

ESTIMATION OF OUTPUT MEASUREMENT VARIANCES FOR PARAMETER ESTIMATION USING ERROR-IN-VARIABLES MODELS

KAVEH ABDI

Error-in-variables (EVM) techniques are used to account for input uncertainties when estimating model parameters. EVM objective functions for parameter estimation contain weighting factors that are reciprocals of the measurement variances for the inputs and outputs, respectively. These variances must be specified using engineering judgment or estimated from data. In conventional least-squares parameter estimation, where model inputs are perfectly known, output variances are straightforward to estimate using replicate experiments. In EVM, however, the issue of replicate experiments is complex because true values of the inputs may be different when multiple attempts are made to repeat an experiment. In the current study, a linearization-based method is proposed for estimating the required input and output variances using “pseudo-replicate” runs where the measurements of the inputs are the same, but unknown true input values are different. The effectiveness of the proposed approach is investigated using a copolymerization example.

PREDICTING MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTION FOR GAS-PHASE POLYETHYLENE PRODUCTION WITH A MULTI-SITE CATALYST

JENNIFER AIELLO

A mathematical model was developed to simulate a laboratory-scale gas-phase ethylene/1-hexene copolymerization process using a multi-site metallocene catalyst. The kinetic scheme includes activation, propagation, chain-transfer to hydrogen, β -elimination, deactivation and reinitiation. A three-site model with 33 parameters was developed to predict number-, weight- and Z-average molecular weights, along with polymerization rate and overall hexene incorporation. In addition, the model predicts the molecular-weight and comonomer-incorporation distributions for the polymer accumulated in the reactor at the end of the batch. Statistical methods were used to rank the kinetic parameters from most-to least-estimable, based on the available industrial data. A mean-squared-error criterion was used to determine the appropriate number of parameters to estimate to obtain reliable model predictions. Parameters were estimated, using gas flow rate and composition data obtained over the course of each experimental run, along with polymer characterization data at the end of each run. Data sets not used for parameter fitting were used for subsequent model validation.

HYBRID NANOPARTICLE-NANO HOLE ARRAY SERS-ACTIVE NANOSTRUCTURES



YAZAN BDOUR

Rapid and highly sensitive SERS-active nanostructures are created from the combination of metallic flow-through nanohole arrays and metallic nanoparticles. The nanohole arrays are used to generate near-surface electrokinetic phenomena to suspend the metallic nanoparticles atop the apertures to produce SERS active hotspots. These hotspots are precisely controlled through the externally-applied voltage, without the need of tags or ligands to control the distance between the nanoparticles and the nanohole arrays to generate ultrasensitive SERS signal. The overall assembly combines nanoplasmonics, and optofluidics to create SERS-active nanostructure that yields Raman signals with enhancement over 80% compared to their individual nanostructures.


THE SYNTHESIS OF ACRYLATE MACROMONOMERS TO PRODUCE STRUCTURED COPOLYMER DISPERSANTS BY SEMI-BATCH RADICAL POLYMERIZATION

LIZZIE BYGOTT

A significant industrial interest is the use of macromonomer rich copolymers to stabilize particles in coatings, dispersants, and adhesives, as the reactive terminal double bond (TDB) units can be used to produce structured architectures such as functionalized branched copolymers and multi-block copolymers. A high temperature starved-feed semi-batch operating policy has been shown to produce poly(acrylates) with high macromonomer content without the use of a catalyst, taking advantage of intrinsic side reactions inherent to acrylate polymerization. This operating strategy was used to polymerize butyl acrylate (BA) over a range of monomer and initiator levels, reaching a maximum macromonomer content of 70%. When the acrylate monomer is switched to isobornyl acrylate (iBoA), the process yields a product of lower dispersity and close to 100% macromonomer content under identical operating conditions. The semi-batch process yields a macromonomer with close to 100% fidelity that has been shown to serve as an excellent addition-fragmentation agent for polymerization of a second monomer.



This presentation will describe the operating conditions required to synthesize acrylate-based macromonomers, as well as their subsequent use to produce blocky copolymers. Challenges related to characterizing TDB content and copolymer structure are addressed using a combination of multi-detector size-exclusion chromatography, differential scanning calorimetry, and nuclear magnetic resonance spectroscopy. The development of a sequential monomer feeding strategy to efficiently synthesize block and comb copolymers by radical polymerization without the use of a mediating agent will eliminate the processing steps required to remove additives, reducing manufacturing costs and environmental impact.



COMPLEX VISCOSITY OF STAR-BRANCHED MACROMOLECULES FROM ANALYTICAL GENERAL RIGID BEAD-ROD THEORY

STEACY COOMBS

The complex viscosity of planar star-branched polymers has been derived from general rigid bead-rod theory, but only for singly-beaded arms. Here, we explore the respective roles of branch functionality, arm length and non-planar arrangements, analytically from general rigid bead-rod theory. For non-planar, we include polyhedral, both regular and irregular. Further, for all structures, we compare with and without the central bead. We fit the theory to complex viscosity measurements on polybutadiene solutions, one quadrafunctional star-branched, the other unbranched, of the same molecular weight. We learn that when general rigid bead-rod theory is applied to quadrafunctional polybutadiene, a slightly irregular center-beaded tetrahedron of interior angle 134° is required to describe its complex viscosity behaviour.

ANION EFFECTS ON ELECTROCHEMICAL CO₂ CONVERSION STABILITY AND SELECTIVITY AT HIGH CURRENT DENSITIES

LUKE KUO

Supported by developments of renewable energy and carbon capture technology, electrochemical CO₂ conversion (ECC) to multi carbon products (C₂₊) exhibits promise as an economically viable CO₂ mitigation technique. It is well known that a successful ECC performance requires a careful control of the local environment at the catalyst surface, namely cations, anions, pH, CO concentration, and CO₂ concentration. While other aspects of the local environment have been explored extensively, research on anion effects remains limited, especially at a high reaction rate. To fill in this gap in the literature, in this work, we investigated how the most prominent ECC anions (HCO₃⁻, SO₄²⁻, Cl⁻, Br⁻, I⁻) affect ECC selectivity and stability at industrially relevant current densities (100-250 mA/cm²). We found that in such current density range, on a polycrystalline Cu catalyst, anions had only a slight influence on C₂₊ selectivity (between 75-80% for all anions). Yet, anions strongly affected catalyst stability, ranging from 15 hours stability in KBr to 6 hours stability in KHCO₃.

Our findings suggest that large halogens (Br⁻ and I⁻), due to their high adsorption affinity toward copper, were able to slow down surface reconstruction, thereby prolonging catalyst stability. Nonetheless, our results also show that excessive halogen absorption can also be disadvantageous for surface stability. Overall, our work provides a basis for anion selection and concentration optimization. Possible approaches to further control surface anion concentration in future designs include using catalyst binders, organic additives, surface coatings, and oxidation techniques.

MASS TRANSFER EFFECTS ON BIOGENIC GREENHOUSE GAS PRODUCTION IN ATHABASCAN OIL SANDS TAILING PONDS

AVERY LING

The oils sands in the Athabasca region of northern Alberta are one of the largest oil deposits in the world. The solid and liquid waste generated from oil sands extraction processes is stored in tailing ponds, which is a source of environmental concerns. This includes biogenically produced greenhouse gas (GHG) emissions, from the depths of the tailing ponds, where dense tailings consolidate over time forming mature fine tailings (MFT). While studies show that GHG are produced by native MFT microbes degrading organics (namely naphtha), there has been little investigation of the impact of mass transfer between the bitumen and water phases in MFT on degradation rates of these organics. Sacrificial 1-D diffusional experiments of O-xylene and 1-methylnaphthalene from bituminous to simulated tailing pond aqueous phases were performed. Accelerated equilibration experiments helped to validate a fugacity-based model which was then used to fix variables in a multicomponent intra-NAPL model.

This model was used to determine mass transfer coefficients for these systems of concern, as well as to provide insight into which systems naphtha degradation may be mass transfer limited. This work also included investigation into the “salting-out” effect that may impede the interfacial transfer of naphtha and may cause preferential sorption to experimental equipment. Florescence spectroscopy was used as the preferred analytical method over gas chromatography for all experiments due to sensitivity, cost, speed, and solution stability in preparation. A multi-phase model was created using mass transfer experimental data, results of multicomponent intra-NAPL modeling, the fugacity-based model, and literature biodegradation data to investigate the effect of mass transfer and biogenic limitations on naphtha degradation. This model is to be improved with specific biogenic experimental data derived from two tailing ponds.

ESTIMATING UNCERTAINTIES AND PARAMETERS FOR FUNDAMENTAL MODELS WITH MULTI-FREQUENCY MEASUREMENTS

QIUJUN (ABBY) LIU

Accurate parameter estimates for fundamental dynamic models are important because accurate model predictions contribute to successful process monitoring and automation. A problem with traditional parameter-estimation methods, based on ordinary differential equation (ODE) models, is the assumption that uncertainties arise from measurement noise, but not from model imperfections. In most process monitoring and control applications, however, substantial model mismatch and unmodeled disturbances can have deleterious influence on the accuracy of the model predictions. In the current research, we focus on parameter-estimation methods for stochastic differential equation (SDE) models that account for unmodeled process disturbances as well as measurement noise.

Recently, Karimi and McAuley developed LAMLE (Laplace Approximation Maximum Likelihood Estimation) and LAB (Laplace Approximation Bayesian) parameter estimation methods for SDE models.

These methods use maximum-likelihood and Bayesian objective functions to simultaneously estimate model parameters and unknown error-covariance matrices for measurements and stochastic process disturbances. The effectiveness of LAMLE and LAB has been tested using a simple two-state CSTR case study, assuming that concentration and temperature measurements are available frequently. Superior parameter-estimation results were found compared to ODE-based Weighted Least Squares (WLS) parameter estimation.

In many chemical processes, some measurements are available more frequently than others. For example, measurements of temperatures, pressures and flow rates are available frequently, whereas concentration measurements made by on-line gas chromatography are available every few minutes, and product properties requiring laboratory analyses may be available every few hours. Therefore, it is important to extend LAMLE and LAB for situations where some measurements are far apart in time. In the current research, updated expressions are derived to estimate disturbance and measurement-noise covariance matrices, along with the parameters, using multi-rate data. The updated LAMLE and LAB methodologies are then tested using the two-state CSTR model using simulated data. Comparisons are made with CTSM, a maximum-likelihood-based SDE approach developed by Kristensen et al. We show that LAMLE and LAB provide reliable results while avoiding convergence problems encountered by CTSM in some situations.

DATA DRIVEN MODELLING AND OPTIMIZATION OF COMPRESSORS IN GAS TRANSPORT NETWORKS

ZAID MARFATIA

The efficient and effective transportation of natural gas has become ever so important due to the world's increasing energy demands, and almost a quarter of that demand is met by natural gas. The fuel cost minimization problem (FCMP) is a heavily researched area within engineering and optimization fields. The problem being addressed asks, 'how to best operate compressor stations and throughput in a pipeline network, such that fuel cost is minimized'. This problem is complex and of great importance. It is estimated that 3-5% of the natural gas being transported is consumed by the compressors used to energize it. In literature it is believed that a 20% reduction in compressor station fuel consumption can be achieved through global optimization of pipeline operation.

Modelling compressor stations is very complex as their behaviour is highly non-ideal and there exists no reliable 1st principles model. Over time researchers have used different formulations to represent the characteristic behaviour of compressors; however, they are inaccurate and deviate from true behaviour. As a result, the solutions derived from such a model warrants several caveats, often deeming the solution infeasible.

In our approach we use data collected directly from characteristic diagrams of compressors to develop high fidelity surrogate models. Surrogate modelling is an approach used to connect the desired output quantities to their related inputs, and the system to be modelled is viewed as black box. We consider different model structures, which are compared in terms of their accuracy and efficiency. We find that deep neural networks (DNN) are a powerful surrogate model structure for compressors, and it achieves the best precision among all model structures under consideration. We also develop a systematic procedure to express the DNN model using mixed-integer linear constraints in the FCMP formulation. Case study of a natural gas transport network will demonstrate the advantage of the DNN model in terms of solution accuracy and efficiency.

ESTIMATING THE BIOACCESSIBILITY OF A HYDROLYTICALLY DEGRADABLE CATIONIC FLOCCULANT

DEREK RUSSELL

Poly(lactic acid) choline iodide ester methacrylate, poly(PLA₄ChMA), is a cationic degradable polymer that can flocculate particles and dewater oil sands from tailings ponds. However, this novel flocculant is not well characterized with respect to potential interactions with sensitive receptors, including humans. Bioaccessibility (bioaccessible fraction) is a measure of the solubility of an ingested contaminant that may be available for systemic absorption. The partially degraded flocculant and its degradation products, modelled using lactic acid and choline chloride, were subjected to a modified physiologically based extraction test (PBET). Bioaccessible fractions were estimated by proton nuclear magnetic resonance (¹H-NMR) spectroscopy and by high-performance liquid chromatography (HPLC). HPLC analysis indicates that the bioaccessibility of lactic acid in gastric solution containing choline chloride is ~100% but slightly dropped to 94% in PBET intestinal solution at a solid-to-liquid ratio of 1:200.


¹H-NMR and gravimetric analyses reveal that the partially degraded poly(PLA₄ChMA) did not degrade further during the PBET and is not solubilized (i.e., 0% bioaccessibility) in the gastric phase. However, the partially degraded polymer is fully solubilized (i.e., 100% bioaccessible) in the intestinal phase. At the end of PBET intestinal digestion, the molar ratio of lactic acid to choline chloride in the presence of degraded poly(PLA₄ChMA) was 2, which is approximately the same as in the initial solution. Thus, lactic acid and choline chloride are solubilized to the same extents in both gastric and intestinal solutions. Results suggest that HPLC can be used to directly estimate the bioaccessibility of lactic acid, whereas ¹H-NMR may be used to indirectly quantify the bioaccessibility of both lactic acid and choline chloride by determining their molar ratio in PBET extracts. In future works, these findings may be applied to the estimation of risks from exposure to poly(PLA₄ChMA) as well as to contaminants flocculated by poly(PLA₄ChMA) in tailings ponds and in other wastewater treatment applications.

NEWTON-SEEKING DISTRIBUTED RESOURCE ALLOCATION

MATTHEW SCHULTZ


When creating control strategies for large-scale systems, real-time optimization (RTO) is a category of closed-loop process control techniques that's focused on increasing process performance and eliminating errors for systems in real time. To create effective strategies, models of the systems are needed that depict the dynamics of the process; because of this, time and money must be spent to create either complex non-linear models, or localized linear estimates. To circumvent this issue, model-free techniques such as Extremum-seeking control (ESC) have been developed that rely on minimizing the unknown cost functions using only the knowledge of the current state and the measurement of the cost function.

Using this optimization methodology, this thesis develops an approach to solve optimal resource allocation problems in a fully distributed fashion where the separable cost function is unknown with dynamics in discrete time.



To accomplish this, we utilize a distributed extremum-seeking scheme that estimates our cost function's gradients and Hessians, allowing us to create Newton step dynamics to asymptotically drive both our primal and dual problems to their optimal values with a user-assignable convergence rate.

The posed strategy is tested using 2 simulations, the first being a small-scale 3-node case highlighting the effectiveness of the strategy while the second is a complex 25-node case that more closely reflects how the strategies would perform in more realistic scenarios.



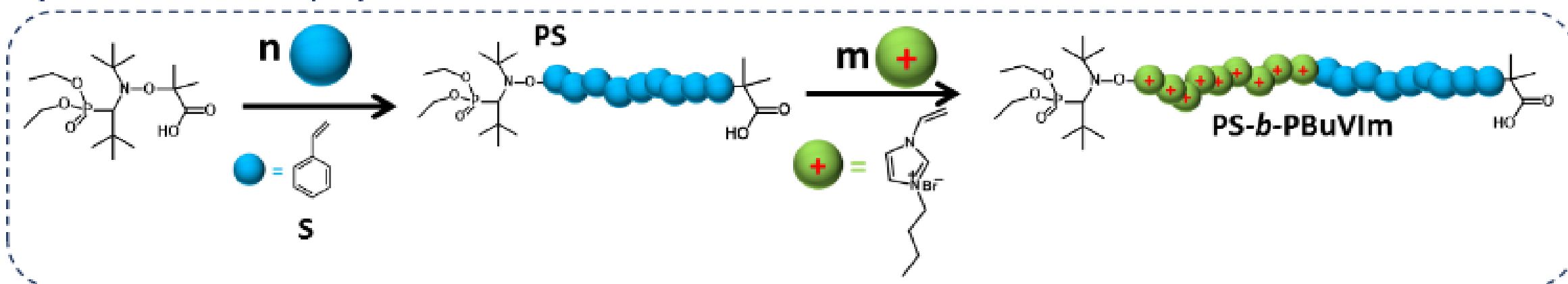
NON-COVALENT POLYMER SURFACE MODIFICATION OF CELLULOSE NANOCRYSTALS USING BLOCK COPOLYMERS

OGLA TORRES ROCHA

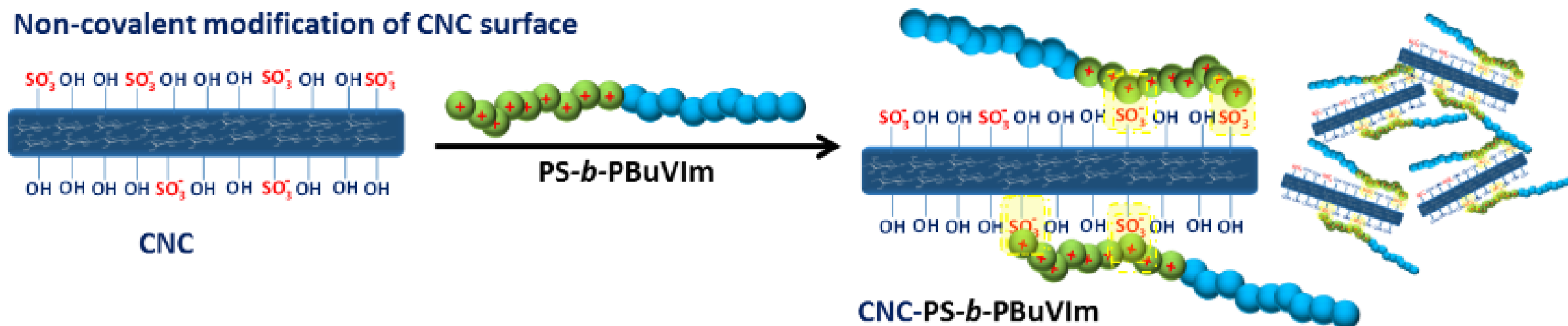
Over the last decade, cellulose nanocrystals (CNCs) have attracted the attention of academic and industrial researchers as their desirable mechanical properties make them a promising candidate in the development of next generation polymer-based advanced composites. Despite their vast potential, CNCs have a highly hydrophilic surface, making them incompatible with most hydrophobic systems. The modification of the CNC surface with polymeric chains increases compatibility with a wide range of hydrophobic systems, including polymer matrices, and expands the potential applications of CNCs. Here we present preliminary results of a simple method to functionalize the CNC surface using block copolymers. Modification of CNCs has been achieved by synthesizing poly(styrene)-*block*-poly(butyl vinyl imidazole bromide) (PS-*b*-PBuVIm) and poly[(poly ethylene glycol ether methacrylate)]-*block*-poly(butyl vinyl imidazole bromide) (PPEGMA-*b*-PBuVIm) block copolymers via nitroxide mediated polymerization (NMP) and then non-covalently complexing the

copolymers with the CNC surface. The cationic butyl-vinyl imidazole block anchors CNCs via complexation to the anionic CNC surface while the other block acts as a hydrophobic stabilizing block, allowing for new dispersibility capabilities in solvents of varying polarity. The functionalization was confirmed via infrared spectroscopy and thermogravimetric analysis. The dispersion of polymer-modified CNC in organic solvents and water was evaluated via dynamic light scattering. The method presented here is simpler and less expensive than modification approaches based on covalent modification (i.e., grafting to, grafting from). The results presented here, open a gate to a new approach to modify CNC with a new series of copolymers that are effectively modifying the surface properties of CNC, potentially leading the development of CNC materials towards industrial applications.

Synthesis of block copolymers



Non-covalent modification of CNC surface



Scheme 1. Synthesis of PS-*b*-PBuVIm and subsequent non-covalent functionalization of CNC.