Terpolymerization Kinetics in Successful Scale-up of The Solution Polymerization of Ethylene and Styrene

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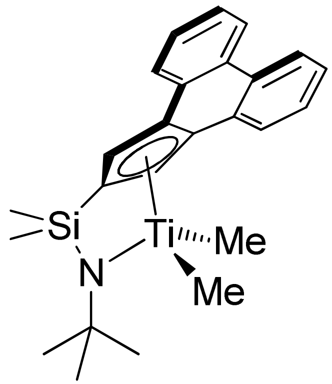
Background

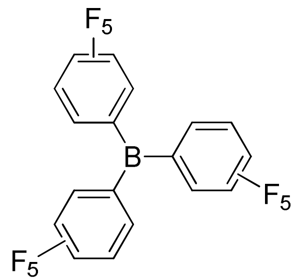
Dow Discovered Catalysts to Copolymerize Ethylene & Styrene in 1989

- Improved Flexibility, Abrasion Resistance, Toughness, Printability, Creep, Compatibility
- Semi-Crystalline (<13 mol% Styrene) to high T_g Glassy (50 mol % Styrene) Products

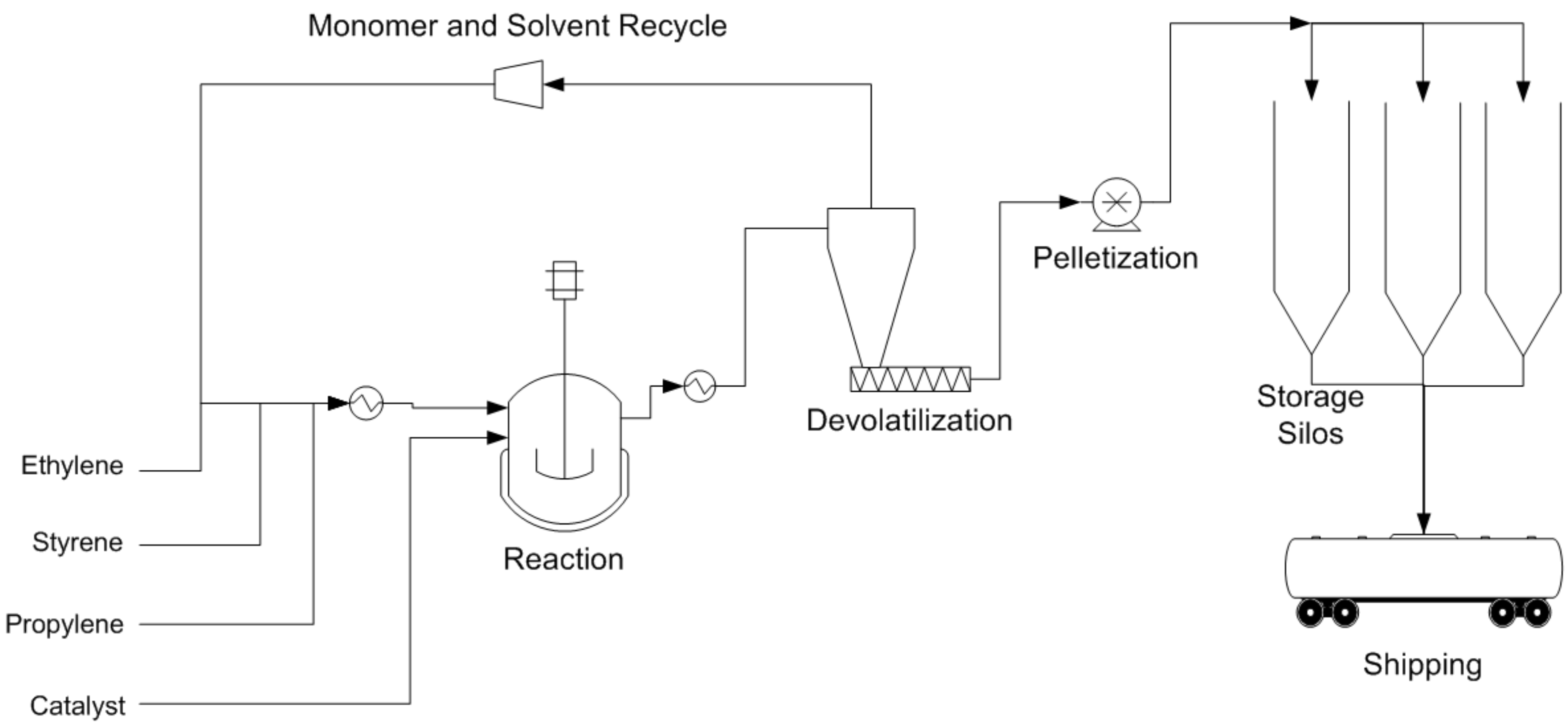


Successfully Scaled Up from Batch to Mini-plant to Pilot Plant to Semi-Commercial Scale

- Commercialization of INDEX™ Interpolymers in 1998
- Stopped Production at Sarnia Product Development Plant in 2002 for Economic Considerations



Solution Polymerization Process



Well-Mixed, Steady-State Reactor
Uses Heat to Devolatilize Polymer
Need to Pelletize, Convey, and Store Product

Practical Copolymerization Models

Ratios of Monomer Polymerization Rates

$$P_{1,n}^{*} + M_1 \xrightarrow{k_{11}} P_{1,n+1}^{*}$$
$$P_{1,n}^{*} + M_2 \xrightarrow{k_{12}} P_{2,n+1}^{*}$$
$$P_{2,n}^{*} + M_1 \xrightarrow{k_{21}} P_{1,n+1}^{*}$$

$$R_{p1} = k_{11} N_1 C_1 + k_{21} N_2 C_1$$
$$R_{p2} = k_{12} N_1 C_2$$

Apply Two Simplifying Assumptions

- Long Chain
  - Neglect Effect of Chain Length on Propagation Rate
  - Neglect Initiation and Termination Reactions
- Steady State Hypothesis for Growing Chains
  - Rate of Production = Rate of Consumption

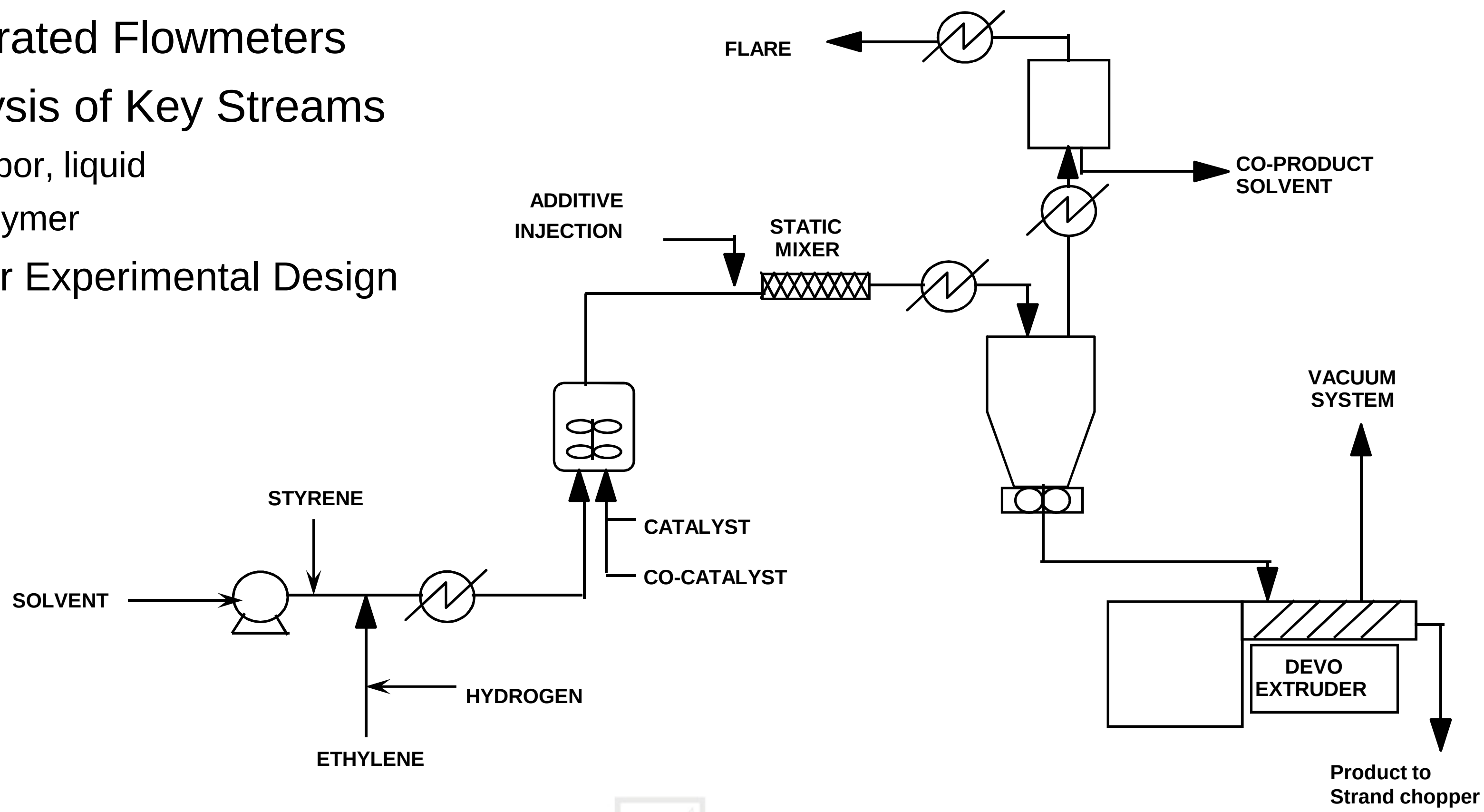
Reactivity Ratios Are Ratios of Propagation Rate Constants

$$r_{ij} = \frac{k_{ii}}{k_{ij}}$$

$$r_s = \frac{k_{21}}{k_{23}}$$

Experimentation at Small Pilot Scale

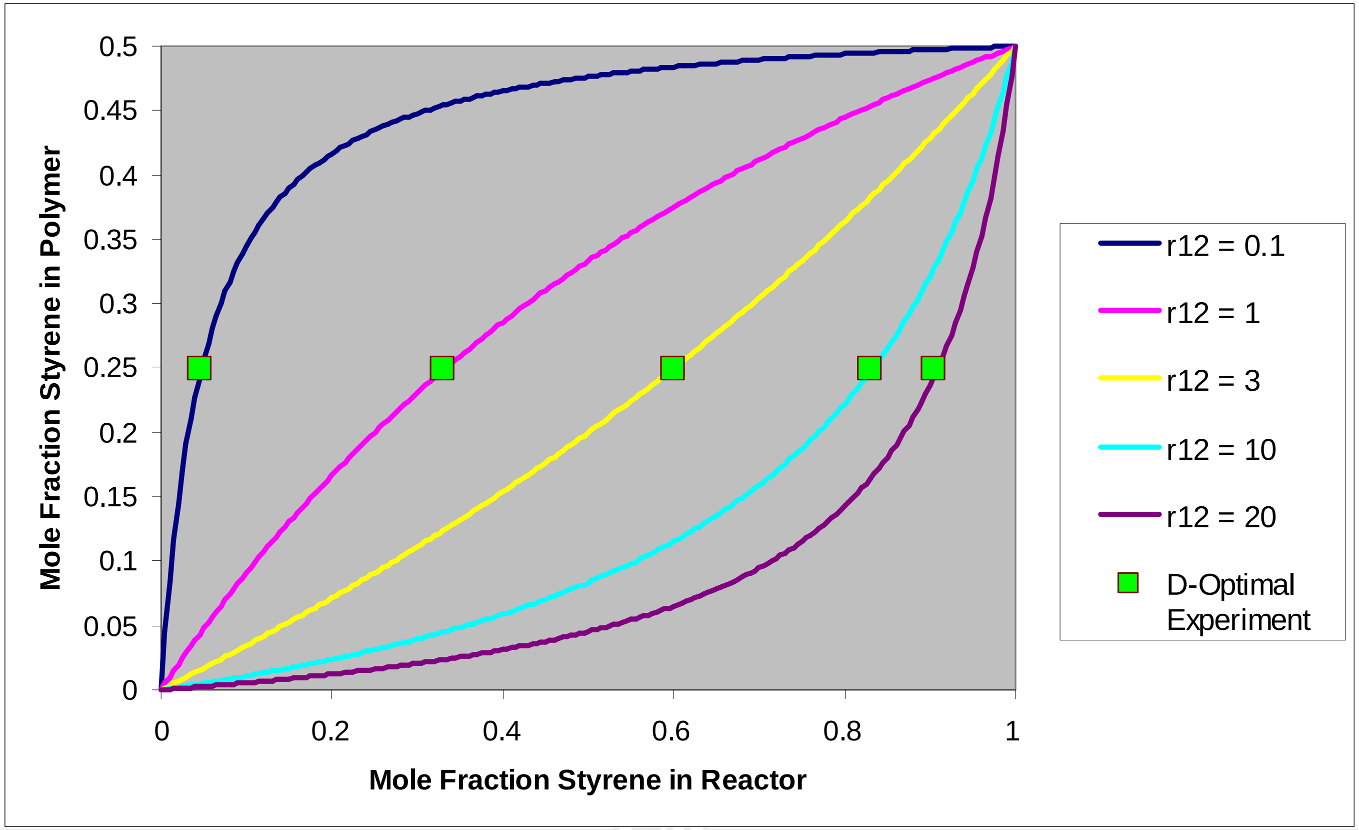
- 2 kg/h Production Rate
- Single Pass, Continuous Well-Mixed Reactor
- Calibrated Flowmeters
- Analysis of Key Streams
  - Vapor, liquid
  - Polymer
- Proper Experimental Design



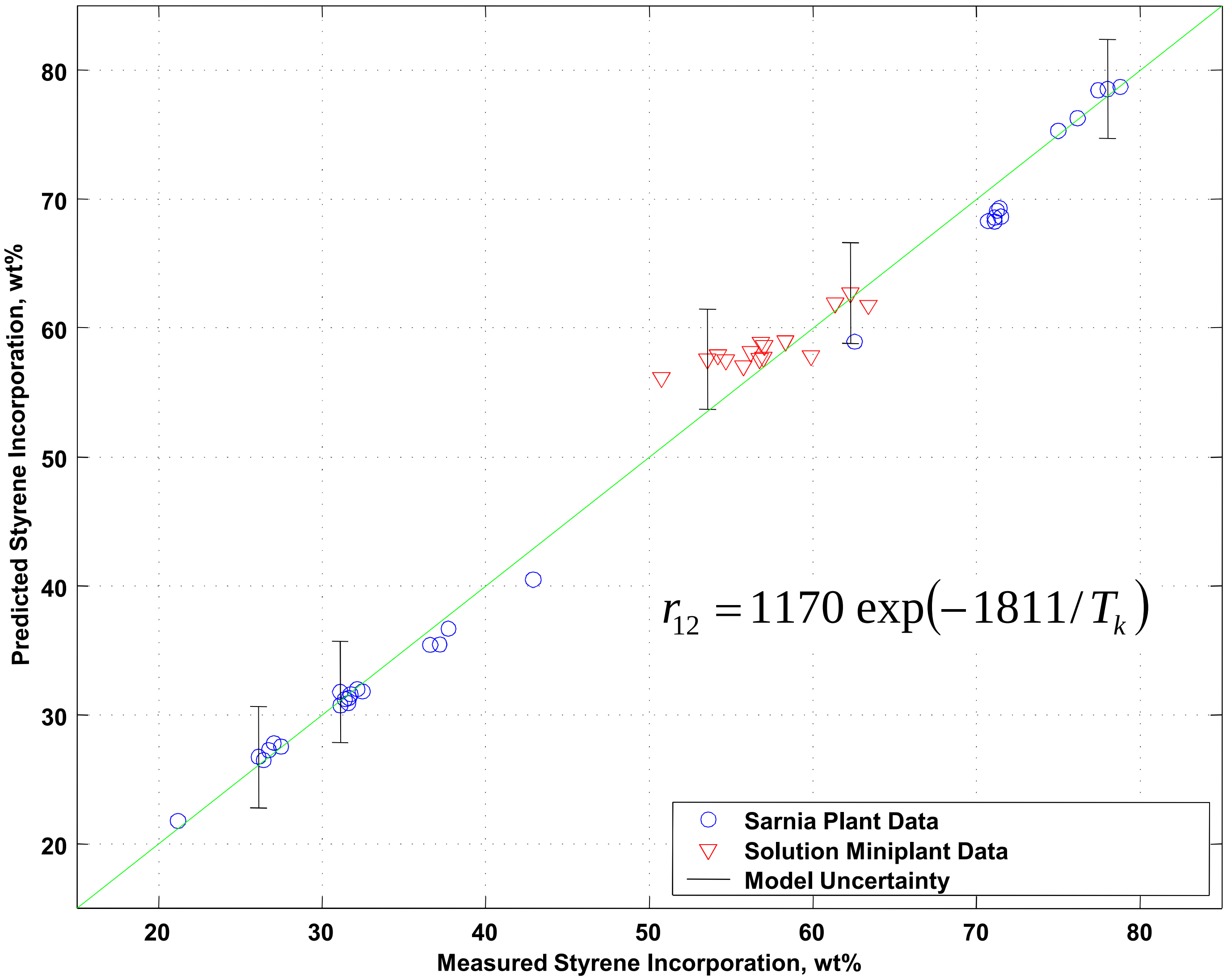
D-optimal Design for E-S Copolymerization

The D-optimal Criterion:

$$\left|\mathbf{F}^T\mathbf{F}\right| = \left(f_2 \frac{1 - f_2}{\left(2 f_2 + r_{12}\left(1 - f_2\right)\right)^2} \right)^2$$



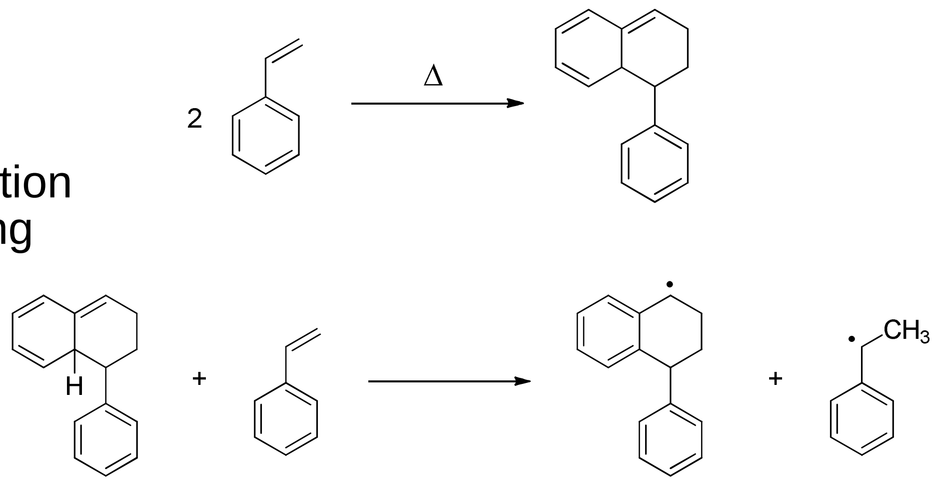
Kinetic Model Scale-Up to Semi-commercial



Challenges of Styrene Monomer

Tendency to auto polymerize

- Stabilizer (4-tert-butyl catechol) Poisons Catalyst
- Undesirable Thermal Polymerization of Styrene during Reactor Loading and Start-up



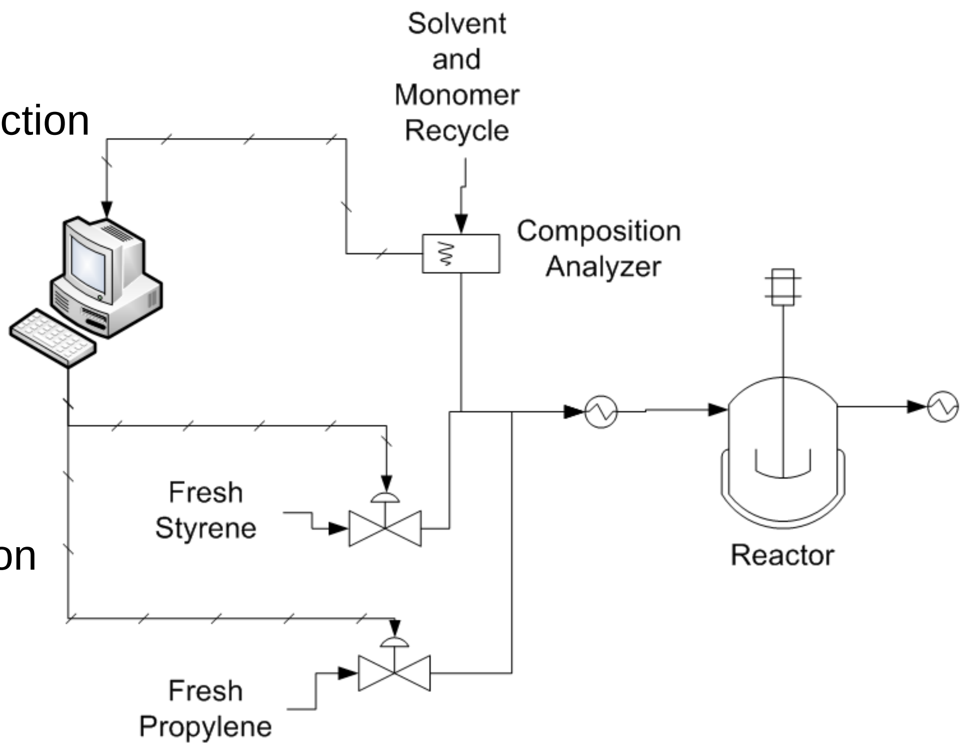
Careful Reactor Startup/Shutdown Methodology Required

- Control Crystallinity of Polymer to Avoid Process Fouling due to Reactor Temperatures Below Polymer Freeze Point
- Minimize Inventory of Styrene in Recycle System

$$R_i = k_d [M]^3$$

Eliminating Excessive Polystyrene Formation

- Avoid High Styrene Concentrations in Process
  - Process not Designed to Handle Polystyrene
  - Plugging of Devolatilization and Material Handling Systems
  - A Method for Controlled Introduction of Styrene
- <u>Use Propylene as a Safe Substitute</u>
  - Control Polymer Composition During Transient Operation
  - Maintain Operability During Shutdown/Startup
  - Need an E/P/S Terpolymerization Model



Ethylene/ Styrene/ Propylene Terpolymerization

Characterize Gross Composition with up to Five Reactivity Ratios and Two Equations

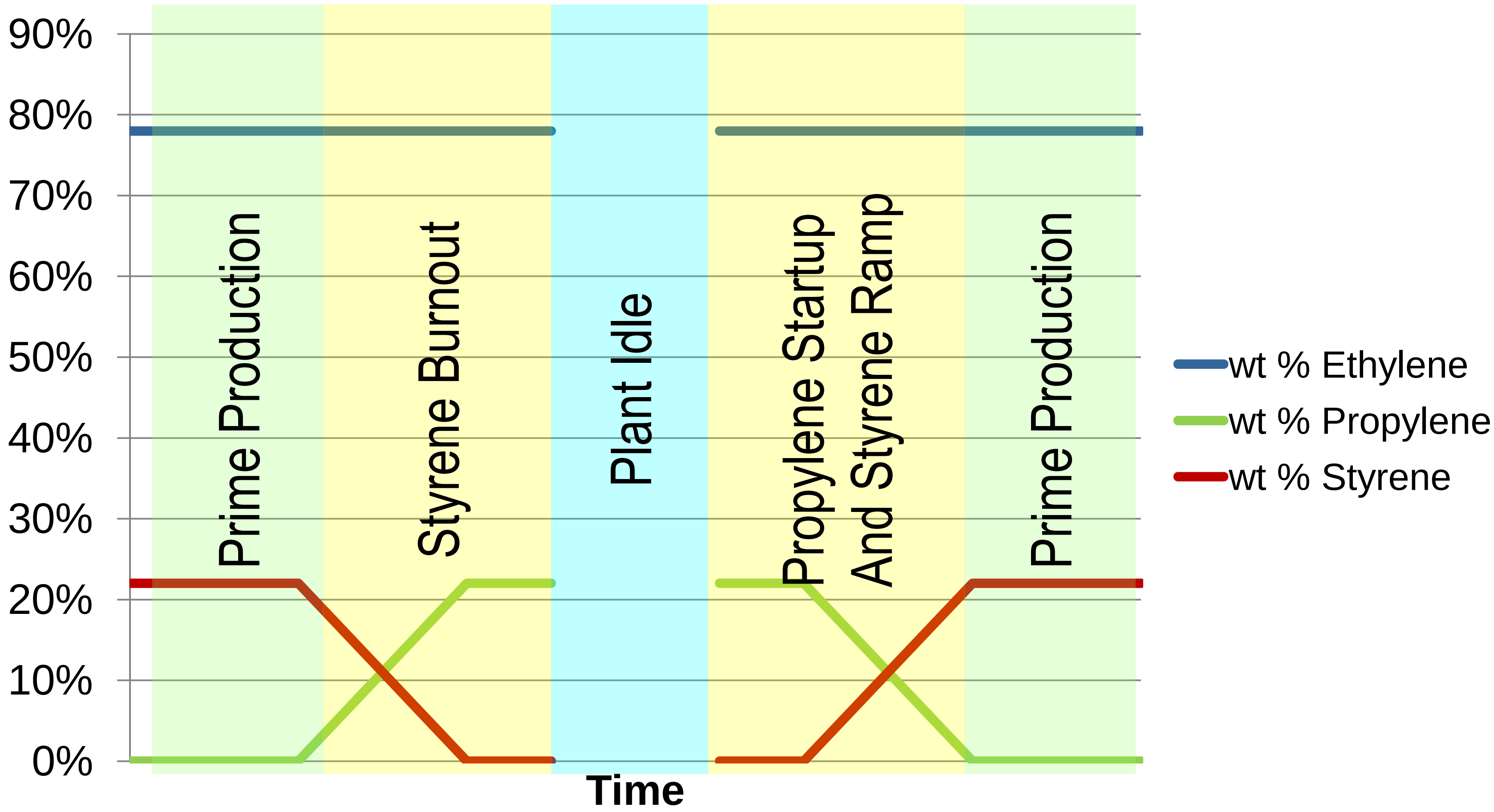
- (Ignore Reverse Insertion of Styrene and Propylene)

$$\frac{F_2}{F_1} = \frac{f_2\left(\frac{f_1}{r_{12}r_{31}} + \frac{f_3}{r_{13}r_{32}} + \frac{f_2}{r_{12}r_{32}}\right)\left(f_1 + \frac{f_3}{r_s}\right)}{f_1\left(\frac{f_3}{r_{31}r_s} + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}}\right)\left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}}\right)} \qquad \frac{F_3}{F_1} = \frac{f_3\left(\frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} + f_3\right)\left(\frac{f_2}{r_{12}r_s} + \frac{f_1}{r_{13}} + \frac{f_3}{r_{13}r_s}\right)}{f_1\left(\frac{f_3}{r_{31}r_s} + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}}\right)\left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}}\right)}$$

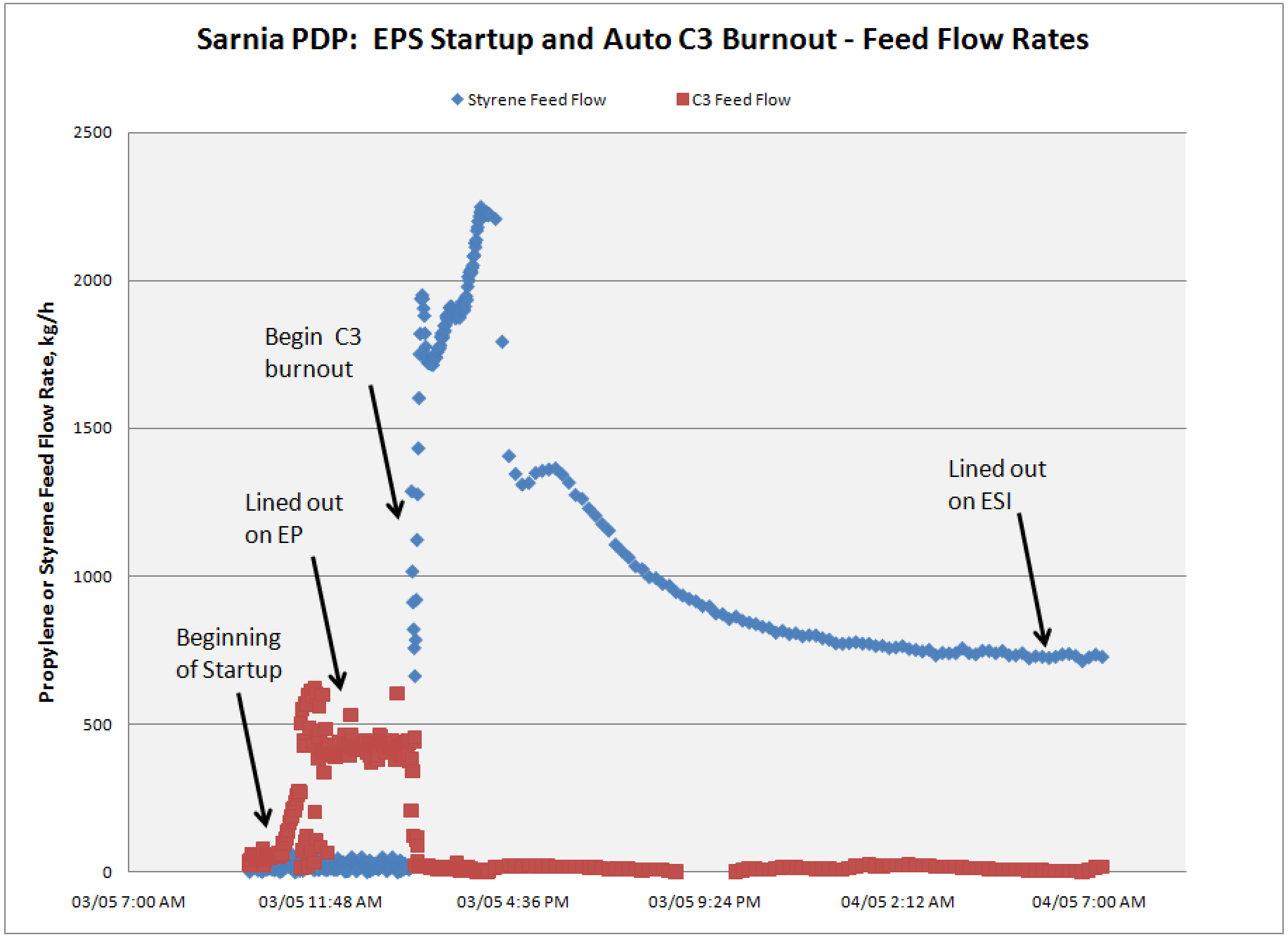
D-Optimal Design

- Five Parameters – Minimum of 5 Experiments
- Numerical Simulation Necessary
  - Maple™ For Analytical Jacobian
  - Excel ™ Solver for Optimization of Conditions

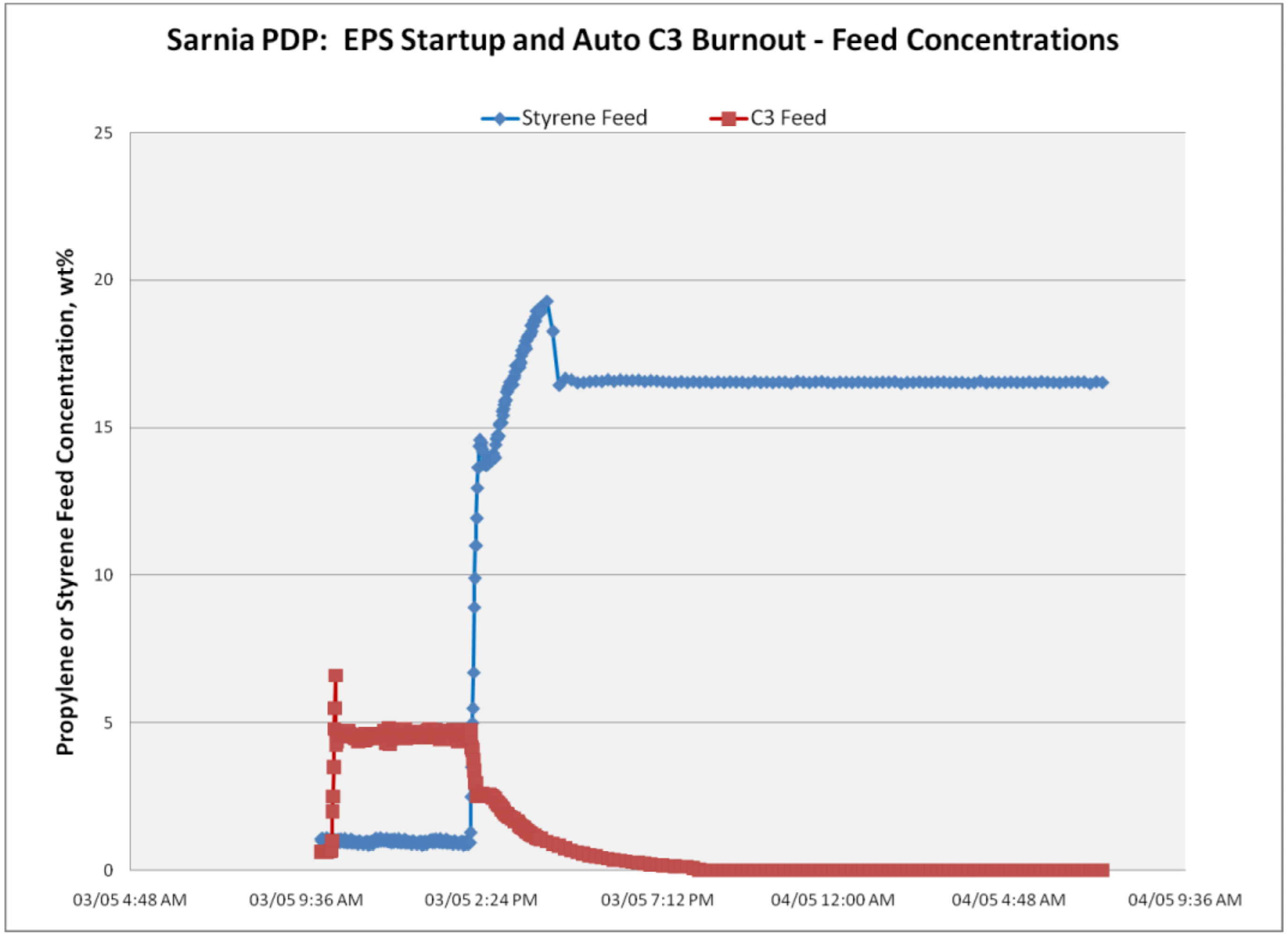
Desired Product Profile Through Shutdown and Startup



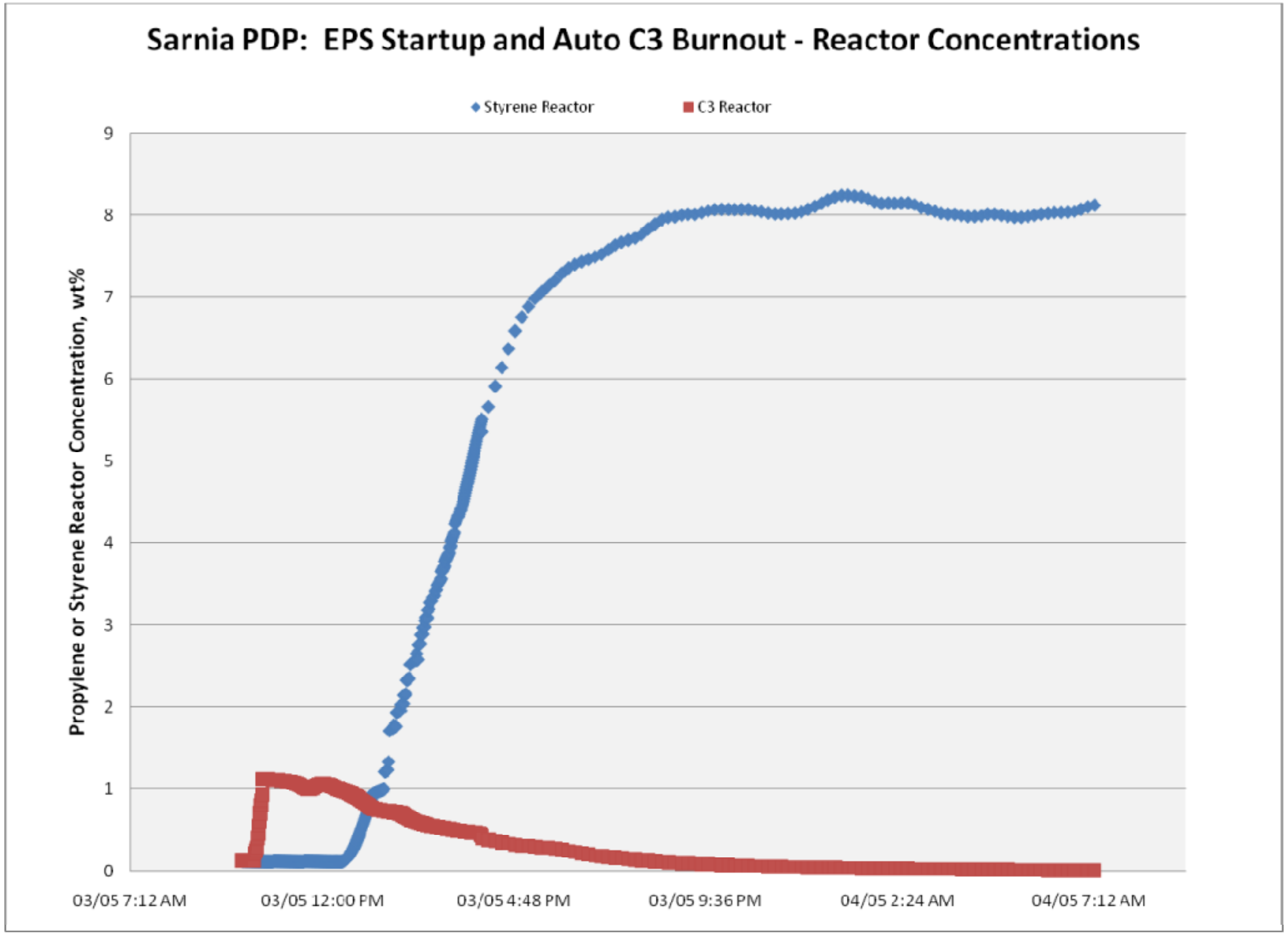
Startup Example – Reactor Feed Flows



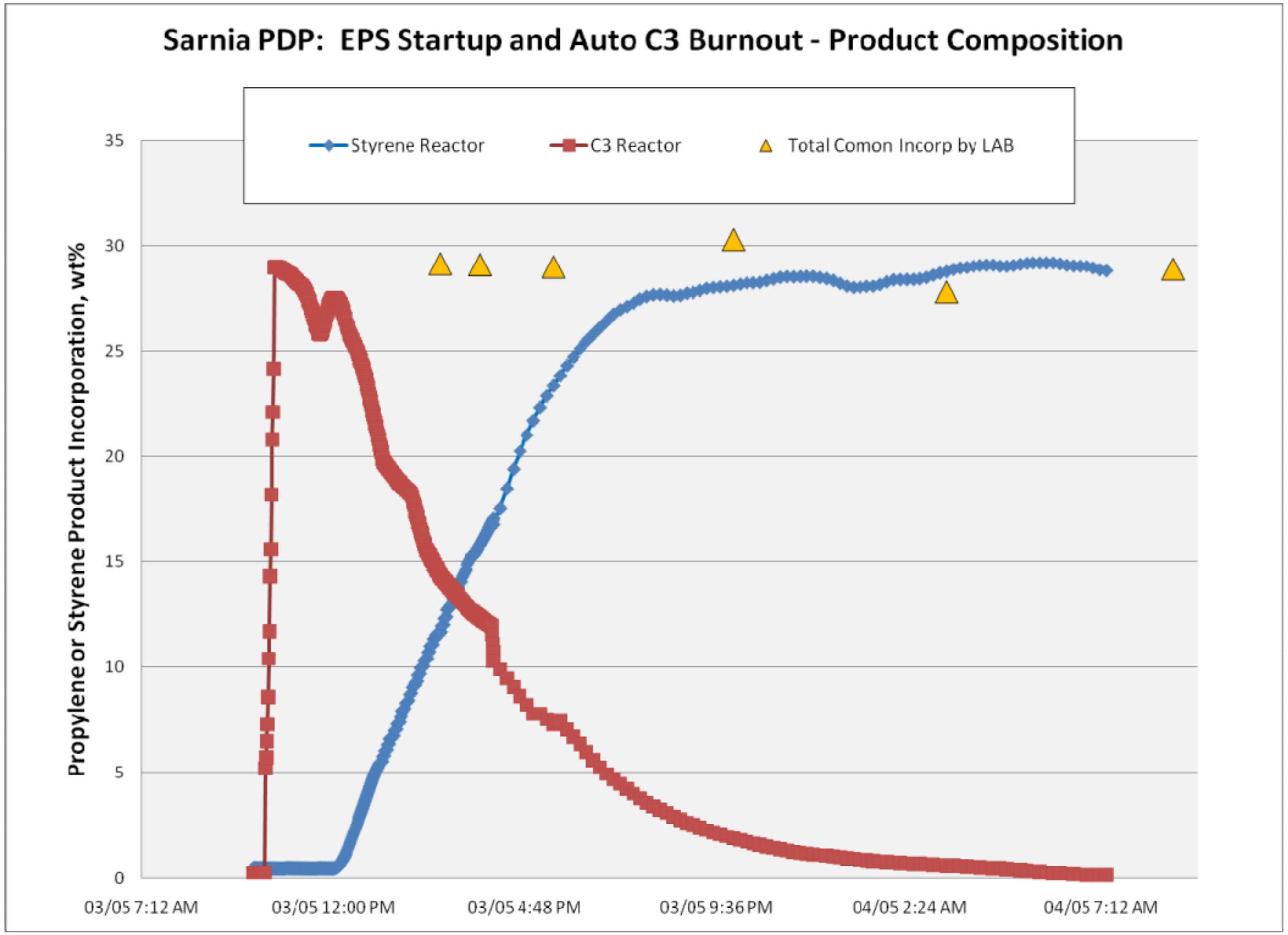
Startup Example – Feed Concentrations



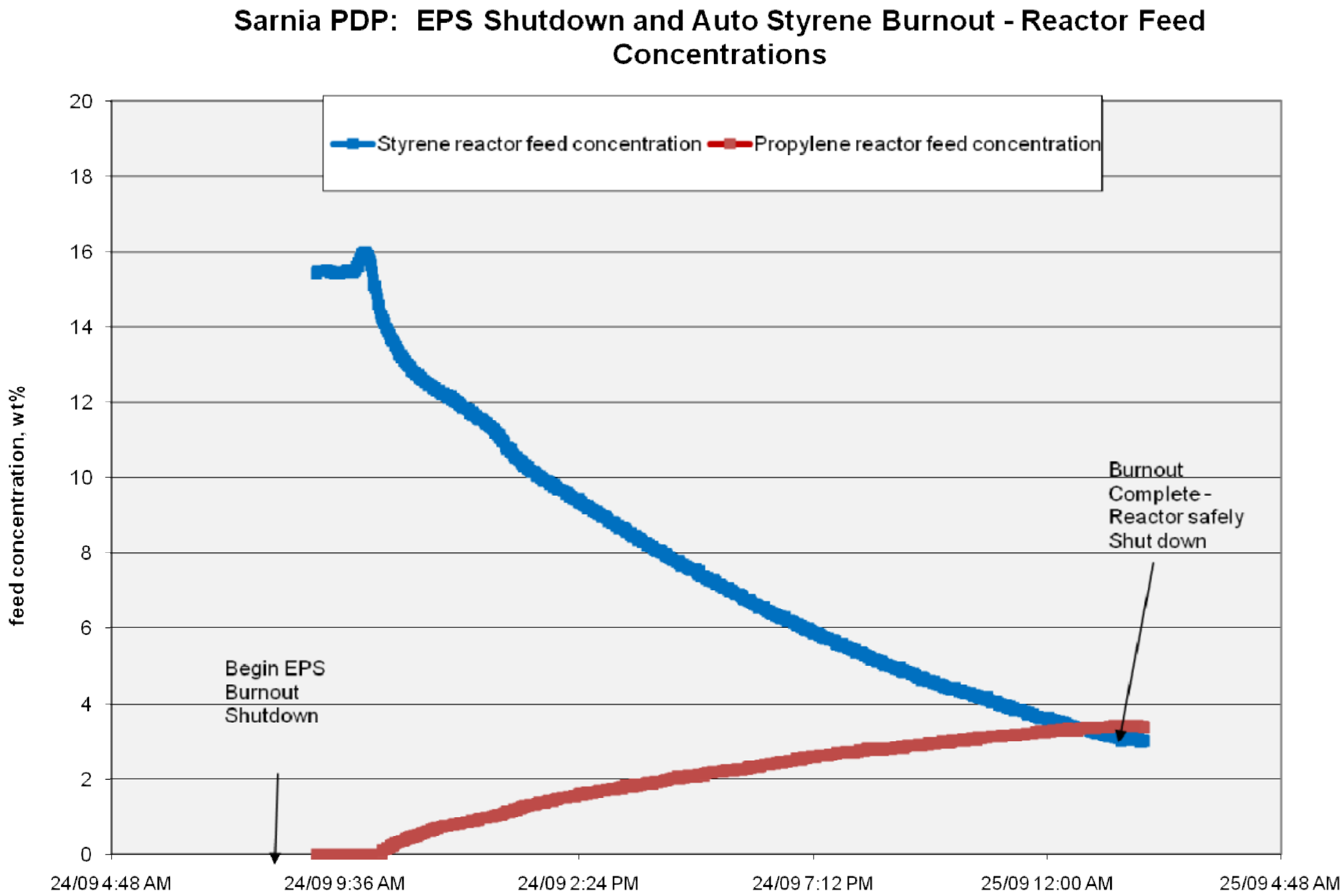
Startup Example – Reactor Concentrations



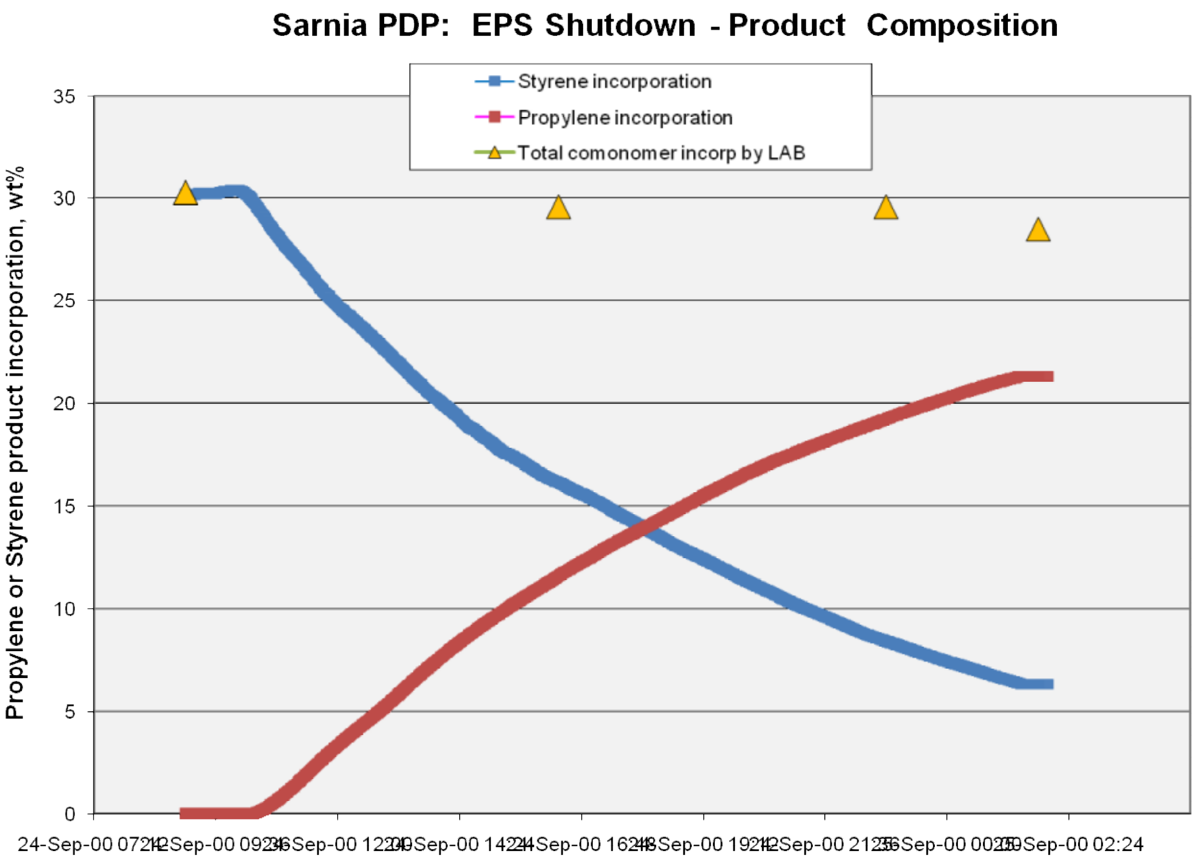
Startup Example – Product Composition



Shutdown Example – Reactor Feeds



Shutdown Example – Product Composition



Conclusions

- Importance of Experimental Design
  - Inefficient Experimentation Wastes Time and Money
  - No Amount of Sophisticated Data Analysis Can Recover Information Not Present in a Dataset
    - The Correct Experimental Design Dictated by Mathematical Structure of Model
    - Carefully Designed Experiments Can Result in Greatly Increased Accuracy

- Practical Value in Reaction Engineering
  - An Accurate Kinetic Model is Available for the Terpolymerization of Ethylene, Styrene, and Propylene
  - A Good Kinetic Model is Critical for Efficiency and Cost-effective Operation at Commercial Scale