Model-based design, scale-up, and operational optimization of fixed bed catalytic reactors and processes

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Introduction to PSE
HISTORY: FROM RESEARCH TO INDUSTRY

1989 – 1997

100s of person-years of R&D with industry
Simulation & modeling, optimization, numerical solutions techniques, supply chain

Company ‘spun out’
Acquires technology
Private, independent company incorporated in UK

1997

Advanced Process Modelling

- Software and services (60:40)
- Major process industry focus – all sectors
- Strong R&D reinvestment
- ~100 people worldwide

2013

USA London HQ Germany Korea Japan

Royal Academy MacRobert Award for Engineering Innovation
UK’s highest engineering award
PSE products & services

1a General process modeling tools

- gPROMS Modeling & solution platform
- ModelBuilder

1b Advanced model libraries

1c Engineering solutions

- gFLARE Safety
- gFUELCELL Fuel cell & hydrogen
- gSOLIDS Solids processes
- gCRYSTAL Crystallisation

1d Advanced thermodynamics

2 Consultancy & services

Process technology & services

General
- Custom Model Development
- Process Design/Optimization

Process-specific
- Safety studies for Oil & Gas Industry
Topic of this year’s forum:

Modeling and simulation of heterogeneous catalytic processes
1. **Scale-up**
   - Laboratory → Pilot → Commercial Plant
   - Maintenance of performance over scales
   - Cost efficiency in investment and operation

2. **Thermal stability** – management of hot spots
   - Adjustment of catalytic bed properties – length, activity, shape of particles, etc
   - Design of cooling system

3. **Catalyst lifetime**
   - Management of catalyst de-activation over operational cycle
All models are wrong

...but some are useful

Characteristics of a useful model for process design

1. Model has the right level of detail needed to simulate key system responses

2. Model parameters are fitted to experimental data

3. Model predictions are accurate enough to support optimization-based process design

4. Model is suitable for scale-up: predicts responses seen in large scale equipment
The Advanced Process Modeling Approach: 4 steps

1. Advanced Process Model with all physics relevant to problem of interest
2. Model-targeted Experimentation + Parameter Estimation
3. Optimization-Based Design
4. Final Adjustments to Equipment Design
The Advanced Process Modeling Approach: Step 1

1. Advanced Process Model with all physics relevant to problem of interest
**Key phenomena: Mass transport and reaction**

- Catalyst pellets/ inert
- Multicomponent solid-fluid mass transfer
- Intra-pore convection
- Multicomponent intra-pore diffusion
- Axial/radial convection in tube-side fluid
- Radial dispersion
- Tube wall
- Thermowell
- Radial dispersion
- Catalyst pellet
- Catalytic reaction on pore surface

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Core model: transport and reaction in catalytic pellets

\[ \nabla N_i = \sum_{k=1}^{NR} v_{ij} r_j \]

\[ -\frac{1}{RT} \nabla p_i = \sum_{j=1}^{NC} x_j N_i - x_i N_j \frac{\varepsilon}{\tau} D_{ij} + \frac{N_i}{D_{iK}} \]

Implemented in spherical or cylindrical coordinates:

- Different particle shapes
- Solid or hollow (for cylinders)
- With or without inert cores
Key phenomena: Heat transfer

- Convective heat transfer in coolant
- Heat transfer between packed bed and wall
- Radial conduction in tube walls
- Heat transfer between tube and coolant
- Radial heat conduction in packed bed
- Axial convective heat transfer in fluid
- Heat transfer between solid and fluid
- Energy carried by solid-fluid diffusive mass transfer
- Intra-pellet heat conduction
FBCR – Heat removal in a tubular fixed bed

Axial & radial variation of bed temperature

Temperatures from center of bed to wall

Effective bed conductivity
Heat transfer coefficient at the bed-wall boundary
Wall-coolant heat transfer coefficient

Distance from the inlet [m]
Example: PSE’s Advanced Model Library for Fixed Bed Catalytic Reactors
Library contents: Axial-flow catalytic bed reactors

- Catalyst Pellet Sections
- Inert Sections
Library contents: Shell-side models

- Fixed coolant
- Cooling jacket
- Multitubular cooling compartment
- Boiling water cooling
Additional building blocks

- Radial flow reactor sections

- Heat integrated annular sections
Assembly of components into reactor model

- Inert packing
- Catalyst/inert ratio #1
- Catalyst/inert ratio #2
- Baffles
- Inert packing
The Advanced Process Modeling Approach: Step 2

1. Advanced Process Model with all physics relevant to problem of interest
2. Model-targeted Experimentation + Parameter Estimation
3.  
4.
Model Validation

Ensuring predictive accuracy through model-targeted experimentation
The purpose of the experiments is not to predict the behaviour of the commercial-sized equipment (that is the job of the validated model).

The objective of the experiments is to find the values of unknown model parameters, minimizing the uncertainty in these values.

**Model-targeted experimentation**
Model parameters *not* derived from first principles

1. **Kinetic parameters** (due to variations in catalyst properties)
   - reaction pre-exponential constants and activation energies
   - reaction orders
   - adsorption constants and heats of adsorption
     - for strongly adsorbing species
   - deactivation model parameters

2. **Bed properties** (due to deviations from ideal of perfectly spherical particles of identical size)
   - coefficients in Ergun equation for pressure drop
   - coefficients in heat transfer parameter correlations
     - bed effective radial conductivity (static and dynamic)
     - bed-wall heat transfer coefficient (static and dynamic)

3. **Particle geometric properties**
   - tortuosity
Reactor model validation
Two-step experimental procedure (ideal)

n-pellet experiment for kinetics identification

Sampling tubes for internal gas composition

Hollow cylinder pellets

Near-isothermal operation

Fixed bed (commercial pellets)

Multiple thermocouples directly in bed

Jacketed tube

Single-tube experiment for heat transfer characterization
Step 1 – Reaction kinetics

1. Laboratory data

2. Lab reactor model

3. Processing of experimental data to evaluate the model parameters

4. Prediction of composition profiles in lab scale experimental reactor

5. Evaluated parameters for the reaction kinetics model
Step 2 – Heat transfer parameters

1. Pilot plant data

2. Processing the experimental data to evaluate the model parameters

3. Parameter estimation tool

4. Evaluation of parameters of the heat transfer model

Prediction of temperature profiles in pilot scale experimental reactor
Lessons from experience: Kinetic parameters (1/2)

- Search literature for kinetic expressions
- Langmuir-Hinshelwood is a good starting point
- Check for chemical equilibrium limitations
- Break correlation between pre-exponential constant and activation energy:

  \[ k_1 = A_1 \exp \left( -\frac{E_1}{RT} \right) \]  

  \[ k_1 = k_{1,\text{ref}} \exp \left( -\frac{E_1}{R} \left[ \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right] \right) \]

- Break correlation between rate constants and adsorption constants:

  \[ r_1 = \frac{k_1 K_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2} \]  

  \[ r_1 = \frac{k'_1 P_A P_B}{\left( \frac{1}{K_A} + P_A + K_{B:A} P_B + K_{C:A} P_C \right)^2} \]
Lessons from experience: Kinetic parameters (2/2)

- Vary temperature, pressure, feed composition
- Include experiments at low conversion
- Perform experiments with co-feed of products that participate in secondary reactions

\[
\begin{align*}
A & \xrightarrow{O_2} B \xrightarrow{2O_2} C \\
3O_2 & \xrightarrow{} \end{align*}
\]

- Perform experiments with co-feed of strongly adsorbing by-products
- Measure temperature at several positions along the catalyst bed
- Characterize carefully the experimental error in outlet composition measurements
Lessons from experience: Bed properties

- Vary gas velocity (to discriminate between static and dynamic contributions)
- Use tubes of different size (to discriminate between bed-wall heat transfer and radial conductivity contributions)
- Cooling jackets preferable to clam shells or electric tape
- Coolant flow rate should be high enough to yield turbulent flow
Lessons from experience: particle properties

- Use reliable laboratory to characterize particle properties
  - Particle size distribution
  - Pore size distribution
  - Porosity

- Conduct experiments with particles of different size to adjust tortuosity factor
Example: Management of catalyst deactivation in Methanol production process
Enhanced methods optimize ownership costs for catalysts

Novel model-based innovation techniques enable simultaneous optimization of catalyst formulations and operating reactors

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Phase I: determining accurate kinetics

■ **Step 1:** Run experiments
  - gradient-free recycle reactor system (Berty reactor)
  - total of 70 steady-state experiments

■ **Step 2:** Validate
  - use model of lab-scale reactor system to obtain accurate kinetic parameters
  - 4 different kinetic models analysed for suitability

Berty reactor flowsheet

Typical parity plot for validated data
Phase II: model the commercial reactor

Megamethanol® process: 2 coupled reactors

Reactor 1: Catalyst inside tubes, cooled by boiling water
Reactor 2: Catalyst in shell side, cooled by process deed
Results: catalyst deactivation predictions (dynamic model)

- Accurate prediction of catalyst de-activation with accumulated production for each reactor

Catalyst activity

Accumulated production (over weeks)
Conclusions

Conclusion 1

- Using validated model, catalyst manufacturer could assist the client to maximise production for a given time period until the end of run (within the given framework of plant constraints)

Conclusion 2

- Catalyst manufacturer could use the models and methodology to optimise their catalyst for this client's requirements
The Advanced Process Modeling Approach: Step 3

1. Advanced Process Model with all physics relevant to problem of interest
2. Model-targeted Experimentation + Parameter Estimation
3. Optimization-based design

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Model-based optimization for design & operation
Multitubular reactor – key design variables

- **Tube side**
  - number, diameter, length of tubes
  - number and length of layers
  - catalyst/inert ratio
  - pellet shape & size
  - .......

- **Shell side**
  - number & positioning of cooling circuits
  - number & positioning of baffles
  - coolant flowrate(s)
Multitubular reactor – objectives and constraints

- Minimize capital/operating costs
- Maximize selectivity
- Maximize catalyst life
- Achieve production target
- Keep pressure drop within limits
- Prevent runaway – keep temperature within limits
- Keep reactor dimensions within limits
  - road transport considerations
- Keep shell-side velocities within limits
  - avoid erosion, vibration, fouling
- Prevent formation of undesirable phase
Optimization-based design procedure (1/2)

1. Add equations that relate model variables to performance indicators:

\[ \text{CapCost} = K (n_{\text{tubes}} \times L_{\text{tube}} \times \pi D_{\text{tube}})^n \]

\[ \text{ProdRate} = F_{\text{out}} \times x_{\text{product}} \times 3600 \text{ s/hr} \times \text{Annual Operating Hours} \]

\[ TAP = \text{ProdRate} \times \text{ProdPrice} - \text{Annual Operating Cost} - AF \times \text{CapCost} \]

2. Select decision variables
   - specify initial guesses (e.g. current design)
   - specify allowable range of variation (continuous/discrete)
3. Select constrained variables
   - any variable calculated by the model
   - specify upper and/or lower bound for constrained variable

4. Launch optimization

5. Inspect results.
   - pay attention to Lagrange Multipliers of decision or constrained variables at bounds: estimates of improvement in objective function that could be achieved by relaxing bounds.

6. Adjust bounds if appropriate, and launch optimization again.
Example: Design of Reactor for Production of Commodity Chemical at a U.S. Refinery
Background

- Reaction Network
  \[ A + B \rightarrow I + C \text{ (exothermic)} \]
  \[ I + B \leftrightarrow P + C \text{ (exothermic)} \]
  \[ B + B \leftrightarrow E + C \text{ (exothermic)} \]
  \[ B \rightarrow W \text{ (high temperature)} \]

- Several catalysts available

- Non-isothermal bench-scale experiments at high conversion

- Challenge: design commercial reactor with only 3 weeks of pilot testing

A : Refinery byproduct
B : Purchased raw material
I : Reaction intermediate
C : Reaction byproduct
E : Reaction byproduct
P : Product
W: Waste
PSE’s approach (1/2)

- Literature review
  - Basis for LH rate expressions
  - Identified species absorbed strongly on catalyst surface
- Re-evaluation of small scale experiments using AML:FBCR
- Designed experiments to be carried out in pilot plant
  - Low conversion experiments
  - By-product co-feed experiments
- Data collected for 17 days. Data collected in the first 15 days was used to derive the model.
PSE’s approach (2/2)

- Commercial design through optimization of validated model, including recycling costs:
  - Number of tubes
  - Tube length
  - Tube pitch
  - Tube diameter
  - Number of baffles
  - Baffle cuts
  - Bed lengths
  - Choice of catalyst for each bed
Results

- Commercial reactors built as designed

- Plant started up in 2010.

- Production target met
Example: HPPO process optimisation
Simultaneous design of reactor and separation section
PLANT DESIGN AND ENGINEERING

Improve engineering via whole-plant design optimization

New simulation methods identify cost-effective advantages early

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Hydrogen Peroxide route to Propylene Oxide (HPPO)

- Multitubular reactor
  - exothermic reaction
- Many distillation columns
  - two reactive distillations
  - one azeotropic distillation
- 25 components
  - reactants, solvent, product, byproducts, impurities
- 2 large recycle streams

\[
\text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{-CH-CH}_2 + \text{H}_2\text{O}
\]
49 continuous and discrete decisions

- Too many decisions for trial-and-error simulation!
- Apply model-based optimisation technique: “MIXED INTEGER NONLINEAR OPTIMISATION”
1. Process design meeting all constraints
   - confidence arising from detailed models & formal model validation
   - good basis for Detailed Engineering & Operational Support

2. Large reductions in annualised cost
   - tens of millions of €/year compared to Base Design
   - two columns eliminated entirely
     - €5m/year saved from one column alone

3. Significant operating cost savings from heat integration
   - attractive ROI: payback < 4 months
The Advanced Process Modeling Approach: Step 4

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Hybrid gPROMS/CFD modeling of multitubular reactors
Hybrid CFD / gPROMS - Overview

**CFD (e.g. ANSYS Fluent®)**
- Complex geometries
- Modeling mixing and turbulence key capability
- Spatial domain discretized in $10^5 - 10^6$ cells
- 10’s of variables per cell
  - Practical limit on number of reactions and species

**gPROMS**
- Relatively simple geometries
- Model processes of arbitrary complexity
  - Population balances
  - Large reaction networks
  - Intraparticle resistances
- $10^2 - 10^4$ variables per discretization element

Combination provides predictive capability of performance of industrial-scale unit operations with practical use of computer resources
Comprehensive performance assessment for commercial-scale multitubular reactors

Wall heat transfer coefficient; coolant temperature throughout shell

Heat flux distribution throughout shell via interpolation of representative tubes

Wall heat transfer coefficient; coolant temperature at surface of representative tubes

Heat flux at surface of representative tubes

→ Highest-accuracy predictive model on both tube-and shell sides

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Outline of the reactor geometry (Fluent)
Flow characteristics

Particle tracks

Velocity magnitude [m/s]

coolant inlet

coolant outlet

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Example of multitubular reactor modelling

Temperature profiles across pilot reactor

\[ x = 0 \] plane

\[ z = 1.05 \text{m} \] plane

- Tube/coolant heat transfer coefficient [W/m\(^2\).K]
  - \( \Delta T = 7 \)

- Coolant temperature [K]
  - \( \Delta T = 7 \)

- Tube surface temperature [°C]
  - \( \Delta T = 16 \)

- Tube centre temperature [°C]
  - \( \Delta T = 60 \)
Example:
Debottlenecking of existing partial oxidation reactor
Geometric configuration

Actual reactor drawings used to build the CFD model
• Maximum horizontal temperature difference: 40°C
• This difference is highly dependent on the coolant temperature difference.
• High temperature regions: around the coolant outlet, around the reactor wall.
Performance Difference between Tubes
Tube Center Temperature and Reactant Mass Fraction

- Different Tube Center Temperature profile between tubes
- Different Feed Consumption behavior in the middle of the tubes
- But similar conversion of feed at the end of tubes
Debottlenecking example – key results

1. Combined CFD/gPROMS model identified tubes prone to high temperatures
   – Improved placement of thermocouples

2. Combined model used to study relationship between feed composition/rate and maximum temperature variations among tubes

3. Combined model allowed to find operating point that increased production while keeping all tube temperatures within safety limits
Closing remarks
1. Model-based design, scale-up, and operational optimization of fixed bed catalytic reactors and processes is being applied in industry today

2. Applications include: catalyst pellet design, reactor design, whole process design, optimization of operation throughout catalyst deactivation cycle

3. Necessary models and modeling platforms are available as commercial, “off the shelf” software
Thank you!