Benefits of Continuous Reactor Operation for Reactivity Ratio Estimation

Alison Scott & Alexander Penidis
Institute for Polymer Research (IPR), Department of Chemical Engineering, University of Waterloo

Research Motivation
- Most copolymerization reactions occur in batch reactors, especially for reactivity ratio estimation (RRE). Limiting assumptions (such as no composition drift) may be necessary, depending on the RRE technique.
- Copolymerization in continuous-stirred tank reactors (CSTRs) is a promising alternative to batch copolymerization for reactivity ratio estimation. CSTR data can be combined with the error-in-variables-model (EVM) methodology for reactivity ratio estimation.

Background Information

Why Use Continuous-Stirred Tank Reactors?
- CSTRs are commonly used in industry for liquid phase reactions (including polymerizations) when production volume warrants their use.
- Steady-state & perfect mixing assumptions; conditions including temperature, concentration, and rate of reaction are not dependent on time or position.
- Composition drift (variation in the instantaneous mole fraction in the polymerizing mixture, f_i, during copolymerization) can be eliminated; CSTRs at steady-state ensure constant copolymer composition.
- Better control over conversion levels; no need to restrict copolymerization to low conversion.
- Instantaneous & cumulative copolymer compositions are equivalent at steady-state (that is, F_i = Σf_i).

Example: batch polymerization of styrene (STY) & glycidyl methacrylate (GMA) in bulk at 110°C, by Wolf et al. (2002).
- Instantaneous copolymer composition equation: F_i = (f_i + 2f_i + 2) / (2 + (2f_i + 2) + f_i + 2).

Why Use the Error-in-Variables-Model?
- Reactivity ratios describe the rate of incorporation of comonomers into the resulting copolymer product.
- The wide variety of (incorrect) RRE methods in literature affects the accuracy of reported values.
- EVM is a non-linear parameter estimation technique that accounts for the errors present in both the measured values and the estimated parameters.
- EVM provides more accurate & precise RRE results, a better understanding of error sources & less correlation between parameter estimates.

I. Continuous-Stirred Tank Reactor
Simulation of CSTR Copolymerization Data
- Typically, during polymerization in CSTRs, something is known about both the inlet & outlet flows:
  - Inlet: mass flow rates of the monomer streams (w_i).
  - Outlet: final monomer concentrations (c_i).
- CSTR Model: mole balances can be solved simultaneously to determine f_i, the number of moles of monomer i incorporated into the copolymer per unit time.

  \[ \begin{align*}
  1 + c_i M_i W_i \left( \frac{1}{V_1} - \frac{1}{V_2} \right) + c_i M_i W_i \left( \frac{1}{V_2} - \frac{1}{V_3} \right) = p_i, \\
  1 + c_i M_i W_i \left( \frac{1}{V_2} - \frac{1}{V_3} \right) + c_i M_i W_i \left( \frac{1}{V_3} - \frac{1}{V_4} \right) = p_i
  \end{align*} \]

- Composition of the polymerizing mixture (f_i = c_i / Σc_i) and copolymer composition (F_i = p_i / Σp_i) are related according to the instantaneous copolymer composition (ICC) equation; a system must satisfy both the mole balances and the ICC.

II. Error-in-Variables-Model
Case Study #1: Acrylamide & Acrylic Acid
- Batch copolymerization by Riahinezhad et al. (2013): r_AAm = 1.33 & f_AAm = 0.23.
- Reactivity ratio estimates from simulated data (n=20) are in perfect agreement with original “true” values.
- Addition of random error: up to ±10% error added to each of the input variables (w_i, w_2, c_i & c_2).
- EVM is able to consider error in all variables; this explains the negligible difference observed in the point estimates and the joint confidence regions (JCRs), even as error is added.

III. Improved Reactivity Ratio Estimates

Case Study #2: Styrene & Glycidyl Methacrylate
- Solution polymerization in xylene by Wolf et al. (2002).
- Preliminary data collected (and reactivity ratios estimated) from low conversion batch experiments.
- Temperature correlation (Arrhenius equation fitted to lower temperature experiments) used to extrapolate to a higher temperature, continuous system.
- Using EVM, reactivity ratios can be re-estimated for the system directly from the continuous data.
- Only 5 experimental data points available at T=190°C, but there is still sufficient information to obtain an accurate estimate of the reactivity ratios.

Improved accuracy visible with EVM estimates.
- Azeotrope prediction is more accurate (based on available data) and copolymer composition model is in better agreement with the experimental data.

Concluding Remarks
- It is straightforward to use CSTR data with EVM for reactivity ratio estimation; requires fewer assumptions & has potential in industry.
- At high conversion levels, EVM gives more accurate results (and better model predictions) than linear parameter estimation techniques or Arrhenius temperature correlations.
- Good agreement between reactivity ratios estimated from batch & continuous data, as expected.

References