Texas A&M Chemical Engineering Research Symposium

Texas A&M University
Chemical Engineering Graduate Student Association
(ChEGSA)

Research Symposium Abstracts

Date: Friday, March 11, 2016

Venue: Memorial Student Center (MSC),

Texas A&M University, College Station, Texas

Track 1

Room: MSC 2500

Session A- I

Time	Presentation
10:00 – 10:20	**A1. Natural Gas to Liquids, Olefins, and Aromatics: A Systematic Approach for the Optimal Production Trade-Offs** *Alexander M. Niziolek, Onur Onel, Christodoulos A. Floudas*
10:20 – 10:40	**A2. Process Synthesis of Natural Gas to Liquid Transportation Fuel Refineries under Price Uncertainty** *Logan R. Matthews, Yannis A. Guzman, Onur Onel, Alexander M. Niziolek, and Christodoulos A. Floudas*

Session A- II

10:50 – 11:10	**A3. Loading Methodologies and Impact on Packing Configurations** *Srikanth Panyaram, David Slivensky,Kenneth Hampton ,Xianchun Wu, Benjamin Wilhite*
11:10 – 11:30	**A4. CFD Simulations of Coupled Endothermic Methane Steam Reforming and Exothermic Combustion of Methane in an Annular Microchannel Reactor (AMR)** *Holly A. Butcher, Peter R. Bossard, Andy Kaldor, and Benjamin A. Wilhite*

Session A- III

2:00 – 2:20	**A5. Optimal Production of Light Olefins from "Wet" Shale Gas: An Integrated NGL Cracking and Dry Gas Reforming Approach** *Onur Onel, Alexander M. Niziolek, and Christodoulos A. Floudas*
2:20 – 2:40	**A6. A New Equation of State Based upon a Rational Form for the Residual Helmholtz Free Energy** *Martin Gomez-Osorio, Robert Browne, Diego Cristancho, James Holste and Kenneth Hall*

Session A- IV

2:50 – 3:10	**A7. Maximizing Production of Fed-Batch and Continuous Biochemical Reactors utilizing Optimal Control Methodologies** *Jonathan P. Raftery and M. Nazmul Karim*
3:10 – 3:30	**A8. Deterministic Optimization Under Uncertainty via Probabilistic Robust Optimization and A Priori Bounds** *Yannis A. Guzman, Logan R. Matthews, and Christodoulos A. Floudas*

A1 - Natural Gas to Liquids, Olefins, and Aromatics: A Systematic Approach for the Optimal Production Trade-Offs

Alexander M. Niziolek[c,a,b], Onur Onel[c,a,b], Christodoulos A. Floudas[a,b]
[a]Artie McFerrin Department of Chemical Engineering, [b]Texas A&M Energy Institute, Texas A&M University, [c]Department of Chemical and Biological Engineering, Princeton University, Princeton

Abstract: Natural gas to liquid transportation fuels processes have been investigated for several decades, but were considered economically unfavorable because of high natural gas costs. Due to recently discovered sources of shale gas, coupled with improvements in the technology used to extract this resource, the abundance of natural gas within the United States soared in recent years. This drastic increase in the supply of natural gas has caused prices to plummet, from $7.99/MMBTU in 2008 to $2.99/MMBTU in 2015. However, the profitability of refineries that produce a wide spectrum of products depends intricately on the ratios of these products. Therefore, we investigate the economic effects of natural gas to liquids, olefins, and aromatics refineries to determine and assess the technological and environmental tradeoffs with multiple alternatives using an important production parameter. An optimization-based process synthesis framework for the conversion of natural gas to liquid transportation fuels, olefins, and aromatics is proposed. Numerous hydrocarbon production alternatives are incorporated, including Fischer-Tropsch refining and methanol synthesis. Multiple commercial and novel technologies for the production of the olefins and aromatics are included. A large-scale nonconvex mixed-integer nonlinear optimization (MINLP) model is formulated to encompass each of these alternatives. The MINLP model is solved using a powerful deterministic global optimization branch-and-bound framework. The key production parameter is a function of the important products output from the refinery, namely, gasoline, diesel, kerosene, aromatics, and olefins. Several case studies are presented to investigate the effect of production ratio on the overall profit of the refinery. The major topological decisions as a function of the production parameter will be discussed and the economic tradeoffs of the refineries will be presented.

A2 - Process Synthesis of Natural Gas to Liquid Transportation Fuel Refineries under Price Uncertainty

Logan R. Matthews[c,a,b], Yannis A. Guzman[c,a,b], Onur Onel[c,a,b], Alexander M. Niziolek[c,a,b], and Christodoulos A. Floudas[a,b]
[a]Artie McFerrin Department of Chemical Engineering, [b]Texas A&M Energy Institute, Texas A&M University, [c]Department of Chemical and Biological Engineering, Princeton University, Princeton

Abstract: Natural gas as a feedstock for producing liquid transportation fuels is appealing due to low costs, growing supply, and greenhouse gas emission levels less than or equal to petroleum processes. Process synthesis of natural gas to liquid transportation fuel (GTL) refineries is a powerful method for optimizing these facilities. A process synthesis superstructure for GTL processing has been developed with various possible conversion routes. Synthesis gas can be produced from natural gas using autothermal or steam reforming, and can be upgraded to fuels via methanol synthesis or Fischer-Tropsch processes. These units, along with other important refinery components, are modeled in a mixed-integer nonlinear optimization problem (MINLP) with simultaneous heat and power integration. A rigorous branch-and-bound algorithm solves the MINLP to global optimality to provide the profit and an optimality gap for the GTL refinery. Refinery feedstocks and products (e.g. gasoline, diesel, and kerosene) have uncertain price parameters that should be accounted for during process synthesis. This uncertainty is incorporated using robust optimization, allowing parameter uncertainty to be included such that global optimum solutions to the process synthesis MINLP can be found with known probabilities of constraint violation. A priori and a posteriori probabilistic bounds for robust optimization allow a substantial reduction in conservatism over worst case values when uncertainty is included. Case studies are conducted on a 50,000 bbl per day facility with uncertainty in the objective function. Using an iterative method for improved robust solutions, the box, interval+ellipsoidal, and interval+polyhedral uncertainty sets are used to gain robust solutions at probabilities of constraint violation from 5% to 95% a priori, and 5% and 30% a posteriori. Profitable plant topologies and diversified product distributions for GTL facilities under price uncertainty are presented.

A3 - Loading Methodologies and Impact on Packing Configurations

Srikanth Panyaram[a], David Slivensky[b], Kenneth Hampton[b] ,Xianchun Wu[b], Benjamin Wilhite[a]
[a]Texas A&M University,College Station
[b]Eastman Chemical Company, Longview

Abstract: Packing algorithm for catalyst particles has been developed using force-displacement models. Structures for spherical and cylindrical catalyst packing are simulated and compared with experimental values. Impact of loading methods on packing configurations is elucidated. The reactor wall affects the porosity variation in packed beds. In addition the cylindrical packing seems to undergo orientation ordering which modify the flow pattern. Impact of loading methodologies on evolution of radial porosity features is evaluated using these algorithms. These investigations help in developing tools to manipulate the heterogeneities in packed beds to mitigate maldistribution and enhance reactor performance.

A4 - CFD Simulations of Coupled Endothermic Methane Steam Reforming and Exothermic Combustion of Methane in an Annular Microchannel Reactor (AMR)

Holly A. Butcher[1], Peter R. Bossard[2], Andy Kaldor[2], and Benjamin A. Wilhite[1]
[1]Artie McFerrin Department of Chemical Engineering, Texas A&M University
College Station. [2]Power and Energy, Inc.

Abstract: Microreactors fulfill the critical need for scalable on-site hydrogen and/or syngas production from natural gas. The coupling of endothermic steam reforming of methane with exothermic combustion of methane allows for stand-alone, self-sustaining operation. Several examples of this reactor and chemistry have been studied, typically consisting of a planar geometry with alternating combustion and steam reforming plates. The authors present a novel annular microchannel reactor (AMR) designed to address the manufacturing challenges associated with planar systems. Computational fluid dynamic models are used to predict performance of the AMR and to determine the efficacy of pairing steam reforming of methane with catalytic combustion of methane in a heat exchanger microreactor. Initially, steam reforming and combustion volumes were modeled separately with an isothermal operation boundary condition imposed at the catalyst coated wall. After appropriate methane capacities and a nominal operating widow was chosen for both volumes, an all-inclusive, non-isothermal model was used to predict and improve performance of the overall system.

A5 - Optimal Production of Light Olefins from "Wet" Shale Gas: An Integrated NGL Cracking and Dry Gas Reforming Approach

Onur Onel[c,a,b], Alexander M. Niziolek[c,a,b], and Christodoulos A. Floudas[a,b]
[a]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station [b]Texas A&M Energy Institute, Texas A&M University, College Station
[c]Department of Chemical and Biological Engineering, Princeton University, Princeton

Abstract: High levels of natural gas production that stemmed from the shale gas industry lowered this feedstock price significantly. Therefore, the wet gas that contains natural gas liquids (NGLs), such as ethane, propane, butane, and natural gasoline, is favorable to extract for commercial purposes. In some wet shale plays, the combined ethane and propane composition can exceed 30%. These trends motivate industrial efforts to build several new ethane crackers with a combined ethylene production capacity of 12.5 million tonnes/year in the United States. Light olefins are valuable petrochemical intermediates and make up two-thirds of the petrochemicals market. These olefins can be produced from alternative feedstocks such as natural gas via reforming. However, extraction of NGLs prior to methane conversion is an opportunity for refineries to maximize carbon conversion towards olefins and avoid high reforming costs. A demethanizer column is utilized to recover more than 83% of ethane and more than 99% of higher hydrocarbons in the wet gas. The NGLs can be cracked or further separated for C3 and C4 dehydrogenation processes to produce light olefins. A rigorous mathematical model is developed for the hydrocarbon cracker using the well-established kinetics in the literature. Dry gas is also converted to light olefins and purified to product quality with an extensive superstructure that considers multiple conversion, production, and purification technologies. The process superstructure that is developed is solved using a novel branch and bound global optimization framework. The objective is to maximize the profit of light olefin production from the integrated NGL extraction and dry gas conversion plant. A techno-economic analysis will be presented with major topological decisions across several case studies. Different natural gas compositions will be shown to present the topological trade-offs for various NGL compositions.

A6 - A New Equation of State Based upon a Rational Form for the Residual Helmholtz Free Energy

Martin Gomez-Osorio, Robert Browne, Diego Cristancho, James Holste and Kenneth Hall
Department of Chemical Engineering, Texas A&M University

Abstract: Chemical process modeling and design requires accurate equations to predict energies, entropies and densities. Cubic equations of state have a simple form that can describe thermophysical properties making assumptions that increase error in the prediction. In other hand, recent multi parametric equations can predict thermodynamic properties with high accuracy by increasing the calculation complexity. This work presents a new equation of state (EoS) having a rational form that can describe properties with accuracy comparable to the best multi-parametric equations with less mathematical complexity. This EoS presents the Helmholtz residual energy as a ratio of two polynomial functions in density (no exponential terms in density are included), which can describe the behavior of pure components. The EoS needs 43 parameters to describe a pure fluid. The EoS can be transformed to describe other thermophysical properties as pressure, compressibility factor, heat capacity and speed of sound. Also this equation can calculate saturated liquid-vapor properties with 20 times less computational time. As one example, this work describes nitrogen data from 66 to 520 K at pressures up to 1000 MPa. The equation can predict compressibility factors within 0.02% for temperatures between 130 K and 520 K. For temperatures below the critical point the uncertainty is around 0.05%, and within the critical region the uncertainty is higher. The model estimates saturated densities within 0.05% for temperatures below 125 K. This EoS also describes reported speed of sound and heat capacity measurements within 1% everywhere except the near critical region. Additionally, a similar equation is developed for Argon data from 100 to 700 K at pressures up to 1000 MPa.

Keywords: Equation of State, Phase equilibria, Helmholtz energy

A7 - Maximizing Production of Fed-Batch and Continuous Biochemical Reactors utilizing Optimal Control Methodologies

Jonathan P. Raftery and M. Nazmul Karim
Artie McFerrin Department of Chemical Engineering, Texas A&M University

Abstract: Fed-batch and continuous operation in biochemical processes can be used to allow for increased cell viability through the mitigation of substrate and product inhibition, thereby increasing the productivity of the desired product. However, this requires knowledge of the operating conditions necessary to achieve the maximum production of a desired product when produced via continuous operation. We will focus on the fed-batch and continuous production of carotenes such as β-carotene, a precursor of vitamin A, which have a structural complexity that makes their chemical synthesis a difficult endeavor, facilitating the need for their biological production. First, a two-step parameter estimation methodology is utilized to develop a reliable kinetic model for the batch production of carotenoids via fermentation to describe the glucose consumption, metabolic product formation and depletion, and the carotenoid production in the Saccharomyces cerevisiae strain mutant SM14 with 20 g/L glucose as the carbon source. These models are then extended to the study of a novel continuous bioreactor system using a two feed configuration that gives the ability to use flowrate and glucose concentration of the feed stream as independent manipulated variables. A two-level optimization algorithm is used to determine the optimal control policy governing the dilution rate and glucose concentration in order to maximize the carotenoid productivity while simultaneously minimizing the overall processing time during fed-batch operation. Finally, a model predictive control methodology utilizing dynamic optimization is proposed to maximize the production of carotenoids during continuous operation to allow for the real-time control of this system.

A8 - Deterministic Optimization under Uncertainty via Probabilistic Robust Optimization and A Priori Bounds

Yannis A. Guzman[c,a,b], Logan R. Matthews[c,a,b], and Christodoulos A. Floudas[a,b]
[a]Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station
[b]Texas A&M Energy Institute, Texas A&M University, College Station
[c]Department of Chemical and Biological Engineering, Princeton University, Princeton

Abstract: The parameters of applied mathematical models often have more than one possible value which they can achieve due to limited information or measurement error. The solutions and objective values produced from optimizing models with uncertain parameters can vary greatly based on which values the uncertain parameters realize. One method of handling uncertain parameters is to guarantee feasibility of the constraints for all possible parameter sets contained within deterministically defined parameter spaces, called uncertainty sets, through robust optimization. The quality of an optimal solution of the robust counterpart relies heavily on methods that define uncertainty sets which are guaranteed to satisfy a particular upper bound on the probability of constraint violation; a tighter probabilistic bound would allow the imposition of a smaller uncertainty set with the same guarantee of feasibility and can drastically improve objective values. We present new a priori bounds on the probability of constraint violation for defining uncertainty sets. The methods apply and are specially tailored to different types of uncertainty sets currently in use. Situations for which the bounds are applicable include (i) bounded uncertain parameters with unknown probability distributions, (ii) bounded and unbounded uncertain parameters with known probability distributions, and (iii) bounded, possibly asymmetrically distributed uncertain parameters with limited information on their means, thus enabling usage of parameters matching the latter scenario for the first time. The novel bounds yield smaller uncertainty sets with the same probability of constraint violation when compared with existing methods. These methods can provide greatly improved objective values and also improve the performance of iterative algorithms which rely on a priori and a posteriori bounds to obtain less conservative solutions.

Track 2

Room: MSC 2502

Session B- I

Time	Presentation
10:00 – 10:20	**B1. Tailored Gelation of Graphene Oxide for Conductive 3D Networks** *Dorsa Parviz, Morgan Plummer, Micah J. Green*
10:20 – 10:40	**B2. Computational Design Aspects of Catalysts for the Synthesis of Single-Walled Carbon Nanotubes** *Jose L. Gomez-Ballesteros, Juan Burgos, Pin Ann Lin, Renu Sharma, Perla Balbuena*

Session B- II

11:50 – 11:10	**B3. The effect of multivalent ions on hydrated polyelectrolyte multilayers** *Dariya Reid, Alex Summers, Josh O'Neal, Avanti Kavarthapu and Jodie Lutkenhaus*
11:10 – 11:30	**B4. Highly Flexible Self-Assembled V_2O_5 Cathodes Enabled by Conducting Diblock Copolymers** *Hyosung An, Jared Mike, Kendall A. Smith, Lisa Swank, Yen-Hao Lin, Stacy Pesek, Rafael Verduzco, and Jodie L. Lutkenhaus*

Session B- III

2:00 – 2:20	**B5. Atomistic Simulation of Molybdenum Disulfide Catalyzed Hydrodesulfurization Reactions** *Narendra Kumar and Jorge Seminario*
2:20 – 2:40	**B6. State Observer Design for Monitoring the Degree of Polymerization in a Series of Melt Polycondensation Reactors** *Chen Ling and Costas Kravaris*

Session B- IV

2:50 – 3:10	**B7. Microwave-Assisted One-Pot Synthesis of Zeolitic Imidazolate Framework (ZIF-8) Membranes** *Gokulakrishnan Ramu, Hyuk Taek Kwon and Hae-Kwon Jeong*
3:10 – 3:30	**B8. Microwave-assisted synthesis of nanomaterial for energy applications** *Yi-Hsien Yu, Xuezhen Wang, Ying-Pin Chen, Zhengdong Cheng*

B1 - Tailored Gelation of Graphene Oxide for Conductive 3D Networks

Dorsa Parviz, Morgan Plummer, Micah J. Green

Abstract: Porous 3D networks of graphene have potential applications in battery electrodes, chemical sensors, oil adsorption and catalysis. These networks could exhibit high surface area and unique mechanical and electrical properties, depending on their preparation method and structure. In this work, a sol-gel technique was used to prepare graphene aerogels from graphene oxide (GO) precursor and their structure was tuned by controlling the synthesis parameters. Through this method, graphene nanosheets form a gel structure by simultaneous crosslinking and reduction of GO nanosheets in presence of the catalyst. Critical point drying was performed on the hydrogels, and then they were annealed at higher temperatures to produce graphene aerogels. The GO concentration and GO/catalyst ratio affect the reduction and crosslinking of the nanosheets, which in turn determine the packing density and pore size distribution in the final aerogels. The nature of the covalent bonds and the inter-sheet "bridges" observed in the SEM images were investigated using FTIR. These aerogels possessed considerably high surface areas in the range of 900-1500 m2/g and electrical conductivities comparable to those of copper and silver. Furthermore, the effect of GO morphology on the aerogel structure was studied by incorporating crumpled graphene oxide (cGO) particles into the hydrogels. cGO particles were prepared by spray drying aqueous GO dispersions during which the nanosheets are compacted from 2D nanosheets to 3D "spherical" particles. As expected, the alteration of the precursor's aspect ratio in a 100% cGO aerogel led to a higher degree of crosslinking and packing density and slight increase in the surface area (1600 m2/g). The synergistic effects of mixed GO/cGO precursors on the structure and properties of aerogels were also explored and characterized.

B2 (P.22) - Computational Design Aspects of Catalysts for the Synthesis of Single-Walled Carbon Nanotubes

Jose L. Gomez-Ballesteros[a], Juan Burgos[a], Pin Ann Lin[b,c], Renu Sharma[b], Perla Balbuena[a].
[a] Department of Chemical Engineering, Texas A&M University, College Station, TX 77843
[b] Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg
[c] University of Maryland – IREAP, College Park

Abstract: Computational catalysis is a useful tool that allows the screening of materials for catalysis in an efficient and cost-effective manner. The important role of catalysis in a variety of industrial processes and cutting-edge technologies for clean energy, transformation of contaminants, high value chemicals, and synthesis of novel materials with specific properties for diverse applications, requires innovative strategies to develop new and better catalysts. Our research focus is the catalytic synthesis of single-walled carbon nanotubes (SWCNTs). SWCNTs are materials with remarkable properties that make them suitable candidates for diverse applications ranging from transistors for faster electronic devices, optical applications and sensors, composite materials, biosensors and drug delivery, among others. We seek to identify and understand the relevant factors that determine selectivity and efficiency of the catalyst for SWCNTs synthesis from a computational perspective. Using density functional theory (DFT) and reactive molecular dynamics (RMD) simulations, we study characteristics of the catalyst such as active surface terminations, metal/carbide phase dynamics, and effect of the catalyst support. The information obtained from simulations is fundamental to assist in understanding the relationship between electronic structure and catalytic properties of materials and ultimately help contribute to the rational design of catalysts.

B3 (P.21) - The Effect of Multivalent Ions on Hydrated Polyelectrolyte Multilayers

Dariya Reid, Alex Summers, Josh O'Neal, Avanti Kavarthapu and Jodie Lutkenhaus

Abstract: Layer-by-layer (LbL) assembly is a commonly studied technique in the production of uniform thin films. The formation of LbL assemblies using model polyelectrolytes, poly(diallyldimethylammonium chloride) (PDAC) and poly(styrene sulfonate) (PSS) has been well studied. We are interested in learning how do multivalent ions impact the structure of LbL multilayers. In addition, when hydrated these films exhibit a thermal transition with features of a glass transition and a lower critical solution temperature transition. The question remains as to how multivalent cations affect the nature of the transition. Here, we present results on the thermal transition and film behavior of PDAC/PSS LbL assemblies exposed to multivalent salts. Quartz crystal microbalance (QCM-D) is used to monitor the film structure and modulated differential scanning calorimetry (MDSC) is used to assess the thermal transition.

B4 - Highly Flexible Self-Assembled V2O5 Cathodes Enabled by Conducting Diblock Copolymers

Hyosung An,[1] Jared Mike,[1] Kendall A. Smith,[2] Lisa Swank,[2] Yen-Hao Lin,[2] Stacy Pesek,[2] Rafael Verduzco,[2] and Jodie L. Lutkenhaus[1*]*

[1]Artie McFerrin Department of Chemical Engineering, Texas A&M University, [2]Department of Chemical Engineering, Rice University

Abstract: Structural energy storage materials combining load-bearing mechanical properties and high energy storage performance are desired for applications in wearable devices or flexible displays. Vanadium pentoxide (V2O5) is a promising cathode material for possible use in flexible battery electrodes, but it remains limited by low Li+ diffusion coefficient and electronic conductivity, severe volumetric changes upon cycling, and limited mechanical flexibility. Here, we demonstrate a route to address these challenges by blending a diblock copolymer bearing electron- and ion-conducting blocks, poly(3-hexylthiophene)-block-poly(ethyleneoxide) (P3HT-b-PEO), with V2O5 to form a mechanically flexible, electro-mechanically stable hybrid electrode. V2O5 layers were arranged parallel in brick-and-mortar-like fashion held together by the P3HT-b-PEO binder. This unique structure significantly enhances mechanical flexibility, toughness and cyclability without sacrificing capacity. Electrodes comprised of 10 wt% polymer have unusually high toughness (293 kJ/m3) and specific energy (530 Wh/kg), both higher than reduced graphene oxide paper electrodes. Electrodes with commercial binder poly(vinylidene difluoride) shows no remarkable improvement.

B5 - Atomistic Simulation of Molybdenum Disulfide Catalyzed Hydrodesulfurization Reactions

Narendra Kumar and Jorge Seminario

Abstract: Molybdenum disulfide, MoS2, is a very versatile material used in several applications of science and engineering. In particular, when supported on alumina is widely used catalyst for hydrotreating processes in petroleum refineries. Stringent environmental norms and uncertainty in import of low sulfur crude oil put pressure on refiners worldwide to develop more efficient catalysts to meet the demand of clean fuel. The hydrodesulfurization of thiophene and dibenzothiophene on both unpromoted and nickel-promoted MoS2 catalyst is analyzed using a multiscale approach including classical molecular dynamics (MD) and density functional theory (DFT). MD simulations are performed on a hydrocarbon mixture containing sulfur compounds in order to determine relative positions of thiophene and dibenzothiophene molecules with respect to the MoS2 catalytic surface previous to possible reactions that are then studied with DFT. The sample box contains a total of 57,515 atoms is able to represent a realistic size of the nanocatalyst process. Under typical hydrodesulfurization conditions, vacancies are needed for adsorption of sulfur compounds and therefore activation of hydrogen becomes an important step. In addition, complexes of MoS2 with graphene and boron nitride, BN, surfaces are also analyzed. MoS2-graphene complexes show improvement in efficiency of adsorption of thiophene on the catalyst edge. Both hydrogenation and direct desulfurization pathways are presented on pristine MoS2 clusters as well as under typical hydrodesulfurization conditions.

B6 - State Observer Design for Monitoring the Degree of Polymerization in a Series of Melt Polycondensation Reactors

Chen Ling and Costas Kravaris

Abstract: A nonlinear reduced-order state observer is applied to estimate the degree of polymerization in a series of polycondensation reactors. The finishing stage of polyethylene terephthalate synthesis is considered in this work. This process has a special structure of lower block triangular form, which is properly utilized to facilitate the calculation of the state-dependent gain in the observer design. There are two possible on-line measurements in each reactor. One is continuous, and the other is slow-sampled with dead time. For the slow-sampled titration measurement, inter-sample behavior is estimated from an inter-sample output predictor, which is essential in providing continuous corrections on the observer. Dead time compensation is carried out in the same spirit as the Smith predictor to reduce the effect of delay in the measurement outputs. By integrating the continuous-time reduced-order observer, the inter-sample predictor and the dead time compensator together, the degree of polymerization is accurately estimated in all reactors. The observer performance is demonstrated by numerical simulations. In addition, a pre-filtering technique is used in the presence of sensor noise.

B7 - Microwave-Assisted One-Pot Synthesis of Zeolitic Imidazolate Framework (ZIF-8) Membranes

Gokulakrishnan Ramu[†], Dr.Hyuk Taek Kwon[†δ] and Dr.Hae-Kwon Jeong[†]*
*[†] Artie McFerrin Department of Chemical Engineering * Materials Science and Engineering Program, Texas A&M University, College Station*
[δ] Currently at School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta

Abstract: Zeolitic Imidazolate Framework (ZIF)'s are polycrystalline membranes with usually zinc or cobalt metal centers coordinated to various organic imidazole ligands. These membranes offer an energy-friendly alternative to distillation processes in the separation of gases with very close properties like propylene/propane. In particular, ZIF-8, with a pore aperture in the size range of propylene, is ideally suited for this commercially important separation. However, their synthesis is not straightforward, involving formation of seed layers on porous supports first, followed by their secondary growth to membranes. To synthesize good quality membranes by this method, strong attachment of seed crystals to the support is essential. Though this has been achieved by our group's Microwave (MW)-Assisted seeding technique, the total time necessary for growing membranes by this method is rather long. So, if membrane-quality films can be obtained after just the initial MW seeding step, the time required for synthesis will be greatly reduced (~ only 2 minutes). This work investigates the feasibility of achieving well-inter grown ZIF-8 films for propylene/propane separation in just a single MW seeding step by varying different parameters like nature of zinc salts, metal salt concentration, modulating agent concentration and MW power.

B8 - Microwave-assisted synthesis of nanomaterial for energy applications

Yi-Hsien Yu[1], Xuezhen Wang[2], Ying-Pin Chen[3], Zhengdong Cheng[1,2,4]
[1] Department of Material Science & Engineering, Texas A&M University, College Station
[2] Department of Chemical Engineering, Texas A&M University, College Station
[3] Department of Chemistry, Texas A&M University, College Station
[4] Mary Kay O'Connor Process Safety Center, Texas A&M University, 3122 TAMU, College Station

Abstract: Microwave heating has been used in organic chemistry for decades, but not been used for growth of nanomaterials until recent years. The merits of microwave techniques are with efficient heating and instantaneous controllable parameters in real time. Hence, the growth of crystals could be significantly accelerated and well-controlled. Microwave-assisted synthesis of α-ZrP and CuO/TiO2 were studied and were found to be useful for energy applications. α-ZrP is well-known as an acidic layered metal salt. By intercalating guest species into the interlayer, the α-ZrP could serve as a host structure or be exfoliated by the guest species. The modified α-ZrP has connected to new applications such as Pickering emulsions. It is for the first time that a rapid microwave-assisted method was developed to synthesize alpha phase of α-ZrP with good control over size and uniformity. We designed a two-step Pickering emulsification procedure to create nano-encapsulated phase changing materials (NEPCMs) using surface modified α-ZrP nano-sheet. The simplicity and low energy consumption of the method suggest promise for scale-up and mass production. NEPCMs exhibit superior mechanical stability and mobility when compared with the well-developed micro-encapsulated phase change materials. NEPCMs find useful applications in thermal management, including micro-channel coolants; solar energy storage media; and thermal transfer fabrics. CuO-deposited TiO2 rods were prepared through a microwave-assisted green method for high efficiency hydrogen evolution. The porous CuO/TiO2 rods with crystallinity and high specific surface area were obtained as-synthesized without calcination. Hydrogen yields were proved to be significantly improved with appropriate amount of CuO deposited onto TiO2 rods. The improved photocatalytic performance was attributed to the synergistic effects of high surface area, specific energy band structure, and enhanced light harvesting at the interface of CuO and porous TiO2 rods.

Track 3

Room: MSC 2504

Session C- I

Time	Presentation
10:00 – 10:20	**C1. Application of Computational Fluid Dynamics (CFD) for Liquefied Natural Gas (LNG) Pool Spreading and Vaporization on Water** *Nirupama Gopalaswami, Konstantinos Kakosimos, Bin Zhang, Yi Liu, R. Mentzer and M. Sam Mannan*
10:20 – 10:40	**C2. Experimental and CFD study of cryogenic vapor formation** *Monir Ahammad, Tomasz Olewski, Luc Vechot and Sam Mannan*

Session C- II

10:50 – 11:10	**C3. The microbiota-metabolite indole attenuates Salmonella virulence and invasion** *Nandita Kohli, Zeni Crisp, Rebekah Davis, Michael Li, Deepa Vijaykumar, Robert C. Alaniz, Arul Jayaraman*
11:10 – 11:30	**C4. Chemotaxis of Escherichia coli to Norepinephrine (NE) Requires Conversion of NE to 3,4-Dihydroxymandelic Acid** *Sasikiran Pasupuleti, Nitesh Sule, Arul Jayaraman, Michael D. Manson*

Session C- III

2:00 – 2:20	**C5. Ammonium nitrate thermal stability study** *Zhe Han, Hans Pasman & M. Sam Mannan*
2:20 – 2:40	**C6. A Fuzzy Logic and Probabilistic Hybrid Approach to Quantify the Uncertainty in Layer of Protection Analysis** *Yizhi Hong, Hans J. Pasman, Sonny Sachdeva, Adam S. Markowski, and M. Sam Mannan*

Session C- IV

2:50 – 3:10	**C7. Investigating Sexual Recombination for Applications in Adaptive Laboratory Evolution toward Industrial Strain Design** *George L Peabody V and Katy Kao*
3:10 – 3:30	**C8. Understanding *Candida albicans* and *Candida glabrata* mixed species biofilm growth** *Michelle L. Olson, Arul Jayaraman, and Katy C. Kao*

C1 (P.5) - Application of Computational Fluid Dynamics (CFD) for Liquefied Natural Gas (LNG) Pool Spreading and Vaporization on Water

Nirupama Gopalaswami, Konstantinos Kakosimos, Bin Zhang, Yi Liu, R. Mentzer and M. Sam Mannan
Mary Kay O'Connor Process Safety Center
Artie McFerrin Department of Chemical Engineering
Texas A&M University System, College Station

Abstract: A marked increase in LNG utilization is forecast with an increase in LNG marine operations. A ship-ship collision of an LNG marine tanker or a rupture of the LNG loading and unloading lines can result in accidental spillage of LNG on water. Upon release, a spreading liquid can form a pool with rapid vaporization, leading to the formation of a flammable vapor cloud. Safety analyses for the protection of the public and property involve the determination of consequences of such accidental releases. The evaluation of consequences resulting from an accidental spill of LNG on water involves the determination of the rate (vaporization rate/source term) at which flammable hydrocarbon vapor is produced and the dynamics of the spreading pool. A specific offshore scenario of rupture of an offloading line is considered resulting in an LNG spill on water, between the space enclosed by the offloading deck and the LNG ship. This scenario was studied experimentally by releasing LNG in a narrow concrete trench filled with water. The experimental study involves the determination of the vaporization rate for a continuous release of LNG in a trench. Along with the vaporization rate, the spreading rate, pool area and pool height were measured. The computational work involves development of a methodology to model the pool spreading and vaporization behavior in Computational Fluid Dynamics (CFD) for the defined scenario. The overall aim of this research is to improve the understanding of pool spreading and vaporization of LNG releases on water.

Keywords: CFD, pool spreading, vaporization, LNG, source term

C2 (P.4) - Experimental and CFD Study of Cryogenic Vapor Formation

Monir Ahammad[a], Tomasz Olewski[b], Luc Vechot[b] and Sam Mannan[a]
Mary Kay O'Connor Process Safety Center
[a]Texas A&M University, College Station
[b]Texas A&M University at Qatar, Education City, Doha, Qatar.

Abstract: One of the key issues of LNG spill consequence studies is accurate estimation of the vapor formation due to heat transfer from the ground. Cryogenic fluids e.g. LNG when spilled on ground undergoes different boiling regimes such as nucleate, transition and film boiling. During the initial stage of spill, due to large temperature difference between the ground and the boiling liquid, film boiling occurs. It also occurs in the spreading pool front of a cryogenic pool. As the ground cools down with time, the boiling mode changes from film boiling to nucleate boiling via a short-living transition boiling. The duration of nucleate boiling is much longer than other regimes, therefore may contribute to significant vapor generation. In this paper, CFD modeling of different boiling regimes i.e. film boiling and nucleate boiling will be addressed along with the experimental findings of cryogenic spill study on concrete substrate. VOF method and Multiphase mixture model is used to model film boiling and nucleate boiling respectively in ANSYS-FLUENT computational environment. The simulated boiling models are compared with literature findings and experimental observations.

Keywords: LNG, Film boiling, Nucleate Boiling, CFD

C3 - The Microbiota-Metabolite Indole Attenuates Salmonella Virulence and Invasion

Nandita Kohli[1], Zeni Crisp[2], Rebekah Davis[2], Michael Li[1], Deepa Vijaykumar[2], Robert C. Alaniz[2],, Arul Jayaraman[1,2,*]*

[1]Department of Chemical Engineering, Texas A&M University, College Station, Texas, U.S.A.

[2]Department of Microbial Pathogenesis and Immunology, Texas A&M Health Science Center, College Station

Abstract: More than 10^{14} microorganisms, collectively known as the microbiota co-exist with the host and colonize the human gastrointestinal tract. The microbiota play an important role in several aspects of health and disease, including preventing pathogen colonization and regulating host defense to infections. Our previous work demonstrated that indole, produced from tryptophan by the microbiota, reduces enterohemorrhagic *Escherichia coli* O157:H7 attachment to epithelial cells and biofilm formation. Here, we report that indole directly attenuates *Salmonella* Typhimurium (*Salmonella*) virulence and invasion as well as increases host cell resistance to *Salmonella* colonization. Indole-exposed *Salmonella* colonized mice less effectively compared to solvent-treated controls. In agreement with the reduced in vivo competitiveness, indole decreased *Salmonella* HeLa epithelial cell invasion by 160-fold and that of J774.A1 macrophages by 2-fold. However, *Salmonella* intracellular survival in J774.A1 macrophages was unaffected by indole. The observed decrease in invasion was mediated by a decrease in expression of four *Salmonella* Pathogenicity Island-1 (SPI-1) genes that are essential for host cell invasion. In addition, indole-treated HeLa cells were resistant to *Salmonella* invasion which was reduced by 70 %, suggesting that indole also increases colonization resistance of epithelial cells. Lastly, indole synergistically enhanced the inhibitory effect of microbiota-derived short chain fatty acids on SPI-1 gene expression. Together, our results demonstrate that indole is an important microbiota metabolite that has direct anti-infective effects on *Salmonella* and host cells, revealing novel mechanisms of colonization resistance.

C4 - Chemotaxis of Escherichia coli to Norepinephrine (NE) Requires Conversion of NE to 3,4-Dihydroxymandelic Acid

Sasikiran Pasupuleti,a Nitesh Sule,a Arul Jayaraman,a Michael D. Mansonb

Department of Chemical Engineering a and Department of Biology,b Texas A&M University, College Station

Abstract: Norepinephrine (NE), the primary neurotransmitter of the sympathetic nervous system, has been reported to be a chemoattractant for enterohemorrhagic *Escherichia coli* (EHEC). Here we show that nonpathogenic *E. coli* K-12 grown in the presence of 2μM NE is also attracted to NE. Growth with NE induces transcription of genes encoding the tyramine oxidase, TynA, and the aromatic aldehyde dehydrogenase, FeaB, whose respective activities can, in principle, convert NE to 3,4-dihydroxymandelic acid (DHMA). Our results indicate that the apparent attractant response to NE is in fact chemotaxis to DHMA, which was found to be a strong attractant for *E. coli*. Only strains of *E. coli* K-12 that produce TynA and FeaB exhibited an attractant response to NE. We demonstrate that DHMA is sensed by the serine chemoreceptor Tsr and that the chemotaxis response requires an intact serine-binding site. The threshold concentration for detection is ≤ 5nM DHMA, and the response is inhibited at DHMA concentrations above 50μM. Cells producing a heterodimeric Tsr receptor containing only one functional serine-binding site still respond like the wild type to low concentrations of DHMA, but their response persists at higher concentrations. We propose that chemotaxis to DHMA generated from NE by bacteria that have already colonized the intestinal epithelium may recruit *E. coli* and other enteric bacteria that possess a Tsr-like receptor to preferred sites of infection.

C5 - Ammonium Nitrate Thermal Stability Study

*Zhe Han, Hans Pasman & M. Sam Mannan**
Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station

Abstract: Ammonium nitrate (AN) fire and explosion hazards present a potentially serious threat to the chemical process industry and the community as incidents related to AN have occurred from time to time, causing the loss of both lives and property. One of the most recent incidents involving AN occurred on April 17, 2013, in West, Texas, killing 15 people and injuring more than 250 people; this incident has caused heated discussion on the safety issues associated with AN including firefighting issues. The thermal stability of AN has been studied. In terms of fire protection, water suppression systems have been widely used in chemical process facilities as an active protection layer, and they have been successful in tackling most of the fires. However, where in most cases of fire, water acts just as a cooling and hence combustion extinguishing agent, in the case of ammonium nitrate within limits it may favor the conditions for explosion. The main objective of this research is to discuss the role of water as a chemical, interfering physically and chemically with AN-related fire scenarios possibly leading to explosion.

Keywords: Ammonium nitrate (AN); Sprinkler system; Explosion; Water; Contamination.

C6 (P.9 PSII) - A Fuzzy Logic and Probabilistic Hybrid Approach to Quantify the Uncertainty in Layer of Protection Analysis

Yizhi Hong[1], Hans J. Pasman[1], Sonny Sachdeva[1], Adam S. Markowski[2], and M. Sam Mannan[1]
[1]Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station
[2]Process Safety and Ecological Division, Faculty of Process and Environmental Engineering, Technical University of Lodz, 90-924 Lodz, ul. Wolczanska 213, Poland

Abstract: Layer of Protection Analysis (LOPA) is a widely used semi-quantitative risk assessment method. It provides a simplified but less precise method to assess the effectiveness of protection layers and the risk of an incident scenario. The outcome frequency and consequence are intended to be conservative by prudently selecting input data, given that design specification and component manufacturer's data are often overly optimistic. There are many influences, including design deficiencies, lack of layer independence, availability, human factors and wear in testing and maintenance, which are not quantified and are dependent on type of process and location. This makes the risk usually overestimated. So, there are different sources and types of uncertainty in the LOPA model that need to be identified and quantified. In this study, a fuzzy logic and probabilistic hybrid approach was developed to quantify the uncertainty of frequency of initiating event and the probabilities of failure on demand (PDF) of Independent Protection Layers (IPLs) based on the available data and expert experience. The method was applied to a distillation system with a capacity to distill 40 tons of flammable n-hexane. The outcome risk of the new method was proven to be more precise comparing to the results of the conventional LOPA approach.

Keywords: Risk Assessment; Layer of Protection Analysis; Fuzzy logic

C7 - Investigating Sexual Recombination for Applications in Adaptive Laboratory Evolution toward Industrial Strain Design

George L Peabody V and Dr. Katy Kao

Abstract: The generation of biofuels and other industrially desirable chemicals can be achieved through the use of biocatalysts. Biocatalysts offer a versatile and environmentally friendly alternative to chemical synthesis. However, industrial production of bio-based compounds faces challenges such as low levels of product yield and titer, and the frequent toxicity of industrially desirable conditions. Biocatalyst robustness in the presence of harsh conditions can be improved by developing tolerant phenotypes. Unfortunately, tolerant phenotype development is often too complex for rational engineering. Adaptive Laboratory Evolution (ALE), serves as a powerful alternative method. ALE has demonstrated substantial success in producing strains that are highly tolerant to various industrially relevant inhibitory conditions and is not limited by knowledge of rational targets for strain design. ALE relies upon mutation and selection to evolve a population toward local or global optima along the organism-of-interest's fitness landscape in the chosen environment. Mutations represent dimensions in the fitness landscape where various mutational combinations lead to changes in fitness. Previous work has attempted to enhance the fitness landscape explored in ALE by introducing sexual recombination to asexual evolving strains, producing a more combinatorial approach. We present experimental evidence of some of the theorized advantages of sexual recombination, including the ability of sexual recombination to reduce genetic load. We then delve into the effectiveness of sexual recombination to better quantify the advantage of a sexual strain and to carry over the results toward strain development and gain a better understanding of the evolutionary process in microbial systems.

C8 - Understanding Candida Albicans and Candida Glabrata Mixed Species Biofilm Growth

Michelle L. Olson, Arul Jayaraman, Katy C. Kao

Abstract: Candidiasis, fungal infection caused by *Candida* species, affects patients of all ages and ranges from thrush in the oral cavity to disseminated deep tissue infections. *Candida* infections may be difficult to treat due to inherent or acquired antifungal resistance and limited number of available therapeutic agents. Biofilms, which are often associated with the pathogenesis of *Candida*, are generally polymicrobial in nature, and are held together by an extracellular matrix (ECM) that is attached to a surface. In the human host, this surface may by a catheter, mucosal surface of the gastrointestinal tract, or lining of the stomach. Biofilms are difficult to treat largely due to the protective ECM, which reduces the penetration and efficacy of antifungal agents. *C. albicans* and *C. glabrata* are the two most commonly isolated species from *Candida* infections, and have been isolated together, which makes polymicrobial populations an interesting and clinically relevant area of study. In this work, we characterize the impacts of co-cultures in biofilm formation and population dynamics using mixed cultures of *C. albicans* and *C. glabrata*. When grown as biofilms, we find that biofilm formation of the polymicrobial population depends on the relative ratio of starting cell concentrations of *C. albicans* and *C. glabrata* in an unexpected manner. The specific ratio we find to yield the highest biomass is when the ratio of *C. albicans* to *C. glabrata* is low. *C. glabrata*, in comparison to *C. albicans*, is not very successful at forming biofilms when grown as a single species. Interestingly, we find that the higher ratios of *C. albicans* to *C. glabrata* in fact result in less biofilm formation. Our results suggest interspecific interactions between these two fungal pathogens, where a polymicrobial population causes unexpected changes in biofilm formation. The underlying mechanisms of these inter-specific interactions are being investigated.

Keywords: Biofilms, Polymicrobial Infection, Commensal Fungi