Pipeline natural gas is the primary fuel of choice for distributed fuel cell-based applications. The concentration of sulfur in odorized natural gas is about 30 ppm, with acceptable levels being <1 ppm for fuel cell applications. Packed bed technology for desulfurization suffers from disadvantages including high pressure drop and slow regeneration rates.

We describe a novel Rapid Temperature Swing Adsorption (RTSA) system utilizing hollow fibers with polymer ‘binder’, impregnated with high loadings of sulfur selective sorbent ‘fillers’. Steam and cooling water can be utilized to thermally swing the sorbent during the regeneration cycles. A dense, thin polymer barrier layer on the outside of fiber sorbents allows only thermal interactions with the regeneration media, minimizing contact between sorbents and thermal swing fluids, thereby promoting consistent sorption capacity over repeated cycles. A simplified flow pattern minimizes pressure drop, porous core morphology maximizes sorption efficiencies, while small fiber dimensions allows for rapid thermal cycles.
We are using Organic Aqueous Tunable Solvents (OATS) to combine the benefits of homogeneous and heterogeneous catalysis while overcoming the limitations of both. We are using the hydroformylation of the hydrophobic $p$-methylstyrene as a model chiral reaction. The reaction is carried out homogeneously in organic-water mixtures using Rh/TPPMS catalytic complex under 30 bars of syngas (1:1 ratio of CO:H$_2$). Reaction rates are improved by an order of magnitude when compared to heterogeneous catalysis. After the reaction, moderate pressures of carbon dioxide are used to induce a phase split, as the gas is almost insoluble in water but completely miscible with most organic solvents. The result is a heterogeneous liquid-liquid system consisting of an aqueous-rich phase and a gas-expanded organic-rich phase. The hydrophobic product partitions into the organic-rich phase, which is decanted and depressurized to yield a facile separation for $>99\%$ recovery. The aqueous-rich phase, which contains 99.9$\%$ of the hydrophilic catalyst, is recycled for the next reaction cycle. This process can be implemented directly in industrial settings with minor or no modifications to existing facilities. OATS reduces the need for prolonged reaction periods and improves the economics of the process while reducing environmental impact.

In this presentation, we shall introduce OATS and discuss the applications and advantages of this system. We shall discuss $p$-methylstyrene hydroformylation in acetonitrile/H$_2$O systems with emphasis on improved reaction rates and facile separations.
CARBON MOLECULAR SIEVE MEMBRANES FOR NATURAL GAS SEPARATIONS

Mayumi Kiyono and William J. Koros
mayumi.kiyono@chbe.gatech.edu

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

Natural gas is one of the growing primary energy sources as an alternative to liquid fossil fuels in the world. The increase in demand for the energy has increased production of high quality natural gas. Raw natural gas contains primarily methane with various impurities, such as carbon dioxide, hydrogen sulfide, water, heavy hydrocarbons, and inert gases. Among the impurities, carbon dioxide is usually the most abundant and can be above 50% in some cases. In order for the natural gas to be fed to the mainline gas transportation system, these impurities must be removed to meet the pipeline standards.

Membrane technology for natural gas processing is attractive due to their lower cost, lower energy consumption, smaller size, and smaller environmental impact. In this work, carbon molecular sieve (CMS) membranes, formed from high temperature pyrolysis of polymeric membranes, are chosen to remove CO₂ from natural gas. CMS membranes have attractive separation performance over polymeric membranes; however, traditional vacuum pyrolysis approaches are difficult to scale up economically.

Our more attractive inert pyrolysis method enables us to achieve attractive separation performance of CMS membranes via doping with trace oxygen. This method involves oxygen exposure during pyrolysis to tune the selective pore windows. This approach provides enhancement of more than 100 times in productivity (CO₂ permeability) and double in efficiency (CO₂/CH₄ selectivity) compared with polymeric membranes. Our successful dense film work was also extended to asymmetric hollow fiber membranes, and the CMS hollow fibers were characterized under realistic feed conditions. Details of the CO₂/CH₄ mixed gas separation performance as well as comparison with a dual mode model prediction are discussed.
Liquid phase processing is used routinely in the fabrication of ICs, MEMS, and nano-structured devices. Aqueous, dilute solutions of hydrofluoric acid (HF) have been used to etch or remove SiO2-based layers in cleaning steps, though they increase exposure times. Also, various equilibria of HF present among a large number of ions in aqueous solutions make selective control of etchant species difficult. In this work, based on an industrial (patented) process, a prototype reactor was designed using Computational Fluid Dynamics (CFD) and fabricated. Simulations have been used to determine the effects of various process parameters. Results from CFD and etch experiments are in good agreement. This process model is appropriate for application to a wide variety of materials and can also be used to enhance process control and optimization schemes.

A large variety of experimental techniques are used to investigate various solution and surface properties. A systematic investigation of various equilibria for characterization of solutions has been carried out using non-aqueous solutions utilizing fluorine containing tetrabutylammonium salts to solvents improve the etch rate uniformity and selectivity of BPSG to thermal oxide relative to aqueous HF solutions.

A spectroscopic reflectometry technique has been implemented in-situ in the prototype reactor to monitor the thickness and/or optical constants. This technique can be used similarly in other reactors/films to monitor thickness/optical constants, in deposition, swelling, dissolution systems. Work is in progress to implement an advanced algorithm (Extended Kalman Filter) for on-line monitoring ER.
Polymer solubility in CO₂ can be enhanced by incorporating carbonyl, silicone, or fluorine groups into the polymer and exploiting specific interactions between these functional groups and CO₂. The quantification of such interactions is essential not only to the design of absorption and polymerization processes involving CO₂ as an absorbate or solvent, but also for modeling phase behavior in polymer + CO₂ systems. This work describes a compressible lattice model for phase equilibria and thermodynamic properties of polymer + CO₂ systems. The model explicitly accounts for specific interactions in these systems using two parameters that can be obtained from FTIR measurements, by correlation of experimental phase equilibrium data, or by molecular modeling. Both ATR-FTIR measurements and molecular modeling were used to quantify the strength of specific interactions in the work described. It is shown that the resulting model can be applied to the prediction of low-pressure as well as high-pressure equilibria, and to predict polymer swelling by CO₂. Furthermore, molecular modeling provides insight into the behavior of isomers and CO₂.
Ordered nanoscale pore systems, such as zeolites, offer unique pore sizes, shapes, topologies, and framework compositions that can facilitate the assembly of guests such as metal oxides and hydroxides. The resulting nanocomposites often exhibit wholly new properties and functionalities that are beneficial for applications in chemical sensors, catalysts, ion exchangers, electrochemical capacitors, and adsorbents. Central to the formation of the nanocomposites is the ability to control microstructure, reactivity, and spatial positioning of metal oxides/hydroxides within or on the zeolite surface.

The directed deposition of magnesium hydroxide (Mg(OH)\textsubscript{2}) nanoflakes on the surfaces of zeolite 4A from an aqueous solution was studied. The mass of Mg(OH)\textsubscript{2} deposited was determined from TGA studies and found to constitute approximately 12 wt % of the total mass of the Mg(OH)\textsubscript{2} – zeolite nanocomposite. No Mg(OH)\textsubscript{2} could be deposited on silica or alumina surfaces, suggesting that Mg(OH)\textsubscript{2} crystals do not adsorb on silanol or aluminol sites, but instead interact with bridging hydroxyl protons (SiOHAl) on the surface. This was confirmed by adsorption experiments, FTIR spectra, and solid state \textsuperscript{1}H, \textsuperscript{29}Si, and \textsuperscript{27}Al NMR analyses. A possible mechanism for the directed assembly of Mg(OH)\textsubscript{2} nanostructures on zeolite surfaces is proposed.
ENHANCEMENT OF BARRIER PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE) BASED ON ANTIPLASTICIZATION

Jong Suk Lee
jong.lee@chbe.gatech.edu

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

The incorporation of small molecular weight additives such as acetanilide and phenacetin into poly(ethylene terephthalate) (PET) improves its barrier properties to oxygen and carbon dioxide gases based on antiplasticization. Barrier Improvement Factor (BIF) is defined as the ratio of permeability of pure polymer to that of antiplasticized polymer and it is used as an indication of barrier efficiency. At a feed pressure of 5 atm, BIF of PET-2.32% phenacetin, and PET-1.95% acetanilide on oxygen was found to be 1.20 and 1.27, respectively. As for carbon dioxide, at a feed pressure of 6 atm, it was 1.31 for PET-2.32% phenacetin and 1.40 for PET-1.95% acetanilide. The reduced permeability coefficient in each antiplasticized PET sample is well justified by the combination of effect of reduced free volume in antiplasticized PET samples and interaction energies of PET with each additive. A less repulsive interaction of PET with additive such as acetanilide in this work requires higher activation energy for diffusional jump. This results in more reduction in permeability even though both PET-2.32% phenacetin and PET-1.95% acetanilide exhibited an almost same level of reduction in free volume. The permeability of a penetrant in a polymer can be expressed as a product of a kinetic (diffusion) and thermodynamic (sorption) coefficient. Our transport study in this work demonstrated that an improved BIF was achieved more due to the reduction in diffusion coefficient than due to the sorption coefficient reduction. The effective equilibrium uptake of penetrant in both antiplasticized PET samples was less than in PET at a given pressure due to the significant reduction of excess free volume. A more repulsive interaction of PET with phenacetin was found to contribute to more reduction in Langmuir capacity constant, $C'_\mu$. 
Finding alternative sources of energy to petroleum is an imperative for a world that relies heavily on this dwindling resource. One such promising alternative that has been considered is lignocellulosic biomass. However, as it consists of polymers with varying chemical make-up (cellulose, hemicelluloses and lignin), conversion to a form that can be integrated into existing petroleum infrastructure can only be achieved by chemical, thermal or biological pretreatments. Production of alternative fuels that can be blended directly to gasoline or diesel blends will require much lower O/C content than is currently present in such intermediate biofuels such as pyrolysis oils. Removal of oxygen can be accomplished by catalytic hydrodeoxygenation.

In this study, we focus on syringaldehyde as a representative compound of an aromatic monomer that can be derived from lignin. This molecule has multiple oxygen-bearing functional groups (aldehyde, ether and phenolic functionalities). This complexity will affect its subsequent reactions. Using a fairly novel HDO catalyst, supported nickel phosphide, it was shown that the aldehydic group was the most reactive in batch experiments using a 50ml Parr reactor pressurized with 1000 psig H₂. Experiments were done at 300°C. Comparison with the much more expensive noble metal catalysts (commercially-available supported platinum and palladium on alumina) showed comparable degrees of syringaldehyde conversion. Product profiles of all these catalysts also showed similar major products formed - with the aldehydic oxygen as the most vulnerable to hydrodeoxygenation of all the oxygen groups present. Maximum yield of toluene in all the tested operating conditions was about 18%. Results demonstrate the utility of the nickel phosphide as an alternative to the more costly commercial noble catalysts.
The goal of this work is to incorporate an elastin mimetic peptide into a PEG-DA hydrogel in an effort to fabricate a tissue-engineered vascular graft (TEVG). The graft will be capable of creating a microenvironment to sustain ECM growth and development leading to better compliance once implanted in vivo. A 23 amino acid, AAKAAKVGVAPGRGDSAAKAACK, and a 19 amino acid, AAKAAKVGVAPGAOKAAKK, sequence peptides were designed to mimic elastin that would be capable of generating functional elastin fibers once incorporated into the TEVG. By isolating key functional groups of elastin, these peptides were engineered to contain crosslinking, cell adhesion, proliferation, and migration motifs. Furthermore, RGDS was introduced in the 23 amino acid sequence to enhance cell adhesion and assist with improving elastin production. The peptides were characterized in vitro in order to assess the deposition of elastin and desmosine, crosslinking domain unique to elastin. Human aortic smooth muscle cells (SMCs) were incubated with either peptides at varying concentrations and the amount of elastin and desmosine deposited was determined after 48 hours. A Fastin assay was used to measure elastin production whereas a competitive enzyme-linked immunosorbent assay (ELISA) was used to quantify desmosine production. The 23 amino acid sequence showed an increasing trend in elastin as well as desmosine deposition. Cell adhesion studies in vitro were also conducted by conjugating the peptides with bovine serum albumin (BSA) to yield either BSA-23 or BSA-19. After 48 hours, a higher SMC adhesion was observed on surfaces coated with BSA-23. With improved cell adhesion as well as elastin and desmosine production in vitro, the 23 amino acid sequence is showing capabilities of generating a microenvironment suitable for vascular growth in a TEVG.
SUPRACHOROIDAL DRUG DELIVERY TO THE BACK OF
THE EYE USING HOLLOW MICRONEEDLES

Samirkumar Patel
Samir.Patel@gatech.edu

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

Drug delivery to the back of the eye is often performed by methods that are poorly targeted or
invasive. Administering a drug to the suprachoroidal space (SCS), between the sclera and
choroid, has been of recent interest because of its close proximity to the choroid and retina which
are the common targets for diseases that cause vision loss. We present here a minimally invasive
method to locally target the SCS using hollow microneedles. The goal of this research is to
understand the distribution and kinetics of the clearance of compounds and particles from the
SCS and compare to currently practiced intravitreal (IV) delivery using flurophotometry.

A single hollow glass microneedle was used to infuse fluorescein, 40 and 250 kDa dextrans, and
20- and 500-nm particle suspensions into the SCS of rabbit eyes in vivo. IV injections of
fluorescein were performed with a 30g hypodermic needle. An ocular flurophotometer was used
to quantify concentrations in the whole eye in situ.

Fluorescence intensity profiles of the eye over time showed that SCS injections were more
localized than IV injections. The half life for SCS and IV injection was 1.3 and 2.4 hours
respectively. Dextran similarly localized in the SCS and cleared the eye within 24 to 48 hours.
Nanoparticle suspensions injected into the SCS resulted in similar localization. However, over
time the nanoparticle concentrations maintained relatively constant levels in the SCS with
minimal exposure to extraneous tissues. At the four-week time point, most particles were still
present and had not cleared from the SCS.

We show here, for the first time, a minimally invasive method utilizing a microneedle to inject
solutions and nanoparticle suspensions into the SCS in-vivo. SCS injections were capable of
localizing the injected material in the back of the eye thus targeting the retinochoroidal surface.
Nanoparticles had residence times of at least one month, which provides the potential for
sustained drug delivery to the back of the eye.
Natural gas processing is one of the largest industrial membrane gas separation applications, almost all for the removal of CO$_2$. Polyimides are a widely studied class of polymers that have very high ideal CO$_2$/CH$_4$ selectivities. However, the performance of polyimide membranes is significantly below the intrinsic membranes under normal operating conditions (mixed gas with high CO$_2$ partial pressure) due to membrane plasticization. High CO$_2$ content can swell the membranes and thus cause drastic losses in selectivity.

Covalent crosslinking has been shown to increase plasticization resistance in dense films. This research focuses on extending success with dense films to asymmetric hollow fibers. Defect-free asymmetric hollow fiber membranes were successfully spun from a novel polyimide and crosslinked by thermally-induced decarboxylation. Under optimum conditions, the crosslinking can be achieved without damaging the selective skin layer on the hollow fibers. The crosslinked hollow fibers were tested with model natural gas feeds at high pressure and showed excellent plasticization resistance against CO$_2$. 
Polymides are glassy polymers with relatively high fractional free volume, and unusually high diffusion coefficients for larger molecules. These properties make them potentially suitable for C4 separation; however higher size and shape selectivity would be desirable. On the other hand, purely inorganic membranes are costly and somewhat fragile. These combined deficiencies can be eliminated by pursuing so-called mixed matrix hybrids comprising inorganic-polymer mixtures.

Past work involving C4 separation has focused on ideal operating conditions such as single gas tests with the downstream under vacuum. Unfortunately, these ideal conditions may give overly optimistic performance estimates. Industrial conditions involve gas mixture with conditions that can prove more challenging and result in lower separation performance of the membrane as compared to ideal conditions.

In this symposium, I will address some of the challenges faced for mixture gas separation. I will also talk briefly about the possible effects of composition, as well as how annealing and mixed matrix membranes can help improve the separation performance.
ELECTRIC CHARGING EFFECTS IN NON-POLAR LIQUIDS BY NON-IONIZABLE SURFACTANTS

Qiong Guo and Sven H. Behrens
qiong.guo@chbe.gatech.edu
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology, Atlanta, GA

Non-polar liquids do not easily accommodate electric charges, but ionic surfactant additives are found to help raise the conductivity and stabilize the immersed solid surfaces. They avoid the large energetic barrier associated with the introduction of small ions in low dielectric media by forming charged micellar aggregates. Here, we study the rarely considered charging effects induced by surfactant molecules without ionizable groups, sorbitan oleate. Precision conductometry, light scattering, and Karl-Fischer titration reveal a distinctly electrostatic action of the nonionic surfactant. The behavior that non-ionizable surfactants induce charge in non-polar oils can be explained by charge disproportionation of molecular surfactant complexes in the sub-CMC regime and reverse micelles above the CMC. Electrokinetic studies of added colloidal particles further exhibit the micelles' ability to create and screen electric charges on the surface of suspended solid particles. Strong particle-charging effects and charge screening are found even at surfactant concentrations below the critical micelle concentration. Our findings suggest that nonionic surfactants can play a key role in the industrially important task of controlling charges in non-polar solvents.
Membranes offer an environmentally benign approach to gas separations, mainly because of reduced process energy requirements. For industrial processes, asymmetric membranes with a thin selective layer on a porous support layer are normally prepared by phase inversion of a polymer solution. This process results in high selectivity, while maintaining a sufficiently high gas throughput. The kinetics of phase separation plays an important role in determining these functionalities, and the objective of our study was to experimentally investigate the kinetics of the phase inversion of polymer solutions during membrane formation.

We present details of a novel microfluidic device that enables us to measure the phase separation kinetics of membrane dopes via video-microscopy. Our device furnishes a well-defined sample geometry and controlled atmosphere for in situ tracking of the phase separation process. We use this technique to quantify the phase separation kinetics of polyetherimide polymer solutions with different concentrations upon contact with an array of relevant nonsolvents. We hypothesize that the process is affected by the micro-rheological and thermodynamic properties of the polymer solution and nonsolvent. To support our hypotheses; we report experimental data on the effective diffusivity of the phase separation front as a function of membrane solution rheology and thermodynamics, i.e. the nonsolvent/solvent/polymer interaction parameter. We also present scaling models based on expanded versions of the Stokes-Einstein relation that incorporate variations in microstructure and thermodynamic properties of the solutions.
Microencapsulation techniques have become increasingly important as an advanced formulation tool with widespread applications in the preparation of functional materials, chemically or biologically active agents, pharmaceuticals, cosmetics, food, and especially as drug delivery agents and cell carriers. One novel technique for encapsulation relies on solid-stabilized emulsions, so-called “Pickering emulsions”, as a template for capsule formation: colloidal particles adsorbed to emulsion droplets are connected into a solid shell enclosing the droplet. The resulting microcapsules, whose shell is composed of solid particles, are known as colloidosomes. Ideally, such capsules should retain and protect an encapsulated agent until delivery conditions are reached in the target environment. Release could be triggered by an external disruption of the system or ideally by a change in the inherent conditions of the delivery medium, such as its temperature, pH, or salinity.

We have developed Pickering emulsion-based microcapsules that dissolve rapidly upon a pH change under mild solution conditions. These capsules combine the sturdiness and pore size control of colloidosomes with the option of triggered disassembly known from stimulus-responsive Pickering emulsions. This work reports the assembly of pH-responsive microcapsules from double Pickering emulsions. The double emulsions are stabilized with nanoparticles, which have been prepared by nanoprecipitation (“Ouzo Effect”). The microcapsules dissolve upon a slight pH change at mild precipitation conditions. Evidence of this triggered response is provided in micrographs demonstrating a fast and complete dissolution of the microcapsules. The permeability of the capsule shell is quantified using Fluorescence Recovery After Photobleaching (FRAP). Capsules with switchable permeability have also been achieved by including an additional polymer in the middle phase and are currently under development.
A new concept for “fiber sorbents” has been investigated. The fiber sorbent is created as a pseudo-monolithic material comprising polymer and zeolite by applying hollow fiber spinning technology. Phase separation of the polymer solution provides an appropriately porous structure throughout the fiber matrix. In addition, the zeolite crystals are homogeneously dispersed in the polymer matrix with high loading. The zeolite mainly contributes to sorption capacity of the fiber sorbent. Mass transfer processes in the fiber sorbent module for hydrogen recovery are analyzed and compared with results for an equivalent size packed bed. The model indicates advantageous cases for application of fiber sorbent module over packed bed technology to allow system downsizing and energy saving by changing the outer and bore diameters to maintain or even reduce the pressure drop. The fiber sorbent was spun successfully with highly porous structure and high CO₂ sorption capacity, so this new approach is attractive for some hydrogen recovery applications as an alternative to traditional zeolite pellets.
DESIGN, CHARACTERIZATION, AND OPTIMIZATION OF SOLID ADSORBENTS FOR CO₂ CAPTURE FROM DILUTE SOURCES

Jeffrey Drese
jeffrey.drese@chbe.gatech.edu

School of Chemical & Biomolecular Engineering
Georgia Institute of Technology, Atlanta, GA

Recent concern over the effect of anthropogenic CO₂ emissions on global climate change has driven research on the investigation of new technologies for capturing CO₂ from dilute sources, such as coal-fired power plants or ambient air. Adsorption is one of these technologies being considered, because of its potential to be less energy-intensive than the current benchmark aqueous amine absorption technology. Of the many different classes of solid adsorbents, we have focused on the use of silica-supported amines for this purpose. We have developed a hyperbranched aminosilica (HAS) with a large amine content per weight of adsorbent, that translates to having a large CO₂ capacity. This inorganic-organic hybrid material is prepared by the ring-opening polymerization of aziridine on mesoporous SBA-15 silica, yielding silica pores functionalized by low molecular weight aminopolymers. Early investigation of the HAS adsorbent revealed a relatively high adsorption capacity of 3.1 mmol CO₂/g at 25 °C from humidified, simulated flue gas, that was fully regenerable over 10 adsorption/desorption cycles. This talk will discuss the effects of modification of certain synthesis parameters such as solvent and reactant concentration on the HAS structure and adsorption properties. By tuning these parameters, we have observed capture capacities above 5 mmol CO₂/g. The effects of these changes on the adsorbent structure, including surface area, pore volume, aminopolymer molecular weight, and ratio of 1°:2°:3° amines will be described.
Glioblastoma multiforme (GBM), is the most malignant and deadly type of brain tumor, with a 5 year survival rate of less than 10%. The ability of GBM cells to rapidly disperse and invade healthy brain tissue coupled with their high resistance to chemotherapy and radiotherapy have resulted in extremely poor prognosis among patients. Nitric oxide (NO) is a small, easily diffusible molecule which, at sufficient concentrations, has shown to induce apoptosis as well as increase radiosensitization in tumor cells.

The aim of this work is the development of controlled release nitric oxide donors for the treatment of GBM. In order to effectively target tumor cells as well as cross the blood brain barriers short peptides sequences and small proteins that were able to specifically bind to tumor cells were used as the basis for this drug delivery system. Two such biomolecules, chlorotoxin and VTWTPQAWFWQV (VTW), were identified from a literature survey. They were reacted with NO gas for 24 hours after which NO release from the biomolecules was measured at 37°C using a free radical detector equipped with a nitric oxide microsensor. It found at physiological pH of 7.4 both the biomolecules were able to release NO for over 6 days.

Cell studies were performed in order to determine the effect of NO concentration on tumor proliferation. Two human glioma cell lines, T98G and U87, as well as normal human astrocytes were cultured at 37 degrees Celsius and 5% carbon dioxide. The cells were seeded in 96-well plates at a density of 25,000 cells/sq. centimeter. After allowing the cells to proliferate for 24 hours they were incubated for 48 hours with varying concentrations of NO reacted chlorotoxin or VTW. After 48 hours a significant decrease in tumor cell viability was observed where as the viability of the astrocytes was not affected significantly.
COMPARISON OF ADAPTED ZYMOMONAS STRAINS ELUCIDATES REQUIREMENTS FOR IMPROVING XYLOSE FERMENTATION

Manoj Agrawal
manoj@gatech.edu

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

Wild-type *Zymomonas mobilis* can only ferment glucose and not xylose to ethanol. Xylose is the second major component in lignocellulosic hydrolysates after glucose. Hence, *Zymomonas* must be engineered for an efficient xylose fermentation to enable industrial use of this extremely promising ethanologen.

We have constructed a xylose utilizing strain of *Zymomonas* by using a unique combination of rational metabolic engineering and adaptive mutation. During the process of adaptive mutation, we isolated two strains – less adapted A1 and more adapted A3. The specific rates of growth, xylose consumption and ethanol production for A3 is higher than A1. By comparing the fermentation byproducts of A3 and A1 and doing comparisons at enzymatic and genetic levels, we have discovered some factors that lead to improvement in xylose fermentation.
HOLLOW FIBER SORBENTS FOR DESULFURIZATION OF PIPELINE NATURAL GAS

Dhaval Bhandari and William J. Koros
dhaval.bhandari@chbe.gatech.edu

School of Chemical and Biomolecular Engineering
Georgia Institute of Technology; Atlanta, GA

Pipeline natural gas is the primary fuel of choice for distributed fuel cell-based applications. The concentration of sulfur in odorized natural gas is about 30 ppm, with acceptable levels being <1 ppm for fuel cell applications. Packed bed technology for desulfurization suffers from disadvantages including high pressure drop and slow regeneration rates.

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SEPARATION OF C4 ISOMER MIXTURES USING POLYIMIDE-BASED DENSE MIXED MATRIX MEMBRANES

Omoye Esekhile and William J. Koros
oesekhile3@gatech.edu

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

Polyimides are glassy polymers with relatively high fractional free volume, and unusually high diffusion coefficients for larger molecules. These properties make them potentially suitable for C4 separation; however higher size and shape selectivity would be desirable. On the other hand, purely inorganic membranes are costly and somewhat fragile. These combined deficiencies can be eliminated by pursuing so-called mixed matrix hybrids comprising inorganic-polymer mixtures.

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COMBINING HOMOGENEOUS REACTIONS WITH HETEROGENEOUS SEPARATIONS FOR HYDROFORMYLATION REACTIONS USING TUNABLE SOLVENTS

Ali Z. Fadhel, Veronica Llopis-Mestre, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert
ali.fadhel@chbe.gatech.edu

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

We are using Organic Aqueous Tunable Solvents (OATS) to combine the benefits of homogeneous and heterogeneous catalysis while overcoming the limitations of both. We are using the hydroformylation of the hydrophobic \( p \)-methylstyrene as a model chiral reaction. The reaction is carried out homogeneously in organic-water mixtures using Rh/TPPMS catalytic complex under 30 bars of syngas (1:1 ratio of CO:H\(_2\)). Reaction rates are improved by an order of magnitude when compared to heterogeneous catalysis. After the reaction, moderate pressures of carbon dioxide are used to induce a phase split, as the gas is almost insoluble in water but completely miscible with most organic solvents. The result is a heterogeneous liquid-liquid system consisting of an aqueous-rich phase and a gas-expanded organic-rich phase. The hydrophobic product partitions into the organic-rich phase, which is decanted and depressurized to yield a facile separation for >99% recovery. The aqueous-rich phase, which contains 99.9% of the hydrophilic catalyst, is recycled for the next reaction cycle. This process can be implemented directly in industrial settings with minor or no modifications to existing facilities. OATS reduces the need for prolonged reaction periods and improves the economics of the process while reducing environmental impact.
The data analysis problem in process systems engineering not only covers the management and understanding of massive volumes of data generated in industries day by day but also the implementation of novel strategies to collect information in experimental or simulated environments. Frequently, the data analysis problem is explored from a purely mathematical and statistical point of view without considering the meaning of the information in terms of chemical engineering. Our research project has been driven looking for a synergistic effect between the physical principles that govern a process and the statistical tools available to analyze the information. Here, we present the results of this philosophy to describe the growth of platinum nanoparticles under supercritical conditions using a statistical tool called Gaussian process regression. The results describe how the understanding of the nanoscale phenomena leads to the dynamic understanding of the process at the manufacturing level and presents future applications of statistical tools for control and optimization of the process.
FIRST-PRINCIPLES STUDY OF PALLADIUM-BASED METAL ALLOYS AS HYDROGEN PURIFICATION MEMBRANES

Sung Gu Kang
skang60@gatech.edu

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

First-principles calculations provide a useful complement to experiments by characterizing hydrogen permeance through dense metal membranes. We report calculations that combine quantum chemistry calculations and cluster expansion methods to describe the solubility, diffusivity, and permeation of interstitial H in fcc Pd-based binary alloys. In particular, we examine Pd₉₆M₄ and Pd₈₉M₁₁ where M = Ir, Nb, Ru, Zr, Hf, and Ta. We analyze Pd-based binary alloys to demonstrate the capability of the cluster expansion approach. Our results make predictions about the properties of these alloys as membranes at moderate hydrogen pressures over the temperature range $600 \leq T \leq 1200$ K.
CARBON MOLECULAR SIEVE MEMBRANES FOR NATURAL GAS SEPARATIONS

Mayumi Kiyono and William J. Koros
mayumi.kiyono@chbe.gatech.edu

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

Natural gas is one of the growing primary energy sources as an alternative to liquid fossil fuels in the world. The increase in demand for the energy has increased production of high quality natural gas. Raw natural gas contains primarily methane with various impurities, such as carbon dioxide, hydrogen sulfide, water, heavy hydrocarbons, and inert gases. Among the impurities, carbon dioxide is usually the most abundant and can be above 50% in some cases. In order for the natural gas to be fed to the mainline gas transportation system, these impurities must be removed to meet the pipeline standards.

Membrane technology for natural gas processing is attractive due to their lower cost, lower energy consumption, smaller size, and smaller environmental impact. In this work, carbon molecular sieve (CMS) membranes, formed from high temperature pyrolysis of polymeric membranes, are chosen to remove CO$_2$ from natural gas. CMS membranes have attractive separation performance over polymeric membranes; however, traditional vacuum pyrolysis approaches are difficult to scale up economically.

Our more attractive inert pyrolysis method enables us to achieve attractive separation performance of CMS membranes via doping with trace oxygen. This method involves oxygen exposure during pyrolysis to tune the selective pore windows. This approach provides enhancement of more than 100 times in productivity (CO$_2$ permeability) and double in efficiency (CO$_2$/CH$_4$ selectivity) compared with polymeric membranes. Our successful dense film work was also extended to asymmetric hollow fiber membranes, and the CMS hollow fibers were characterized under realistic feed conditions. Details of the CO$_2$/CH$_4$ mixed gas separation performance as well as comparison with a dual mode model prediction are discussed.
Mineral dust aerosols play an important role in warm clouds due to their ability to serve as effective Cloud Condensation Nuclei (CCN). However, predicting the complex effect of mineral dusts on clouds and climate requires integrating observational knowledge into theoretical mathematical parameterizations. Current climate models, use traditional Köhler theory to describe supersaturation required for dust activation based on its soluble fraction, and completely ignore interactions of hydrophilic insoluble core with water vapor. In this work, we show improvements in current understanding of mineral dusts interactions with clouds by coupling laboratory CCN activation measurements of regional dust samples with advancements in numerical parameterizations to describe dust-cloud interactions in global aerosol climate models.

We investigate the CCN activation behavior of mineral dusts from Northern America, African soils, and East Asian soils in the laboratory simulated conditions to determine their respective affinity for water. To assess the role of the mineralogy on dust CCN activities, we also compare CCN activities of various individual minerals (clays and carbonates) with those of regional mineral dust samples. The results obtained from these measurements will be used to constrain the parameters in the new parameterization algorithm developed to address the activation of insoluble dust particle using multilayer Frenkel-Halsey-Hill (FHH) adsorption isotherm model modified to account for particle curvature (Kumar et al., 2009). A comparison of different aerosol-water vapor interaction mechanisms (traditional Köhler theory vs adsorption activation theory) associated with fresh mineral dust suggests potential differences in CCN number, parcel maximum supersaturation and cloud droplet number. This new framework of aerosol-water interaction by the “adsorption activation” has been incorporated into aerosol-cloud interaction parameterization for mineral dust activation.
The incorporation of small molecular weight additives such as acetanilide and phenacetin into poly(ethylene terephthalate) (PET) improves its barrier properties to oxygen and carbon dioxide gases based on antiplasticization. Barrier Improvement Factor (BIF) is defined as the ratio of permeability of pure polymer to that of antiplasticized polymer and it is used as an indication of barrier efficiency. At a feed pressure of 5 atm, BIF of PET-2.32% phenacetin, and PET-1.95% acetanilide on oxygen was found to be 1.20 and 1.27, respectively. As for carbon dioxide, at a feed pressure of 6 atm, it was 1.31 for PET-2.32% phenacetin and 1.40 for PET-1.95% acetanilide. The reduced permeability coefficient in each antiplasticized PET sample is well justified by the combination of effect of reduced free volume in antiplasticized PET samples and interaction energies of PET with each additive. A less repulsive interaction of PET with additive such as acetanilide in this work requires higher activation energy for diffusional jump. This results in more reduction in permeability even though both PET-2.32% phenacetin and PET-1.95% acetanilide exhibited an almost same level of reduction in free volume. The permeability of a penetrant in a polymer can be expressed as a product of a kinetic (diffusion) and thermodynamic (sorption) coefficient. Our transport study in this work demonstrated that an improved BIF was achieved more due to the reduction in diffusion coefficient than due to the sorption coefficient reduction. The effective equilibrium uptake of penetrant in both antiplasticized PET samples was less than in PET at a given pressure due to the significant reduction of excess free volume. A more repulsive interaction of PET with phenacetin was found to contribute to more reduction in Langmuir capacity constant, $C'_\mu$. 
THE SUSTAINABLE AND SCALABLE SYNTHESIS OF
PIPERYLENE SULFONE:
A “VOLATILE” AND RECYCLABLE DMSO SUBSTITUTE

Gregory Marus, Eduardo Vyhmeister, Pamela Pollet, Megan E. Donaldson,
Veronica Llopis Mestre, Leslie Gelbaum, Charles L. Liotta, and Charles A. Eckert
gmarus@gatech.edu

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

In this work, we established a road-map to the sustainable and scalable synthesis of piperylene sulfone, a potentially important new solvent for the pharmaceutical industry. Polar aprotic solvents, such as DMSO, offer many advantages to the pharmaceutical industry, such dissolution of inorganic salts from organic reactions. However, solvent removal and further product purification are not trivial due to high boiling points or sizable waste generation. PS has solvent properties very similar to DMSO, but is a fully recyclable dipolar aprotic solvent that undergoes a retro-cheletropic reaction at 110 °C, permitting facile solvent removal and recycle. When we showed the advantages of this solvent, a number of industrial firms asked for larger quantities, and one specialty chemical company offered to make kilogram or larger quantities if we could provide a method.

Due to the commercial unavailability of PS, we synthesized laboratory quantities using a method not sustainable on a large scale due to significant waste generation during the synthesis. We have now established a route to permit the cost- and environmentally competitive synthesis of piperylene sulfone for commercial use. The work presented here aims at maximizing reaction efficiency and minimizing undesirable side reactions. First, the reaction was optimized through studying the kinetics of piperylene sulfone formation in terms of time, dilution, and radical inhibitor. Second, the separation of piperylene sulfone from the inhibitor and un-reacted isomer was separately optimized. In conclusion, we report the sustainable and scalable synthesis of a fully recyclable dipolar aprotic solvent capable of replacing traditional solvents, like DMSO, yet offering the advantages of benign separation and recycle in pharmaceutical processes.
Membranes offer an environmentally benign approach to gas separations, mainly because of reduced process energy requirements. For industrial processes, asymmetric membranes with a thin selective layer on a porous support layer are normally prepared by phase inversion of a polymer solution. This process results in high selectivity, while maintaining a sufficiently high gas throughput. The kinetics of phase separation plays an important role in determining these functionalities, and the objective of our study was to experimentally investigate the kinetics of the phase inversion of polymer solutions during membrane formation.

We present details of a novel microfluidic device that enables us to measure the phase separation kinetics of membrane dopes via video-microscopy. Our device furnishes a well-defined sample geometry and controlled atmosphere for in situ tracking of the phase separation process. We use this technique to quantify the phase separation kinetics of polyetherimide polymer solutions with different concentrations upon contact with an array of relevant nonsolvents. We hypothesize that the process is affected by the micro-rheological and thermodynamic properties of the polymer solution and nonsolvent. To support our hypotheses; we report experimental data on the effective diffusivity of the phase separation front as a function of membrane solution rheology and thermodynamics, i.e. the nonsolvent/solvent/polymer interaction parameter. We also present scaling models based on expanded versions of the Stokes-Einstein relation that incorporate variations in microstructure and thermodynamic properties of the solutions.
The goal of this work is to incorporate an elastin mimetic peptide into a PEG-DA hydrogel in an effort to fabricate a tissue-engineered vascular graft (TEVG). The graft will be capable of creating a microenvironment to sustain ECM growth and development leading to better compliance once implanted in vivo. A 23 amino acid, AAKAAKVGVAPGRGDSAAKAKK, and a 19 amino acid, AAKAAKVGVAPGAAKAKK, sequence peptides were designed to mimic elastin that would be capable of generating functional elastin fibers once incorporated into the TEVG. By isolating key functional groups of elastin, these peptides were engineered to contain crosslinking, cell adhesion, proliferation, and migration motifs. Furthermore, RGDS was introduced in the 23 amino acid sequence to enhance cell adhesion and assist with improving elastin production. The peptides were characterized in vitro in order to assess the deposition of elastin and desmosine, crosslinking domain unique to elastin. Human aortic smooth muscle cells (SMCs) were incubated with either peptides at varying concentrations and the amount of elastin and desmosine deposited was determined after 48 hours. A Fastin assay was used to measure elastin production whereas a competitive enzyme-linked immunosorbent assay (ELISA) was used to quantify desmosine production. The 23 amino acid sequence showed an increasing trend in elastin as well as desmosine deposition. Cell adhesion studies in vitro were also conducted by conjugating the peptides with bovine serum albumin (BSA) to yield either BSA-23 or BSA-19. After 48 hours, a higher SMC adhesion was observed on surfaces coated with BSA-23. With improved cell adhesion as well as elastin and desmosine production in vitro, the 23 amino acid sequence is showing capabilities of generating a microenvironment suitable for vascular growth in a TEVG.
ENHANCING ENZYME PERFORMANCE FOR CONVERTING CELLULOSE TO ETHANOL

John Reye, Kendra Maxwell, and Sujit Banerjee
John.Reye@ipst.gatech.edu
Kendra.Maxwell@ipst.gatech.edu
School of Chemical and Biomolecular Engineering
Georgia Institute of Technology, Atlanta, GA

The addition of a cationic polyelectrolyte to either the amylase mediated hydrolysis of cornstarch or the hydrolysis of wood fiber by cellulase can enhance the initial hydrolysis rates. Cationic polyelectrolytes serve as accelerants and can improve the efficiency of both amylase and cellulase systems. The initial amylase rate approximately doubles; the analogous cellulase hydrolysis rate increases by about 40%. The polyelectrolyte has been found to increase the binding of enzyme to substrate. The technology has been licensed to Akzo Nobel and is being prepared for commercialization.
EVALUATION OF NOVEL ENOATE REDUCTASES AS POTENTIAL BIOCATALYST FOR ENANTIOMERICALLY PURE COMPOUND SYNTHESIS

Yanto Yanto¹ and Andreas Bommarius¹,²,³
yanto.yanto@chbe.gatech.edu

¹School of Chemical & Biomolecular Engineering
²Parker H. Petit Institute of Bioengineering and Biosciences
³School of Chemistry and Biochemistry
Georgia Institute of Technology, Atlanta, USA

Biocatalysis has emerged as a key toolbox in the industrial synthesis of bulk chemicals, pharmaceuticals intermediates, food ingredients, and agrochemicals in the past 20 years. Due to its exquisite regio- and stereoselectivities, largest role of biocatalysis is in production of chiral pharmaceutical reagents. Among the available enzymes, enoate reductases are a subfamily of flavoenzymes that capable to catalyze asymmetric reduction of C=C bonds and creates up to two chiral carbon centers. The ability to selectively reduce enones, nitroesters, and nitroaromatic compounds have make enoate reductases an interesting area of study for biotransformations.

Nitroreductase activity on aromatic compounds is also often observed[1]. In this study, we have characterized several enzymes for their reduction potential on various nitro-substituted compounds. High degrees of conversion, along with high regio- and stereo-selectivity were obtained in the reduction of substrates such as 1-nitro-2-phenylpropene. In order to broaden the applicability of these enzymes, we investigated the substrate specificity using wide range of C=C activating groups including aldehyde-, ketone-, imide-, and carboxylic acid- moieties. The study explored the possibilities of reduction amination of nitro-substituted alkenes for efficient synthesis of amines.

![Scheme 1: Nitrobenzene reduction to aniline using nitroreductase from Salmonella typhimurium.](image1)

Scheme 1. Nitrobenzene reduction to aniline using nitroreductase from Salmonella typhimurium.

![Scheme 2: Asymmetric reduction of nitroalkenes using enoate reductase.](image2)

Scheme 2. Asymmetric reduction of nitroalkenes using enoate reductase.

Polymer solubility in CO₂ can be enhanced by incorporating carbonyl, silicone, or fluorine groups into the polymer and exploiting specific interactions between these functional groups and CO₂. The quantification of such interactions is essential not only to the design of absorption and polymerization processes involving CO₂ as an absorbate or solvent, but also for modeling phase behavior in polymer + CO₂ systems. This work describes a compressible lattice model for phase equilibria and thermodynamic properties of polymer + CO₂ systems. The model explicitly accounts for specific interactions in these systems using two parameters that can be obtained from FTIR measurements, by correlation of experimental phase equilibrium data, or by molecular modeling. Both ATR-FTIR measurements and molecular modeling were used to quantify the strength of specific interactions in the work described. It is shown that the resulting model can be applied to the prediction of low-pressure as well as high-pressure equilibria, and to predict polymer swelling by CO₂. Furthermore, molecular modeling provides insight into the behavior of isomers and CO₂.