Support of Fuels/Reformer R&D with Computational Fluid Dynamics (CFD) Modeling

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Overall Objective of Reformer Modeling Program

Develop/validate a CFD model of a reformer that can be used to evaluate the interaction between and the impact of fuels (composition) and design/operating parameters on reformer performance.

What does a Computational Fluid Dynamics (CFD) Model Do?

- Solves the laws of conservation of mass, momentum, energy, and atomic species within a flow domain
- *Couples* the conservation laws with other physical & chemical processes (reaction, vaporization, turbulence, etc.) to provide a characterization of major processes within the flow domain
- Computes primary variables throughout the domain: T,P,**U,** ρ, h, k, ε, Y_i

Technical Approach

- Develop a reformer model utilizing ANL's multiphase reacting flow CFD codes
  - Incorporate kinetic models for POX, shift, and PROX reactions
- Model selected micro reactors and prototype reformers
  - Use CFD models to extract local kinetic rate constants for postulated reduced reaction models
- Validate reformer model
  - With available data over wide parameter space
- Use validated model to conduct parametric, sensitivity, optimization and scale up studies
  - Identify most promising fuel composition and associated optimal operating and design parameters
  - Quantify impact of key operating and design parameters on reformer performance
  - Explore design options to maximize performance

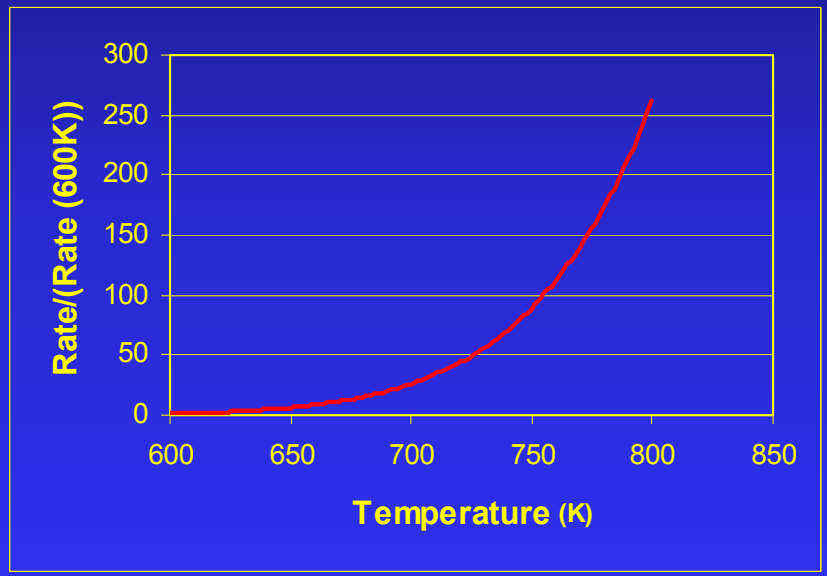
A CFD Model is an Invaluable Tool to Study Fuel/Reformer Interactions

- Fuel constituent reaction rates are characterized by the Arrhenius equation:

$$\frac{\partial C_i}{\partial t} = -K_i \left(\prod_r C_r^{n_r} \right) \exp\left(\frac{-E_i}{RT} \right)$$

Where C_r = concentration of reactants, T = temperature, K_i = preexponential constant, n_r = order of reaction for species r, E_i = activation energy for reaction i

Reaction rates are very sensitive to temperature

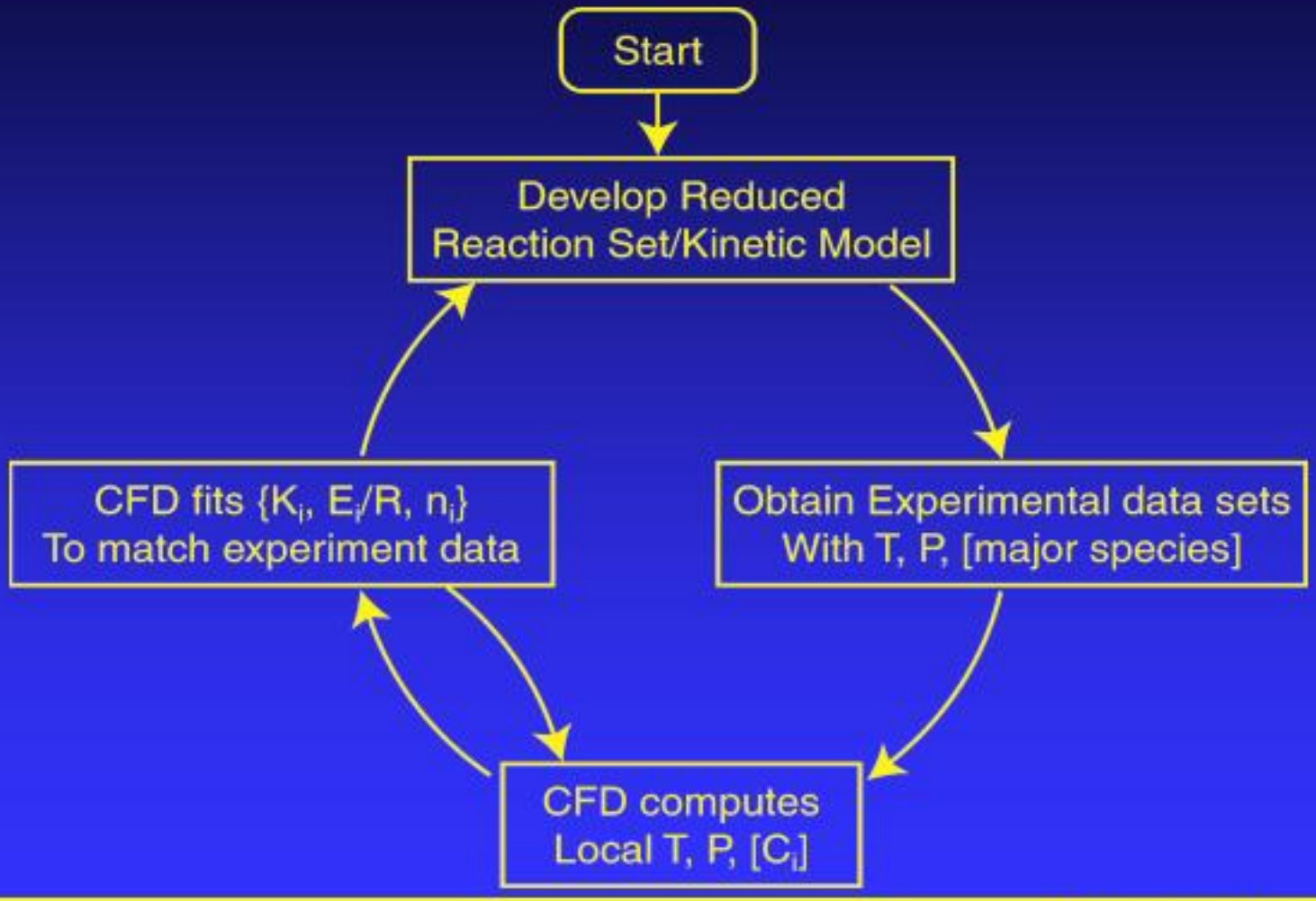


A CFD Model computes the local and exit values of the flow parameters & reaction rates and thus the overall reformer performance

Fuels Composition and Reformer Design Together Determine Overall Reformer Performance

- Critical issues/parameters impacting reformer performance
  - Operating windows exist with respect to coking limits & catalyst heat tolerance determined by fuel composition, Air/Fuel ratio & Steam/Carbon ratio
  - Reforming reaction rates of individual fuel constituents
  - Controlling reforming reactions
  - Incomplete mixing of reactant streams at catalyst inlet (determined by entry region design)
  - Heat losses at component boundaries (creates T distribution that impacts reaction rates)
  - Reformer volume (size)/residence time
- CFD models can be used to help identify optimal fuels/blends and investigate the impact of such issues in a cost effective manner

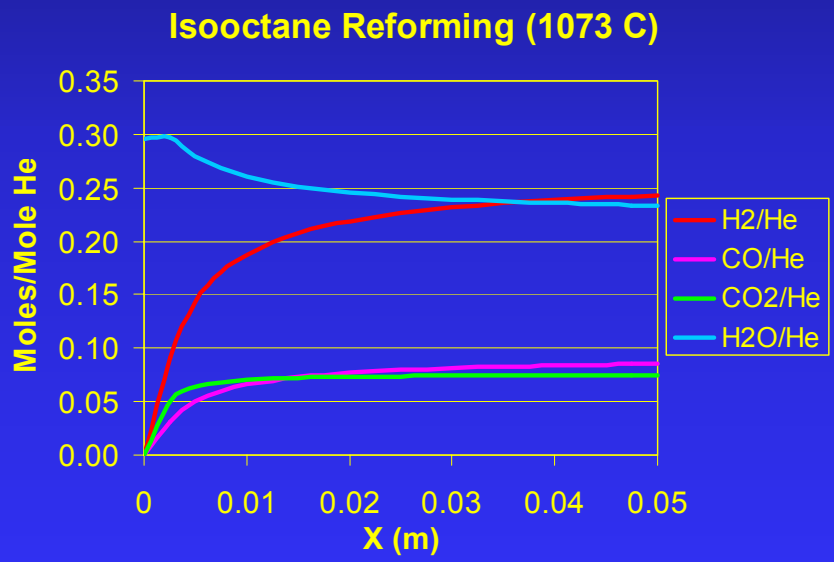
Kinetic Model Development and Rate Constant Extraction with CFD



Reduced Isooctane Kinetics Model From Micro Reactor Experiments

- Reduced reaction set for C_8H_{18} reforming
  - POX: $C_8H_{18} + 4\ O_2 \rightarrow 8\ CO + 9\ H_2$
  - Oxidation: $C_8H_{18} + 25/2\ O_2 \rightarrow 8\ CO_2 + 9\ H_2O$
  - Reforming: $C_8H_{18} + 16\ H_2O \rightarrow 8\ CO_2 + 25\ H_2$
  - Reforming: $C_8H_{18} + 8\ H_2O \rightarrow 8\ CO + 17\ H_2$
  - Shift: $CO + H_2O \rightarrow CO_2 + H_2$

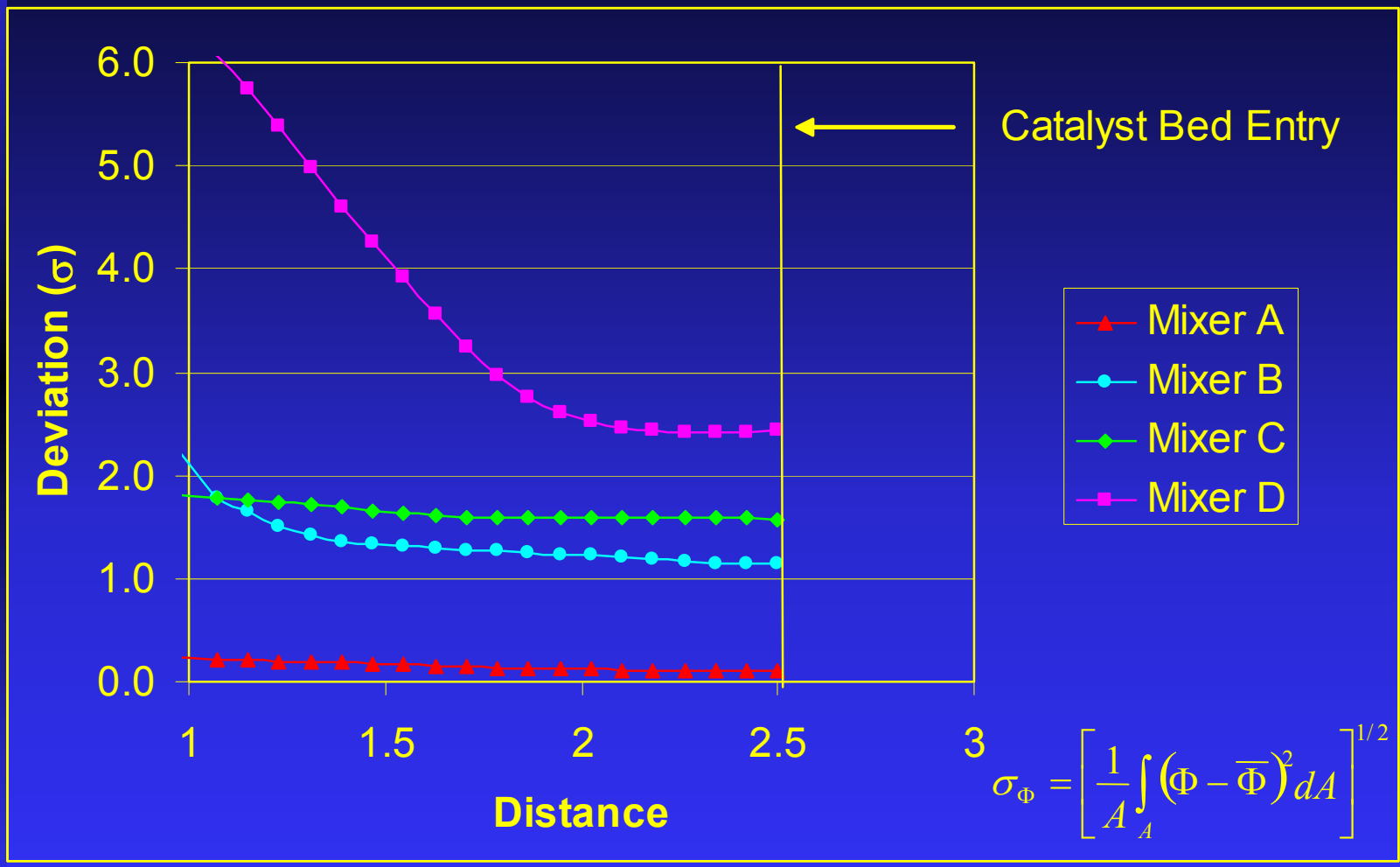
Typical Predicted Model Yield Trends in Micro Reactor



Approach Taken to Evaluate Impact of Reactant Maldistribution at Catalyst Bed Entry on Reformer Performance

- Defined/modeled four different reactant injection designs
  - Proprietary to industrial partner
  - Designated as Mixer A, B, C, D
- Coupled entrance models to specified autothermal reformer geometry
- Used isooctane reaction model
- Computed reformer H_2 yields
- Compared results with baseline having uniform reactant distribution at catalyst entry

Deviation From Uniform Equivalence Ratio Over Axial Cross Sections in Mixers up to Catalyst Bed Entry



$$\sigma_{\Phi} = \left[\frac{1}{A} \int_{A} \left(\Phi - \overline{\Phi} \right)^2 dA \right]^{1/2}$$

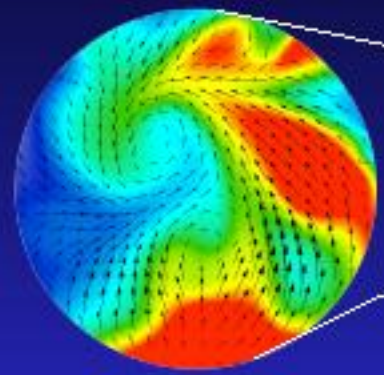
Effect of Incomplete Mixing on Hydrogen Formation in an ATR Catalyst Bed (Based on Mixer D)

Micro Reformer

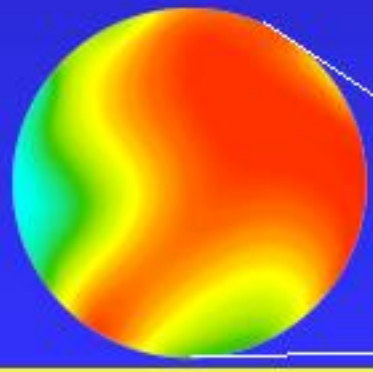
Fuel/Air mixture ratio at start of catalyst bed

Uniform mixing prior to entering catalyst bed leads to hydrogen formation in entire bed area

Hydrogen concentration

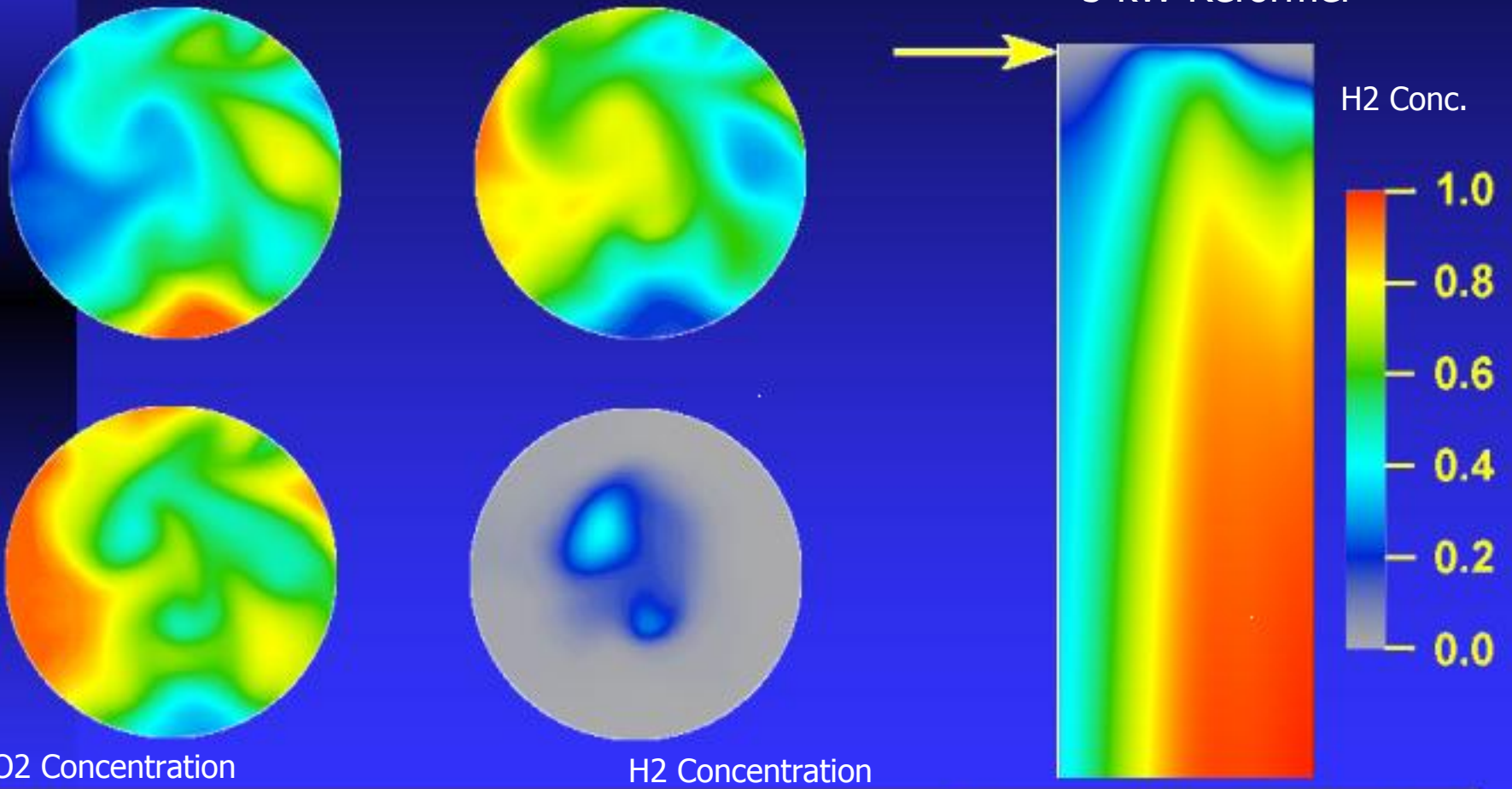


Non-uniform mixing prior to entering catalyst bed leads to uneven hydrogen formation

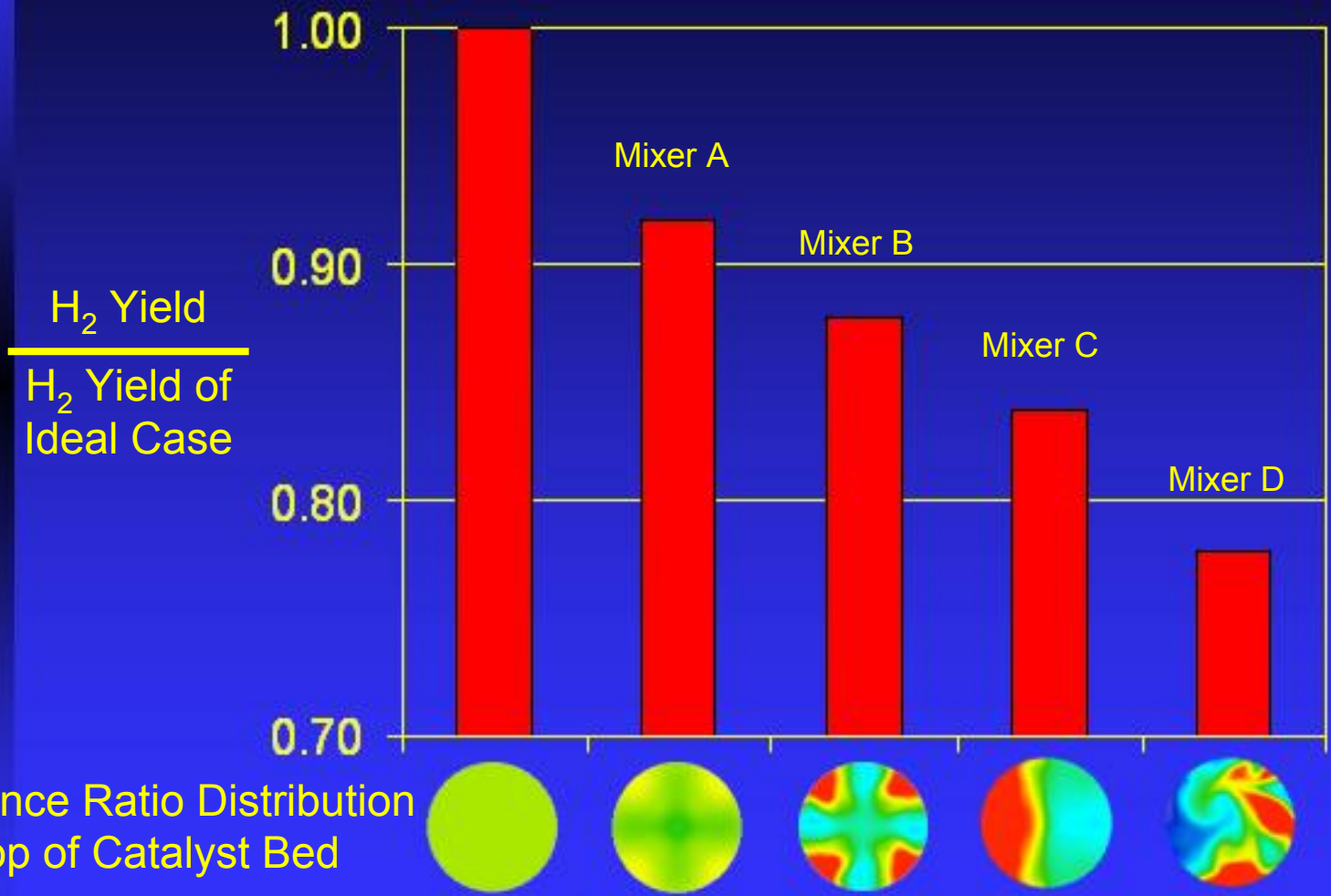


5 kW Reformer

Distributions Traveling Through the Catalyst Bed for Mixer D

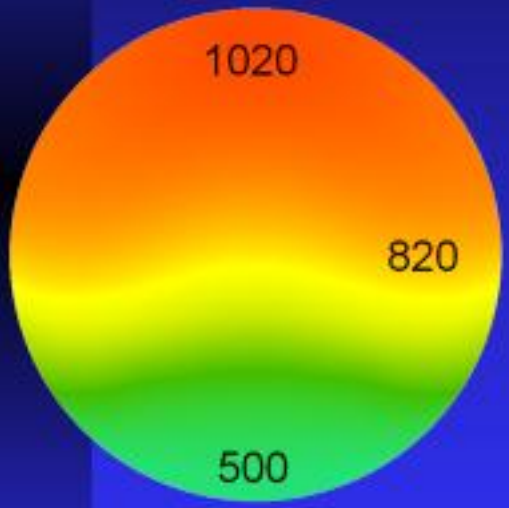


Hydrogen Yield Ratios Compared to Ideal Mixing Case

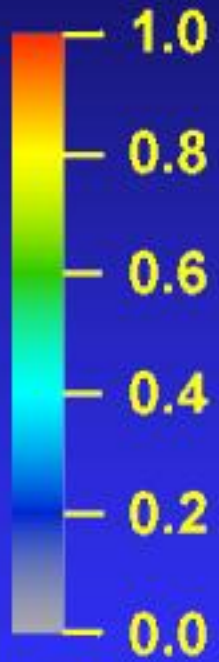


Experimental Thermal Couple Well Temperatures Compared to Computed Trends

Position at 1/5
Catalyst Bed Length

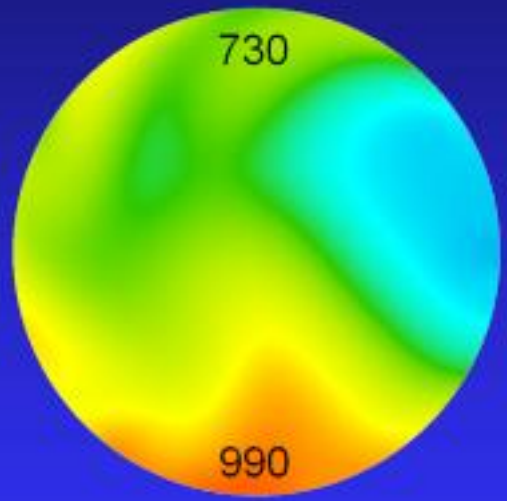


Mixer C



T/T_{max}

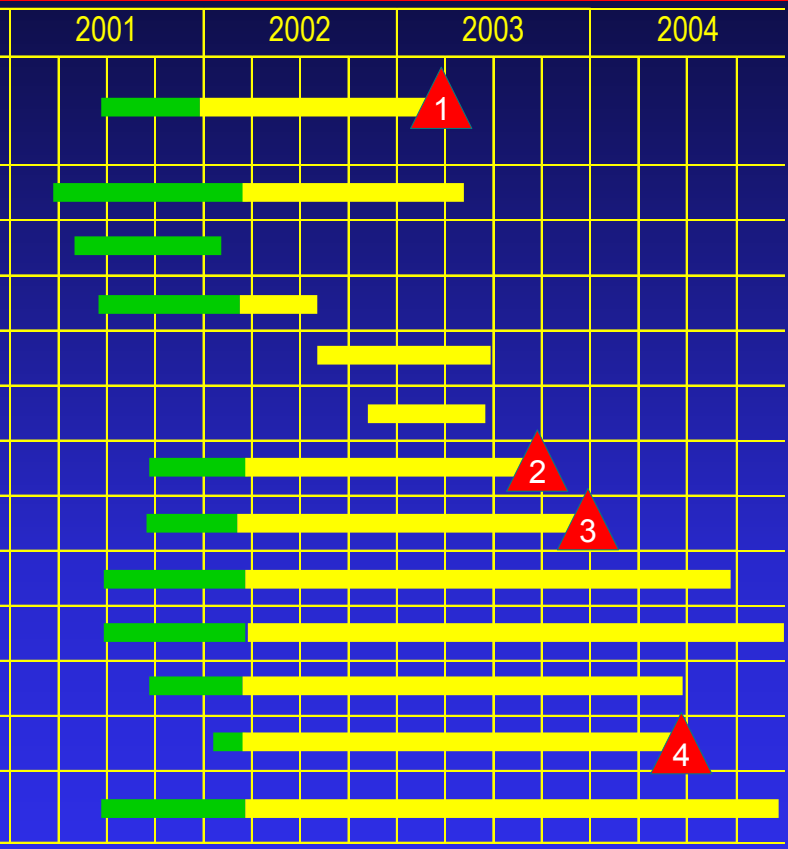
Position at 1/5
Catalyst Bed Length



Mixer D

Program Schedule/Milestones

Task	Task Description
1.	Construct reduced reaction models for selected fuels (constituents)
2.	Construct CFD reformer component models
	Entrance (reactant injection) region
	Auto thermal reactor
	Water-gas shift reactor
	PROX reactor
3.	Merge component models into reformer model
4.	Validate component/reformer models
5.	Parametric, sensitivity and optimization studies
6.	Modeling support of reformer R&D programs
7.	Parallelize codes for high fidelity simulations
8.	Develop transient/component/reformer models
9.	Technology transfer/support industrial programs



Major milestones:

Completed work:

1. Reduced reaction models for gasoline fuel developed
2. Overall reformer model completed
3. Component/reformer models validated
4. Transient reformer model completed

Planned Activities for Next Period

- Develop reduced reaction models for selected fuels
  - Focus on gasoline
    - Start from isooctane model reduced reaction set
    - Identify/use data available from labs and industry
- Finish monolith catalyst model
  - Add reaction to flow and heat transfer model
  - Fully couple to mixing zone computation
- Continue transient fast start heat up model development for ATR and water-gas-shift reactor
- Continue ongoing modeling support and CFD analysis activities consistent with guidance and available resources