APM 2013

The Advanced Process Modeling Forum

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Use of APM for Design and Scale-Up of Multitubular Fixed Bed Catalytic Reactors

From lab to commercial scale

Alejandro Cano – Head of Consulting

All models are wrong

…but some are useful

George E.P. Box, *Empirical Model-Building and Response Surfaces*, 1987

Key engineering problems

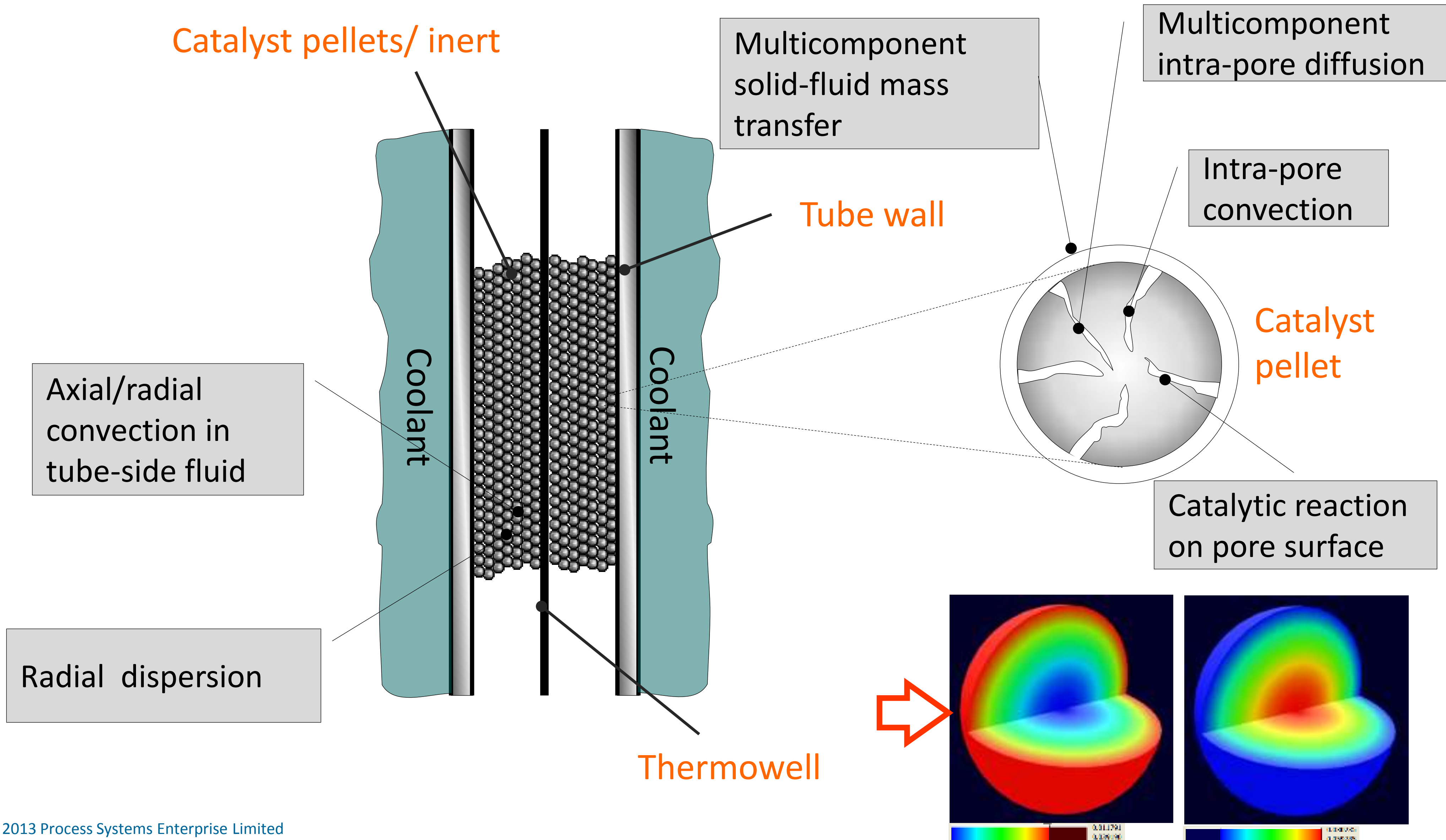
1. **Scale-up**
   - Laboratory → Pilot → Commercial Plant
   - Maintenance of performance over scales
   - Cost efficiency in investment and operation
2. **Thermal stability – elimination of hot spots**
   - adjustment of catalytic bed properties – length, activity, shape of particles, etc
   - design of cooling system
3. **Catalyst lifetime**
   - Management of catalyst de-activation over operational cycle

The Advanced Process Modeling Approach: 4 Steps

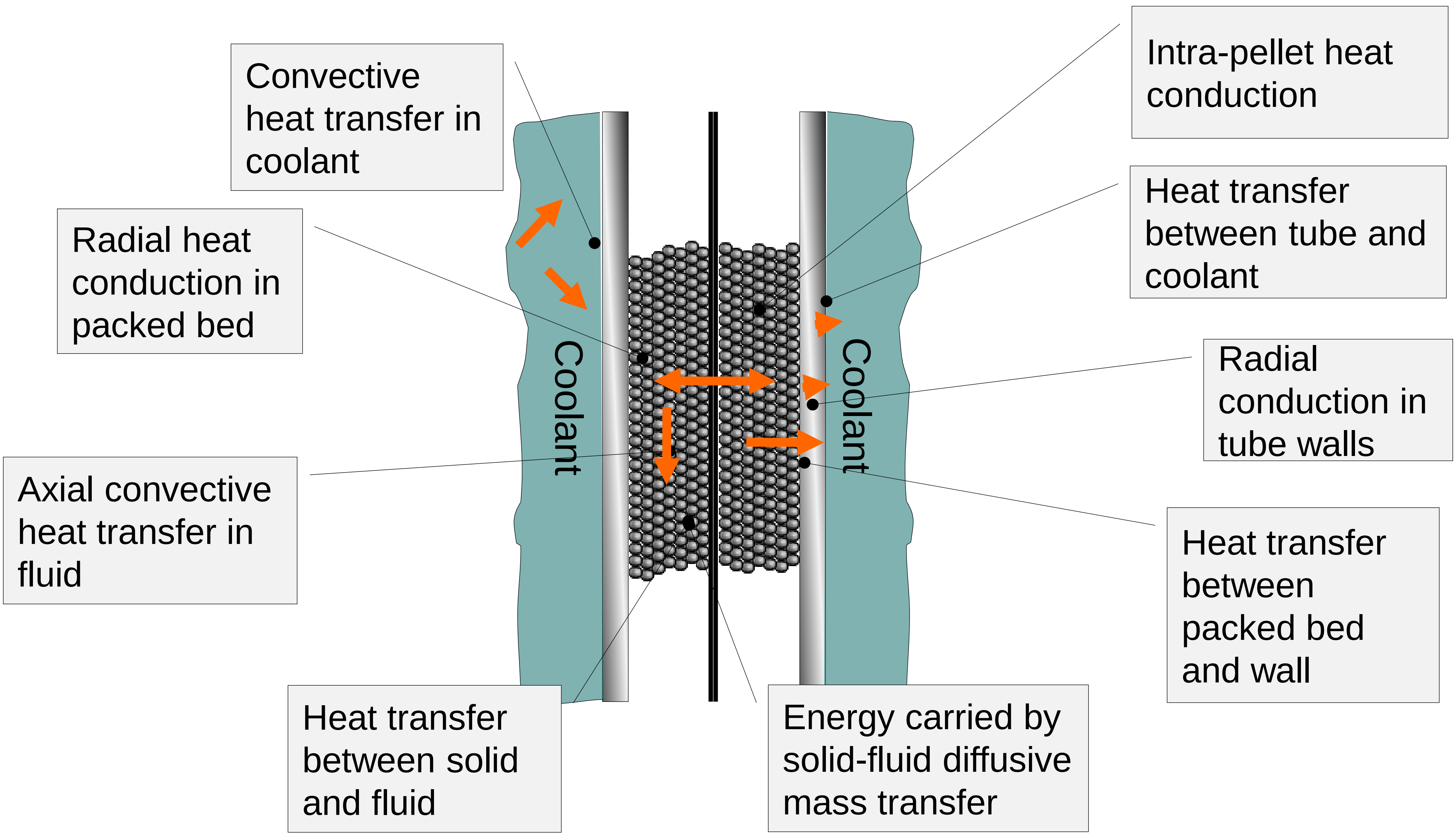
1 | 2 | 3 | 4

Advanced Process Model with all physics relevant to problem of interest

Key phenomena: Mass transport and reaction

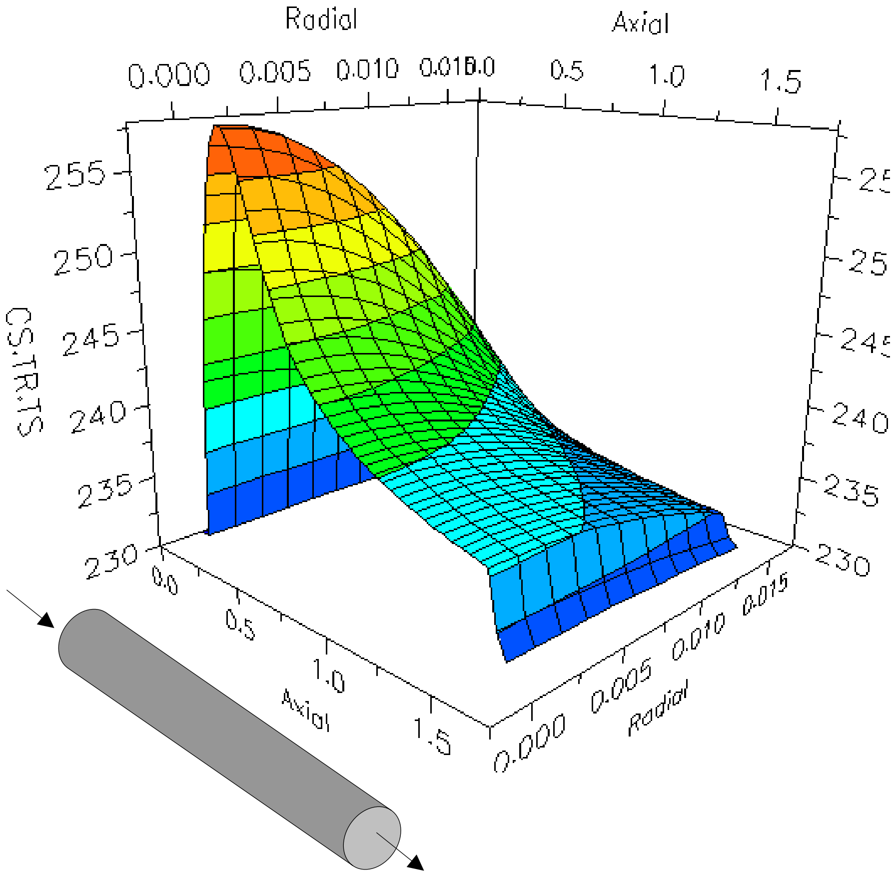


Key phenomena: Heat transfer

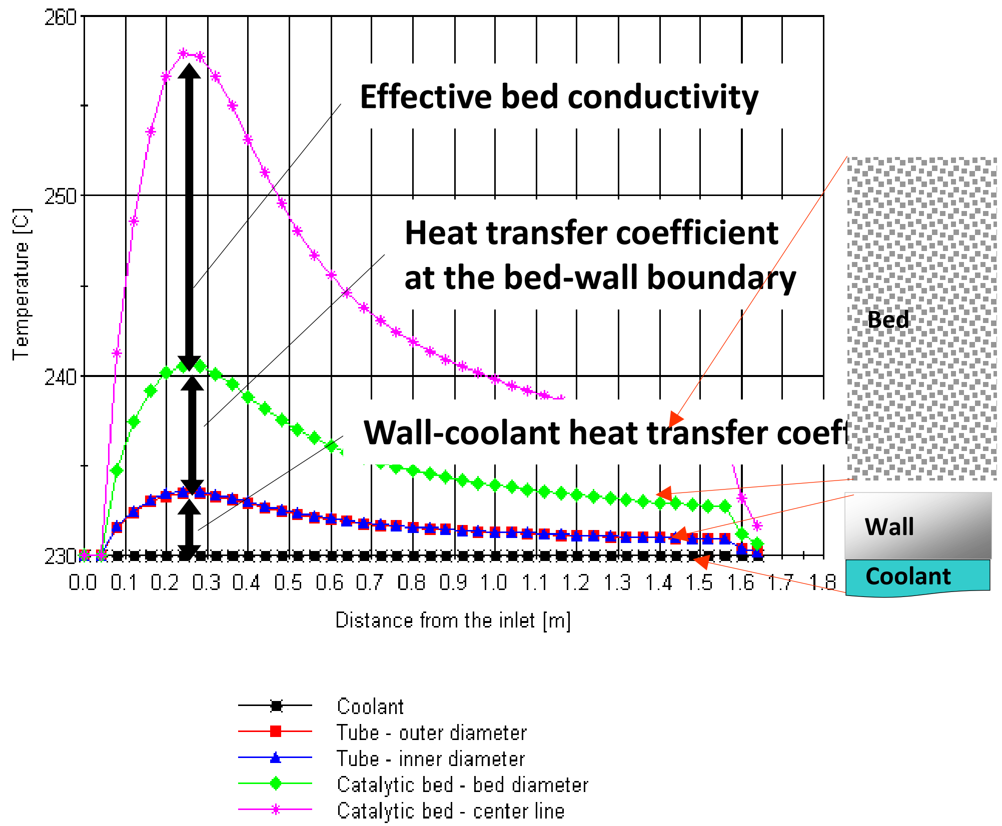


FBCR – Heat removal in a tubular fixed bed

Axial & radial variation of bed temperature



Temperatures from center of bed to wall



1

Advanced **M**odel **L**ibrary

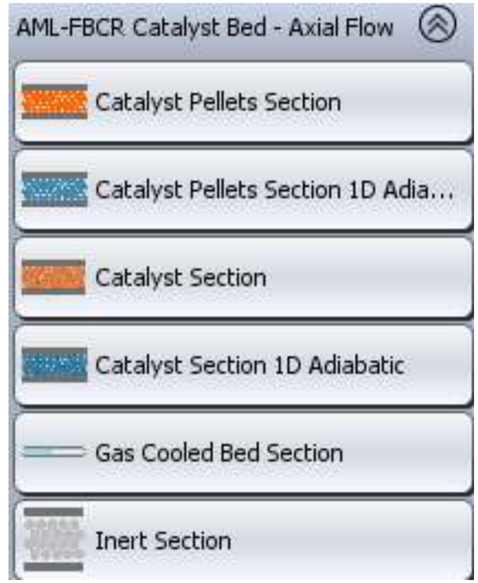
AML:FBCR

Fixed **B**ed **C**atalytic **R**eactors

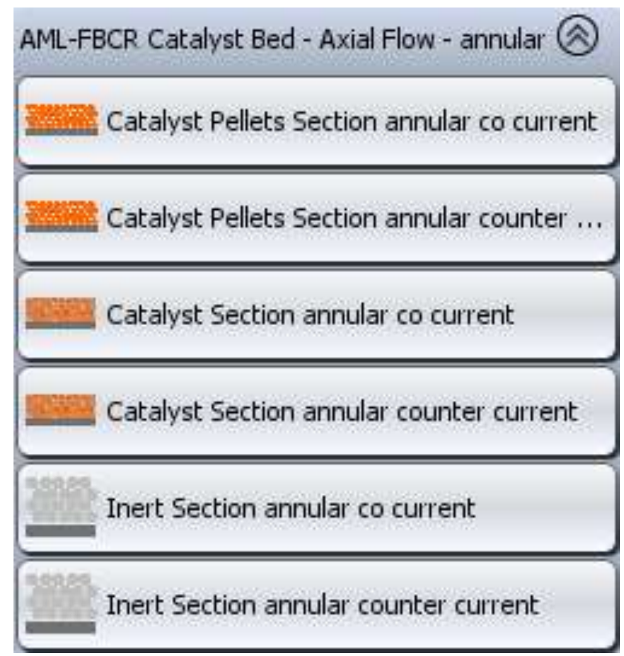
Library scope

Library contents: Axial-flow catalytic bed reactors

- Catalyst Pellet Sections
- Inert Sections

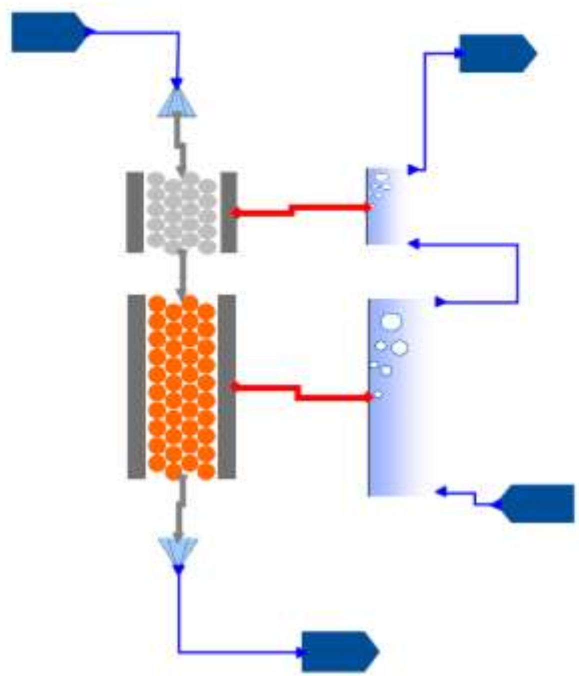


- Heat integrated annular sections



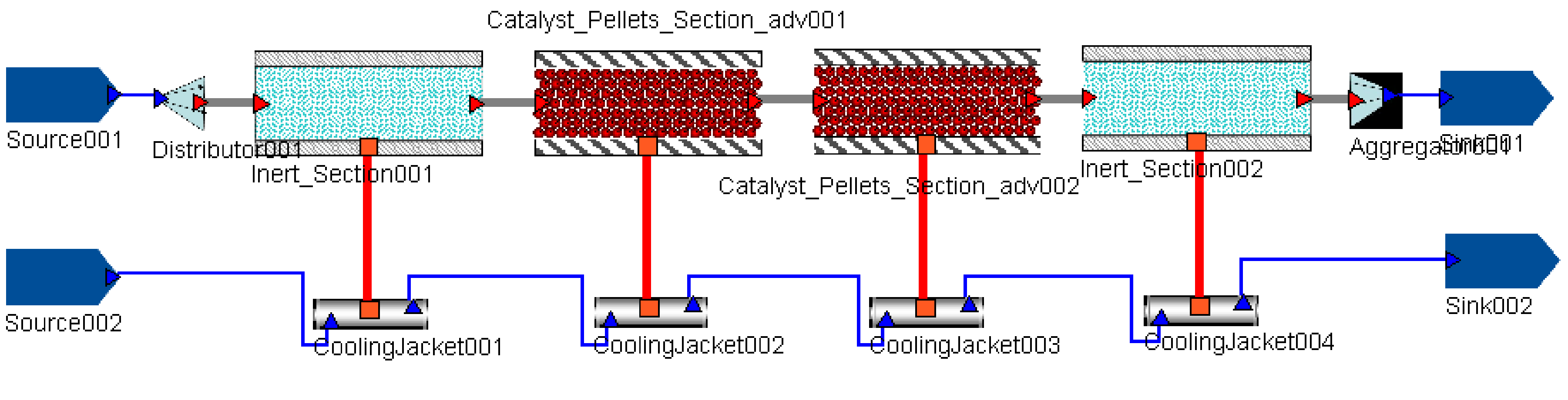
Library contents: Shell-side models

- Fixed coolant
- Cooling jacket
- Multitubular cooling compartment
- Boiling water cooling

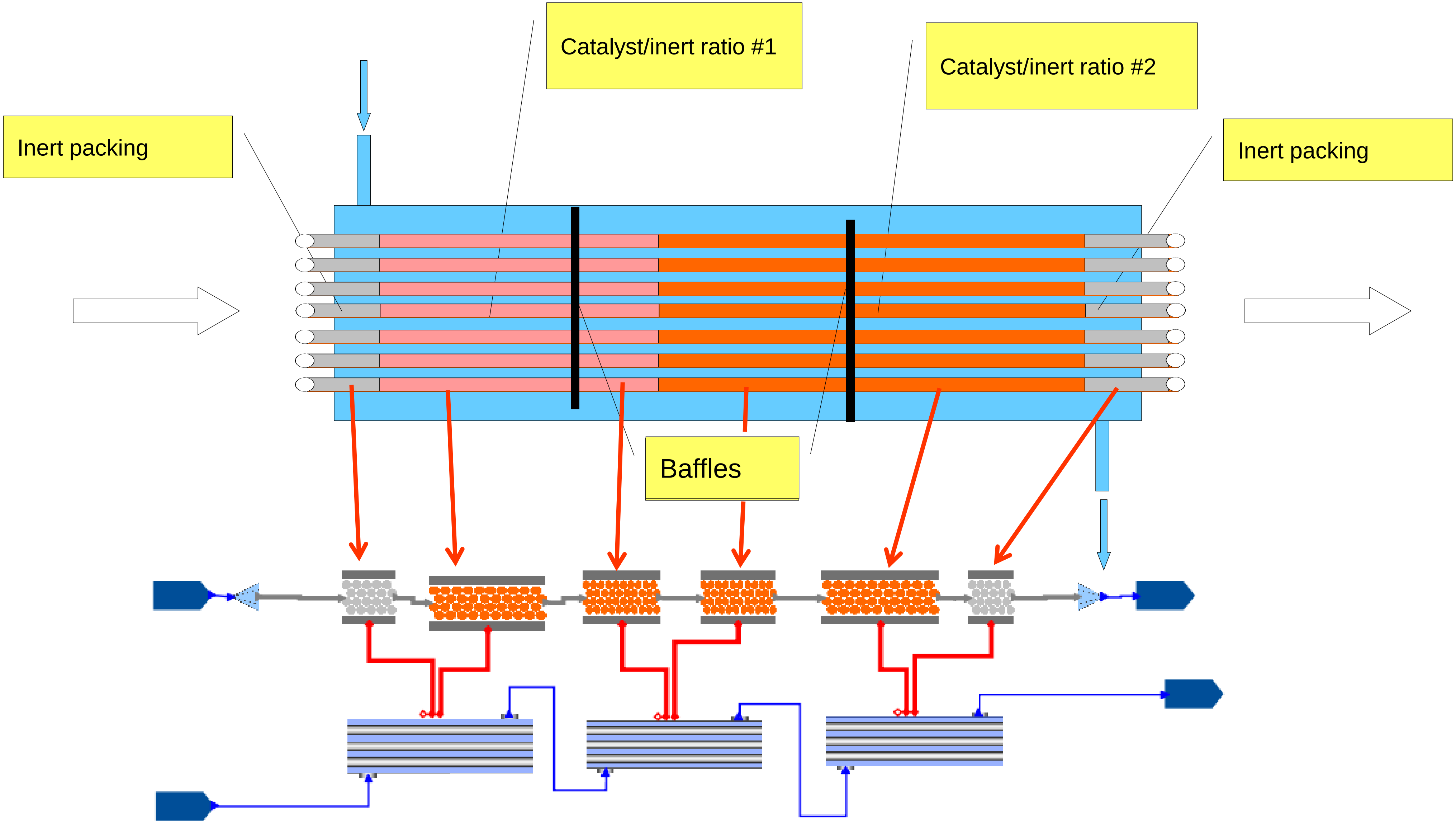


Assembly of components into unit operation models

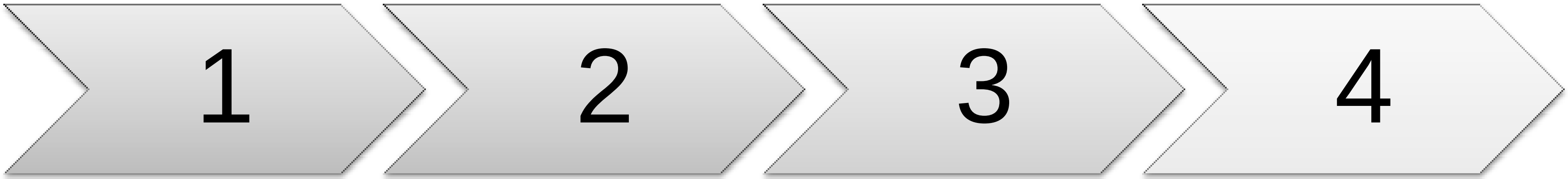
- Jacketed single-tube pilot plant reactor



A more realistic FBCR configuration



The Advanced Process Modeling Approach: Step 2



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

2

gPROMS AML:FBCR

Model Validation

Ensuring predictive accuracy through model-targeted experimentation

Experimentation in the APM approach

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
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

Estimation of multiple parameters from multiple experiments: a standard feature in gPROMS

Practical advice: 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:

$$\cancel{k_1 = A_1 exp\left(-\frac{E_1}{RT}\right)} \qquad k_1 = k_{1,T_{ref}} exp\left(-\frac{E_1}{R}\left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right)$$

- Break correlation between rate constants and adsorption constants:

$$\cancel{r_1 = \frac{k_1 K_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2}} \qquad r_1 = \frac{k_1{}' P_A P_B}{\left(\frac{1}{K_A} + P_A + K_{B:A} P_B + K_{C:A} P_C\right)^2}$$

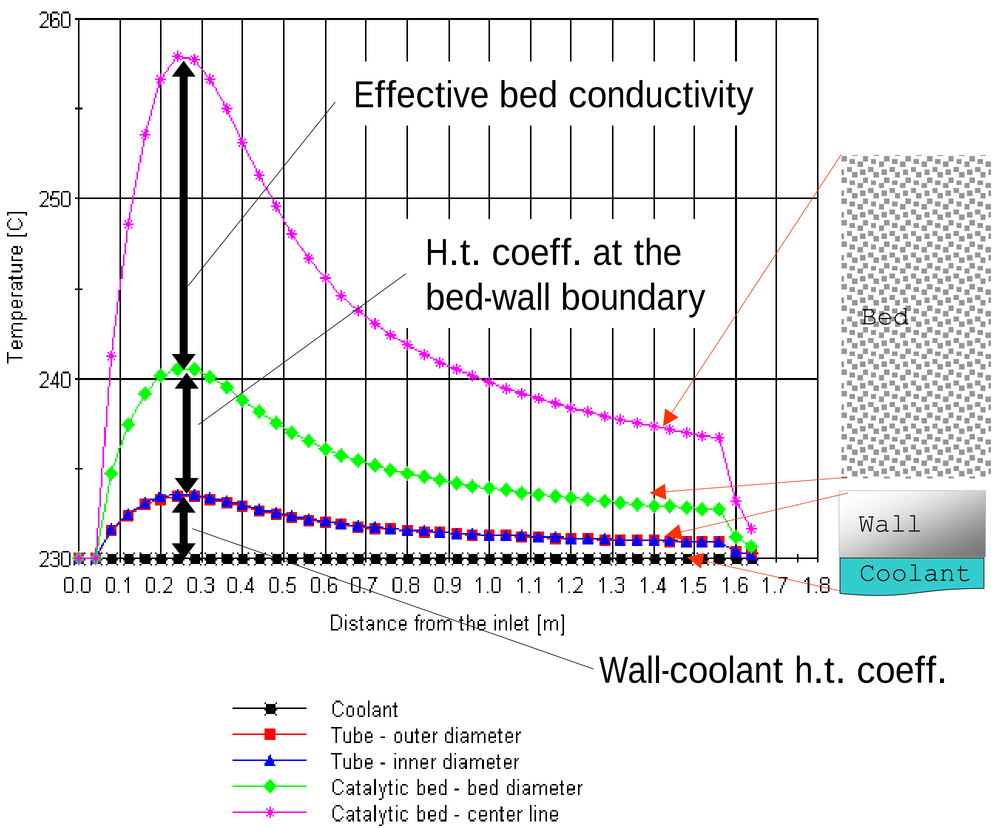
Practical advice: Kinetic parameters (2/2)

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

$$\begin{tikzcd} A \arrow[r, "O_2"] \arrow[rr, bend right, "3O_2"'] & B \arrow[r, "2O_2"] & C \end{tikzcd}$$

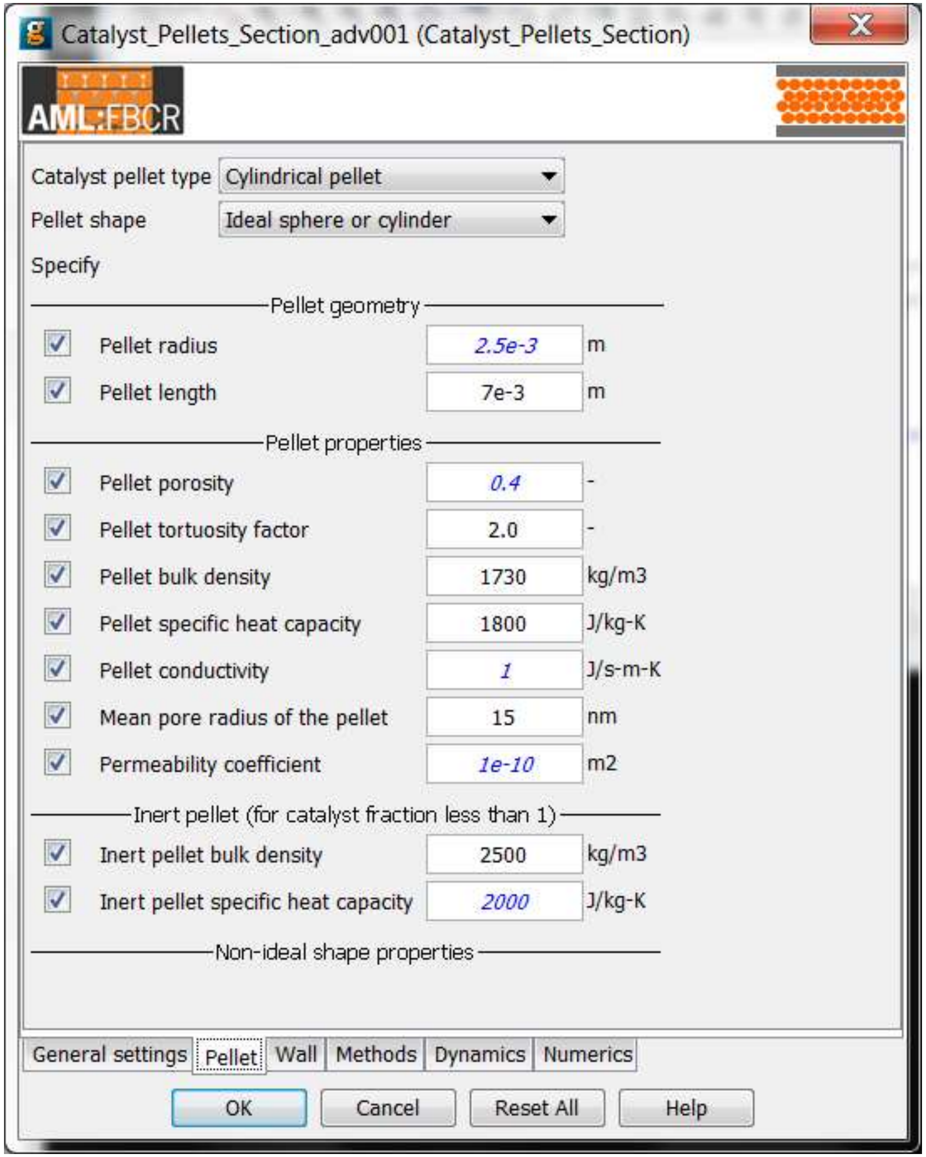
- Perform experiments with co-feed of strongly adsorbing by-products
- Measure temperature at several positions along the catalyst bed
- Characterize carefully the experimental error in outlet composition measurements

Practical advice: 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

Practical advice: particle properties



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

- Conduct experiments with particles of different size to adjust tortuosity factor

What have we achieved so far?

- Theoretical model + experimental stage + data processing **= fully predictive model of a single tube of catalytic bed**

- Now: **any coolant side equipment model** can be thermally coupled with the tube model for the reactor design study

The Advanced Process Modeling Approach: Step 3

1	2	3	4
Advanced Process Model with all physics relevant to problem of interest	Model-targeted Experimentation + Parameter Estimation	**Optimization-based design**	

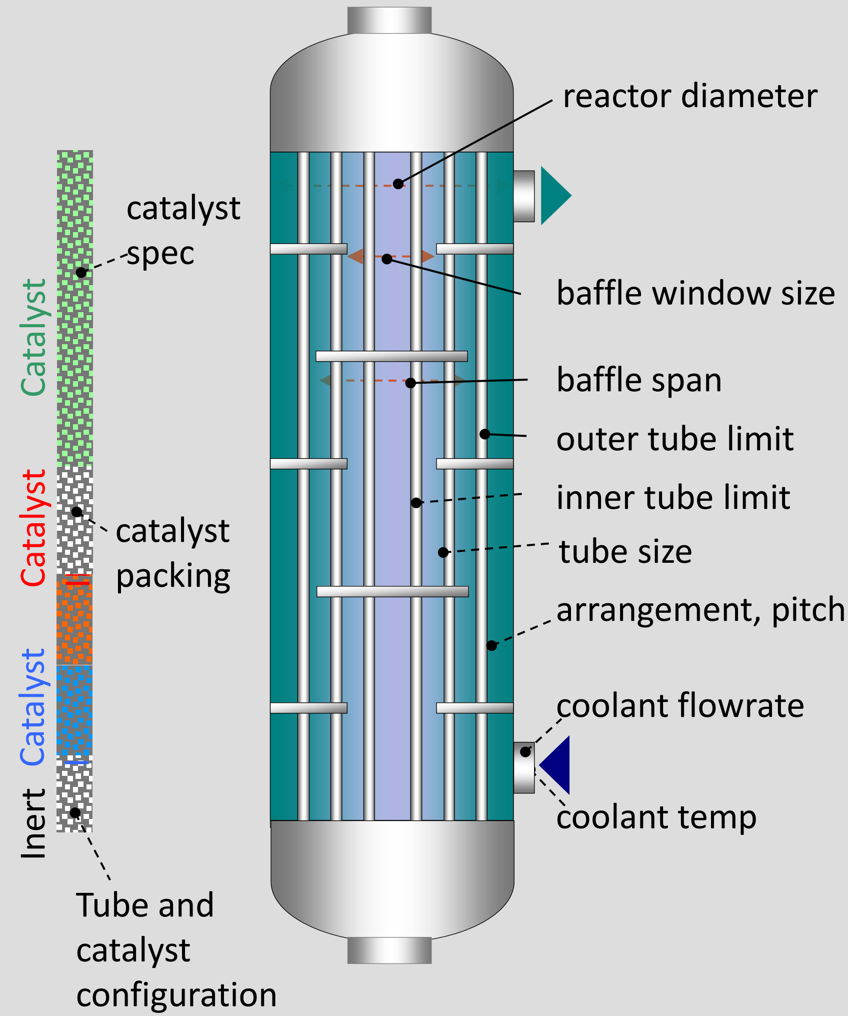
3

gPROMS AML:FBCR

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

**Solution of optimization problems with multiple decision variables and constraints:
a standard feature in gPROMS**

Optimization-based design procedure (1/3)

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

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

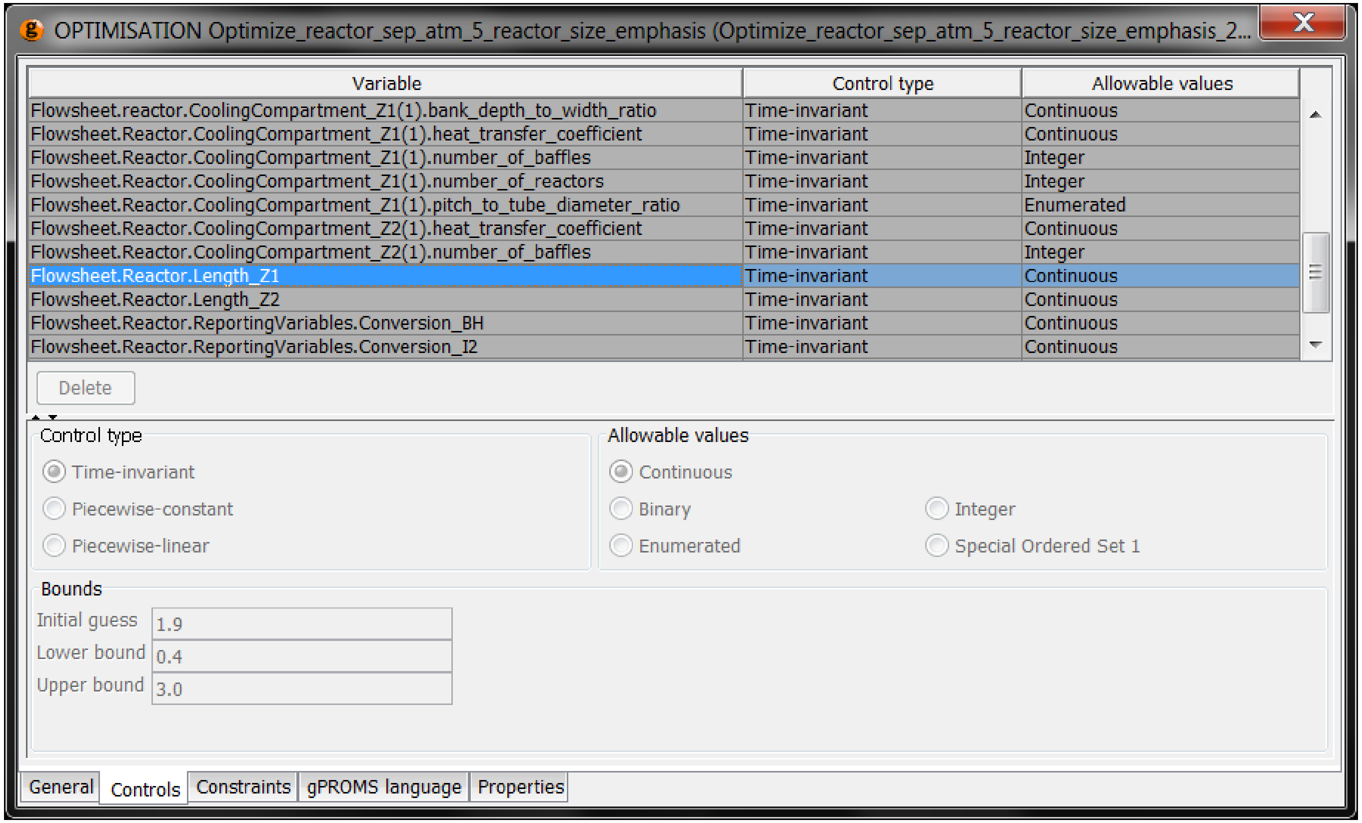
$$ProdRate = F_{out} \times\ x_{product} \times \text{3600 s/hr} \times \text{Annual Operating Hours}$$

$$TAP = ProdRate \times ProdPrice - Annual\ Operating\ Cost\ - AF \times CapCost$$

2. Select decision variables
   - specify initial guesses (e.g. current design)
   - specify allowable range of variation (continuous/discrete)

Optimization-based design procedure (2/3)

3. Select constrained variables
   - any variable calculated by the model
   - specify upper and/or lower bound for constrained variable



Optimization-based design procedure (3/3)

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.

OPTIMISATION REPORT Optimize_reactor_sep_hiP_4_2_2 (Optimize_reactor_sep_hiP_4_2_2_20100614_125001)

Constrained Variable	Type	Time	Value	Lower Bound		Upper Bound	
				Value	Lagrange Multiplier	Value	Lagrange Multiplier
Flowsheet.Reactor.ReportingVariables.Source_pressure_bar	End Point	0.0000	1.6000	$-1.0000\times10^{+30}$	0.0000	1.6000 *	1.0053

Report | Properties

6. Adjust bounds if appropriate, and launch optimization again.

The Advanced Process Modeling Approach: Step 4

1 Advanced Process Model with all physics relevant to problem of interest

2 Model-targeted Experimentation + Parameter Estimation

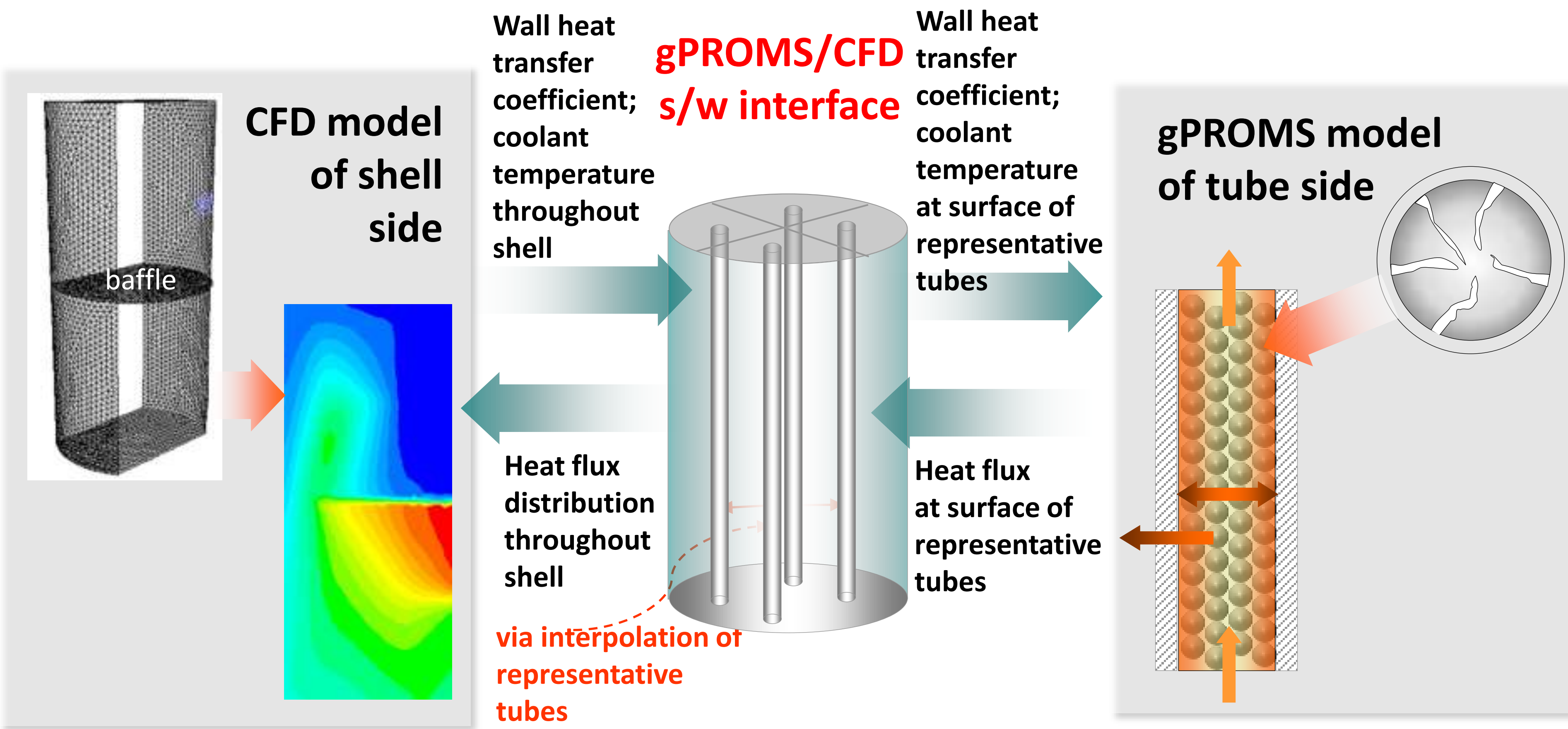
3 Optimization-Based Design

4 **Final Adjustments to Equipment Design**

gPROMS AML:FBCR

Hybrid gPROMS/CFD modeling of multitubular reactors

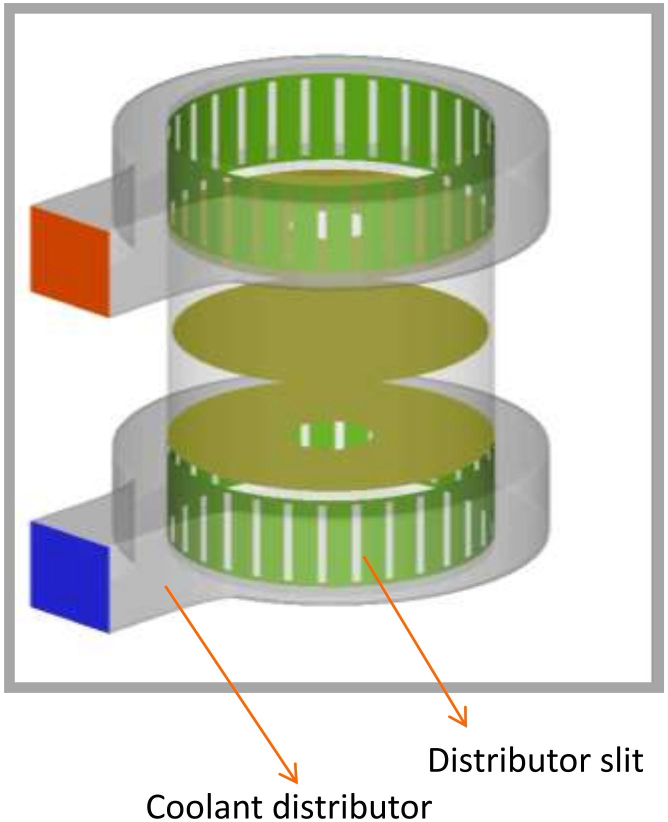
Comprehensive performance assessment for commercial-scale multitubular reactors



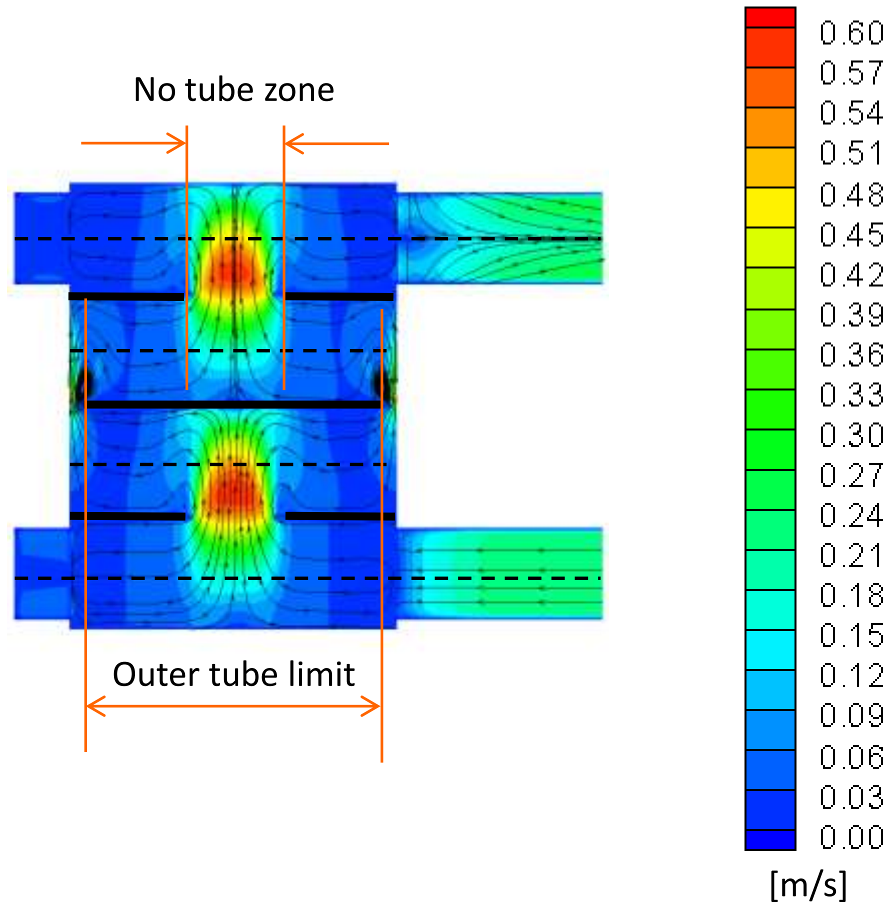
→ Highest-accuracy predictive model on both tube-and shell sides

AML:FBCR off-the-shelf add-on

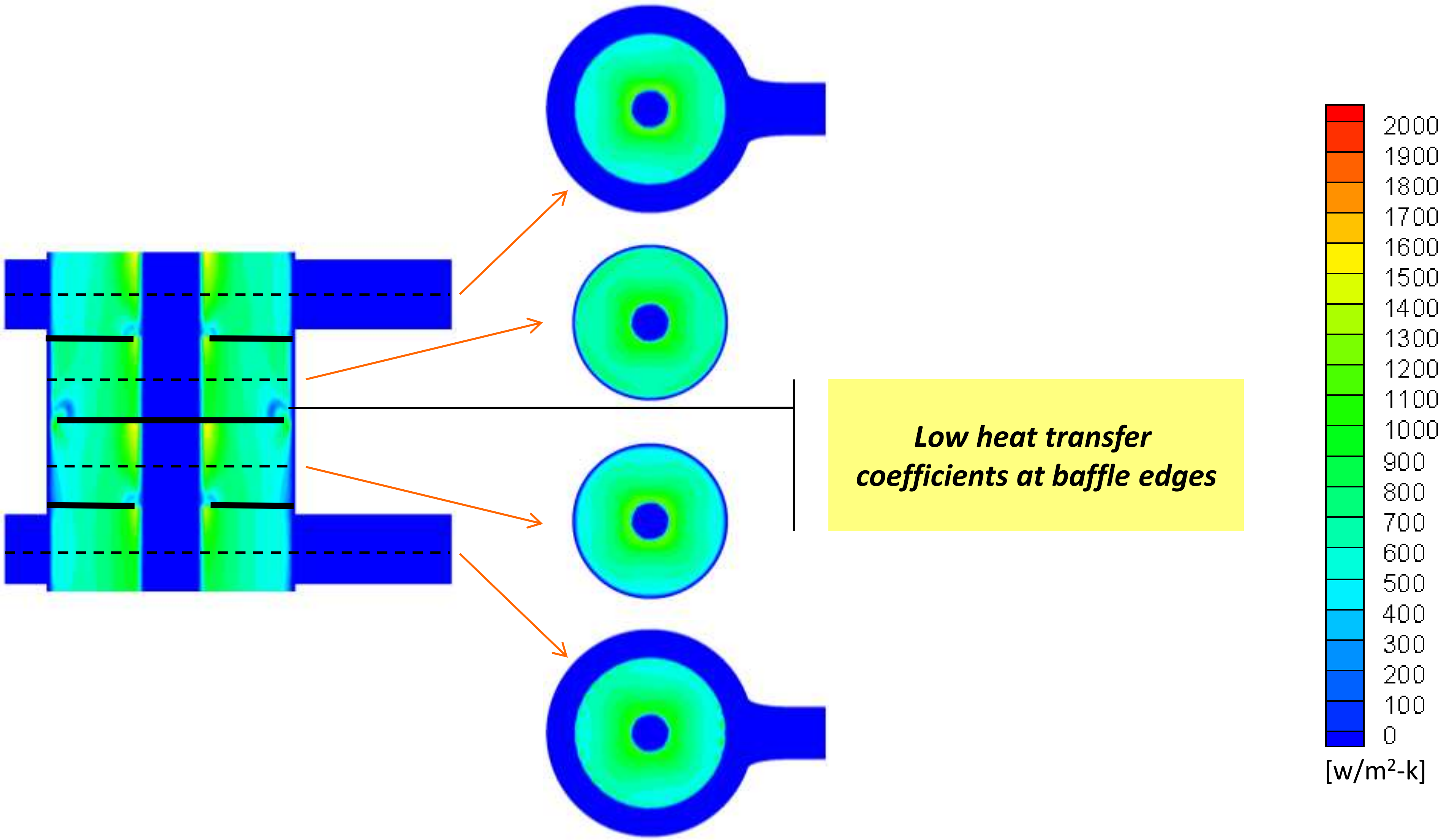
CFD model (implemented in Fluent®)



Velocity magnitude and streamlines

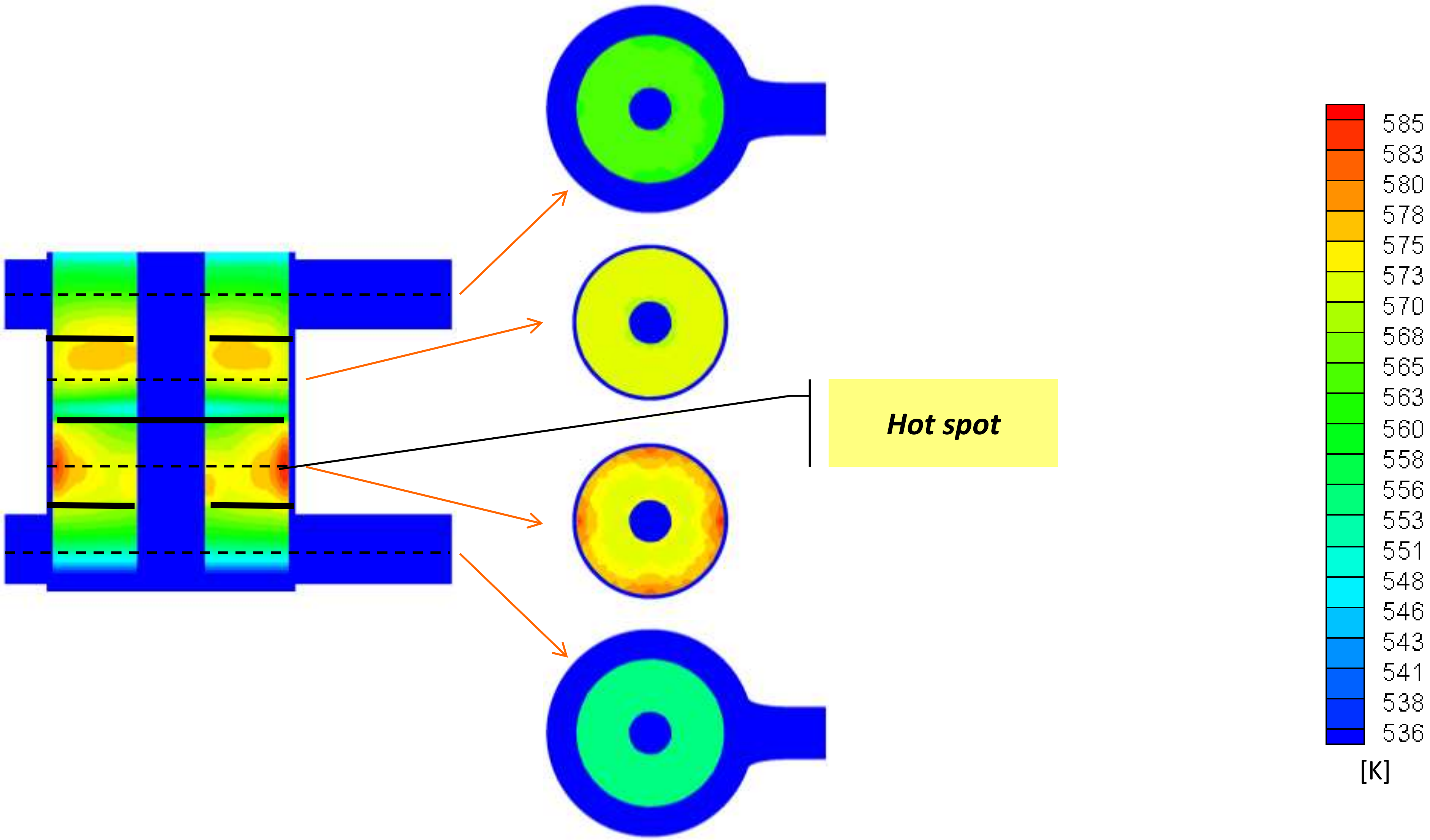


Heat transfer coefficient



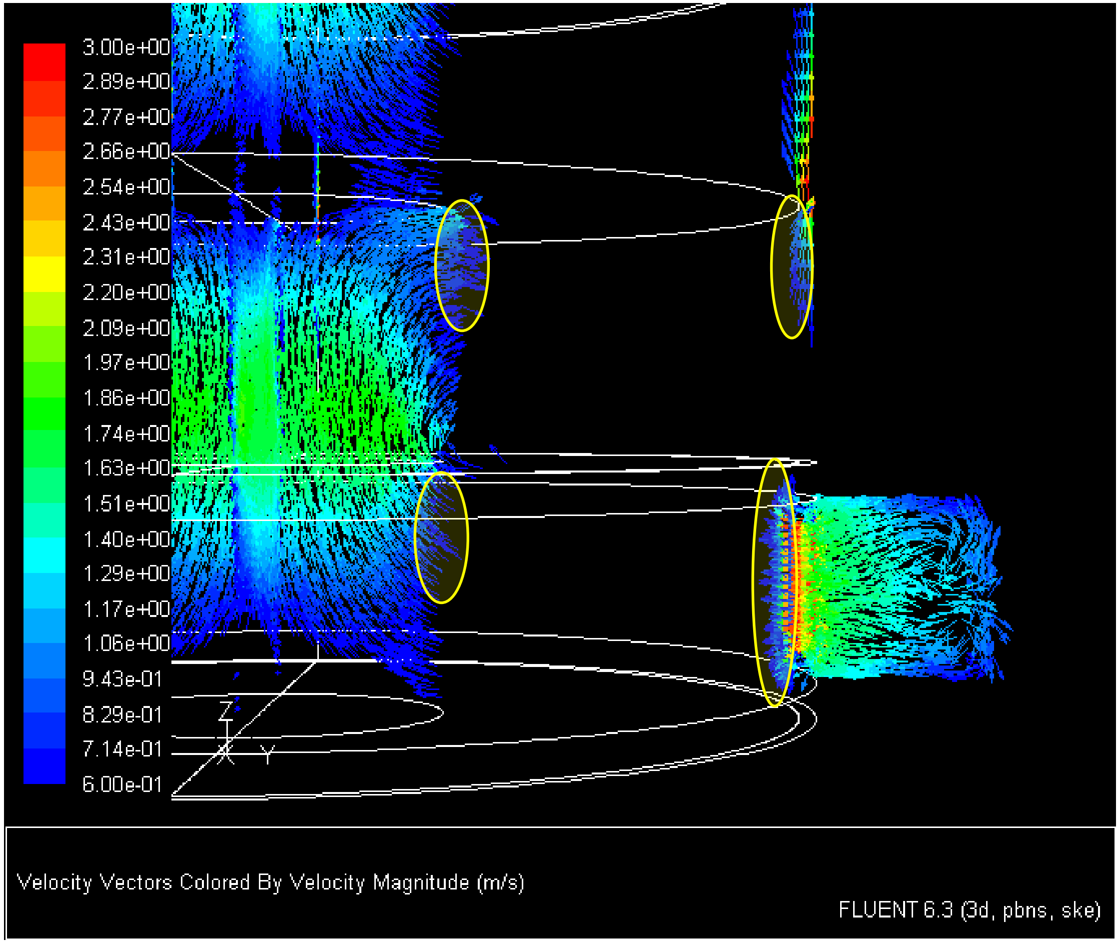
Hybrid gPROMS/CFD simulation results

Tube center temperature I



Check mechanical performance: Example

- $V > V_{max}$ at distributor inlets, inner boundary, outer boundary (axial)
- Minor changes to distributor and baffle geometry to meet mechanical constraints



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  Tom Williams, Ying-Sheng Cheng: CFD Multitubular interface

  Entire team: Parameter Propagation, Non-Uniform Grids, Identity Elimination, Ordered Sets, Initialization Procedures, etc.
- **Customers**

Arkema · BP · Gas2 · Gaylord Chemical · IDESA ·
Hanwha Chemical Company · Hunt Refining · Hyosung · INEOS Nitriles ·
LG Chem · Maruzen · Repsol · Samsung - BP Chemicals · Shell · SCG ·
SK Chemicals · Süd-Chemie · United Technologies / Clearedge Power ·
Wacker Chemie

Thank you!

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