

Infineum Experience: Using Advanced Process Modeling to Optimize Chemical Processes

Advanced Process Modeling Forum 2013

Thomas Skourlis

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Performance you can rely on.



Who are we?



- Infineum is one of the World's leaders in the development, manufacture and marketing of petroleum additives for fuels and lubricants.
- Established in January 1999, Infineum is a 50/50 joint venture between ExxonMobil and Shell, bringing their respective Petroleum Additives Divisions together.
- Infineum additive technology is underpinned by a world-wide research and development, manufacturing and supply network.
- Our customers are primarily oil companies and other lubricant and fuel marketers.
- Employing approx. 1600 colleagues world-wide and having an annual revenue in excess of \$2 billion.

What do we do?



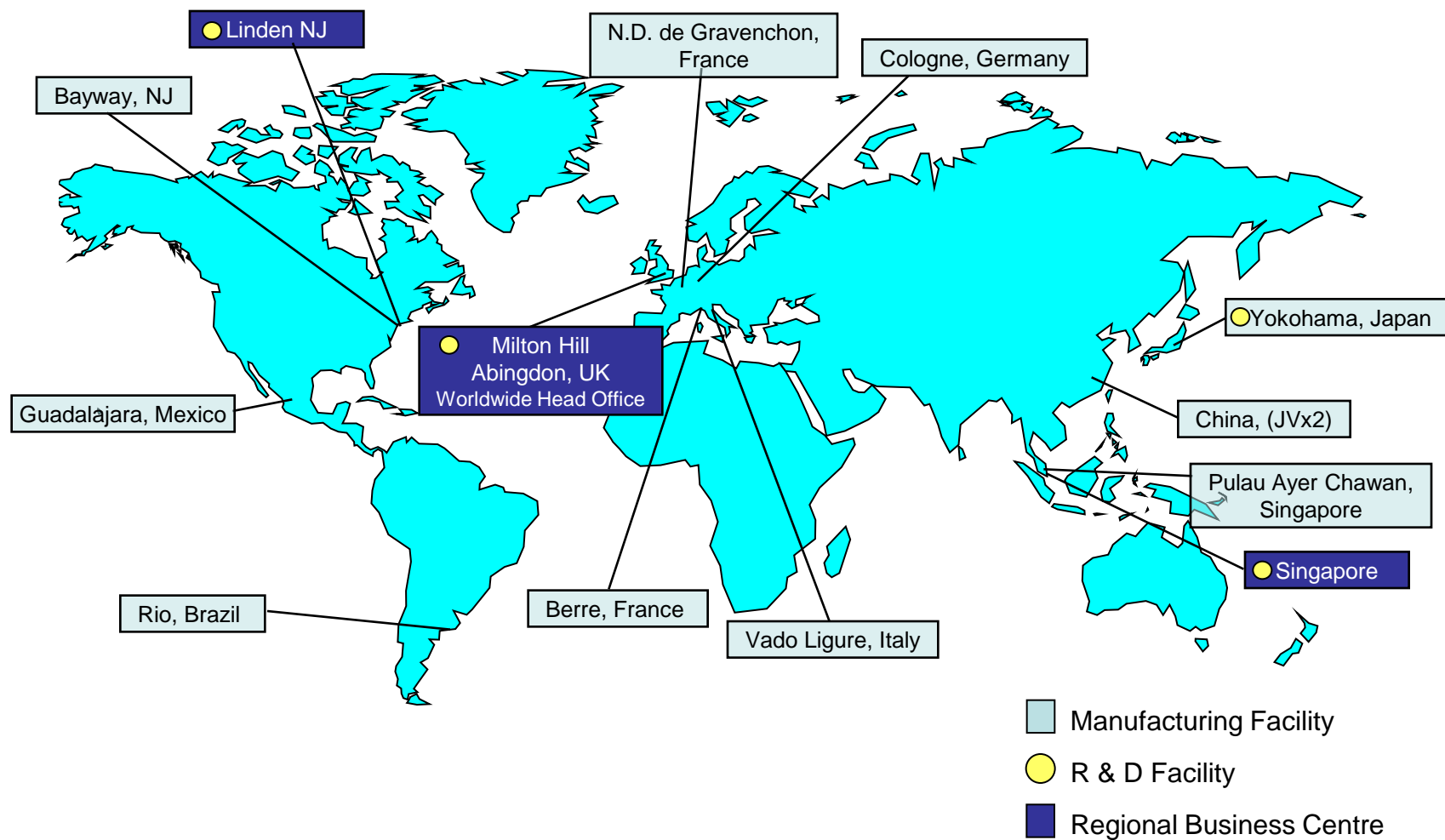
- Infineum develops and manufactures petroleum additives, and markets them globally, in three main product areas:
- Crankcase lubricant additives:
 - Passenger Car Motor Oils; Heavy Duty Diesel Oils; Viscosity Modifiers and Lubricant Flow Improvers
 - Components include: Antifoamants, Demulsifiers, Rust/Corrosion Inhibitors, Antioxidants, Antiwear, Friction Modifiers, Detergents, Dispersants
- Fuel additives:
 - Middle Distillate, Heavy Fuel and Crude Oil Flow Improvers; Corrosion Inhibitors; Combustion Improvers; Lubricity Improvers and Premium Diesel, Gasoline and Heating Oil Additives
- Speciality lubricant additives:
 - Two and Four Stroke Engine Oils; Transmission and Gear Oils; Marine Oils; Railroad Lubricants; Gas Engine Oils and Industrial Products


Infineum in our everyday life

- Our Crankcase additives are in 1 in 3 vehicles on the road
- Our Automatic Transmission Fluid additives are in the fastest growing OEM transmissions
- Our Two-Stroke additives are in 70% of the water cooled small engines in North America
- Our Marine additives (TPEO) are in over 50% of large vessels
- Our Fuel additives treat more than 150 Million tons of diesel fuel/year



Global footprint



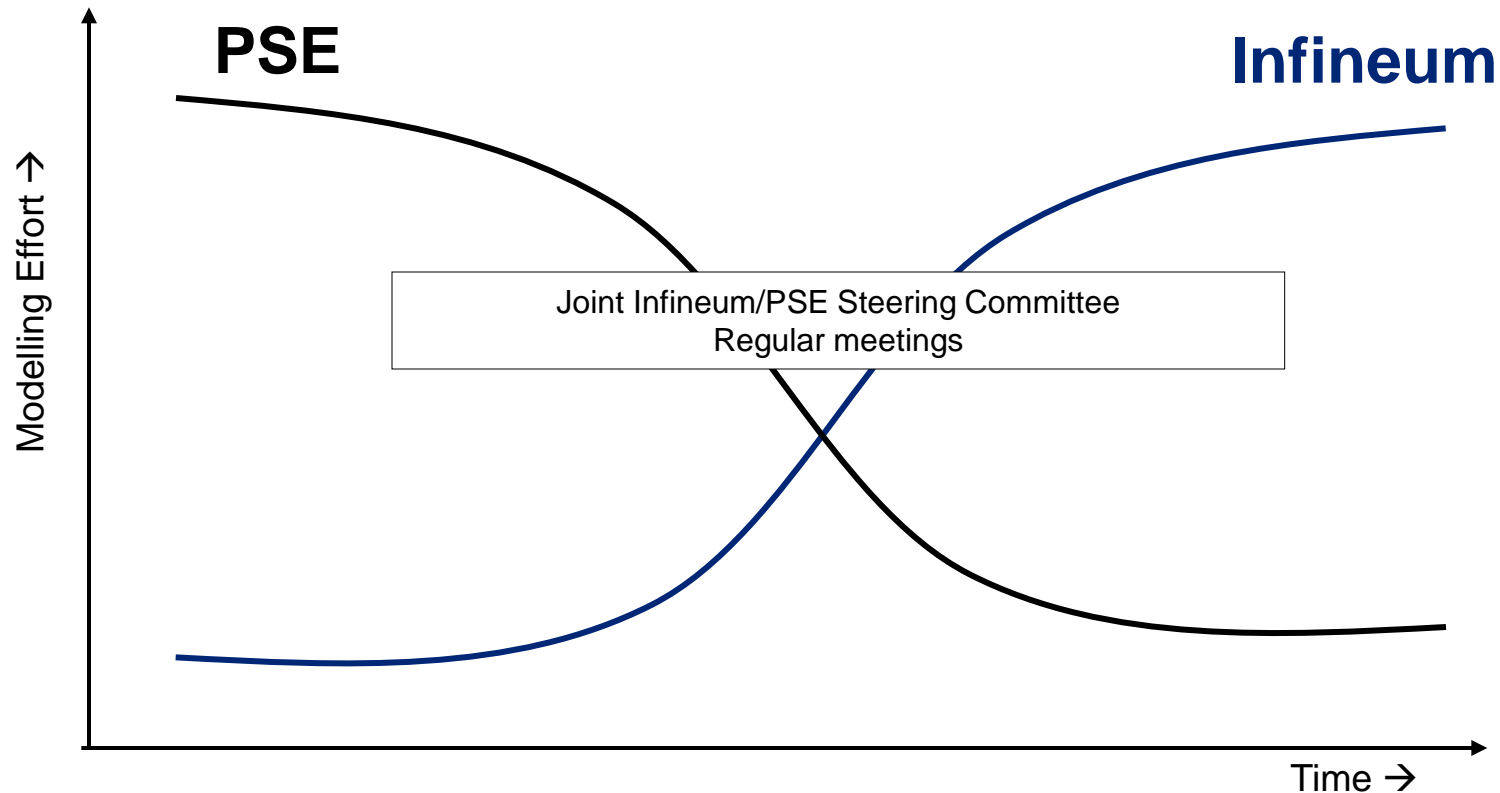
1. **Understanding** process-structure-performance interactions
 - Increased process-structure understanding  Reduced development time new/modified products
2. Existing plant **process optimization**
 - Cycle time reduction
 - Operational improvements:
 - Batch to batch variability reduction by adjusting to raw material variations
 - Improved reactor T control
3. **New plant design** for existing products
 - Shift from batch to continuous processes
4. **Knowledge transfer** tool
 - Learning tool for operators and engineers

Why did we choose g-PROMS



1. Need **dynamic** simulations
 - Majority of Infineum applications (reactions/separations) are batch processes
2. Need flexibility in **user specified** kinetics and mass transfer
 - Very complex kinetic mechanisms
 - Multiple phases present
3. Need an **integrated parameter estimation** and optimization tool
 - Large amounts of data from lab and commercial plant units are available-parameter estimation is challenging
4. Need a tool suitable for **polymerization kinetics**
 - g-PROMS allows user to follow individual species
 - Majority of Infineum products are in the oligomer –low MW polymer range

- Initial Project in 2007-08: Ethylene-Vinyl Acetate (EVA) free radical co-polymerization model developed by PSE
 - Modeling work was done by PSE based on Infineum supplied data
 - Report was used for Infineum plant expansion project
- Based on initial benefits PSE chosen to evaluate further modeling opportunities in 2008-09
 - 37 potential processes evaluated (mostly current processes)
 - Simple esterification model developed and used by Infineum
- 3 processes selected and initiated in 3Q09:
 1. Free Radical Copolymerization
 2. Formaldehyde Based Poly-condensation
 3. Polymer Functionalization
 - PSE led modeling effort with knowledge transfer to Infineum key deliverable of projects and overall relationship
- Initial version and documentation for all 3 models completed by 3Q12



PSE effort during the transition

- modelling project planning & leadership
 - occasional, dedicated, on-site training & software support

PSE residual effort

- software support & on-going training
 - advice on modelling approach for very challenging projects

- **Process/Chemistry understanding:** Gaps in model data requirements... learning what we do not really know
- **Data collection:** Effort required in data collection needs to be integrated into development process (i.e. resource intensive to “redo” experiments)
 - Model forces us to ask questions about mass balance and side reactions previously considered negligible
 - Thermodynamic experiments (no reaction) are required
 - Experiments at conditions on the boundaries of the operating window might be required to be able to quantify side reactions
- **Cross functional engagement:** between chemists-process specialists and modelers critical to success of model development.
 - Mechanisms need to be revisited after initial data and parameter estimation is completed
 - New experiments need to be performed and included in PE

CASE 1: Free Radical Copolymer Process

Process Optimization Based on
Process-Impurities-Structure

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Fumarate – Vinyl Acetate Chemistry

PROCESS:

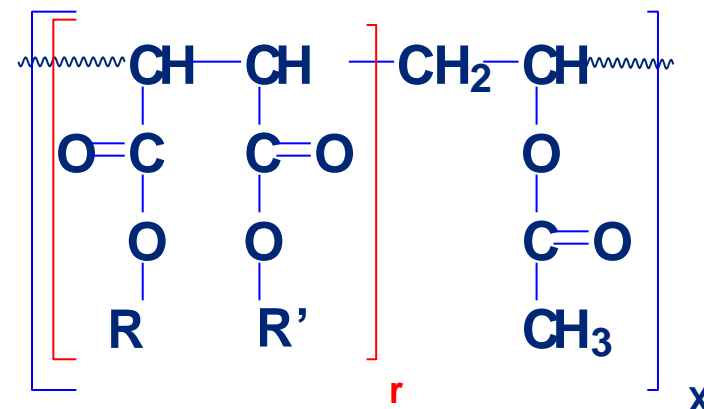
- Free radical polymerization of Vinyl Acetate (VA) & Dialkyl Fumarate (DAF)
- Peroxide initiator

PRODUCT

- Copolymer characteristics

Determined by polymerization process

- Molecular Weight (x) distribution
- DAF conversion
- DAF/VA copolymer ratio (r)



IMPURITIES: Process variability due to impurities from DAF esterification (i.e. reaction between fumaric acid and alcohols):

- Catalyst Residue
- Water
- Alcohol

Process Sequence

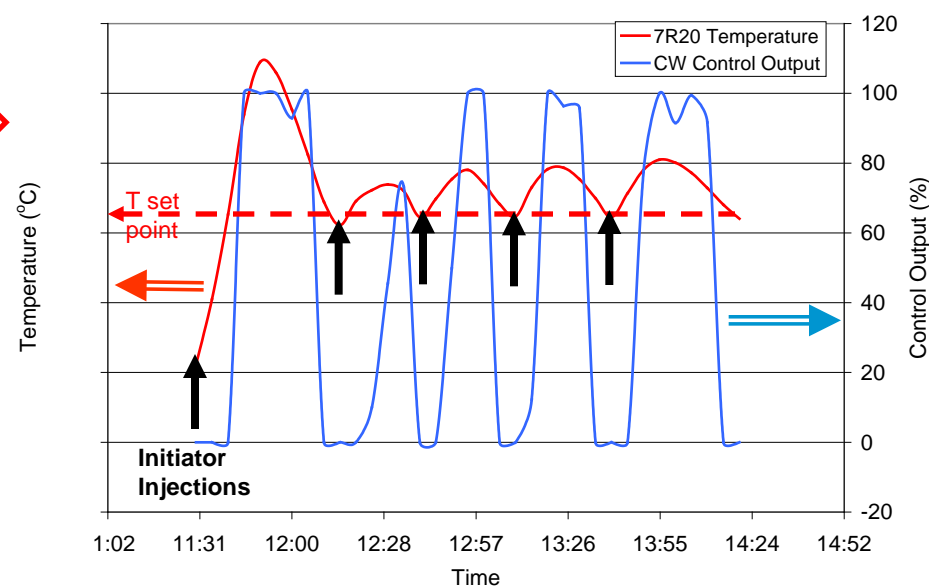
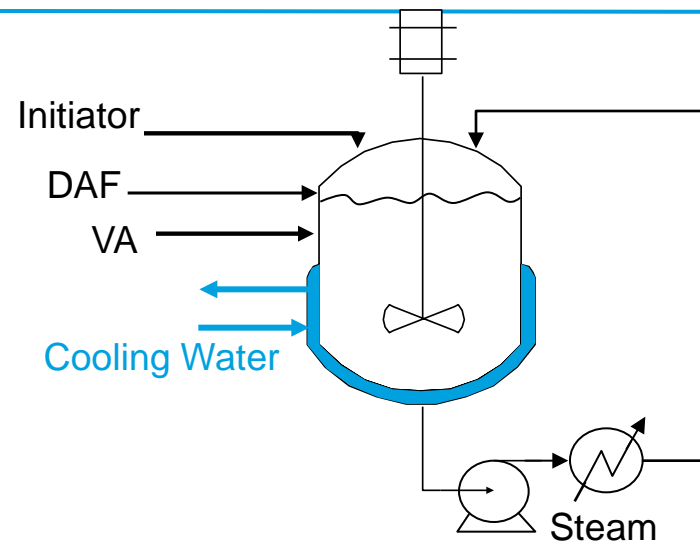
Material Charge

Reactor Heat Up

Polymerization

6 Initiator injections (exotherms)
Cooling water to control T

Increase T to kill initiator (soak)
Reactor strip with N_2 under vacuum

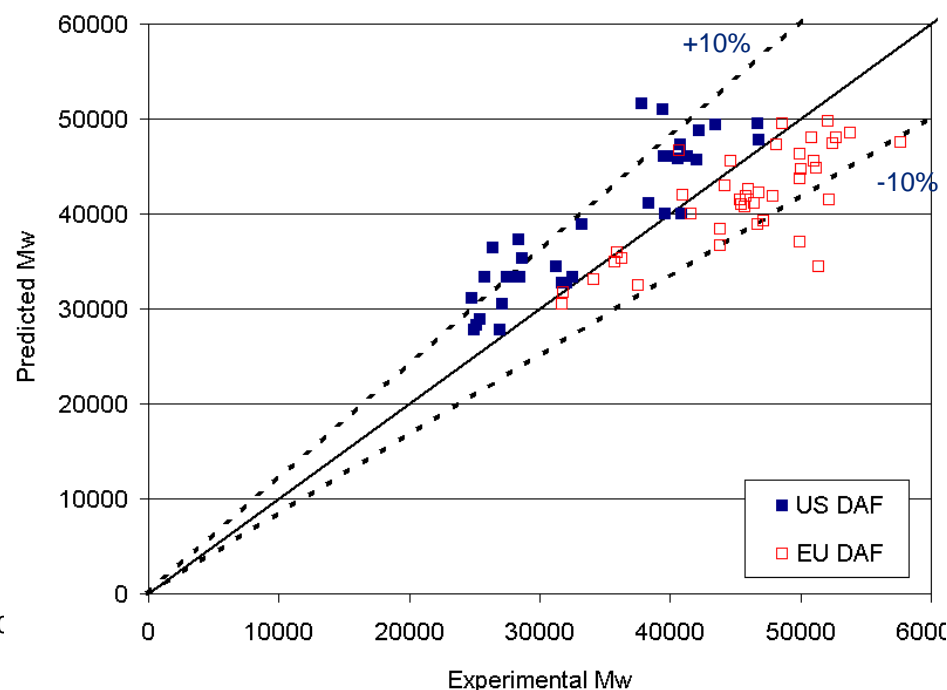
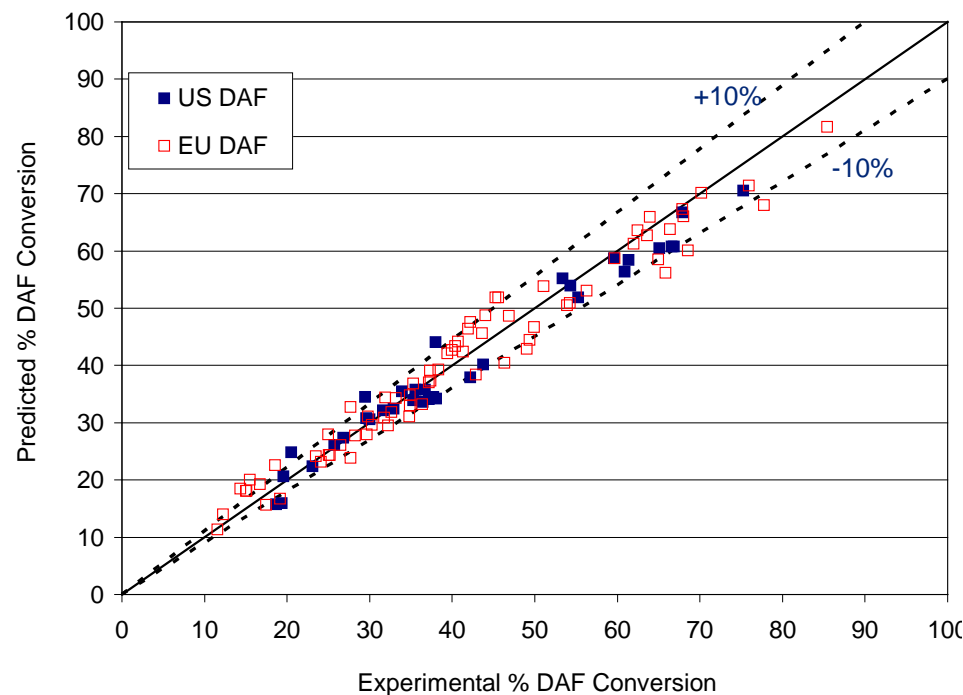


- Kinetic mechanism includes several elementary steps
 - Initiator decomposition
 - Radical initiation
 - Propagation (VA-VA, VA-DAF, DAF-VA, DAF-DAF)
 - Radical termination by combination
 - Radical termination by disproportionation
 - Radical transfer to monomer
 - Radical transfer to (esterification) catalyst and alcohol w/o re-initiation
- Chain transfer mechanisms w/o re-initiation reduce both rate and MW
- Chain transfer w/ re-initiation to monomer or a solvent reduces MW w/o reducing polymerization rate

Isothermal Single Injection Kinetic Data



- Parr reactor used with 3 process parameters varied :
 - Temperature
 - Amount of initiator
 - Monomer charge ratio
- Kinetic data are based on GPC and NMR of intermediate samples



Heat Balance -Validation

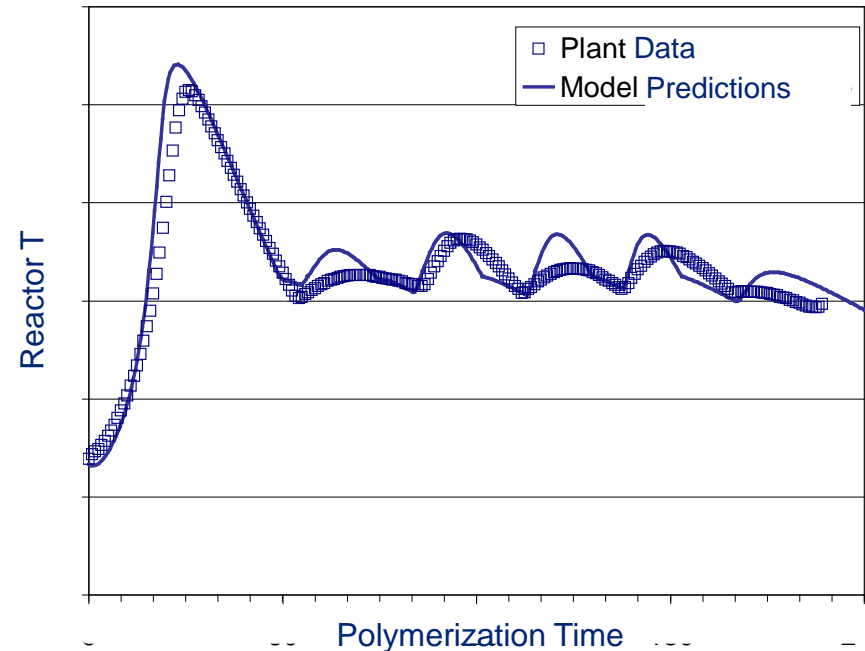
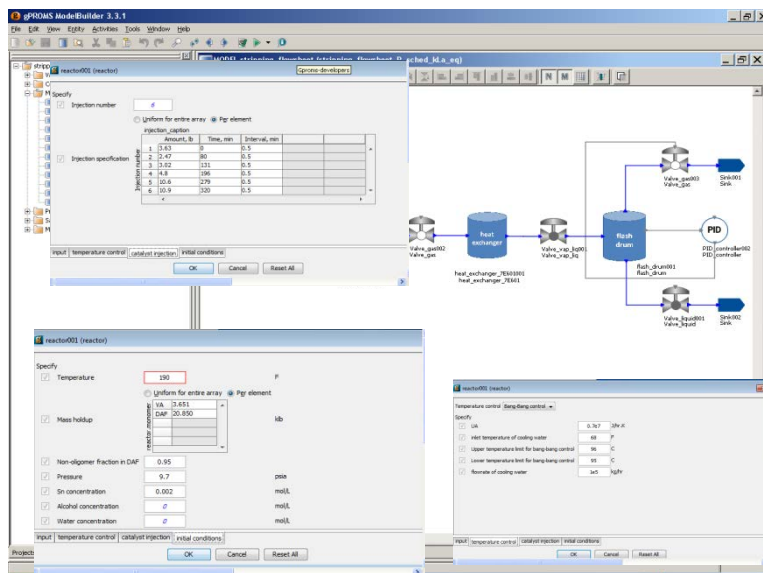
- Heat balance requires: ΔH_{rxn} and heat transfer coefficient UA

$$mc_p \frac{dT}{dt} = V(-\Delta H_{rxn})r_A + UA(T - T_{cw}) + Q_{loss}$$

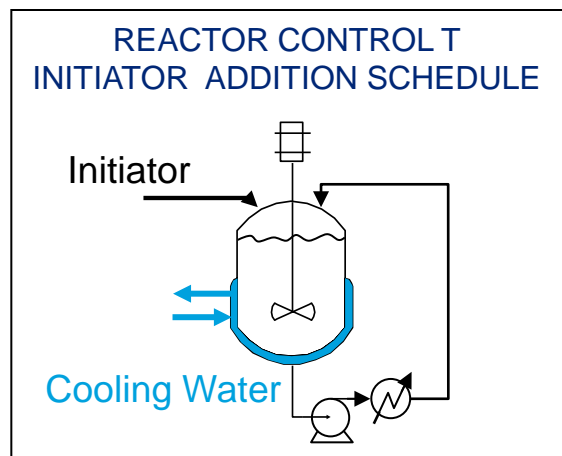
- Calorimetry
- Literature

- Lab kinetics
- Isothermal data

- Correlations
- Fitting of plant T profiles

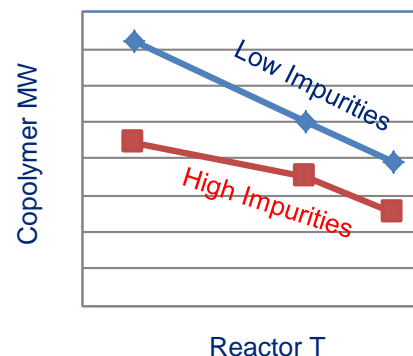
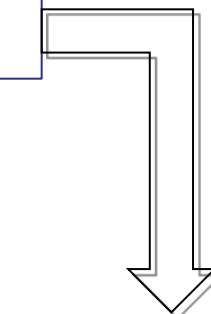
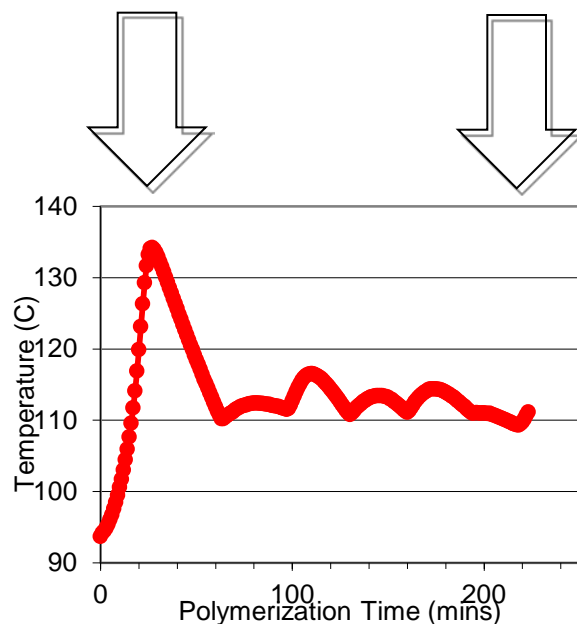


Model Predicted –Impurity/Process Interactions



DAF IMPURITIES

- Esterification Catalyst
- Free Alcohol
- Water



Product
MW
KV100

- Learnings from Kinetics
 - Polymer MW is weak function of amount of initiator
 - MW is strong function of temperature (Higher MW at lower T)
 - Transfer is dominant (monomer, esterification catalyst and alcohol)
- Process Improvement/Optimization
 - Improved reactor T control
 - More isothermal process -T spikes increase product variability
 - Enhanced heat transfer or modified control strategy
 - Modified Initiator addition profile
 - Initiator schedules can be optimized for desired conversion and MW
 - DAF variability response strategy
 - Initiator addition & T control can be used to respond to monomer variability
 - Reduction in cycle time
 - Stripping section of the model couples VA conversion and mass transfer limited stripping

CASE 2: Formaldehyde Based Poly-condensation Process

Design of a new Continuous Process based on Batch Data

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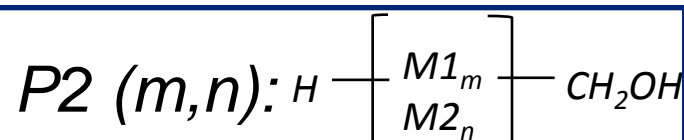
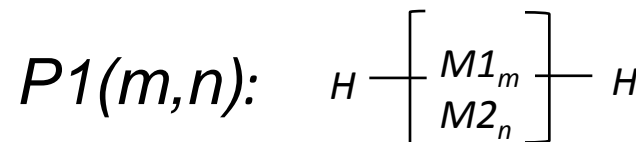
- Semi-Batch reaction between monomer solution in toluene & formaldehyde
- Water generated by reaction removed via Dean-Stark trap-toluene refluxed
- Two types of bridges can be formed between monomer units:
 - Methylene bridge (Formaldehyde based acid catalyzed poly-condensation)
 - Acetal bridge (formed via reversible reaction)

- **2 basic monomer units used:**

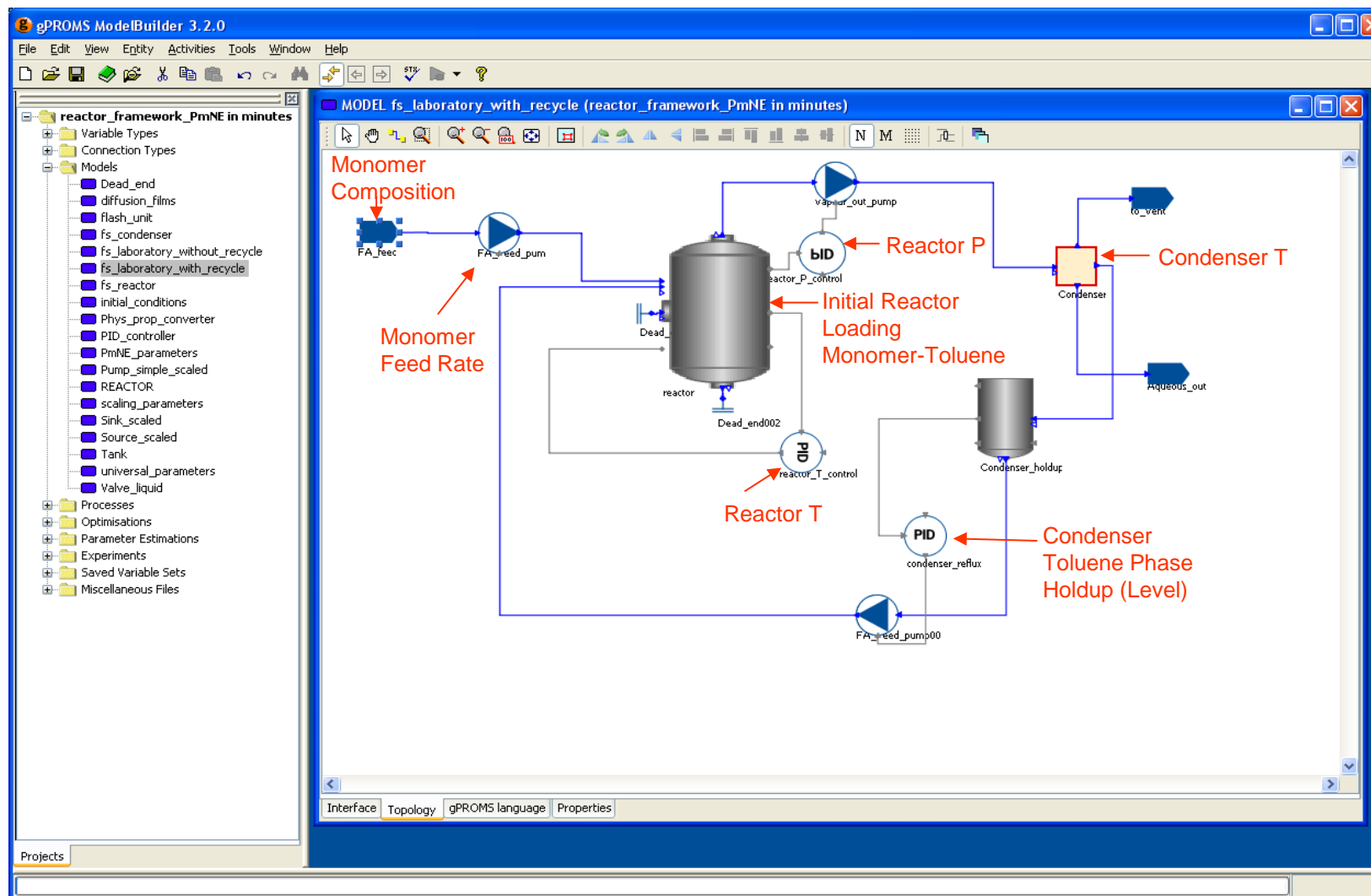
Methylene bridge
Monomer M1

Acetal bridge
Monomer M2

- 2 types of polymer arrays were followed



Batch Flow Sheet



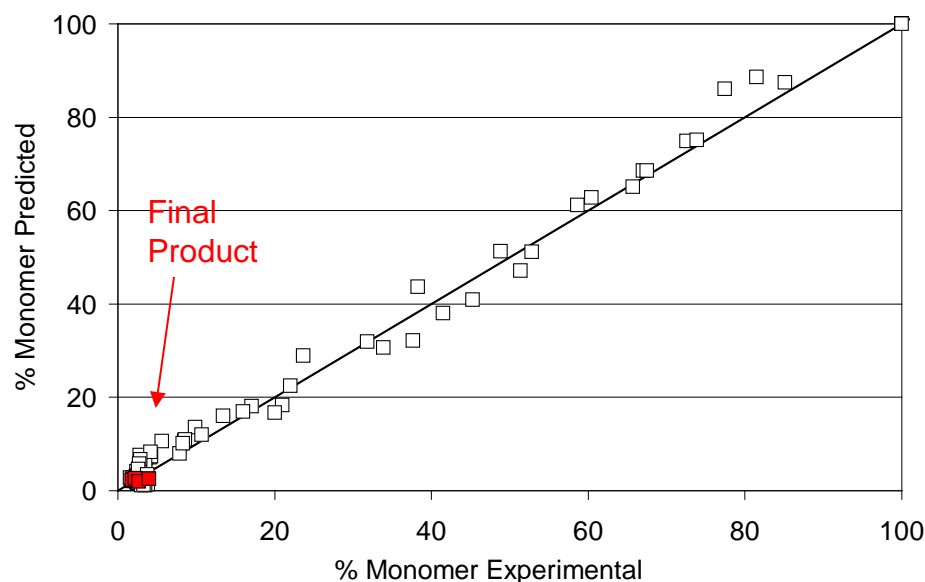
- Polymer Structure Captured By the Model (as a function of time):
 - MW info from GPC fingerprint: Up to 4 Unit Oligomers, MWD
 - Acetal to methylene bridge ratio from NMR
- Kinetic Mechanisms with Arrhenius T dependence:
 - Formaldehyde addition
 - Methylene bridge formation
 - Acetal bridge formation/hydrolysis
- Kinetic Data Collection:
 - 9 Experiments were designed varying T and formaldehyde addition rate
 - Samples were taken every 20 minutes and analyzed via GPC and NMR
- Thermodynamic Data Collection
 - UNIQUAC activity coefficient model- Needed interaction parameters for monomer
 - Separate experiment w/o catalyst provided interaction parameters: to predict water solubility in reactor and aqueous phase production

Parameter Estimation Results: Monomer and MW

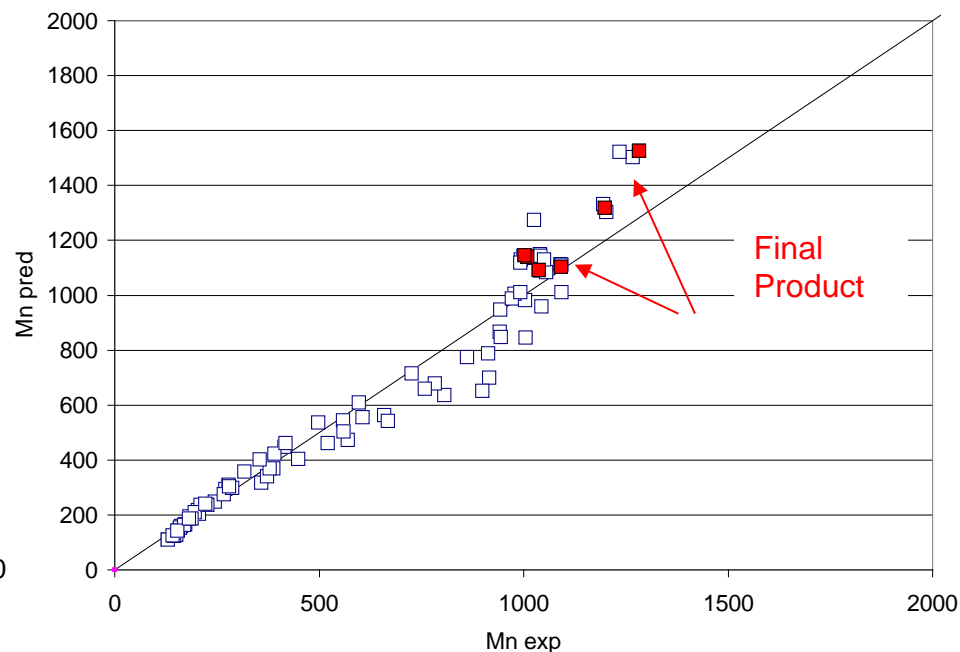


- Intermediate samples provide insight in the reaction mechanism and product structure evolution
- Monomer Conversion and MW fits well across a wide range

Unreacted Monomer Amount Parity Plot

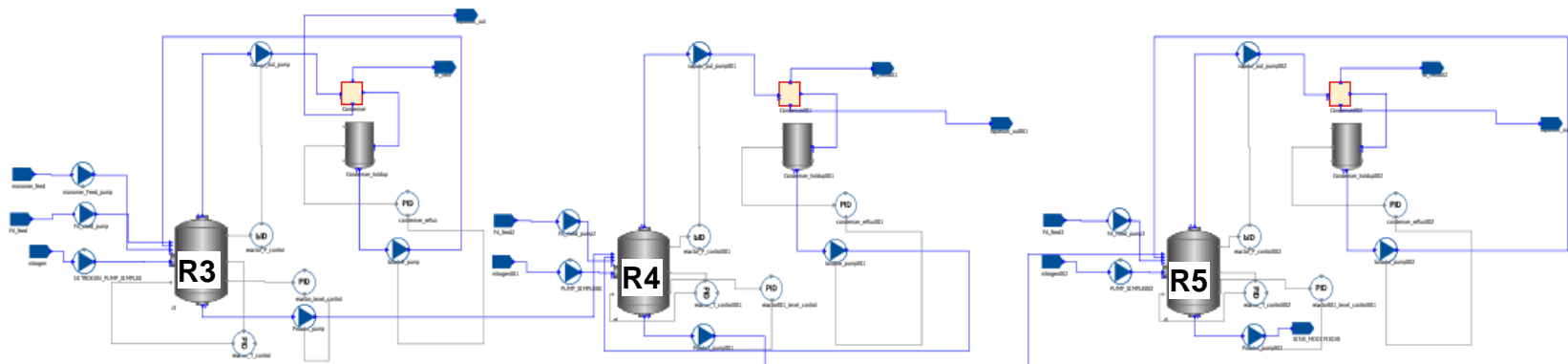


Mn Parity Plot

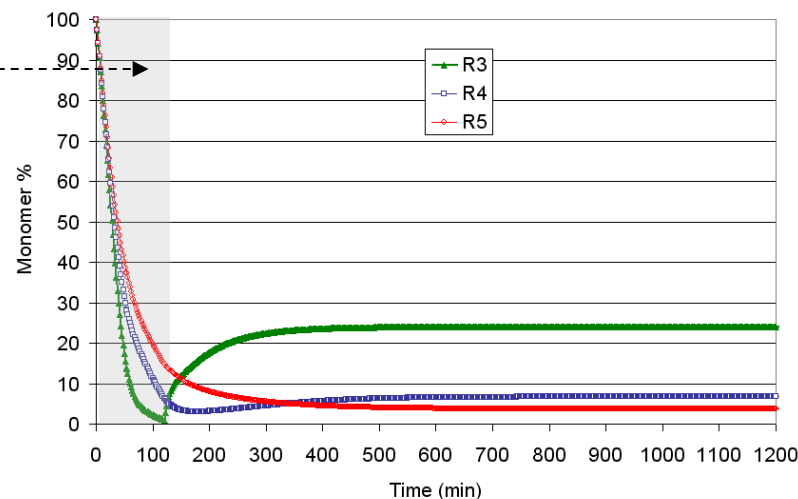


- Process was evaluated for continuous operation based on following perceived advantages:
 - Process intensification potential: smaller volume equipment
 - Reduced plant footprint
 - Reduced capital cost of (smaller) equipment
 - Improved product quality through reduced inter-batch variation
- Design was based on series of CSTRs to replace existing Batch Process
- Model was modified to account for inlet and outlet streams. This allowed for combinations of CSTRs in series
- g-PROMS simulation advantages at the early design stage:
 - 2-3 Days lab work replaced by ½ hour of simulation
 - Dozens of “simulation experiments” were done in just a few days
 - New concepts like higher pressure and 5-6 CSTRs were tried

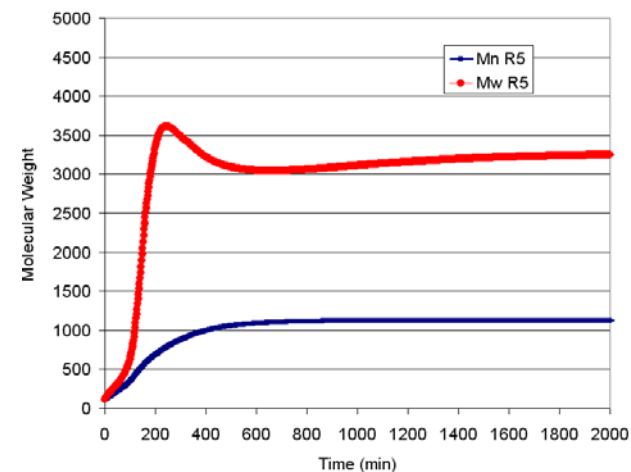
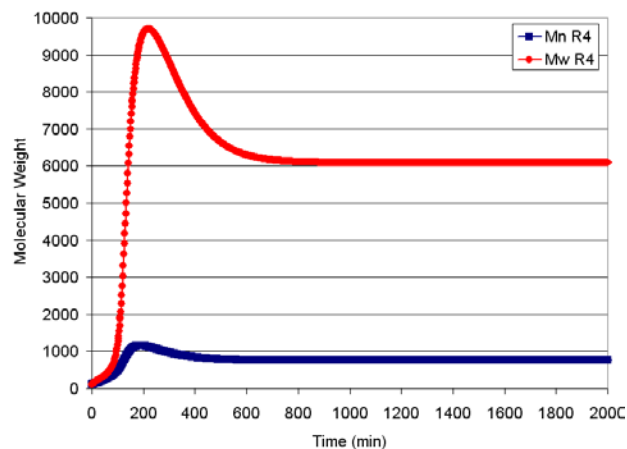
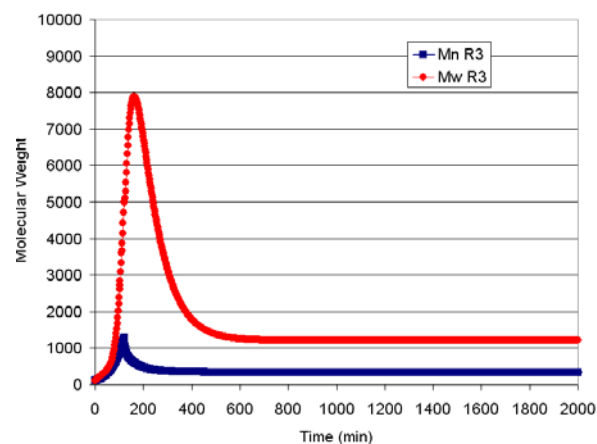
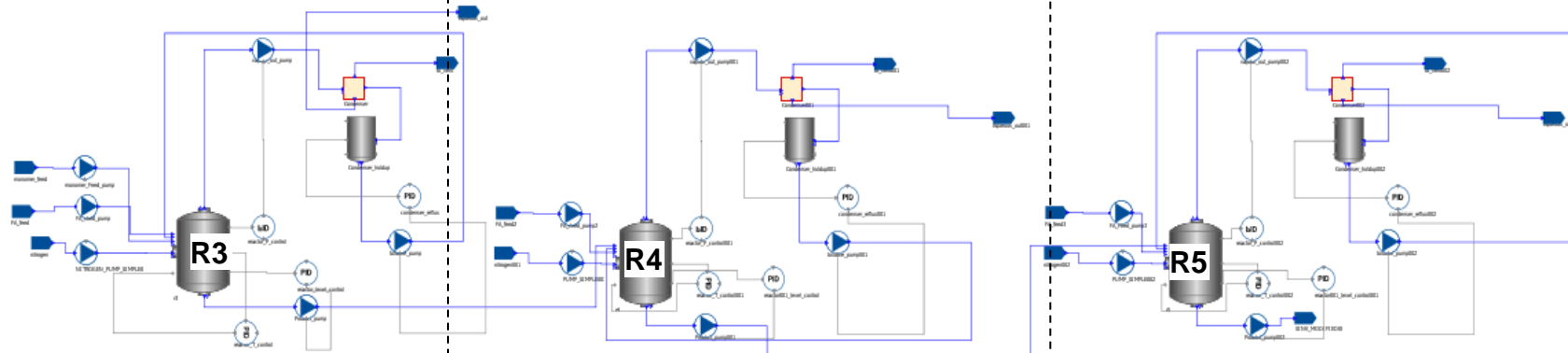
3 CSTR in Series g-PROMS Model



- Monomer+ Toluene + Catalyst Fed to R3
- Formalin added to R3 and R4
- Startup (to build polymer inventory) followed by continuous operation



MWD in Continuous CSTR System



- Kinetic/Thermodynamic learnings:
 - Closing the formaldehyde mass balance and evaluating water solubility allowed us to understand the mechanism especially for the acetal bridge
 - Fitting the oligomer fingerprint as well as the average MW showed gaps in our understanding and need for more data and improved analyticals
 - Data Collection should include thermodynamic (equilibrium) data
 - Taking samples can affect the kinetics so sampling should be included in PE
- Preliminary design results
 - Continuous operation results in increased polydispersity (M_w/M_n)
 - Reducing final product PDI can be a challenge- Model shows possible solutions
 - High residence time and/or T and P in last reactor
 - More CSTRs
 - Modeling results can provide baseline for new products (i.e. different monomer-formaldehyde chemistry)

CASE 3: Poly-Iso-Butylene Functionalization Reaction

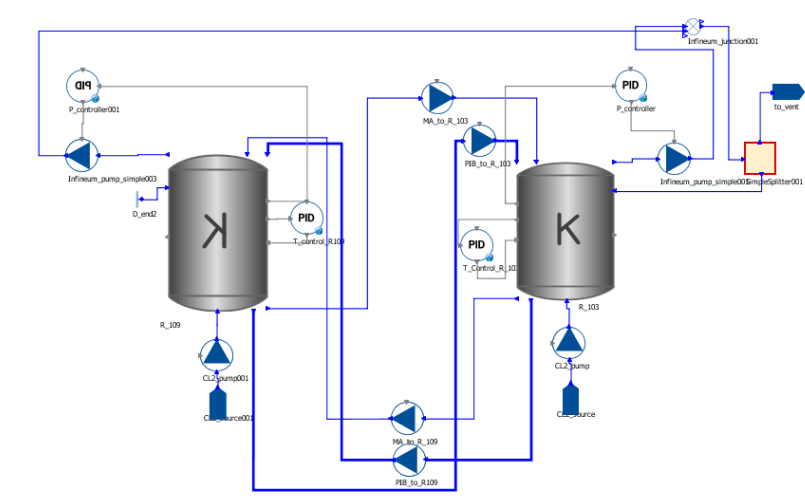
Process Optimization

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Problem Description/Motivation

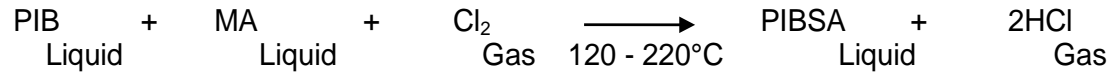


- Functionilization reaction between Poly-Iso-Butylene (PIB) and Maleic Anhydride (MA) using chlorine gas to form functionalized PIB (PIBSA)
- Existing commercial (Combo) reactor overhead condenser replacement: Need understanding of how the chemistry and process impact on the condenser loading
- Model needs to predict product characteristics as a function of processing conditions including raw material charging strategies
 - Degree of functionality
 - Active ingredient %
 - Reactor off gas flowrates
- Model should predict condenser deltaP as a function of process conditions



How did we model this Process

- Overall Reaction



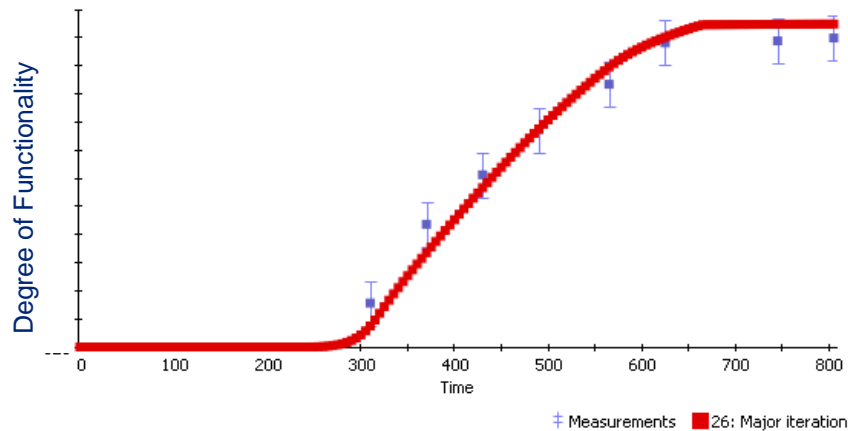
- Modeling required 129 individual reactions/ 12 groups assumed at same reactivity
- Rate equations for all reactions

$$r_j = k_j \pi C_{i,j}^n$$

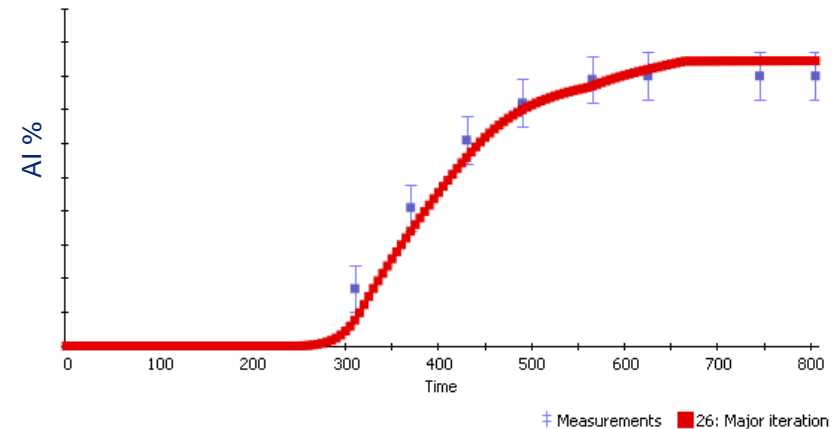
- Reaction orders all stoichiometries (n=1)
- 3-phase Vapor-Liquid-Liquid (VLLE) System
- Non-equilibrium mass transfer controlled three phase system
- Thermodynamic model
 - PSRK EOS (Predictive Sloan-Rednick-Kwong Equation of State)
 - UNIFAC Group Contribution Methods

- Lab Experiments
 - Intended to separate the kinetics and mass transfer effects
- Plant trials at 7 conditions: intermediate samples used for parameter estimation
 - 27 total parameters including kinetic constants and mass transfer coefficient

PIBSA Functionality



Active Ingredient %



- Kinetic Understanding
 - Critical aspects of the kinetics captured but modifications had to be made
 - Balance competing olefin reaction and polymer side-reaction
 - Added side reaction right product functionality
 - Mechanism for closure of chlorine balance had to be added
- Model Used for Commercial Reactor Replacements
 - Predict reactor offgas rates
 - Information used by exchanger vendor to size/design equipment
- Process Optimizations
 - Manipulating temperature profiles and chlorination rates via simulations
 - Predict impact on off gas rates and residual chlorine levels
 - Test potential cycle time reductions

- 3 Models have been deployed and are available to plant engineers
- Cultural shift required to utilize the models to their full potential
- Current emphasis on in-house new model development using PSE consultancy and building on 3 original models
- Current Infineum modeling team:
 - 3 existing modelers- 1 new member
 - 10 other users
- 4 new models for existing and new processes are being developed:
 - Modified monomer condensation polymerization model
 - Phenol alkylation model
 - Cationic polymerization model
 - Modified (Thermal) PIB functionalization model
- Existing process unit (PML) library and thermodynamic database are being re-used for new models

Infineum Modelers: Mike Minotti, Kwok Tse, Claire Fitter, Alasdair Graham

PSE Consultants: Praveen Lawrence, Diogo Narciso, Gang Wang, Simon Leyland, Apostolos Giovanoglou

Other Infineum Contributors/Users: David Birse, Jim Grundy, Bogdan Barboiu, Mark Ossowski, Jun Hua, Tushar Bera, Jack Emert, Ramdas Venkatram, Eric Blythe, Bob Kleist

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