

APM 2013



The Advanced Process Modeling Forum

5–6 June 2013, New York

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



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



**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

Multicomponent
intra-pore diffusion

Intra-pore
convection

Tube wall

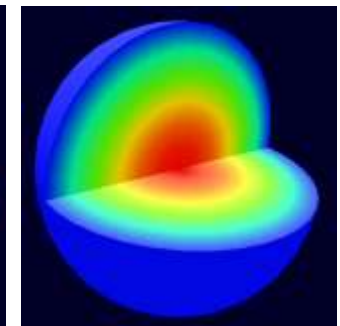
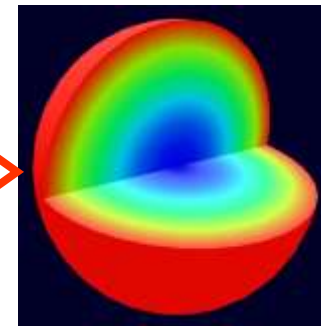
Catalyst
pellet

Axial/radial
convection in
tube-side fluid

Catalytic reaction
on pore surface

Radial dispersion

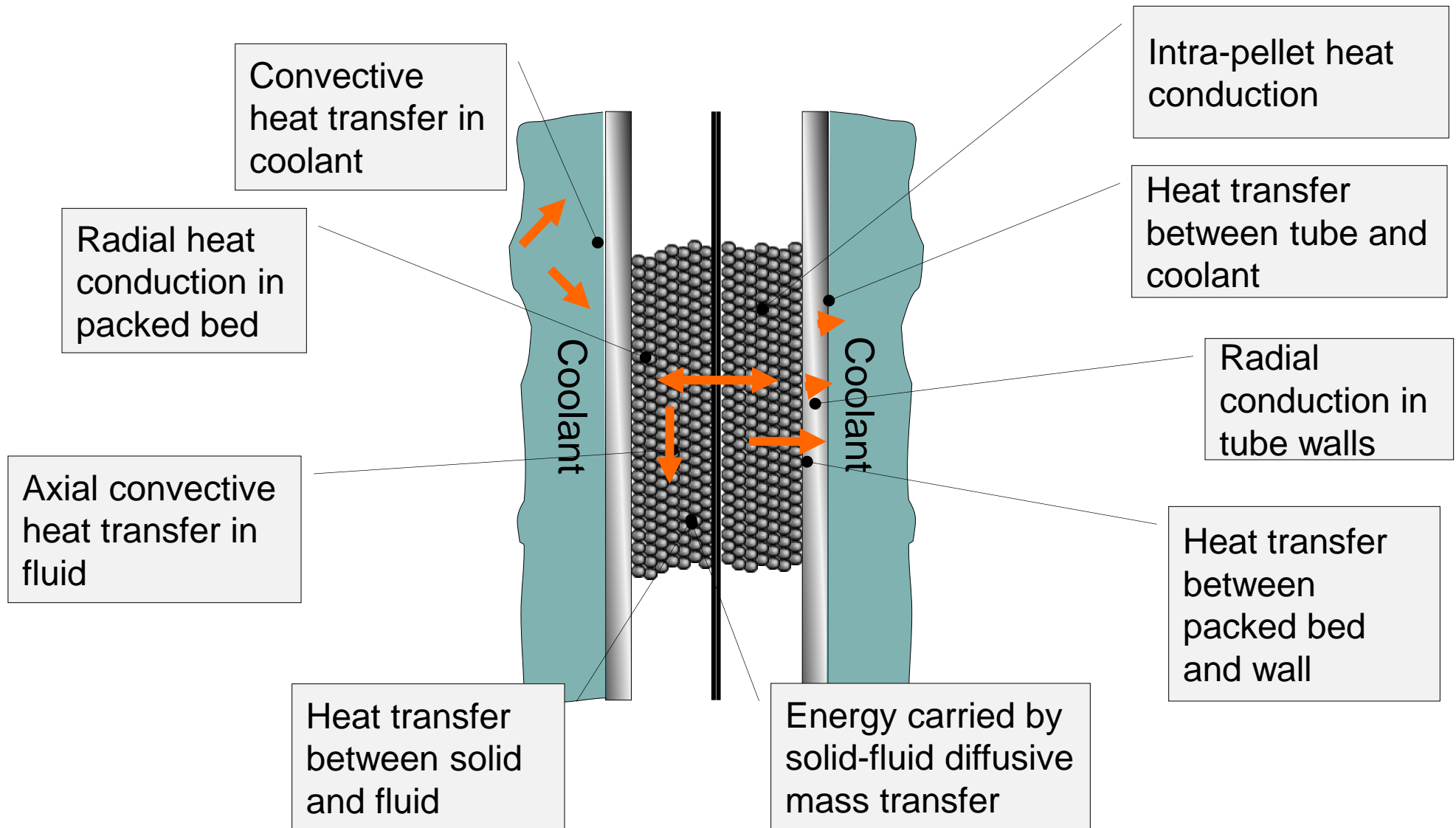
Thermowell



0.011294
0.000000

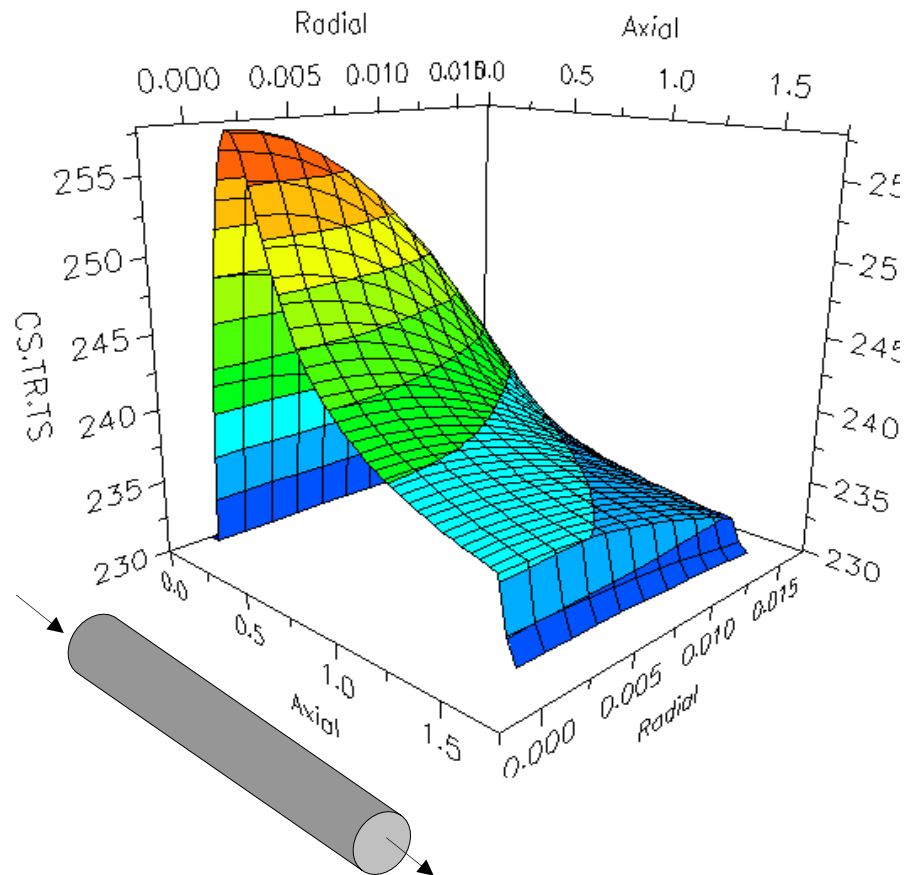
0.000000
0.000000

Key phenomena: Heat transfer

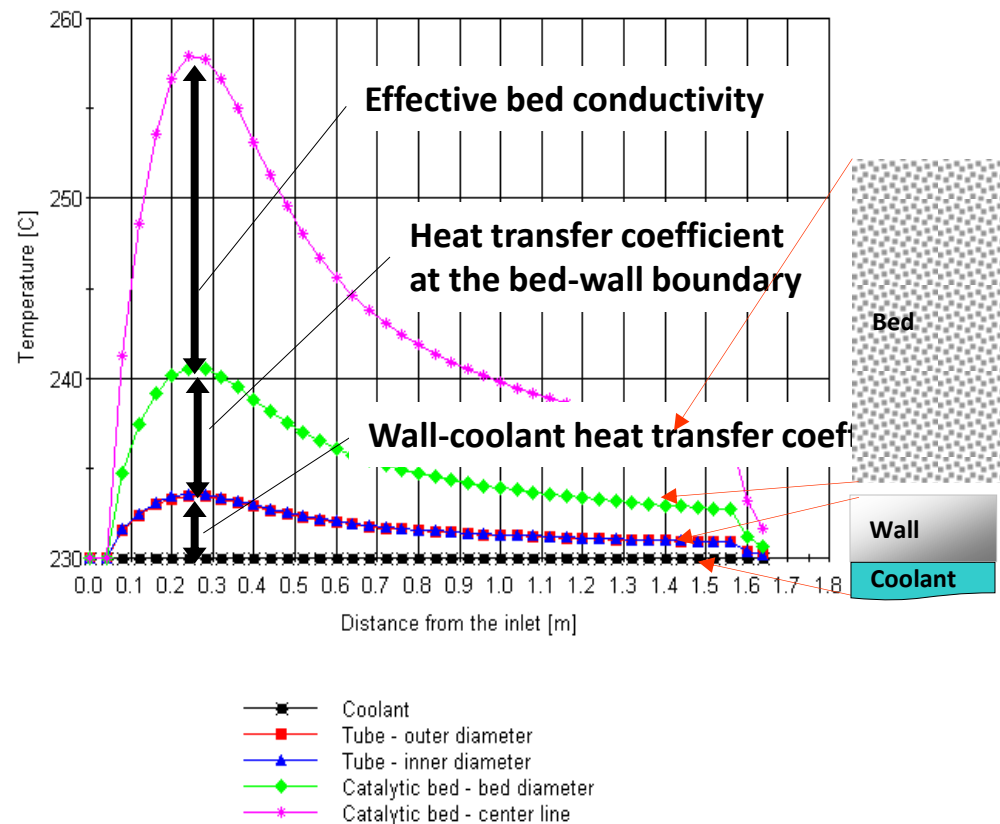


FBCR – Heat removal in a tubular fixed bed

Axial & radial variation of bed temperature



Temperatures from center of bed to wall



Advanced Model Library



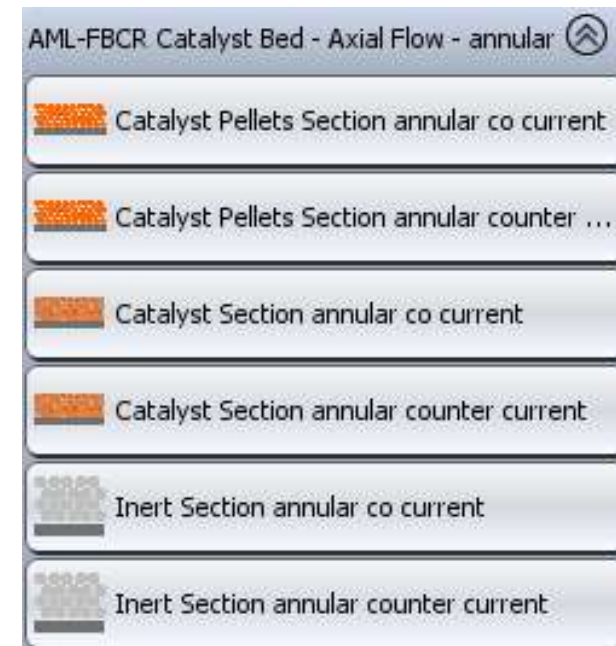
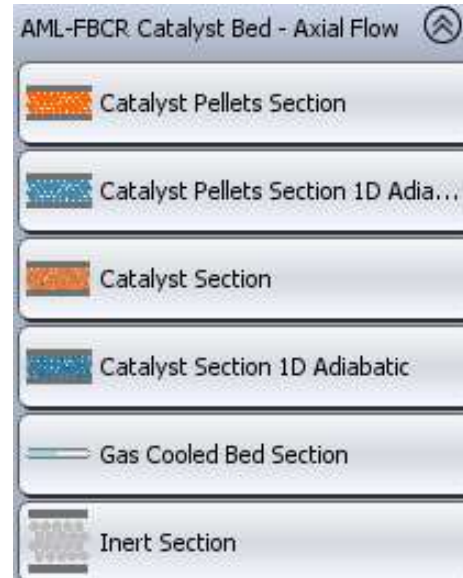
Fixed Bed Catalytic Reactors

Library scope

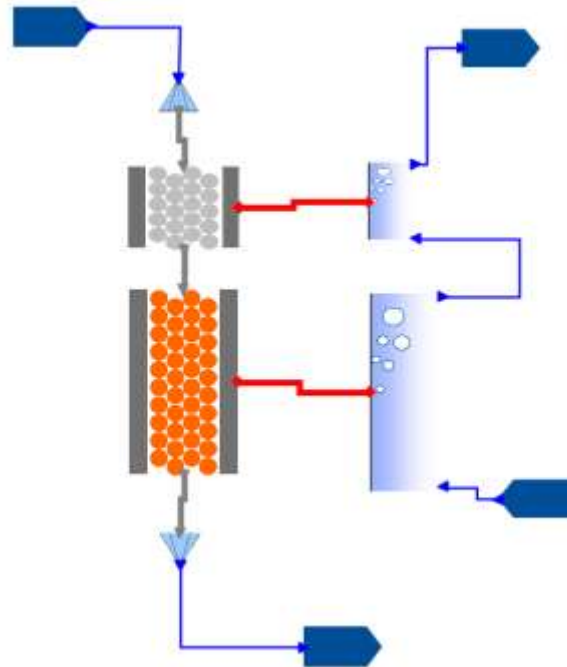
Library contents: Axial-flow catalytic bed reactors



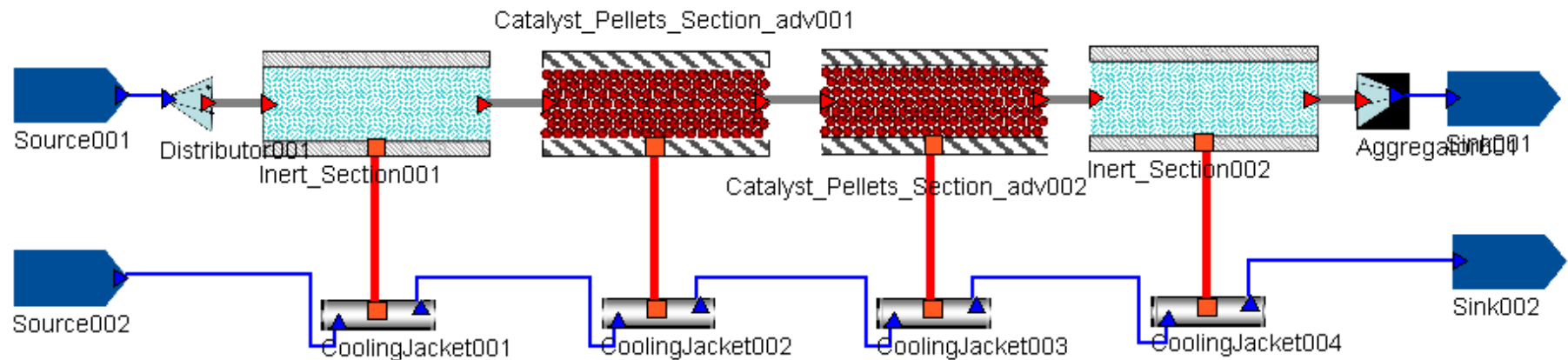
- Catalyst Pellet Sections
- Inert Sections
- Heat integrated annular sections



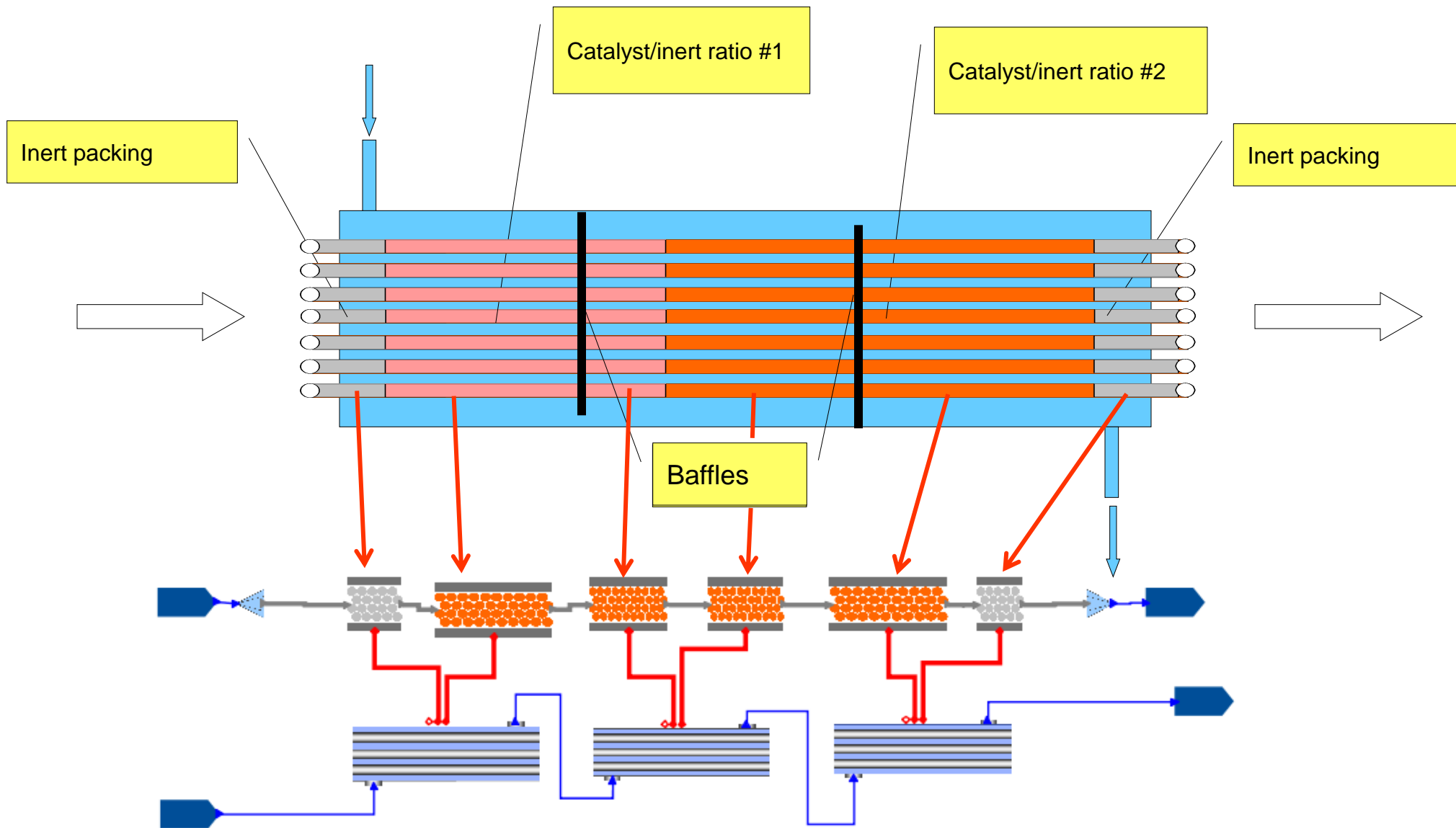
- Fixed coolant
- Cooling jacket
- Multitubular cooling compartment
- Boiling water cooling



■ Jacketed single-tube pilot plant reactor



A more realistic FBCR configuration



The Advanced Process Modeling Approach: Step 2



Advanced Process
Model with all
physics relevant
to problem of
interest

**Model-targeted
Experimentation
+
Parameter
Estimation**

gPROMS AML:FBCR 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
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:

~~$$k_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)$$~~

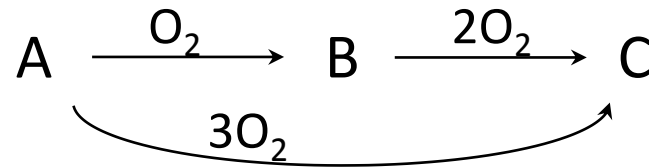
$$k_1 = k_{1,T_{ref}} \exp\left(-\frac{E_1}{R} \left[\frac{1}{T} - \frac{1}{T_{ref}}\right]\right)$$

- Break correlation between rate constants and adsorption constants:

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

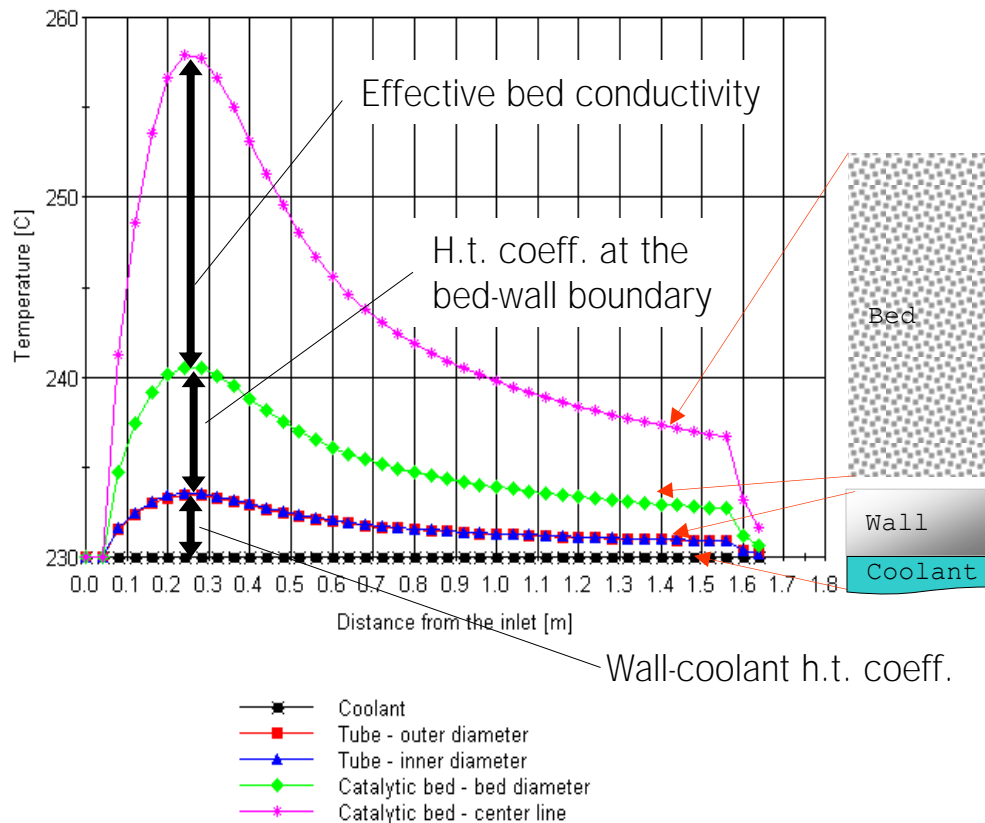
$$r_1 = \frac{k_1' P_A P_B}{\left(\frac{1}{K_A} + P_A + K_{B:A} P_B + K_{C:A} P_C\right)^2}$$

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



- 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



Catalyst_Pellets_Section_adv001 (Catalyst_Pellets_Section)

AML:FCBR

Catalyst pellet type: Cylindrical pellet

Pellet shape: Ideal sphere or cylinder

Specify

Pellet geometry

- ☒ Pellet radius: $2.5e-3$ m
- ☒ Pellet length: $7e-3$ m

Pellet properties

- ☒ Pellet porosity: 0.4 -
- ☒ Pellet tortuosity factor: 2.0 -
- ☒ Pellet bulk density: 1730 kg/m³
- ☒ Pellet specific heat capacity: 1800 J/kg-K
- ☒ Pellet conductivity: 1 J/s-m-K
- ☒ Mean pore radius of the pellet: 15 nm
- ☒ Permeability coefficient: $1e-10$ m²

Inert pellet (for catalyst fraction less than 1)

- ☒ Inert pellet bulk density: 2500 kg/m³
- ☒ Inert pellet specific heat capacity: 2000 J/kg-K

Non-ideal shape properties

General settings | Pellet | Wall | Methods | Dynamics | Numerics

OK Cancel Reset All Help

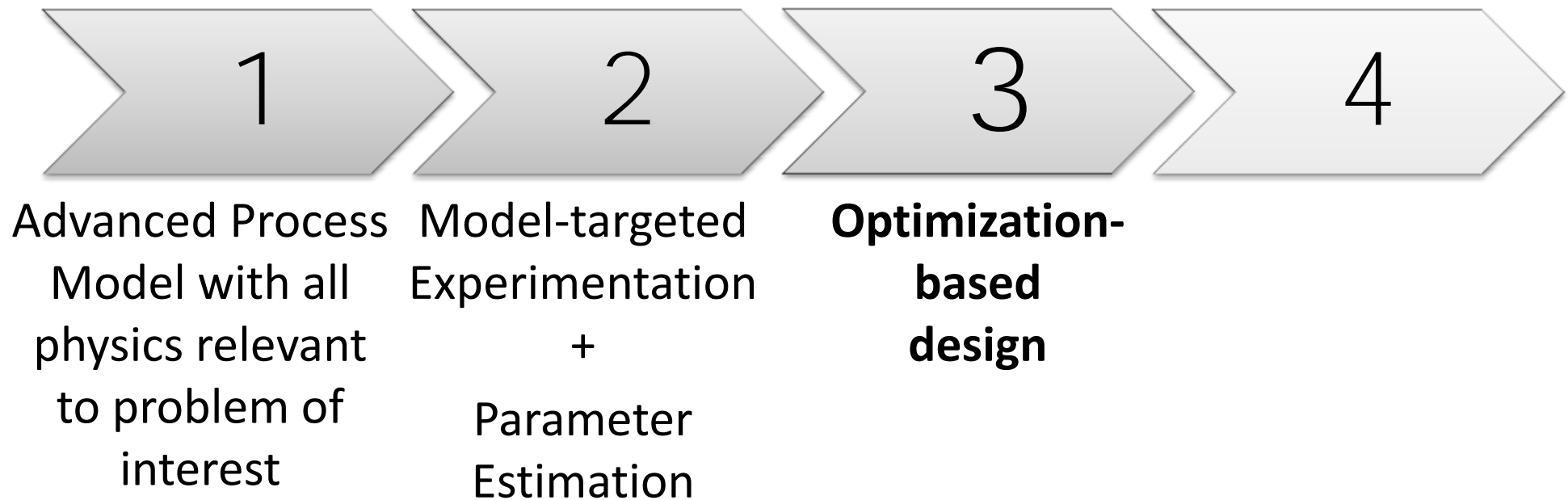
- Use reliable third-party laboratory to characterize particle properties
 - Particle size distribution
 - Pore size distribution
 - Porosity
- Conduct experiments with particles of different size to adjust tortuosity factor

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





gPROMS AML:FBCR

Model-based optimization for design & operation

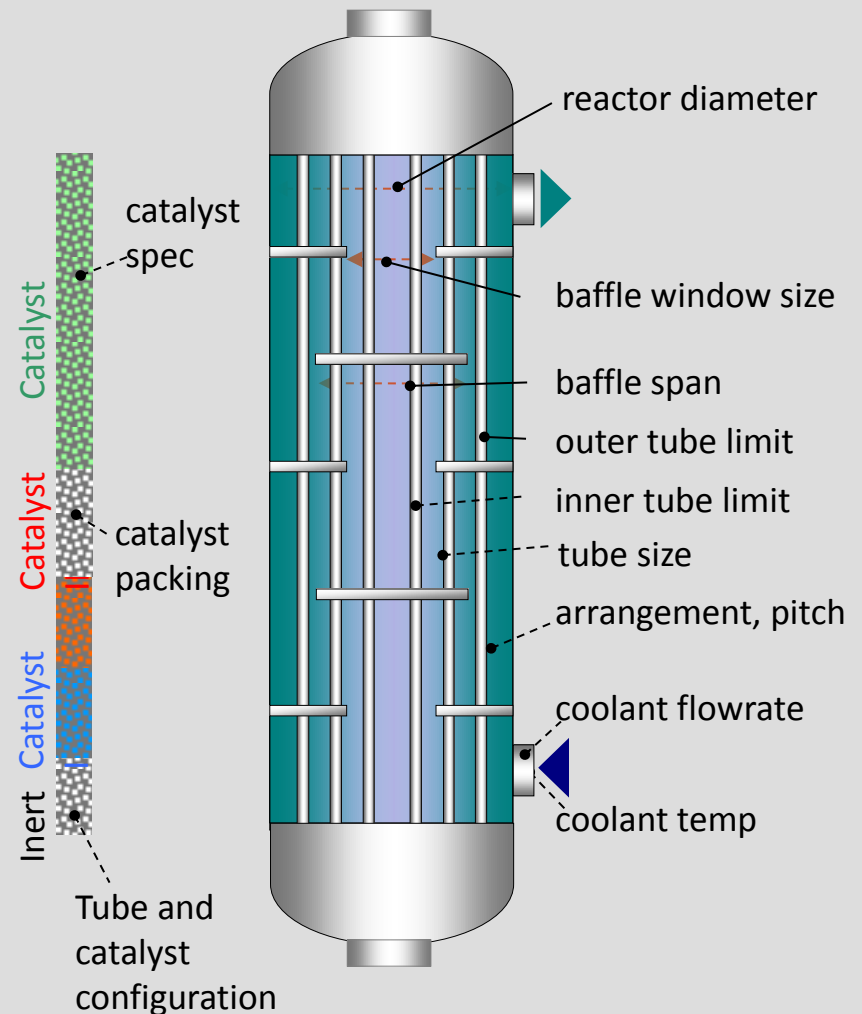
Multitubular reactor – key design variables

■ 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

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

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

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

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

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

The screenshot shows the 'OPTIMISATION' window for the file 'Optimize_reactor_sep_atm_5_reactor_size_emphasis'. The window contains a table of variables and their properties, and a detailed configuration panel for the selected variable 'Flowsheet.Reactor.Length_Z1'.

Variable	Control type	Allowable values
Flowsheet.Reactor.CoolingCompartment_Z1(1).bank_depth_to_width_ratio	Time-invariant	Continuous
Flowsheet.Reactor.CoolingCompartment_Z1(1).heat_transfer_coefficient	Time-invariant	Continuous
Flowsheet.Reactor.CoolingCompartment_Z1(1).number_of_baffles	Time-invariant	Integer
Flowsheet.Reactor.CoolingCompartment_Z1(1).number_of_reactors	Time-invariant	Integer
Flowsheet.Reactor.CoolingCompartment_Z1(1).pitch_to_tube_diameter_ratio	Time-invariant	Enumerated
Flowsheet.Reactor.CoolingCompartment_Z2(1).heat_transfer_coefficient	Time-invariant	Continuous
Flowsheet.Reactor.CoolingCompartment_Z2(1).number_of_baffles	Time-invariant	Integer
Flowsheet.Reactor.Length_Z1	Time-invariant	Continuous
Flowsheet.Reactor.Length_Z2	Time-invariant	Continuous
Flowsheet.Reactor.ReportingVariables.Conversion_BH	Time-invariant	Continuous
Flowsheet.Reactor.ReportingVariables.Conversion_I2	Time-invariant	Continuous

Below the table is a 'Delete' button. The configuration panel for 'Flowsheet.Reactor.Length_Z1' includes:

- Control type:** Radio buttons for Time-invariant (selected), Piecewise-constant, and Piecewise-linear.
- Allowable values:** Radio buttons for Continuous (selected), Binary, Integer, Enumerated, and Special Ordered Set 1.
- Bounds:** Input fields for Initial guess (1.9), Lower bound (0.4), and Upper bound (3.0).

At the bottom are tabs for General, Controls, Constraints, gPROMS language, and Properties.

Optimization-based design procedure (3/3)



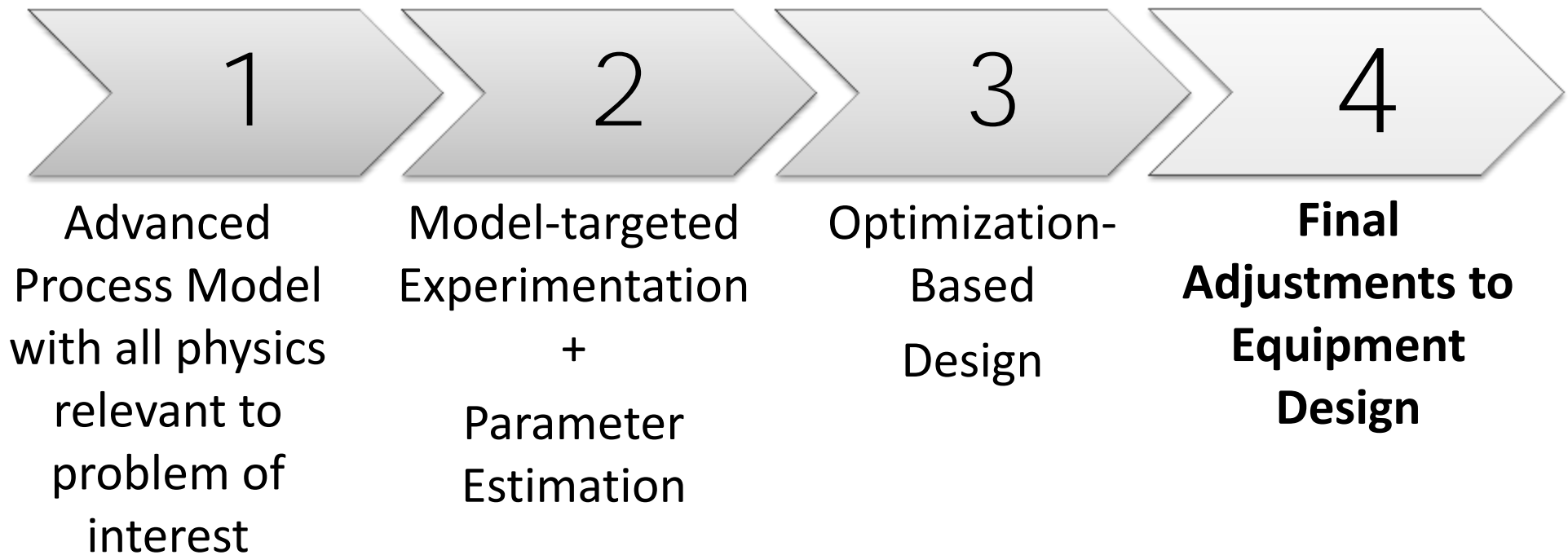
4. Launch optimization
5. Inspect results.
 - pay attention to Lagrange Multipliers of decision or constrained variables at bounds: estimates of improvement in objective function that could be achieved by relaxing bounds.

The screenshot shows an optimization report window with a table of results. The table has columns for Constrained Variable, Type, Time, Value, Lower Bound (Value and Lagrange Multiplier), and Upper Bound (Value and Lagrange Multiplier). The data row shows a constrained variable 'Flowsheet.Reactor.ReportingVariables.Source_pressure_bar' at an 'End Point' with a value of 1.6000. The lower bound is -1.0000x10⁺³⁰ with a Lagrange Multiplier of 0.0000. The upper bound is 1.6000* with a Lagrange Multiplier of 1.0053.

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	-1.0000x10 ⁺³⁰	0.0000	1.6000 *	1.0053

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

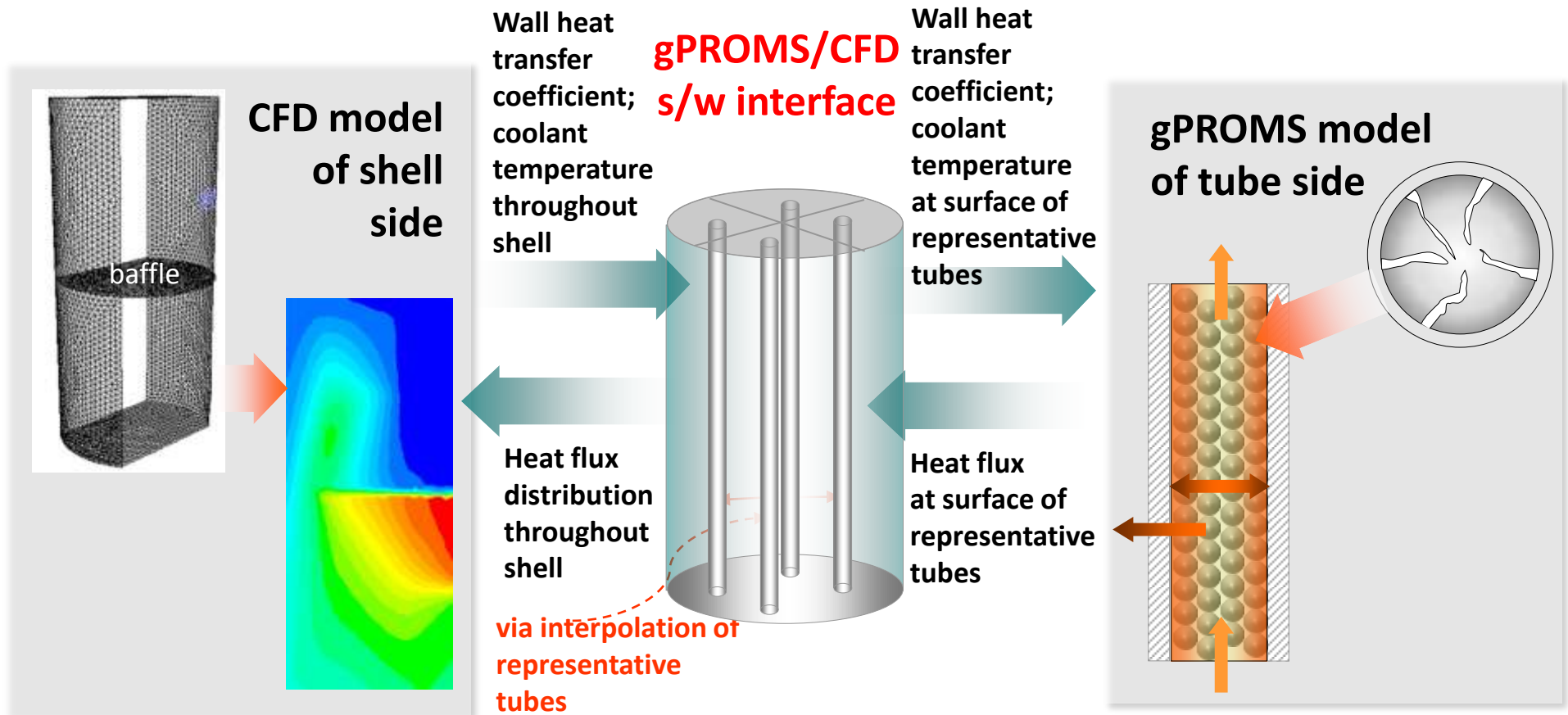
The Advanced Process Modeling Approach: Step 4



gPROMS AML:FBCR

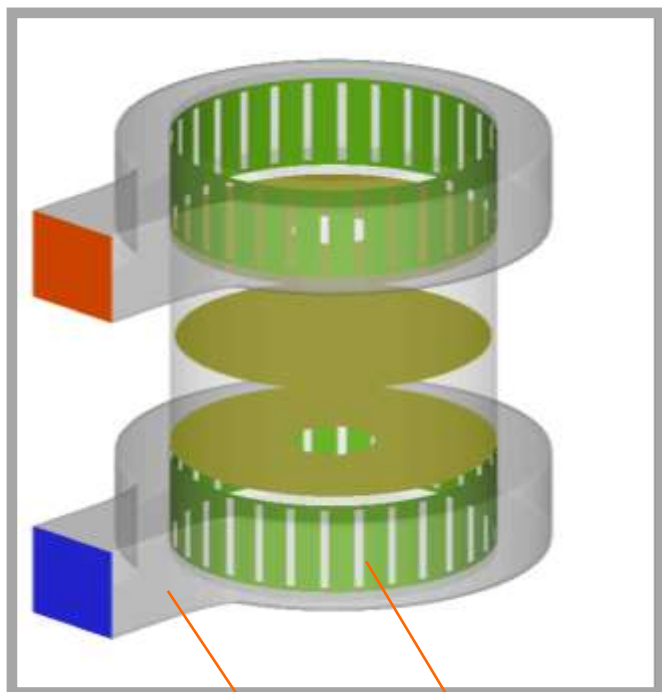
Hybrid gPROMS/CFD modeling of multitubular reactors

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

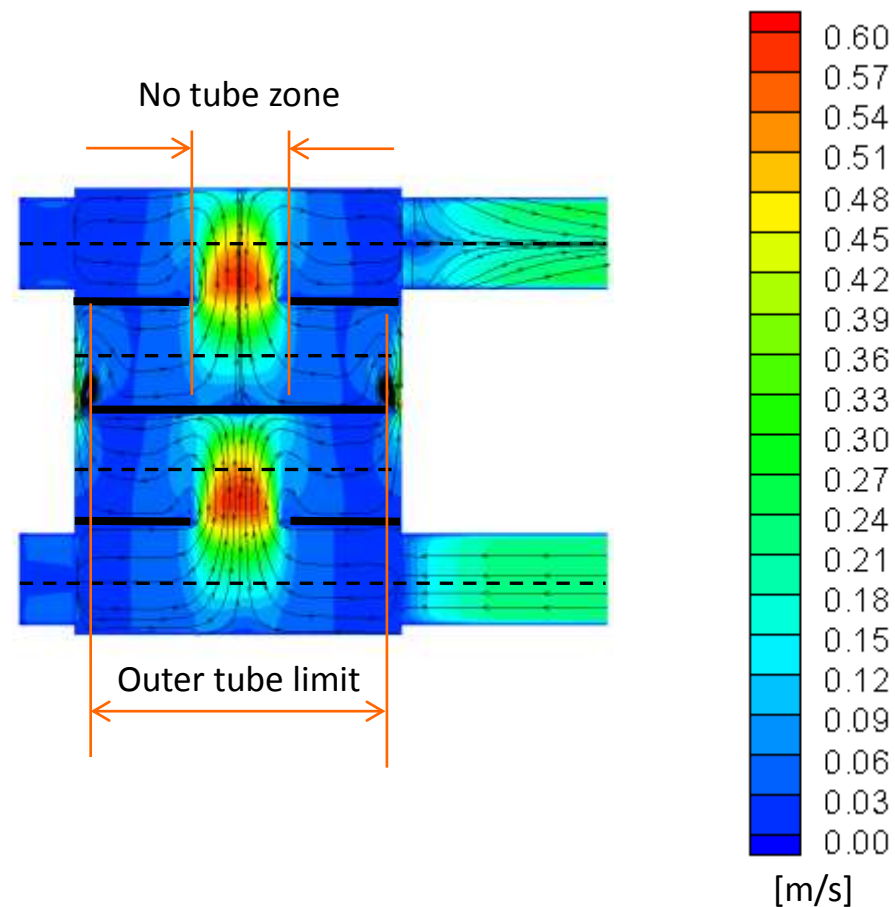
CFD model (implemented in Fluent®)



Coolant distributor

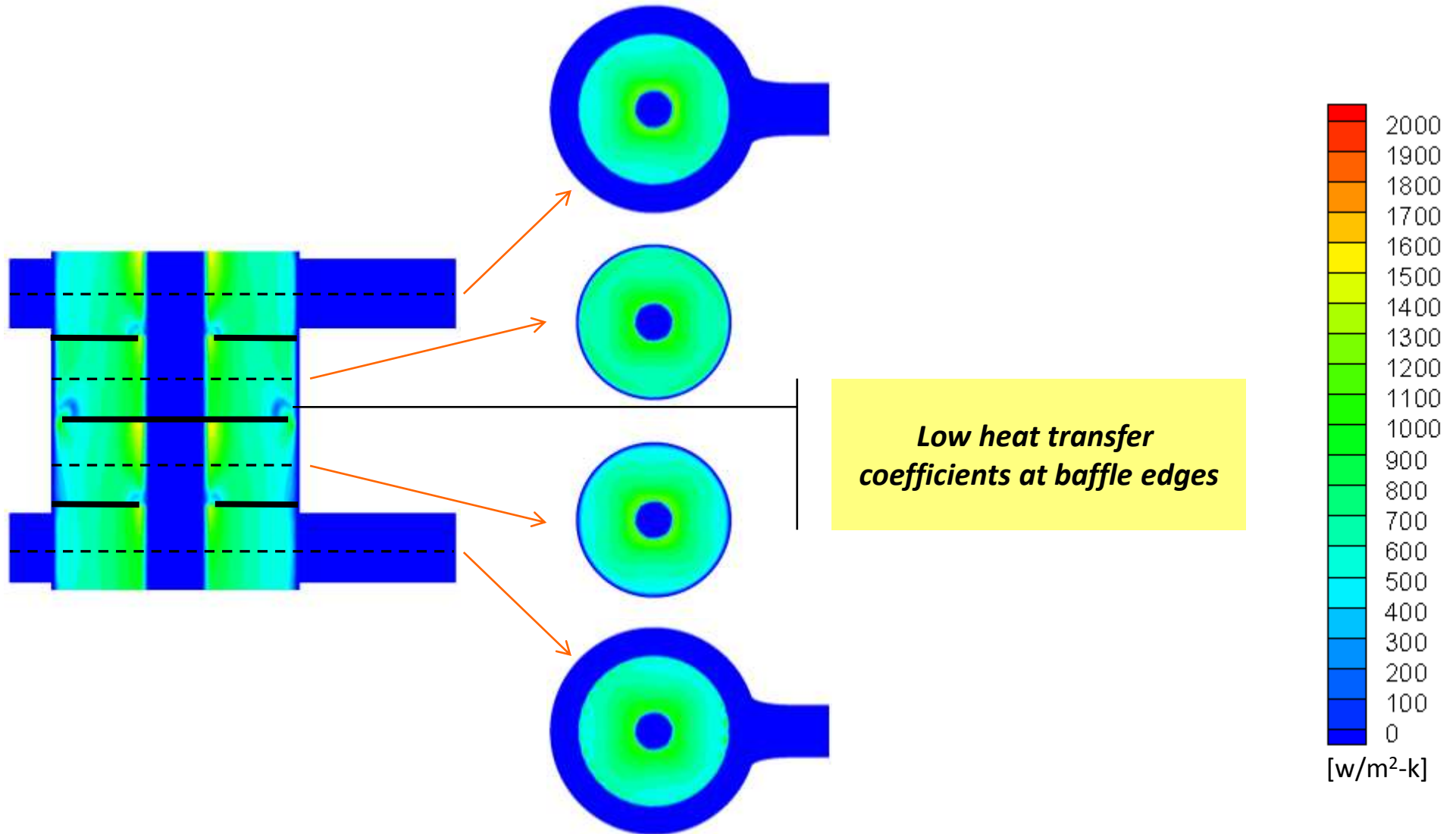
Distributor slit

Velocity magnitude and streamlines



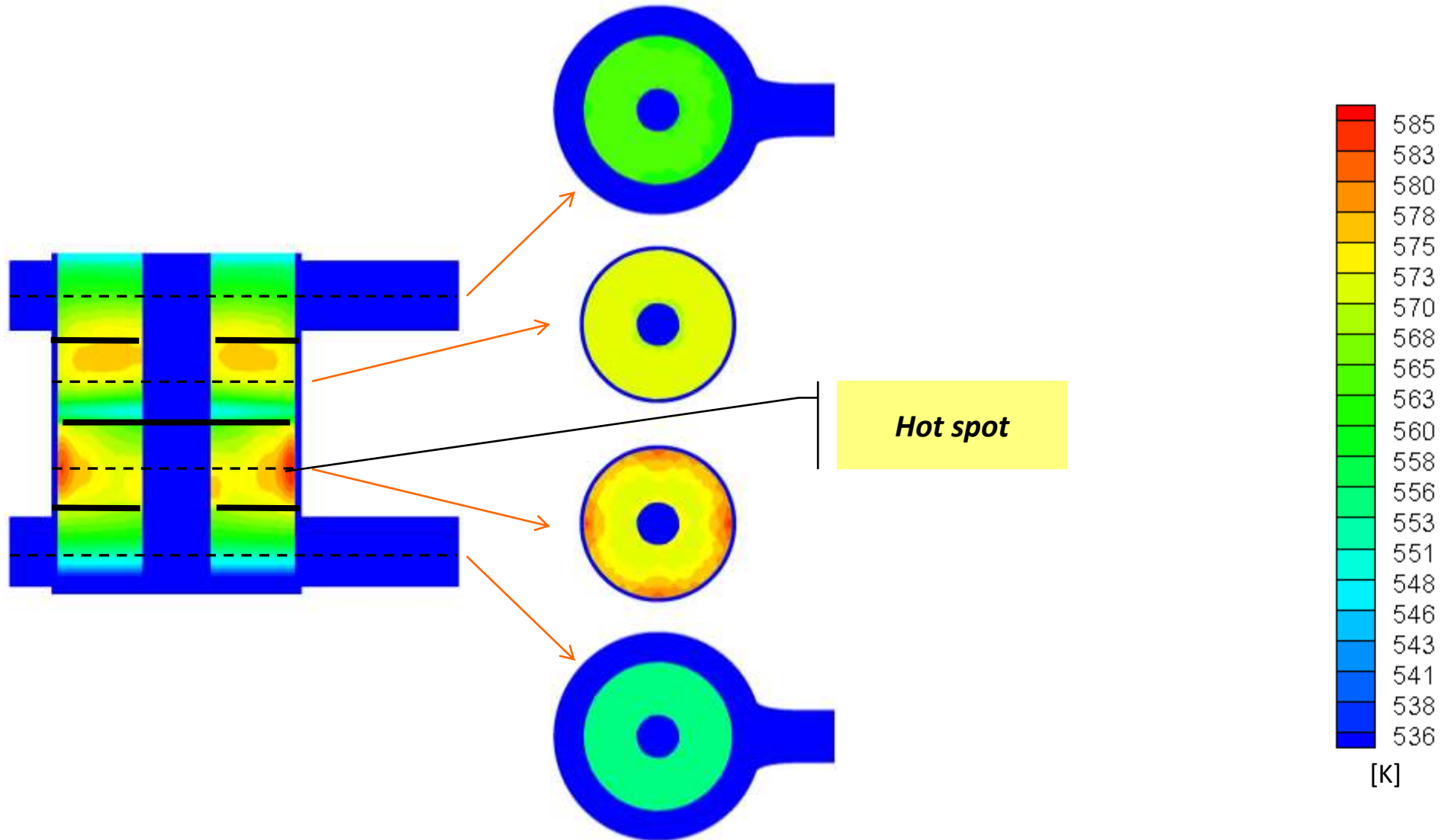
Hybrid gPROMS/CFD simulation results

Heat transfer coefficient



Hybrid gPROMS/CFD simulation results

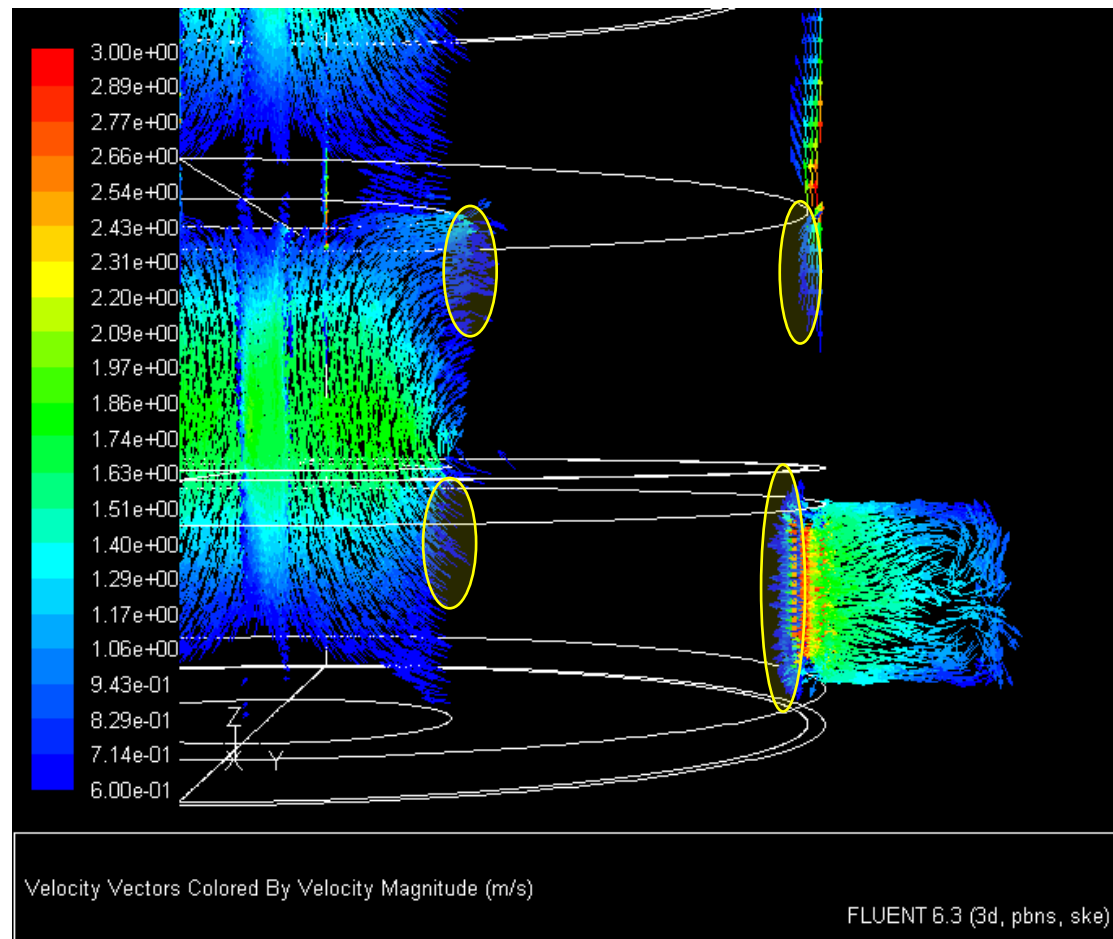
Tube center temperature I



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



- **AML:FBCR authors:** Zibi Urban, Stepan Spatenka

- **PSE Consultants:** Phil Han, In Seon Kim, Sujin Lee, Praveen Lawrence, Pieter Schmal, Sreekumar Maroor

- **PSE Software Technology Group**

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!



APM 2013

The Advanced Process Modeling Forum