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CHEMICAL ENGINEERING GRADUATE STUDENT ASSOCIATION

5th ANNUAL RESEARCH SYMPOSIUM
ABSTRACT BOOK



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A. ORAL PRESENTERS

i) MORNING SESSION

1. Rapid One-Pot Microwave Synthesis of Mixed Linker Hybrid Zeolitic-Imidazolate Framework Membranes for Tunable Gas Separations

Febrian Hillman¹, Jordan Brito¹, and Hae-Kwon Jeong^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Department of Material Science and Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Separating a crude component into a more valuable purer product is a major part of many industrial chemical plants. Typically these processes utilize distillation, which account to 10 – 15 % of world's energy consumption. One alternative solution that can reduce energy consumption is through membrane separation using porous solid material such as metal organic frameworks (MOFs). Zeolitic-imidazolate frameworks (ZIFs), a subclass of MOFs, in particular have attracted many attentions due to their chemical/thermal stabilities, their ultra-miroporosities, and high surface area when compared to other MOFs material. ZIFs are frameworks consisting transition metals bridged by imidazolate-derived ligands. A common drawback for membrane gas separation is the limited availability of pore size and functionalities. Furthermore, the slow fabrication of MOF membranes restricts their commercialization. Studies have shown that through mixing linkers, one can continuously tune the ZIFs (termed hybrid ZIFs) properties to match with the characteristic of specific gas mixture.

Herein we report a rapid one-step microwave-assisted synthesis of mixed linker ZIF-7-8 membranes in under ~ 90 seconds. ZIF-7-8 consists of Zn²⁺ metal nodes bridged by a mixture of benzimidazolate (bIm, ZIF-7 linker) and 2-methylimidazolate (mIm, ZIF-8 linker) linkers. To the best of our knowledge, this is the fastest synthesis of any polycrystalline MOF membranes reported up to now. Furthermore, the gas separation performances (separation factor and permeance) of hybrid ZIF-7-8 membranes were systematically tuned by varying the bIm-to-mIm ratio incorporated into the framework. The unprecedentedly rapid synthesis of ZIF-7-8 membranes with tunable molecular sieving properties is an important step.

2. Micro-encapsulation with Nanoplatelet Surfactant

L. Eric Zhang^{1,2} and Zhengdong Cheng^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

We demonstrated the possibility to employ both microfluidics and Janus nanoplatelets to fabricate capsules at micrometer level. Conventional encapsulation technologies apply polymer material as shell structure, which complicates the manufacturing procedure and increases cost of micro capsules. In our work, utilizing the Janus nanoplatelet surfactant developed in our lab, we are able to simplify the encapsulation procedure by integrating the shell material and the emulsifier. The geometry of the capsule comprises a layer of Janus platelet shell, a swellable hydrogel core and encapsulated active ingredient. During the manufacturing the Janus platelet can serve as an emulsion stabilizer and the precursor of the shell structure. With a coaxial microfluidics device, we are able to encapsulate hydrogel and water soluble active ingredients with the Janus nanoplatelet surfactant, and then polymerize the capsules with UV-initiator. The release of active ingredients can be controlled by hydrogel swelling. Several applications with this technique are demonstrated. Such a Janus particle microencapsulation technique has a potential to be applied in biomedical, cosmetic and oil & gas industry.

3. Multifunctional Charge Transfer-Based Supramolecular Materials with Tunable Thermochromism

Tianyu (Kelvin) Yuan¹, Lei Fang^{1,3}, and Mark A. Olson²

¹*Department of Materials Science and Engineering, Texas A&M University, College Station, TX, USA, 77843*

²*School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China*

³*Department of Chemistry Texas A&M University, College Station, TX, USA 77843*

Abstract:

Stimuli-responsive materials, such as thermochromics, have found mass usage and profitability in manufacturing and process control. Imparting charge transfer-based functional supramolecular materials with tunable thermochromism, emerges as an ideal strategy to construct optically responsive multifunctional assemblies. A new series of thermochromic charge transfer-based supramolecular materials assembled in water has been developed. These assemblies are composed of a bis-bipyridinium-derived acceptor and a series of commercially available donors – namely, the neurotransmitter melatonin and its analogue bioisosteres. By tailoring the chemical structure of the donors, the strength of the charge transfer interactions can be tuned. Thermochromic aerogels and inks of these materials are prepared, with a large selection of colors, in environment-friendly solvents and demonstrate tunable thermochromic transition temperatures ranging from 45 to 105 °C. Stamped and inkjet-printed thermochromic patterns can be prepared from their aqueous solutions which also showed favorable compatibility with commercial inks. Mechanistic studies reveal that the two types of water molecules were bound to the supramolecular complexes with different strength, and the more weakly bound water is responsible for the thermochromic transitions.

Overall, this work presents a novel series of donor-acceptor CT-based supramolecular materials which feature versatile processability and tunable thermochromic properties. The unfolded design principles and underlining mechanism in this work provide essential insights for the future development of reversible and recyclable thermochromic supramolecular materials.

4. Relative Abundance of *Candida Albicans* and *Candida Glabrata* in *In Vitro* Co-culture Biofilms Impacts Biofilm Structure and Formation

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

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Candida is a member of the normal human microbiota and often resides on mucosal surfaces such as the oral cavity or the gastrointestinal tract. In addition to their commensality, *Candida* species can opportunistically become pathogenic if the host microbiota is disrupted or if the host immune system becomes compromised. An important factor for *Candida* pathogenesis is its ability to form biofilm communities. The two most medically important species - *Candida albicans* and *Candida glabrata* - are often co-isolated from infection sites, suggesting the importance of *Candida* co-culture biofilms. In this work, we report that biofilm formation of the co-culture population depends on the relative ratio of starting cell concentrations of *C. albicans* (Ca) and *C. glabrata* (Cg). When using a starting ratio of Ca:Cg of 1:3, a ~6.5- and ~2.5-fold increase in biofilm biomass was observed relative to Ca monoculture and a Ca:Cg ratio of 1:1, respectively. Confocal microscopy analysis revealed heterogeneity and complex structures composed of long Ca hyphae and Cg cell clusters in the co-culture biofilms, and qRT-PCR studies showed an increase in the relative expression of the *HWPI* and *ALS3* adhesion genes in the Ca:Cg 1:3 biofilm compared to Ca monoculture biofilm. Additionally, only the 1:3 Ca:Cg biofilm demonstrated increased resistance to the antifungal drug caspofungin. Overall, the results suggest that interspecific interactions between these two fungal pathogens increase biofilm formation and virulence-related gene expression in a co-culture composition-dependent manner.

5. Modulation of Ultrasensitive Signaling in Bacteria by Viscous Load on Flagellar Motor

Jyot Antani and Pushkar Lele

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Mechanical forces are known to influence signaling in several biological systems. In recent years, several mechanosensitive proteins have been implicated in bacterial colonization and pathogenesis. Our earlier work showed that the bacterial flagellum, an appendage that enables motility, is an adaptive mechanosensor (Lele et al., PNAS, 2013). Recent results from our lab suggest that the mechanosensitive force-generators within the flagellar motor are activated through a catch-bond type mechanism (Chawla et al., Sci Rep, 2017). We have found additional mechanosensitive functions of the flagellar motor: a molecular flagellar switch, which enables reversals between clockwise (CW) and counterclockwise (CCW) directions of rotation, is also modulated by mechanical signals. This modulation is likely important for chemotaxis and bacterial swarming (Lele et al., Sci Adv, 2016), but the molecular mechanisms remain unknown. Here, we determined how viscous loads (mechanical forces) modulate the activity of the flagellar switch by controlling its ultrasensitive response to an allosteric response regulator, CheY-P. We employed the popular tethered-bead assays as well as tethered cell techniques to apply varying magnitudes of viscous loads on individual motors. Next, we measured the switch activities in a large population of cells and employed a statistical distribution technique to determine the dose-response relations ($CW_{\text{bias}}[\text{CheY-P}]$) as a function of load. Our preliminary observations suggest that modulation either occurs through the control of the flagellar switch structure or via the mechanosensitive response of stator-units involved in motor rotation.

6. Stochastic Modeling of CTB-GM1 Binding Kinetics

Dongheon Lee^{1,2}, Alec Mohr¹, Joseph S. Kwon^{1,2}, and Hung-Jen Wu¹

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843*

Abstract:

Cholera toxin (CTx) is a toxin protein, which can lead to lethal cholera. CTx is an AB₅ protein that consists of an enzymatic A-subunit and five identical cholera toxin B-subunits (CTB). CTB binds with gangliosides such as GM1 on host cell membrane, which facilitates the endocytosis of CTx and the development of cholera. How cholera toxin subunit B (CTB) binds to its receptor on host cell membrane is still not fully understood due to its complex nature. Since the binding events highly depend on the current surface configuration, the kinetic Monte Carlo methodology is applied to simulate the complex interactions between CTB and GM1 microscopically. The proposed kMC model considers receptor migration, CTB attachment and detachment, and surface forward and backward reactions as discrete microscopic events. At every moment, an event to be executed is selected randomly based on the rates of all possible events, and this procedure continues till the end of simulation. In summary, we utilize theoretical modeling to explore cholera pathogenesis and offers a systematic tool for the biomedical community to reveal the pathogenesis of other diseases.

7. Optimal Design of Energy Systems using Constrained Grey-Box Multi-objective Optimization

Burcu Beykal^{1,2}, Fani Boukouvala³, Christodoulos A. Floudas^{1,2}, and Efstratios N. Pistikopoulos^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843*

³*School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332*

Abstract:

The (global) optimization of energy systems, commonly characterized by high-fidelity and large-scale complex models, poses a formidable challenge partially due to the high noise and/or computational expense associated with the calculation of derivatives. This complexity is further amplified in the presence of multiple conflicting objectives, for which the goal is to generate trade-off compromise solutions, commonly known as *Pareto-optimal* solutions. We have previously introduced the p-ARGONAUT system,

parallel Algorithms for Global Optimization of constrained grey-box computational problems, which is designed to optimize general constrained single objective grey-box problems by postulating accurate and tractable surrogate formulations for all unknown equations in a computationally efficient manner. In this work, we extend p-ARGONAUT towards multi-objective optimization problems and test the performance of the framework, both in terms of accuracy and consistency, under many equality constraints. Computational results are reported for a number of benchmark multi-objective problems and a case study of an energy market design problem for a commercial building, while the performance of the framework is compared with other derivative-free optimization solvers.

8. Integration of Design, Scheduling, and Control of Combined Heat and Power Systems: A Multiparametric Programming Based Approach

Baris Burnak^{1,2}, Justin Katz^{1,2}, Nikolaos A. Diangelakis², and Efstratios N. Pistikopoulos^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Texas A&M Energy Institute, Texas A&M University, College Station TX, 77843

Abstract:

The operation of multiproduct/multipurpose processes involves decisions at different time scales; such as short-term for control, medium-term for scheduling, and long(er)-term for design. At all these scales, uncertainty plays a key role with fluctuations in product demand, prices, availability of units, as well as raw materials and product specifications. While it has been widely accepted that simultaneous decision making at these three layers are expected to deliver cost-effective and intensified/integrated processes; such an integration still poses formidable challenges due to the order of magnitude differences in the time-scale, the often-conflicting objectives at the different layers, etc. However, recent advances in this area provide a sound basis for further development.

In this work, we present a unified framework towards this direction for the case of multiproduct/multipurpose processes. Based on the PAROC (PARAMetric Optimization and Control) framework featuring (i) a single high-fidelity model, (ii) multi-parametric Rolling Horizon Optimization (mpRHO) policies to readjust for the changing market structures, (iii) multi-parametric Model Predictive Control (mpMPC) for efficient set point tracking and, (iv) a surrogate model formulation to bridge the time gap between mpRHO and mpMPC, we derive (i) design dependent and scheduling aware control strategies, and (ii) scheduling strategies that are design dependent and control aware. The multi-parametric formulation of the integrated scheduling and control schemes yields offline maps of optimal actions that enable design and operational optimization under uncertainty. The framework is illustrated on a combined heat and power (CHP) system, involving two CHPs operating in tandem to satisfy the time-variant heat and electricity demand from multiple residential units. We utilize the proposed methodology to simultaneously determine (i) the optimal size of the internal combustion engine, (ii) the decentralized control schemes for different operating policies, and (iii) the coordination of the parallel operations of the CHP units.

9. Simultaneous Process Network Synthesis and Process Intensification Using Block Superstructure

Jianping Li, Salih Emre Demirel, and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Process synthesis is used in obtaining the best processing route among many alternatives by assembling units into a process network with the goal of optimizing either economic, environmental, and/or social objectives. Current optimization-based process synthesis methods are unable to automatically construct and identify novel intensified equipment as they require pre-specified equipment configurations. Furthermore, whenever a new problem is addressed, a different superstructure needs to be postulated. To address these challenges, we propose a new block-based superstructure instead of classical unit-operation based one. Each block represents a unit use of materials with a specific function (reaction, separation, storage). The existence of connecting streams between adjacent blocks and jump flows among all blocks enables the necessary interactions between different blocks via material and energy flows. An assembly of the same blocks results in a classical unit operation, while intensified units are realized with assembly of multiple different blocks. This allows a systematic identification, representation and generation of intensification alternatives at the flowsheet level without *a priori* postulation of their existence. The proposed approach not only identifies different process equipment, but also automatically generates the corresponding flowsheet. We pose the unified synthesis and intensification problem

as a mixed-integer nonlinear optimization (MINLP) problem. The objective is to synthesize a process with intensified units by minimizing or maximizing a process metric given the feed and product specifications, feed and product prices, material properties and bounds on flow rates. We also demonstrate that the simultaneous synthesis and intensification approach leads to substantially smaller, cleaner, safer, and more energy-efficient designs.

10. Adsorption of Carbon on Partially Oxidized Cu Surfaces - Applications to Graphene Synthesis

Behnaz Rahmani Didar and Perla B. Balbuena

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Currently, the Catalytic Chemical Vapor Deposition is the most popular method for the synthesis of graphene and carbon nanotubes. Copper (Cu) as the catalyst in this process has shown much potential for growing high quality fragments of graphene. Experimentally, it has been observed that predosing Cu substrates with oxygen before graphene growth has a cleaning effect on the substrate. We study and discuss this process using DFT on two surfaces of Cu; (100) and (111). Our results show that on both surfaces, an incoming carbon atom has the ability to replace and completely desorb a previously surface-adsorbed oxygen atom producing CO and CO₂ molecules in the gas phase. By comparison, the (111) surface is better suited for oxygen desorption, and an incoming carbon atom can more easily bond to and desorb oxygen atoms even at low oxygen coverages. We also examine this mechanism at two different temperatures for both surfaces at 0.5 ML oxygen coverage.

Our results in this study shows first-principles evidence of the cleaning effect of oxygen on Cu surfaces in the presence of carbon with applications to graphene and carbon nanotubes synthesis. Conversely, adsorption and diffusion of carbon atoms, both of which are necessary for the nucleation and growth of carbon nanotubes, may be hindered by the presence of the oxidized or partially oxidized surfaces. Such desorption of carbon as CO or CO₂ in partially or totally oxygenated surfaces may be one of the reasons for the undesired termination of carbon nanotube growth.

11. Calorimetric Study of Graphene Oxide Thermal Stability

Pritishma Lakhe¹, Devon Kulhanek², Wanmei Sun², Bin Zhang¹, Micah J. Green², and M. Sam Mannan¹

¹*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

Large-scale production of graphene is of increasing commercial and academic interest because graphene has shown immense potential in energy storage and composite filler applications. Synthesis routes that involve graphene oxide (GO) are predominantly used because this method has shown potential for bulk production at high yield. This method involves the oxidation of graphite to GO and its subsequent reduction to reduced graphene oxide (rGO). However, prior studies have shown that GO can undergo explosive decomposition under certain conditions. There is no documented process safety incident related to GO so far, but GO is an energetic material that can undergo explosive thermal reduction. The motivation of this research is to investigate potential process safety issues with bulk GO storage and handling because the industry is ramping up large-scale manufacturing of GO. Our data shows increasing GO mass decreases the temperature at which material decomposes. We quantified the pressure release rate and pressure generation during decomposition. We also discussed the underlying causes of the explosive behavior of bulk GO and proposed safer storage and handling conditions. Studies were conducted in Advanced Reactive System Screen Tool (ARSST). We compared the GO decomposition made in lab using modified Hummers method to the commercially available GO. Finally, we used the Frank Kamenetskii model to obtain the critical density and mass necessary for GO decomposition. This research will be beneficial in assessing the hazards of GO and enhancing the safety of rGO production processes over their life cycles.

12. Toward Optimal Synthesis of Renewable Ammonia and Methanol Processes

C. Doga Demirhan^{1,2}, William W. Tso^{1,2}, and Efstratios N. Pistikopoulos^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843*

Abstract:

The conversion and storage of renewables into useful and transportable energy vectors is an outstanding challenge in transitioning to a sustainable energy future. Ammonia and methanol are two promising vectors due to their proven production and transportation infrastructures. Individual processes consuming fossil fuels have been improved and optimized over the years, but there is no clear path forward for incorporating renewables or their coproduction. In this work, we introduce a deterministic global optimization-based process synthesis framework to determine the minimal cost for the coproduction of ammonia and methanol from hardwood biomass and natural gas. This will provide the guideline for future studies into solar and wind energy. A process superstructure with several competing technologies and integration routes is modeled and described. A customized branch-and-bound algorithm is used to solve the resulting mixed-integer nonlinear nonconvex optimization model. Results indicate that the biomass incorporated processes are cost-competitive with pure fossil fuel based processes, and the integration of ammonia and methanol production leads to 4-7% savings.

ii) **AFTERNOON SESSION**

13. Surface-Agnostic Highly Stretchable and Bendable Conductive MXene Multilayers

Hyosung An¹, Touseef Habib¹, Smit Shah¹, Huili Gao², Miladin Radovic^{2,3}, Micah J. Green^{1,3}, and Jodie L. Lutkenhaus^{1,3}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843*

³*Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

Stretchable, bendable, and foldable conductive coatings are crucial for wearable electronics and biometric sensors. Such coatings should maintain functionality while simultaneously interfacing with different types of surfaces undergoing mechanical deformation. MXene sheets as conductive 2D nanomaterials are promising for this purpose, but it is still extremely difficult to form surface-agnostic MXene coatings that can withstand extreme mechanical deformation. Herein, we demonstrate conductive and conformal MXene multilayer coatings that can undergo large-scale mechanical deformation while maintaining a conductivity as high as 2000 S/m. MXene multilayers are successfully deposited onto flexible polymer sheet, stretchable poly(dimethylsiloxane), nylon fiber, glass, and silicon. The coating shows a recoverable resistance response to bending (up to 2.5 mm bending radius) and stretching (up to 40% tensile strain). We demonstrated that the MXene multilayer films could be used as strain sensors to topographically sense objects or materials deformation.

14. 3D Graphene Oxide Gel Assembly: Effects of Nanosheet Morphology and Ammonia on Gel Properties and their use as Structural Electrodes for Energy Storage

Smit A. Shah¹, Dorsa Parviz², Morgan G. Odom³, Wanmei Sun¹, Devon Kulhanek¹, and Micah J. Green^{1,3}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139*

³*Department of Materials Science and Engineering, Texas A&M University, College Station, TX, 77843*

Abstract:

3D graphene oxide (GO) based gels synthesized using sol-gel technique have gained remarkable interest because of their ability to retain individual nanosheet properties. The high specific surface area and electrical conductivity of these 3D gel networks makes them suitable active material for electrochemical energy storage applications. However, 3D GO gel's electrical conductivity, surface area and density depend on the crosslink type and density. Here we investigate the role of ammonia and precursor nanosheet morphology on the crosslink type and density of 3D GO gels. Our results indicate that ammonia strongly affects the formation of inter-sheet bridging structures as well as the deoxygenation and reduction of nanosheets during gelation. Thermal annealing of GO gels result in an increase in their electrical conductivity and displacement of nitrogen. We also altered the GO nanosheet morphology to obtain crumpled GO (CGO) nanosheets and prepared 3D aerogels with mixtures of GO-CGO nanosheet dispersions. The properties of these gels demonstrate how the GO morphology can allow for an additional handle in creating GO-based gels with tunable density, electrical conductivity, and surface area. We investigated the composites of GO gel with aramid nanofibers (ANFs) to obtain improved mechanical properties for their application as structural supercapacitor electrodes.

15. High Efficient Oil-Water Separation using Surface-Programmable Membranes

Glenn Zeng¹, Lecheng Zhang¹, Dali Huang², and Zhengdong Cheng^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843

Abstract:

The challenge of separating emulsified oil from water has sparked enormous research interests in developing advanced membrane technology. One of the most crucial elements to achieve high separating efficiency lies in the design of interfacial structure of membranes. Herein, we present a surface-programmable membrane for separating oil-water emulsions. Owing to the precise control on the surface chemistry of membranes, the hybrid membrane not only separates the oil-water mixture with high efficiency (>99.2%), but also demonstrates high versatility for many advanced applications, e.g., self-healing and heavy metal removal. This research opens up new opportunities in developing multifunctional membrane-based materials.

16. Synthetic, Functional Thymidine-Derived Polydeoxyribonucleotide Analogues from a Six-Membered Cyclic Phosphoester

Yi-Yun Timothy Tsao¹⁻³, Travis H. Smith¹⁻³, and Karen L. Wooley¹⁻³

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Department of Chemistry, Texas A&M University, College Station, TX 77843

³Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843

Abstract:

A grand challenge that crosses synthetic chemistry and biology is the scalable production of functional analogues of biomacromolecules. We have focused our attention on the use of deoxynucleoside building blocks bearing non-natural bases to develop a synthetic methodology that allows for the construction of high molecular weight deoxynucleotide polymers. Our six-membered cyclic phosphoester ring-opening polymerization strategy will be demonstrated, by an initial preparation of novel polyphosphoesters, comprised of butenyl-functionalized deoxyribonucleoside repeat units, connected *via* 3',5'-backbone linkages. Computational modeling of the six-membered 3',5'-cyclic phosphoester ring derived from deoxyribose indicated strain energies at least 5.4 kcal/mol higher than the six-membered monocyclic phosphoester. These calculations supported the hypothesis that the strained 3',5'-cyclic monomer can promote ring-opening polymerization to afford the resulting polymers with low dispersities. Regioregularity is a crucial property in the synthesis of DNA analogues, as natural DNA is synthesized exclusively in the 5' to 3' direction. The regioisomeric preference was investigated by comparison to synthesized model compounds of 3',3'-, 3',5'-, and 5',5'-linkages. 31P NMR spectra revealed the major connectivity in the polymer backbone to be 3',5'-linkages, with $\leq 30\%$ of other isomeric forms. Model reactions employing a series of alcohol initiators imparting various degrees of steric hindrance were then conducted to afford the corresponding ring-opened unimer adducts and to gain understanding of the regioselectivity during the ring-opening polymerization. 1H-31P heteronuclear multiple-bond correlation spectroscopy showed ethanol and 4-methoxybenzyl alcohol initiation to yield only the P-O5' bond cleavage product, whereas attack by isopropyl alcohol afforded both P-O3' and P-O5' bond cleavage products, supporting our hypothesis that the increased steric hindrance of the propagating species dictates the regioselectivity of the P-O bond cleavage. Overall, this work provides a fundamental understanding of the polymerization behavior of six-membered cyclic phosphoesters and broadens the scope of DNA analogues from the ring-opening polymerization of 3',5'-cyclic phosphoesters.

17. Polymer-Clay Nanocomposite Coatings as Efficient, Environment-Friendly Surface Pretreatments for Aluminum Alloy 2024-T3

Pilar C. Suarez-Martinez¹, Jerome Robinson², Hyosung An¹, Robert C. Nahas², Douglas Cinoman², and Jodie L. Lutkenhaus¹

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Axalta Coating Systems, Experimental Station E402/2131, Wilmington, DE 19803*

Abstract:

Surface pretreatment coatings are a research area in continuous transformation. Moving away from the well-known chromium conversion coatings (CCC) toward an environment-friendly alternative is of great interest. Materials such as the aluminum alloy 2024-T3 (AA2024-T3) used in aircraft, for example, provide good mechanical performance but lack good corrosion resistance. Here, we present a polymer-clay coating made from branched polyethylenimine (BPEI) and montmorillonite (MMT) clay as a potential CCC substitute, and we examine this for the corrosion protection of AA2024-T3. This polymer-clay coating is applied by airbrushing an aqueous BPEI/MMT mixture onto any substrate. With this approach, application time is significantly reduced in comparison to other techniques (e.g. layer-by-layer assembly), and the structure of the polymer-clay coating is finely tuned by controlling the polymer-clay ratio. Results from electrochemical measurements and salt spray testing reveal good long-term (40d) corrosion protection of AA2024-T3 provided by a 1.8 μm thick coating with a 20:80 polymer-clay ratio. This polymer-clay ratio yields a highly ordered multilayered brick and mortar structure, where MMT (bricks) provides a physical barrier for the diffusion of corrosive agents/corrosion products within the coating, and BPEI (mortar) provides structural support and decelerates the corrosion process through surface buffering.

18. Water and Ion Pairing Universally Influence the Glass Transition of Polyelectrolyte Complexes

Yanpu Zhang¹, Piotr Batys^{2,4}, Joshua T O'Neal², Fei Li¹, Maria Sammalkorpi³, and Jodie L. Lutkenhaus^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Materials Science and Engineering, Texas A&M University, College Station, TX, USA, 77843*

³*Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, 00076 Aalto, Finland*

⁴*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, PL-30239 Krakow, Poland*

Abstract:

The glass transition of a polyelectrolyte complex is long known to be influenced by hydration and salt doping. For example, it is generally accepted that increasing water content or salt doping depresses the glass transition temperature (T_g). However, there lacks a quantitative and physically meaningful relationship among these parameters that captures the behavior across more than one polyelectrolyte complex system. Here, modulated differential scanning calorimetry and all-atom molecular dynamic simulations are cooperatively exploited to investigate complexes paired from poly(diallyldimethylammonium chloride) and poly(sodium 4-styrenesulfonate). This relationship reveals that the glass transition is quantitatively controlled by the number of water molecules surrounding polyelectrolyte-polyelectrolyte ion pairs. Because this relationship also holds for another different polyelectrolyte complex system, it suggests that it might be considered “universal”. Simulations reveal the extent of water clustering around different types of ion pairs during the glass transition process. These results explain broadly the fundamental - but nontraditional - plasticization influence of water, which impacts current interpretations of PECs for humidity annealing, temperature-responsive platforms, swelling, and sensing for a wide range of applications.

19. Shale Gas Techno-economic Analysis: Designing Separation Units to Handle Feedstock Variability

Eric Bohac¹, Mahmoud El-Halwagi¹, and Debalina Sengupta²

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*The Gas and Fuels Research Center, Texas A&M Engineering Experiment Station, College Station, TX 77843*

Abstract:

One of the key challenges with shale gas is the wide variability in its composition and flow rate. The composition and flow rate, both between wells, and within the same well over time, can differ significantly. This is a challenge when designing a plant of optimal size. In general plants with larger process equipment are more flexible, and are able to handle a wider range of inlet compositions, however these plants also have higher fixed and operating costs.

In this work compositional variability is considered when designing a dehydration, NGL recovery, and fractionation train facility for a plant with a fixed inlet flowrate. A range of compositions are considered known. Conventional technology is used A plant is then designed for this base case process and is then simulated using ProMax, and fixed and variable costs are estimated using Aspen Process Economic Analyzer. Next five other cases representing the range of wellhead compositions in this region are run through the base case process design, assuming the same inlet flowrate, and any needed process modifications are made. Then revenue from the sale of shale gas and NGLs are compared with the additional fixed and variable costs for each case. The determination is then made based on process economics whether each case is worth treating or not. Safety impacts of the various cases are also considered, as is an additional case with a high acid gas content.

20. Model Approximation in Multiparametric Optimization and Control – A Computational Study

Justin Katz^{1,2}, Nikolaos A. Diangelakis², and Efstratios N. Pistikopoulos^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843*

Abstract:

The development of a high fidelity model to accurately describe a dynamical system can lead to a complex structure of (partial) differential algebraic equations. Incorporating these highly complex, coupled, and nonlinear systems into optimization and control studies may often lead to an intractable problem. Reduction of such large scale systems into more tractable forms is typically done via model approximation; for example in control studies some form of linearization or complexity reduction is performed. Such model approximations are also at the heart of the Parametric Optimization and Control (PAROC) framework for the derivation of explicit/multiparametric controllers and/or online (e.g. MPC) explicit strategies. A key question that remains open within the PAROC framework is *what constitutes a suitable approximate model for the derivation of explicit control strategies with multiparametric programming?*

In this work, we present a computational study towards addressing this question. In particular, we study system identification, and piece-wise linearization, in order to gain fundamental insights on the impact of the model approximation on (i) the solution of the multiparametric optimization problem, and (ii) the derived explicit control strategies. A computation study which features a detailed comparison based on error metrics is proposed in the following steps. Open loop dynamic optimization is first performed on a variety of high fidelity models of increasing complexity to ascertain the 'desired' optimal trajectories. These optimal trajectories are then compared to the trajectories determined from advanced control strategies, including explicit/multiparametric MPC, which are based on model approximations. Key error metrics include model accuracy, controller accuracy, and deviations from the 'desired' optimal trajectory. Two systems are used as a basis for this computational study: (i) a linear tank system with minimal complexity utilized to highlight the main principles of this approach, and (ii) a CSTR system where the reaction mechanisms are manipulated to increase the model complexity.

21. Systematic Analysis and Optimization of Water-Energy Nexus

Spyridon D. Tsolas, M. Nazmul Karim, and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

We present a scalable and systematic method for the design and optimization of complex water-energy nexus using graph theory-based network representation and a novel water-energy nexus (WEN) diagram. The graph-theoretic approach defines a nexus as a directed bipartite graph with two product flows, namely water and energy. The network representation allows decomposing a complex nexus into essential and redundant components. We show that for specified external grid demands, the optimal nexus configuration with minimum generation is the one without any redundant subgraphs with closed cycles. We then propose a systematic method to identify and eliminate redundant cycles, flows and entities within a nexus leading to (i) minimum generation/extraction of water and energy resources from the environment, or (ii) maximum yield of water and energy to meet external demands. Our proposed graphical approach is simple to implement and results in optimal nexus configurations. The approach is demonstrated using case studies on national and regional water-energy systems.

22. Improved Flare Radiation Criteria in Terms of Solar Radiation Contribution

Ankita Taneja¹, Delphine Laboureur^{1,2}, Bin Zhang¹, and M. Sam Mannan¹

¹*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*The von Karman Institute for Fluid Dynamics, Belgium*

Abstract:

At chemical processing plants, a flare stack is used to get rid of unwanted or excessive gases and relieve the system of excess pressure by combustion, thus causing high heat to radiate to atmosphere. Heat radiated from flare is important for siting flare at a proper location. The heat radiation should not exceed recommended threshold level so that people on-site and the equipment are not affected. Thus, to have a well-designed flare, knowledge of total radiation emitted from a flare is important to know. It will aid in accurately estimating the flare height and the area near the flare which would sustain high level of thermal radiation.

A common point of contention while calculating radiation level emitted from flare is the decision of including solar radiation (SR) in the calculations. API 521 mentions it to be discretionary upon the flare design company. However, some literature states that for all practical purposes, solar radiation contribution can be discounted.

The work performed aims at presenting a framework which quantitatively addresses aforementioned obscurity. The analysis helps flare designers to more objectively decide whether to include SR or treat it insignificant. The work studies the factors that cause variation in SR value: location, time, and orientation of the surface. Considering all these parameters, an appropriate value of SR is chosen to be the contribution of Sun to thermal radiation from flare. The effect of SR to design of flare is quantified by studying the change in effect distance near the flare and the height of flare. Consequence analysis software PHAST is used to obtain these calculations. In addition, the outcome that SR inclusion will have on the risk posed by the flare due to thermal radiation on personnel is also examined. This is studied by measuring the change in lethality and heat stress caused by radiation exposure.

23. Predicting Influence of Packing Shape and Loading Methodology upon Fixed-bed Structures

Srikanth Panyaram and Benjamin Wilhite

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Fixed beds are ubiquitous in chemical industry, finding use for gas-solid, liquid-solid, gas-liquid solid catalytic as well as gas-liquid mass transfer processes (absorption, distillation). The local packing structure of the fixed-bed provides surface area for fluid mass transfer, house catalyst material for reactions and dictates local flow patterns. Heterogeneities in packing configurations may result in increased pressure drop, fluid maldistribution and/or under-utilization of catalyst material, making an understanding of packed-bed structure essential to the efficient operation of these units.

Bed-packing algorithms have been developed for generating detailed three-dimensional maps of local bed structure. The algorithm has been tailored to study two widely used shapes in industry; spheres and cylinders. The study provides important insights into the global and local properties of the fixed-bed as a function of particle size, shape and loading methodology. Shape and size distribution of the particle sample influences the global and radial voidage. An essential component of this study is to understand how loading methods can influence the evolution of the properties exhibited by the beds. Different loading methods have been used to study the influence of particle-particle and particle-wall interactions. These interactions have shown to influence the voidage and orientation effects within the packing structures. Finally, the effect of these parameters on the evolution of fluid flows in fixed beds is elucidated. These investigations help in developing tools to manipulate the heterogeneities in packed beds to enhance reactor performance.

24. A Sustainable Process Design Approach for On-purpose Propylene Production and Intensification

Ashwin Agarwal¹, Debalina Sengupta², and Mahmoud M. El-Halwagi^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*The Gas and Fuels Research Center, Texas A&M Engineering Experiment Station, College Station, TX 77843*

Abstract:

The advent of Shale Gas and the increasing spread between the supply and demand curves for propylene present an opportunity for adopting alternative pathways to produce propylene. This study aims to investigate a sustainable process design approach to on-purpose propylene production. A hierarchical approach to sustainable process design is proposed and implemented in a case study. An initial evaluation of different propylene production technologies yielded propane dehydrogenation (PDH) as the most profitable route and hence, is the process under consideration. A base case design was developed, and process integration and intensification techniques were applied to reduce dependence on external utilities and to lower the overall capital investment. Waste heat recovery and off gas recycle were additional options used to intensify the overall energy consumption of the process. Emissions from the process were calculated from the EPA's guidelines. Economic and environmental metrics were then used to study the impact of integration and intensification techniques. Up to 70% reductions in CO₂ emissions were achieved as a result of this approach to sustainable design. The Sustainability Weighted Return on Investment (SWROI) metric was evaluated for all cases. Multi-objective decision making for the optimum design was facilitated by the sustainability metrics augmented with the traditional economic criteria.

B. POSTER PRESENTERS

i) MORNING POSTER SESSION

1. Polymerized Ionic Liquid Triblock Terpolymers: Synthesis and Characterization

Patrick M. Lathrop and Yossef A. Elabd

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Polymerized ionic liquid (PIL) block copolymers are a distinct set of block copolymers that incorporate the unique physiochemical properties of PILs (*e.g.*, high solid-state ionic conductivity, high chemical, thermal and electrochemical stability, and widely tunable physical properties) into block copolymer architecture, which allows for self-assembly into a range of nanostructures, where morphology type and domain size are tunable. To date, PIL block copolymers have been synthesized by a number of research groups and have shown distinct conductivity-morphology relationships as it relates to various applications. Several block chemistries have been explored, yet almost all reports are exclusive to (AB) diblock copolymers. Although AB diblock copolymers can provide orthogonal properties of high ion conduction and high mechanical strength in a solid-state material, there are limitations to AB diblock copolymers, such as limited set of morphologies, domain sizes, and a lack of means to achieve a combination of more than two properties simultaneously (*e.g.*, conductivity, strength, flexibility). Moreover, spatially connected 3D network morphologies, which often result in the highest ion conductivities, occur only over a small compositional range in AB diblock copolymers.

In this study, a PIL (ABC) triblock terpolymer was synthesized to explore a PIL-containing polymer with a richer compliment of properties, a wider diversity of cation/backbone chemistries, and a broader compositional range to obtain a variety of continuous 3D network morphologies. Specifically, poly(MMA-*b*-MEBIm-Br-*b*-HMA) was synthesized *via* sequential reversible addition-fragmentation chain-transfer (RAFT) polymerization and subsequently quaternized, where A block = methyl methacrylate (MMA), B block or PIL block = 1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide] (MEBIm-Br), and C block = hexyl methacrylate (HMA). Reaction kinetics of this PIL ABC triblock terpolymer were investigated and these results were utilized in scaling up the polymerization reaction to > 2 g quantities with narrow polydispersities and controllable block compositions. Chemical, thermal, morphological, and ion conductive properties were characterized using ¹H nuclear magnetic resonance (NMR) spectroscopy, elemental analysis (EA), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and electrical impedance spectroscopy (EIS).

2. Aramid Nanofiber/Functionalized Graphene Composite Electrodes for Structural Energy and Power

Paraskevi Flouda¹, Dimitris C. Lagoudas^{2,3}, and Jodie L. Lutkenhaus^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843*

³*Department of Aerospace Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

Flexible, structural or even wearable electronics have recently become a significant and inseparable part of our everyday life. This has led to an urgent need for structural energy storage systems, such as structural batteries and supercapacitors. Therefore, the development of structural electrodes, electrodes that can simultaneously bear mechanical loads while storing energy, is crucial for the design of next generation electronics. Here, we report on multifunctional electrodes for supercapacitors, consisting of functionalized graphene oxide (f-GO) and aramid nanofibers (ANFs) fabricated through vacuum filtration. Graphene has remarkable properties such as high theoretical electrical conductivity, high surface area and excellent mechanical properties. On the other hand, recently developed aramid nanofibers, nanoscale Kevlar® fibers, are of great interest due to their exceptional mechanical properties, such as ultimate strength and stiffness. Functionalized graphene and ANFs were combined to create mechanically strong supercapacitor electrodes, where ANFs interact with f-GO through extensive hydrogen bonding and pi-pi interactions. The electrodes were characterized through scanning electron microscopy (SEM), Raman, and X-ray photoelectron

spectroscopy (XPS). The effect of the addition of ANF, as well as, of the functionalization of the GO sheets with different functional groups (-COOH and -NH₂) on the mechanical and electrochemical properties, was examined. Tensile testing, cyclic voltammetry and galvanostatic charge-discharge tests were conducted to evaluate the mechanical and electrochemical performance of the fabricated structural electrodes.

3. Radio Frequency Curing of Pre ceramic Polymers Loaded with Nano-fillers to Silicon Carbide Preforms

Nutan Patil¹, Micah J. Green¹, and Mohammad Saed²

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, TX 79409*

Abstract:

Silicon carbide (SiC) structures are deployed to meet a wide range of defense and aerospace applications. These materials are often prepared by sintering but may also be prepared by high-temperature curing of pre ceramic polymers like polycarbosilanes. The limitation of polymer routes is slower curing processes and non-uniform curing due to heat transfer gradients. In this method, we are using carbon nanotubes (CNTs) as RF susceptors and heating CNT-polycarbosilane mixtures using RF sources. This leads to rapid curing of the polymers. In order to keep the mechanical integrity of the sample, we propose deposition and curing of thin layers. This technique has a wide scale application in additive manufacturing of SiC and mold casting as well. RF thermal spectroscopy technique developed by our group was used to find resonant frequency. Study of curing behavior of polymer for varying CNT loading and power was done. The extent of curing was shown by TGA and SEM.

4. Approach to Retard Oxidation During Processing of Colloidal Ti₃C₂ MXenes

Touseef Habib¹, Smit Shah¹, Yexiao Chen², Wanmei Sun¹, Miladin Radovic², and Micah J. Green¹

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

MXenes are a relatively new class of nanosheets and they have gained significant interest due to their unique chemical, dielectric and transport properties. Since their discovery in 2011, they have shown to be promising in a wide range of applications such as batteries, supercapacitors, electromagnetic shielding, and water desalination. However, Ti₃C₂ MXenes are prone to oxidation, which causes them to chemically degrade to TiO₂ over time and become impractical for desired applications. This makes processing of Ti₃C₂ MXenes difficult. In this study, we investigated oxidation of Ti₃C₂ MXenes in air, liquid media, and solid media. We characterized oxidation by monitoring TiO₂ content and conductivity of the processed films. We show Ti₃C₂ MXenes in solid media oxidize at lower rates relative to other media.

5. Ab-Initio Investigation of Dimethyl Disulfide as an Additive for Lithium-Sulfur Batteries

Ethan P. Kamphaus and Perla B. Balbuena

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Energy storage technology is an important field of study with strong economic and environmental driving forces. Batteries are ubiquitous and critical for much of modern technology like cell phones and electric vehicles. The current leader in rechargeable battery technology is the lithium ion (Li) battery. However, the Li battery is close to the theoretical limit of its energy storage but our technology requires more capacity. One promising battery system is the Lithium-Sulfur (LiS) battery which can surpass the Li battery by about 3 times the energy density.

Unfortunately, the LiS battery faces several challenging problems before it can be utilized commercially. One problem is known as the polysulfide shuttle reaction. This reaction is the consequence of the solubility of reaction products in the electrolyte. The polysulfide shuttle causes active material loss from the cathode and passivates both electrodes. Donghai Wang's group at Penn State University recently published a new strategy to counteract this effect: use a different electrolyte. Their new electrolyte

consisted of 50% DME and 50% dimethyl disulfide (DMDS) which showed increased battery performance. Wang et. al's experiment postulated several potential reasons for why they saw increased performance but were not able to determine exactly why.

We used density functional theory (DFT) to explore the theory and fundamentals behind DMDS's effect on battery performance to complement Wang et al's experimental work. Computational chemistry calculations were completed with Gaussian to determine reaction thermodynamics on the new reaction pathway that DMDS forms with the traditional sulfur reduction. We also investigated the passivation of the electrodes with the DMDS modified reduction pathway by solid state calculations with VASP. Electronic structure of the final reduction products that precipitate on the cathode were determined including DOS and other charge carrier calculations.

6. Ferrocene-Based Redox Switches for Reversible Single-Molecule Magnet Behavior in Dysprosium(III) and Erbium(III) Bis-Diamidoferrocene Complexes

Courtney M. Dickie¹, Alexander L. Laughlin², Joshua D. Wofford¹, Nattamai S. Bhuvanesh¹, and Michael Nippe¹

¹*Department of Chemistry, Texas A&M University, College Station, TX 77843*

²*Department of Chemistry and Biochemistry, University of California, Los Angeles, CA 90095*

Abstract:

Single-molecule magnets (SMMs) are considered feasible candidates for next-generation high density data storage applications. SMMs featuring switchability of their magnetization dynamics are particularly attractive with respect to use in devices. This poster presentation will show that transition metal-based redox events may be used to influence slow magnetic relaxation at nearby anisotropic lanthanide(III) ions. The anionic homoleptic bis-diamidoferrocene complexes of Dy³⁺ (oblate) and Er³⁺ (prolate) may be reversibly oxidized by one electron to form the neutral species. The Dy³⁺ system can function as either an "on"/"off" or a "slow"/"fast" switch in the absence or presence of an applied dc field respectively, whereas the Er³⁺ system functions as an "on"/"off" switch in the presence of an applied dc field. Furthermore, results from ⁵⁷Fe Mössbauer spectroscopy, cyclic voltammetry and UV-Vis-NIR spectroscopy indicate the presence of significant electronic communication between Fe ions in the mixed valent compounds.

7. Systematic Process Intensification using Building Blocks

Salih Emre Demirel, Jianping Li, and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Process intensification combines multiple operations in a single unit, and leads to substantially smaller, cleaner, safer, and more energy-efficient technologies. Current superstructure-based process synthesis relies on pre-specified equipment configurations which hinders automatic identification of intensified equipment configurations. Phenomena based process intensification, allows to approach processes from a lower aggregation level which enables identification, screening and incorporation of intensification opportunities, but this approach often requires sequential or decomposition based solution strategies to solve large models, which can lead to suboptimal solutions. In this work, a unified process synthesis and intensification method that utilizes an original building block-based superstructure is proposed. Proposed superstructure is an ensemble of building blocks, where each block represents a unit use of a material. An intensified unit is realized by selecting and assembling multiple neighboring blocks with different functionalities. This enables to incorporate many intensification alternatives, including divided wall column distillation, reactive distillation, reactive absorption and membrane reactor, within the same superstructure without any a priori postulation. The overall process intensification model is formulated as a single mixed-integer nonlinear optimization (MINLP). Hence, given feed and product specifications and available materials, building block-based superstructure is able to generate intensified process flowsheets with optimum operating conditions.

8. A Novel Derivative-Free Optimization Method on Single Dimension Projection

Ishan Bajaj and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

With the advent of high-fidelity, complex process modeling and simulation in many areas including computational fluid dynamics-based reactor design, Nonlinear Algebraic and Partial Differential Equations (NAPDE)-based multiscale optimization, data-driven methods are gaining more importance than ever. Most often, these optimization problems are formulated as black-box problems where the objective function and/or constraints cannot be expressed analytically as explicit functions of decision variables. This implies that the values of the objective and/or constraints become available only after performing a full-scale expensive simulation. To this end, derivative free optimization (DFO) has emerged as a promising approach to optimize black-box problems.

In this work, we present an algorithm to address multi-dimensional black-box problems based on projection onto a one-dimensional space. Specifically, we consider a problem of minimizing $G(t)$, which can be interpreted as the projection of the original objective function $f(x_i)$, $i = 1, \dots, n$ taken in the t -space such that $i=1 \rightarrow x_i=t$. We show that the minimum of $G(t)$ also corresponds to the minimum of $f(\mathbf{x})$. This enables us to solve the original optimization problem in two steps. The first step involves identifying $G(t)$ and is referred as the inner loop. In this work, the inner loop is applied at discrete values of t (t_1, t_2, \dots, t_k). Once the solution at the previous t (t_{k-1}) is known, sensitivity theorem is utilized to obtain close solution for the inner loop at next t (t_k). The second step is optimizing the univariate function $G(t)$ to find the solution of the original problem. The algorithm is applied to a large set of test problems and compared to existing model-based DFO solvers.

9. Modeling, Simulation and Optimization of Hybrid Adsorption-Reaction Systems

Akhil Arora, Ishan Bajaj, Shachit S. Iyer, and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Intensified adsorption-reaction processes have shown promise for obtaining higher reaction conversions, and better process efficiency and integration in equilibrium-limited reactions. In these processes, in-situ removal of the reaction byproducts from the gas phase reaction mixture, by a solid adsorbent, favors further production of non-adsorbed product. Hydrogen has been produced via sorption-enhanced steam methane reforming (SE-SMR) and sorption-enhanced water gas shift (SE-WGS); these intensified reactions have shown significant reduction in temperature, and higher hydrogen product purity and limiting reactant conversions in comparison to the conventional reactions. Therefore, the practical utility for efficient designing of reactor-adsorber systems using high-fidelity mathematical models is indispensable. However, the dynamic nature of such processes, and the complex and coupled multiphysics nature of the systems make their modeling and simulation a complicated task.

In this work, we have developed a high-fidelity generalized reaction-adsorption modeling and simulation (GRAMS) framework. For demonstrating the capabilities of GRAMS, the simulations are performed for several configurations of the column containing (i) pure catalyst, (ii) pure adsorbent, (iii) heterogeneously-compartmentalized adsorbent and catalyst, and (iv) homogeneously-distributed uniform mixture of adsorbent and catalyst. The model predictions show excellent agreement with experimental observations for SE-SMR, SE-WGS, conventional SMR and pressure swing adsorption. GRAMS is then coupled with in-house black-box optimization solvers for simultaneous identification of optimal sequence and types of process steps, and optimal process operating conditions including pressure, temperature, steps duration, feed composition and flow rate, and adsorbent-to-catalyst ratio.

10. Toward a Systematic Framework for the Synthesis of Safely Operable Process Intensification Systems

Yuhe Tian¹, M. Sam Mannan^{1,2}, and Efstratios N. Pistikopoulos^{2,3}

¹Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

³Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843

Abstract:

Modular process intensification offers the promise to involve multifunctional phenomena at different time and spatial scales to efficiently overcome process limitations and maximize synergy effects. However, this highly integrated scheme often reduces the degrees of freedom for safe operation and process control, thus arousing concerns from process safety and operability perspective. Despite increasing efforts in recent publications towards a systematic strategy to deliver intensified processes, there is a lack of approach to simultaneously synthesize intensified but safely operable systems. To address this challenge, we will present an integrated framework, which embeds inherent safety, flexibility, and controllability analysis in a phenomenological representation framework to derive intensified designs with guaranteed safety and operability performance.

The proposed framework features (i) superstructure-based process synthesis using Generalized Modular Representation Framework to give the resulting design configurations, where multifunctional mass/heat exchange modules are employed as building blocks; (ii) high-fidelity dynamic modeling and simulation; (iii) operability analysis, comprising flexibility analysis for accommodation of uncertainty, risk assessment for inherent safety evaluation, together with controller design in multi-parametric model-based predictive control (mp-MPC) scheme following the PAROC framework; and (iv) in-silico closed-loop validation to bridge between steady-state synthesis and dynamic modeling and to ensure targeted performance during both operation modes. As the first step of a broader scope of process intensification systems, we apply the proposed framework to a case study on heat exchanger network (HEN) synthesis, which opens up the potential for thermal process intensification, as well as can be expanded to mass/heat exchanger network synthesis. The results indicate that significant improvements in HEN design configurations can be obtained to enhance safety and operability.

11. Effect of Carbon Dioxide-Sustained Adsorption using Ion-Exchange Resin on Mixed-Acid Fermentation

Haoran Wu, Samarпита Roy, Kefan Yang, and Mark Holtzaple

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

The carboxylate platform is a biomass-to-energy process that converts biomass into hydrocarbon fuels or chemicals. Using mixed-cultures of microorganisms, five mixed-acid fermentation systems were established. Carbon dioxide-sustained resin adsorption column was designed and the effects of carbon dioxide flowrate in carboxylic acids uptake capacity were measured. Different amount of weak base anion-exchange resin (Amberlite IRA-67) were employed to adsorb the carboxylic acids produced from the established fermentation systems in the presence of carbon dioxide. The conversion, yield and selectivity with or without adsorption in each system were calculated and compared.

12. Fire Incidents in Offshore Oil and Gas Rigs: Analyses of Incident Investigation Reports

Zohra Halim, Sunder Janardanan, Tatiana Flechas, and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

In order to learn from past incidents and prevent future disasters from occurring, it is important to identify underlying factors that led to the incidents. Fire incidents are rather common on offshore oil and gas facilities. In an attempt to identify the common causes behind such incidents, the current work focuses on analyzing 137 investigation reports on fires that occurred on offshore oil and gas facilities located in the Gulf of Mexico, made available by Bureau of Safety and Environmental Enforcement (BSEE). These reports have been analyzed using a systematic methodology to generate statistical data on leading causes and lagging measures

arising from various technical, operational, human and organizational issues that contributed to the incidents. Initially, the investigation reports had categorized the findings into 9 direct causes (equipment failure, human error, external damage, slip/trip/fall, weather related, leak, upset H₂O treating, overboard drilling fluid and other), of which equipment failure and human error were found to be the most common ones. However, our analysis of the narrative parts of the reports found that apart from the 9 broad causes, there were many other factors that contributed to these causes. The most recurring contributing factors were job safety analysis, procedure (including procedural deviation and improper procedure) and maintenance related issues. Others such as improper supervision, improper communication, design flaw etc. were also identified. This work thus provided a deeper insight about the issues that led to the past incidents and helped identify the areas of concern that needs improvement to achieve process safety excellence in offshore facilities to prevent future disasters from recurring.

13. Calorimetry Studies of Benzoyl Peroxide

Yueqi Shen, and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Organic Peroxides (OP) are widely used in petrochemical industry as initiators. Their unstable O-O bonds make them very useful, but also hazardous due to highly exothermic nature of decomposition, which can result in runaway reactions. Benzoyl peroxide (BPO) is one of the most commonly used OPs in industry and the hazards associated with its processing, storage and transport are revealed in many incidents. Benzoyl peroxide can decompose under favorable conditions and release large amounts of energy in short time. The decomposition reaction can ultimately lead to runaway reaction, posing great hazard of high temperature and high pressure. The most critical control factors of thermal decomposition and possible explosion of benzoyl peroxide are temperature, structure, and impurities or extraneous matter. This research is a comprehensive study of the runaway behavior of BPO hybrid system using isothermal and adiabatic calorimeters. The aim is the advancement of understanding the thermal decomposition of BPO under various conditions from both experimental and theoretical aspects. More specifically, this research will systematically study and develop thermodynamic and kinetic parameters related to decomposition of BPO, and further the use of this particular knowledge to mitigate the risks in storage, transportation and manufacturing process.

14. Safety Assessment of Secondary Alcohol Oxidation with Hydrogen Peroxide

Yue Sun¹, Lei Ni², Maria Papadaki³, Wen Zhu¹, Juncheng Jiang², and M. Sam Mannan¹

¹*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Jiangsu Key Laboratory of Hazardous Chemicals Safety and Control, College of Safety Science and Engineering, Nanjing Tech University, Nanjing 210009, China*

³*Department of Environmental & Natural Resources Management, School of Engineering, University of Patras Seferi 2, Agrinio 30100, Greece*

Abstract:

Ketones are produced on massive scale in industry as solvents, polymer precursors, and pharmaceuticals. Current ways of producing ketone through alcohol dehydrogenation are energy intensive and usually expensive, hazardous and toxic due to employing strong oxidizing agents. In 1997, Kazuhiko Sato, et al., found a way of producing ketones via 30 % hydrogen peroxide oxidation of alcohol, and tungstate as catalyst along with a phase transfer catalyst. This method is considered as 'green chemistry' since it is organic solvent- and halide-free. Lots work has been done later focusing on different catalysts and experimental conditions as well as their effects on yields of different ketones in laboratory.

However, there are safety concerns for scale-up regarding this reaction system because of its runaway potentials. Thus, the purpose of this project is to conduct a comprehensive study of thermal and kinetic behavior of this reaction system. Calorimeters, such as DSC and Phi-Tec, are used to help study, experimentally and theoretically, these reactions under normal operating and runaway conditions. Here, we report the thermal hazard assessment of these reactions and discuss the DSC results as well as GC/MS analysis of chemicals that produced through the test. The findings will be further used to propose measures for safer design and scale-up of this reaction process with runaway potentials.

15. Studying The Effects of Obstacle Configuration and Fire Suppressants on Flame Propagation Regimes

Cassio B. Ahumada¹, Eric Petersen², and M. Sam Mannan¹

¹Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Department of Mechanical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

In respect of vapor cloud explosions, there are two main combustion modes: deflagration and detonation. Deflagrations occur when the flame front travels at subsonic speeds leading to overpressures with the same order of magnitude as the atmospheric pressure. Unlike deflagrations, detonations are characterized by supersonic flame propagation velocities and significant overpressures. Several experimental studies have shown that, when the proper conditions are met, the flame front may accelerate reaching the detonation combustion mode; a phenomenon known as deflagration-to-detonation transition (DDT). However, more recent large-scale tests have demonstrated that intermediate states between laminar deflagrations and CJ detonations are more likely to happen for fuels with low and medium reactivity, such as methane and propane. Therefore, this research project focus on studying experimentally and numerically intermediate combustion regimes during deflagration-to-detonation transition. The ultimate goal is to understand the effects of layout and fire suppressants on the final flame speed.

16. Predicting the Stability of Pt^{II}-Based Molecular Gyroscope Isomers

Andreas Ehnbon, Lisa M. Pérez, Michael B. Hall, and John A. Gladysz

Department of Chemistry, Texas A&M University, College Station, TX 77843

Abstract:

Recent efforts to synthesize molecular gyroscopes containing a platinum core have unveiled several competing molecular architectures (see abstract graphics, compounds a-d). We sought to understand if there exists any thermodynamic preference for one of these species, but moreover, to probe how the linker length (n) and ligand set ($L = F, Cl, Br, I, H, Me, Ph$) would impact the relative stability of a-d as this could help us steer the experimental endeavors in a clear direction. Density functional theory was used to probe these issues using both gas-phase calculations and solvent corrected models. Dispersion corrections were also implemented to account for the dispersion interactions that were of particular importance for compounds with large linker length ($n = 18, 20, 22$). Calculation data were compared to experimentally harnessed X-ray structures, which showed good structural agreements. It was concluded that for short-medium linker lengths ($n = 10, 12, 14$), the gyroscope architecture (a) proved to be the most stable isomer in the presence of small to medium sized ligands ($L = H, F, Cl, Br, I$). However, the "parachute" structure (b) was favored for larger ligands ($L = Me, Ph$) with short linker lengths. The "ear-type" structures (c, d) were high in energy relative to a-b with short linker length species ($n = 10-14$) due to steric effects exerted in two of the smaller macrocycles, or "ears". Interestingly, c and d are closer in energy to a when the linker length increases ($n \geq 16$), and this tendency have also been experimentally observed. These investigations will help us to direct the synthesis to specifically target a-d by providing a rationale for the stereoelectronic underpinnings on how components such as ligand type and linkage length impact the relative stabilities.

17. Study on the Interfacial Interaction between Carbon Nanotubes and Catalyst, and the Effect in Tube Diameter

Mauricio Carvajal Diaz and Perla B. Balbuena

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Single-walled carbon nanotubes (SWCNTs) are seamless cylinders of graphene that have been at the forefront of nanotechnology research for the past two decades. They possess a range of exceptional properties including high strength (~37 GPa), thermal conductivity (~3500 W/m/K) and ballistic electronic transport. Importantly, they can have semiconducting, semi-metallic, or metallic conductivity depending on their chiral angle (χ), i.e. the angle between the tube axis and the edge of the graphene lattice. While mass-produced SWCNT powders are adequate for some applications, many emerging applications require stricter control over SWCNT properties and architectures, necessitating targeted growth, i.e. tailoring the physical properties of the SWCNTs (diameter, orientation/architecture, etc.) during synthesis to match the requirements of a particular application.

This project attempts to prove the key role of the catalyst – graphene interaction in the chirality selectivity of carbon nanotubes (CNT) and therefore, the intrinsic relation between catalyst size and nanotube diameter. We work on the assumption that the curvature energy is one of the most influential factors in the nanotube's formation reaction and a decisive step to determine the diameter of the nanotube during the growth. The calculation of interlayer binding energies using density functional theory (DFT) and pseudopotential functions has been valuable to find the transition diameter between fullerene and tube. Also, we propose a new relation that links theory to measurable thermodynamic properties such the surface tension, and surface energy. This is just the first step to bring light to the yet undiscovered reigning principle in the nanotube's diameter stability during nucleation.

ii) AFTERNOON POSTER SESSION

18. Electrochemical Investigations of Electroactive Redox Polymer for use in Energy Storage Devices

Kasturi Sarang¹, Hysoung An¹, Andrea Miranda³, Jodie L. Lutkenhaus^{1,2}, and Rafael Verduzco^{3,4}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843

³Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005

⁴Department of Materials Science and NanoEngineering, Rice University, Houston, TX 77005

Abstract:

Future is dependent on electrochemical energy storage (EES) systems which will have a tremendous role in technical applications like computers, communication devices, electric vehicles, laboratory equipment etc. Fossil fuels are depleting, and we can already see the world moving towards EES systems. Polymers have a prominent place in EES, not just as an electrolyte, but also in solid state batteries, especially electrodes. Recent focus is on organic polymers since they are sustainable, nontoxic and its possible to fabricate lightweight flexible devices. This study introduces an organic pi-conjugated redox active polymer, poly(fluorene-alt-naphthalene diimide) (PFNDI), which can be a potential n-type polymer in EES systems. N-type polymers have shown to lack electrochemical stability and have very high impedance, thus making them unsuitable for fast charge/discharge kinetics. However, we have shown that PFNDI can be stably and reversibly doped with high ion and electron conductivity, thus enabling realization of fast rechargeable batteries. PFNDI has a redox active unit which assist in doping process and a pi-conjugated unit which assists in electron and ion transfer. Energy is storage via exchange of dopants and electrons during charge/discharge. We have done a detail fundamental study of energy storage in n-type polymer. We evaluated this polymer as a charge storage material for rechargeable Li batteries and it delivers 92% of its theoretical capacity at very high rate of 1000C. This study introduces a new organic polymer which has a potential application in all polymer flexible battery and/or capacitor.

19. Saturated N-heterocyclic Cationic Polymers: Synthesis and Stability

Rui Sun and Yossef A. Elabd

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Polymers containing unsaturated N-heterocyclic cations (i.e., imidazolium) have been synthesized and investigated for various applications, including alkaline fuel cells and batteries. Recently, results have shown higher alkaline chemical stability for polymers bearing a saturated N-heterocyclic cation (pyrrolidinium) versus an unsaturated imidazolium cation. Additionally, several studies on small molecules have reported increasing stability with increasing saturated N-heterocyclic cation size and this was attributed to decreasing ring strain with increasing cation size. However, to date, few studies have systematically investigated polymers containing saturated N-heterocyclic cations, specifically N-heterocyclic cations with larger ring sizes (i.e., azepanium, azocanium, azonanium). In this study, styrene-based saturated N-heterocyclic cationic (SNHC) polymers with various covalent attached cations (methylpyrrolidinium, methylpiperidinium, methylazepanium) were successfully synthesized to investigate the influence of ring size/strain on the properties of SNHC polymers. Functionalization of poly(vinylbenzyl chloride) was employed to covalently attach cations onto polymer backbone, followed by anion exchange metathesis, resulting in polymers with bromide counter anions. Alkaline chemical stability, temperature and humidity dependent water uptake, and ion conductivity of these SNHC polymers were measured and will be reported in regards to the relationship with ring size/strain. This work provides a fundamental understanding of the ring size/strain effect in SNHC polymers and further introduces a promising chemistry for producing highly stable and ion conductive solid-state separators for alkaline fuel cells and batteries.

20. High-Resolution Scalable Propylene/Propane Separation for ZIF-8 Polycrystalline Membranes on Ceramic Tubular Support

Jingze Sun and Hae-Kwon Jeong

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Zeolite-imidazole frameworks (ZIFs) have been extensively studied as a new membrane material for gas separations due to their robust synthesis protocols, chemical and thermal stability, and well-defined ultra-micropores (~ 2 to 5 Å).^{1, 2} ZIFs are comprised of metal centers (Zn, Co, and Cd) and bridging imidazole-based ligands. ZIF-8, composed of zinc nodes and 2-methylimidazole linkers, has been shown very promising for propylene/propane separations since its effective aperture size lies in between propylene (~ 4 Å) and propane (~ 4.2 Å).³ In fact, some of the polycrystalline ZIF-8 membranes synthesized by various methods have been reported to exhibit impressive propylene/propane separation factors up to 200.^{4, 5} These highly propylene-selective ZIF-8 membranes were supported mostly on alumina disks or occasionally on hollow fibers (polymer or ceramic).

For their large-scale industrial applications, however, the productivities of ZIF-8 membranes must be significantly improved. One way to increase the membrane productivity is to increase membrane area per volume. As such, current disk supports are not desirable. Though hollow fiber supports (either polymer or ceramic) are most desirable, they are unlikely to be used for large-scale applications in near future. This is because ceramic hollow fibers are highly fragile while polymer hollow fibers require much more development. While hollow fiber supports are transformative, ceramic tubular supports are readily available for large-scale applications. For example, ceramic tubular supports have been used for commercial polycrystalline zeolite membranes.⁷ Though ZIF-8 membranes on ceramic tubular supports were reported, none of those membranes showed promising propylene/propane separation capabilities.

Here, we would like to present polycrystalline ZIF-8 membrane supported on alumina tubes showing high propylene/propane separation performances. The tubular membranes were synthesized using our microwave seeding and secondary growth method. The effects of the synthesis parameters on the microstructures of tubular ZIF-8 membranes will be presented. Finally, the propylene/propane separation performances of ZIF-8 membranes supported on alumina tubes will be discussed.

21. Application of Electrochemical Impedance Spectroscopy for The Study of Degradation Behavior of Nanowire Thin Films in Simulated Industrial Environments

Pranav Kannan^{1,2}, M Sam Mannan^{1,2}, and S. Vaddiraju^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

Silicon (Si) and Copper (II) Oxide (CuO) Nanowires (NWs) are substrates which offer the possibility for diverse applications in battery anodes, gas-sensing, PV modules, etc. due to their ease of surface modification, large surface area to volume ratio and scalable production. An important limitation is the lack of understanding of fouling and degradation processes in aggressive field environments such as those faced in the oil and gas industry. To improve the understanding of the electrochemical processes, two environments, 3.5% NaCl and simulated produced water (brine solution) were utilized in a three-electrode configuration with a high-internal resistance potentiostat to generate impedance spectra over a 24-hour period. The Nyquist plots indicated the presence of diffusion limitations at low frequencies for the silicon nanowires, and at high frequency there were contributions from external connections and ionic conductions to exhibit pure resistive behavior. The intermediate frequencies exhibited the individual contributions from the nanowire elements to the surface resistance. The Nyquist plots for the copper oxide nanowires indicated the increase in the surface resistance with time, which is attributable to the formation of passive film due to hydroxide formation. In contrast, the silane hydrolysis can be attributed to the decrease in surface resistance with time for the silicon nanowires. The equivalent circuit models for both the systems are utilized for further explanation of the surface processes.

22. Cone Calorimeter Analysis of Flame Retardant Poly(Styrene) Nanocomposite

Lubna Ahmed², Bin Zhang², Ruiqing Shen³, Zhengdong Cheng¹, Qingsheng Wang³, and M. Sam Mannan^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

³Fire Protection & Safety Engineering Technology, Oklahoma State University, OK 74078

Abstract:

The widespread application of polymers in the domestic and industrial life of people necessitates the study of its flammability. Polymer, being hydrocarbon, is a source of fuel in any fire scenarios. Flame retardant nanofiller can be one potential barrier to deteriorate the flame spread at the event of a fire. In the present study, silica and montmorillonite nanofillers will be embedded via *in-situ* method within the polystyrene matrix for forming fire retardant polymer nanocomposite. Polymer-nanocomposites have been chosen since they have demonstrated improvement in terms of thermal and mechanical stability, optical and electric properties when compared to the micro and macro varieties. To study the flammability of nanocomposites and analyze the reaction of the same to the fire, cone calorimeter has been used. Both neat polystyrene and polystyrene nanocomposites have shown the trend of a thermally thick charring polymer in the heat release rate over time data. The nanocomposites had an overall better flame retardancy than the neat polystyrene in terms of lower peak heat release rate, lower average mass loss rate and enhanced char formation. The nanocomposites had also reduced smoke emission with lower CO and CO₂ yield compared to the neat polystyrene. The overall flame retardancy was enhanced as the nanofiller loading was increased for both the nanosilica and MMT nanocomposites.

23. Combined High Stretchability and Gas Barrier in Hydrogen-Bonded Multilayer Nanobrick Wall Thin Films

Shuang Qin, Yixuan Song, Michael E. Floto, and Jaime C. Grunlan

Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Stretchable gas barrier coatings, that can maintain their barrier performance when subjected to high strain, are highly desired for flexible electronics protection, pressurized systems (e.g. tires and gas seals) and various types of food and pharmaceutical packaging. In this study, we demonstrate a stretchable high oxygen gas barrier nanocoating prepared with water-soluble and environmentally benign materials using layer-by-layer assembly. Polyethylene oxide (PEO) was alternately deposited from water with an aqueous mixture of polyacrylic acid (PAA) and montmorillonite (MMT) clay. The oxygen impermeable MMT platelets were highly exfoliated and aligned within the PEO/PAA polymer matrix. Ten bilayers of this multilayer nanocoating, with a thickness of 432 nm, improves the oxygen barrier of a 1mm polyurethane rubber by more than 50X after exposure to a 20% strain. This system, which provides the best stretchable oxygen barrier to-date in the open literature, shows great potential for use in a number of everyday products.

24. Advancing the Production of Olefins and Aromatics from Natural Gas Via Methanol: Chemical Looping for Syngas Generation

William W. Tso^{1,2}, C. Doga Demirhan^{1,2}, Alexander M. Niziolek³, Onur Onel³, Christodoulos A. Floudas[†], and Efstratios N. Pistikopoulos^{1,2}

¹Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

²Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843

³Department of Chemical & Biological Engineering, Princeton University, Princeton, NJ 08544

Abstract:

Due to technological advances in the shale gas industry, the supply of natural gas in the United States has greatly increased (37% since 2008) and its price has significantly dropped (\$2.52/MMBtu in 2016). The shale gas boom has not only revitalized the U.S. economy, but also rejuvenated interests in C1 catalysis toward the production of chemicals typically derived from petroleum

refining. Olefins (ethylene, propylene, butane isomers, butadiene) and aromatics (benzene, toluene, xylenes) are examples of valuable chemicals in high demand.

A judicious utilization of natural gas resources necessitates a systematic analysis of all available processing routes. To this aim, a gas to olefins and aromatics (GTOA) superstructure has been developed and includes several olefins and aromatics production technologies. Previous works investigated reforming as the primary method to convert natural gas to syngas and demonstrated the profitability of GTOA processes. Recently, the benefits of chemical looping for syngas generation have been observed in lowering the breakeven oil prices for a gas to liquids (GTL) process. In this work, we incorporate chemical looping into the GTOA superstructure as an alternative to reforming and study its impact on chemicals production.

Process synthesis of the GTOA superstructure forms a large-scale nonconvex mixed-integer nonlinear model (MINLP). A tailored deterministic global optimization branch-and-bound algorithm is used to solve the MINLP and determine optimal natural gas refineries with the highest profit. Several case studies are investigated to compare chemical looping against reforming for natural gas conversion. The effect of different plant capacities and product ratios are explored as well. Key topological selection of process technologies will be discussed.

25. Fault Detection and Diagnosis of Continuous Processes via Non-linear Support Vector Machine Based Feature Selection

Melis Onei^{1,2}, Chris A. Kieslich³, Yannis A. Guzman^{1,2,4}, Christodoulos A. Floudas^{1,2}, and Efstratios N. Pistikopoulos^{1,2}

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Texas A&M Energy Institute, Texas A&M University, College Station, TX 77843*

³*Coulter Department of Biomedical Engineering, Georgia Institute of Technology, Atlanta, GA 30332*

⁴*Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544*

Abstract:

Advances in sensor and data collection technologies has valorized data-driven modeling approaches in process monitoring and fault detection in process systems engineering. Today, machine learning and pattern recognition techniques play a significant role in attaining actionable insights and decision-making from the vast amounts of available process data by building accurate and robust data-driven models. One of the most popular machine learning techniques is Support Vector Machines (SVMs) which allows the use of high dimensional feature sets for learning problems such as classification and regression. Yet reducing the dimensionality of the feature space in data-driven modeling, known as dimensionality reduction and feature selection, is still a key task in improving model accuracy as well as decreasing *a priori* data collection, which in turn yields enhanced efficiency in chemical processes.

In this work, we present the application of a novel non-linear (kernel-dependent) SVM-based feature selection algorithm to process monitoring and fault detection of continuous processes. The developed methodology is derived from sensitivity analysis of the dual SVM objective and utilizes existing and novel greedy algorithms to rank features that also guides fault diagnosis. Here, we train two-class SVM models to detect known faults where the manipulated and measured variables of the process constitute the input feature space, and instances of normal and faulty operation yield training samples for our SVM models. The feature selection algorithm is used to improve the accuracy of fault detection models and perform fault diagnosis. We present results for the Tennessee Eastman process as a case study and compare our approach to existing approaches for fault detection and diagnosis.

26. Multi-scale Optimization of a Novel Separation and Storage Technology for Natural Gas

Shachit S. Iyer, Salih E. Demirel, and M. M. Faruque Hasan

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Significant efforts have been undertaken in the past for the separation, storage and transportation of methane from sources such as natural gas, shale gas, landfill gas and biogas which can often have high impurity content. Existing adsorption-based separation processes involve multiple pressure changes at different steps and multiple individual units resulting in additional cost. We propose a novel combined separation and storage (CSS) technology to simultaneously separate and store methane in a single column while

eliminating separate steps^[1]. However, the following challenges remain: (i) materials and technologies with high selectivity for methane separation often do not have high capacity for storage, and (ii) materials and technologies with high capacity for methane storage often do not have high selectivity for separation. For application in the CSS process, the adsorbent material should simultaneously possess both high methane selectivity and storage. Design of such a technology requires a rigorous multi-scale modeling and optimization approach. The adsorption of gases in the column is described using a non-linear algebraic partial differential equation model which is discretized over space and time domains to formulate and solve an optimization problem. The optimal operating conditions and adsorbents which would maximize storage of methane while maintaining a desired level of purity can then be obtained. Solutions from simulations are provided as warm starts to the optimization algorithm to aid in convergence.

27. Multi-objective Stochastic Optimization for Preventive Maintenance Planning in Chemical Plants

Christopher Gordon, Monir Ahammad, and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Maintenance planning and process operations in chemical manufacturing facilities are subject to several sources of uncertainty ranging from volatile feedstock prices to uncertainty in the level of demand. In the context of assuring the integrity of assets in ageing chemical plants, the present research focuses on uncertainty in equipment availability and develops a novel multi-objective stochastic mixed-integer nonlinear optimization algorithm for preventive maintenance planning. The algorithm factors in uncertainty to arrive at robust optimal solutions in contrast with other approaches such as risk-based inspection and deterministic optimization. In addition, it simultaneously considers the two competing objectives of cost minimization and system availability maximization to decide on the optimal maintenance frequency, set of online equipment and process flowrates at each time stage.

The proposed approach consists of two main steps. In the first step, the system is represented as a dynamic Bayesian network to capture complex interactions between system components, identify critical failure pathways, and characterize the overall risk of system failure. In the second step, the multistage stochastic optimization subproblem is formulated over a shrinking time horizon to progressively incorporate decisions and information from prior time stages into the decision-making process. Following system representation and problem formulation, the overall multi-objective optimization problem is solved using the epsilon-constrained method to obtain the optimal maintenance policy. The overall optimization problem is non-convex and large-scale and computational difficulties are tackled within the algorithm using structure-based decomposition strategies such as Generalized Benders decomposition, or via metaheuristic optimization techniques such as simulated annealing.

The results of the research include: (i) obtaining a robust optimal expected preventive maintenance plan and operating schedule, and (ii) provision of a Pareto front of optimal solutions from which the decision maker can select. This robust approach combining the techniques of Bayesian network-based risk assessment and nonlinear stochastic programming is illustrated with a case study and can be used to improve overall equipment availability and maximize plant productivity.

28. Identify Weak Signals using Data Mining Techniques

Mengxi Yu, Noor Quddus, and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Despite accumulated process safety knowledge and analysis tools of safety management, catastrophic incidents in process industries still occur. Most incidents are led by an incubation period when a chain of discrepant events develops and accumulates unnoticed. Some weak signals are only recognized after incident investigations, but are difficult to be recognized and interpreted before the incidents occur. On the other hand, a large volume of different types of data exist in process industries, including process data, maintenance and inspection data, incident reporting data and so on. Thus, the study is aimed to learn from historical database in process industries by using data mining to identify weak signals and predict occurrence of unwanted events/incidents. In current phase of the study, data is generated by modeling and simulation to be analyzed by data mining. The study will be decomposed to few tasks: define weak signal, understand and analyze the human/ organizational/ technological functions involved in a methyl

methacrylic polymerization process, generate data for the involved functions and corresponding scenarios, and finally develop a predictive model using data mining techniques to identify weak signals.

29. Mapping Review of Reactive Chemicals Hazards Research

Hallie Graham and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

Reactive chemicals are a major hazard affecting both the processing, storage, and handling of chemicals, powders, and pharmaceuticals that can lead to serious consequences such as fires, explosions, and toxic gas releases. In the 2003 Chemical Safety Board's Reactive Hazard Investigation of 167 serious accidents over 40 classes of chemicals were identified with no one dominating class involved and most were not even listed as reactive chemicals. This mapping review takes a systematic approach to review the study of reactive chemicals. A comprehensive look at the field of reactive chemical comparing the types of chemical, equipment, and computational techniques used to understand and handle their highly volatile nature. The review shows the most common types of reactive chemical studied in literature. The comparison of the laboratory equipment such as calorimeters used and the computational techniques available. Mapping the use of the different techniques within different classes of reactive chemicals to identify gaps.

30. Developing Probabilistic Barrier Failure Models to Predict Kicks while Drilling

Nafiz Tamim¹, Delphine Laboureur¹, A. Rashid Hasan² and M. Sam Mannan¹

¹*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Harold Vance Department of Petroleum Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

Predicting a kick timely and efficiently is often a challenging task due to the complexities of drilling and other well intervention activities. Leading indicators based probabilistic barrier failure models for different stages of drilling are developed in this work to assess performance of primary well control barrier – hydrostatic head. These models would help to determine the probabilities of kick initiating events and identify key leading indicators for predicting kicks and preventing blowouts. The key causal factors for primary well control barrier (hydrostatic head) failure have been identified by conducting fault-tree analysis and analyzing historical incident data. Abnormal pore pressure and swabbing are found to be the major contributors for low hydrostatic head or mud column failure. To predict abnormal pore pressure and swabbing events effectively, leading indicators model are developed combining organizational, operational and real-time indicators. A Bayesian network tool is used to construct probabilistic well barrier failure models for these causal elements. The probability distribution for observing changes in real-time parameters when a kick is developing due to abnormal pore pressure or swabbing are also determined. These parameters are function of both kick initiating events and some influencing organizational factors. This study would allow both predictive (causes to effect) and diagnostic (effect to causes) reasoning of kicks and blowouts for better understanding of well control system while drilling. Developed risk models enable informed decision making with a relatively clear picture of the risk of barrier failure and provide useful information on actions required to prevent escalation of well control events.

31. Thermal Decomposition of Mono-Nitrated Toluene (MNT) with Additives

Wen Zhu and Chad V. Mashuga

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

On September 21st 1992, an explosion happened in Castleford, UK, at the distillation unit, owned by Hickson & Welch Ltd. The incident killed 5 people and caused nearly 200 injuries. The main reason is due to the decomposition of mono-nitrated toluene (MNT). Nitrated aromatic compounds present a potential run-away reaction threat to the chemical process industry, due to its unstable structure and extensive heat release during upset situations. This study employs the Advanced Reactive System Screening

Tool (ARSST) to study the effects of various common contaminants on MNT's thermal decomposition, including sodium nitrate, sodium hydroxide, and sodium carbonate. Experimental parameters and results such as 'onset' temperature, pressure increase rate, temperature increase rate and maximum temperature are present.

32. Optimization of Flame Retardants on Commercial Aircrafts

Mazdak Mina and M. Sam Mannan

Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

To ensure the long-term health of pilots and flight attendants on planes, while also keeping planes safe, an optimization analysis, risk assessment, and root cause analysis literature review, with some lab work, on the flame retardant chemicals and additives used on planes needs to be done. Flame retardants are known carcinogens that are widely used on household and commercial materials to prevent the ignition and spread of fires in homes and businesses. Due to their carcinogenic design, overexposure to flame retardants over an extended period of time has also been shown to cause cancer, most recently involving long-term workers (pilots and flight attendants) on commercial planes. In order to balance the safety risk of a plane catching fire with the health risk for the workers on a plane, an optimization analysis needs to be done to confirm the optimum level of flame retardant chemicals is needed to minimize both risks and save the most lives. In addition, both a risk assessment and a root cause analysis needs to be done to determine where the biggest risks lie, what the greatest causes of injury or health effects are, and where optimization would be most effective. Finally, some lab work can also be done to find less carcinogenic or non-carcinogenic flame retardants that may also be effective as a long term solution to this problem. Overall, by doing the previously mentioned literature review and analyses, a solution to the problem of balancing safety and risk involving flame retardants on planes can be found.

33. Formation of Multi-layer Graphene Nanosheets with Strong Sulfur-Carbon Interaction and Enhanced Sulfur Reduction Zones for Lithium-Sulfur Battery Cathodes

Saul Perez Beltran and Perla Balbuena

Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843

Abstract:

The Lithium-sulfur battery is one of the most promising alternatives to allow rechargeable batteries do the big leap of rechargeable batteries from portable consumer electronics to high demanding energy applications. Before commercial implementation, however, much work must be still done to make improvements concerning cycle-life, stability, and electrochemical activity. A common strategy to implement sulfur-based cathodes is using sulfur-carbon composite materials. These composite structures might help to solve one of the most common issues the Li/S batteries face, the insulating nature of sulfur and the formation of soluble lithium sulfide intermediates. Deeper understanding of the lithiation mechanisms of these composite cathodes is still needed.

In this work we present a novel sulfur/graphene architecture emulates the electrochemical behavior of the Li-S battery cathode, promoting the S-C interaction through the edges of graphene sheets. Structural stabilization and S reduction calculations are performed with classical reactive molecular dynamics and density functional theory. This methodology allowed us to account for the collective behavior of the S and graphene structures. The S encapsulation induces ring opening, and the S phase evolves into a distribution of small chain-like structures interacting with C through the graphene edges. The lithiation calculations showed the Li₂S phase grows around ensembles of parallel graphene sheets during S reduction. No diffusion of S or Li between graphene sheets are observed and extended Li₂S domains bridging the space between carbon ensembles are suppressed. The results emphasize the importance of morphology on the electrochemical performance of the composite material. The sulfur/graphene model outlined here provides new understanding of the graphene effects on the S reduction behavior and the role that van der Waals interactions may play in favoring S reduction reactions and enhanced polysulfide trapping.

34. Magnetically Driven Functionalized Nanoplatelets Pickering Emulsion for Removal of Oil Contaminants from Water

Dali Huang², Minxiang Zeng², Lecheng Zhang², Arun Sabapathy², Janet Sajan², and Zhengdong Cheng¹

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, TX 77843*

²*Department of Materials Science and Engineering, Texas A&M University, College Station, TX 77843*

Abstract:

There is an immense need for efficient cleanup and recovery of industrial grade oil in today's society. Incidents like the BP Deepwater Horizon oil rig explosion in the Gulf of Mexico in 2010 and Sanchi tanker collision in East China Sea in Jan. 2018 have caused huge oil spill and tremendous harm to the environment. This has resulted in the loss of billions of dollars due to the loss of products and cleanup efforts, which now has drawn considerable attentions for the environmental merits. The purpose of our research is to develop an effective and inexpensive method to absorb crude oil from oil-water mixtures. Functional magnetic nanoplatelets can be designed as Pickering emulsion surfactant for targeting removal oil contaminants from seawater. After introducing magnetic nanoparticles into water-oil mixtures, small oil droplets will be stabilized by two-dimensional Pickering nanoemulsifier and can be easily controlled to move by the external magnetic field. The advantage of utilizing magnetic particles to extract oil droplets from mixture is that oil droplets can move as designed direction and easily be reclaimed for use. Small stable oil droplets are relatively hard to remove and costly, but adding magnetic nanoparticles and establishing an application with magnetic field can restore large amount of extracted oil with a high speed. This magnetic particle approach can be considered as an environmental and promising technology for oil water separation.

35. Microfluidic Microbiologically Influenced Corrosion (M-MIC) Models

Susmitha Purnima Kotu¹, Sam Mannan¹ and Arul Jayaraman¹

¹*Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843*

Abstract:

Several industries such as oil and gas, chemical, marine and aviation industries impacted by microbiologically influenced corrosion (MIC) expend millions of dollars either for understanding MIC mechanisms or mitigation of MIC. In MIC, interplay of microorganisms, metal and surrounding environment results in corrosion. Microorganisms exist as biofilms attached to the corroding metal at the sites of MIC. Since there is no single mechanism for MIC, understanding mechanisms and the mitigation strategies should be oriented towards site-specific evaluations. Microfluidic microbiologically influenced corrosion (M-MIC) models were developed that can be used for investigation of mechanisms and development effective mitigation strategies. These models consist of a metal coated glass slide bonded to a transparent polymer imprinted with a rectangular micro-flow channel. Some advantages of the continuous flow M-MIC models are capabilities for real-time monitoring and high-throughput testing in addition to minimal reagent usage. For investigation of MIC mechanisms, the model uses two electrode system with corroding metal and non-corroding metal electrodes in parallel. This enables investigation of the biofilm growth, corrosion mechanisms and indicators of corrosion on metal surface using confocal laser scanning microscopy (CLSM), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). For development of effective mitigation strategies, a modified version of the model has been developed such that instead of two different metals there is only one metal (corroding metal). This allows evaluation of biofilm viability grown either from field inocula or laboratory cultures to biocide treatments on the corroding metal surface to determine biocide effectiveness. To summarize, these M-MIC models can be used to non-destructively and simultaneously monitor biofilm development and corrosion mechanisms on metal surfaces both for laboratory and field applications to better investigate and mitigate MIC.