



Annual Chemical Engineering Research Symposium

Tuesday, September 17, 2013
Celebration Hall Conference Center

Annual Chemical Engineering Research Symposium

Tuesday, September 17, 2013
Celebration Hall Conference Center

8:45 am	Coffee and Registration		
9:00 am	Opening Remarks		
9:15 am	Session 1	Section Leader: Abhishek Kar	
		<i>Colloidal engineering of nanofluids</i>	Saba Lotfizadeh
		<i>OPTO/Acoustic tweezers: Microfluidic particles/cell concentrating and patterning</i>	Yuliang Xie
		<i>Multifunctional organic nano-micro biomaterials for targeted drug delivery to brain tumors.</i>	Pouria Fattahi
		<i>Cell shape regulates epithelial-myofibroblast transition</i>	Joseph O'Connor
10:35 am	Break		
10:45 am	Session 2	Section Leader: Pouria Fatathi	
		<i>Alcohol, the amazing mechanical (and social!) lubricant</i>	Anthony Barthel
		<i>Using droplet microfluidic to synthesize nanomaterials</i>	Nicholas Sturgis
		<i>Development of hybrid-MD/MC methods to investigate oxide formation on Pd catalysts</i>	Thomas Senftle
		<i>Influence of structure and electronic properties of Ni-Zn bimetallic catalysts for Acetylene Semi-Hydrogenation</i>	Charles Spanjers
12:05 pm	Lunch		
		Lunch – Celebration Hall	
1:00 pm	Session 3	Section Leader: Nymul Khan	
		<i>Nanoparticle-filled solid polymer electrolytes</i>	Lalitha Ganapatibhotla
		<i>Polymer semiconductor for photovoltaic applications</i>	Changhe Guo
		<i>Domain compositions govern charge recombination and device performance in polymer/fullerene solar cells</i>	Sameer Vajjala Kesava
2:00 pm	Session 4	Section Leader: Chris Lee – Section Leader	
		<i>Adaptive and responsive nanoparticle amphiphiles</i>	Sun Hae Ra Shin
		<i>Comparative genome-scale modeling of the metabolic potential of Cyanobacteria <i>Cyanothece</i> sp. ATCC 51142 and <i>Synechocystis</i> sp. PCC 6803.</i>	Rajib Saha
		<i>Determining the structure of cellulose and hemicellulose in the primary plant cell wall using small angle neutron scattering [SANS]</i>	Shih-Chun Huang
3:00 pm	Break		
3:10 pm	Session 5	Section Leader: Charlie Spanjers	
		<i>Coarse-grained simulation of primary cell wall polysaccharides</i>	Bingxin Fan
		<i>Engineering microbial consortia for conversion of lignocellulosic biomass to fuel</i>	Trevor Zuroff
		<i>Transient gene expression and bioreactor design to improve plant propagation of cacao.</i>	Sergio Florez
		<i>Process design for the production of an alternative biofuel and development of <i>Rhodobacter capsulatus</i> as a platform organism</i>	Nymul Khan
4:30 pm	Poster Session – Happy Hour & Awards		

Colloidal Engineering of Nanofluids

Presenter: Saba Lotfizadeh

Advisor: Themis Matsoukas

In heat transfer literature, nanofluid is a term used to entitle a suspension of nanoparticles in a fluid. Replacing common cooling fluids, which usually have low thermal conductivities, with nanofluids is an efficient way to elevate the low heat transfer rates in different industrial applications. The standard classical model to predict this enhancement is Maxwell's mean field theory, which is borrowed from electricity. Assuming particles to be motionless and well dispersed, the theory predicts that the conductivity of the suspension depends only of the volume fraction of the particles but not their size. Inconsistencies between experiments and theory have been the focus of many studies. Different explanations were introduced to account for higher enhancements in experimental measurements in compare to the theoretical prediction.

Thermal conduction in a system with different phases is dominated by the conductivity of the continuous phase. Therefore, depending on whether the continuous phase is the fluid or the particles, Maxwell standard theory predicts two limiting bounds. Lower bounds, which is usually more quoted in literature as Maxwell prediction, represents the configuration where the particles are well dispersed in the fluid as the continuous phase. Whereas upper bound demonstrates a configuration where the particles construct the continuous phase by forming chain-like networks connected extensively in the fluid. The fluid trapped in between the particle's chains represents the dispersed phase. This situation is analogous to a colloidal gel. Since colloidal particles invariably suffer from aggregation, aggregate networks are thought to increase conductivity somewhere between the two bounds of the Maxwell theory. Direct experimental tests of this hypothesis have not been made because controlling the degree of aggregation in typical colloids in a systematic way is not possible. Here have employed a colloidal system with the ability to undergo reversible aggregation/deaggregation and produced stable aggregates of desired size, all the way from fully dispersed nanoparticles (40nm in diameter) to fully gelled systems (infinite size). Thermal conductivity measurements are provided for different size of stable aggregates in the fluid for different volume fractions.

Also, we have employed a computational model to explain the experimental results and quantify the effect of aggregation on thermal conductivity. We generate model clusters in a base fluid and evaluate the thermal conductivity of the system using a Monte Carlo algorithm. Briefly, we discretize the aggregate and embed a large number of random walkers whose displacement is biased by the thermal conductivity in the vicinity of their location. The thermal diffusivity and heat conduction are then obtained from the average mean-squared displacement. We vary the degree of aggregation in a systematic way and find the conductivity increases up to 30% above the lower Maxwell bound. The results suggest that manipulation of the microstructure of particle-fluid systems has the potential to produce enhanced thermal properties and provide an explanation for the "anomalous" enhancements often reported by experimentalists who do not control the state of aggregation in suspension.

OPTO/Acoustic tweezers: Microfluidic particles/Cell concentrating and patterning**Presenter:** Yuliang Xie**Advisor:** Tony Jun Huang

We present a programmable, biocompatible technique for dynamically concentrating and patterning particles and cells in a microfluidic device. We name it “optoacoustic tweezers” since our technique utilizes opto-thermally generated, acoustically activated, surface bubbles. Our demonstrated optoacoustic tweezers are capable of concentrating particles/cells at any prescribed locations in a microfluidic chamber without the use of permanent structures, rendering it particularly useful for the formation of flexible, complex cell patterns. Additionally, this technique has demonstrated excellent biocompatibility and can be conveniently integrated with other microfluidic units. In our experiments, micro-bubbles were generated by focusing a 405 nm diode laser onto a gold-coated glass chamber. By properly tuning the laser, we demonstrate precise control over the position and size of the generated bubbles. Acoustic waves were then applied to activate the surface bubbles, causing them to oscillate at an optimized frequency. The resulting acoustic radiation force allowed us to locally trap particles/cells, including 15 μm polystyrene beads and HeLa cells, around each bubble. Cell-adhesion tests were also conducted after cell concentrating to confirm the biocompatibility of this technique. In conclusion, by integrating optothermal effect, acoustic waves using a microbubble, several important cell operations were demonstrated, such as: concentrating, culturing, and patterning. These operations will much benefit the future cell research. More in-depth biological research is being carried on using this platform.

Multifunctional organic nano-micro biomaterials for targeted drug delivery to brain tumors.

Presenter: Pouria Fattahi

Advisor: Ali Borhan

Despite significant progress in development of new chemotherapeutic agents and methods of drug delivery, the effective therapy for treatment of brain tumors remains a challenge. To overcome the blood brain barrier problem, high doses of systemic intravenous delivery of anticancer drugs are required, that can cause adverse side effects. It is becoming clear that a major unmet challenge for the field is to develop methods that allow effective and local delivery of chemotherapeutic agents in cellular level. Many 'solutions' to this problem have been published on this subject during the last decade, but we yet have to see an effective delivery technology.

In this study we report a new method for local and on-demand release of 1,3-bis(2-chloroethyl)-1-nitrosourea (BCNU) using electrical actuation of conducting polymer on the surface of microelectrodes. This innovative modified-electrode allows for a more precise control of anticancer agent releases at the tumor sites. The fabrication process involves electrostatic spraying of BCNU-loaded biodegradable poly (lactic-co-glycolic acid) (PLGA) microspheres on a gold substrate, followed by electrochemical polymerization of conductive polymers poly (3,4-ethylenedioxythiophene) (PEDOT) on the gold substrate and around the BCNU-loaded PLGA microspheres. We can control the diameter of the PLGA spheres by controlling the electrospraying parameters such as polymer concentration, flow rate, voltage, needle gauge, and distance between the syringe and target plate. Field Emission Scanning Electron Microscopy (FESEM) revealed that the size of BCNU-loaded PLGA spheres and the wall thickness of PEDOT spherical cups ranged from 700 nm to 5 μ m and 150 nm to 200 nm, respectively. By changing the polymerization time, we can reproducibly control the opening size of the conducting polymer shell and create either fully coated PEDOT (double layer sphere) or partially coated PEDOT (spherical cup). We anticipate that BCNU can be released from conducting polymer microspherical structure in a controlled fashion by actuation of PEDOT during electrical stimulation (\sim 1V). In addition, we also measured drug release profiles and developed mathematical models to estimate the effective diffusion coefficient of BCNU in different PLGA microspheres. The BCNU release profile for microspheres was found to be in good agreement with model predictions for drug release as a result of drug diffusion and degradation of PLGA microspheres.

10:15 AM

Cell shape regulates epithelial-myofibroblast transition

Presenter: Joseph O'Connor

Advisor: Esther Gomez

Myofibroblasts, specialized cells within the body that aid in normal wound healing processes, exert large contractile forces on their microenvironment with the primary job of these cells being to assist in the closure of wounds. Aberrant and chronic activation of myofibroblasts can lead to the development of pathological conditions including fibrosis and cancer. Mechanical tension is thought to be crucial for the activation of myofibroblasts from other cell types; however, a mechanistic understanding of how biophysical cues regulate myofibroblast phenotype is not clear. Here, we employ a microfabrication approach to investigate the role of cellular shape and tension in the development of myofibroblasts. We find that cell shape controls the subcellular localization of key mechanoresponsive molecules and subsequent expression of cytoskeletal proteins that contribute to the increased contractile features characteristic of activated myofibroblasts. Results provide insight into how mechanical signals can control the development of myofibroblasts and may suggest ways to engineer therapeutic and diagnostic solutions for fibrosis and cancer.

10:45 AM

Alcohol, the amazing mechanical (and social!) lubricant

Presenter: Anthony Barthel

Advisor: Seong H. Kim

Boundary lubrication involves lubricating surfaces that are in intimate contact with one another and is important to many mechanical systems. Adsorbed vapor-phase molecules are a promising candidate for conformal lubrication in the boundary lubrication regime. To investigate this, the effect of alcohol vapor on the friction and wear between surfaces was studied using a ball-on-flat tribometer and infrared spectroscopy on a variety of different material substrates. Linear chain alcohols, as well as branched and unsaturated alcohols, were found to physisorb onto oxide, metal, and ceramic surfaces. The adsorption isotherm for these alcohols revealed that a monolayer quickly forms at low vapor partial pressure (p/p_{sat}), followed by slower adsorbed growth at intermediate p/p_{sat} and finally rapid adsorbed layer growth as saturation is approached. The adsorbed alcohol molecules drastically influence friction and wear for all materials, and have a nearly identical affect across a range of materials. Wear ceases and the friction coefficient reaches a value of 0.2 during sliding tests, irrespective of the material's behavior in a dry environment. This often resulted in a friction coefficient decrease, such as with steel, copper, or silicon surfaces, but could also increase friction, such as with diamond-like carbon surfaces. Some physisorbed alcohol molecules can also react under sliding to form a tribopolymer which imparts additional lubrication.

Using droplet microfluidics to synthesize nanomaterials

Presenter: Nick Sturgis

Advisor: Rob Rioux

There is little known about the formation mechanism of nanomaterials because the conditions for nanoparticle nucleation, crystallization and growth typically require high temperatures and occur in solution phase, both of which create conditions that are not easily amenable to direct, in-situ characterization. Therefore, the deduction of a reaction mechanism relies mostly on observations of the nanomaterial after they have formed. Traditional synthetic approaches to producing nanomaterials often rely on injection methods that introduce temperature and thermal gradients to the system. The fluxes associated with these systems and the rapid kinetics makes for a difficult to characterize synthetic method.

Droplet-based microfluidics overcomes the drawbacks of batch syntheses by providing a system with minimal mass and heat transfer effects. Droplets provide a mechanism of mixing otherwise unavailable at low Reynolds number and the small flow streams rapidly equilibrate with the surrounding device temperature. Carrying reactions within droplets also isolates reagents as they flow through the device by preventing the droplets from contacting the walls, providing characteristics approaching an ideal plug flow reactor. Additionally, the continuous nature of microfluidics allows the coupling of reaction progression to spatial coordinates on a device; observation at a fixed point provides a snapshot of the reaction progression that is independent of time. This means the timescale for an analytical technique does not have to be faster than the reaction kinetics. Using these microreactors we can efficiently and reproducibly probe the phase space of a reaction system by having the ability to finely tune the time, temperature, and concentration of reactions. In addition to studying the effect these variables have on the final structure, we have coupled this method with synchrotron techniques to provide in-situ reaction characterization.

Development of hybrid-MD/MC methods to investigate oxide formation on Pd catalysts**Presenter:** Thomas Senftle

Advisor: Michael Janik and Adri C.T. van Duin

Oxide formation on palladium surfaces impacts the activity and selectivity of Pd-based catalysts, which are widely employed under oxygen rich operating conditions. To investigate oxidation processes over Pd catalysts at time and length scales inaccessible to quantum based computational methods, we have developed a Pd/O interaction potential for the ReaxFF reactive force field. Using the resulting potential, we conducted molecular dynamics simulations of oxide formation on Pd(111), Pd(110), and Pd(100) surfaces. The results demonstrate good agreement with previous experimental observations; bulk oxidation below Pd(111) and Pd(100) surfaces is kinetically hindered by surface oxides, whereas bulk oxidation occurs readily over Pd(110). Additionally, we developed a ReaxFF-based hybrid grand canonical Monte Carlo/molecular dynamics (GC-MC/MD) approach to assess the thermodynamic stability of oxide formations. This method is used to derive a theoretical phase diagram for the oxidation of Pd₉₃₅ clusters in temperatures ranging from 300 K to 1300 K and oxygen pressures ranging from 10-14 atm to 1 atm. We observe good agreement between experiment and ReaxFF, which validates the Pd/O interaction potential and demonstrates the feasibility of the hybrid GC-MC/MD method for deriving theoretical phase diagrams. The GC-MC/MD method developed is novel to ReaxFF, and is well suited to studies of supported-metal-oxide catalysts, where the extent of oxidation in metal clusters can significantly influence catalytic activity, selectivity, and stability.

Influence of Structure and Electronic Properties of Ni-Zn Bimetallic Catalysts for Acetylene Semi-Hydrogenation

Presenter: Charles Spanjers

Advisor: Rob Rioux

The catalytic semi-hydrogenation of acetylene to produce ethylene is a common method for the removal of trace acetylene (~1%) in ethylene feed streams destined for ethylene polymerization. Acetylene impurities in ethylene produced from naphtha can cause deactivation of the polymerization catalyst if not removed from ethylene prior to polymerization. An effective catalyst for this reaction converts all of the acetylene to ethylene without further converting any ethylene to ethane such that there is a net increase in the amount of ethylene. Well-dispersed Pd supported on aluminum oxide exhibits high activity for acetylene removal, but limited selectivity and long-term stability. Pd-Ag alloys, and more recently, intermetallic Pd-Ga compounds, demonstrate high selectivity towards ethylene and long-term stability. Improved selectivity is a result of isolation of active Pd hydrogenation sites which reduces the ability of the catalyst to over hydrogenate to form ethane, produce oligomerization products, and form coke on the catalyst surface. Recent efforts have demonstrated that intermetallic NiZn may be a suitable replacement for Pd-based catalysts based on DFT calculations and experimental validation. Replacing precious metal Pd-based catalysts with base metal Ni-based catalysts would be highly beneficial in terms of cost. We report on the catalytic selectivity of unsupported bulk intermetallic Ni-Zn catalysts for acetylene semi-hydrogenation. The addition of Zn to Ni results in a higher selectivity for the desired product, ethylene, and a decrease in the formation of higher molecular weight compounds.

Nanoparticle-filled Solid Polymer Electrolytes for Lithium Ion Batteries

Presenter: Lalitha Ganapatibhotla

Advisor: Janna Maranas

We explore the influence of nanoparticle surface chemistry and aspect ratio on performance of nanofilled solid polymer electrolytes (SPEs). SPEs are the key to light-weight and energy-dense rechargeable lithium ion batteries but suffer from low room temperature ionic conductivities. Spherical ceramic fillers are known to improve SPE conductivity and mechanical properties. Our experiments on acidic and neutral spherical particle filled SPEs indicate highest conductivity enhancement at eutectic composition and temperature, which is independent of filler surface chemistry. These findings can be explained by a new mechanism, via stabilization of alternating layers of PEO and highly conducting PEO₆:LiClO₄ tunnels at the filler surface. More such structures would be stabilized at a filler surface with high aspect ratio. Consistent with this hypothesis, gamma-Al₂O₃ nanowhiskers (2-4 nm in diameter and 200-400 nm in length) intensify the effect of gamma-Al₂O₃ nanoparticles. At the eutectic composition, they increase conductivity more than the nanoparticles, and at non-eutectic compositions, they decrease conductivity more than the nanoparticles. The diameters of the two fillers are similar, but the change in aspect ratio (1 to 100) improves conductivity by a factor of 5. The influence of morphology and PEO segmental dynamics on conductivity enhancement will be presented. Morphology is examined using electron microscopy, segmental dynamics is determined using quasi-elastic neutron scattering and conductivity is measured using dielectric spectroscopy. All measurements are performed at a series of Li compositions, temperatures and nanoparticle loadings.

1:20 PM

Conjugated block copolymer photovoltaics

Presenter: Changhe Guo

Advisor: Enrique Gomez

Bulk heterojunction organic solar cells rely on intricate morphologies within the active layer for efficient photogeneration of charges. State-of-the-art devices are composed of donor/acceptor mixtures and rely on kinetically trapped non-equilibrium morphologies. In contrast, the self-assembly properties of block copolymers have the potential to create unique nanoscale structures for efficient photovoltaic operation. Using a poly(3-hexylthiophene-2,5-diyl) - poly((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(thiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) conjugated block copolymer (P3HT-b-PFTBT), we demonstrate that devices comprised of donor-acceptor block copolymer active layers can function as solar cells with efficiencies around 3%. The combination of resonant soft X-ray scattering (RSOXS) and grazing-incidence wide-angle X-ray scattering (GIWAXS) demonstrates that the block copolymer mesophase dominates the thin-film structure, thereby exhibiting lamellar morphologies and transforming mostly edge-on crystalline orientations for neat P3HT to face-on orientations for P3HT within block copolymers.

***Domain compositions govern charge recombination and device performance in
polymer/fullerene solar cell***

Presenter: Sameer Vajjala Kesava

Advisor: Enrique Gomez

Charge separation and recombination in polymer/fullerene solar cells is highly dependent on the microstructure of donor-acceptor interfaces. Unfortunately, the ubiquitous presence of mixed phases in mixtures of organic semiconductors utilized in the active layer of polymer/fullerene solar cells creates multiple morphologically distinct interfaces which are capable of charge photogeneration or recombination. We have examined the microstructure of poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]germole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] (PGeBTBT)/[6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) mixtures using energy-filtered transmission electron microscopy and resonant soft X-ray scattering to examine the microstructure and domain compositions. PGeBTBT is a low band gap polymer (1.5 eV) belonging to cyclopentadithiophene-based polymer family that has been shown to produce high short-circuit currents when employed as the active layer of organic solar cells. Structural characterization shows that the microstructures of the mixtures do not change significantly with the overall composition of the film. Composition maps generated from energy-filtered electron microscopy experiments, however, demonstrate that fullerene domain compositions vary significantly with the overall film composition. Furthermore, the amount of PGeBTBT in the fullerene-rich domains is anti-correlated with device performance. Photo-induced absorption studies using ultrafast infrared spectroscopy (URIR) demonstrate that at 1 ps after photoexcitation the polaron concentration is highest when fullerene domains contain the least amount of polymer. Thus, the purity of the fullerene-rich domains is critical for efficient charge photogeneration. Our results suggest that controlling the composition of mixed phases in polymer/fullerene active layers is critical for the device performance of organic photovoltaics.

Integration of magnetic nanoparticles into bilayer structures via adaptive surface chemistry

Presenter: Sun Hae Ra Shin

Advisor: Kyle Bishop

This talk presents the spontaneous incorporation of amphiphilic magnetic nanoparticles into the walls of surfactant vesicles. Cobalt ferrite nanoparticles (~10 nm in diameter) were functionalized with mixed monolayers of hydrophilic and hydrophobic ligands, which are known to redistribute dynamically on the particle surface in response to changes in the local environment. When the cobalt ferrite nanoparticles are mixed with preformed vesicles, the hydrophobic ligands on the particle surface interact favorably with the hydrophobic core of the bilayer structure and guide the incorporation of particles into the vesicle walls. Unlike previous magnetic field-responsive vesicles that rely on localized heating of the magnetic particles, the vesicles described here respond to directly applied fields through the strong coupling between the particles' internal magnetic moments and their asymmetric surface chemistry. The field-induced response of the vesicles will be investigated via magnetic field-triggered contents release.

***Comparative Genome-Scale Modeling of the Metabolic Potential of Cyanobacteria
Cyanotheca sp. ATCC 51142 and Synechocystis sp. PCC 6803***

Presenter: Rajib Saha

Advisor: Costas Maranas

A number of trail-blazing metabolic models of cyanobacterial systems have been developed over the past decade. While these models have offered valuable insights into cyanobacterial biology, they remain incomplete in many ways: 1) They do not cover the full range of essential metabolism, 2) The descriptions of biomass used in these models are incomplete and/or derived from measurements of unrelated strains, and 3) The metabolic reactions contained within these models are not directly associated with genes and proteins and are often not elementally and charge-balanced. In addition, the similarities and differences between cyanobacterial metabolisms have not been addressed through comparative modeling.

Here, we assemble, update and compare genome-scale models (iCyt773 and iSyn731) for two phylogenetically related cyanobacterial species, namely *Cyanotheca sp. ATCC 51142* and *Synechocystis sp. PCC 6803*. While *Cyanotheca 51142* is a potent unicellular diazotroph that produces large amounts of H₂ photosynthetically, *Synechocystis 6803* is the first sequenced photosynthetic organism and is a workhorse organism for cyanobacterial synthetic biology. In our models, all reactions are elementally and charge balanced and localized into four different intracellular compartments (i.e., periplasm, cytosol, carboxysome and thylakoid lumen) and biomass descriptions are derived based on experimental measurements of these two strains. We have added new reactions absent from earlier models (266 and 322, respectively) that span most metabolic pathways with an emphasis on lipid biosynthesis. All thermodynamically infeasible loops are identified and eliminated from both models.

Comparisons of model predictions against gene essentiality data reveal a specificity of 0.94 (94/100) and a sensitivity of 1 (19/19) for the *Synechocystis iSyn731* model. The diurnal rhythm of *Cyanotheca 51142* metabolism is modeled by constructing separate (light/dark) biomass equations and introducing regulatory restrictions over light and dark phases. Specific metabolic pathway differences between the two cyanobacteria alluding to different bio-production potentials are reflected in both models. Additionally, we have applied these models to identify targets for metabolic engineering of *Synechocystis 6803* to overproduce biofuel molecules including isoprene and n-alkanes.

Determining the structure of cellulose and hemicellulose in the primary plant cell wall using small angle neutron scattering [SANS]

Presenter: Shih-Chun Huang

Advisor: Janna Maranas

Previous works have established the importance of hemicellulose in primary cell wall. Hemicellulose interacts with cellulose microfibrils to form a complicated nano-composite, and become the major body of primary cell wall. Further definition on hemicellulose or cellulose alone from the nano-composite is challenging by using traditional methods. In this work, we provide new insight on the structure of the primary cell wall by using small angle neutron scattering combined with contrast matching. We determine the structural arrangement in primary cell walls of wild-type and xyloglucan-deficient [xxt1xxt2] *Arabidopsis Thaliana*. Cellulose microfibril measurements share features with SEM and AFM. The interfibril spacing of cellulose microfibril is 30% less in xxt1xxt2 *Arabidopsis*. Hemicellulose measurements reveal structure of extended coils and exterior microfibril coating. Extended coils characteristic in a good solvent are observed in both samples. But significant hemicellulose coating is only observed in the wild type sample. Some of us recently suggested how different region of hemicellulose influence biomechanical strength [Park and Cosgrove, 2012, Plant Physiology]. Now we have a strong evidence to conclude that the xyloglucan coating layer has an impact on wall mechanical strength.

3:10 PM

Coarse-grained simulation of primary cell wall polysaccharides

Presenter: Bingxin Fan

Advisor: Janna Maranas

Cellulose microfibrils are recalcitrant toward dissolution, thus it is difficult to extract and characterize them without modifying their native state. To study the molecular level behavior of microfibrils over 100 sugar residues, we construct a coarse-grained model of solvated cellulose I β microfibril using one bead per sugar residue. We derive the coarse-grained force field from atomistic simulation of a 36 chain, 40-residue microfibril by requiring consistency between the chain configuration, intermolecular packing and hydrogen bonding of the two levels of modeling. Coarse-grained force sites are placed at the geometric center of each glucose ring. Intermolecular van der Waals and hydrogen bonding interactions are added sequentially until the microfibril crystal structure in the atomistic simulation is achieved. This requires hydrogen bond potentials for pairs that hydrogen bond in cellulose I β , as well as those that can hydrogen bond in other structures, but not in cellulose I β . Microfibrils longer than 100 nm form kinks along their longitudinal direction, with an average periodicity of 70 nm. The behavior of kinked regions is similar with a bending angle of approximately 20°. These kinked regions might be linked to observations of periodic disorder from small angle neutron scattering and acid hydrolysis.

Engineering microbial consortia for conversion of lignocellulosic biomass to fuel**Presenter:** Trevor Zuroff

Advisor: Wayne Curtis

A symbiotic microbial consortium was developed which improves conversion of both cellulose and lignocellulose (switchgrass) to ethanol. The consortium was specifically designed as a solution for achieving consolidated bioprocessing (CBP) or the simultaneous biological enzyme production, hydrolysis and fermentation of lignocellulose to biofuel. CBP systems are limited by the lack of a suitable single organism to complete the required hydrolysis and fermentation steps. As an alternative to single culture bioprocessing, mixed cultures or consortia represent a potential solution to achieve the appropriate combination of metabolic and hydrolytic properties. However, the stability of such consortia and lack of simplistic bioprocessing are often cited as inhibitors of this type of approach. The advances made in this work demonstrate how inducing cooperation within microbial consortia may overcome these challenges. A symbiotic consortium of the cellulolytic mesophile, *Clostridium phytofermentans*, and a cellodextrin fermenting yeast *Saccharomyces cerevisiae* cdt-1, was developed. Cooperation was induced through diffusion of oxygen into culture medium which acts to inhibit the growth of the obligate anaerobe, *C. phytofermentans*. When provided a soluble carbon source from *C. phytofermentans* hydrolysis of cellulose, the yeast metabolizes oxygen relieving the inhibitory effect. The symbiotic consortium outperforms mono-cultures by producing about two times more ethanol from purified cellulose and 50% more from *Panicum virgatum* (switchgrass). This presentation will discuss the design, verification and application of this consortium in the context of a new, consortia-mediated, paradigm of biofuels production. Ultimately, the successful development of a microbial consortium for CBP of lignocellulosic biomass may make renewable biomass-based fuels a reality.

Transient gene expression and bioreactor design to improve plant propagation of cacao.**Presenter:** Sergio Florez

Advisor: Wayne Curtis

Somatic embryogenesis (SE) is a way to make superior plants with a desired trait. SE allows the reprogramming of a somatic cell to form a new plant. This extremely complex system is tightly controlled by a network of regulating factors in the plant's signaling mechanism. This network can be tweaked by environmental changes or more recently by the introduction of transcription factors to activate or repress specific pathways. This manipulation can be done through an agrobacterium mediated gene transfer however, very precise timing and control is necessary to prevent abnormal development or the production of transgenic plants. As a result, transient expression, the introduction of a gene into the plant for a short period of time, is a critical tool that can be used to increase productivity of SE. Using cacao (chocolate tree) as a plant model, this strategy is being implemented and has shown an increase embryo production by using the transcription factor Babyboom. These results suggest a new genetic method of plant propagation that can bypass extensive tissue culture work to obtain somatic embryos. In addition to the modified genetic environment, an optimal culture environment is essential for the successful implementation of this process at a scaled-up or commercial scale. Plant tissue bioreactors provide a way to control this environment but are often prohibitively expensive. A bioreactor system has been fabricated for plant tissue culture propagation which utilizes low-cost plastic bags combined with gravity driven flows as an approach to achieving scale-up and reducing costs. These temporary immersion bioreactors (TIB) provide for complete media-tissue contacting while minimizing boundary layer mass-transfer resistances and water-logging the plant tissue.

Process design for the production of an alternative biofuel and development of Rhodobacter capsulatus as a platform organism

Presenter: Nymul Khan

Advisor: Wayne Curtis

In the US approximately 13.6 million bbl of gasoline is consumed every day to run the vehicles. And the demand for liquid transportation fuel is not predicted to go down in the foreseeable future. This consumption of fossil fuel releases about 2 billion metric tons of CO₂ to the atmosphere each year. We are working on a technology to sustainably capture the energy of the gaseous molecule into a high-energy liquid fuel that can be a viable alternative to petroleum. C₃₀ hydrocarbons (botryococenes), natively produced by the algae *Botryococcus braunii* Race B, is an ideal fuel molecule due to its high energy density, hydrophobicity and similarity to petroleum crude. These properties make it easy to separate from water, simply by decanting, thus saving the large cost of separation. It can be used as a drop-in feedstock for the current petroleum industry, obviating the need for new infrastructure for processing. The goal of this project is to produce this botryococenes via a biological process from H₂, O₂ and CO₂ as the primary substrates.

Rhodobacter capsulatus is a purple non-sulfur chemolithotroph capable of growing on these gases and has been chosen as the platform for engineering the associated pathway for the production of botryococenes from *B. braunii* Race B. We have successfully engineered *R. capsulatus* to produce botryococenes at a titer levels in excess of 10 mg/L. This is primarily achieved by augmenting the prokaryotic MEP pathway already existing in *R. capsulatus* for the production of Farnesyl Pyrophosphate (FPP), the immediate precursor to botryococcene, with additional copies of the important genes from the pathway along with the Botryococcene Synthase (BS) gene from *B. braunii* Race B. Optimization of the genetic engineering is ongoing to obtain much higher levels of titer. This includes introducing the entire MVA pathway (mainly exists in eukaryotes for the production of isoprenoids) into *R. capsulatus*, introducing promoters that are induced by autotrophic conditions, optimizing the process conditions etc.

We are using economic considerations of the envisioned process to help drive research priorities in addition to the goal of genetically engineer the botryococenes pathway into *R. capsulatus*. We have developed a detailed model for the process including a bioreactor with mass-transfer limited bacterial growth, incorporating the energetics of the bacteria and fuel production. Our goal is to analyze various scenarios and evaluate the overall capital and operating cost of the process to draw conclusion on the viable economic options. The results of this project thus far challenge the typical paradigm of working with organisms that are inherently fast growing and easy to culture. We suggest that as genetic engineering capabilities extend to more difficult organisms, some of the more fringe 'tougher, more efficient' organisms may be better suited for fuels production than their fast-growing 'easy to manipulate' counterparts.

Happy Hour Poster Session

A comprehensive approach to engineering microbial consortia for lignocellulosic biofuels production**Presenter:** Trevor Zuroff

Advisor: Wayne Curtis

A symbiotic microbial consortium was developed which improves conversion of both cellulose and lignocellulose (switchgrass) to ethanol. The cellulolytic mesophile, *Clostridium phytofermentans*, and a cellodextrin fermenting yeast, *Saccharomyces cerevisiae* cdt-1, cooperate based on diffusion of oxygen into the culture medium. Oxygen acts to inhibit the growth of the obligate anaerobe, *C. phytofermentans*, but when provided a soluble carbon source from *C. phytofermentans* hydrolysis of cellulose, the yeast metabolizes oxygen relieving the inhibitory effect. This cooperative behavior results in a stable, controllable consortium which improves the conversion of both cellulose (two-fold increase) and lignocellulose (50% increase) to ethanol. This consortium was specifically designed as a solution for achieving consolidated bioprocessing (CBP) or the simultaneous biological enzyme production, hydrolysis and fermentation of lignocellulose to biofuel. This poster focuses on the comprehensive approach taken to understand, control and apply this microbial consortium to CBP of lignocellulose. This involved understanding the microscopic structure of biofilms (surface attached microbial communities) formed on the cellulose surface, modeling the kinetics of cellulose degradation and consortium function and applying the consortium to high-intensity cellulose and lignocellulose fermentations. This work sets the stage for more advanced microbial systems for economically efficient and environmentally friendly production of fuels and chemicals from plant biomass.

Output feedback control of distributed parameter systems using adaptive model reduction**Presenter:** Davood Pourkargar

Advisor: Antonios Armaou

The problem of output feedback control of distributed parameter systems with limited number of continuous measurement sensors is investigated using adaptive proper orthogonal decomposition (APOD) method. Specifically, APOD is used to recursively construct locally accurate low dimensional reduced order models (ROMs). The controller is designed by combining a robust state controller with a dynamic observer of the system states to reduce measurement sensors requirements. The asymptotic stability of the closed-loop system is proven using Lyapunov stability arguments and hybrid system stability analysis without assuming the separation principle between controller and dynamic observer holds. The proposed method is successfully used to regulate the Kuramoto-Sivashinsky equation (KSE) at a spatially invariant open-loop unstable steady state profile when the process exhibits significant nonlinear behavior.

Disorder in organic small molecule single crystals and its effect on charge mobility

Presenter: Jwala Adhikari

Advisor: Enrique Gomez

Remarkable charge mobilities ($> 5 \text{ cm}^2/\text{Vs}$) have been observed in organic field-effect transistors when active layers are comprised of single crystals. The high mobilities can be a consequence of eliminating grain boundaries which can be detrimental for charge transport in some systems. Nevertheless, processing can strongly affect measured mobilities; for example, it has been reported that charge mobilities in devices comprised of organic single crystals are higher when the active layer is deposited through thermal evaporated versus solution-processing. To explore the underlying phenomena which modulate charge mobilities as a function of processing, we measure the cumulative disorder in single crystals using X-ray diffraction. Our studies examine the relationship between solution processing (i.e. solvent choice and casting temperature), disorder, and charge mobilities within organic single crystals.

Correlation between degree of sulfonation and polymer-ion dynamics in PEO-based single-ion conductors.

Presenter: David Caldwell II

Advisor: Janna Maranas

PEO-based ionomers reduce concentration polarization in solid polymer electrolytes by binding the anion to the polymer backbone. Ionomers have significant ion aggregation compared to PEO/salt systems, and the influence of these aggregates is unclear. When ion transport is coupled to the segmental dynamics of the polymer, aggregation will always reduce ion motion and conductivity. However, the conductivity of PEO ionomers is not sensitive to the degree of aggregation. By using ion aggregates as conducting channels, the charge mobility becomes partially decoupled from the segmental dynamics of the host matrix. This mechanism, dubbed superionic conduction, has been seen in ceramic materials but has not been seen in polymers. Determining the optimum conditions for ion conducting channels reduces the constraints imposed by the segmental dynamics when designing future materials. We present results of molecular dynamics simulations where ion content and temperature is systematically varied. We consider the influence of ion content and temperature on ion aggregation, polymer mobility, cation motion, and superionic conductivity.