

Chemical Engineering Seminar Series



Validation, Evaluation and Standardization of a Solid-Phase Extraction Method for the Separation of Algal Lipid Classes

Elizabeth Claudio Pachecano

ABSTRACT

Algae have been extensively studied and used as a renewable resource for bioenergy production; specifically, algal oils as feedstocks for the production of biodiesel. These can be obtained using one of several extraction techniques, such as Soxhlet extraction. A critical issue is the presence of compounds that cannot be used for biodiesel production in the crude extract; i.e. pigments and phospholipids. While solid-phase extraction (SPE) has been successfully standardized for the fractionation of lipids from animal and human sources, it has not been widely applied for algal lipid classes. Therefore, SPE should be evaluated, validated and standardized for algal biomass to improve the feedstock quality for biofuel production. This work investigates the efficiency of different SPE cartridges (Supelco LC-NH₂, Phenomenex Strata NH₂ and Strata SI-1 Silica). To recover the crude algal extract, Soxhlet extractions were performed on *Scenedesmus sp.* SPEs were performed under different conditions, namely the initial extract amount, vacuum-assisted extractions, solvent-washing cycles and cartridge volume. The elution solvent-system ratios and their volumes were modified and evaluated for each fraction. Three fractions were obtained, A: Non-polar lipids; B: Phospholipids, Ceramides, Pigments, and others; and, C: Free Fatty Acids, where A and C are the fractions of interest for biodiesel production. The fractions were characterized by ¹H and ¹³C NMR. Preliminary results indicated that while the greatest total yields of fractions A and C were obtained using Strata NH₂ (26.3%), Strata SI-1 yielded approximately 89% of the total useful lipids in a single elution. In order to select the most promising conditions the user must generally compromise between total yield, and solvent and time consumption. These results will be key to optimize the SPE algal crude extract recovery methodology and be used as an accurate reference to determine the total useful lipid content for comparison to other extraction techniques.

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A novel method for the treatment of hydraulic fracturing flowback fluid utilizing extractive membrane bioreactors

Nathan Mullins

ABSTRACT

The process of hydraulic fracturing involves the use of horizontal drilling techniques and high pressure liquid injections, to stimulate the production of natural gas through the propagation of micro-networks produced in tight formations. The use of proprietary blends of chemicals for well stimulation along with the dissolution of autochthonous organic and inorganic compounds creates a variable composition of chemicals within the subsurface. High volume hydraulic fracturing (HVHF) consumes large volumes of water, which upon release, returns to the surface as flow-back or produced water. In addition to the intentionally-added fracturing chemical blends, HVHF industrial wastewaters often contain a myriad of chemicals such as polyaromatic hydrocarbons, aromatic hydrocarbons, geogenic inorganic material, and naturally occurring radioactive material (NORM). The diversity and variation of recalcitrant compounds within HVHF wastewater has made them difficult to remediate, and there is a lack of effective remediation/disposal strategies surrounding this practice. Synthetic HVHF flowback was generated according to a comprehensive analysis of quantitative peer-reviewed and industrial literature in an effort to replicate industrial effluent samples. Extractive membrane bioreactors, which consist of a microbial consortium capable of degrading organic contaminants and *in situ* polymeric tubing through which the organic/inorganic HVHF flows utilize tailored polymeric membranes that can selectively transport and/or sequester organic versus inorganic compounds via thermodynamic partitioning. Operated in batch or continuous mode, EMBs significantly improve bio-treatment processes by eliminating microbial inhibition arising from the presence of high concentrations of inhibitory organic substrates, while also sequestering high salt concentrations within the tubing and away from the microbial cells. Research on this topic has had two components: the characterization of transport of organic/inorganic species across the polymeric tubing membrane, and subsequent biodegradation of the HVHF organics by a selectively enriched microbial consortium in an EMB. Several grades of DuPont Hytrel polymeric tubing were tested for their ability to transport organics, and inability to transport inorganic species across the membrane. Also, a microbial consortium was isolated from contaminated soil which is capable of degrading key organics present in HVHF fluid.

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Magnetotactic bacteria: microscale interactions and macroscale applications

Saeed Rismani Yazdi

ABSTRACT

Magnetotactic bacteria (MTB) are a unique class of prokaryotic cells with the ability to orient along the Earth's magnetic field lines through a chain of magnetite nanocrystals in their body. Using their flagella acting as a propeller, this ability allows MTB to swim towards a magnetic pole, a behavior called magnetotaxis. MTB live in complex and heterogeneous habitats (e.g. water columns and sediments), where fluid flow is ubiquitous, and play a crucial role in biogeochemical processes, including the Earth's iron and sulfur cycles. In the first part of this talk, we will discuss the migration behaviour of magnetotactic bacteria in porous micromodels. In particular, using microfluidics and video microscopy, we demonstrate that directed MTB can circumvent curved obstacles by traveling along the boundaries, and pass flat obstacles by repeatedly switching between forward and backward runs. We demonstrate that magnetotaxis enables directed motion of MTB through heterogeneous porous micromodels, overcoming tortuous flow fields with local velocities as high as $250 \mu\text{m s}^{-1}$. Our findings bring new insights into the migration behaviour of MTB in their natural habitats, and their potential *in vivo* applications as microbiorobots. In the second part of this talk, we will present biologically-driven magnetic actuation of droplets on a superhydrophobic surface using magnetotactic bacteria. MTB were exploited to transport droplets along various paths with actuation speeds as high as 30mm s^{-1} , and sequentially merge and mix multiple droplets. Our results suggest that MTB-actuation can be used for droplet transport in lab-on-a-chip platforms.

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Distributed Observer Design for Linear Time-Invariant Systems

Mohammad Jahvani

ABSTRACT

This work presents a distributed observer scheme for estimating the states of lumped Linear Time-Invariant systems. It is assumed that a group of agents equipped with processing units have access to local measurements from the system and can simultaneously exchange information with each other through a network with a pre-specified topology. The objective of each agent is to generate an asymptotically correct estimate of the states of the system at an arbitrary but preassigned convergence rate. We will study the problem of existence of linear distributed observers when the underlying communication network is strongly connected

Modeling Polycondensation Equilibrium for Nylon 6 and Nylon 6,6

Fei Liu

ABSTRACT

Key Words: polycondensation, equilibrium constant, nylon 6, nylon 6,6 and nylon 6/6,6 copolymer

A new model equation is developed to describe the complex influence of water W and temperature T on the condensation equilibrium of commercially important nylon polymers (i.e., nylon 6, nylon 6,6 and nylon 6/6,6 copolymer). As shown in Figure 1, the apparent nylon 6 equilibrium constant K_a is small at very low $[W]$ (e.g., $[W] < 0.1 \text{ mol kg}^{-1}$), increases to a maximum value for $[W]$ near 1 mol kg^{-1} and then decreases with increasing $[W]$.^[1] Also, K_a decreases with increasing T . This complex behaviour of K_a has long been a topic of mystery and practical concern because reliable values of K_a are important for simulating and optimizing nylon reactor systems.^[1-3] Until now, no literature models have been able to capture the overall trend of nylon 6 and 6,6 equilibrium data. A new model equation is developed based on the extended nylon 6 reaction scheme in Table 1, where the polycondensation reaction R1 involving amine ends A , carboxyl ends C , amide links L and W is accompanied by four additional reactions involving amidine ends I and hydrated carboxyl ends C^* . Amidine ends form via the reverse of R2 and R3 when $[W]$ is very low and T is high.^[4,5] Hydration of carboxyl ends becomes important when $[W]$ is large.^[3] Based on the mechanism in Table 1 and two reactions (similar to R2 and R3) that occur during nylon 6,6 polymerization,^[6,7] an expression for K_a is developed and fitted using all literature nylon 6 and 6,6 equilibrium data over a wide range of conditions ($0.06 \leq [W] \leq 52 \text{ mol kg}^{-1}$; $220 \leq T \leq 300 \text{ }^\circ\text{C}$).^[1,2] The resulting expression (used to obtain the curves in Figure 1) was developed by recognizing that experimental values of K_a are obtained using titrations where basic amidine ends are counted as if they are amine ends and hydrated carboxyl ends are counted as if they are regular carboxyl ends, so that $K_a = [L][W]/\{([C]+[C^*])([A]+[I])\}$. A good fit was obtained for all 144 data points used to estimate the five parameters that appear in the final expression (i.e., values of K_1 , K_2 and K_4 at a reference temperature of $240 \text{ }^\circ\text{C}$ and reaction enthalpies for R1 and R2). The resulting relatively simple equation will be used in ongoing model development for nylon 6/6,6 copolymerization.

Figure 1 Comparison of predictions for K_a at $220 \text{ }^\circ\text{C}$ and $260 \text{ }^\circ\text{C}$ with nylon 6 equilibrium data of \circ Wiloth and \blacksquare Giori and Hayes.

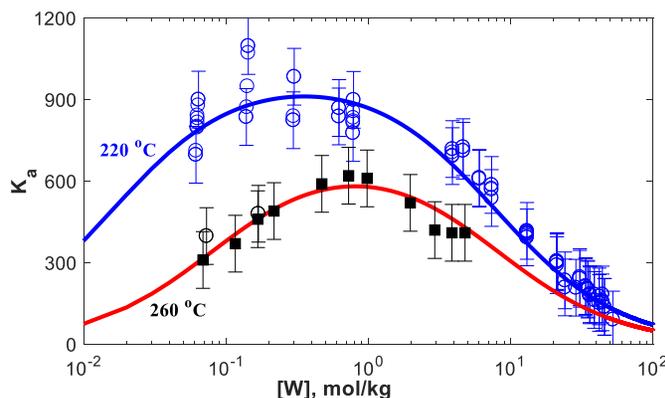
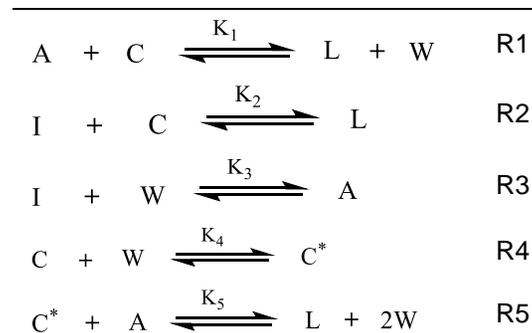


Table 1 Nylon 6 Reaction Mechanism used to Derive Polycondensation Equilibrium Expression for K_a



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Use of Beta Zeolites for the Hydroisomerization of Oleic Acid to Branched Chain Fatty Acids

Samantha Duff

ABSTRACT

The environmental impacts of the finite fossil fuel resources are a growing global concern, and alternatives to petrochemical materials are needed. Lubricants and waxes are conventionally derived from crude oil, and are an important global commodity. Bio-based products made from vegetable oils and animal fats can offer renewable alternatives to these petroleum-based products. The application of these naturally occurring vegetable oils is limited, however, by their oxidation stability and cold flow properties. Hydroisomerization of vegetable oil free fatty acid content has the potential to overcome the technical challenges surrounding biolubricants by producing branched chain isomers. Branched chain fatty acids have improved characteristics for the development of biolubricants. This work focuses on catalytic conversion of oleic acid to modify its structure. Work done by Azko Nobel Chemicals (2004) has shown that acidic zeolites are promising catalysts for high yields of branched fatty acid products. As well, catalysts that consist of both an acid site and a hydrogenation site can increase the yield of favorable saturated branchchain fatty acid products. Zeolite catalysts, with large pores and strong, adjustable acidity, are a common catalyst used in the petroleum industry for the isomerization of straight chain hydrocarbons. Work conducted by researchers at the University of British Columbia (Reaume and Ellis, 2011) has shown encouraging results using mesoporous zeolites, particularly the Beta structure. This work focuses on these aluminosilicate zeolites as a backbone support, combining hydrogenation catalysts such as platinum through incipient wetness impregnation to develop a dual function hydroisomerization catalyst. Catalysts have been characterized using Brunauer–Emmett–Teller (BET) physisorption techniques and Neutron Activation Analysis (NAA). Reactions were conducted in an Autoclave Stirred Pressure Vessel, and the fatty acid products analyzed using Attenuated Total Reflection (ATR) Infrared Spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy to measure the degree of branching and by-product formation.