UNIVERSITY OF DELAWARE
ENGINEERING

DEPARTMENT OF CHEMICAL
AND BIOMOLECULAR ENGINEERING

DEPARTMENTAL RESEARCH REVIEW

4TH YEAR TALKS

WEDNESDAY, JUNE 01, 2022

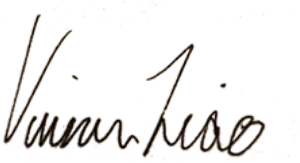
ABSTRACTS AND SCHEDULE GUIDE

PERKINS STUDENT CENTER | 325 ACADEMY STREET • NEWARK DE 19716

Welcome to our Annual Winter Research Review. We are pleased that you can join us. The focus of today's program—research presentations by our fourth-year graduate students— provide one of the best opportunities to learn about the research of our senior graduate students and their faculty advisors. Throughout the day you can also visit research posters presented by our third-year students.

Our graduate program is the center of our principal missions of scholarship, education, service, and innovation. We hope that you will enjoy this opportunity to learn more about our department and its activities, as well as to meet the students and faculty.

Eric M. Furst
Professor and Department Chair
Department of Chemical and Biomolecular Engineering



Vinson Liao
President of Colburn Club
The Graduate Student Organization

Colburn Club is the graduate student organization in the Chemical and Biomolecular Engineering Department, which is comprised of representatives from each year as well as a number of members filling specialized roles. The primary functions of the club are to organize research reviews and social events for the department, in addition to serving as one line of contact between the students and the faculty. We hope you enjoy this event and can join us again in the future.

The Colburn Club

www/che.udel.edu/cc

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2021 – 2022 WINTER RESEARCH REVIEW

8:00 AM – 8:50 AM	BREAKFAST	West Lounge
8:50 AM – 9:10 AM	Welcome & Opening Remarks Colburn Club and Department Chair, Eric Furst	Rodney Room
10:45 AM – 11:45 AM	Poster Session	East Lounge
11:45 AM – 1:00 PM	LUNCH Feature Speaker: Kevin Solomon	West Lounge
4:00 PM – 5:15 PM	Industry Mixer	West Lounge

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2021 – 2022 WINTER RESEARCH REVIEW

Location: **RODNEY ROOM**
Schedule of Talks and Abstracts

8:50 AM	**Welcome & Opening Remarks**	**RODNEY ROOM**
9:20 AM	Forder, James **Quantitative Prediction of MAb Interactions with Experimental and Computational Approaches** Advisor: Christopher Roberts Committee Members: Arthi Jayaraman & Eric Furst	
9:40 AM	Green, Erica **High-yielding Processes for Transient and Stable Expression of the SARS-CoV-2 Receptor Binding Domain in HEK293 Cells** Advisor: Kelvin Lee Committee Members: April Kloxin & Millicent Sullivan	
10:00 AM	Herman, Chase **Behavior of Host-cell Protein Particulates in Protein A and Ion-exchange Chromatography** Advisor: Abraham Lenhoff Committee Members: Eric Furst & Kelvin Lee	
10:20 AM	Butler, Neil ***De Novo* Biosynthesis and Site-Selective Ribosomal Incorporation of a Nitroaromatic Non-Standard Amino Acid** Advisor: Aditya Kunjapur Committee Members: Wilfred Chen & Eleftherios Papoutsakis	
10:40 AM	**BREAK & POSTER SESSION**	**EAST LOUNGE**
11:45 AM	**LUNCH (feat. Kevin Solomon)**	**WEST LOUNGE**

1:10 PM	Jones, Michaela **Profiling of Putative Threonine Transaldolases for Biosynthesis of Non-Standard Amino Acids** Advisor: Aditya Kunjapur Committee Members: Wilfred Chen, Millicent Sullivan, & Ethan Garner (Harvard)
1:30 PM	Sen, Sabyasachi **Development of an Engineered *Escherichia Coli* N-Degron Pathway for Enhanced Control of Post-Translational Protein Fate** Advisor: Aditya Kunjapur Committee Members: Wilfred Chen & Kelvin Lee
1:50 PM	Woodward, Ian **3D Printed Lattices for Next-Gen Pulmonary Therapeutics** Advisor: Catherine Fromen Committee Members: April Kloxin, Abraham Lenhoff, & Jason Gleghorn
2:10 PM	Thomson, Will **The Nature and Physiological Impact of Small RNA Cargo in Microparticles from Megakaryocytes and Chinese Hamster Ovary Cells** Advisor: Eleftherios Papoutsakis Committee Members: Catherine Fromen & April Kloxin
2:30 PM	**BREAK** **EAST LOUNGE**
2:50 PM	Otten, Jonathan **Syntrophic Co-Cultures of *Clostridium* Organisms to Produce C6-C8 Alcohols and Carboxylic Acids** Advisor: Eleftherios Papoutsakis Committee Members: Wilfred Chen, Catherine Fromen, & Aditya Kunjapur
3:10 PM	Meisenhelter, Joshua **Truncated Coiled-Coil Peptides as a Building Block for Hierarchical Material Synthesis** Advisor: Christopher Kloxin Committee Members: April Kloxin, Darrin Pochan, & LaShanda Korley
3:30 PM	Cassel, Samantha **Lentiviral Reporters for Temporal Characterization of Cell Activation in Response to Dynamic Stimuli** Advisor: April Kloxin Committee Members: Catherine Fromen & Wilfred Chen
4:00 PM	**INDUSTRY MIXER** **WEST LOUNGE**

Quantitative Prediction of MAb Interactions with Experimental and Computational Approaches

James K. Forder
Advisor: Christopher J. Roberts
Committee Members: Arthi Jayaraman, Eric M. Furst

Monoclonal antibodies (MAbs) are a prominent sector of the biopharmaceutical industry, with dozens of FDA-approved therapies for treating diseases including a range of cancers and autoimmune disorders. Many challenges remain in the process of developing MAb therapies including candidate selection and formulation development, which are both multiparameter optimization problems that span an intractable space of possibilities. Rational and efficient workflows are essential for choosing a developable candidate (i.e., one that can be developed into a drug product free from debilitating issues in manufacturing, stability, or efficacy), and successfully determining the formulation conditions (e.g., pH, co-solutes and ionic strength) of the final drug product. There is a demand for tools that can be used to predict experimental properties relevant to developability of a given protein candidate, with less time- and material-intensive methods. Of particular concern is irreversible aggregation, a common but not well-understood form of MAb degradation that reduces shelf life and can lead to a detrimental immunogenic response in patients. MAb self-interactions at low and high protein concentrations are of interest as they are at least phenomenologically related to the mechanisms of aggregation and other problematic behaviors such as phase separation and high viscosity.

Recent work used low-concentration self-interaction experimental data in the form of static light scattering (SLS) to parameterize low-resolution coarse-grained simulations that can quantitatively predict high-concentration self-interactions for a subset of behaviors. Additionally, prior experimental work has semi-quantitatively connected SLS to aggregation rates for formulations as a function of pH and salt concentration. Each of these studies motivates further investigation that captures a broader range of MAbs, especially those with net attractive self-interactions. This presentation will focus on coarse-grained molecular simulations at low and intermediate resolution that provide quantitative predictions of high-concentration MAb self-interactions. Experimental low- to high-concentration SLS measurements are used to parameterize the models and validate the computational predictions, while dynamic light scattering measurements provide an independent measurement of self-interactions that also includes hydrodynamic interactions.

High-yielding processes for transient and stable expression of the SARS-CoV-2 receptor binding domain in HEK293 cells

Erica A. Green
Advisor: Kelvin H. Lee
Committee Members: April M. Kloxin and Millicent O. Sullivan

Human embryonic kidney 293 (HEK293) cells are an important host platform for production of therapeutic proteins and viral vectors. While other mammalian cell lines such as Chinese hamster ovary (CHO) and murine myeloma (NS0) cells generally can produce therapeutics at higher titer, the use of HEK293 cells is advantageous when proteins with humanized post-translational modifications are desired. Over the last few decades, HEK293 cells have been more widely used in scalable, serum-free protein expression systems, but further work in vector engineering and cell line development is needed to improve transient and stable protein production processes.

We established transient and stable process development workflows for production of the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) spike protein receptor binding domain (RBD). HEK293 was selected as the expression system because of the need to produce recombinant RBD (rRBD) protein with human characteristics. Transient process development involved screening of vector elements, transfection conditions, and process parameters to identify the most productive rRBD expression workflow. Stable cell line development involved the generation of a rRBD-expressing pool and generation of clonal cell lines that were screened for rRBD titer. Bio-layer interferometry (BLI) and enzyme-linked immunosorbent assay (ELISA) methods used to measure rRBD concentrations in unpurified supernatant samples enabled efficient comparison of the titers from different processes and clones. Ultimately, these methods can be used to develop transient and stable production processes for other proteins expressed in HEK293 cells.

Behavior of host-cell protein particulates in protein A and ion-exchange chromatography

Chase Herman
Advisor: Abraham Lenhoff
Committee Members: Eric Furst and Kelvin Lee

Host-cell proteins (HCPs) represent an important class of impurities that downstream bioseparations are designed to remove, and recent studies have shown that aggregated particulates in monoclonal antibody (mAb) processes may be rich in HCPs. We investigate the composition and chromatographic behavior of these particulates to better understand their implications for downstream bioprocessing. Clarified harvest cell culture fluid (HCCF) and protein A eluate (PAE) pools from a mAb manufacturing process were fractionated using size exclusion chromatography, demonstrating that both relatively large and somewhat smaller particulates may survive the protein A capture operation. Proteomic analysis of these particulates reveals that hundreds of constituent HCP species may be present, despite low overall HCP concentrations. Many of the constituent HCPs were shared among HCCF and PAE pools, including several species that have been deemed to represent a high risk to therapeutic products. This suggests that particulates partially mediate HCP persistence, and batch adsorption experiments were performed to survey this phenomenon using confocal laser scanning microscopy. Experiments with mAb Select Sure LX, a protein A resin, indicate that HCCF particulates adsorb at neutral pH and coelute at low pH. Comparison of samples with and without added mAb suggests that the particulates compete with the mAb for the resin surface, which may be exploited to partially clear impurities using high-pH washes, and further experiments demonstrate the ability of anion-exchangers to sequester particulates that remain in the PAE.

De Novo Biosynthesis and Site-Selective Ribosomal Incorporation of a Nitroaromatic Non-Standard Amino Acid

Neil Butler
Advisor: Dr. Aditya Kunjapur
Committee Members: Dr. Wilfred Chen, Dr. E. Terry Papoutsakis

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Nitroaromatic functional groups can impart valuable properties to chemicals and to biological macromolecules including polypeptides. The nitroaromatic amino acid p*ara*-nitro-L-phenylalanine (pN-Phe) in particular has been applied in proteins as an immune stimulating and fluorescence quenching residue. Currently, nitroaromatic chemical synthesis methods, including that of pN-Phe, do not follow green chemistry principles and limit the use of pN-Phe in engineered bacterial cells for *in situ* applications. To this point, metabolic engineering efforts toward *de novo* nitro-product biosynthesis and investigation into nitro-forming enzymes has been limited. Through the development of metabolic synthesis pathways for pN-Phe paired with orthogonal translational machinery, bacteria can be engineered to autonomously utilize an expanded genetic code with nonnative chemistries.

In this work, I present an integrated *de novo* heterologous pathway for the production of pN-Phe in *Escherichia coli.* Here, I utilized previously characterized genes for the biosynthesis of an amine precursor (*para*-aminophenylalanine) with a newly discovered nitro-synthesizing enzyme identified through screening of putative diiron monooxygenases from nature. Further optimization of the chassis, plasmid constructs, and media conditions, enabled me to improve pN-Phe biosynthesis to near millimolar levels in relevant culture conditions. Then, through fluorescence-based screening, I identified orthogonal translational machinery capable of selective incorporation of pN-Phe within proteins. Through integration of the metabolic pathway with this orthogonal translational machinery, we have created an *E. coli* strain capable of *in situ* use of an expanded, nitroaromatic amino acid-containing genetic code.

Profiling of putative threonine transaldolases for biosynthesis of non-standard amino acids

Michaela Jones
Advisor: Dr. Aditya Kunjapur
Committee Members: Dr. Wilfred Chen, Dr. Millicent Sullivan, Dr. Ethan Garner (Harvard)

Beta-hydroxy non-standard amino acids (β-OH-nsAAs) have broad utility as small molecule drugs, precursors for beta-lactam antibiotics and building blocks for introducing novel functionality into proteins. Despite the valuable applications for these non-standard amino acids, organic synthesis routes are expensive and documented for only a limited number of β-OH-nsAA and existing biosynthetic approaches are limited by unfavorable equilibrium dynamics. A recently discovered enzyme class of threonine transaldolases can address the current limitations for β-OH-nsAA biosynthesis through a stereo-selective and thermodynamically favorable aldol condensation of an aromatic aldehyde and L-threonine. We have probed the substrate specificity of a TTA from *Pseudomonas fluorescens* to access novel β-OH-nsAAs. To explore the specificity of this enzyme class more broadly, we have expressed and characterized naturally occurring, putative TTAs. Through the screen of putative TTAs, we have identified different enzymes with broader substrate scope, lower threonine affinity, and faster initial reaction rates. To characterize the broad specificity of many TTAs, we optimized a high-throughput absorbance-based assay that couples an alcohol dehydrogenase with a TTA to produce a measurable output of enzyme activity. We have also produced β-OH-nsAAs in metabolically active, engineered *E. coli* cultures, a novel chassis for β-OH-nsAA production. Overall, our work helps identify new candidate enzymes that could enable biological synthesis of valuable small molecules and building blocks that expand protein functions.

Development of an engineered *Escherichia coli* N-degron pathway for enhanced control of post-translational protein fate

Sabyasachi Sen
Advisor: Aditya Kunjapur
Committee Members: Wilfred Chen & Kelvin Lee

From biocontainment to biosensing, modern synthetic biology research requires unprecedented control over the expression and depletion of proteins. As we seek to engineer tight, transient changes in protein concentration, there remains a need for genetic tools that can carefully monitor and manipulate protein fate. Notably, challenges in the space such as undesired protein persistence can be better resolved at the downstream post-translational stage as opposed to the upstream transcriptional stage. Our focus rests on creating degradation tools that are modular in strength, minimally invasive to the protein's function, and can be conditionally activated to initiate proteolysis. Towards this end, we are developing a protein degradation tool that is built upon the *Escherichia coli* N-degron proteolysis pathway. To achieve this, we engineer the interactions between expressed proteins carrying short, conditionally destabilizing N-terminus motifs (N-degrons) and the proteins that modify, enhance, and initiate proteolysis (N-recognins) within a model organism. From there, we combine synthetic biology principles and natural-to-synthetic design to better understand the capabilities of the degradation pathway, and then subsequently expand its functionality.

In this talk, I will outline my work to develop and characterize a dual fluorescent protein reporter assay that monitors protein degradation. Working towards a robust and accessible tool, we characterized protein accumulation phenomena to provide an understanding of long-term protein fate within the cell. To expand our knowledge of pathway substrates, we tested a series of natural and synthetic degrons. Additionally, I will outline our prototypes of novel degradation systems driven by heterologous expression of eukaryotic N-recognins. I will conclude by outlining ongoing work regarding engineering the conditional and complete depletion of essential proteins in a biocontainment application.

3D Printed Lattices for Next-Gen Pulmonary Therapeutics

Ian R. Woodward
Advisor: Catherine A. Fromen
Committee Members: April M. Kloxin, Abraham M. Lenhoff, and Jason P. Gleghorn

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3D printing and additive manufacturing have seen rapid development in recent history, making the technology relevant across a variety of research and industrial sectors. In addition to on-demand manufacturing and reduced waste, 3D printing facilitates the realization of highly intricate structures like periodic lattice networks. These structures are accessible through a wide range of design parameters, which has made them useful in the contexts of catalysis, thermal management, structural support, biomedical devices, and even consumer products. Simultaneously, the COVID-19 pandemic has highlighted the difficulties of treating respiratory illnesses, which have been the leading causes of death worldwide, for over 30 years. This is due in part to the complexity of the lungs, which exhibit a range of length scales, transport phenomena, and biological responses–all of which are difficult to characterize *in vivo* and prohibitively challenging to fully replicate *in vitro*. As a result, modern inhalable therapeutics stem from *in vitro-in vivo* correlations (IVIVCs) developed in the mid-to-late 20th century. Here, we will showcase the ways in which we are leveraging 3D printing to drive innovation in inhalable therapeutics, to develop not just devices for administration but also platforms to approximate the full lung space.

In this talk, we demonstrate a method for generating lattice structures capable of conforming to an arbitrary configuration. Using a Carbon M1 3D printer, we assessed printability at unit cell length scales ranging from 0.5 to 3.5 mm and strut diameters ranging from 0.11 to 1.05 mm. Upon characterization, we identified trends in dimensional deviations that depend on length scale and resin chemistry, and we implemented a method to compensate for these defects at the design stage. We further investigated the fluid properties of two common lattice geometries in pipes ranging from 12 to 52 mm in diameter and compared the measured pressure gradient to published correlations. Finally, we will discuss the performance of these lattice structures in heterogeneous systems and the implications for 3D printed devices in pulmonary medicine. Through these continued developments, this work supports the promise of 3D printing to bring tailored solutions to any application and the potential to design the next generation of IVIVCs informed by patient-specific metrics and dynamics.

The Nature and Physiological Impact of Small RNA Cargo in Microparticles from Megakaryocytes and Chinese Hamster Ovary Cells

Will Thompson
Advisor: Eleftherios Papoutsakis
Committee Members: Catherine Fromen, April Kloxin

Extracellular vesicles—lipid bilayer-bound particles of less than one micron in diameter—are produced by every cell type and increasingly recognized as key to intercellular communication. Subcategorized as "exosomes" (derived from late endosomes) and "microparticles" (derived from the plasma membrane), these vesicles transport proteins, lipids, and nucleic acids between cells. Small RNA cargo—thought to be most responsible for inducing phenotypic change in target cells—is of particular note.

The properties of microparticles derived from megakaryocytes (platelet-producing cells) are well-defined. These vesicles promote the proliferation and subsequent megakaryopoiesis of hematopoietic stem and progenitor cells, even in the absence of thrombopoietin, an important finding for both *in vitro* and *in vivo* platelet production efforts. This function is primarily due to the action of two small RNAs: hsa-miR-486-5p and hsa-miR-22-3p. However, while increased shear stress (similar to that experienced by megakaryocytes *in vivo*) is known to promote microparticle production by megakaryocytes, the impact of this stress—and additional relevant factors, such as culture age—on the microparticles' small RNA levels has never been studied. To this end, we investigate and contrast methods for shear-induced megakaryocytic microparticle production, giving special attention to variation in the particles' small RNA profiles. The collective findings suggest a synchronicity between microparticle loading and release machinery which changes over time and becomes disturbed by various culture stresses, including shear stress. We observe a similar dynamic in microparticles released from Chinese hamster ovary cells, themselves the workhorses of the biopharmaceutical industry. The way forward, then, involves manipulating culture stressors and other microparticle harvest conditions such that the particles' cargo can be selectively enriched or depleted in a scalable process. Enriched megakaryocytic microparticles offer promise as ultra-powerful inducers of stem cell growth and megakaryopoiesis, which, as described previously, is crucial for platelet production. Meanwhile, depleted such particles offer excellent unsullied vehicles for targeted delivery of choice exogenous cargo to stem cells.

Syntrophic Co-Cultures of *Clostridium* Organisms to Produce C6-C8 Alcohols and Carboxylic Acids

Jonathan Karl Otten
Advisor: Eleftherios T. Papoutsakis
Committee Members: Wilfred Chen, Catherine Fromen, Aditya Kunjapur

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Synthetic syntrophic co-cultures provide several advantages for the renewable production of target biofuels and chemicals. Engineering all desired metabolic pathways into one organism is difficult, but in a co-culture, each organism can specialize according to their natural and engineered capabilities while sharing metabolites and proteins. This project explores co-cultures of *C. acetobutylicum* (*Cac*), an industrial solventogen that produces ethanol, butanol, and acetate; *C. kluyveri* (*Ckl*), which can elongate acetate into longer-chain carboxylic acids; *C. ljungdahlii* (*Clj*), an acetogen that can capture carbon dioxide to produce ethanol and acetate; and *C. saccharolyticum* (*Csac*), which can quickly produce large amounts of ethanol and acetate. Butanol, hexanol, and octanol, as well as their respective carboxylic acids, are common industrial chemicals, but they are currently produced from petroleum-based processes. Syntrophic co-cultures of *Clostridia* promise a sustainable and green replacement.

In these co-cultures, an engineered high-ethanol-producing strain of *Cac* consumes glucose and produces ethanol, acetate, carbon dioxide, butyrate, and butanol. The ethanol and acetate are elongated by *Ckl* to create valuable hexanoate and octanoate, which can be converted by either *Cac* or *Clj* into their respective alcohols, which are easier to extract from the media. Co-cultures of *Cac* and *Ckl* and *Csac* and *Ckl* have been studied. *Clj* can be added to these co-cultures to capture the carbon dioxide produced by the co-culture organisms, which raises carbon efficiency and lowers costs. Notably, this work has resulted in the highest-observed hexanoate production from *Ckl* without concurrent in-reactor capture. Co-cultures of *Csac* and *Ckl* produce more hexanoate more quickly than any published co-culture. This work also provides more insight into co-culture biology, as both flow cytometry and fluorescent microscopy have provided evidence of cell contact and protein sharing between co-culture members of different species. Altogether, this work elucidates how co-cultures can expand the metabolic space by unlocking and better utilizing the capabilities of all co-culture members so that we can deploy more environmentally sustainable means of chemical production.

Truncated Coiled-Coil Peptides as a Building Block for Hierarchical Material Synthesis

Joshua Meisenhelter
Advisor: Christopher Kloxin
Committee Members: April Kloxin, Darrin Pochan, LaShanda Korley

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Proteins achieve incredibly complex tasks which we often cannot mimic by modern materials. The intricate functions of proteins arise from their hierarchical structure and the presence of various chemical handles in exact locations based on the folding of the protein; However, proteins are often limited in their materials applications due to the difficulty of modification for specific applications. This work investigated using a peptide-based material to utilize the exact display of chemistry and self-assembling properties of proteins, while allowing for diverse modifications to expand the toolkit of synthesis pathways for hierarchical peptide materials.

The peptides used in this work were computationally designed to form 29amino acid residue coiled-coils that are stable as an individual unit and have an exact display of chemistry that can be modified for a multitude of applications. Previous work demonstrated the ability to use this coiled-coil peptide system and from a rigid-rod structure through N-terminal modifications. This work expands upon this work by truncating the 29 amino acid coiled-coil sequence to 15 amino acids. By reducing the size of the repeat unit, the degree of modification that can be achieved in hierarchical material is increased. The sub-unit stability was investigated through circular dichroism, and displayed random coil behavior; However, upon covalent linkage two 15 amino acid peptides by their N-termini, the peptides were able to polymerize into a rigid-rod of coiled-coils. These rigid-rod polymers were observed to have a width of <6nm and a length >2μm as characterized by cryo-electron microscopy. The proposed mechanism of assembly relies on the transient formation of unstable coiled-coils with overhanging 15 amino acid peptide strands that act as the initiation and propagation site for polymerization into rigid-rods. This unique assembly pathway resulted in rods longer than those previously reported, which previously reached lengths on the order of 1μm, which is less than half what was observed in truncated sequence rods. The newly developed 15 amino acid peptide sequence creates the possibility of unique material assembly pathways and polymer distributions resulting in broader applicability of this system to further materials applications that would have previously been inaccessible.

Lentiviral reporters for temporal characterization of cell activation in response to dynamic stimuli

Samantha Cassel
Advisor: April Kloxin
Committee Members: Catherine Fromen, Wilfred Chen

Fibrosis, a class of diseases characterized by accumulation of scar tissue, is driven by the differentiation of fibroblasts, among other cell types, into activated myofibroblasts. This activation is crucial to healthy healing after injury, where myofibroblasts facilitate wound contraction and secrete matrix proteins for tissue regeneration. However, when activation persists after complete wound healing, excessive protein deposition leads to increased tissue stiffness and eventual organ failure. This persistence is multifaceted and thought to be driven by mechanical feedback loops that continually activate fibroblasts, as well as through crosstalk that encourages myofibroblastic differentiation of surrounding cell types such as epithelial cells. Activation is often assessed by characterizing the expression of a cytoskeletal protein called alpha smooth muscle actin (αSMA), traditionally quantified through destructive end-point techniques that provide population averages. These methods (RT-qPCR, western blot, immunostaining) are often limited by large error owing to the inherent heterogeneity of myofibroblast populations and highlight the need for more sophisticated tools to capture these dynamics. In this work, we demonstrate use of lentiviral reporters to assess individual and collective fibroblast activation for characterizing real-time cell response to mechanical and biochemical cues.

The reporter system utilized provides low-level constitutive expression of DsRed fluorescent protein, while ZsGreen fluorescent protein is conditionally expressed as the cell produces αSMA. Two versions of the virus were tested: one with a destabilized ZsGreen, where fluorescence dissipates quickly after expression, and a stable ZsGreen, where fluorescent protein accumulates and fluorescence persists over longer timescales. With emphasis on different timescales of interest (e.g., hours to days), each system provides unique insights into dynamic activation behavior not captured with static assessment of αSMA protein expression. This reporter system can be utilized across a wide array of cell types and can further be applied to patient-derived human cells, providing a complementary approach to transgenic reporter animal models. Work is ongoing to implement these reporters in dynamically modulated systems for more insights into fibroblast activation and persistence, aiming to move towards developing more representative *in vitro* disease models. With tools like these, we can improve our understanding of fibrosis progression and motivate new approaches for treatment.

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Location: **EWING ROOM**
Schedule of Talks and Abstracts

9:20 AM	Oliveira, Nicholas **Evidence for Caffeine's Positive Impact on HOR/HER Activity Through Water Rearrangement as Opposed to Direct Impact on the Interfacial Electric Field** Advisor: Yushan Yan Committee Members: Marat Orazov & Feng Jiao	
9:40 AM	Matz, Stephanie **Electrochemically-Driven CO2 Separation from Ambeint Air using Hydroxide Exchange Membranes** Advisor: Yushan Yan Committee Members: Raul Lobo & Dionisios Vlachos	
10:00 AM	Overa, Sean **Pure and Concentrated Acetate Production Via Electrochemical CO2/CO Reduction** Advisor: Feng Jiao Committee Members: Raul Lobo & Dionisios Vlachos	
10:20 AM	Shin, Haeun **Understanding Acetate Selectivity in Electrochemical CO Reduction** Advisor: Feng Jiao Committee Members: Dionisios Vlachos & Yushan Yan	
10:40 AM	**BREAK & POSTER SESSION**	**EAST LOUNGE**
11:45 AM	**LUNCH (feat. Kevin Solomon)**	**WEST LOUNGE**
1:10 PM	Ding, Haoran **Electrochemical Generation of Reactive Intermediates as a Tool for Aromatics Upgrading** Advisor: Marat Orazov Committee Members: Raul Lobo & Feng Jiao	

1:30 PM	Steinman, Eric **Ethylbenzene via Consecutive Oxidative Dehydrogenation of Ethane and Benzene Alkylation** Advisor: Marat Orazov Committee Members: Douglas Buttrey & Yushan Yan
1:50 PM	Surendhran, Roshaan **Developing an Encapsulated Hydrogenation Catalyst for the Direct Conversion of Glucose to Ethylene Glycol** Advisor: Marat Orazov Committee Members: Raul Lobo & Dionisios Vlachos
2:10 PM	Baker-Fales, Montgomery **Microwave Heating-Induced Temperature Gradients in Liquid-Liquid Biphasic Systems** Advisor: Dionisios Vlachos Committee Members: Abraham Lenhoff & Raul Lobo
2:30 PM	**BREAK** **EAST LOUNGE**
2:50 PM	Kurdziel, Sophia **Beyond Semi-Empirical Energy Scaling: Correlations and Theory for Vibrational Frequencies and Thermochemical Quantities** Advisor: Dionisios Vlachos Committee Members: Raul Lobo & Marat Orazov
3:10 PM	Lee, Seungyeon **Theoretical Insights into the Heterogeneous Hydroformylation of Ethylene on Atomically Dispersed Rh-Oxide Promoter Pairs** Advisor: Dionisios Vlachos Committee Members: Raul Lobo & Marat Orazov
3:30 PM	Zong, Xue **Statistical-learning-aided Multiscale Modeling of Structure-sensitive Catalytic Reactions** Advisor: Dionisios Vlachos Committee Members: Antony Beris & Feng Jiao
4:00 PM	**INDUSTRY MIXER** **WEST LOUNGE**

Evidence for Caffeine's positive impact on HOR/HER activity through water rearrangement as opposed to direct impact on the Interfacial Electric Field

Nicholas Oliveira
Advisor: Yushan Yan
Committee Members: Professor Marat Orazov and Professor Feng Jiao

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The inexplicable pH dependence of HOR/HER leading to the apparent 2 orders of magnitude loss in Platinum Group Metal (PGM) activity has plagued both our practical design of electrochemical devices as well as our fundamental understanding of electrode/electrolyte interfaces.[1] Explanations for this effect have ranged from the presence of adsorbates specific to alkaline conditions,[2] shifts in the electrode potential of zero free charge (pzfc) and subsequent strengthening or weakening of the interfacial electric field,[3] the orientation of interfacial water molecules and changes in the binding energy of reaction intermediates.[4–6] Recently, several innovative *in situ* techniques have been used to probe these theories, ranging from Fourier Transform Infrared Spectroscopy (FTIR) to X-Ray Absorption Spectroscopy (XAS), as well as novel computational studies to isolate the contributions of surface adsorbed hydroxide and water.[2–4,7] Additionally, the identification of Caffeine as a "double-layer dopant" capable of improving HOR/HER activity 5-fold on Pt(111) by Intikhab et al. has provided the field with a model system with which to systematically test these theories.[8] In this work, we demonstrate that specifically adsorbed caffeine does change the strength of the interfacial electric field as measured through CO stark tuning in Attenuated Total Reflection-Surface Enhanced Infrared Reflection Absorption Spectroscopy, though this change, which is also found for numerous other compounds, is not responsible for the increased activity. Further, SEIRAS's high surface sensitivity allows direct probing of the interfacial water's hydrogen bonded structure, highlighting the changes that occur on addition of HOR/HER promoting species such as caffeine.

The electrochemical interface is traditionally viewed as a double layer model, with specific electrochemical adsorbates existing in the Inner Helmholtz Plane and the first layer of non-adsorbates at the Outer Helmholtz Plane. FTIR studies of CO stark tuning have long been used as a direct probe of the interfacial electric field strength, dictated by the majority species in the OHP.[9,10] Surface sensitive IR shows peaks corresponding to surface bound caffeine, as well as losses of Free-Water on CO, suggesting caffeine is the main occupant of the OHP in CO stark tuning studies. The low ST rate of 22 $cm^{-1}V^{-1}$ is similar to that found for varying concentrations of crown ethers and acetonitrile, implying IEF changes are not responsible for increased HOR/HER activity. However, differences in the ν(O-H) stretching mode of water suggest caffeine's impact is to change the interfacial water structure, allowing for more facile kinetics, the main parameter responsible for the "apparent pH dependence" of PGM HOR/HER.

Electrochemically-Driven CO2 Separation from Ambient Air using Hydroxide Exchange Membranes

Stephanie Matz
Advisor: Yushan Yan
Committee Members: Raul Lobo and Marat Orazov

In a hydroxide exchange membrane fuel cell (HEMFC), hydroxide produced at the cathode readily reacts with CO_2 in air due to its acid-base reaction. The CO_2 in (bi)carbonate form then transports across the hydroxide exchange membrane to the anode where bicarbonates build up lowering the local pH until CO_2 evolution reactions become favorable. The pH gradient across the cell results in lower voltage output, decreasing fuel cell efficiency; however, this cell can effectively separate CO_2 from air. By focusing on CO_2 separation, rather than power production, an electrochemically-driven CO_2 separator (EDCS) was developed using a poly(aryl piperidinium) membrane. The EDCS only requires a small hydrogen stream to power separation of ambient levels of CO_2 from air at moderate temperatures. The EDCS product streams are a CO_2-depleted air stream and a CO_2-concentrated stream contaminated with a small amount of unreacted hydrogen and pure water. Compact, efficient, and continuous CO_2 separation technologies, like the EDCS, are needed for various applications such as direct air capture, air pretreatment for HEMFC stacks in vehicles, and life support systems in submarines and manned spacecrafts.

This work will demonstrate the ability of the EDCS to effectively and continuously remove CO_2 from air at ambient levels while minimizing hydrogen consumption. The effect of various operating conditions on CO_2 separation performance of the innovative EDCS will be explored, such as flow rates and current density. A carbon-ionomer interlayer added between the catalyst layer and membrane will be shown to improve CO_2 capture by creating an accessible volume for hydroxide and CO_2 gas to react. Additionally, various design features of the cell will be investigated to reduce gas-phase mass transport resistance such as flow fields and gas diffusion layers. An optimized single-cell 25 cm^2 EDCS achieves > 99% CO_2 removal from 3.2 sLpm air containing 400 ppm CO_2 for over 150 h while maintaining a hydrogen consumption of 0.05% of air processed. The EDCS operating conditions and design is also evaluated for different applications as their requirements for air flow, CO_2 concentrations, operating conditions, hydrogen availability, and size restraints differ and must be taken into account.

Pure and concentrated acetate production via electrochemical CO_2/CO reduction

Sean Overa
Advisor: Feng Jiao
Committee Members: Raul Lobo, Dionisios Vlachos

The electrochemical conversion of CO_2 to value-added products is a promising approach to mitigate rising CO_2 levels. Direct electrochemical CO_2 conversion to high-value multi-carbon (C_{2+}) products, such as ethylene, alcohols, and acetate, still lacks development and has poor selectivity and durability. However, electrochemical CO_2 conversion to CO is durable and highly selective in low- and high-temperature reactors. As a result, significant interest has been invested in the electrochemical conversion of CO to valuable C_{2+} products, allowing for a tandem CO_2-to-CO-to-C_{2+} system. Here we present our work on designing and scaling a CO electrolyzer capable of producing acetate and ethylene at >90% selectivities. We first demonstrate the system's feasibility by constructing a 5 cm^2 membrane electrode assembly (MEA) electrolyzer. Through reactor, membrane, and catalyst design, this system achieved the state of the art acetate production from CO, producing > 3 M acetate at a purity of 98% for > 100 hours at a cell voltage of < 2.24 V and an operating current density of 200 mA cm^{-2}. This system also achieved a peak acetate concentration of 7.7 M (57 wt%) at a molar purity of 99.3%, both the highest weight percent and purity of acetate demonstrated by CO reduction. The system's feasibility was demonstrated through selective acetate production directly from CO_2 via a two-step electrolysis method, where >25% of fed CO_2 was converted to acetate. Lastly, this work highlights our future efforts in scaling the CO reactor system from the bench scale to the pilot scale. We will highlight our work developing a 25 cm^2 reactor and designing more stable catalysts to achieve a total current of 7.5 A with > 130-hour durability. This system is then further scaled to 100 cm^2 in preparation for developing a CO MEA stack operating at the kW scale.

Understanding Acetate Selectivity in Electrochemical CO Reduction

Haeun SHin
Advisor: Feng Jiao
Committee Members: Dr. Dionisios Vlachos and Dr. Yushan Yan

Electrochemical carbon monoxide (CO) reduction is one of the promising technologies in carbon capture, utilization, and storage (CCUS) by converting carbon dioxide into valuable chemicals. With renewable electricity, carbon-neutral chemical production can be rationalized. Unlike direct electrochemical carbon dioxide (CO_2) reduction, electrochemical CO reduction can operate in a highly alkaline environment leading to the high selectivity of multi-carbon products, ethylene, ethanol and acetate, on copper-based catalysts without electrolyte consumption due to carbonate formation. Moreover, recent development in flow-cell designs has allowed industrially relevant high current density by overcoming the low solubility of CO in aqueous electrolytes. However, tuning selectivity towards target products is still challenging because there is no consensus on the mechanism for the selectivity amongst multi-carbon products leading to difficult catalyst/reaction designs. In this study, we propose the comprehensive transport model elucidating the mechanism behind the acetate formation supported with catalyst loading and electrolyte pH experiments. The variations of catalyst loading and electrolyte pH in electrochemical CO reduction suggested that the transport properties of a ketene, the stable intermediate of multi-carbon products, defined selectivity towards acetate rather than the intrinsic activity of copper catalysts. The electrolyte pH study showed an increase in acetate production with an increase in electrolyte pH because the high concentration of [OH^-] facilitated the intermediate to react with [OH^-] in the solution regardless of catalyst morphologies. The loading variations with different sizes of copper particles, therefore different surface roughness, suggested that the rate of a desorbed form of ketene (H_2CCO_{aq}) being re-adsorbed (H_2CCO^*) onto the catalyst surface changed the acetate selectivity as the acetate formation occurred with [OH^-] in a solution phase. The results showed that an increase in roughness lowered the acetate production because the high surface area of the catalyst favors re-adsorption of H_2CCO_{aq} implying the critical role of H_2CCO mass transport in determining multi-carbon products. The insight into the comprehensive mechanism provided the rational designs to steer the selectivity of acetate during electrochemical CO reduction which is critical to maximizing energy utilization.

Electrochemical Generation of Reactive Intermediates as a Tool for Aromatics Upgrading

Haoran Ding
Advisor: Marat Orazov
Committee Members: Raul F. Lobo, Feng Jiao

Functionalization of simple aromatics such as benzene, toluene, xylenes, ethylbenzene, and styrene substantially expand the utility of such commonly available building blocks. Traditional upgrading methods include electrophilic aromatic substitution, partial oxidation, and halogenation of side chains. Such reactions often require harsh conditions like elevated temperature and pressure, corrosive solutions and vapors, and reactive reagents such as halogens. Electrosynthesis employs electrochemical potential as the driving force of reactions, allowing operation near ambient temperatures, with conventionally unreactive reagents, thus providing alternative pathways to aromatic functionalization that avoid harsh conditions.

The electrochemical upgrading of aromatics often involves reactive intermediates such as radicals or carbocations, which can be produced by Kolbe electrolysis of carboxylic acids or direct activation of aromatics. Reactive carbon-centered radicals are produced in Kolbe electrolysis of carboxylic acids [1]. While simple, symmetric radical coupling products have limited commercial interest, directing such radicals towards addition to C=C double bonds in styrene is a promising approach to extend electrosynthesis to complicated upgraded aromatic products. Such reactions have been reported in several studies [2-3], but the undesired side reactions, such as self-coupling and radical-initiated polymerization, often led to low selectivity and rapid catalyst deactivation. We developed a current-pulse technique to mitigate deactivation of the electrodes caused by deposition of insulating oligomers, improving the carbon balance and reducing the energy input. Several parameters such as the current density, temperature, electrode material, pulse length and frequency were investigated and optimized. The reaction mechanism was confirmed to involve a radical intermediate using a radical trap. Direct oxidation of aromatic substrates is another way to generate reactive intermediates electrochemically. The electrooxidation of alkylbenzenes is believed to proceed via a radical carbocation intermediate [4]. We showed that performing such electrooxidations in anhydrous carboxylic acid solvents lead to the formation of corresponding aromatic esters without substantial solvent oxidation under high oxidation potentials. With p-xylene as substrate and acetic acid as solvent, the major product, p-methyl benzyl acetate was produced at 65% Faradaic efficiency and 70% selectivity. Further oxidation produced a mixture of partially oxidized products, including substantial quantities of aromatics functionalized on both alkyl groups.

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Ethylbenzene via Consecutive Oxidative Dehydrogenation of Ethane and Benzene Alkylation

Eric Steinman
Advisor: Marat Orazov
Committee Members: Douglas Buttrey and Yushan Yan

While vapor-phase zeolite-catalyzed benzene alkylation is a mature industrial process, current methods produce ethylene through energy intensive processes and require expensive intermediate separations before benzene alkylation. Ethylene can be produced via oxygen-oxidized oxidative dehydrogenation of ethane (ODHE) to reduce external energy needs, enable operation at lower temperatures, remove significant thermodynamic limitations, and mitigate coking compared to ethylene production via ethane cracking. One can envision consecutive reactors for ODHE and benzene alkylation to convert from ethane to ethylene and ethylene to ethylbenzene, respectively. Operating ODHE as a standalone process for the production of ethylene below full ethane conversion at scale would require cryogenic distillation or advanced membranes to separate product ethylene from unreacted ethane similar to those used for ethane cracking. Separation costs can be mitigated in the consecutive process if benzene alkylation can operate at high ethylene conversion and be agnostic toward feed ethane. Thereby, the ethane-ethylene separations can be replaced with much easier ethane-BTEX separations.

In an ideal embodiment, the downstream alkylation process would be compatible with all reactants and products of the upstream ODHE process. Unfortunately, the presence of oxygen leads to deactivation of the parent zeolite for the standard alkylation catalyst. Since industrial alkylation catalysts are already highly efficient and optimized, it is desirable to avoid making major alterations to the alkylation catalyst. Thus, ODHE needs to be operated at high oxygen conversion which can hurt the performance and longevity of ODHE catalysts. ODHE catalyst selection and reaction engineering is needed to overcome these hurdles. In this presentation, we will show a proof of concept for our novel consecutive process.

Developing an encapsulated hydrogenation catalyst for the direct conversion of glucose to ethylene glycol

Roshaan Surendhran
Advisor: Dr. Marat Orazov
Committee Members: Dr. Raul Lobo, Dr. Dionisios G. Vlachos

With a global production capacity of 42 million tons in 2019 and a global market value of 30.4 billion USD in 2018[1], ethylene glycol (EG) is a high-volume chemical used primarily as a reagent in the synthesis of polymers, as a solvent, and as a heat-transfer fluid. The most prevalent process for producing EG is via the epoxidation of ethylene, followed by the hydration of the ethylene oxide intermediate, which requires multiple reactors and separation units[2]. Over 95% of the global EG supply is produced through this method utilizing ethylene sourced predominantly from non-renewable natural gas, naphtha, coal, and more recently from bioethanol[1]. The overall financial and environmental cost for sourcing ethylene and subsequently converting it to EG incentivizes the development of a technology that can directly convert the feedstock to EG. To this end, the direct conversion of cellulose or glucose to EG has been the subject of research in the recent years, with a sequential retro-aldol–hydrogenation strategy being particularly appealing.

The retro-aldol reaction required for this strategy is equilibrium limited and favors the hexose (glucose) over the smaller fragments (glycolaldehyde and erythrose). To overcome this limitation, we pursue a tandem strategy that irreversibly transforms the glycolaldehyde to EG via size-selective hydrogenation by encapsulated catalysts. Such a strategy requires the simultaneous use of two catalysts, one for the retro-aldol reaction, and one for the selective hydrogenation of glycolaldehyde. However, typical hydrogenation catalysts like Ni/SiO_2 are not size-selective and catalyze the reduction of both glucose and glycolaldehyde. By encapsulating the active Ni nanoparticles inside zeolitic frameworks, we can achieve size-selective hydrogenation of glycolaldehyde by limiting the transport of glucose to the active site. MFI framework type materials, with largest pore diameter of 5.5 Å, can exclude glucose[3] due to its larger size and provide the necessary selectivity for glycolaldehyde reduction to EG. In this work, we have explored the preparation and application of such MFI encapsulated Ni catalysts for size-selective hydrogenation.

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Microwave Heating-Induced Temperature Gradients in Liquid–Liquid Biphasic Systems

Montgomery Baker-Fales
Advisor: Dionisios G. Vlachos
Committee Members: Abraham Lenhoff, Raul Lobo

Microwaves (MWs) can enable the electrification and intensification of chemical manufacturing. They have been applied to various unit separations, such as drying, distillation, and extraction, entailing gas–liquid and solid–liquid systems. However, a limited quantitative understanding of MW-heated liquid–liquid biphasic systems related to extraction exists. This work measures the temporal and spatial temperature difference between an aqueous and an organic phase in batch and continuous microfluidic modes. We demonstrate permanent temperature differences between phases over 35 °C and spatiotemporal periodic and quasiperiodic oscillations modulated by the flow patterns. The temperature differences are primarily driven by the faster absorption rate of MW irradiation by the aqueous phase versus the slower heat transfer from the aqueous phase to the organic phase. These are amplified by low specific interfacial area and modifications of the electromagnetic field. We employ a multiphysics model to predict the temperature difference in a batch system. The model is in good agreement with the experiments. We demonstrate a strong effect of input power, dielectric properties of organic solvents, the volume of solvents, and the volume ratio between phases on the temperature difference. A simple analytical model describes the temperature difference and provides design principles. The combined approach offers new insights into the design and optimization of the MW-heated biphasic systems.

Beyond Semi-Empirical Energy Scaling: Correlations and Theory for Vibrational Frequencies and Thermochemical Quantities

Sophia Kurdziel
Advisor: Dr. Dionisios G. Vlachos
Committee Members: Dr. Raul F. Lobo, Dr. Marat Orazov

Semi-empirical energy correlations, such as linear scaling relationships (LSRs) and transition-state scaling (TSS) / Brønsted-Evans-Polanyi (BEP) relationships, are often used to circumvent expensive density functional theory (DFT) computations of electronic energies. These models are well established for AH_X (A = C, N, O) adsorbates and reactions across transition-metal surfaces; however, other Arrhenius parameters are often taken as constants to avoid quantum calculations. Our group developed vibrational scaling relationships (VSRs) which correlate metal-adsorbate driven vibrational modes between AH_X species across metal surfaces, and recently expanded to transition-state VSRs (TSVSRs) which scale metal-adsorbate driven modes between local minima and transition states for AH_X reactions. (TS)VSRs, and by extension, thermochemical property scaling relations, offer a pathway to estimate vibrational thermochemical contributions for larger species or at transition states.

Using *d*-band theory and linear muffin tin orbital theory, we discuss the derivation of the TSVSR slopes from the corresponding TSS relations and pertinent geometric data for AH_X diffusions and dehydrogenations. For AH_X diffusions, we incorporate variation between binding sites into TSVSR slope predictions. For bond breaking reactions, namely for AH_X dehydrogenations, we examine changes in relevant adsorbate orbital overlap with metal atomic *d* orbitals between local minima and transition states, and predict both the slopes of the TSSs and TSVSRs. Finally, we demonstrate thermochemical property scaling across metal surfaces and a homologous series as an application of TSVSRs to estimate pre-exponentials and temperature corrections to DFT energies. Extension to larger species and transfer from one catalyst to another are also discussed.

Theoretical insights into the heterogeneous hydroformylation of ethylene on atomically dispersed Rh-oxide promoter pairs

Seungyeon (aka Lina) Lee
Advisor: Dion Vlachos
Committee Members: Raul Lobo, Marat Orazov

Atomically dispersed late-transition state metals on oxide supports have emerged as a new frontier in catalysis as they combine the advantages of both homogeneous and heterogeneous catalysts.[1] Successful heterogenization of the hydroformylation reaction, an industrially significant process for aldehyde production conventionally performed on homogeneous Rh or Co complexes,[2] has been reported recently for atomically dispersed Rh on oxide supports.[3-4] Interestingly, the presence of oxide promoters on the support seems to enhance the catalyst's selectivity for hydroformylation versus hydrogenation of the olefin. Ro et al.[3] have demonstrated that Rh-ReO_x pairs atomically dispersed on γ-Al_2O_3 are more selective for the hydroformylation of ethylene than Rh alone.

I present a theoretical study of ethylene hydroformylation by Rh atomically dispersed on γ-Al_2O_3(110) in the absence and presence of two oxide promoters, ReO_x and WO_x, and evaluate the developed mechanisms by comparing the predicted kinetic observables (selectivity, apparent activation energies, and reaction orders) with experimental values. I analyze how the promoters modify the electronic properties of the Rh(I) active site and elucidate their role in the catalyst's enhanced selectivity for the hydroformylation pathway. The Re(VII) promoter seems to induce no electronic changes to Rh that are related to the latter's catalytic function, and it only blocks the dehydrogenation pathway by posing a steric hindrance. On the other, the W(VI) promoter have a more profound electronic effect as it must be reduced to the W(V) state before it is activated.

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Statistical-learning-aided Multiscale Modeling of Structure-sensitive Catalytic Reactions

Xue Zong
Advisor: Dionisios G. Vlachos
Committee Members: Antony N. Beris, Feng Jiao

Heterogeneous catalytic reactions are commonly structure sensitive and dependent on the size and shape of catalyst particles. However, the structure sensitivity of surface reactions has been a long-studied problem, and often debated experimentally even for a simple chemical reaction due to the difficulty in identifying catalyst surface structures in situ. The ability to predict a priori which reactions are structure sensitive and under what conditions has not been in general possible. This challenge arises from being difficult to make materials with arbitrary and stable structures and the need to perform numerous first principles calculations on various facets, build kinetic models, and compare the rates. To our knowledge, while in principle possible, structure dependent models for complex catalytic reactions have not been achieved yet because the effort of building a first-principles kinetic model is already significant. Recently published work either chooses several common facets [1] or develops a structure-dependent model for archetypical simple reactions, such as CO oxidation [2]. There is a need to create suitable kinetic models for describing structure sensitivity of complicated reactions.

In this work, we introduce statistical learning tools to develop a novel structure-descriptor-based kinetic model for complete methane oxidation based on first-principles calculations. Structure-reactivity scaling relationships, reminiscent of the generalized coordination number (GCN) [3], are developed using statistical learning techniques. By incorporating these correlations into kinetic models leveraging our in-house developed software DescMAP, we predict the experimental observables, such as turnover frequencies (TOF) and apparent activation energies, at a dramatically reduced computational cost compared to first-principles calculations. Additionally, uncertainty quantification is applied for exploring the effects of errors in structure-reactivity scaling relations on variable catalyst facets. This methodology enables the rapid prediction of kinetics on arbitrary structures for complicated catalytic reactions and quantifies the uncertainties due to the catalyst structure for the first time.

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UNIVERSITY OF DELAWARE
ENGINEERING
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2021 – 2022 WINTER RESEARCH REVIEW

Location: **COLLINS ROOM**
Schedule of Talks and Abstracts

9:20 AM	Ye, Mingchun **Novel and Valuable Chemicals from Renewable Feedstocks through Catalysis** Advisor: Raul Lobo Committee Members: Dionisios Vlachos, Christopher Kloxin, Donald Watson, & Hari Sunkara
9:40 AM	Kim, Doyoung **Metathesis, Molecular Redistribution of Alkanes, and the Chemical Upgrading of Low-Density Polyethylene** Advisor: Raul Lobo Committee Members: Bingjun Xu, LaShanda Korley, Marat Orazov, & Mary Watson
10:00 AM	Lee, Jason **Mechanistic Studies of Hydrocarbon Dehydrogenation and Cyclization in Acid Zeolites Using Density Functional Theory** Advisor: Raul Lobo Committee Members: Marat Orazov, Feng Jiao, & Stavros Caratzoulas
10:20 AM	Chen, Tso-Hsuan **Computational Study of the Solvent Effects for Fructose Dehydration in Biphasic Systems** Advisors: Dionisios Vlachos & Stavros Caratzoulas Committee Members: Marat Orazov & Rual Lobo
10:40 AM	**BREAK & POSTER SESSION** — **EAST LOUNGE**
11:45 AM	**LUNCH (feat. Kevin Solomon)** — **WEST LOUNGE**
1:10 PM	Hsiao, Yung-Wei **Cost and Energy Efficient Cyclic Separation and Upgrade of 5-Hydroxymethyl Furfural in a Microfixed Bed** Advisor: Dionisios Vlachos Committee Members: Raul Lobo & Marianthi Ierapetritou

1:30 PM	Jariwala, Soham **Modeling Rheology of Aggregating Colloidal Suspensions: Perspectives from Population Balances and Non-Equilibrium Thermodynamics** Advisors: Antony Beris & Norman Wagner Committee Members: Bertrum Diemer & Eric Furst
1:50 PM	Chen, Yingjie **A Framework of Surrogate-based Multi-objective Optimization with Adaptive Sampling for Continuous Pharmaceutical Manufacturing Processes** Advisor: Marianthi Ierapetritou Committee Members: Bertrum Diemer & Arthi Jayaraman
2:30 PM	**BREAK** **EAST LOUNGE**
2:50 PM	Heil, Christian **Computational Study of Structure, Self-Assembly, and Optics of Bio-Inspired Nanoparticles** Advisor: Arthi Jayaraman Committee Members: Catherine Fromen, Eric Furst, & Ali Dhinojwala
3:10 PM	Wu, Zijie **Computational Studies of Macromolecular Materials with Directional and Specific Interactions** Advisor: Arthi Jayaraman Committee Members: April Kloxin & LaShanda Korley
4:00 PM	**INDUSTRY MIXER** **WEST LOUNGE**

Novel and Valuable Chemicals from Renewable Feedstocks through Catalysis

Mingchun Ye
Advisor: Dr. Raul F. Lobo
Committee Members: Dr. Dionisios G. Vlachos, Dr. Christopher J. Kloxin, Dr. Donald A. Watson and Dr. Hari B. Sunkara (DuPont)

To mitigate the environmental impact of plastic waste and reduce our dependence on fossil fuels, we must find renewable alternatives with desirable combinations of physical and chemical properties. Recent reports have shown that bifuran-based polyesters could afford such materials: poly(ethylene bifuroate), for example, has attractive UV blocking and gas barrier properties. This bifuroate can be prepared by the selective C-C homocoupling of methyl furoate via the Heck reaction, but this requires halide substitution and inert reaction atmosphere. To prepare the bifuroate from less expensive ingredients alternatives to the C-C homocoupling need to be found. Here we investigate the feasibility of oxidative coupling of furoate using homogeneous Pd(II) catalysts. We have simplified the reaction composition, determined important steps of the reaction mechanism and optimization of the oxidative coupling of the methyl furoate. Using homogeneous Pd(II) catalysts we have obtained acceptable yields (11.4%), good selectivity (85%) and very high turn-over-frequency (TOF) (544 h^{-1}). Kinetic analyses revealed that the mechanism fitted the so-called bimetallic mechanism of oxidative coupling. It was found that the solubility of the product, Dimethyl 2,2'-bifuran-5,5'-dicarboxylate (DMBF), was greatly temperature dependent and shown that this property can be used for effective scale up of the reaction.

Metathesis, Molecular Redistribution of Alkanes, and the Chemical Upgrading of Low-Density Polyethylene

Doyoung Kim
Advisor: Raul F. Lobo
Committee Members: Bingjun Xu, LaShanda T. J. Korley, Marat Orazov, Mary P. Watson

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The negative environmental impact of plastic waste requires the urgent development of effective and economic plastic recycling and upgrading processes. Polyethylene (PE) is the largest portion of the plastics waste stream and presents major challenges to chemical recycling due to the stability of the polymers' C-C bonds. Numerous investigations utilizing various catalytic reactions for PE upgrading have been reported recently. Catalytic alkane metathesis chemistry—comprising tandem (de)hydrogenation and olefin metathesis—has been explored as an alternative to direct deconstruction methods (*e.g.*, pyrolysis or hydrocracking) due to its moderate operating temperature (~200 °C) and absence of reactive gases (*i.e.*, H_2) in the process, two factors favorable for economic viability of a metathesis-based chemical recycling process.

While alkane metathesis-based PE deconstruction processes have been demonstrated in the literature, the approach typically relies on a rhenium oxide catalyst for the olefin metathesis reaction. Rhenium oxide is expensive, cannot be applied at the high temperatures at which reaction kinetics are most favorable (due to the high volatility of surface rhenium oxide species), and can be complex to regenerate. We sought to substitute this catalyst with a silica-supported tungsten oxide (WO_x/SiO_2), a relatively inexpensive material that addresses the adverse features of rhenium oxide. Olefin metathesis and alkane metathesis using WO_x/SiO_2 have been applied in PFR-type flow systems and are generally known as molecular weight redistribution processes; but there have been no reports of the application of this catalyst for either olefin or alkane metathesis reactions in a batch reactor system nor for PE deconstruction. A batch reactor may be preferable to a flow reactor for PE upgrading to address challenges of converting mixed plastics waste; therefore, understanding the conditions needed for catalyst operation in a closed system is key to the development of successful upgrading processes.

Herein, we develop model reactions of catalytic olefin and alkane metathesis using a WO_x/SiO_2 catalyst in a batch system. Using these model reactions, we evaluate the role of zeolite 4A absorbent in facilitating catalyst activation and reaction in a closed batch system. We demonstrate that because WO_x/SiO_2 can operate in the range of temperatures that are inaccessible to rhenium oxide, shorter reaction times can achieve high conversion of the surrogate reactant. High conversion of 1-hexadecene (96 %) and n-hexadecane (92 %)—surrogates of long-chain molecules—demonstrate the high reactivity of WO_x/SiO_2 metathesis catalyst for olefin and alkane metathesis reactions, respectively, at moderate reaction temperatures of 300 °C for 2 to 3 h. Pretreatment temperature and length of short alkane chain solvent have significant effects on metathesis reactivity and selectivity. The WO_x/SiO_2-driven alkane metathesis system demonstrates remarkable potential for the chemical upcycling of PE at short reaction time (3 hours) using short chain alkane (6 g) required to convert the unit mass of LDPE, and the capacity to produce solid products of homogenous molecular weight distributions with the greatest reduction in the average molecular weight (Mw) by 99 % and polydispersity over 6-fold.

Mechanistic Studies of Hydrocarbon Dehydrogenation and Cyclization in Acid Zeolites Using Density Functional Theory

Jason Lee
Advisor: Raul Lobo
Committee Members: Marat Orazov, Feng Jiao, Stavros Caratzoulas

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Despite the ubiquity of zeolite catalysts in various industrial processes for converting light alkanes into other hydrocarbon products, many questions remain unanswered about specific catalytic mechanisms. For example, decades ago, UOP/BP and ExxonMobil each developed processes around acid zeolite catalysts capable of direct synthesis of aromatic hydrocarbons from methanol, ethane, or propane. Currently, disagreements continue over the details of the complex reaction network often referred to as the "carbon pool" mechanism. In several different zeolite frameworks, olefins are thought to grow via sequential methylation, forming an "olefin pool". Cyclization of the longer alkene chains in this pool results in the formation of desirable aromatic products as well as an "aromatic pool". However, no proposed mechanism satisfactorily explains the elementary steps of cyclization or any cyclic intermediates. Understanding of mechanistic details would contribute greatly towards catalyst development and improvement.

In this work, density functional theory (DFT) was used to develop a new mechanism for the cyclization of 1,3,5-hexatriene. This is the simplest model compound for conjugate trienes, which have been shown in the literature via in situ IR and UV-Vis to be prevalent in acid zeolites during aromatization. Faujasite (FAU), with its single crystallographically unique Brønsted acid site (BAS) and large pores, was chosen as a model zeolite for studying how intermediates and transition states of the proposed cyclization mechanism interact with DFT cluster models of the BAS. From these calculations, a quantitative reaction coordinate diagram was constructed for the proposed reaction network. Microkinetic modelling was used to identify dominant surface species and to estimate relative reaction rates. The proposed mechanism also attempts to reconcile contradicting experimental observations on cyclic carbocation rearrangements made very early in the literature by the groups of Olah and Sorensen.

Similarly, there has also been renewed interest in extra-framework metal-modified zeolites, such as Ga- and In-CHA (chabazite), for ethane and propane dehydrogenation, due to rising costs of precious metal (Pt) catalysts. Although the mechanism for Ga-ZSM-5, a framework with a larger pore than CHA, has been well studied in the literature, the details that explain the higher reactivity in Ga- vs In-CHA appear to be more complex. The second half of this talk focuses on possible explanations for the differences in reactivity using a similar DFT-based approach.

Computational Study of the Solvent Effects for Fructose Dehydration in Biphasic Systems

Name: Tso-Hsuan Chen
Advisor: Dionisios G. Vlachos, Stavros Caratzoulas
Committee Members: Marat Orazov, Raul F. Lobo

The partial deoxygenation of fructose to platform molecules, 5-hydroxymethylfurfural (HMF), is critical for the economic production of biofuels and chemicals from non-edible lignocellulosic biomass. Efforts have been made over the past few decades to identifying solvents, catalysts, and reaction conditions that could enable the selective production of such intermediate. Previous study from Román-Leshkov et al. has initiated the exploration of biphasic reactive extraction systems for fructose dehydration, reporting unprecedented improvements in the selectivity to HMF. In such biphasic system, HMF is continuously extracted into a non-polar organic phase, allowing the separation between the products and the catalysts and suppressing further side reactions. Despite the significant enhancement in the yield of HMF, the mechanistic understanding of fructose dehydration in the biphasic system remains lacking. Even the well-studied effects of polar aprotic co-solvents on the rate and selectivity of the monophasic fructose dehydration are difficult to extrapolate to the non-polar solvents used in biphasic systems.

In this work, we investigated the nature of the enhanced dehydration of fructose to HMF in the water and methyl isobutyl ketone (MIBK) biphasic microfluidic system computationally. Classical molecular dynamics simulations (MD) were performed to understand the partition of water between fructose and HMF in the mixture of organic solvents and water. Hybrid quantum mechanics/molecular mechanics (QM/MM) MD was applied to study the proton-fructose and proton-HMF interactions in the organic solvents. Finally, we applied the linear response theory to estimate the relative solvation free energy ($\Delta\Delta G_{sol}$) between the reactant and product states and further understand the change of their relative stability in different solvents. Among the major conclusion from our simulations are: (a) When both fructose and HMF co-exist in non-polar organic solvents, water preferably coordinates near the highly hydrophilic fructose substrate, limiting the water available for HMF rehydration. (b) The formation of a tight hydrophilic domain around the substrate enables strong proton-substrate interactions in the organic solvent-rich environment and further enhance the reaction rates. (c) In the aqueous mixture of the non-polar organic solvents, the formation of the side product (levulinic acid) is suppressed and thus increases the selectivity towards HMF.

Cost and Energy Efficient Cyclic Separation and Upgrade of 5-Hydroxymethyl Furfural in a Microfixed Bed

Yung Wei Hsiao
Advisor: Dionisios G. Vlachos
Committee Members: Raul Lobo and Marianthi Ierapetritou

The efficient separation of 5-hydroxymethyl furfural (HMF) – a platform chemical in biomass valorization – from the reactive aqueous mixture of sugars is key to improving its economic production. Here we demonstrate a cyclic fixed-bed process that selectively adsorbs HMF from the aqueous phase, purifies the solute, and enables its subsequent desorption using a suitable solvent for downstream applications. This intensified process bypasses the traditional energy-intensive recovery of HMF via vacuum distillation. The adsorption and desorption performances of a commercially available polymer-based spherical activated carbon (PBSAC) are quantified in batch and continuous systems. The effects of temperature (25 – 90 °C) and the co-existence of other components from the fructose dehydration reaction (fructose, formic acid, and levulinic acid) on adsorption are evaluated. It is demonstrated that HMF can be selectively purified and recovered, and the adsorption column can be reused for at least seven cycles tested here. A simple economic analysis further showcases nearly tenfold cost and energy savings for HMF separation. The cyclic mechanism promotes flexible solvent choice. An intensified downstream hydrodeoxygenation (HDO) reaction using the desorbed HMF is demonstrated using an inexpensive copper-based catalyst, achieving a high >95% yield under continuous operation. The Cu catalyst was characterized using XRD, XPS, TEM, and TPR to understand its structure-activity relationship. The framework outlined here highlights the potential for modular biorefineries and can be applied to other biomass solutes.

Modeling rheology of aggregating colloidal suspensions: perspectives from population balances and non-equilibrium thermodynamics

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Committee Members: R. Bertrum Diemer, Eric M. Furst

Aggregating colloidal suspensions can be encountered in a large number of materials; examples include food products, biological fluids, printer inks, paints, and slurries [1]. Modeling of these suspensions remains challenging as their rheology directly connects to the mesoscale structure and aggregation kinetics. Transient flows in such suspensions show complex dynamics due to yield stress, viscoelasticity, and flow history dependence, i.e., thixotropy. Structure kinetics, where a scalar is used to track the changes in mesoscale structure, remains a popular approach to describe these phenomena. It has been shown recently that such ad hoc phenomenologically constructed models may violate the second law of thermodynamics [2, 3], indicating a need for more robust microstructurally-based models.

Mwasame et al. [4, 5] have shown that one can more accurately describe the rheology of aggregating suspensions by taking advantage of microstructure-based relationships and rigorously derived aggregation kernels for shear flow and Brownian motion. This approach provides a bottom-up particle level description; however, it is limited only to shear flows and cannot be generalized for arbitrary flow types.

In this work, we outline the development of a thermodynamically consistent, microscopically-based model by incorporating the principles of population balances in the framework of nonequilibrium thermodynamics [6]. This top-down approach uses the entropy of mixing associated with agglomerate formation to generate a model of the aggregation and breakup processes along with a conformation tensor-based viscoelastic description of the elastic particle networks. We explore how this modeling approach can be extended further to capture phenomena such as flow inhomogeneities and stress-induced migration that are commonly observed in such systems.

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A Framework of Surrogate-based Multi-objective Optimization with Adaptive Sampling for Continuous Pharmaceutical Manufacturing Processes

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Committee Members: Prof. R. Bertrum Diemer, Prof. Arthi Jayaraman

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Incentivized by increasing market competition and encouragement from regulatory agencies to develop agile, flexible, and robust manufacturing lines, pharmaceutical manufacturing processes are experiencing a shift from batch to continuous operations [1]. With considerable efforts, progress has been made in mathematical modeling of solid-based continuous manufacturing processes, supporting their design, analysis, and optimization. However, as the complexity of models increases to represent process dynamics more accurately, computational burden also rises. To address the problem, a surrogate-based optimization strategy has been proposed, where a surrogate that approximates the complicated model is developed and iteratively updated with the adaptive sampling step that searches for new promising points based on certain infill criteria. The workflow continues until a stopping criterion is met, and the final surrogate with low approximation error is used for optimization [2]. Previous work has applied this approach in continuous pharmaceutical manufacturing by using a weighted expected improvement (EI) function as an infill criterion to guide the search of new points towards feasible regions with low objective values, followed by a modified EI on the objective to search for global optimum within the feasible region [3]. Although the work demonstrates high accuracy in obtaining the optimum, it has only applied to single-objective problems.

In this talk, I will present the work on an updated framework of surrogate-based, feasibility-driven, multi-objective optimization with adaptive sampling. Each objective is approximated using a surrogate, and the constraints are grouped into a feasibility function based on maximum constraint violation, which is also substituted with a surrogate. For the infill criteria, both the centroid method that computes EI based on the first moment of the joint probability density function of the objectives, and the expected hypervolume improvement function that seeks for Pareto solutions based on the difference in hypervolumes, are implemented. With the identified Pareto front, a goal programming approach is used to decide for the best solution. The effectiveness of the framework is demonstrated with a benchmark case and a study from the continuous pharmaceutical manufacturing process. As the framework can obtain accurate results under a smaller sample size, it can be effectively used to investigate multiple competing objectives under constraints, allowing for a better decision-making strategy.

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Computational Study of Structure, Self-Assembly, and Optics of Bio-Inspired Nanoparticles

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Nanoparticle self-assembly is relevant to engineering materials for a wide array of applications including optics, catalysis, biomedicine, sensing, and electronics. Directed self-assembly of nanoparticles near surfaces/interfaces (e.g., in thin films, droplets in emulsion assembly) enables formation of 3-dimensional "supraparticle" assemblies that are used in optics and photonics applications. Such supraparticle assemblies produce structural colors by constructive interference of specific wavelengths of light as it moves through the assembled structure. The direct relationship between the assembled supraparticle structure and resulting optical properties requires structural characterization as a necessary step during the design of materials with tailored optical or photonic properties. Structural characterization of assembled nanoparticles is performed primarily using microscopy and scattering techniques. While microscopy is beneficial for visualizing the nanoparticle assemblies, both transmission electron microscope**,** TEM, and scanning electron microscope, SEM, suffer from limited sample area and probe limited length scales. In contrast, small angle scattering techniques characterize structures over a broader range of length scales and present ensemble averaged information from the sample. Interpreting the small angle scattering output data, $I(q)$ vs. q, typically requires fitting the scattering data with an appropriate analytical model that is relevant for the material under consideration; however, for some supraparticle assemblies (e.g., high packing fraction, amorphous structure) the existing analytical models may be too approximate. One part of my thesis work has been focused on development of a computational method called CREASE (computational reverse-engineering analysis for scattering experiments) for interpreting supraparticles' structure from small-angle scattering without relying on analytical models. In the first part of my talk, I will describe the genetic algorithm (GA) based optimization used in CREASE to analyze the $I(q)$ from structural arrangement of the assembled spherical nanoparticles within a supraparticle. I will demonstrate how we validate our approach using *in silico* experimental scattering profiles from prior simulations of supraparticles composed of binary mixtures of spherical nanoparticles by comparing the output of our GA approach to the known structure. In the second part of my talk, I will present our recent extensions of CREASE to interpret small angle scattering profiles from systems (e.g., concentrated solution of micelles) where both the form factor of the particle (i.e., micelle) and the assembled structure of the particles are unknown to the experimentalist and determined by CREASE.

Computational studies of macromolecular materials with directional and specific interactions

Zijie Wu
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Committee Members: Prof. April Kloxin, Prof. LaShanda Korley

Hydrogen bonding interaction is an important inter-molecular interaction that drives assembly in many families of polymer chemistries (e.g., polysaccharides, polysulfamides, polypeptides, oligonucleic acids). Researchers using molecular modeling and simulations to study these macromolecules face the challenge of simultaneously capturing the localized directionality induced by hydrogen bonding at monomer-scale and the larger length and time scales associated with polymer relaxation and ordering/assembly. The overarching goal of my thesis is to develop appropriate multiscale models and computational methods to probe assembly and structure formation in macromolecules driven primarily by hydrogen-bonding interactions. In this talk, I will highlight my recent work aimed at thermoresponsive self-assembly of methylcellulose (MC) solutions, widely used in food, medical and biological industries, where hydrogen bonding interactions stabilize various observed structures in experiments. MC chains in aqueous solutions remain soluble at room temperature and assemble into fibrils at elevated temperatures. Experiments [e.g., *Macromolecules,* 2018, **51**, 7767-7775] show constant average fibril diameters upon varying MC molecular weight and concentration. Using a combination of recently developed coarse-grained models [*J. Chem. Theory Comput*. 2020, **16**, 7, 4599-4614] and a recently developed computational method called CREASE [*J. Am. Chem. Soc*. 2019, **141**, 14916−14930], my work is focused on unraveling the molecular mechanism of the assembly and the packing of individual MC chains within the fibrils, both of which remain unclear. In this talk I will describe how we apply genetic algorithm (GA) part of CREASE to extract MC fibril dimension (diameter, flexibility, dispersity) from small-angle X-ray scattering (SAXS) profiles for MC fibrils obtained experimentally by Bates, Lodge and coworkers [*Macromolecules,* 2018, **51**, 7767-7775] without the need for *a priori* analytical models. Using the molecular reconstruction part of CREASE, I will show our prediction of chain packing driven by both directional hydrogen bonding effects and isotropic hydrophobic effects within the fibril contour. Our work provides insight into the self-assembly of MC chains in solution and generally, fibrillar network formation of semiflexible polymers with a combination of directional and isotropic molecular interactions.

POSTER PRESENTERS

Nikolas Angyal	"Valorization of Plastic Waste via Low Temperature Oxyfunctionalization" **Advisor: Marat Orazov**
Oluwadare Badejo	"Integration of Tactical Supply Chain and Process Operations using Data-driven Feasibility Analysis" **Advisor: Marianthi G. Ierapetritou**
Matthew Becker	"Determination of the Binding Behavior of Problematic Host Cell Proteins to Industrial Monoclonal Antibodies" **Advisor: Abraham M. Lenhoff**
Soumitra Bhoyar	"Investigating Yield Loss During High pH Wash In Protein A Chromatography" **Advisor: Abraham M. Lenhoff**
Chaoying Ding	"A Novel Framework of Surrogate-based Feasibility Analysis for Establishing Design Space of Twin-column Continuous Chromatography" **Advisor: Marianthi G. Ierapetritou**
Róisín Donnelly	"Exploring Temperature Activated Hydrogen Deuterium exchange of proteins with SANS and Neutron Spin Echo" **Advisors: Norman J. Wagner and Yun Liu**
Antonio Goncalves	"Assembly of a Modular and Tunable Worm-like Protein Nanostructure using a Bottom-up Approach" **Advisors: Wilfred Chen and Millicent O. Sullivan**
Yagya Gupta	"Upgrading Food Waste to High Commercial Chemicals" **Advisor: Dionisios G. Vlachos**
Quentin Kim	"Low Temperature Oxyfunctionalization of Propane" **Advisor: Marat Orazov**
Mi Jen Kuo	"Selective Synthesis of 4, 4′-Dimethylbiphenyl from 2-Methylfuran" **Advisor: Raul F. Lobo**
Vinson Liao	"Characterization of Supported Subnanometer Clusters via Computational Infrared Spectroscopy" **Advisor: Dionisios G. Vlachos**

POSTER PRESENTERS

Shizhao Lu	"Modeling and Simulation of Polymer Nanocomposites containing Nanorods" **Advisor: Arthi Jayaraman**
Yuqing Luo	"Biorefinery Process and Supply Chain Design Optimization under Uncertainty" **Advisor: Marianthi G. Ierapetritou**
Ahmad Naqi	"Multi-material Fused Filament Fabrication via Core-Shell Die Design" **Advisor: Michael E. Mackay**
Alexandra Oliveira	"Anode-Fed Anion Exchange Membrane Electrolyzers for Hydrogen Generation Tolerant to Anion Contaminants" **Advisor: Yushan Yan**
Brian Paul	"Crystal, Liquid, or Gel: Phase Behavior in Dilute Protein Solutions with Increasing Electrolyte Concentrations" **Advisors: Norman J. Wagner, Eric M. Furst, Abraham M. Lenhoff, Susana C.M. Teixeira**
Mruthula Rammohan	"Stabilizing mRNA-lipid nanoparticles using photo-responsive polymers" **Advisors: Thomas H. Epps and Millicent O. Sullivan**
Esun Selvam	"Microwave-assisted depolymerization of PET over heterogeneous ZnO catalysts" **Advisor: Dionisios G. Vlachos**
Terrance Shoemaker	"Assessing Impact of Hinge Flexibility on Predicted Antibody Interactions" **Advisor: Christopher J. Roberts**
Sanjana Srinivas	"Spin-Crossing in Heterogeneous Catalysis By Atomically Dispersed Transition Metals: Ethane Dehydrogenation By Co/SiO2" **Advisors: Dionisios G. Vlachos and Stavros Caratzoulas**
Huayu Tian	"Characterization and Propagation of RTD uncertainty for Continuous Solid-Based Drug Manufacturing Process" **Advisor: Marianthi G. Ierapetritou**
Brandon Vance	"Developing a Mechanistic Framework for Polyolefin Hydroconversion" **Advisor: Dionisios G. Vlachos**

POSTER PRESENTERS

Noah Willis	"Separate, Separated, Together: Transcriptional Program of a Clostridium Syntrophy" **Advisor: Eleftherios T. Papoutsakis**
Yu-Tai Wong	"Exploring the Relationship Between Architecture and Mechanics in Lignin-Derivable Polymer Networks" **Advisor: LaShanda T. Korley**
Yurong Wu	"Dynamics of Brønsted acidity over the Pt-WOx/SiO2 Inverse Catalyst" **Advisor: Dionisios G. Vlachos**
Piaoping Yang	"Structure Sensitivity of Catalytic Transfer Hydrogenation of Furfural over Metal-N-C Catalysts" **Advisor: Dionisios G. Vlachos**
Kewei Yu	"Ethane Non-oxidative Dehydrogenation over Co/SiO2 – Pretreatment and Regeneration" **Advisor: Dionisios G. Vlachos**
Jiahua Zhou	"Tuning Oxygen-Containing Functional Groups and Reactivity of Carbon Surfaces" **Advisor: Dionisios G. Vlachos**

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