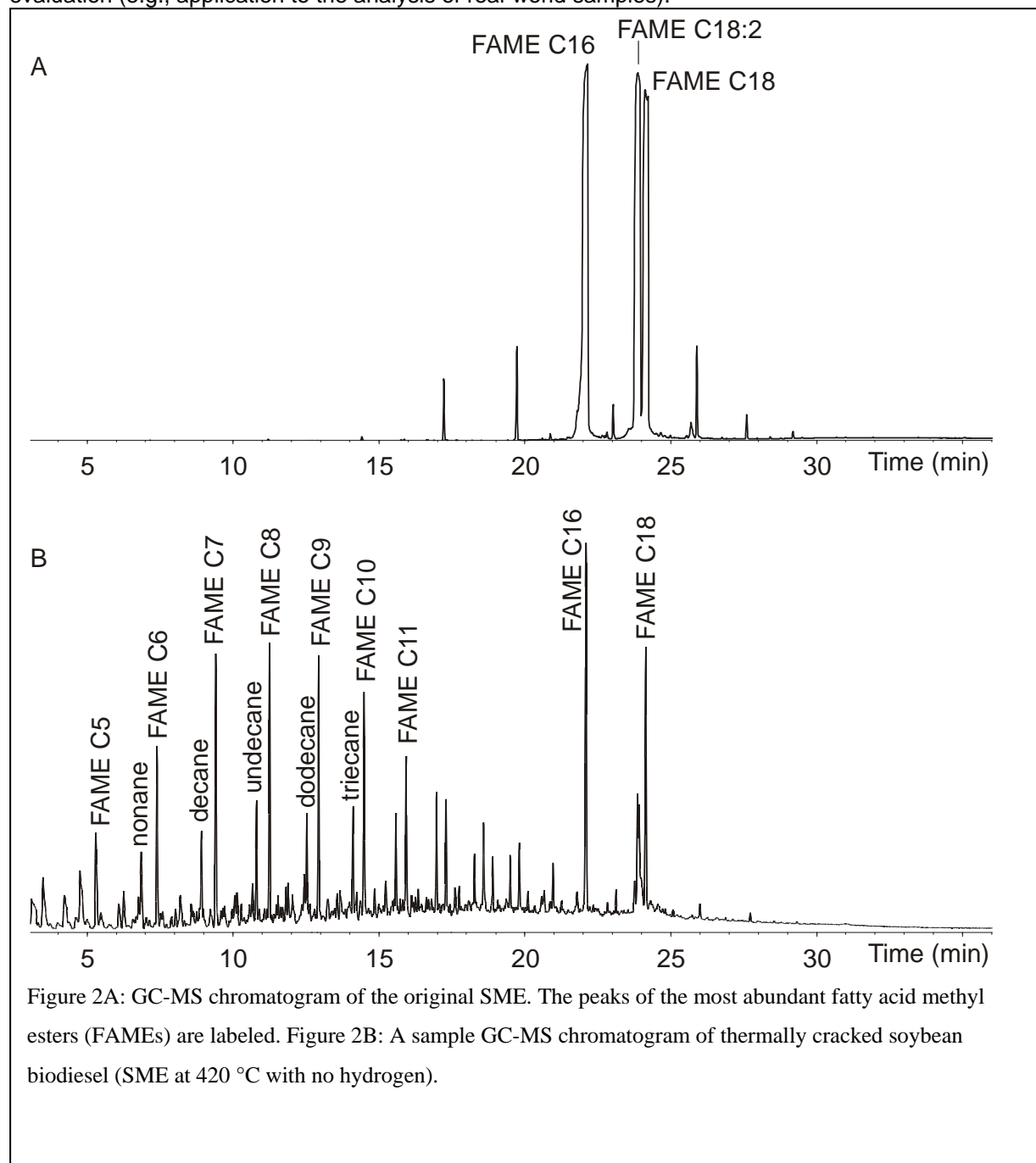


Figure 1. Data generation using AAS.

Chromatographic Characterization of Biofuels – Mentors: A. Kubatova (Chem.) and D. Muggli

(Chem. E.)

To characterize various biofuels produced from crop oils, an exact composition of the reaction products is needed. Currently, a comprehensive chromatographic method is being developed using GC with a simultaneous FID and MS detections (the former is essential for the analyte quantification whereas the latter provides accurate identification). An example is provided in Figure X. However, the reports obtained by this method consist of more than 200 data points for each sample, which need to be organized in systematic manner to enhance the speed of data processing. Thus, in this project an REU student will develop the required macro for Microsoft Excel and would collaborate with an analytical chemist on its evaluation (e.g., application to the analysis of real-world samples).



E.) Currently, we are developing several catalysts to enhance the production of biofuels from soybean and canola oil. This project involves the making of improved catalysts, testing their performances, and analyzing the quality of the resulting bio-derived fuel. Another goal of this project is to design, build, and test a sixteen-reactor system that will allow for rapid screening of catalysts for various reactions that are important in biofuels production.

Developing a New Catalyst for Photocatalytic Oxidation – Mentor: Darrin Muggli (Chem. E.)

Organophosphorous Compounds (OPCs) are pollutants posing a serious risk to human health due to their use as pesticides, insecticides, detergents, and chemical warfare agents. The objective of the proposed project is to develop a promising new type of catalysts, TiO₂ nanotubes, for the photocatalytic oxidation (PCO) of these compounds (then, their use will be expanded to advanced oxidation of chemicals obtained upon biomass conversion during the sustainable energy production). To do this, students will work with Dr. Muggli and Masters student Jordan Grasser to synthesize TiO₂ nanotubes and test their photocatalytic activity based on the following hypotheses: 1) TiO₂ nanotubes can be synthesized to possess an optimum composition of intimately mixed anatase and rutile phases, which will increase activity for OPC oxidation, 2) Doping TiO₂ nanotubes with metals will increase PCO activity, and 3) Incorporating nitrogen in TiO₂ nanotubes will make them significantly more active when exposed to both visible and ultraviolet light, which will improve destruction rate of OPCs.

High-throughput Experimentation and Combinatorial Chemistry for the Development of Catalysts for Biofuels Production - Mentors: Darrin Muggli and W. Seames (Chem. E.) and Evguenii Kozliak (Chem.)

The application of combinatorial methods with High-Throughput Experimentation (HTE) and allows the rapid synthesis and testing of catalysts. The application of these techniques in the biofuels production area is an ideal fit, as very little catalyst development work has occurred. Students interested in this project will work in one of several areas, depending on student interest. Research areas include: developing a combinatorial catalyst synthesis procedure, building and testing of the high-throughput reaction system, testing catalyst formulations, enhancing throughput by developing efficient catalyst evaluation methods, and applying statistical design of experiments to HTE methods.

Development of New Organometallic Catalysts – Mentor: Irina Smoliakova (Chem.)

Development of new efficient catalysts is of great importance for studies of fuels and chemical products from non-traditional, renewable sources. Complexes of Pd(II), particularly air and moisture stable cyclopalladated compounds, have attracted a considerable interest as catalysts in hydrogenation, polymerization of alkenes, Heck reaction, and a number of other processes.

Our research project has two major objectives: (i) synthesis and characterization of new types of cyclopalladated complexes and (ii) determination of their catalytic activity in polymerization of vinyl esters, vegetable oil cracking and other processes. Students will perform synthesis of organic ligands, preparation of organometallic derivatives and their spectral (IR, ¹H, ¹³C, ³¹P and 2D NMR) characterization.

Applications of Silica-based Nanocatalysts – Mentors: J. Zhao and D. Pierce (Chem.)

The project will focus on applications of newly developed cutting-edge electrochemical catalysts for energy conversion. While the nanocatalysts could serve as efficient catalysts in a variety of energy-related applications, the principle application will be toward direct-methanol fuel cells.

The template synthesis developed in this project has significant advantages for producing high-performance bimetallic catalysts. An important bimetallic catalyst used for energy conversion is the Pt/Ru anode material of direct-methanol fuel cells (DMFCs). A combinatorial approach to bimetallic synthesis and EIS testing will be used to optimize Pt/Ru alloy nanocatalysts as DMFC anode materials. The following effects on methanol oxidation rate and mechanism will be investigated by preparing Pt/Ru

nanocatalysts with the required morphologies: 1) different average size of Pt/Ru nanoclusters, 2) different Pt:Ru ratios, 3) different Pt/Ru loading, 4) different silica nanoparticle sizes, 5) degree of metal reduction.

Study of Fundamental Chemistry of Silica-based Nanocatalysts – Mentors: J. Zhao (Chem.) and D. Muggli (Chem. E.)

The objective here is to learn how the nanoscale surface structure affects catalytic activity. For this purpose, electro-oxidation of methanol will be used to evaluate the catalytic activity of Pt nanocatalysts. This reaction has been widely studied with a variety of platinum catalysts – including Pt-modified nanomaterials – which makes it an excellent model.⁶⁻¹⁷ Electrochemical impedance spectroscopy (EIS) will be used to extract both thermodynamic and kinetic parameters associated methanol oxidation by Pt nanocatalysts and to identify any enhanced functionality associated with their structure. This work will be supported by vigorous chemical/structural characterization using electron microscopy (TEM, SEM), X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), mass spectrometry-inductively coupled plasma spectrometry (MS-ICP), and dynamic light scattering.

Synthesis of Silica-based Nanocatalysts – Mentor: J. Zhao (Chem.)

Understanding of the fundamental chemistry underlying the formation and behavior of the silica-based nanocatalysts is critically needed. A detailed study of metal and metal-ion chemistry at the nanoscale will include crystalline structures, thermodynamic/optical properties and catalytic activity. This work will identify key functional differences in catalytic behavior associated with nanoscale structure. Furthermore, the nanoparticles developed here may open new avenues in the field of nanotechnology.

The project will focus on syntheses of nanodimensional silica-based metal nanocatalysts. A series of highly efficient and low cost metallic silica nanocatalysts will be developed (with the subsequent aim of using them in processing of chemicals obtained as a result of vegetable oil and biomass pyrolysis). Compared to traditional metal-particle catalysts, the planned nanocatalysts will have three advantages: (a) higher catalytic efficiency, (b) lower cost, and (c) more controllable properties. The significance of the proposed work lies on the new approach for preparing low cost and high activity metallic nanomaterials for energy-related catalysis.

Computational Chemistry Research in Coal – Mentor: Dr. Mark Hoffmann (Chem.).

Our research group has interest in quantum mechanical descriptions of the electronic structures of molecules and reactions of relevance to the understanding of combustion processes. Our primary focus is on chemical reactions that are difficult or impossible to measure accurately in the laboratory, so that the computational results are critical to developing a correct understanding of the chemical systems. We are able and interested in examining reactions that involve excited electronic surfaces, as a result of thermal or photochemical processes. We are particularly interested in reactions that involve O₂, O₃, and oxides of nitrogen with coal-mimetic molecules and compounds of trace elements found in coal (e.g., Se, As). Recent work has extended our prior interest in homogeneous reactions to reactions on clusters that mimic surfaces. The student will become involved in one of the ongoing projects and will work closely with the mentor and one of his upper division undergraduate research students, graduate students or postdoctoral research associates. The student will develop familiarity with the use of well established main techniques of modern quantum chemistry (e.g., Self Consistent Field (SCF) method, hybrid density functional methods such as B3LYP, and second-order Møller-Plesset perturbation theory), and novel multireference perturbation theory approaches developed at UND, in the context of a combustion-relevant chemical problem. The results to be obtained will be matched with the experimental results obtained by chemists (Kozliak) and chemical engineers (Seames).

Optimization of Material Formulation for Efficiency of Nanobiocomposite Organic Photovoltaic – Mentor: R. Parker (Chem. E.)

This project utilizes biopolymers for photonic-electronic conversion, organic nano-semiconductors [such as carbon nanotubes, poly(styrenesulfonate), poly(3,4-ethylenedioxythiophene)], for charge carrier transport to improve charge carrier mobility, and formulation ingredients such as surfactants and thickeners. The objective is to develop optimal formulations and treatments for the organic photovoltaic devices.

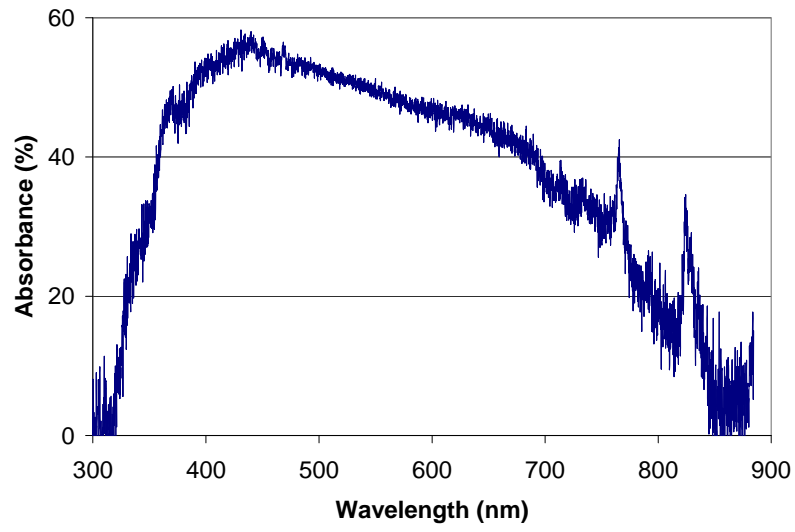


Figure 3. Absorption spectrum of a typical nanobiocomposite organic photovoltaic material