



# McWhirter Graduate Research Symposium

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*Friday, September 15, 2017*

*The Nittany Lion Inn*

# Penn State Chemical Engineering Research Symposium

Friday, September 15, 2017

<b>10:00 AM</b>	<b>Registration</b>	
<b>10:30 AM</b>	<b>Session 1</b>	<b>Ballroom AB</b>
	<i>Hydrothermal Demetallation of Algal Biocrude Oil and Hemin</i>	Jimeng Jiang
	<i>An Automated Model Test System for Systematic Development and Improvement of Gene Expression Models</i>	Alexander Reis
	<i>Molecular and Lumped Products from Hydrothermal Liquefaction of Protein</i>	James Sheehan
	<i>Lipid Membrane and Zinc Oxide Thin-Film Transistor Based Biosensors</i>	Akanksha Gupta
<b>12:00 PM</b>	<b>Lunch – Boardroom</b>	
<b>1:00 PM</b>	<b>Session 2</b>	<b>Ballroom AB</b>
	<i>Resonant Soft X-ray Scattering of Cellulose Microstructure in Plant Primary Cell Walls</i>	Dan Ye
	<i>The Pathway Map Calculator: Accelerating Multi-Enzyme Pathway Engineering with Automated Kinetic Model Parameterization</i>	Sean Halper
	<i>Polarized soft X-ray Scattering Reveals Chain Orientation within Block Copolymer Lamellae</i>	Joshua Litofsky
	<i>Thermally Regenerative Batteries: A Story of Capturing Low-Grade Thermal Energy as Electricity</i>	Mohammad Rahimi
<b>2:30 PM</b>	<b>Keynote Speaker – Dr. Huda Jerri – Boardroom</b>	
<b>3:15 PM</b>	<b>Poster Session – Ballrooms AB</b>	
<b>3:45 PM</b>	<b>Session 3</b>	<b>Ballroom AB</b>
	<i>Identifying Atomic Arrangement in <math>\gamma</math>-Brass Intermetallics to Design Site Isolated Catalysts</i>	Anish Dasgupta
	<i>Mechanochemistry at Tribological Interfaces: Polymerization of Adsorbed Molecules by Mechanical Shear</i>	Xin He
	<i>Probing the Dehydration-Induced Alteration of Cellulose Organization in Primary Cell Walls using Sum Frequency Generation (SFG) Vibrational Spectroscopy</i>	Shixin Huang
	<i>Genome Scale Mapping Models and Algorithms for Stationary and Instationary MFA Based Metabolic Flux Elucidation</i>	Saratram Gopalakrishnan
<b>5:00 PM</b>	<b>Reception</b>	

## Session 1

# Hydrothermal Demetallation of Algal Biocrude Oil and Hemin

**Presenter:** Jimeng Jiang (jxj289@psu.edu)

**Advisor:** Phillip E. Savage (psavage@engr.psu.edu)

Hydrothermal Liquefaction (HTL) converts wet biomass into a renewable crude bio-oil that could be further treated to become acceptable for processing in petroleum refineries. HTL takes advantage of the properties of hot and compressed water near its critical point to break down biomacromolecules in the feedstock into smaller molecules. One barrier that prevents the substitution of HTL biocrude for petroleum is the presence of high concentrations of metals. Metal impurities can cause plugging, deposition, coke formation, and catalyst deactivation. Among all the metals present in biocrude, iron gets the most attention due to its high abundance in the crude bio-oil and difficulty to be removed. Iron has been found to plug the head of the catalyst beds that are used to hydrotreat algal biocrude oil (Jarvis et al., 2016).

Using *Nannochloropsis sp.* algae as a renewable feedstock, here we report how different HTL processing conditions (temperature, holding time, algae loading, and water volume) can influence the metal concentrations in the algal biocrude and in the post-HTL aqueous phase product. We also studied the effect of different recovery solvents and heterogeneous catalysts. In the end, by using different heterogeneous catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, activated charcoal, and CoMo/Al<sub>2</sub>O<sub>3</sub>) in addition to one of the recovery solvents during HTL, we were able to produce algal biocrude oil that had just 3% of the Fe content that would otherwise be present from HTL of the algal biomass (Jiang and Savage, 2017).

In addition to this work with an actual renewable biomass feedstock, we used hemin, a porphyrin model compound that represents the molecular forms of iron in microalgae cells (Marchetti and Maldonado, 2016), as a starting material. We explored the effect of different isothermal HTL conditions and the same catalysts used with algae biomass on iron distribution in hemin oil. Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> was able to reduce most of the iron contents but it then introduced additional nickel into the oil. Activated charcoal and CoMo/Al<sub>2</sub>O<sub>3</sub> reduced the iron content to some extent but were not as effective on hemin as they were on algae biomass. We characterized the hemin oil by GC-MS and FT-ICR-MS to identify some of the reaction products and used SEM-EDS to locate the iron particles on the spent catalyst.

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2. Jiang, Jimeng, and Phillip E. Savage. "Influence of process conditions and interventions on metals content in biocrude from hydrothermal liquefaction of microalgae." *Algal Research* 26 (2017): 131-134.
3. Marchetti, A., Maldonado, M.T., 2016. Iron, in: Borowitzka, M.A., Beardall, J., Raven, J.A. (Eds.), *The Physiology of Microalgae*. Springer International Publishing, Cham, pp. 233–279.

# An Automated Model Test System for Systematic Development and Improvement of Gene Expression Models

**Presenter:** Alexander C. Reis (alex.reis@psu.edu)

**Advisor:** Howard M. Salis (salis@psu.edu)

Synthetic biology is an emergent field with the goal of engineering genetic systems, or novel biological devices implemented using proteins and other bio-macromolecules, to help solve humanity's challenges in areas such as the environment, energy, and health. Common examples of genetic systems include engineered metabolic pathways for chemical overproduction<sup>1</sup> or genetic circuits integrated with sensing and actuating capabilities to respond to a changing environment<sup>2</sup>. Early strategies for building and testing these systems relied on shared, standard biological parts<sup>3</sup>, however these parts often function unpredictably in different system contexts and are therefore unreliable for robust design. More recently, synthetic biologists have turned to sequence-function models to predict the behavior of a designed genetic system from sequence or to design DNA sequences *de novo* with target functions. Gene expression models are a key class of predictive tools that predict DNA sequence-function relationships to quantitatively predict protein levels within a genetic system<sup>4</sup>. Improved models are needed to engineer more complex systems, however it has been a challenge to identify and quantify new mechanisms controlling gene expression.

To address this challenge, we developed an automated model test system that combines machine learning and a database of 27903 characterized genetic systems to measure model accuracies, accept or reject mechanistic hypotheses, and identify areas for model improvement. We compared the accuracies of six existing models of bacterial translation initiation, and rejected several hypothetical, long-suggested mechanisms controlling translation initiation. We improved existing, and identified new, determinants of gene expression including initiation from non-canonical start codons and an energetic penalty as a result of the nucleotide-specific polymer rigidity of the spacer sequence. We compiled these changes and other parameter updates into a new version of RBS Calculator (v2.1) for increased model accuracy across a wide range of functionally diverse sequences. Lastly, we used feature selection to identify ribosome drafting<sup>5</sup> and mRNA degradation as two determinants of gene expression currently unaccounted for in the existing state-of-the-art models. Automated model test systems will dramatically accelerate the development of improved gene expression and regulation models, and thereby transition synthetic biology into a mature engineering discipline.

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2. Brophy, J. A. N. & Voigt, C. A. Principles of genetic circuit design. *Nat. Methods* **11**, 508–520 (2014).
3. Canton, B., Labno, A. & Endy, D. Refinement and standardization of synthetic biological parts and devices. *Nat. Biotechnol.* **26**, 787–793 (2008).
4. Salis, H. M., Mirsky, E. A. & Voigt, C. A. Automated design of synthetic ribosome binding sites to control protein expression. *Nat. Biotechnol.* **27**, 946–950 (2009).
5. Espah Borujeni, A. & Salis, H. M. Translation Initiation is Controlled by RNA Folding Kinetics via a Ribosome Drafting Mechanism. *J. Am. Chem. Soc.* **138**, 7016–7023 (2016).

# Molecular and Lumped Products from Hydrothermal Liquefaction of Protein

**Presenter:** James D. Sheehan (jds574@psu.edu)  
**Advisor:** Phillip E. Savage (psavage@enr.psu.edu)

Hydrothermally processing low-value, wet biomass feedstocks such as food waste, municipal sludge, livestock manure, and microalgae is a step toward producing fuels and chemicals from these renewable resources. The reaction environment of hot compressed water decomposes the macromolecular constituents of biomass into a mixture of chemical products that can include amino acids, fatty acids, potential nutrients (e.g., ammonia, nitrates, phosphates), fuel gases, and renewable crude bio-oils. Hydrothermal processes are attractive for valorizing wet biomass because they obviate an otherwise energy-intensive drying step generally required by other processes (e.g., pyrolysis, lipid extraction).

Generally, low-value, wet biomass feedstocks can be rich in proteins. Thus, in the present study we examined the decomposition of and product formation from a model protein, bovine serum albumin (BSA), under hydrothermal conditions. BSA forms smaller polypeptides as it decomposes, primarily via hydrolytic cleavage of the peptide bonds. It also forms insoluble aggregates in high yields at mild conditions, which subsequently decompose. There were no polypeptides (MW > 5 kDa) remaining after 5 min at 350 °C, but smaller peptides persisted in yields of about 15 wt%. The total yield of free amino acids was typically < 3 wt%, but nearly reached 6 wt% at 250 °C and 60 min. Glycine and glutamic acid were the most abundant amino acids in the aqueous phase products. The yields of primary and secondary amines reached 50 wt% and generally increased with time and temperature. Up to 40 mol% of the nitrogen in the BSA appeared as NH<sub>3</sub> in the aqueous phase, and the NH<sub>3</sub> yields increased with both time and temperature. Biocrude yields increased with reaction severity until reaching a maximum of about 20 wt%. Cyclic dipeptides were the most abundant GC-elutable components in the biocrude.

# Lipid Membrane and Zinc Oxide Thin-Film Transistor Based Biosensors

**Presenter:** Akanksha Gupta (aug269@psu.edu)

**Advisor:** Esther Gomez (ewgomez@engr.psu.edu) & Thomas Jackson (tnj1@psu.edu)

Cell membrane components regulate a variety of biological functions including vesicle trafficking, intercellular and intracellular signaling and have been implicated as important mediators of disease. [1] Developing robust and label-free electronic biosensors to monitor membrane interactions would not only help in membrane biological studies but also enable new modalities for medical diagnostics and drug screening. Electronic biosensors would provide a path to simple, sensitive, and selective detection of pathogens if practical device platforms and molecular recognition systems can be developed. In this work, we present zinc oxide thin film transistors (ZnO TFTs) combined with lipid membrane bio-interfaces that provide unique advantages for designing sensors for real world applications. ZnO TFTs allow flexibility in device layout and can be fabricated on polymeric substrates. The lipid membranes used for bio-functionalization of ZnO TFTs mimic the cell membrane environment and provide a platform to apply this biosensor approach to target proteins and also with other bio-materials such as oligonucleotides or aptamers. Here, we report integration of lipid membrane assemblies with ultra-thin channel (~10 nm thick) bottom-gate ZnO TFTs. The goal is to use the bio-functionalized TFT to measure changes in electronic charge related to membrane proteins and surface and membrane interactions which are otherwise difficult to characterize.

ZnO TFTs are grown using photolithography and wet etching. ZnO layer is grown by plasma enhanced atomic layer deposition. We demonstrate lipid membrane functionalization of ZnO TFTs with alkyl-phosphonic acid hydrophobic self-assembled monolayers in fluid channels. We enclose the ZnO TFTs in a polymethylglutarimide (PMGI) microfluidic channel sealed with a coverslip to simplify bio-functionalization of ZnO TFTs and allow convenient fluid exchange for device functionalization.

We characterize the uniformity of lipid monolayer and bilayer functionalized Al<sub>2</sub>O<sub>3</sub>-passivated ZnO TFT surfaces using fluorescence recovery after photobleaching (FRAP). Bio-functionalized ZnO TFTs coated monolayer lipid membranes supported on a self-assembled monolayer of an alkylphosphonic acid, exhibit a shift in the turn-on voltage and in the TFT on-current compared to unfunctionalized transistors. We also characterize the response of TFTs coated with different concentrations of charged lipid bilayers to the response of TFTs coated with neutral lipid.

The data demonstrate that electrical characteristics of the TFTs are sensitive to binding of species to their surfaces using lipid membranes. Addition of charge within the membrane shifts the electrical characteristics of the ZnO TFTs.

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## Session 2

# Resonant Soft X-ray Scattering of Cellulose Microstructure in Plant Primary Cell Walls

**Presenter:** Dan Ye (dyy5022@psu.edu)

**Advisor:** Enrique D. Gomez (edg12@psu.edu) & Esther W. Gomez (ewgomez@enr.psu.edu)

Cellulosic biomass is the most abundant raw material available for the production of sustainable biofuels. Breaking down cellulose is the rate-limiting step in economical biofuel production; therefore, a detailed understanding of the microscopic structure of plant cell walls is required. Primary cell walls are key determinants of plant growth and mechanics. Their structure is complex and heterogeneous, making it difficult to elucidate how various components such as pectin, hemicellulose, and cellulose contribute to the overall structure. The electron density of these components is similar; such that conventional hard X-ray scattering does not generate enough contrast to resolve the different elements of the polysaccharide network. The chemical specificity of resonant soft X-ray scattering allows contrast to be generated based on differences in chemistry of the different polysaccharides. By varying incident X-ray energies, we have achieved increased scattering contrast between cellulose and other polysaccharides from primary cell walls of onions. By performing scattering at certain energies, features of the network structure of the cell wall are resolved. From the RSoXS results, we obtained the packing distance of cellulose microfibrils embedded in the polysaccharide network.

# The Pathway Map Calculator: Accelerating Multi-Enzyme Pathway Engineering with Automated Kinetic Model Parameterization

**Presenter:** Sean Halper (sxh456@psu.edu)

**Advisor:** Howard Salis (salis@psu.edu)

Engineered heterologous metabolic pathways can convert low-cost feedstock into high-value products, though it remains a significant challenge to reliably and efficiently maximize end-product biosynthesis, particularly when many enzymes must be co-expressed together. When current approaches are applied to many-enzyme pathways, the construction and characterization process is highly iterative and laborious, while generating high-dimensional datasets that remain difficult to analyze for forward engineering efforts. To overcome these challenges, we developed a new algorithm that determines the highly non-linear and high-dimensional relationship between a pathway's enzyme expression levels and its end-product productivity from a small number of commonly acquired measurements. We combined kinetic metabolic modeling, elementary mode analysis, model reduction, de-dimensionalization, and genetic algorithm optimization into an automated procedure that parameterizes accurate kinetic metabolic models from sparsely characterized libraries of pathway variants with varied expression levels. The resulting Pathway Maps are used to predict optimal expression levels, determine rate-limiting steps, identify the presence of allosteric interactions, rank-order enzyme kinetics, and prioritize protein engineering efforts. We demonstrate the Pathway Map Calculator algorithm on three experimental datasets, a 5-enzyme NADPH regeneration pathway, a 3-enzyme carotenoid biosynthesis pathway and a 9-enzyme limonene biosynthesis pathway, as well as a series of in silico pathway examples to rigorously demonstrate the algorithm's accuracy, linear scaling, and high tolerance to measurement noise. The algorithm is formulated to be used on diverse pathways that use arbitrary genetic parts to vary expression level in arbitrary host organisms, broadening its applications. By greatly reducing experimental efforts and providing quantitative forward engineering predictions, the Pathway Map Calculator has the potential to dramatically accelerate the engineering of many-enzyme heterologous metabolic pathways.

# Polarized soft X-ray Scattering Reveals Chain Orientation within Block Copolymer Lamellae

**Presenter:** Josh Litofsky (jhl182@psu.edu)

**Advisor:** Enrique Gomez (edg12@psu.edu)

Fully conjugated block copolymers, consisting of covalently bonded donor and acceptor blocks, can serve as the active layer in organic photovoltaics and other organic electronic devices. The use of Resonant Soft X-Ray Scattering (RSoXS) allows for studies into the molecular orientation and domain spacing of the polymers within lamellae by tuning the X-ray energy and polarization to examine various components of block copolymers. Using the conjugated block copolymer system of poly(3-hexylthiophene)-block-poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl), P3HT-b-PFTBT, and PFTBT derivatives, we can examine the effects of various polymer blocks on the differences of morphology between the donor and acceptor. Polarized Soft X-Ray Scattering (PSoXS) allows us to quantify the type of orientation of chains within block copolymer domains in thin films. Further examination of the anisotropy in PSoXS data provides a clear signature of the block copolymer microstructure. Radial distribution and Fourier transform calculations of model polymer structures corroborate this concept of block copolymer domains. Based on our early findings, we believe that within our P3HT-b-PFTBT block copolymer films, the crystalline P3HT blocks orient parallel to the block copolymer interface, and we confirm that the domain spacing extracted from PSoXS scales with the end-to-end distance of the blocks.

# Thermally Regenerative Batteries: A Story of Capturing Low-Grade Thermal Energy as Electricity

**Presenter:** Mohammad (Mim) Rahimi (mxr460@psu.edu)

**Advisor:** Bruce Logan (blogan@psu.edu)

A vast amount of low-grade thermal energy (temperature < 130 °C) is available globally at industrial plants and from solar and geothermal sources. Converting these sources of energy to electricity has drawn increasing attention in recent years. Solid-state thermoelectrics (SSTs) and liquid-based thermoelectrochemical systems (TECs) have been widely investigated as means of converting low-grade waste heat to electrical energy. However, despite much progress in both the methods, these systems have failed to produce high power densities, and have not been cost-effective. A recently developed thermally regenerative ammonia batteries (TRAB) showed a significantly higher power production (~12 times more) than both SSTs and TECs [1-4]. In a TRAB, electrical power is obtained from the formation of metal ammine complexes, which are produced by adding ammonia to the anolyte, but not to the catholyte. After the cell discharges, ammonia is separated from the anolyte using a conventional technology, such as distillation with low-grade waste heat, and then added to the other electrolyte for the next discharge cycle. The previous TRAB based on copper electrodes and a copper salt electrolyte showed a relatively high power production. However, unbalanced rates of anode dissolution and deposition of copper on the cathode limited the use of copper in closed-loop cycles. To address the reversibility issue, a silver-based TRAB was developed as an alternative to the copper-based TRAB. With silver, the cathodic and anodic coulombic efficiencies of the TRAB were the same (~100%), resulting in a reversible system for converting low-grade waste heat into electricity over many successive cycles. The developed silver system produced a net maximum power density of 30 W m<sup>-2</sup>-electrode area, with a net energy production of 490 Wh m<sup>-3</sup>-anolyte in a flow cell with an optimal hydraulic retention time (HRT) of 2 s. Successive deposition and dissolution cycling (i.e., the electrode reversibility) showed the system was stable over a hundred cycles. An initial economic analysis of the system showed that the price of electricity produced based on materials costs was 1.8 times more than the average electricity price in the U.S. (\$ 120 MWh<sup>-1</sup>), due primarily to the cost of the membrane as well as silver. However, this could be reduced to \$ 120 MWh<sup>-1</sup> if the cost of a membrane used in the system could be reduced to \$10 m<sup>-2</sup>. Other potential benefits, such as elimination of air pollution, and beneficial issues related to health and climate change were not included in the comparison. Although the cost of building and operation relative to energy production of Ag-TRAB is currently higher than that of conventional technologies, this approach could generate a cleaner method of electrical power generation using a waste source of heat if the commercial cost of ion exchange membranes could be significantly reduced.

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4. X. Zhu, M. Rahimi, C.A. Gorski, B. Logan; A thermally-regenerative ammonia-based flow battery for electrical energy recovery from waste heat, *ChemSusChem*, 9 (2016) 873-879.

## Session 3

# Identifying Atomic Arrangement in $\gamma$ -Brass Intermetallics to Design Site Isolated Catalysts

**Presenter:** Anish Dasgupta (aud224@psu.edu)

**Advisor:** Robert Rioux (rmr189@psu.edu)

Semi-hydrogenation of acetylene in a 1:100 ethylene rich stream destined for polyethylene manufacturing plant serves the dual purpose of removing acetylene (to <5 ppm) which acts as a poison for the polymerization catalyst and also enhancing the ethylene feed concentration making it commercially beneficial to design active and selective acetylene semi-hydrogenation catalysts. Such a catalyst should bind acetylene strongly but not ethylene. This may be achieved through active site isolation [1]. However, the binding strength of acetylene and ethylene on transition metals are positively correlated leading to an activity-selectivity optimization challenge [2].

We investigate the possibility of designing selective and active semi-hydrogenation catalysts by utilizing the unique  $\gamma$ -brass phase crystal structure of Ni-Zn and Pd-Zn (15.4-24 at% Ni/Pd) where the active sites (Ni/Pd) are isolated in an inert Zn matrix. We employ neutron diffraction and DFT calculations to identify the arrangement of atoms in the crystal at different M:Zn ratios (M=Ni/Pd). We further utilize model reactions ( $H_2$ - $D_2$  exchange and ethylene hydrogenation) along with Wulff constructions to identify the atomic arrangement on the surface, which effectively governs catalysis. The over-arching purpose of this work is to study (and ideally optimize) the effect of the size of active sites on activity and selectivity.

Neutron diffraction analysis on the Ni-Zn catalysts indicates that while only completely isolated Ni “monomers” exists in  $Ni_8Zn_{44}$  (15.4 at% Ni), Ni-Ni-Ni trimers are present in the bulk at higher Ni concentrations. In Pd-Zn  $\gamma$ -brass phase also, Pd-Pd-Pd trimers occur only if the Pd concentration exceeds 15.4 at% while just Pd monomers are present in  $Pd_8Zn_{44}$  (15.4 at% Pd). However, for this transition from monomer to trimer active sites to be catalytically relevant it must occur at the exposed surface and not just the bulk.

All four Ni-Zn catalysts behave equivalently (in terms of activity and activation barrier) for both  $H_2$ - $D_2$  exchange and ethylene hydrogenation indicating that only Ni monomers are exposed (because  $Ni_8Zn_{44}$  is precluded from having trimers) irrespective of Ni concentration. However,  $Pd_8Zn_{44}$  behaves differently from the other Pd-Zn catalysts. It had a noticeably higher activation barrier for  $H_2$ - $D_2$  exchange and displayed no activity towards ethylene hydrogenation whereas the other Pd-Zn catalysts showed appreciable hydrogenating ability. Moreover, the specific hydrogenation activity was seen to increase almost linearly from  $Pd_9Zn_{43}$  to  $Pd_{11}Zn_{41}$  while the activation barrier remained invariant, thereby suggesting that Pd trimers are exposed on the surface at Pd concentration greater than 15.4 at% and the number of surface trimers increases in a commensurate manner with stoichiometry. DFT surface energy calculations and Wulff construction confirmed our experimental results. The Ni trimer containing (1 -1 0) facet in  $Ni_9Zn_{43}$  was found energetically unfavorable to be exposed whereas in  $Pd_9Zn_{43}$  the trimer containing (1 -1 0) surface was most stable.

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# Mechanochemistry at Tribological Interfaces: Polymerization of Adsorbed Molecules by Mechanical Shear

**Presenter:** Xin He (xuh118@psu.edu)

**Advisor:** Seong Kim (shk10@psu.edu)

Physisorbed molecules at a sliding solid interface could be activated by mechanical shear and react with each other to form polymeric products that are often called tribopolymers. The dependence of the tribopolymerization yield on the applied load and adsorbate molecular structure was studied to obtain mechanistic insights into mechanochemical reactions at a tribological interfaces. An Arrhenius-type analysis of the applied load dependence of the tribopolymerization yield revealed how the critical activation volume ( $\Delta V^*$ ) varies with the structure of adsorbed molecules. Analysis of the experimental results in the context of mechanically assisted thermal reaction theory, combined with the atomistic details available from the simulations, suggested that some degree of distortion of the molecule from its equilibrium state is necessary for mechanically induced chemical reactions to occur and such a distortion occurs during mechanical shear when molecules are covalently anchored to one of the sliding surfaces. The surface material dependence of tribo-chemical reaction was investigated as well. The tribopolymer film synthesized in situ at the sliding interface exhibited an excellent boundary lubrication effect in the absence of any external supply of lubricant molecules.

# Probing the Dehydration-Induced Alteration of Cellulose Organization in Primary Cell Walls using Sum Frequency Generation (SFG) Vibrational Spectroscopy

**Presenter:** Shixin Huang (szh200@psu.edu)

**Advisor:** Seong Kim (shk10@psu.edu)

Cellulose is the most abundant natural polymer in biosphere with vast applications among food, paper and bioenergy. Although cellulose has great importance in human activities, its native structure and organization in plant cell walls are not fully understood. Our approach is using a non-linear optical method which called sum frequency generation (SFG) vibrational spectroscopy to study the meso-scale (~100s nm) arrangement of cellulose in plant cell walls.

We recently applied SFG to the comparison of dried primary cell walls which are originally hydrated during cell expansion and fully developed secondary cell walls. The SFG spectra from dried primary cell walls showed significant differences in the alkyl (CH, CH<sub>2</sub>) stretch region (2700-3000 cm<sup>-1</sup>) which indicated that those cellulose microfibrils in dried primary cell walls may have different assembly. To investigate whether cellulose organization was modified by dehydration, we used SFG, complemented with x-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and atomic force microscopy (AFM) as the techniques and onion epidermal walls as the sample model. Our results showed that the arrangement of cellulose microfibrils can be altered by the shrinking process of the pectin gel network in onion epidermal walls during dehydration and this alteration is reversible once the dried wall is fully rehydrated.

# Genome Scale Mapping Models and Algorithms for Stationary and Instationary MFA Based Metabolic Flux Elucidation

**Presenter:** Saratram Gopalakrishnan (sxg375@psu.edu)

**Advisor:** Costas D. Maranas (costas@engr.psu.edu)

Metabolic models used in  $^{13}\text{C}$  metabolic flux analysis ( $^{13}\text{C}$ -MFA) generally include a limited number of reactions primarily from central metabolism, neglecting degradation pathways and atom transition contributions for reactions outside central metabolism. This study addresses the impact on prediction fidelity of scaling-up core bacterial and cyanobacterial mapping models to a genome-scale metabolic mapping (GSMM) models, imEco726 (668 reaction and 566 metabolites) and imSyn617 (684 reactions, 615 metabolites) for *E. coli* and *Synechocystis* PCC 6803, respectively, representing a ten-fold increase in model size. The GSMM models are constructed using the CLCA algorithm following reduction of the corresponding metabolic models, iAF1260 and iSyn731, using experimentally measured biomass and product yield during growth on glucose and  $\text{CO}_2$ , respectively. The mapping models are then deployed for flux elucidation using isotopic steady-state MFA for *E. coli* to recapitulate experimentally observed labeling distributions of 12 measured amino acids, and isotopic instationary MFA for *Synechocystis*, to recapitulate labeling dynamics of 15 central metabolites. In both models, 80% of all fluxes varies less than one-tenth of the basis carbon substrate uptake rate primarily due to the flux coupling with biomass production. Overall, we find that both the topology and estimated values of the metabolic fluxes remain largely consistent between the core and GSMM models for *E. coli*. Stepping up to a genome-scale mapping model leads to wider flux inference ranges for 20 key reactions present in the core model. The glycolysis flux range doubles due to the possibility of active gluconeogenesis, the TCA flux range expanded by 80% due to the availability of a bypass through arginine consistent with labeling data, and the transhydrogenase reaction flux was essentially unresolved due to the presence of as many as five routes for the inter-conversion of NADPH to NADH afforded by the genome-scale model. By globally accounting for ATP demands in the GSMM model the unused ATP decreased drastically with the lower bound matching the maintenance ATP requirement. A non-zero flux for the arginine degradation pathway was identified to meet biomass precursor demands as detailed in the iAF1260 model. Significant flux range shifts were observed using a GSMM model compared to a core model in *Synechocystis* arising from the inclusion of 18 novel carbon paths in the GSCM model. In particular, no flux is channeled through the oxidative pentose phosphate pathway, resulting in a reduced carbon fixation flux. In addition, a higher flux is seen through the Transaldolase reaction, serving as a bypass route to Fructose biphosphatase. Serine and glycine are found to be synthesized from 3-phosphoglycerate and the photorespiratory pathway, respectively. Pyruvate is synthesized exclusively via the malate bypass with trace contributions from pyruvate kinase. Furthermore, trace flux is predicted through the lower TCA cycle indicating either pathway incompleteness or dispensability during photoautotrophic growth. Despite these differences, 80% of all reactions in both genome-scale models are resolved to within 10% of the respective substrate uptake rate due to the presence of 411 and 407 growth-coupled reactions in *E. coli* and *Synechocystis*, respectively. Flux ranges obtained with GSCM models are compared with those obtained upon projecting core model ranges on to a genome-scale metabolic model to elucidate the loss of information and erroneous biological inferences about pathway usage arising from assumptions contained within core models, reaffirming the importance of using mapping models with global carbon path coverage in  $^{13}\text{C}$  metabolic flux analysis.

## Poster Session

# Effect of Zinc Chloride and PEG Concentrations on the Critical Flux during Tangential Flow Microfiltration of BSA Precipitates

**Presenter:** Zhao Li (zzl5215@psu.edu)

**Advisor:** Andrew L. Zydney (alz3@psu.edu)

There is renewed interest in the possibility of using precipitation for initial capture of high value therapeutic proteins as part of an integrated continuous downstream process. These precipitates can be continuously washed using tangential flow filtration, with long term operation achieved by operating the membrane modules below the critical filtrate flux for fouling. Our hypothesis was that the critical flux for the precipitated protein would be a function of the properties of the precipitate as determined by the precipitation conditions. We evaluated the critical flux using a flux-stepping procedure for model protein precipitates (bovine serum albumin) generated using a combination of a crosslinking agent (zinc chloride) and an excluded volume precipitant (polyethylene glycol). Data were obtained using 0.2  $\mu\text{m}$  pore size hollow fiber polyethersulfone microfiltration membranes. The critical flux varied with shear rate to approximately the  $1/3$  power, consistent with predictions of the classical polarization model. The critical flux increased significantly with increasing zinc chloride concentration, going from 60 L/m<sup>2</sup>/hr for a 2 mM ZnCl<sub>2</sub> solution to 200 L/m<sup>2</sup>/hr for an 8 mM ZnCl<sub>2</sub> solution. In contrast, the critical flux achieved a maximum value at an intermediate polyethylene glycol (PEG) concentration of around 6 weight percent at a fixed ZnCl<sub>2</sub> concentration of 3.5 mM. Independent measurements of the effective size and viscosity of the protein precipitates were used to obtain additional understanding of the effects of ZnCl<sub>2</sub> and PEG on the precipitation and the critical flux. These results provide important insights into the development of effective tangential flow filtration systems for processing large quantities of precipitated protein as would be required for large scale continuous protein purification by precipitation.

# Modified Equation-free Control of Distributed Parameter Systems with Model Mismatch

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Many chemical and material industry processes exhibit spatial variation of the state variables because of diffusion, convection and reaction. These processes can be mathematically described by partial differential equations based on conservation equations. This kind of system is called distributed parameter system (DPS). To achieve economic profit and improve the product quality, controlling DPS is important. Since the infinite dimensional state space dynamics of DPS makes controller design nontrivial, a standard way to tackle the issue is to construct a reduced order model (ROM) using Galerkin's method. Then controller and observer can be designed based on the ROM with less computational cost. However, most of the established methods require a mathematical model of the system.

To relax the requirement on the mathematical model, in [1] we proposed an equation-free method to control systems when the knowledge of the governing law is unavailable or incomplete and the actuator effect is known. This method was developed based on the feature of discrete empirical interpolation method (DEIM) [2] that the selection of the interpolation indices can limit the growth of the error of the approximation by DEIM. A set of snapshots (observation of the system) is assumed available. Estimation of the dynamics can be made using these previous observations and continuous measurement on limited number of locations.

In this presentation, we improve the accuracy of the estimation of the dynamics when the system dynamics no longer match previous observations [3]. A correction term is added to reduce the error of the estimation of the system dynamics. The difference between the expected value of the state and the actual value is used to update the correction term. The modified version is applied to a diffusion reaction process.

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# Chemical Degradation of Polyacrylamide during Hydraulic Fracturing

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Polyacrylamide (PAM) based friction reducers are a primary ingredient of slickwater hydraulic fracturing fluids. Little is known regarding the fate of these polymers under downhole conditions, which could have important environmental impacts including strategies for reuse or treatment of flowback water. The objective of this study was to evaluate the chemical degradation of high molecular weight PAM, including the effects of shale, oxygen, temperature, pressure, and salinity. Data were obtained with a slickwater fracturing fluid exposed to both a shale sample collected from a Marcellus shale outcrop and to Marcellus core samples at high pressures/temperatures (HPT) simulating downhole conditions. Based on size exclusion chromatography analyses, the peak molecular weight of the PAM was reduced by two orders of magnitude, from roughly 10 MDa to 200 kDa under typical HPT fracturing conditions. The rate of degradation was independent of pressure and salinity but increased significantly at high temperatures and in the presence of oxygen dissolved in fracturing fluid. Results were consistent with a free radical chain scission mechanism, supported by measurements of sub- $\mu\text{M}$  hydroxyl radical concentrations. The shale sample adsorbed some PAM (~30%), but importantly it catalyzed the chemical degradation of PAM, likely due to dissolution of  $\text{Fe}^{2+}$  at low pH. These results provide the first evidence of radical-induced degradation of PAM under HPT hydraulic fracturing conditions without additional oxidative breaker.

# Random Pore Model & Langmuir-Hinshelwood Kinetics Applied to Industrial Coal Gasification

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Random pore model (Bhatia and Perlmutter, 1980; 1981; 1983) has been applied extensively to both char oxidation systems (Su and Perlmutter, 1985) and char gasification systems with CO<sub>2</sub> (Bhatia, 1981) and H<sub>2</sub>O (Chi and Perlmutter, 1989). The model solutions developed in these works assume the reaction to be first order in the reactant gas composition. But it is well known that coal char systems are highly porous and the gasification reactions follow the Langmuir-Hinshelwood (LH) kinetics (Ergun, 1955).

There have been attempts to combine random pore model with LH kinetics for competing CO<sub>2</sub> and H<sub>2</sub>O gasification reactions (Umemoto et. al., 2013). But these efforts are restricted to the low temperature kinetically controlled regime. There is a need to extend the combined model to systems at higher temperature that are pore diffusion controlled to better understand the industrial systems of coal gasification.

In this work we extend the random pore model with transport and diffusion effects to incorporate LH kinetics first to CO<sub>2</sub> gasification systems with varying amounts of CO using multi-species reaction diffusion modeling. We then study the H<sub>2</sub>O gasification systems in presence of H<sub>2</sub>O, CO and H<sub>2</sub>. Finally we combine both these efforts to study the complete industrial gasification systems that involve both CO<sub>2</sub> and H<sub>2</sub>O in the presence of all four gases: CO<sub>2</sub>, CO, H<sub>2</sub>O and H<sub>2</sub>. Using this model we gain important insights into optimizing the feed compositions to obtain the final product: syngas, with the desired specifications.

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