CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Modeling CFP Catalyst Regeneration in BFCC Units

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Bruce Adkins   Oak Ridge National Laboratory
Yupeng Xu, Mehrdad Shahnam and Jordan Musser   National Energy Technology Laboratory

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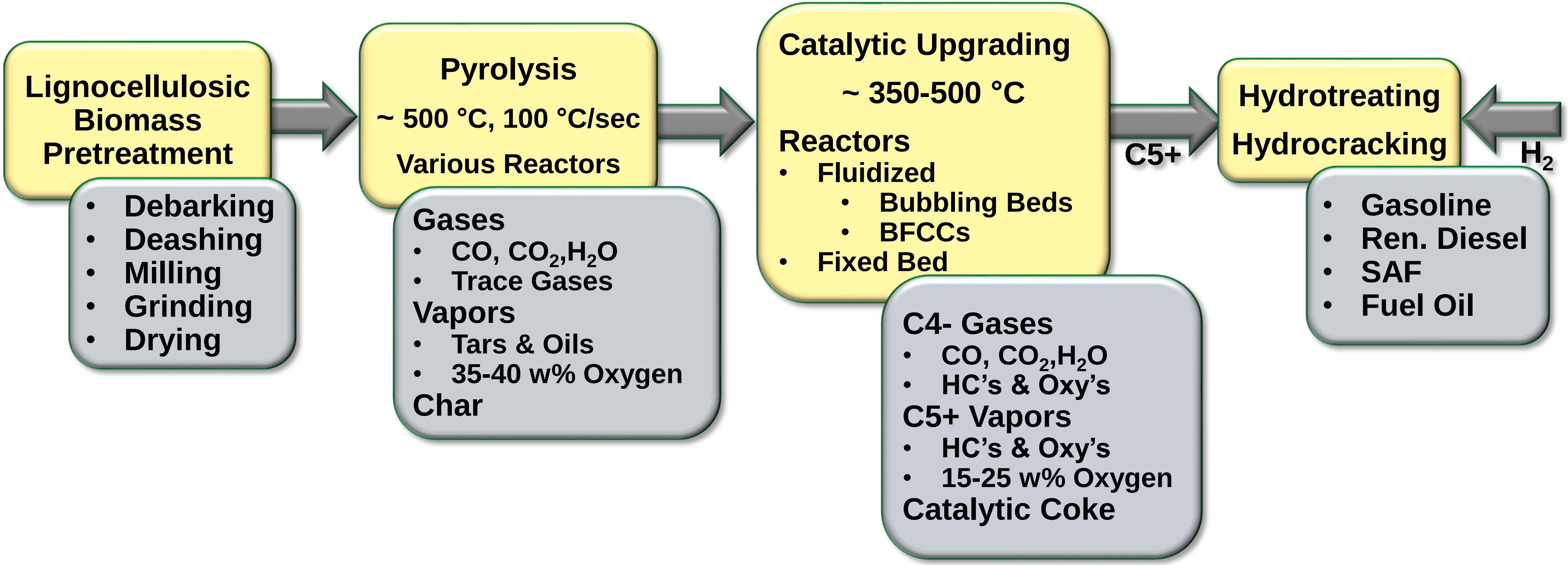
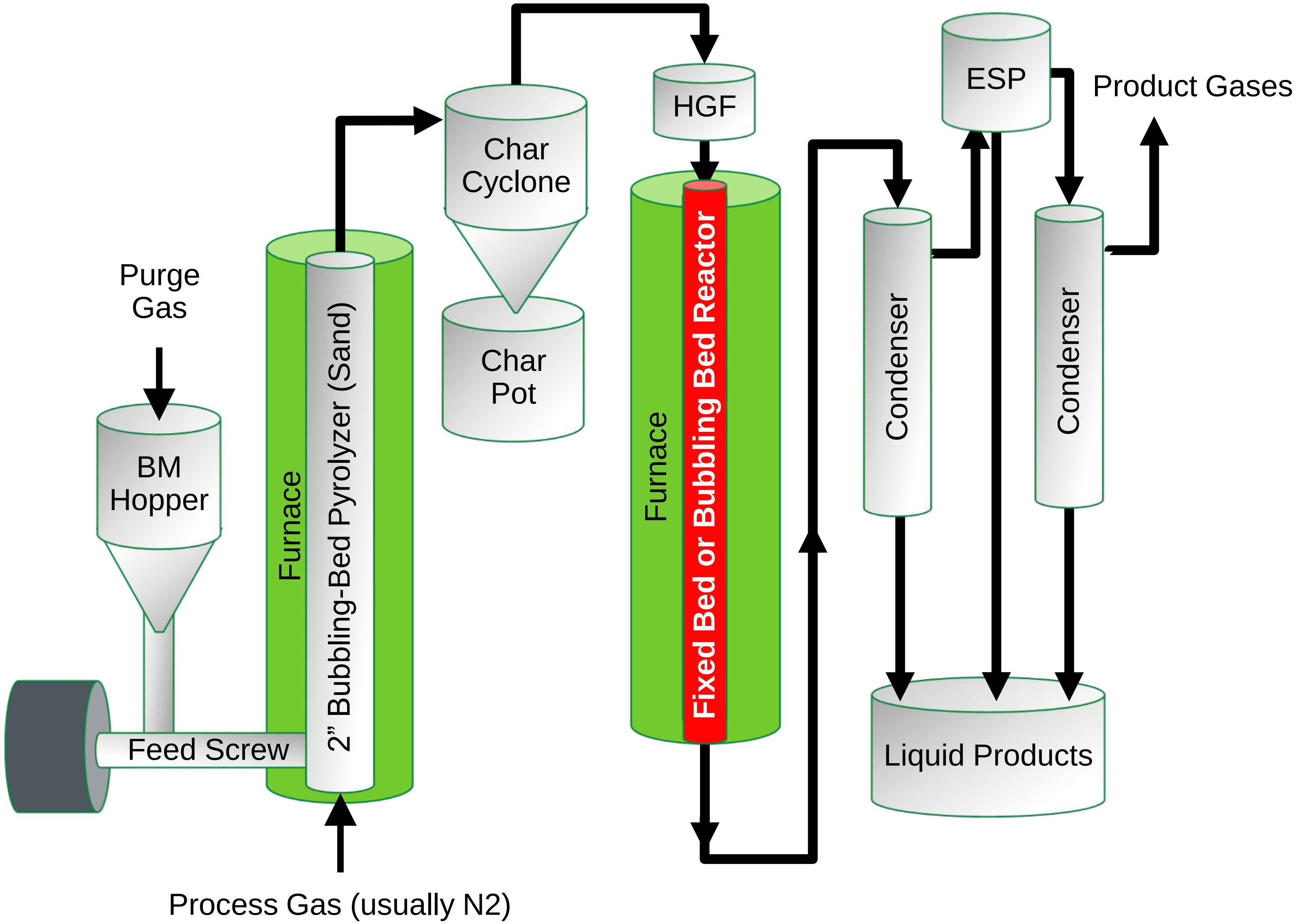
Catalytic Fast Pyrolysis (CFP)



NREL's "2FBR": A Flexible CFP Unit



ZSM-5 Based Catalysts Used in 2FBR Bubbling-Bed Upgrader

80% ZSM-5
20% Alumina

+/- P-promotion
(2.5 wt%)

Geldart B
Dp = 500 – 800 μm

Spent Catalyst:
9-13 wt% CoC
(Coke on Catalyst)

1 Extensive laboratory characterization of coked catalyst: TPO, NMR, microscopy….

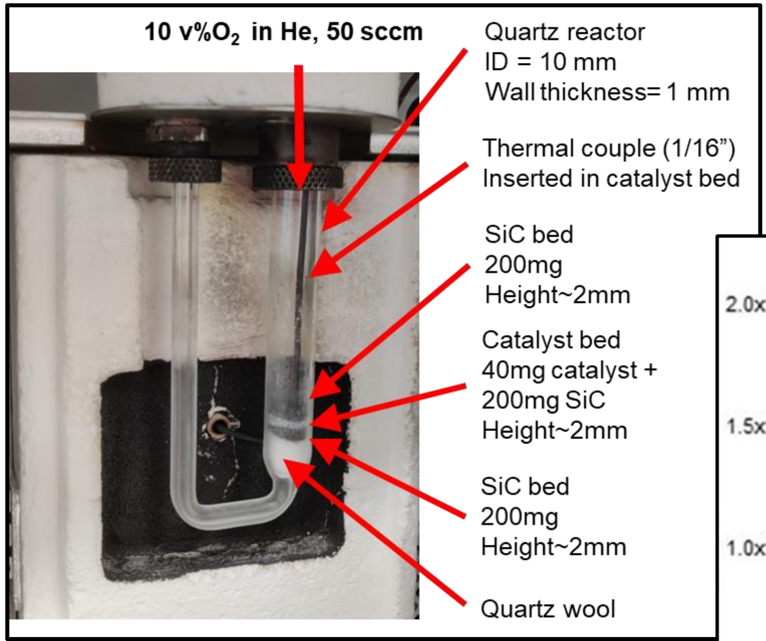
2 Develop kinetics for coke oxidation from TPO data using FEM fixed bed models

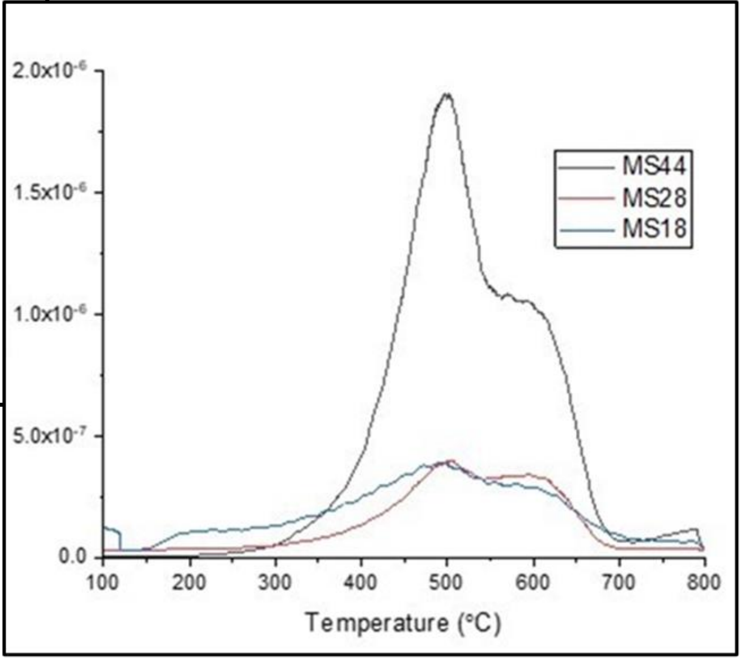
3 Extend to FCC catalyst, i.e. Geldart A particles with much lower CoC

MODEL BFCC REGENERATOR IN BARRACUDA

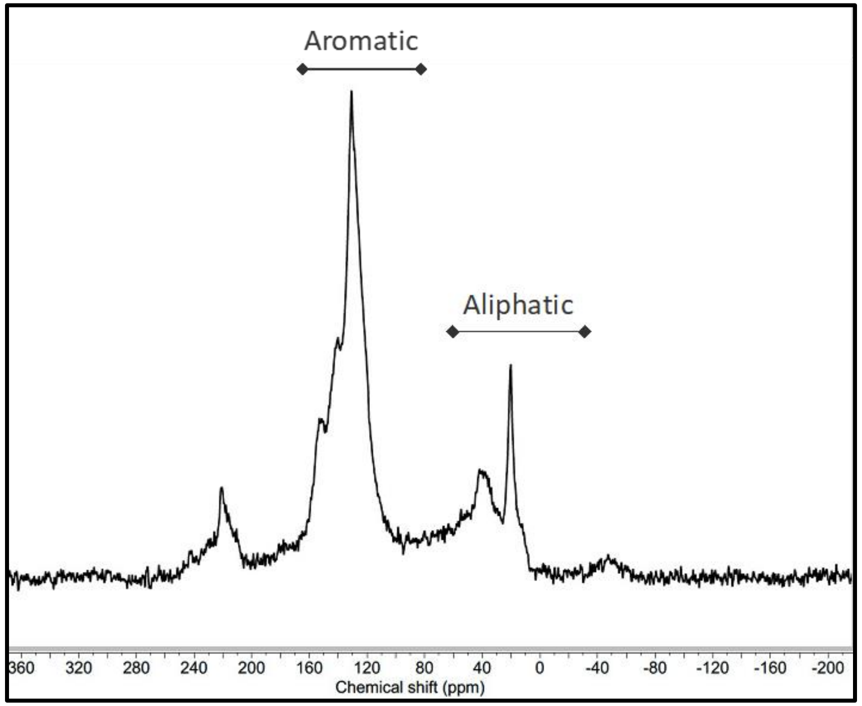
Unpromoted Catalyst: Coke Chemistry and Combustion Behavior

TPO
"Low" and "High" Temperature Carbon





^{13}C-NMR
Aromatic and Aliphatic Carbon



Whole Pellets (~600 μm)
vs
Crushed (< 100 mesh)

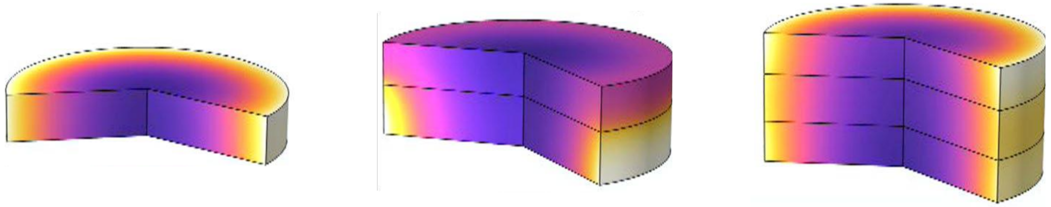
Consortia Acknowledgements:

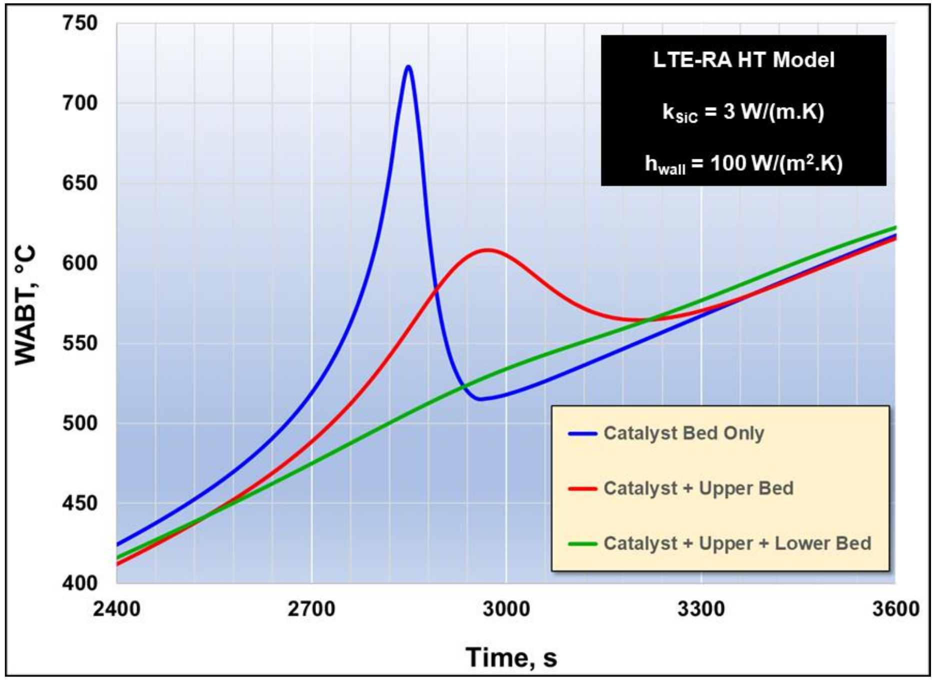
CDM: Catalyst Deactivation Mitigation

ACSC: Advanced Catalyst Synthesis and Characterization

TPO Finite Element Modeling

Bed Heat Transfer





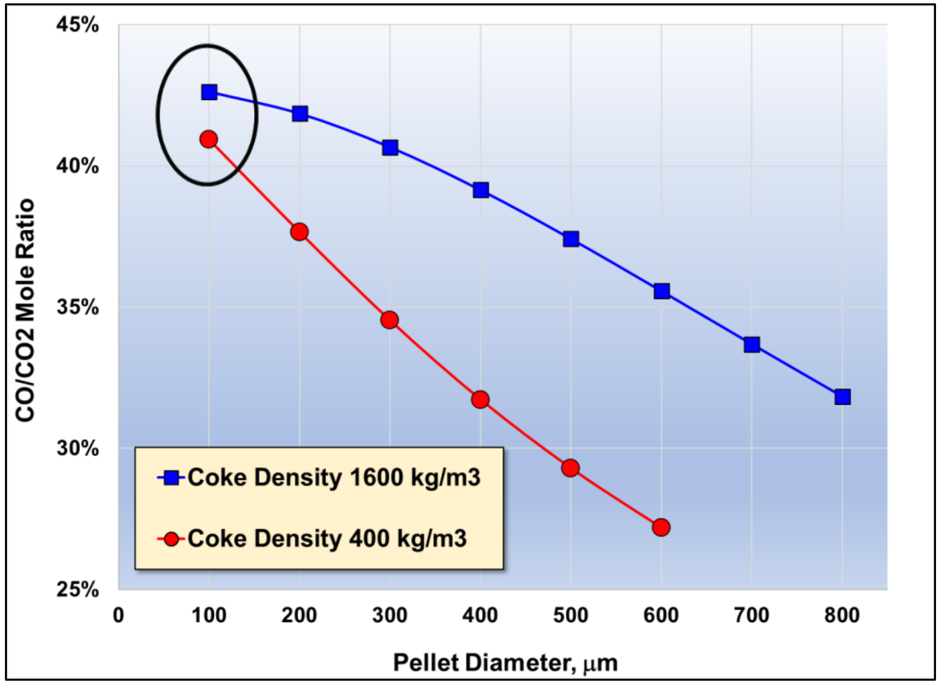
Coke Density and Pellet Mass Transfer

$$V_{f,coke} = m_{coke} \cdot \frac{S_{cat}}{\rho_{coke}}$$

$$\varepsilon_s = \varepsilon_f - V_{f,coke}$$

$$MPD_s = MPD_f \cdot \left({}^{\varepsilon_s}/_{\varepsilon_f} \right)^{1/pore\_dim}$$

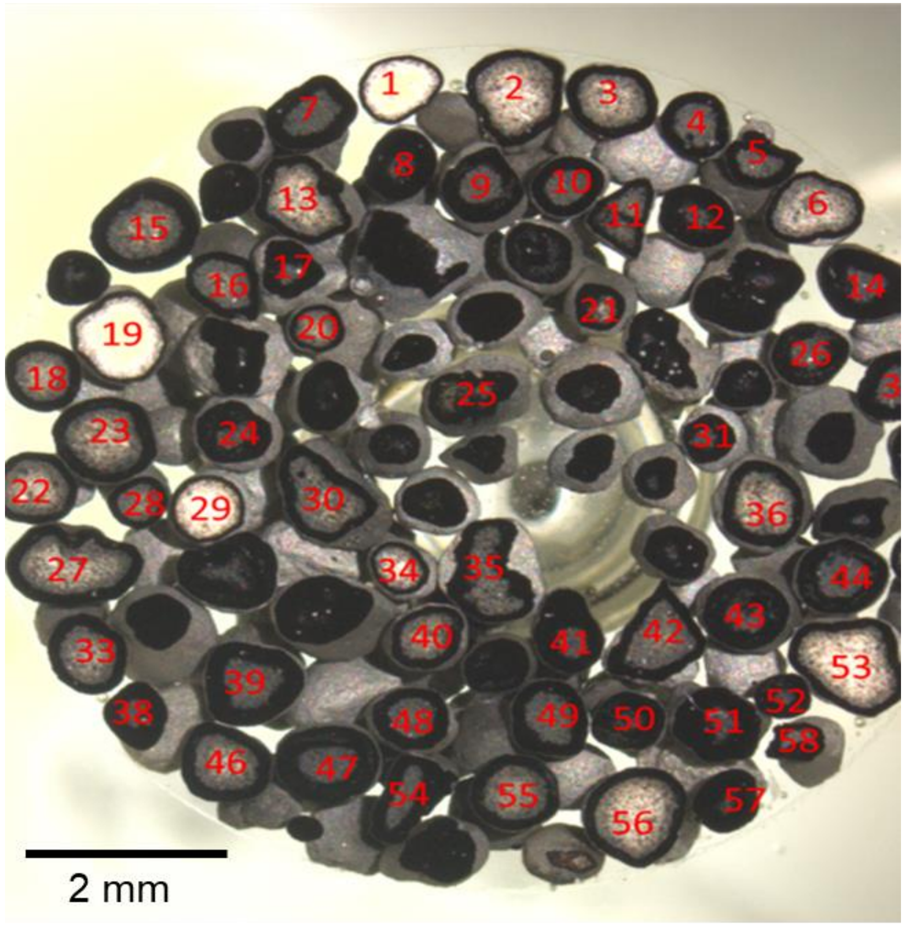
$$MPD_s = MPD_f \cdot \sqrt{{}^{\varepsilon_s}/_{\varepsilon_f}}$$



Coke: Physical Distribution

Pellet Cross-Sections

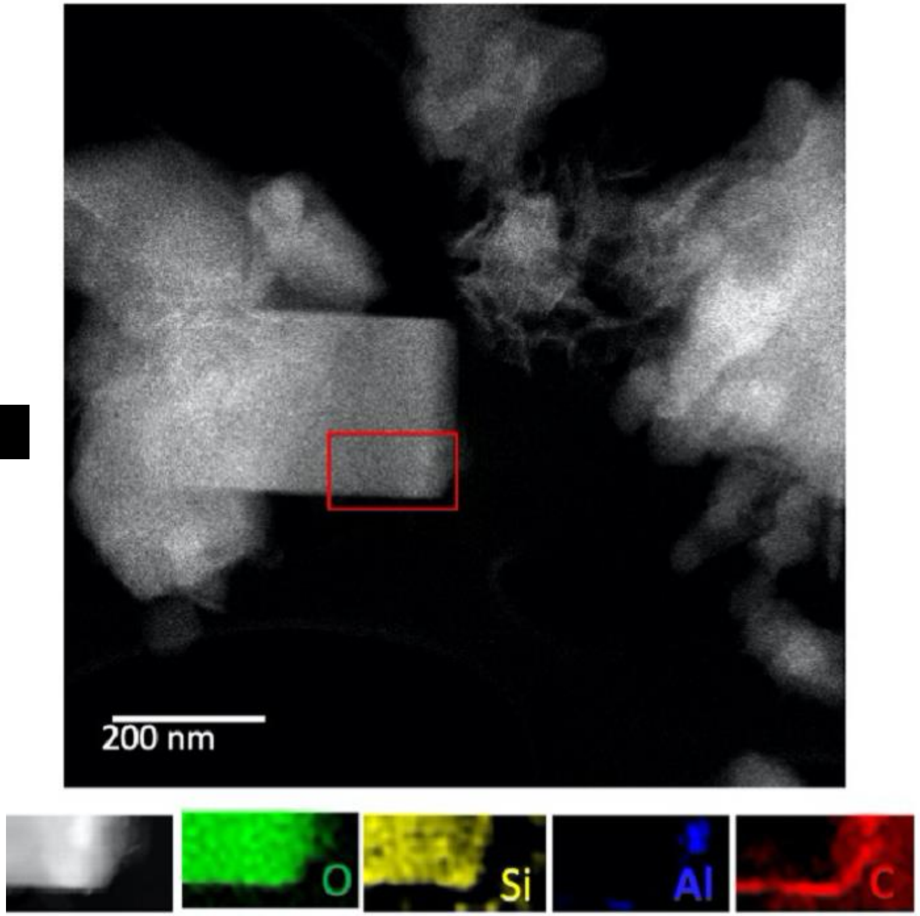
Mix of “Core-Shell” and Uniform



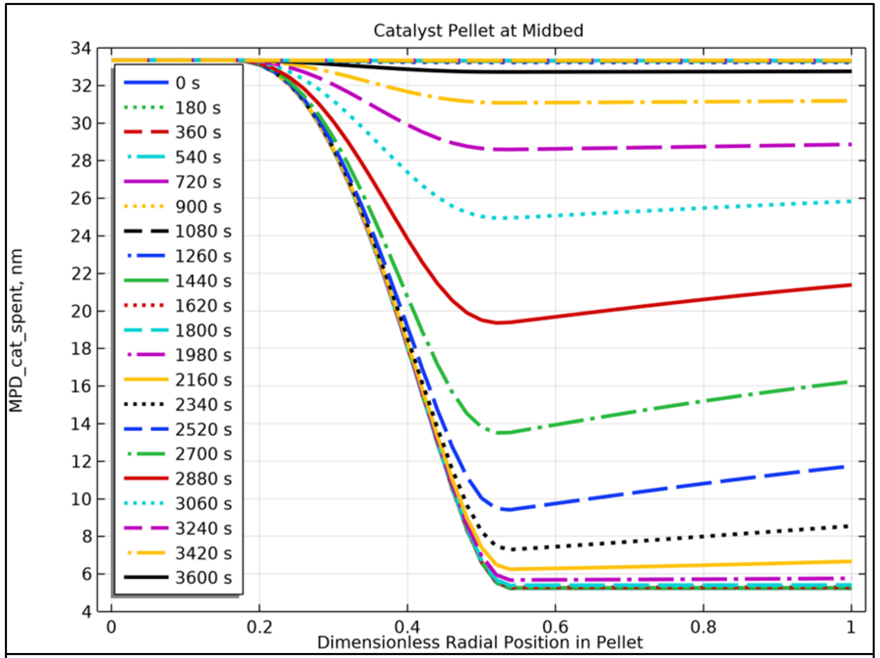
Courtesy ACSC

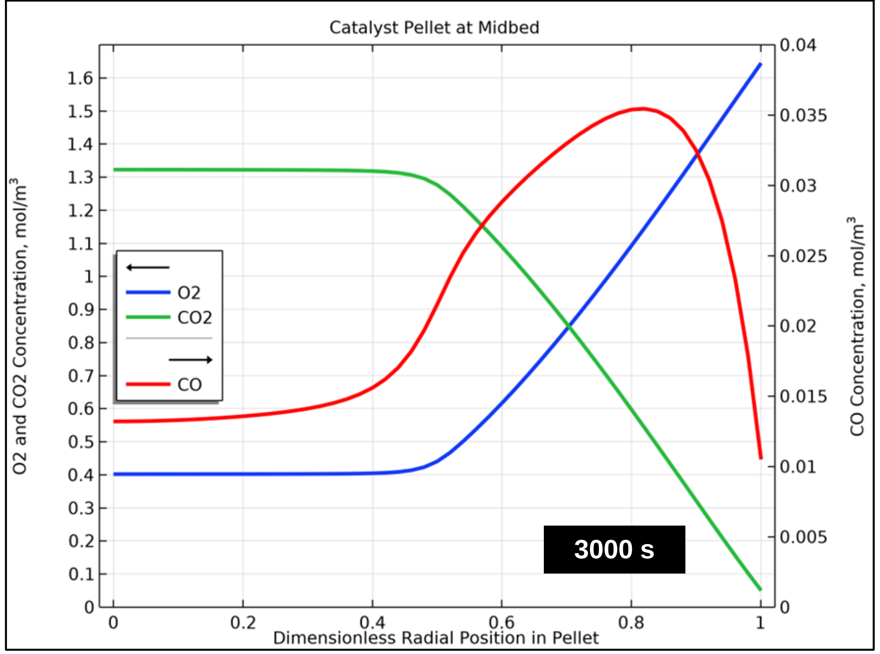
STEM-EELS

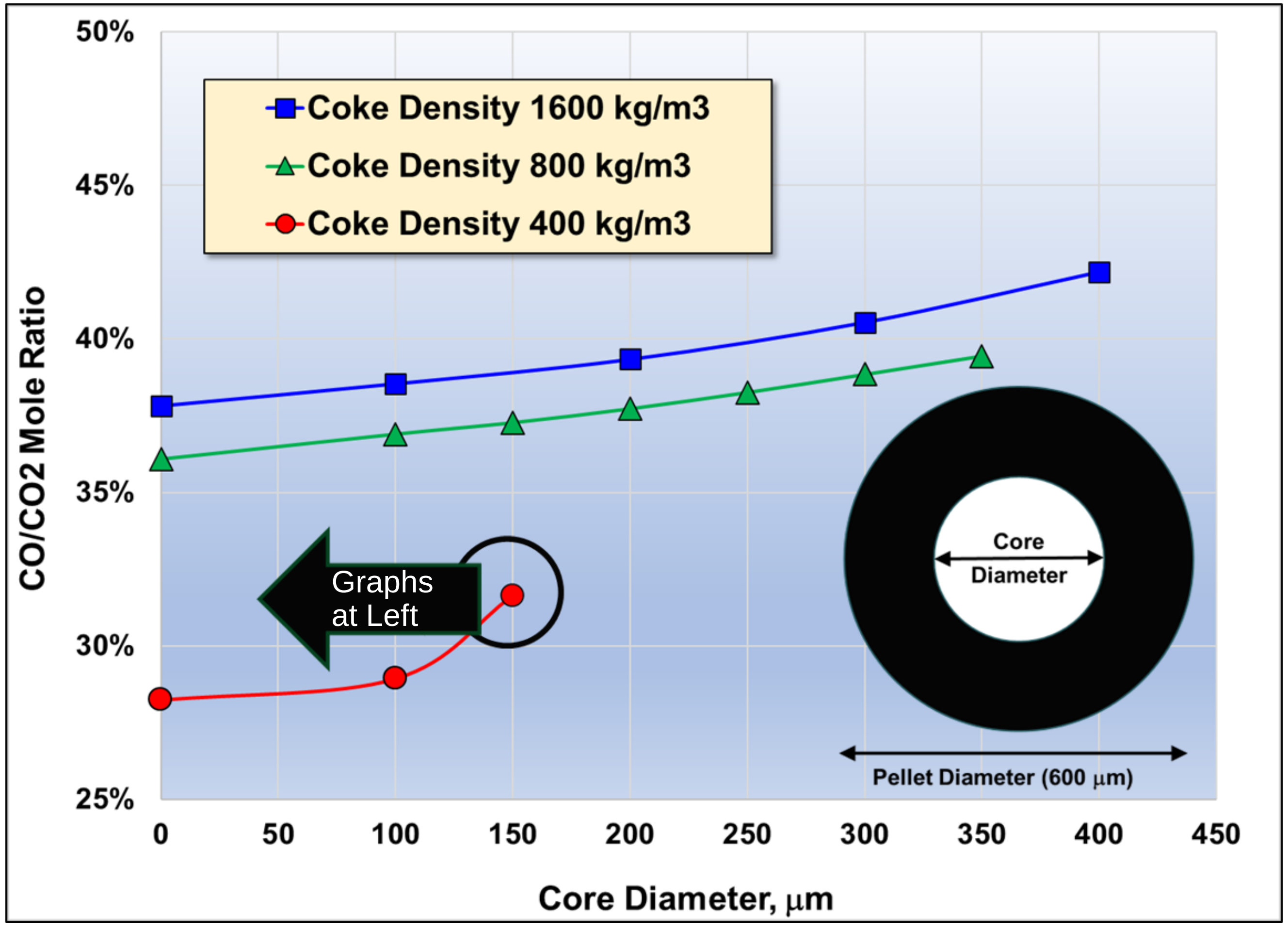
Essentially No Coke Inside Zeolite Crystals



Modeling Core-Shell Coke Distribution







Unpromoted Catalyst
Coke Combustion Kinetic Model

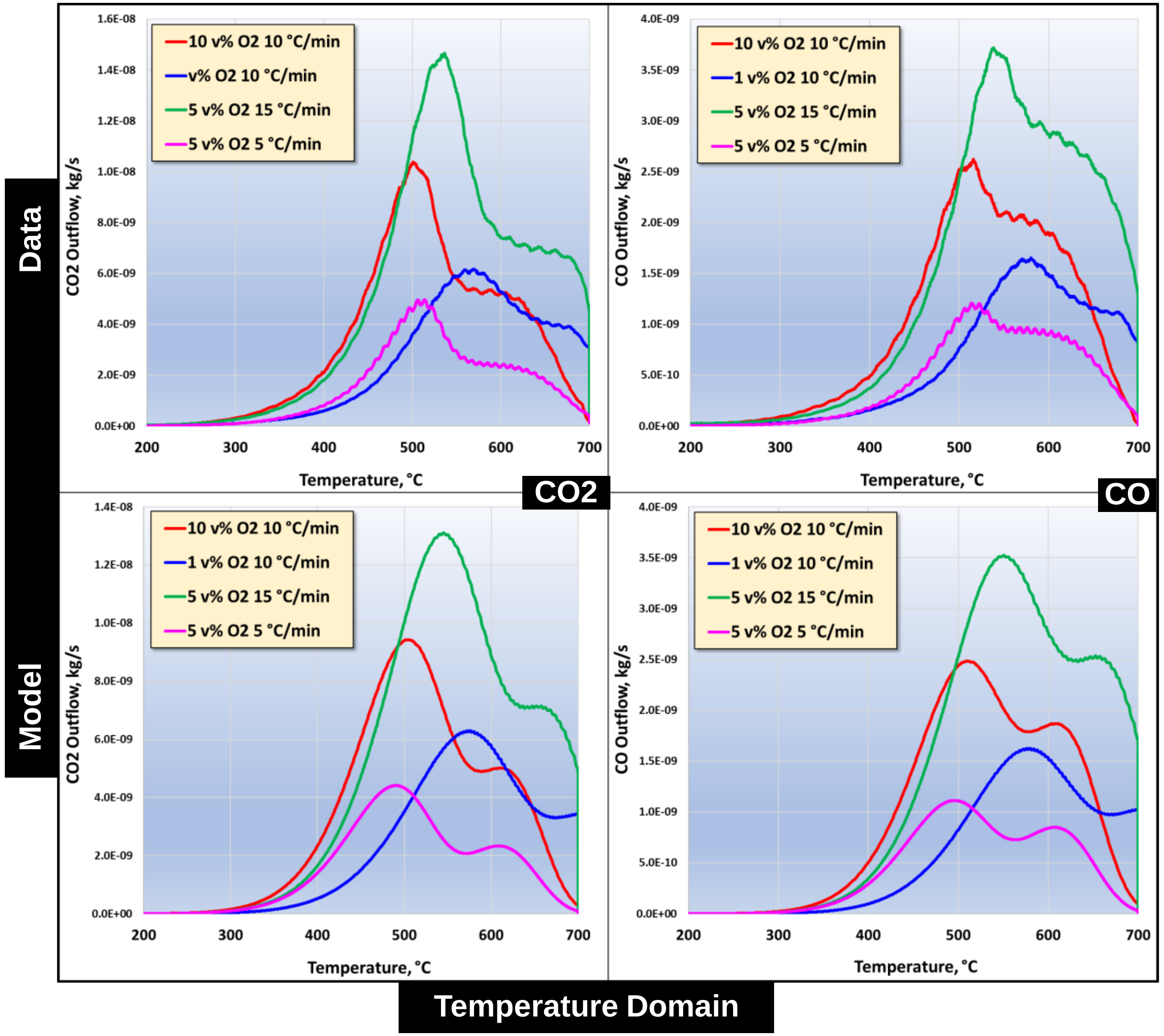
	Reaction	Rate Equation	Units
1	Low temperature CO_2 formation on surface	$R_{CO2\_low} = a_{CO2\_low}\, cC_{low}\, cO_2^{b_{CO2\_low}}\, e^{\frac{-Ea_{CO2\_low}}{RT}}$	$mol/(m^2.s)$
2	High temperature CO_2 formation on surface	$R_{CO2\_hi} = a_{CO2\_hi}\, cC_{hi}\, cO_2^{b_{CO2\_hi}}\, e^{\frac{-Ea_{CO2\_hi}}{RT}}$	
3	Low temperature CO formation on surface	$R_{CO\_low} = a_{CO\_low}\, cC_{low}\, cO_2^{b_{CO\_low}}\, e^{\frac{-Ea_{CO\_low}}{RT}}$	
4	High temperature CO formation on surface	$R_{CO\_hi} = a_{CO\_hi}\, cC_{hi}\, cO_2^{b_{CO\_hi}}\, e^{\frac{-Ea_{CO\_hi}}{RT}}$	
5	CO oxidation	$R_{CO\_CO2} = a_{CO\_CO2}\, \rho_p\, cCO\, cO_2^{b_{CO\_CO2}}\, e^{\frac{-Ea_{CO\_CO2}}{RT}}$	$mol/(m^3.s)$

1. *Pool the CO and CO2 outflow data from TPO runs and fit model parameters using a "0D" (gradientless) spreadsheet model and SOLVER*

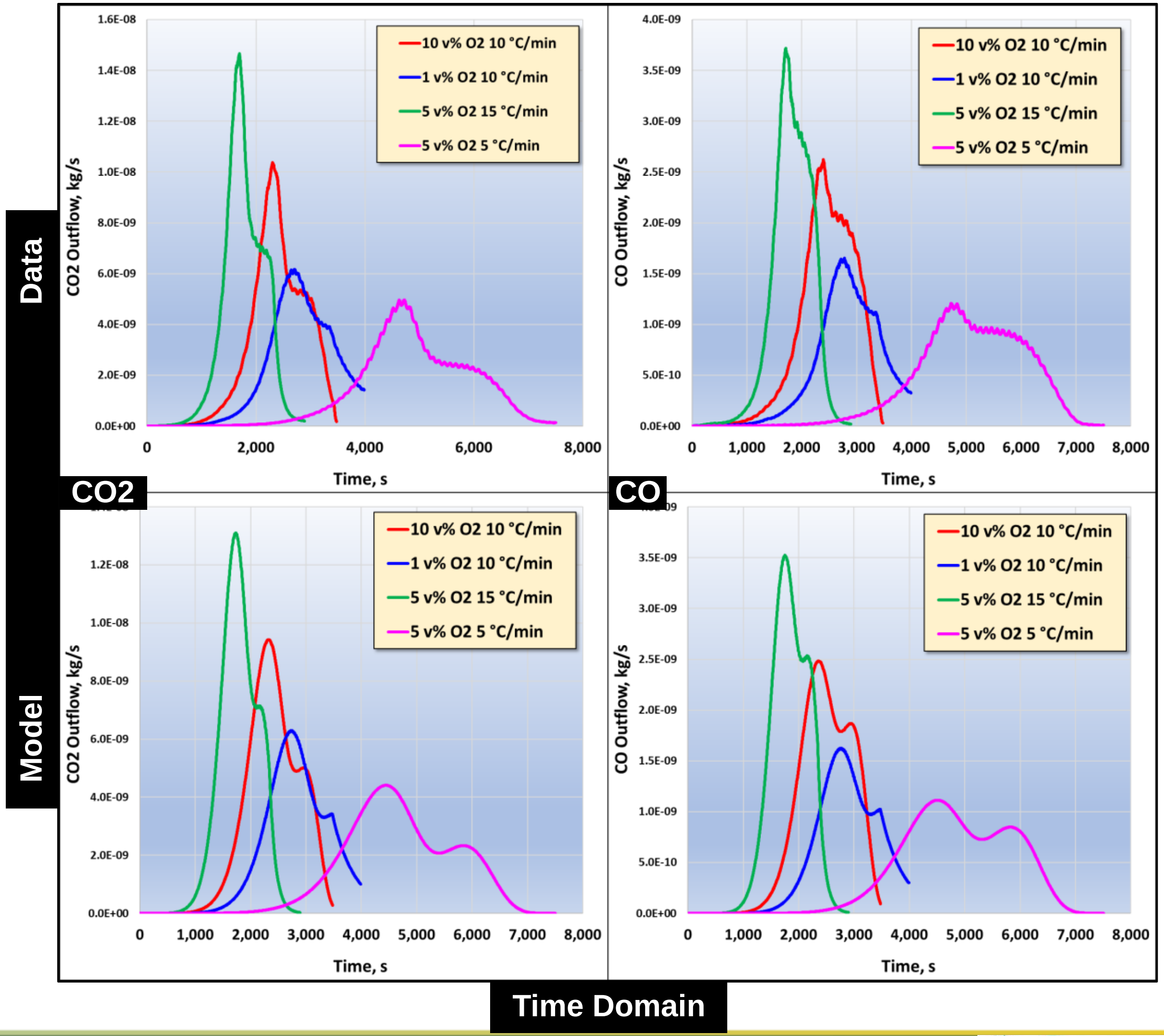
2. *Use 2D full-gradient COMSOL FEM model to adjust the CO oxidation constant to account for mass transfer effects (mainly, of CO concentration)*

Parameter	Units	Value
a_{CO_CO2}	$m^3/(kg.s)$	0.2925
a_{CO2_low}	1/s	1,087
a_{CO2_hi}		5,102
a_{CO_low}		33,881
a_{CO_hi}		594,715
b_{CO_CO2}	-	0.0695
b_{CO2_low}		0.5384
b_{CO2_hi}		0.4793
b_{CO_low}		0.6650
b_{CO_hi}		0.9739
Ea_{CO_CO2}	J/mol	14,680
Ea_{CO2_low}		88,103
Ea_{CO2_hi}		118,987
Ea_{CO_low}		109,677
Ea_{CO_hi}		143,340

Quality of Fit: Four TPO Runs



Crushed -100 Mesh



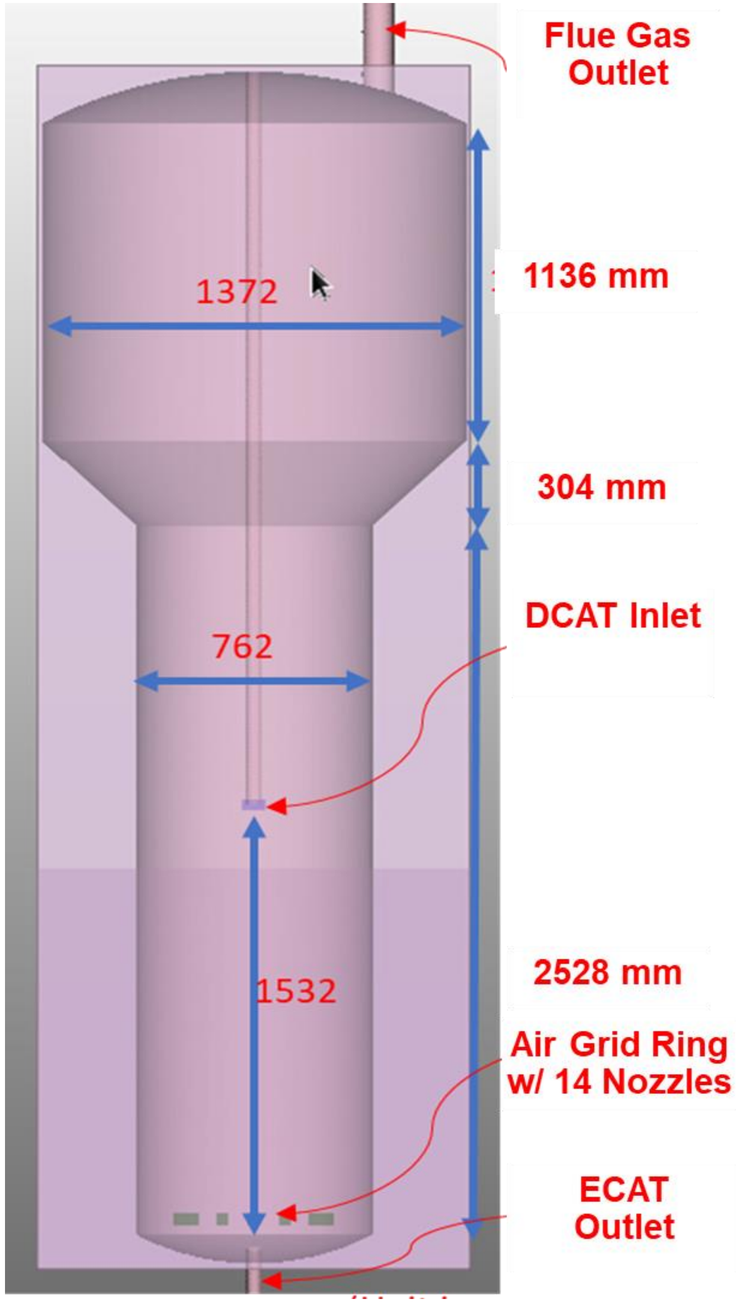
Translate Model to Barracuda: 80 μm BFCC Particles with 1 wt% CoC

1. Assume the coke profile inside the 80 μm particle is uniform → AVOID MODELING THE PARTICLE INTERIORS
   - At 100 μm SED, the FEM model shows almost no difference at lowest and highest coke densities, even at 13% wt% CoC: see slide 7
   - At 1 wt% CoC, the coke profile is likely to be more uniform than at 13 wt%
   - The 80% ZSM-5, 20% Al2O3 formulation is too high in Z/M (too many active sites and too low in mesoporosity → Thiele number is too high). This very likely leads to the core-shell coke profile. THE REAL BFCC CATALYST SHOULD HAVE LOWER Z/M!!!

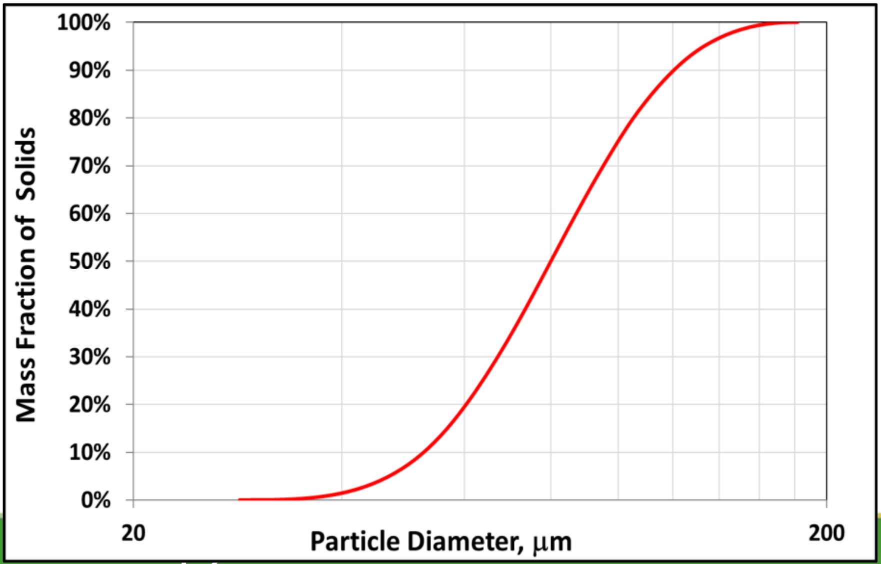
2. Convert reaction expressions to volume concentrations (mass/volume) instead of surface concentrations (mass/area)
   - Used the "single particle in one grid cell" method to validate the conversions
   - CPFD training!

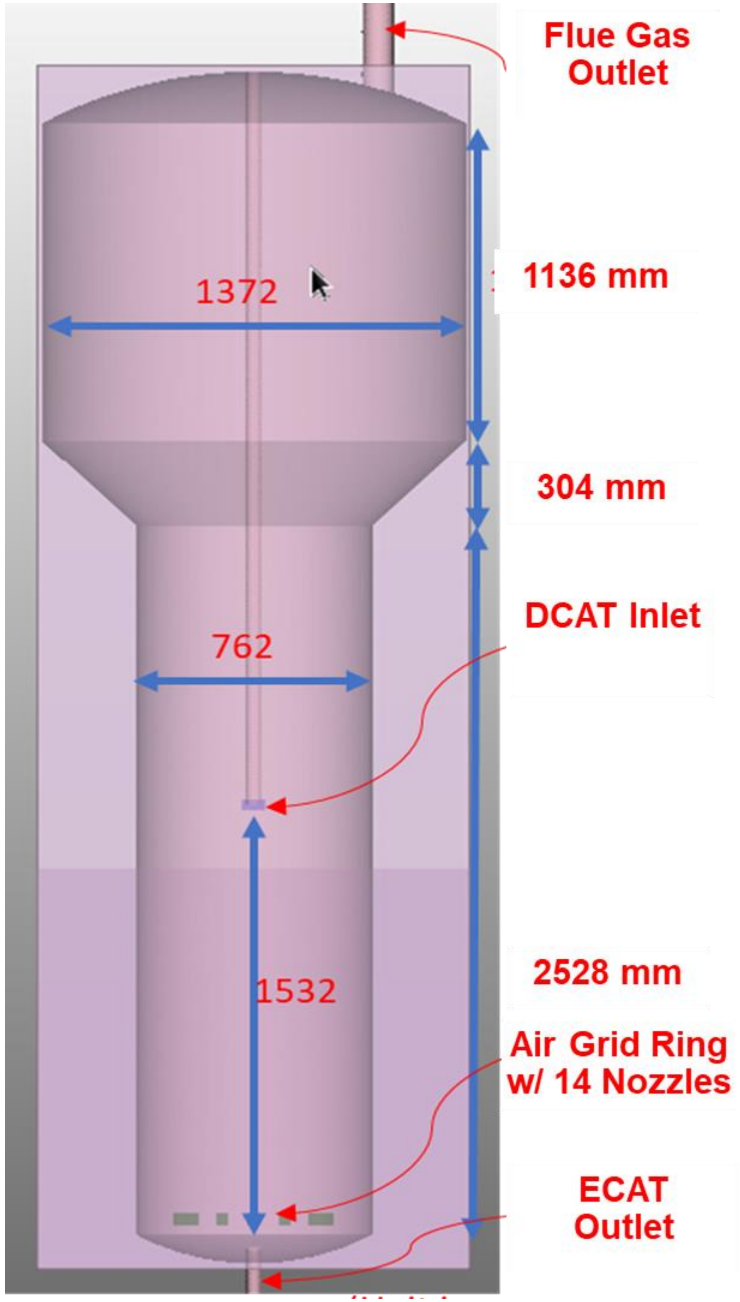
Parameter	Units	COMSOL	Barracuda
a_{CO_CO2}	$m^3/(kg.s)$	0.2925	0.6107
a_{CO2_low}	1/s	1,087	90,689
a_{CO2_hi}		5,102	425,663
a_{CO_low}		33,881	2.827E+06
a_{CO_hi}		594,715	4.962E+07
b_{CO_CO2}	-	0.0695	
b_{CO2_low}		0.5384	
b_{CO2_hi}		0.4793	
b_{CO_low}		0.6650	
b_{CO_hi}		0.9739	
Ea_{CO_CO2}	J/mol	14,680	
Ea_{CO2_low}		88,103	
Ea_{CO2_hi}		118,987	
Ea_{CO_low}		109,677	
Ea_{CO_hi}		143,340	

BFCC Regenerator: 5 mTPD Demo Unit



Fixed Parameter	Units	Value
Biomass Feedrate	mT/day (dry basis)	5.0
Catalyst Circ Rate		45.0
Catalyst/Biomass	-	9.0
Coke Yield	wt%	9.0
DCAT Coke on Catalyst (CoC)	wt%	1.00
DCAT CoC “Low” Form		0.61
DCAT CoC “High” Form		0.39
Base Catalyst Inventory	kg	325
Stoichiometric Airflow	kg/s	0.06
Nominal Pressure	kPa	274
Catalyst Particle Density	kg/m^3	1,380





Variables Studied

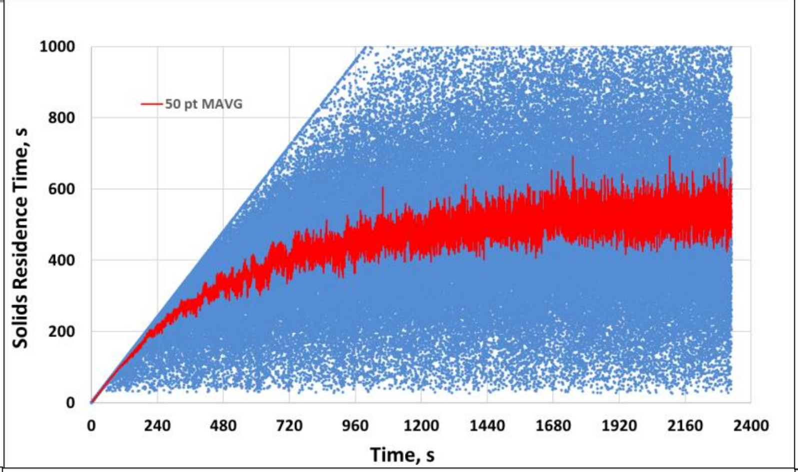
Variables	Units	Range
Relative Airflow (Stoichiometric = 1)	-	1.0, 1.1, 1.3
Relative Catalyst Inventory (Base = 1)		1.0, 1.3, 1.6
DCAT Temperature *Effect of Riser Outlet Temp (ROT) and/or catalyst cooler*	°C	450, 500, 530, 544

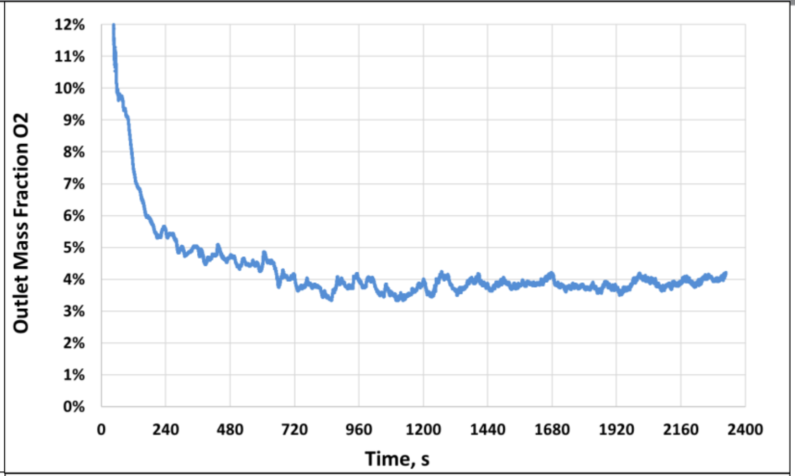
Important Outputs

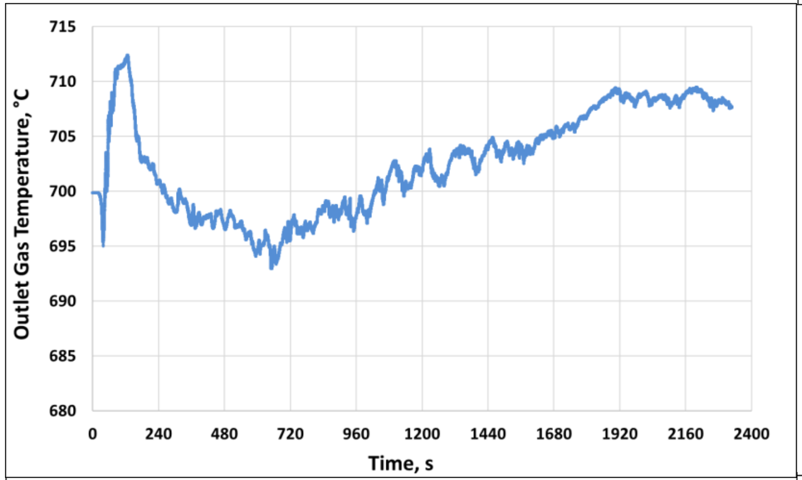
Variables	Units	Significance
ECAT CoC	wt%	Sets the ***activity*** of the catalyst returning to the riser
Flue Gas CO	v%	An indication of the potential for ***afterburn*** (CO combustion in freeboard)

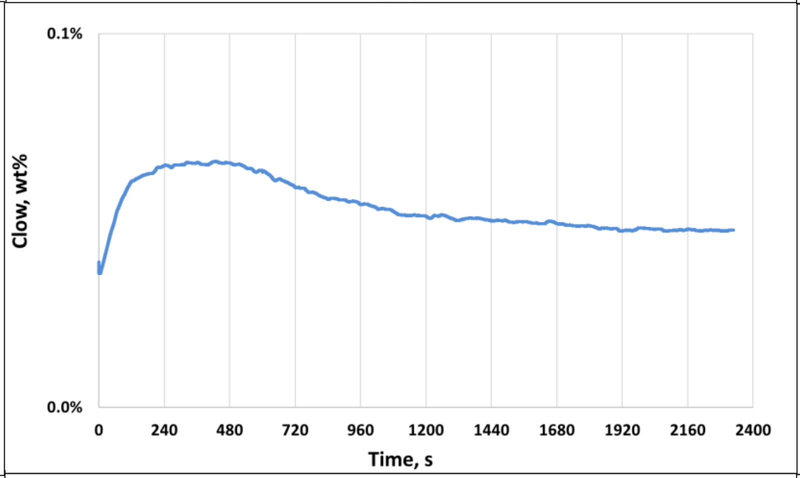
Typical Solution Behavior

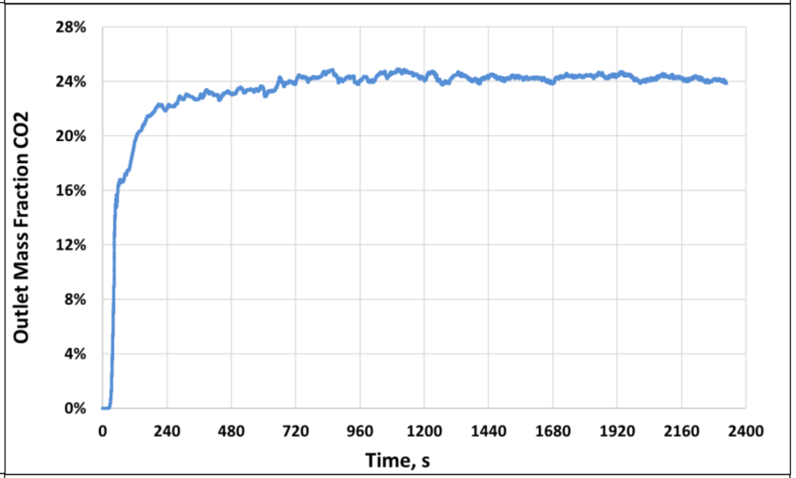
Relative Airflow = 1.0
Relative Catalyst Inventory = 1.0
DCAT Temperature = 530°C

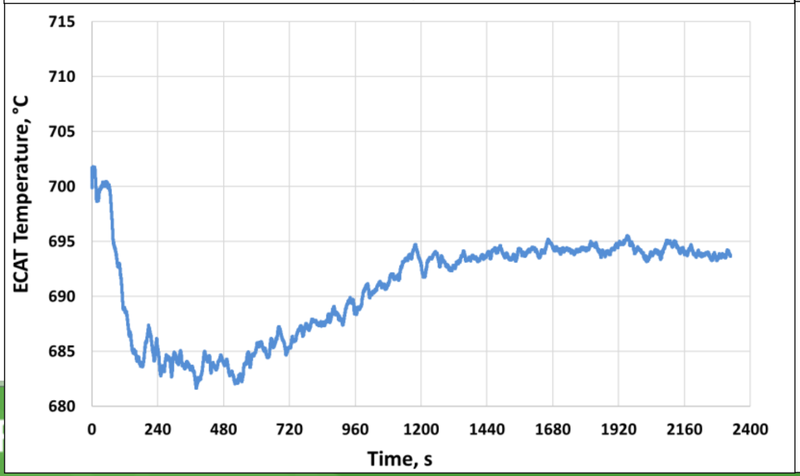


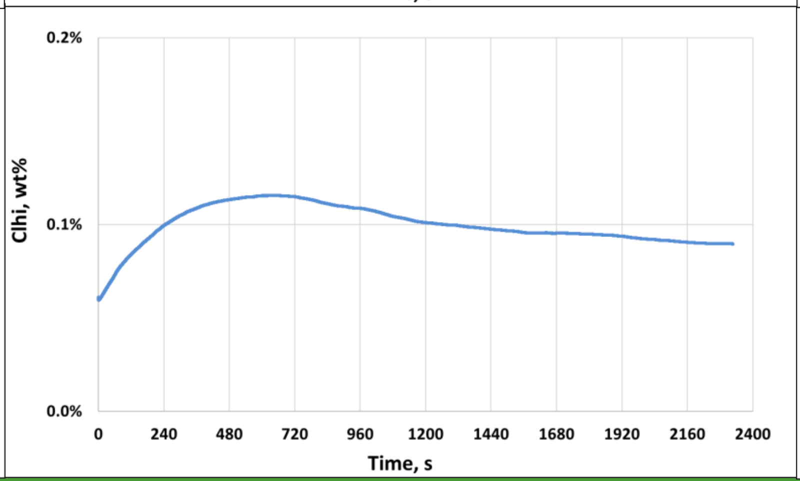


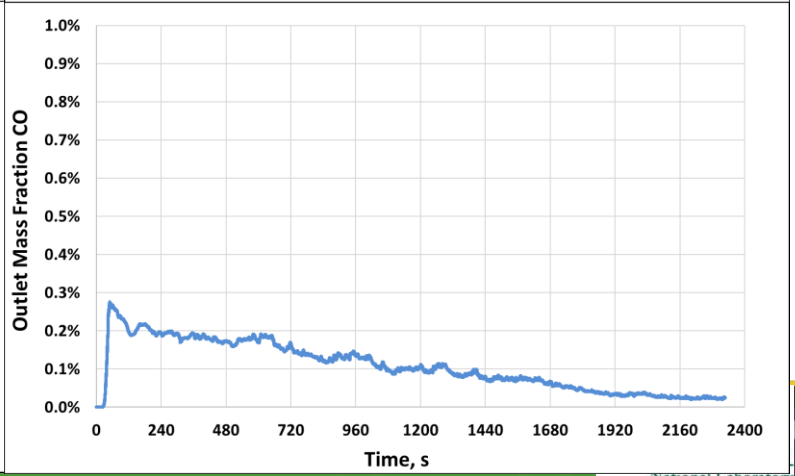




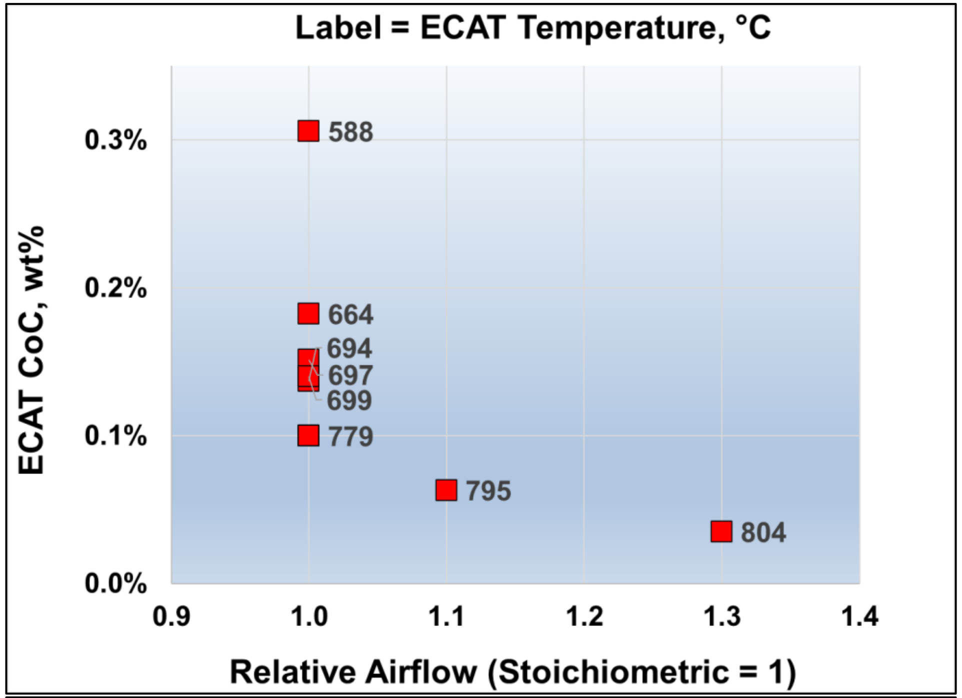


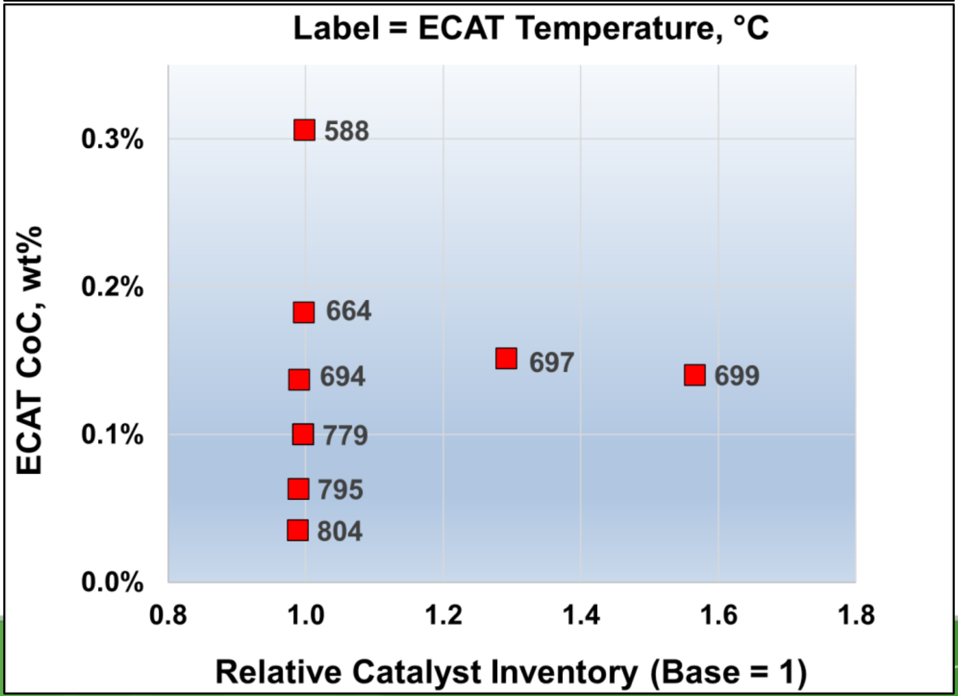


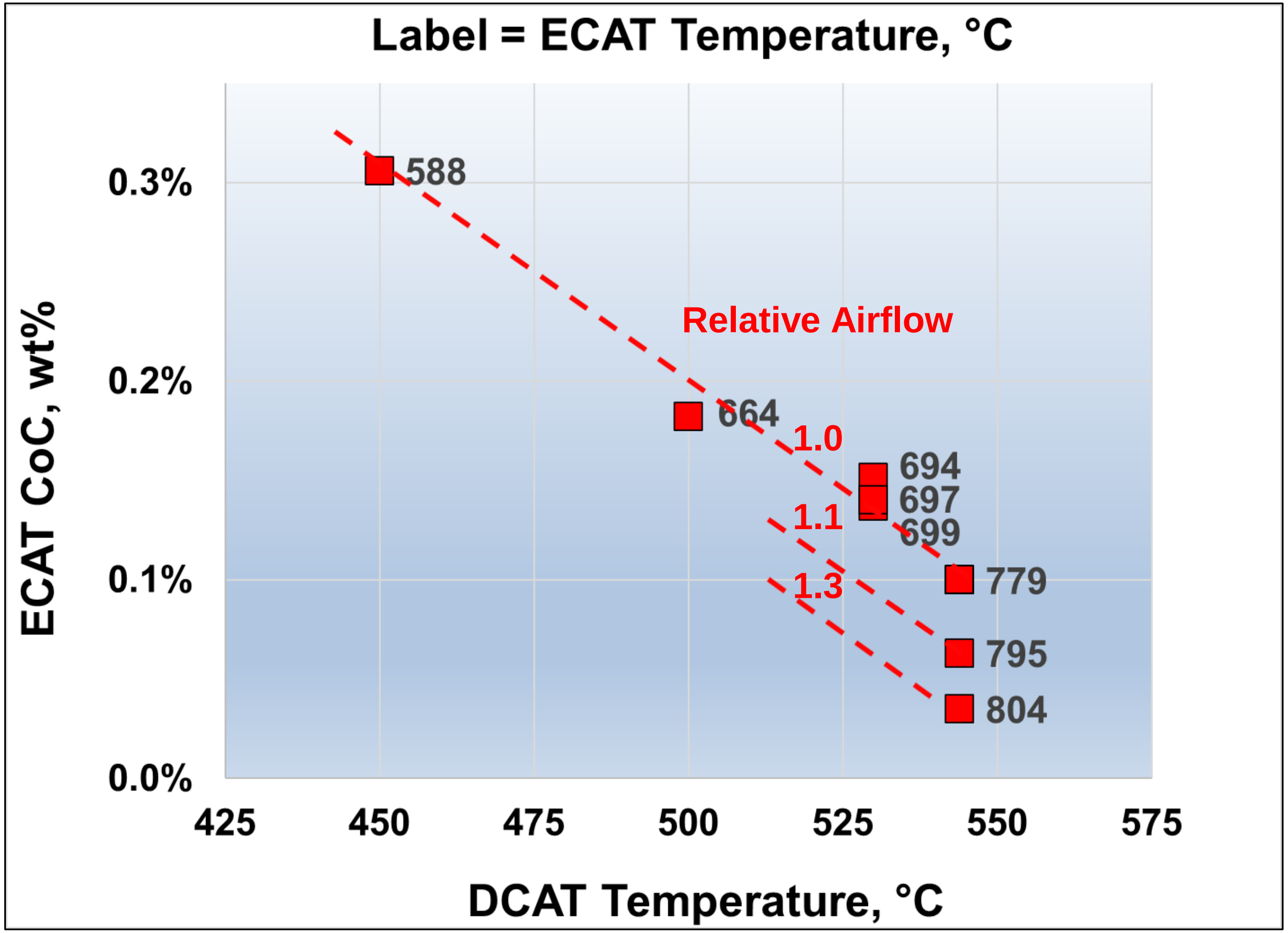




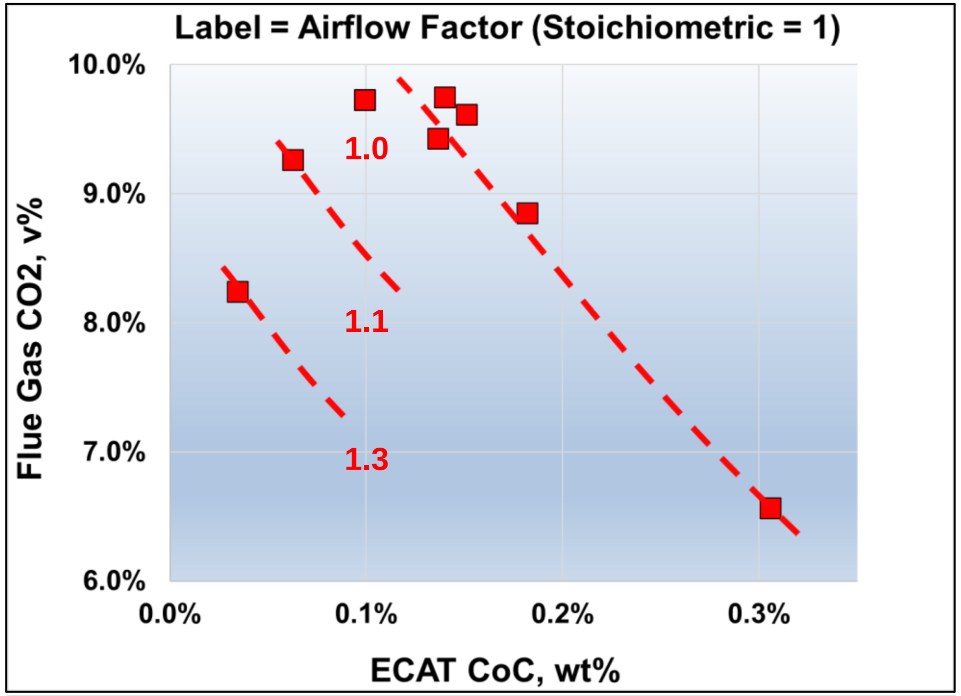
ECAT Carbon on Catalyst (CoC)

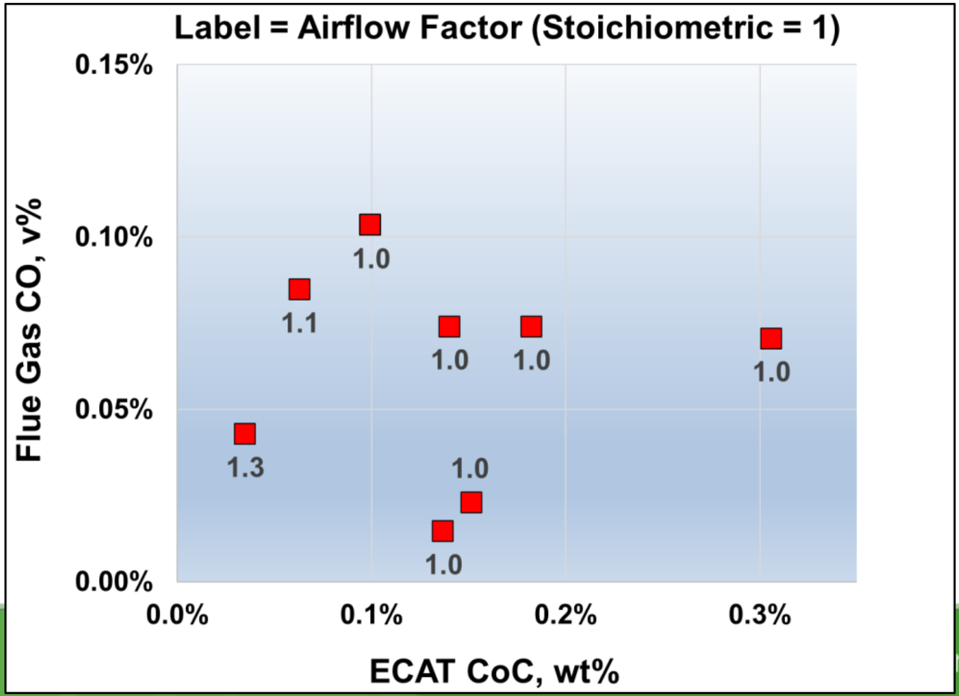


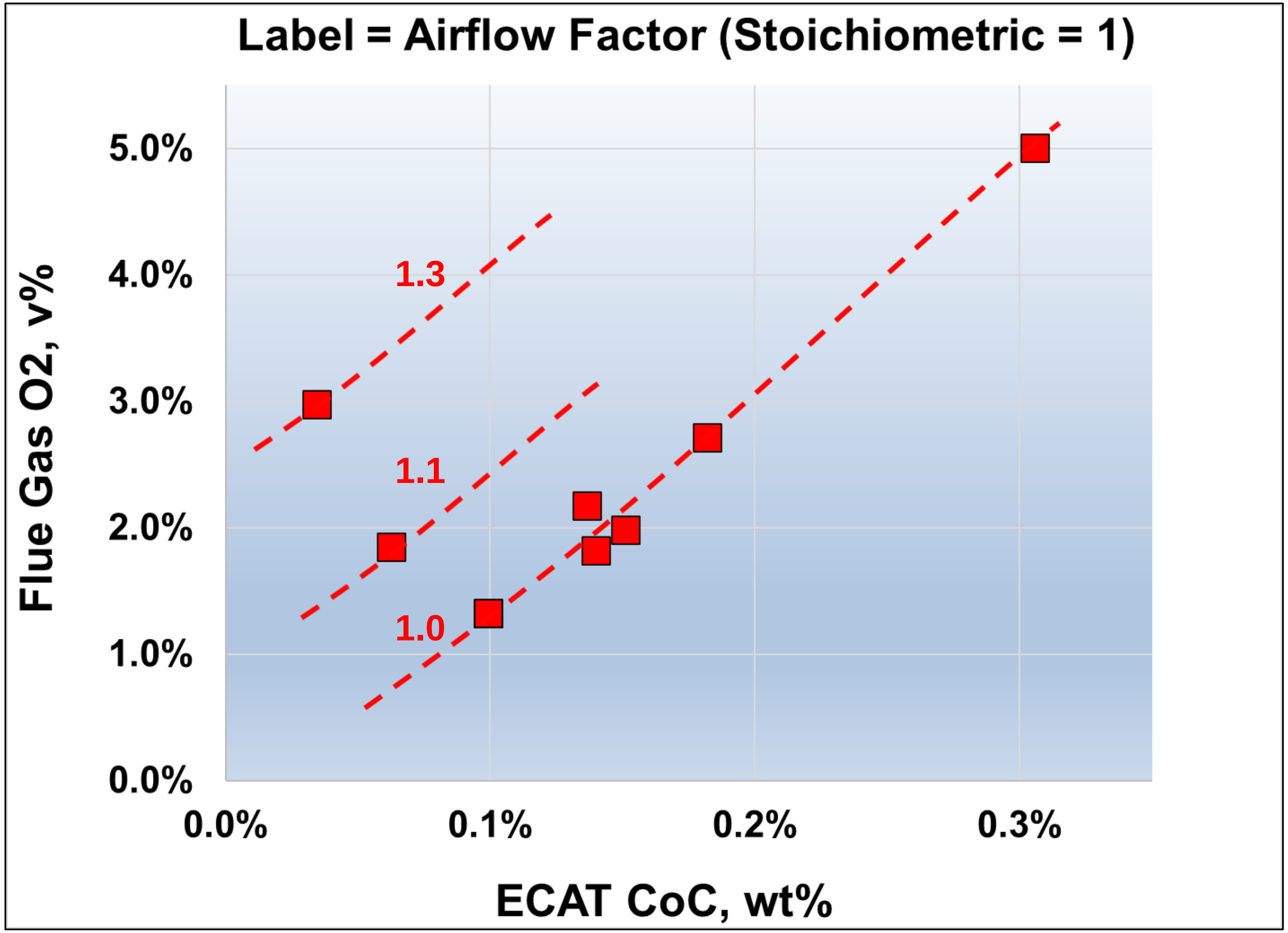




Flue Gas Composition





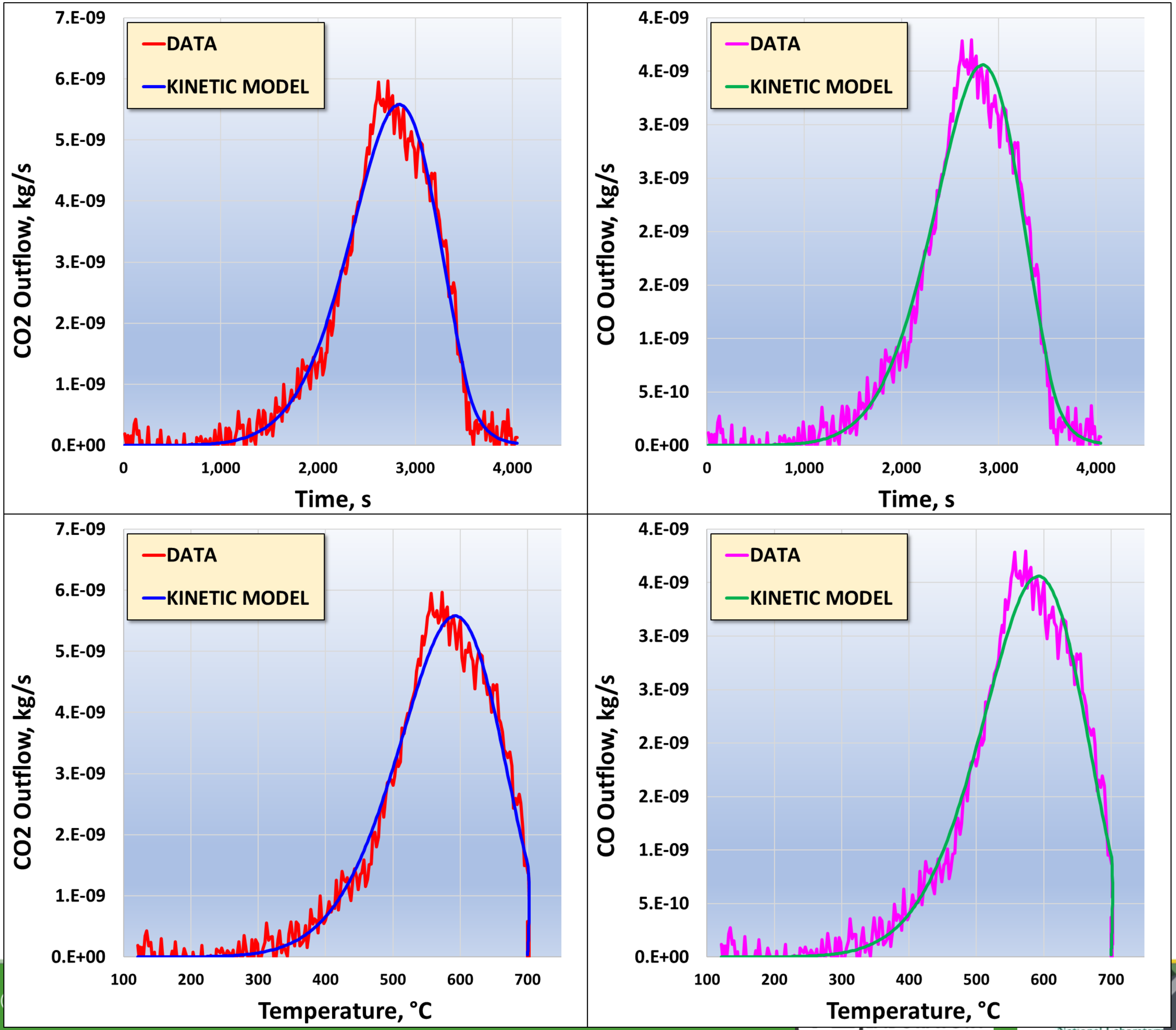


P-Promoted Catalyst

TPO Data and Kinetic Model

Parameter	Units	Value
a_{CO_CO2}	$m^3/(kg.s)$	0.1852
a_{CO2}	1/s	40.851
a_{CO}		171.58
b_{CO_CO2}	-	0.06993
b_{CO2}		0.6776
b_{CO}		1.0
Ea_{CO_CO2}	J/mol	20,729
Ea_{CO2}		76,029
Ea_{CO}		83,117

- *Only one form of carbon, somewhat intermediate but closer to the "low" species in unpromoted catalyst*
- *Simpler kinetic model!*



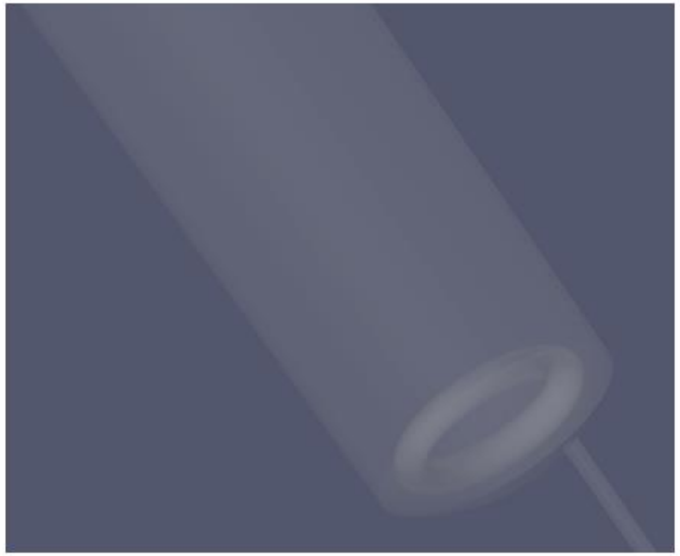
Conclusions

- **Unpromoted catalyst**
  - Initial results indicate that excessive temperatures (≥ 780°C) could be needed to reduce ECAT CoC below 0.1 wt%.
    - Tradeoff: ECAT activity vs long-term hydrothermal deactivation of zeolite (also activity)
    - Full analysis should include the activity effect, required circulation rate, etc.
  - At demo scale (5 mTPD) risk of afterburn is low
    - Need to consider commercial scale
- **P-promoted catalyst**
  - TPO data suggests a combustion promotion effect of P, essentially eliminating the “high” coke species
    - Should correspond to a lower regeneration temperature at equal ECAT CoC
    - Barracuda comparison in progress

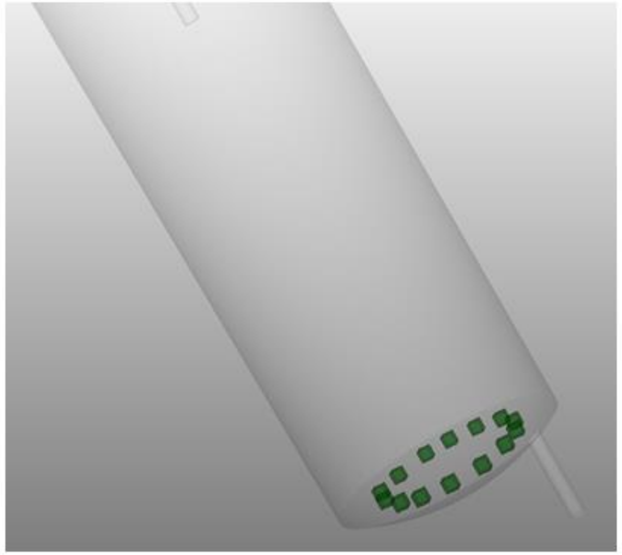
Future Work

- Complete the Barracuda simulation of the P-promoted kinetics in 5 mTPD demo
- Include H → H_2O reaction (some data still pending)
- Extend the study to commercial scale
  - NETL team building an MFiX-Exa model

Exa



MFiX



- MFiX uses point source for the air inlet, while Exa can resolve the circular air grid in much more details.

Acknowledgements

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