ChemCatBio

Chemical Catalysis for Bioenergy

Computational Fluid Dynamic Study of Biomass Vapor-Phase Upgrading Process

Xi Gao, **Tingwen Li**, William Rogers, Rupen Panday, Jonathan Higham, Greggory Breault, Jonathan Tucker

National Energy Technology Laboratory, Morgantown, WV, United States

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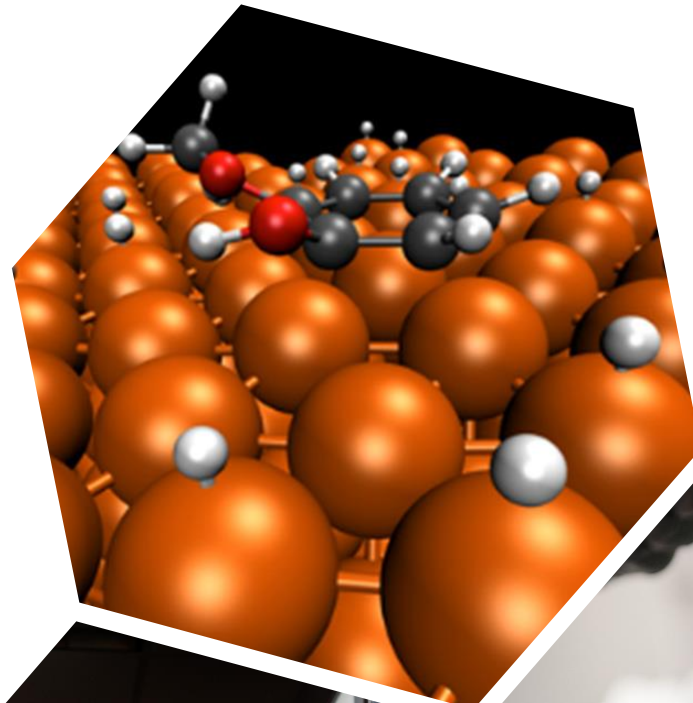

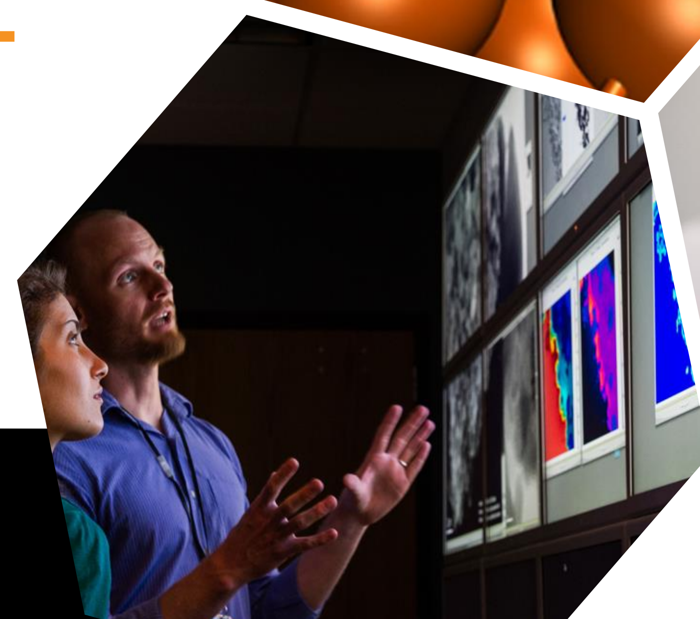

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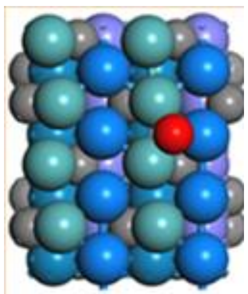
Presentation Outline

- **Background and motivation**
- **Simulation Setup** - Determine and validate the optimal catalyst particle drag model
- **Simulation Setup** - Validate Residence Time Distribution (RTD) calculations by comparing to experimental data
- **Simulation Application** - Predict gas and catalyst RTDs in the NREL VPU reactor over a range of operating conditions
- **Conclusions and next steps**

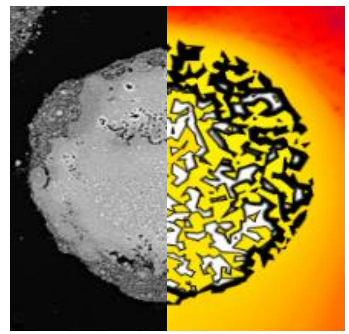
Consortium for Computational Physics and Chemistry (CCPC)

Atomic Scale Catalysis Modeling



Investigating novel catalyst material combinations and understanding surface chemistry phenomena to guide experimentalists

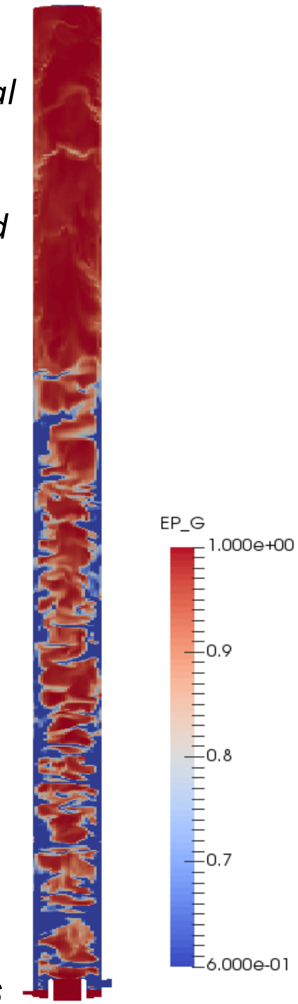
Meso Scale Particle Modeling



Understanding mass transport of reactants/products and coking and degradation processes

Process Scale Reactor Modeling

Determining optimal residence time distributions for maximum yield and enabling scale-up



ChemCatBio Enabling Projects

CCPC

www.cpcbiomass.org

ACSC
Advanced Catalyst Synthesis & Characterization

CCM
Catalyst Cost Model

ChemCatBio
Chemical Catalysis for Bioenergy

Vision: *The computational toolset developed by CCPC facilitates the modeling of biomass industrial technologies from atomic to process scales, thereby reducing the cost, time, and risk in commercializing bioenergy technologies*

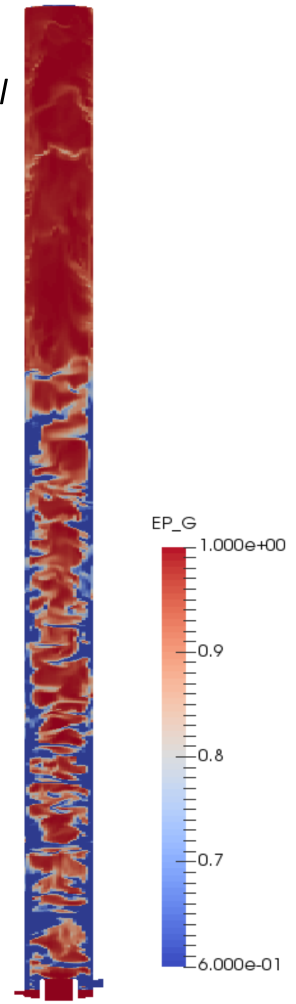
Background and Motivation

Process Scale Reactor Modeling

- **Goal of this work**: Use reactor-scale multiphase computational fluid dynamics simulations of catalytic upgrading of biomass pyrolysis vapor to provide:
  - Detailed modeling of hydrodynamics, chemistry, and heat transfer
  - Model validation using experimental data
  - Determine gas and catalyst **residence time distributions** for use in reduced-order reactor models and to help guide experiments
  - Provide a validated computational tool to support reactor design, scale-up, and optimization

- Models use the NETL MFiX Software Suite
  - MFiX – **M**ultiphase **F**low with **i**nterphase e**X**changes
  - CFD software for reacting, multiphase flow developed and supported by NETL
  - Open-Source, available to the public

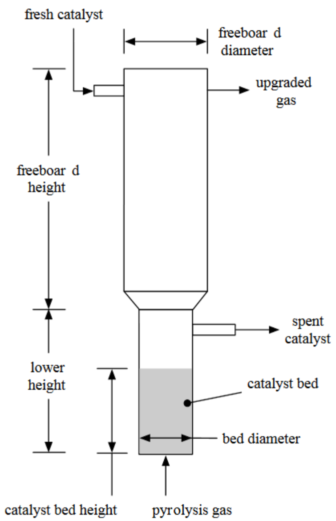
Determining optimal residence time distributions for maximum yield and enabling scale-up



Background and Motivation

- CCPC reactor simulations study a broad range of NREL reactor scales

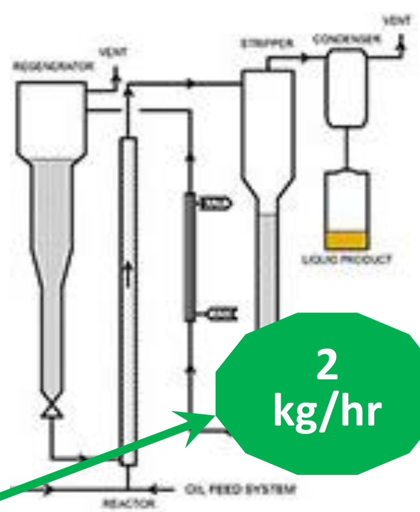
2" Fluidized Bed Reactor Upgrader*



0.5 kg/hr

Relevant to new BETO catalysts

Davison Circulating Riser (DCR) Reactor*

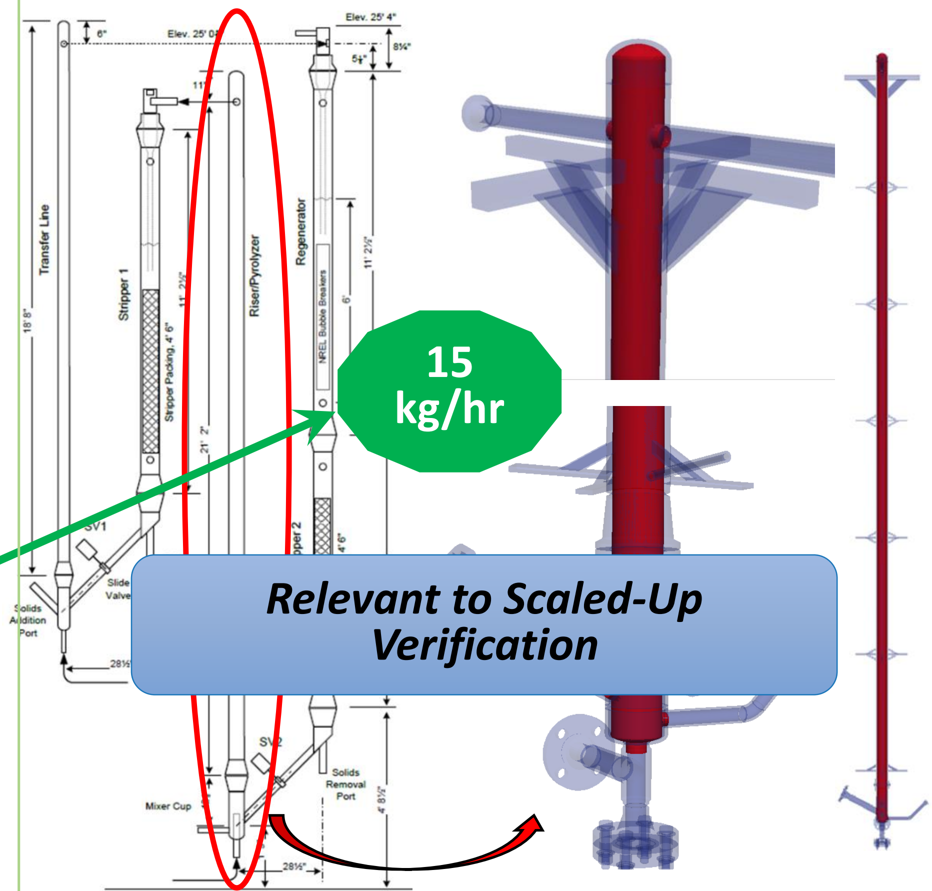


2 kg/hr

WR Grace

Relevant to Industry

TCPDU R-Cubed Upgrader*



15 kg/hr

Relevant to Scaled-Up Verification

PSRI (redesign)

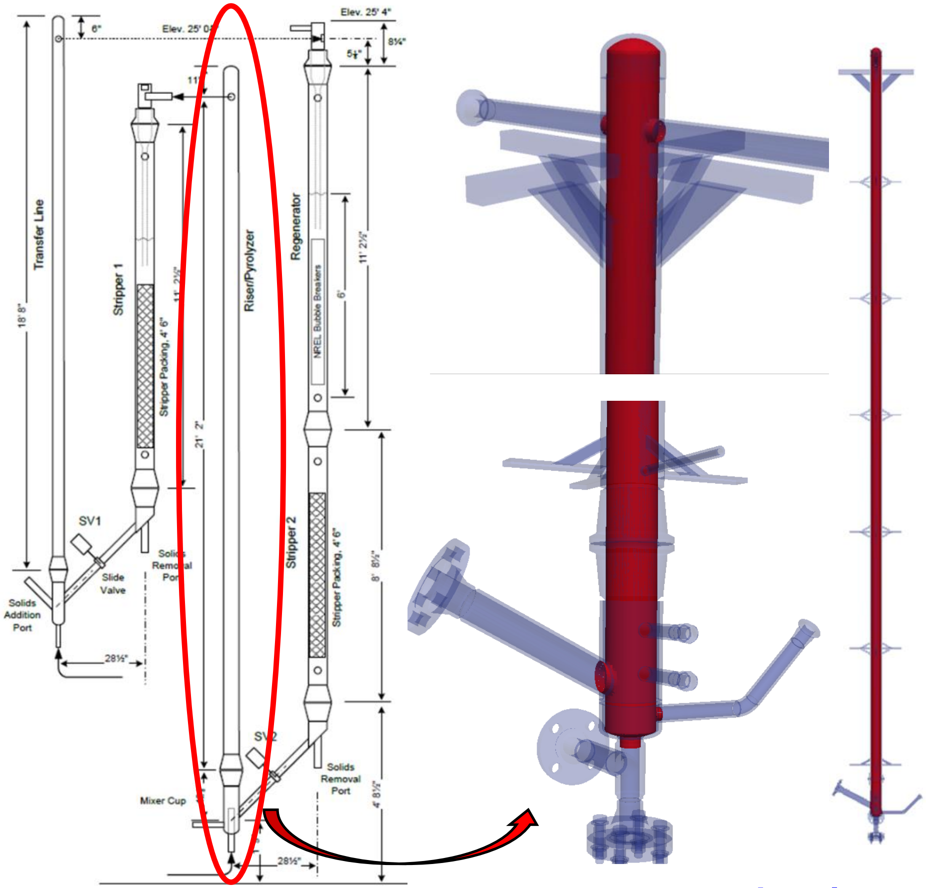
Computational Domain in Red

***All (3) Reactors at NREL**

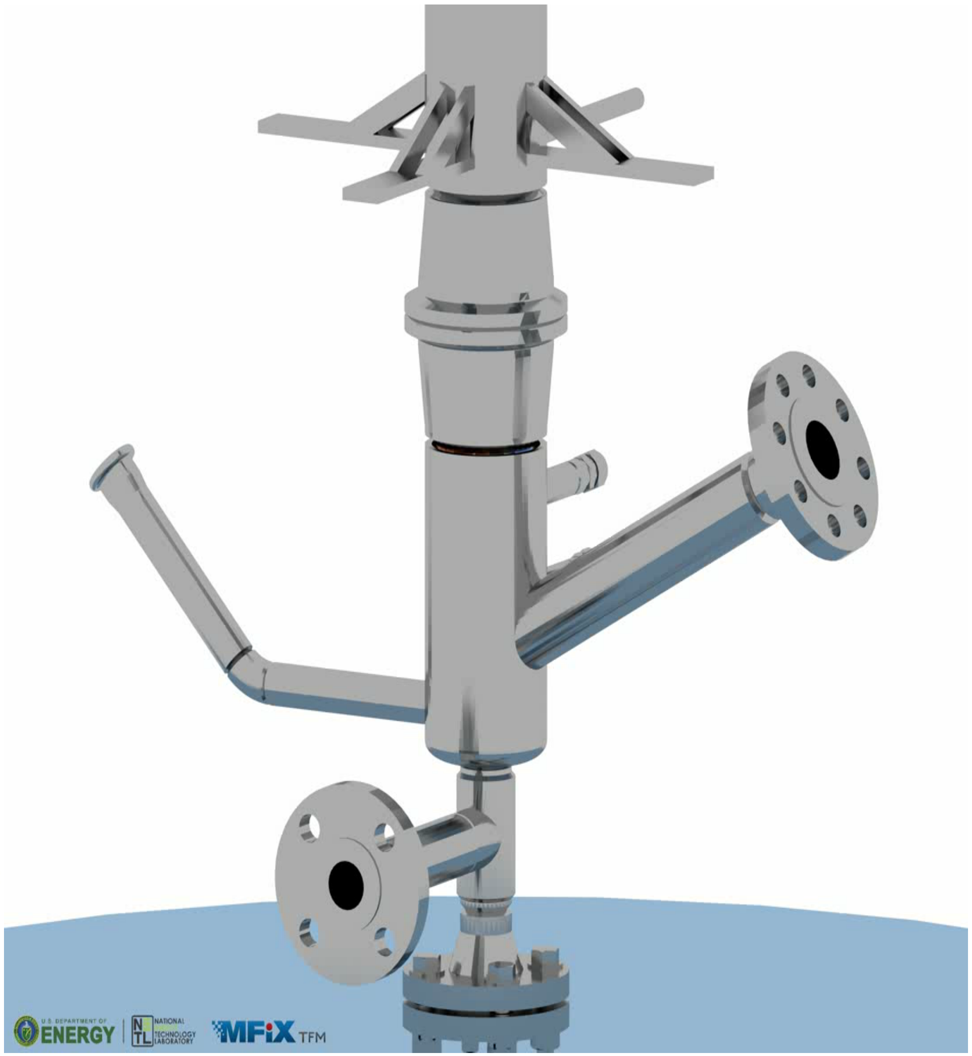
Background and Motivation

- The NREL R-Cubed Vapor Phase Upgrader (VPU) Riser is the subject of this study

TCPDU R-Cubed Upgrader

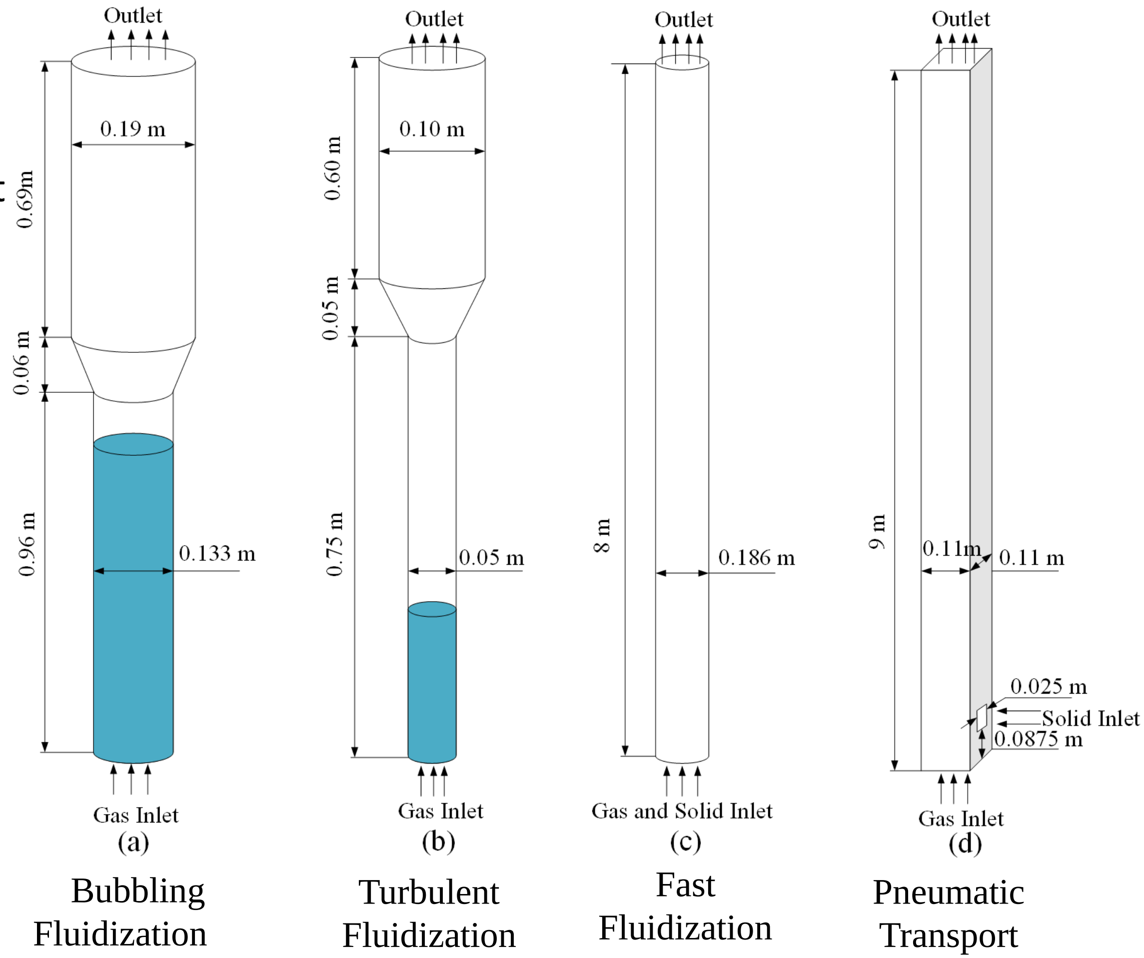


Computational Domain in Red



Simulation Setup – Determine and validate the optimal catalyst particle drag model

- The VPU system is challenging to model
  - Small H-ZSM-5 (ECAT) particles need special consideration - Geldart A classification
  - Wide range of hydrodynamics encountered in full-loop CFBs
  - Limited grid resolution due to computational cost
- A comprehensive evaluation of drag models for Group A particles was performed
  - Eight drag models were evaluated over a range of fluidization regimes
  - Detailed, three-dimensional simulations were conducted
  - Model results were compared to experimental data
    - Axial profiles of time-averaged gas volume fraction were basis of comparison
    - Data from literature



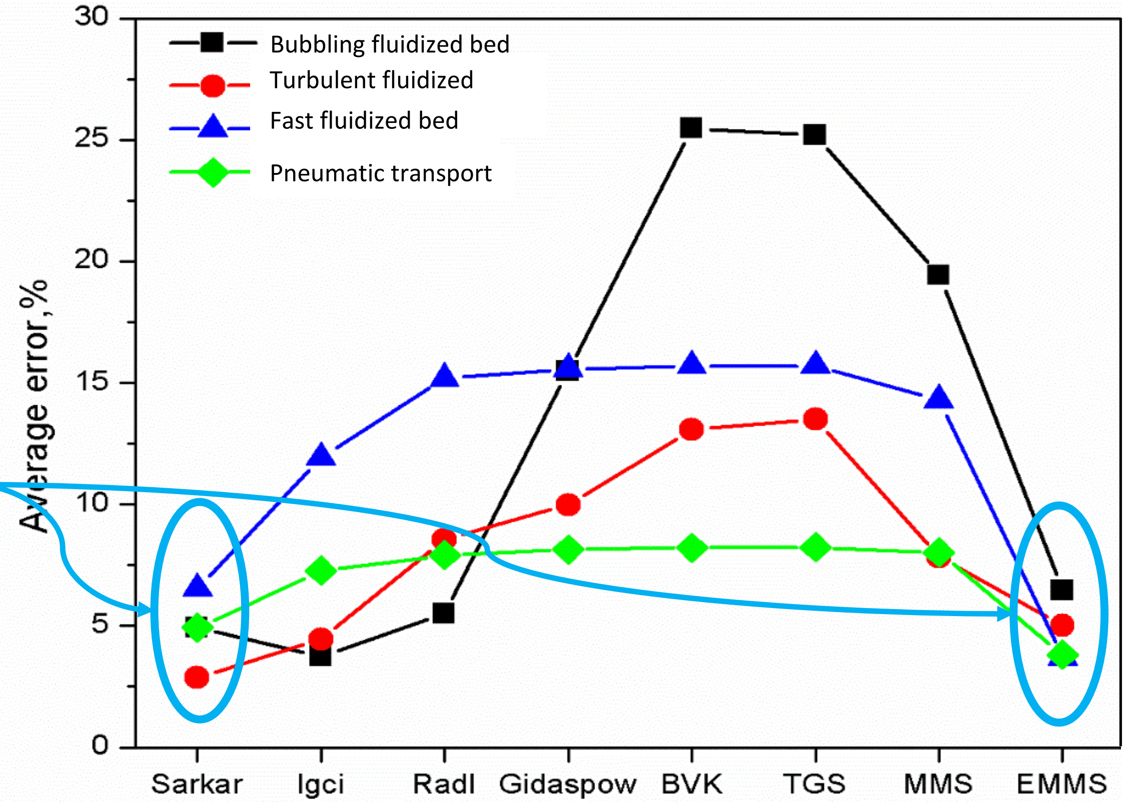
Different fluidization regimes for Geldart Group A particles were studied

Simulation Setup – Determine and validate the optimal catalyst particle drag model

- Evaluate the agreement for all fluidization regimes
  - Define an average error

$$E_{abs} = \sum_{i=1}^{N} \frac{\left|\alpha_{g,sim}^{i} - \alpha_{g,\exp}^{i}\right|}{\alpha_{g,\exp}^{i} N}$$

  - Based on this metric, the filtered model of **Sarkar et al.** (2014) and the **EMMS** (Li and Kwauk, 1994) models yield the best agreement for all fluidization conditions



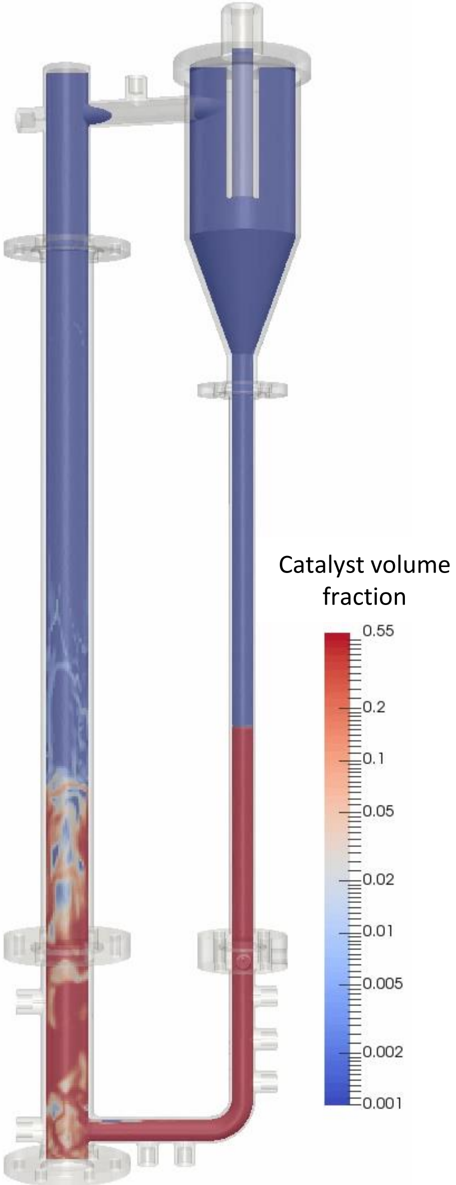
- However, EMMS is system and operation dependent
  - A new drag expression is needed for each operating condition
  - Depends on temperature, solid circulation rate, superficial gas velocity, etc.
- Sarkar et al. (2014) is a universal model, **it was selected as the best option for large-scale VPU simulations**

Sarkar A., Sun X., Sundaresan S. (2014) Verification of sub-grid filtered drag models for gas-particle fluidized beds with immersed cylinder arrays. Chemical Engineering Science, 114, 144–154.

Li, J., Kwauk, M., (1994), Particle-Fluid Two-phase Flow, The Energy-Minimization Multi-Scale Method, Metallugical Industry Press, Beijing, China.

Simulation Setup – Determine and validate the optimal catalyst particle drag model

- Validate the drag model
  - Conduct experiments with ECAT zeolite in an NETL CFB
    - measure key performance parameters
  - Model the experiment with MFiX to validate the selected drag model
- Small-scale CFB for ECAT zeolite
  - Height: 0.61m (2 ft)
  - Riser diameter: 0.0254m (1in)
  - Standpipe diameter: 0.0127m (0.5in)
  - Accurate measurements and accurate flow control
  - Use the NREL ECAT zeolite material
    - Mean particle diameter: 86µm
    - Particle density: 1560 kg/m^3
- Measurements
  - Transient pressure drop for different bed sections
    - Indicates solids “hold up” for the bed section
  - Transient bed height in the standpipe

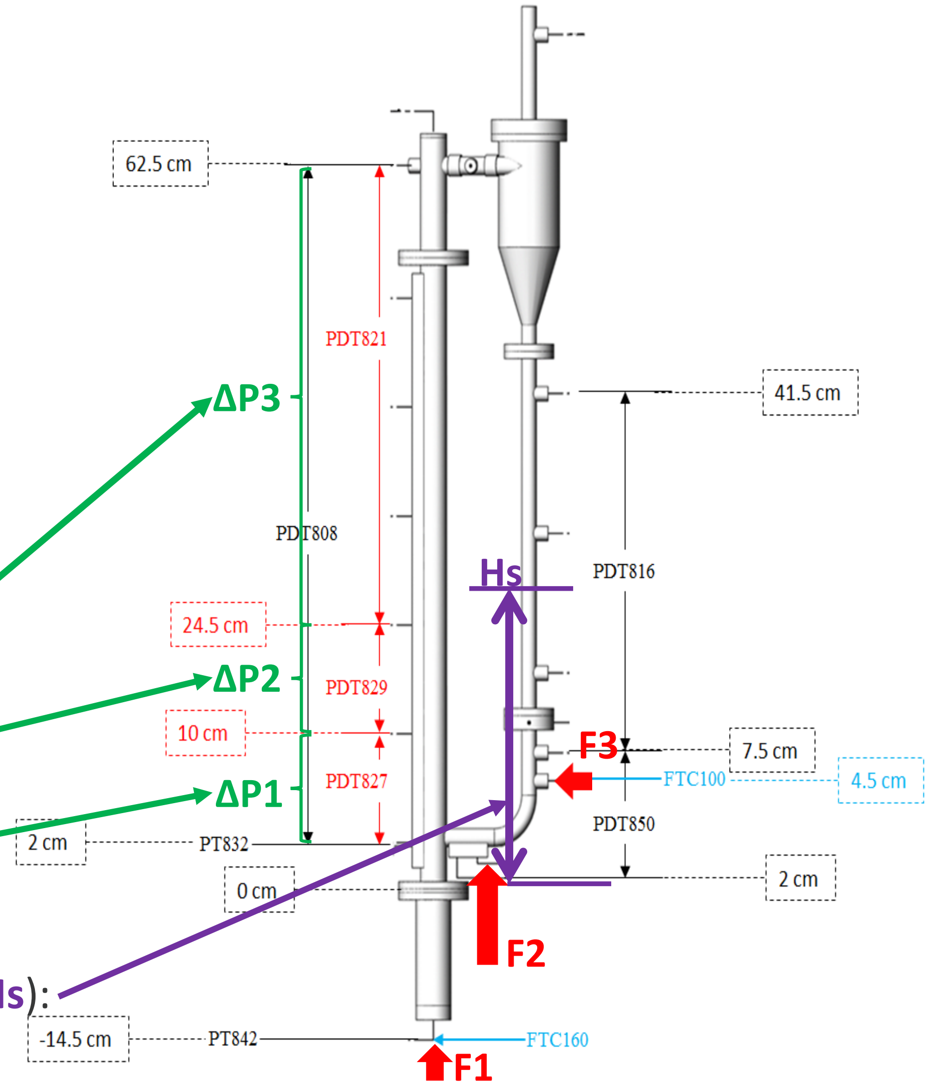


Simulation Setup – Determine and validate the optimal catalyst particle drag model

- **Small-scale CFB operating conditions**
  - Riser Flow, **F1**: 10 slpm
  - L-Valve Flow, **F2**: 0 slpm
  - Standpipe Flow, **F3**: 0.02 slpm
  - Bed Inventory: 80 g

- **Comparison of Measurement and Model prediction**
  - Time-averaged pressure drop

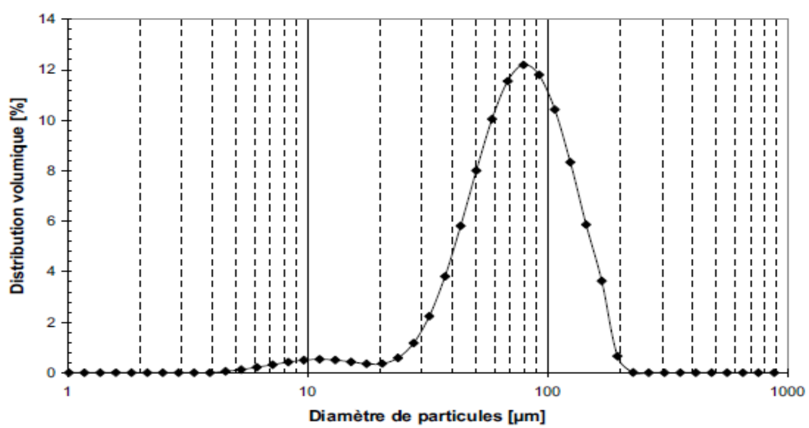
	Measurement	Prediction
ΔP3 (Pa)	5	7
ΔP2 (Pa)	263	372
ΔP1 (Pa)	436	477

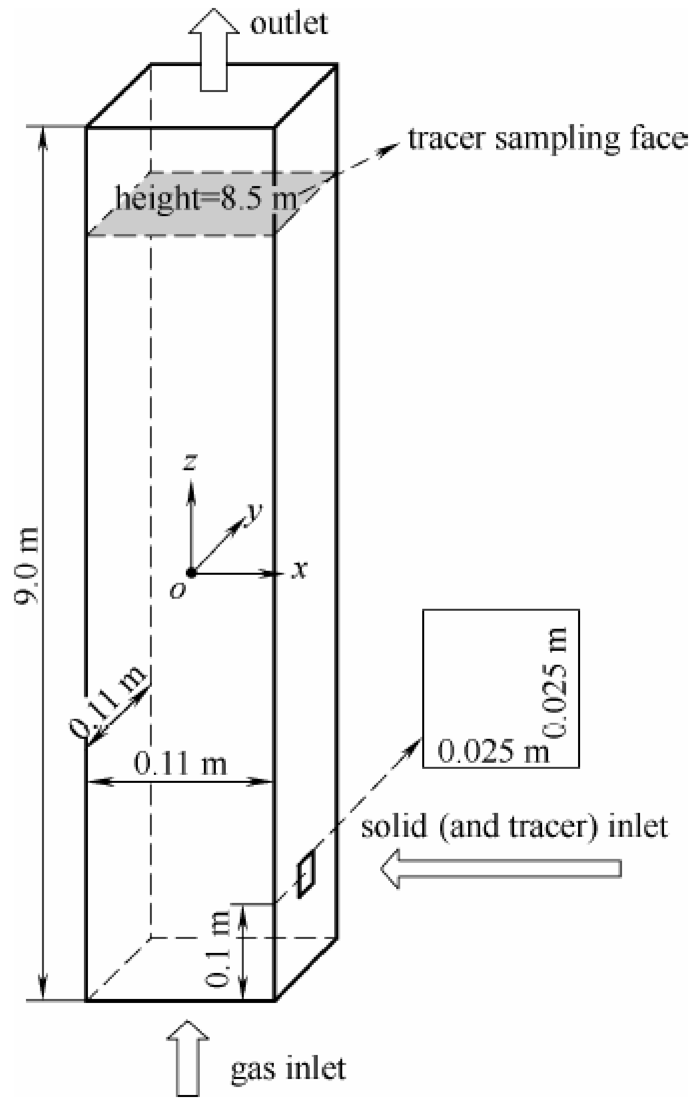


  - Time-averaged solids height in standpipe (**Hs**):
    - 23 cm (exp.) vs. 25 cm (model)

Simulation Setup – Validate RTD calculation

- Compare simulation to the data from CFB experiment of Andreux et al. 2008
  - Riser geometry: 0.11m×0.11m×9 m
  - Particle mean diameter, $d_{p,50}$: 70µm
  - Particle density, ρ_p: 1400kg/m^3
  - Gas inlet velocity, Ug: 5, 7m/s
  - Solids mass flux, Gs: 76, 133 kg/m^{2}s
  - Salt tracer used with pulse injection at inlet
  - Tracer detection near top





Andreux, R., Petit, G., Hemati, M., Simonin, O., 2008, Hydrodynamic and solid residence time distribution in a circulating fluidized bed: Experimental and 3D computational study, Chemical Engineering and Processing, Vol. 47, pp. 463-473.

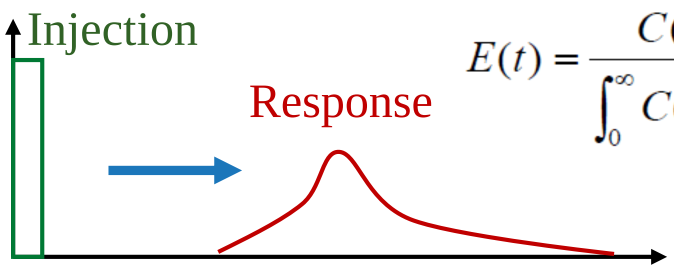
Simulation Setup – Validate RTD calculation

All simulations use the optimal Sarkar et al. (2014) drag model

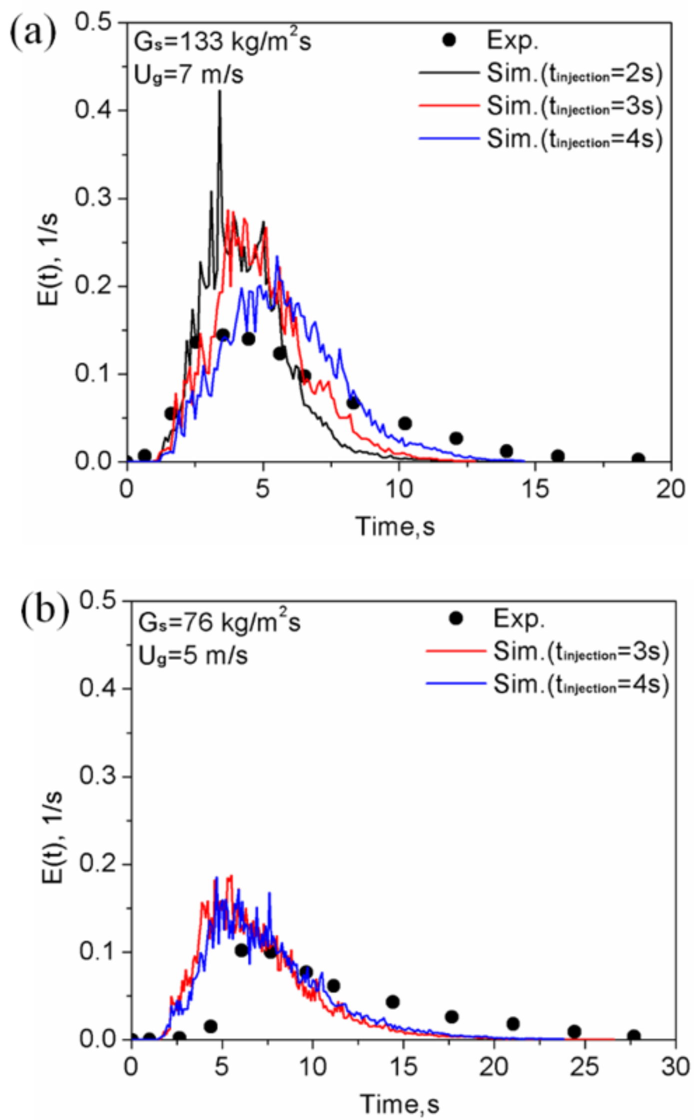
- Catalyst hold-up in the riser was validated by comparing measured and predicted pressure drop – *error <5%*

Pulsed solids phase tracer injection at the inlet

- Solid tracer is a "labeled" solids flow
- **Pulse injection** of **50g** solid tracer over **2~4s** time period
- Tracer concentration monitored at 8.5m near exit



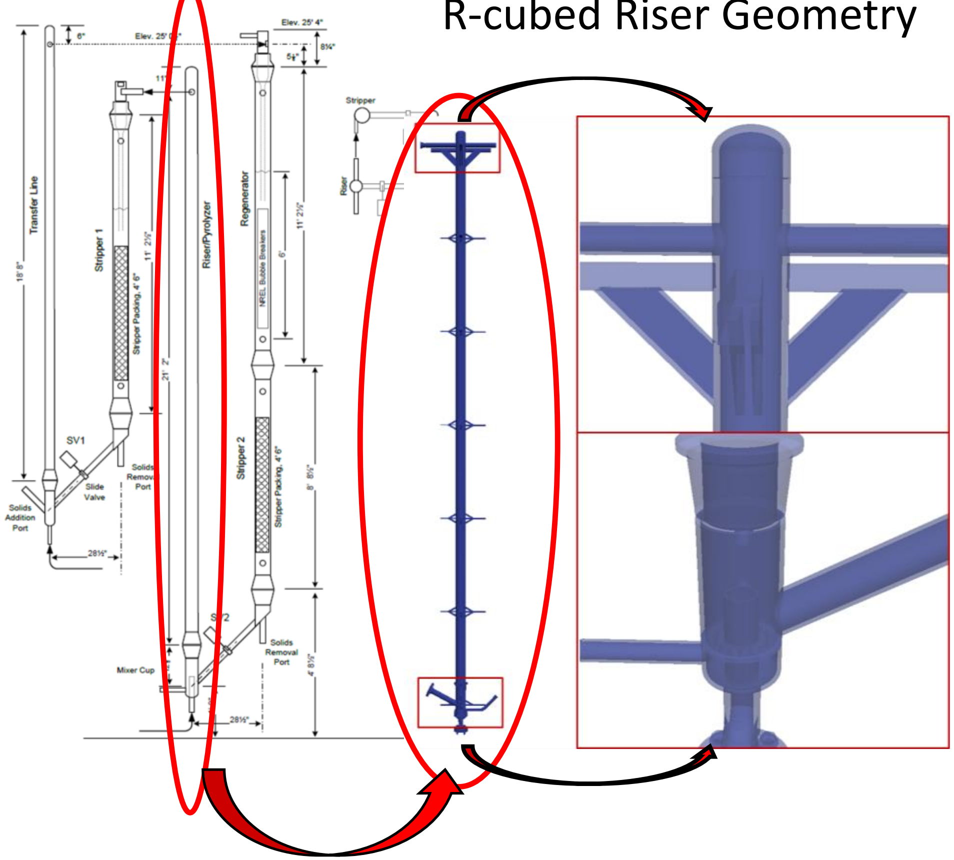
$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt}$$



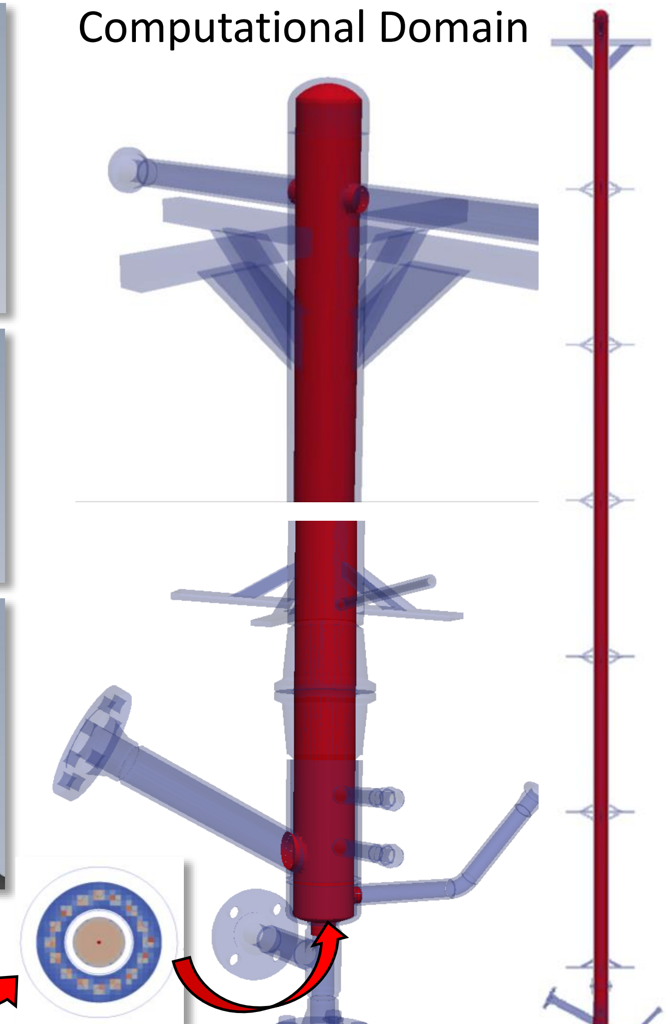
Simulation Application – RTD calculation in the VPU riser

TCPDU Process

R-cubed Riser Geometry



Computational Domain

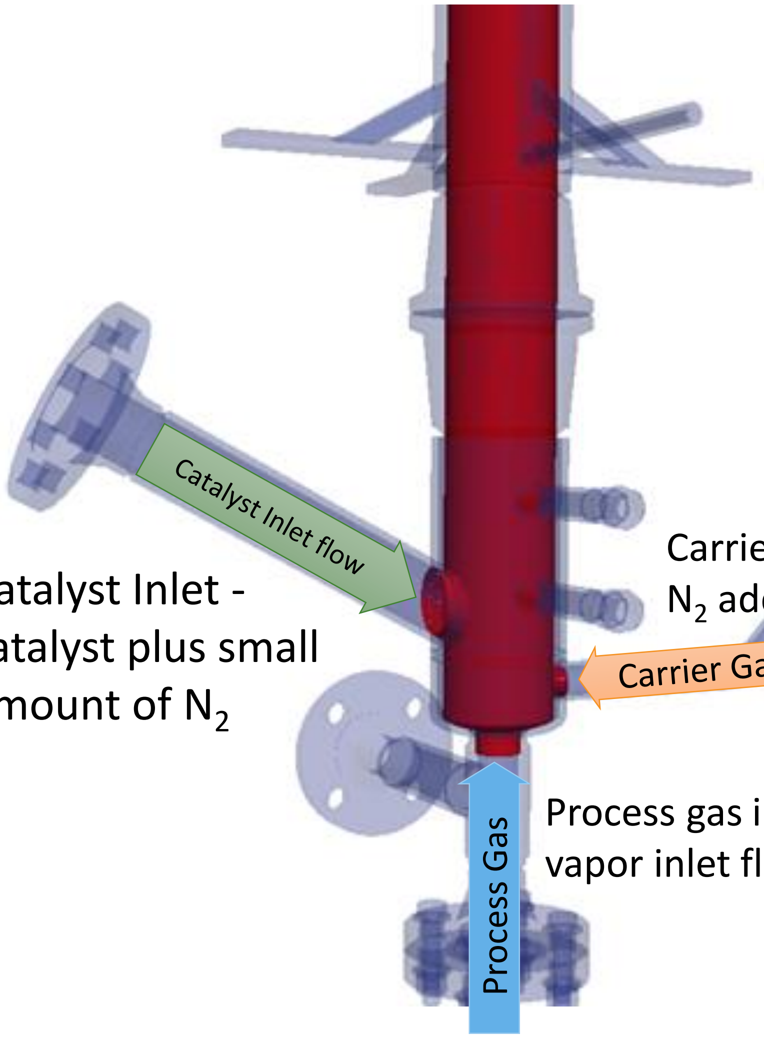


Inlet holes are resolved

- Riser: Height: 7.05 m, diameter: 0.092 m
- Outlet diameter: 0.038 m
- Solids inlet diameter: 0.049 m
- Pyrolysis vapor inlet diameter: 0.047 m
- Distributor: 16 holes with diameter of 0.00625 m

Simulation Application – RTD calculation in the VPU riser

Inlet configuration

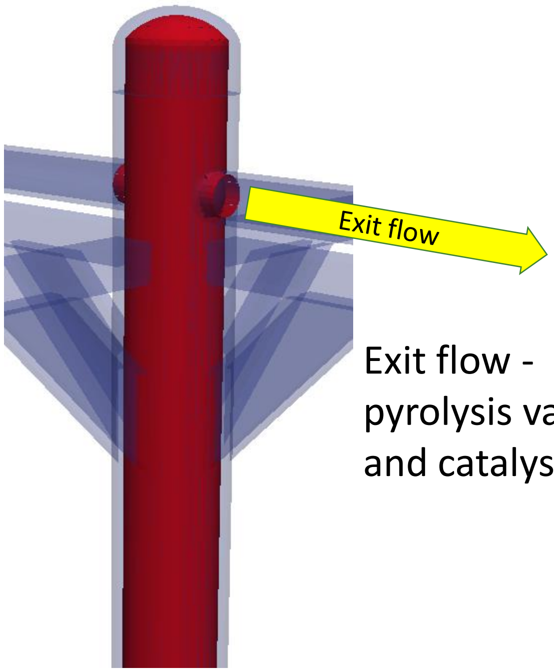


Catalyst Inlet - catalyst plus small amount of N_2

Carrier gas inlet -additional N_2 added to riser flow

Process gas inlet - pyrolysis vapor inlet flow

Outlet configuration



Exit flow - pyrolysis vapor and catalyst

Simulation Application – RTD calculation in the VPU riser

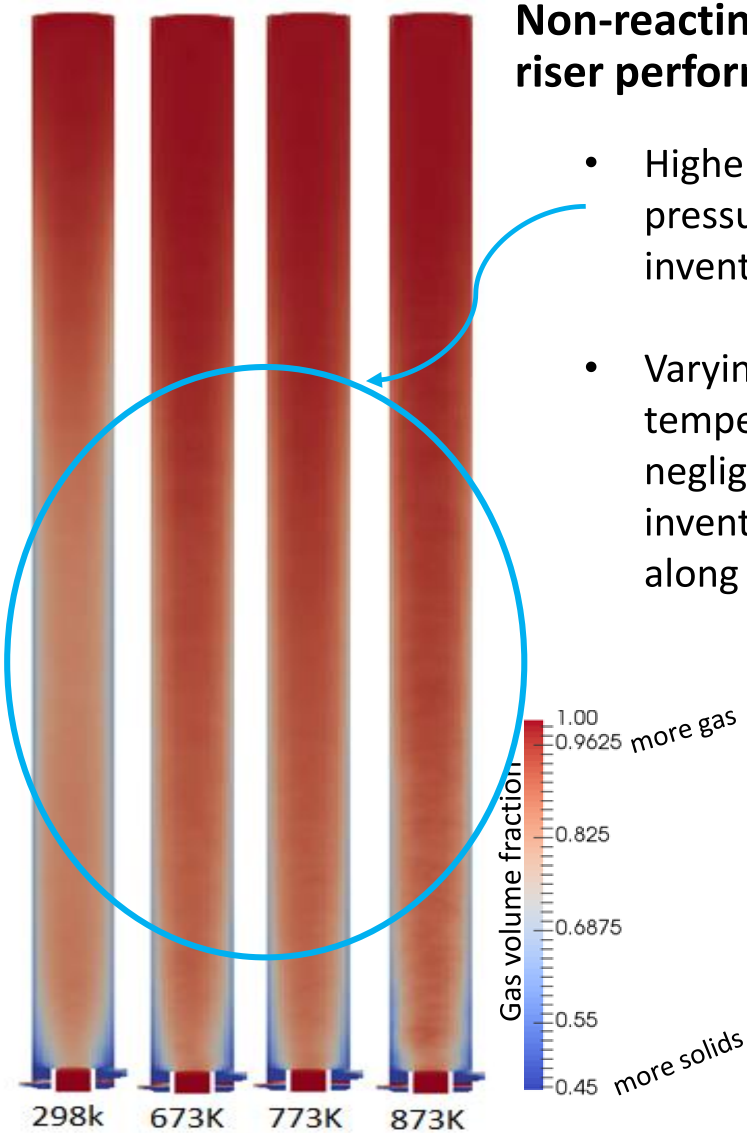
Baseline operating conditions based on design specifications

Parameters	Values	Parameters	Values
Inlet pyrolysis vapor volumetric flow rate, Qg (slpm)	580	Inlet pyrolysis vapor temperature (K)	773
Inlet catalyst mass flow rate, Gs (g/s)	46.1	Inlet catalyst temperature (K)	773
Average riser pressure (kPa)	150	Catalyst particle density (kg/m^3)	1560
Catalyst particle diameter (SMD) (microns)	86	Carrier gas volumetric flow rate (slpm)	5
J-leg gas flow rate (slpm)	5		

First parametric study varies operating pressure, gas inlet temperature, and catalyst inlet temperature – all at non-reacting conditions

Case number	Description
Case A	All inlet temperatures 298K and riser pressure at 101kPa
Case B	All inlet temperatures 773K and riser pressure at 150kPa (Baseline conditions)
Case C	Gas inlet temperature 773K, inlet catalyst temperature 673K and pressure at 150kPa
Case D	Gas inlet temperature 773K, inlet catalyst temperature 873K and pressure at 150kPa

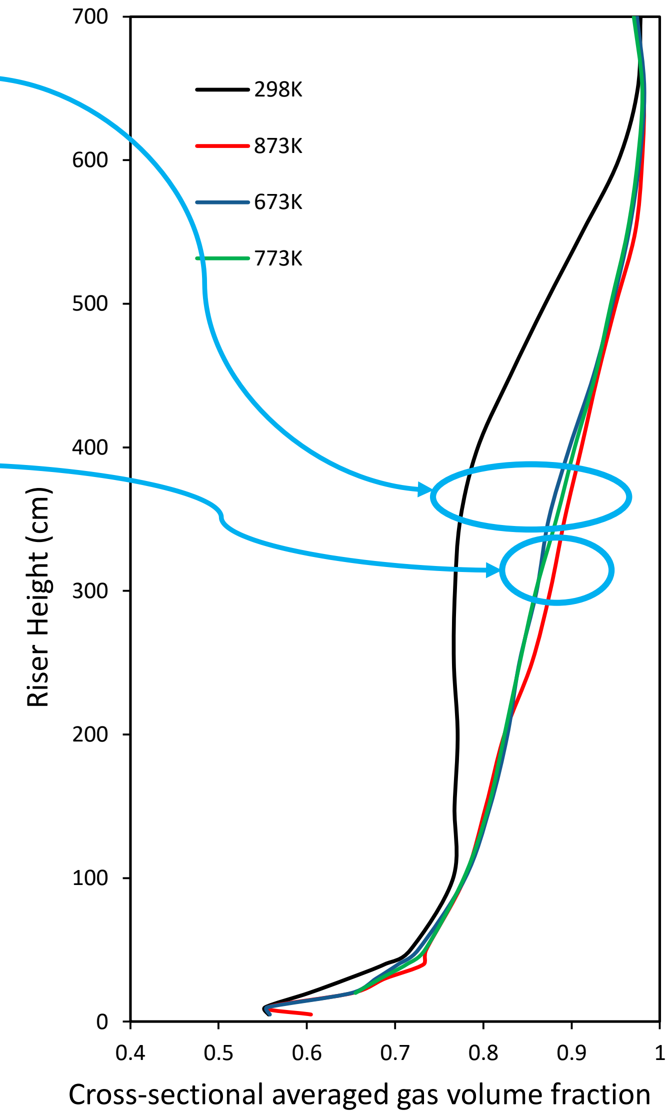
Simulation Application – RTD calculation in the VPU riser



Time-averaged contours of gas volume fraction

Non-reacting flow - Effect of catalyst inlet temperature on riser performance

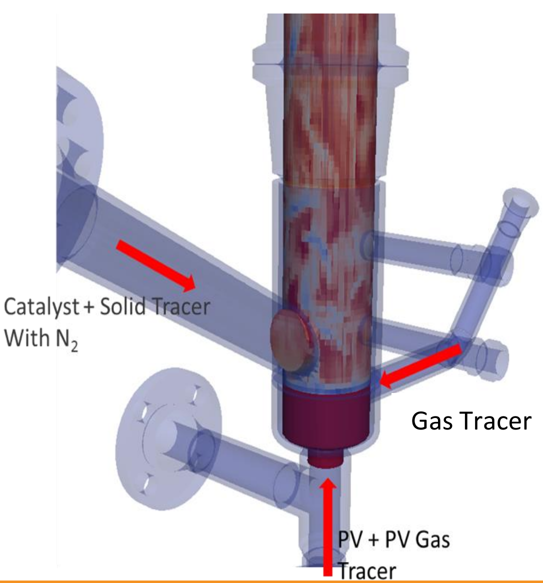
- Higher riser temperature and pressure reduces catalyst inventory
- Varying the catalyst inlet temperature by +/-100K has negligible impact on catalyst inventory and distribution along the riser



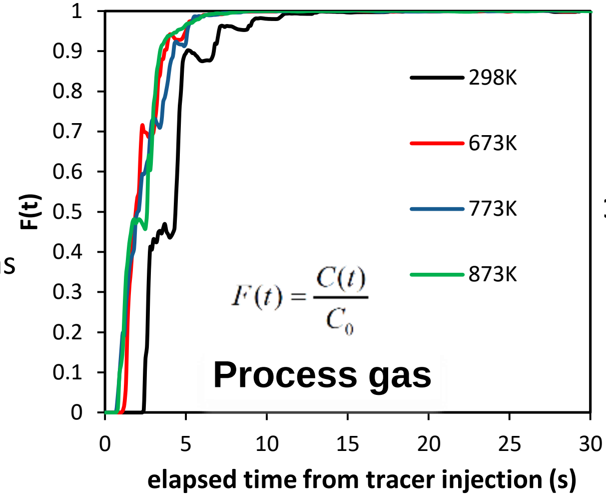
Simulation Application – RTD calculation in the VPU riser

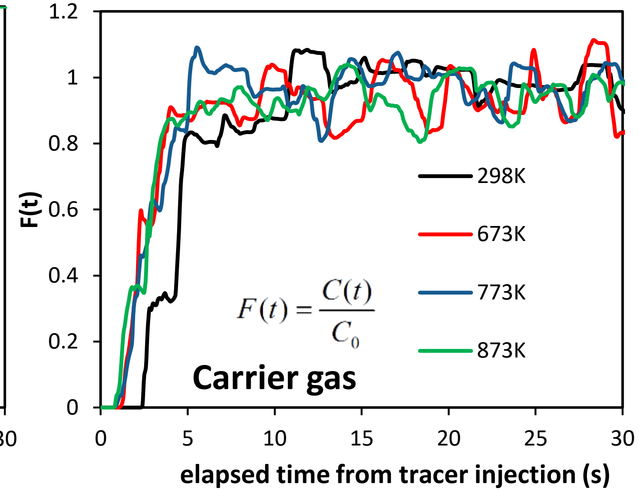
Tracer injection for non-reacting flow RTD

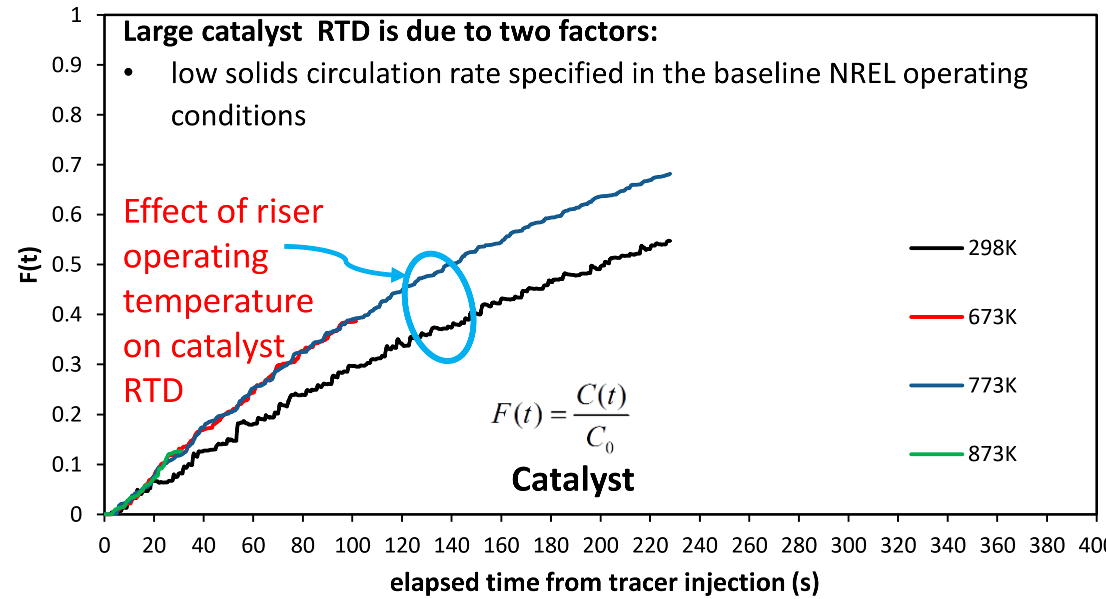
- Continuous (*step*) gas and catalyst tracer injections
- Gas tracers are given the same properties as process gas and carrier gas
- The solid tracer is given the same properties as the catalyst
- A volume fraction of 5% was used for each tracer
- The tracer outlet concentration is monitored at the top exit



Cumulative RTD for gas and catalyst tracers – from simulation





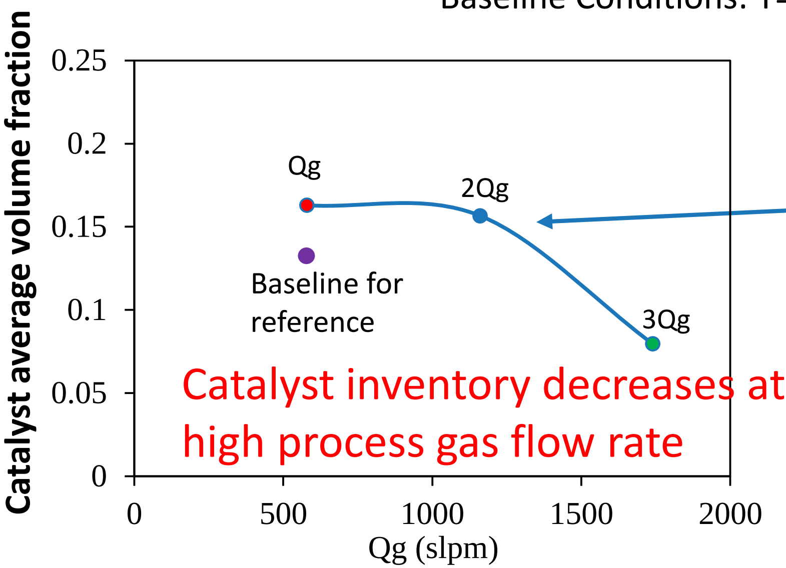


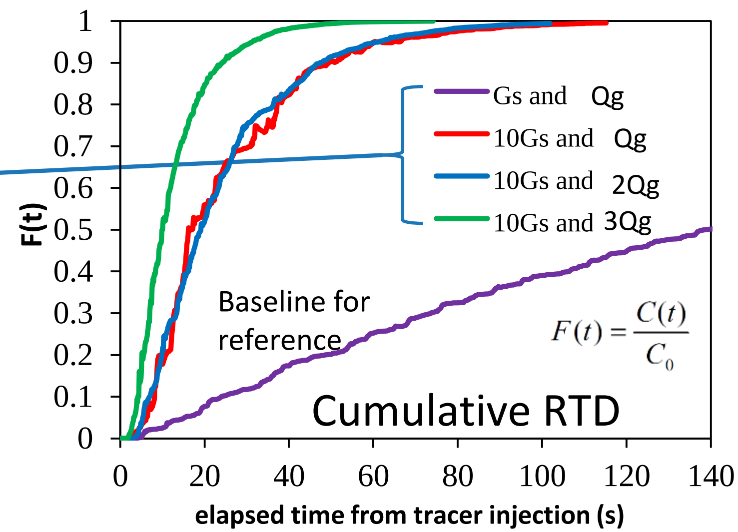
Simulation Application – RTD calculation in the VPU riser

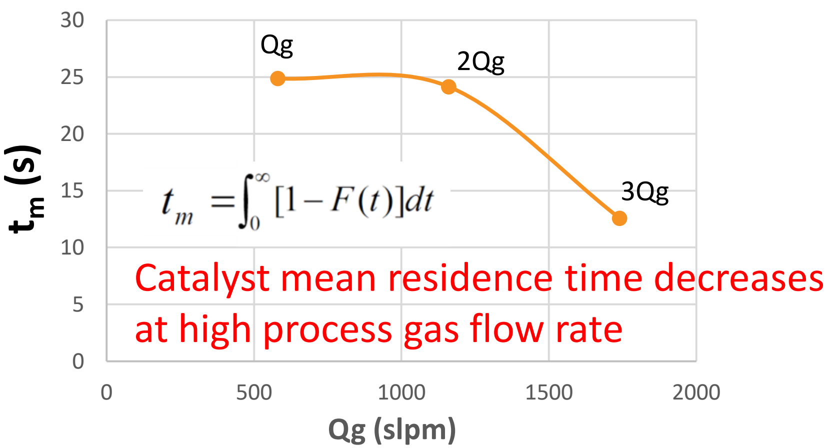
Study effect of process gas flow rate on catalyst RTD –high temperature, non-reacting flow

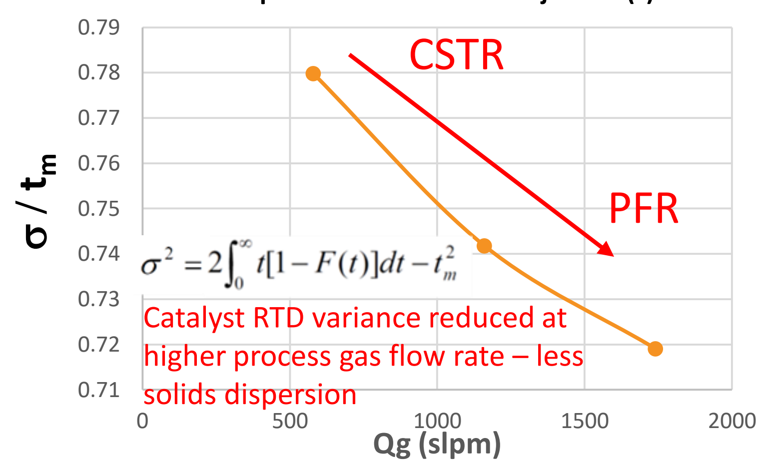
- Evaluate the effect of process gas (pyrolysis vapor) flow rate – 2x and 3x baseline gas flow rate
- Mean catalyst residence time is impacted at high process gas flow rate

Baseline Conditions: T=773K, Gs=46.1 g/s, Qg=580 slpm







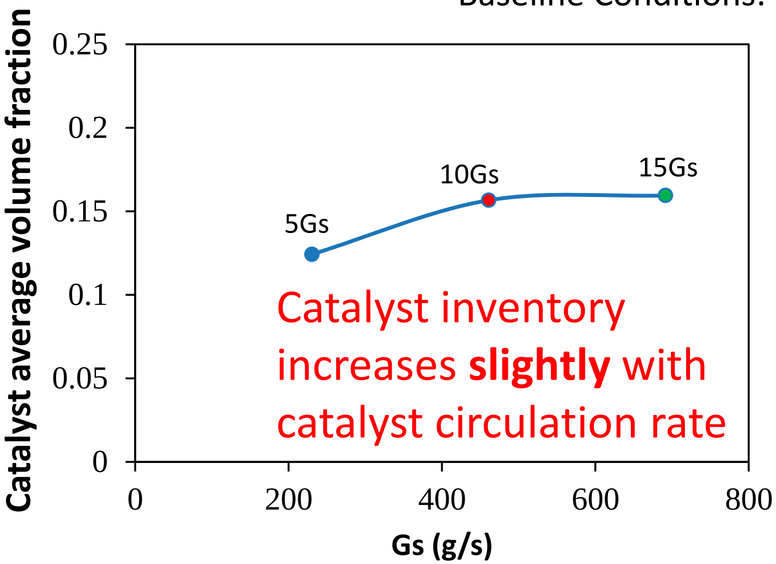


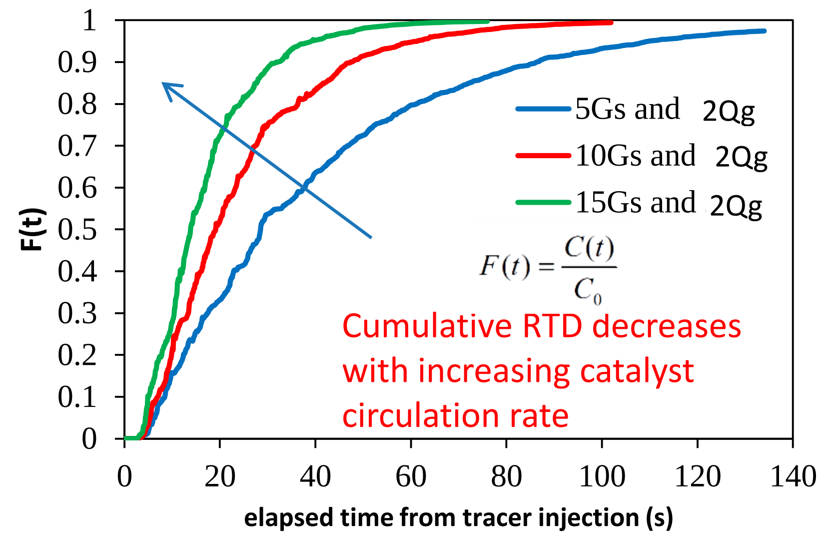
Simulation Application – RTD calculation in the VPU riser

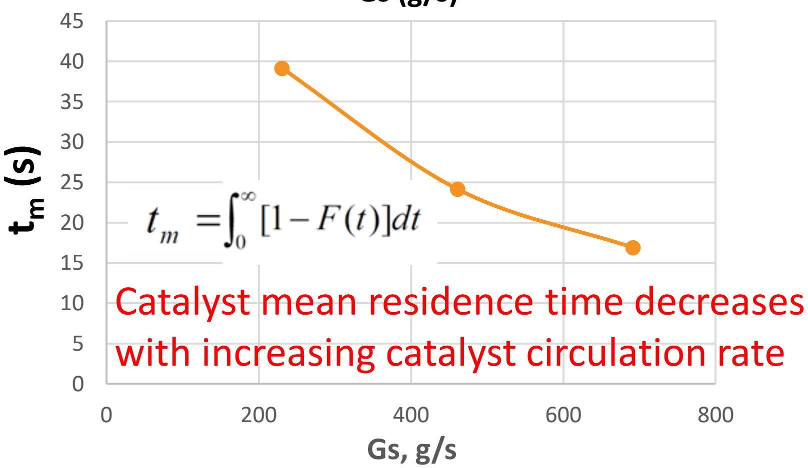
Effect of catalyst inlet flow rate on catalyst RTD – high temperature, non-reacting flow

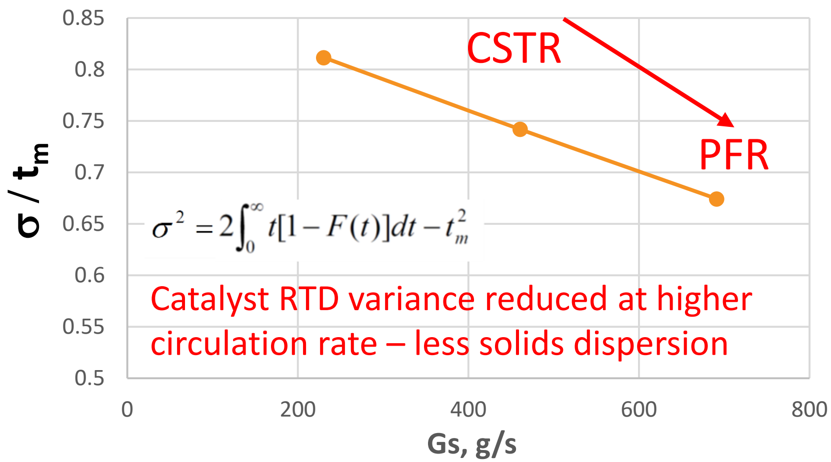
- Catalyst inventory increase is small with increasing circulation rate at 5x, 10x, 15x baseline catalyst flow
- Catalyst mean residence time decreases with increasing circulation rate

Baseline Conditions: T=773K, Gs=46.1 g/s, Qg=580 slpm



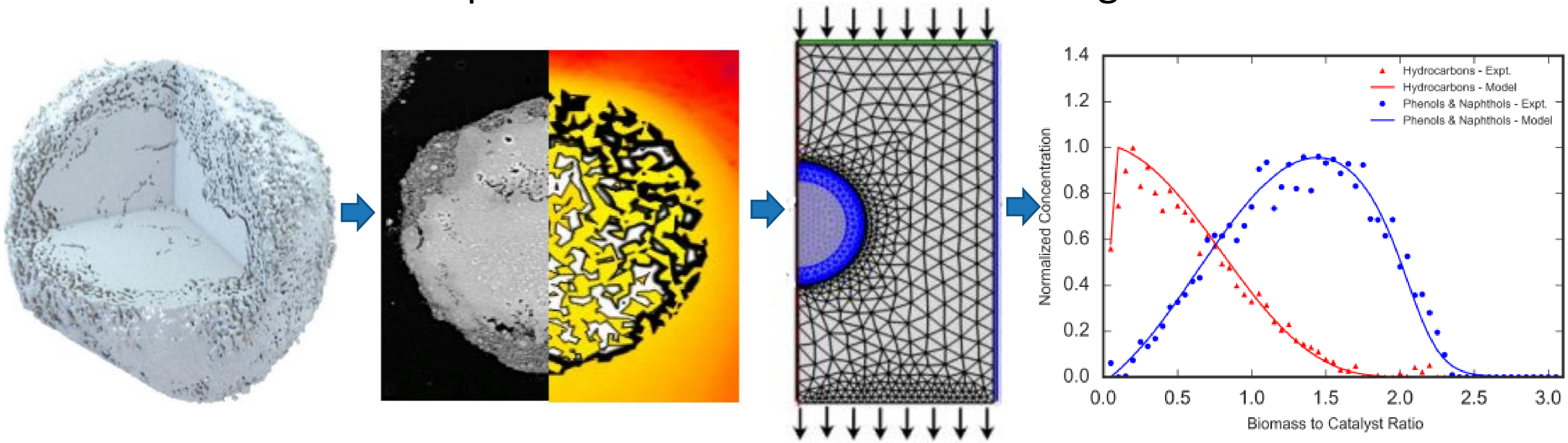


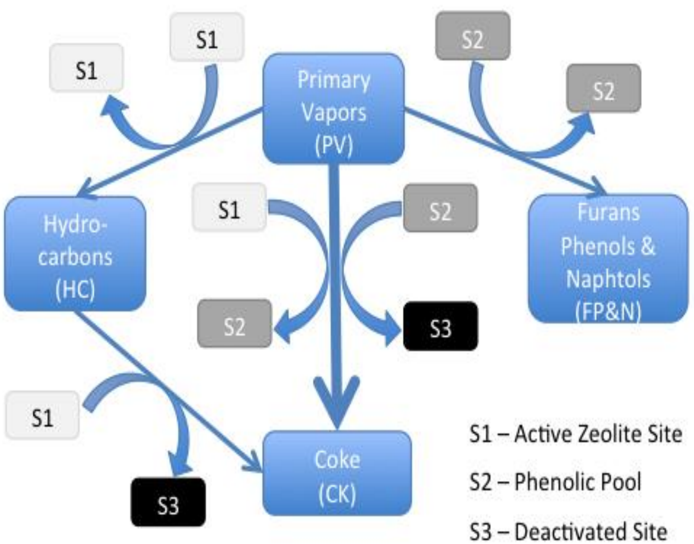




Simulation Application – Next step is reacting flow

- Kinetics from NREL experiments and mesoscale modeling*





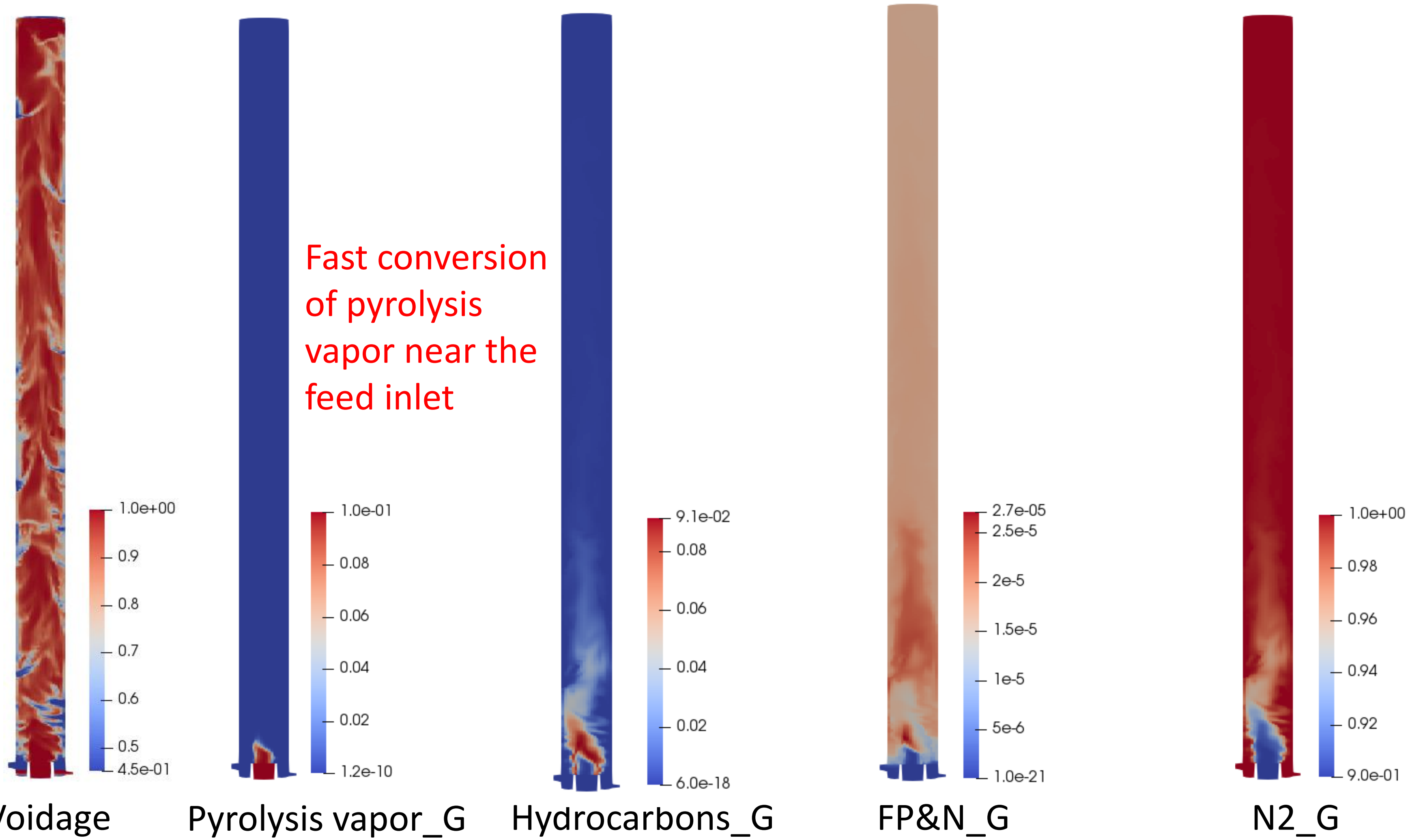
	Reaction	Rate Constant @500 °C [m³/(mol.s)]
1	PV + S1 → HC + S1	76.646
2	PV + S1 → CK + S2	4.4673
3	PV + S2 → FP&N + S2	16.690
4	PV + S2 → CK + S3	0.7207
5	HC + S1 → CK + S3	0.2167

*NREL 2017 Q4 report.

Simulation Application – Next step is reacting flow

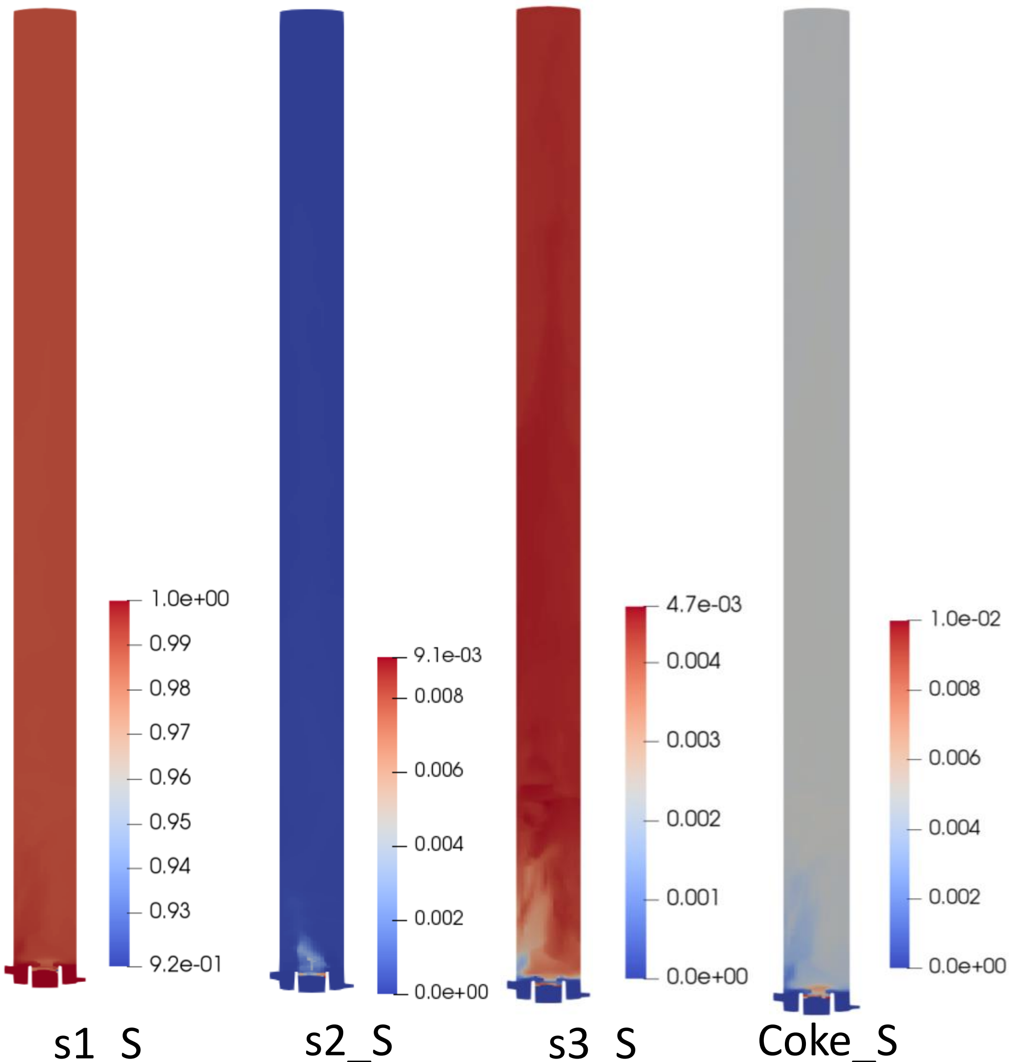
- Inflow: mixture of 10% volatiles and 90% N2
- Operating condition: 773K, 150kPa, 10xGs, 2xVg

Transient results at 47 s

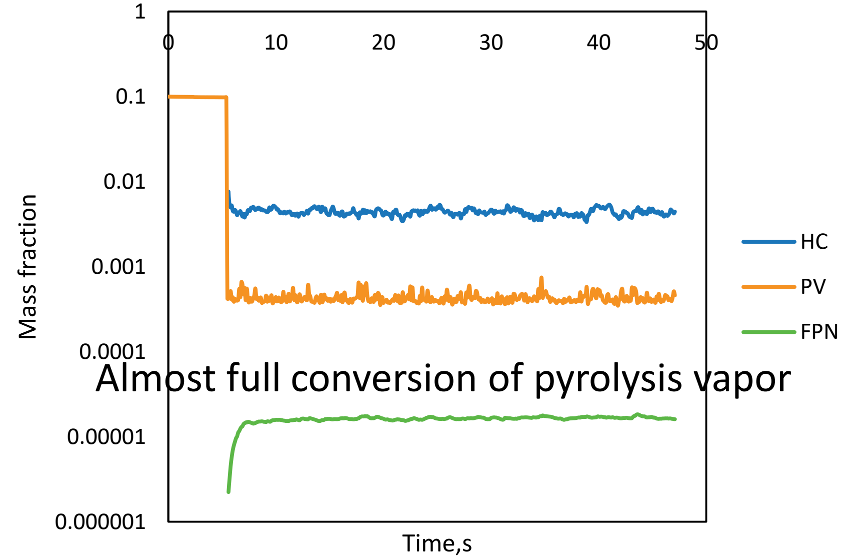


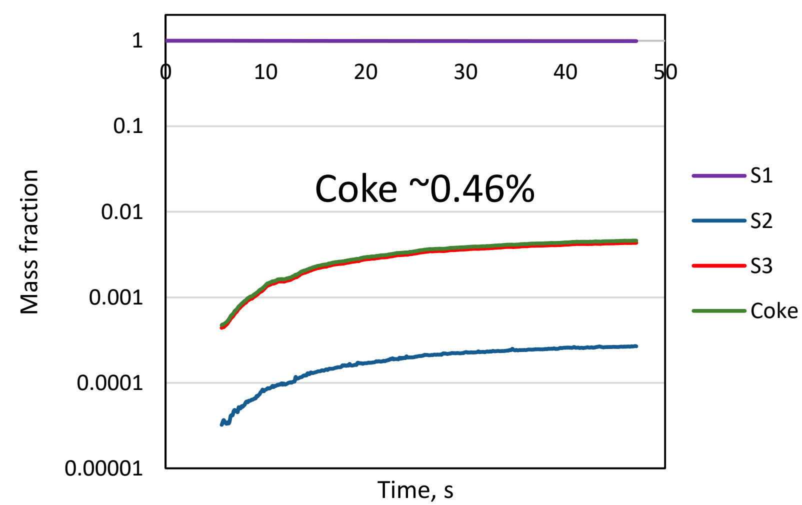
Simulation Application – Next step is reacting flow

Mass fraction of solid species



Composition of exit flow





Conclusions and Next Steps

- A comprehensive evaluation was conducted to determine the optimal drag model for ECAT catalyst particles over the full range of fluidization regimes
- The selected drag model was validated with inhouse experiments for ECAT particles in a small CFB application
- Simulations of the VPU riser were performed for a broad range of operating conditions to study flow hydrodynamics and gas/solid RTDs
- Results of this study are being used by NREL to help guide instrumentation and future testing of the pilot VPU plant
- Next Steps:
  - Validate reactor scale model hydrodynamics using data from cold flow experimental tests at NREL
  - Incorporate meso-scale transport models and chemical kinetics in the reactor-scale simulations
  - Validate reactor-scale model with meso-scale chemistry using NREL data

Acknowledgements

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Cong Liu
Dale Pahls

Industry Advisory Panel

David Dayton (RTI), George Huff (MIT, retired BP), Jack Halow (Separation Design Group), Mike Watson (Johnson Matthey), Steve Schmidt (WR Grace), Tom Flynn (Babcock & Wilcox)

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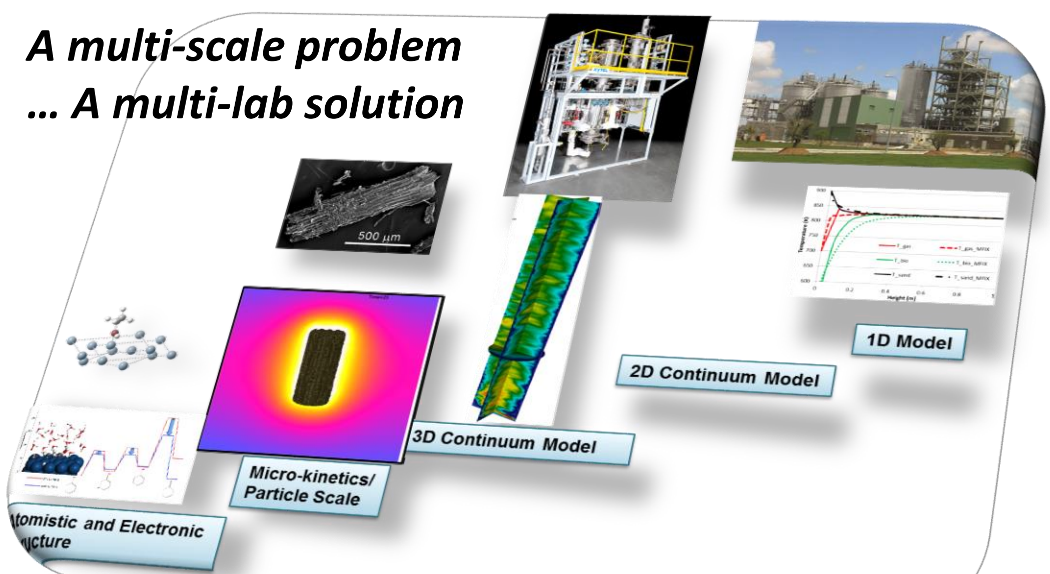
A multi-scale problem
… A multi-lab solution



NETL 2018 Workshop on Multiphase Flow Science

At University Houston, Houston, TX on **August 7-9, 2018**

Abstract submission at workshop@mfix.netl.doe.gov by **June 1, 2018**

Cosponsored by NETL, U. Houston and Louisiana State U.

Thank you.

Questions?

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