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

CFP Regenerator Model Development

tcBiomass2024

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ChemCatBio
Chemical Catalysis for Bioenergy

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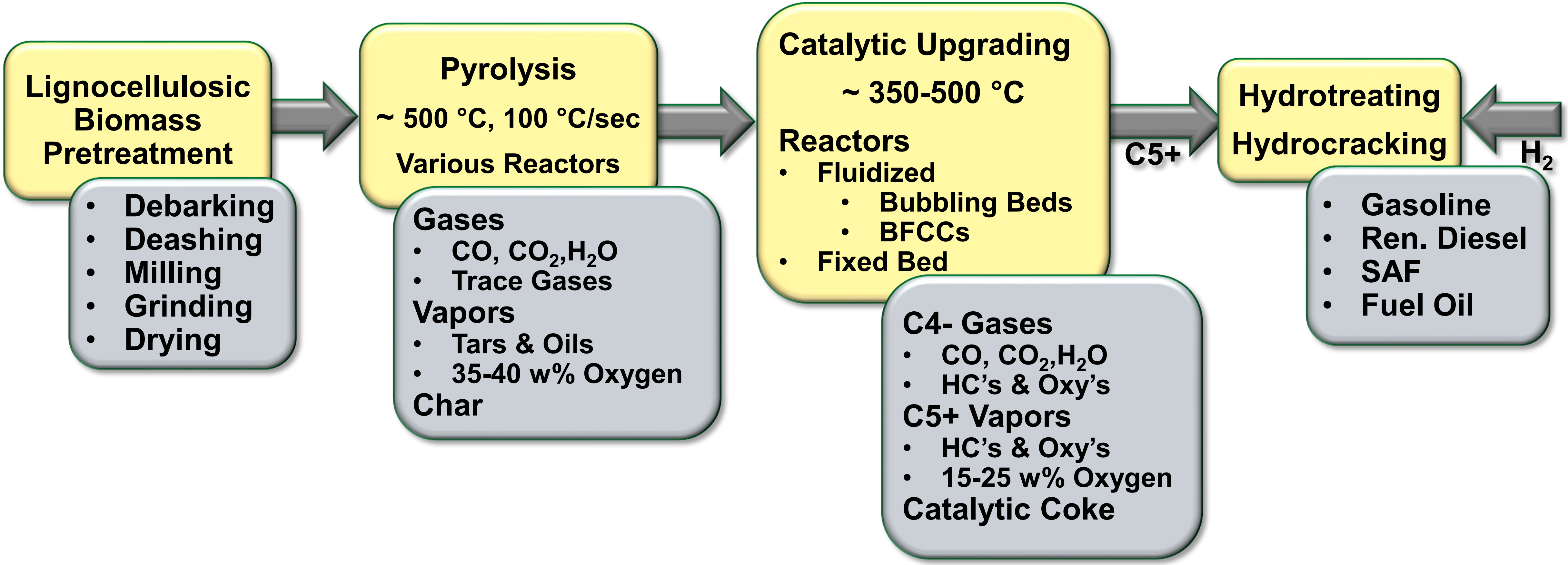
Catalytic Fast Pyrolysis (CFP)



Lignocellulosic Biomass Pretreatment

- Debarking
- Deashing
- Milling
- Grinding
- Drying

Pyrolysis

~ 500 °C, 100 °C/sec

Various Reactors

Gases
- CO, CO_2,H_2O
- Trace Gases

Vapors
- Tars & Oils
- 35-40 w% Oxygen

Char

Catalytic Upgrading

~ 350-500 °C

Reactors
- Fluidized
  - Bubbling Beds
  - BFCCs
- Fixed Bed

C4- Gases
- CO, CO_2,H_2O
- HC's & Oxy's

C5+ Vapors
- HC's & Oxy's
- 15-25 w% Oxygen

Catalytic Coke

C5+

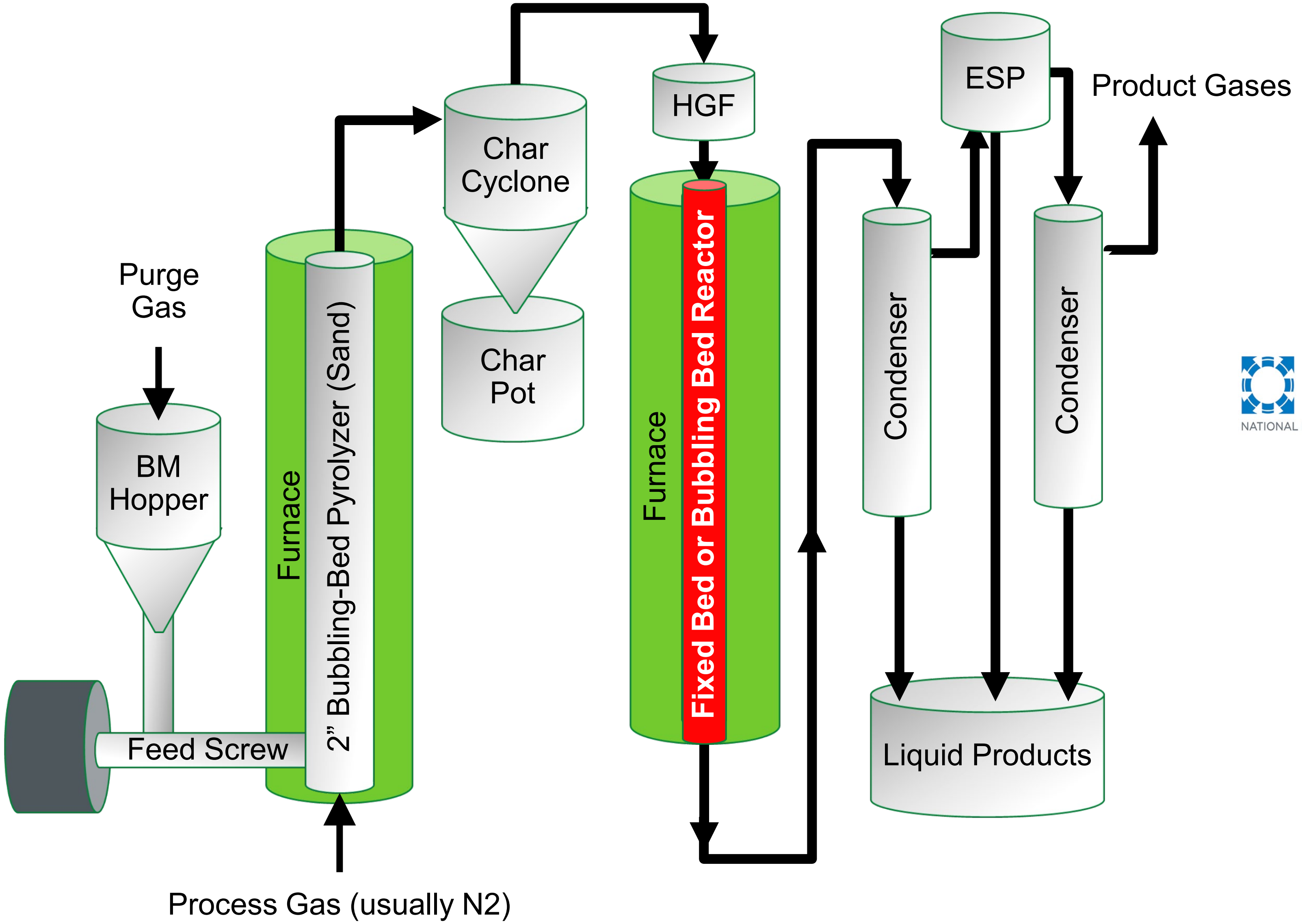
Hydrotreating

Hydrocracking

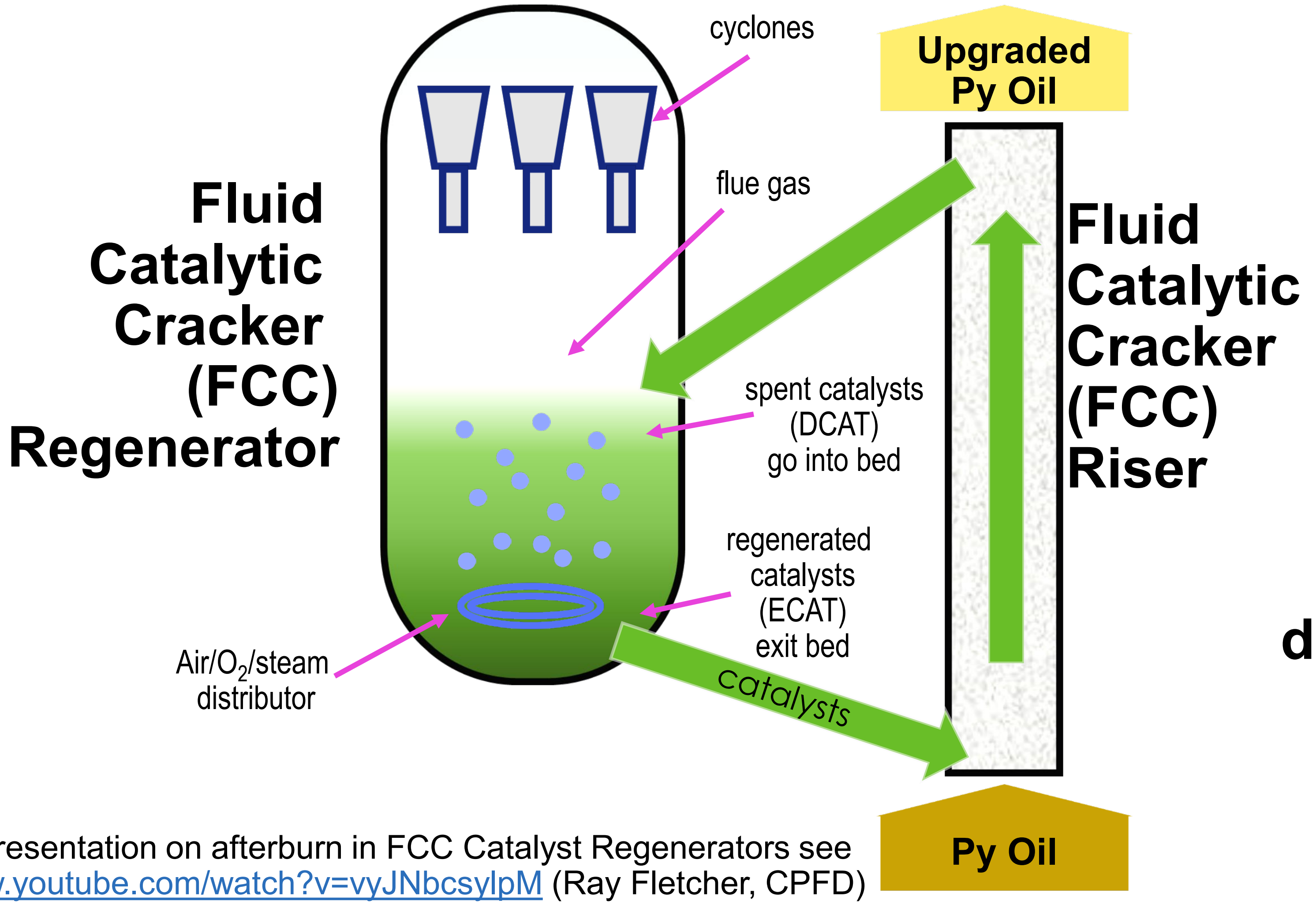
H_2

- Gasoline
- Ren. Diesel
- SAF
- Fuel Oil

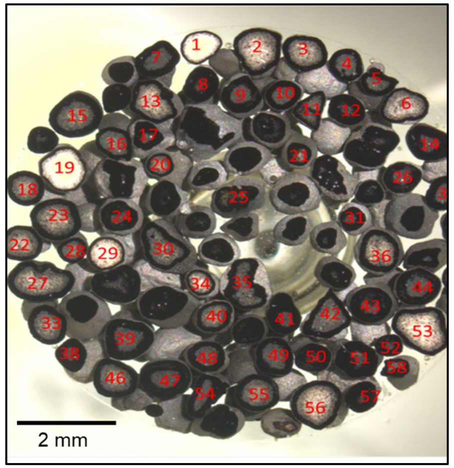
NREL's "2FBR": A Flexible CFP Unit



Mitigating risks for scale up of Catalytic Fast Pyrolysis catalyst regeneration requires accurately capturing CO and CO_2 kinetics



Coked catalysts from Catalytic Fast Pyrolysis ChemCatBio team



When bio-coke combusts during catalyst regeneration (de-coking) does it make CO or CO_2?

For nice presentation on afterburn in FCC Catalyst Regenerators see https://www.youtube.com/watch?v=vyJNbcsylpM (Ray Fletcher, CPFD)

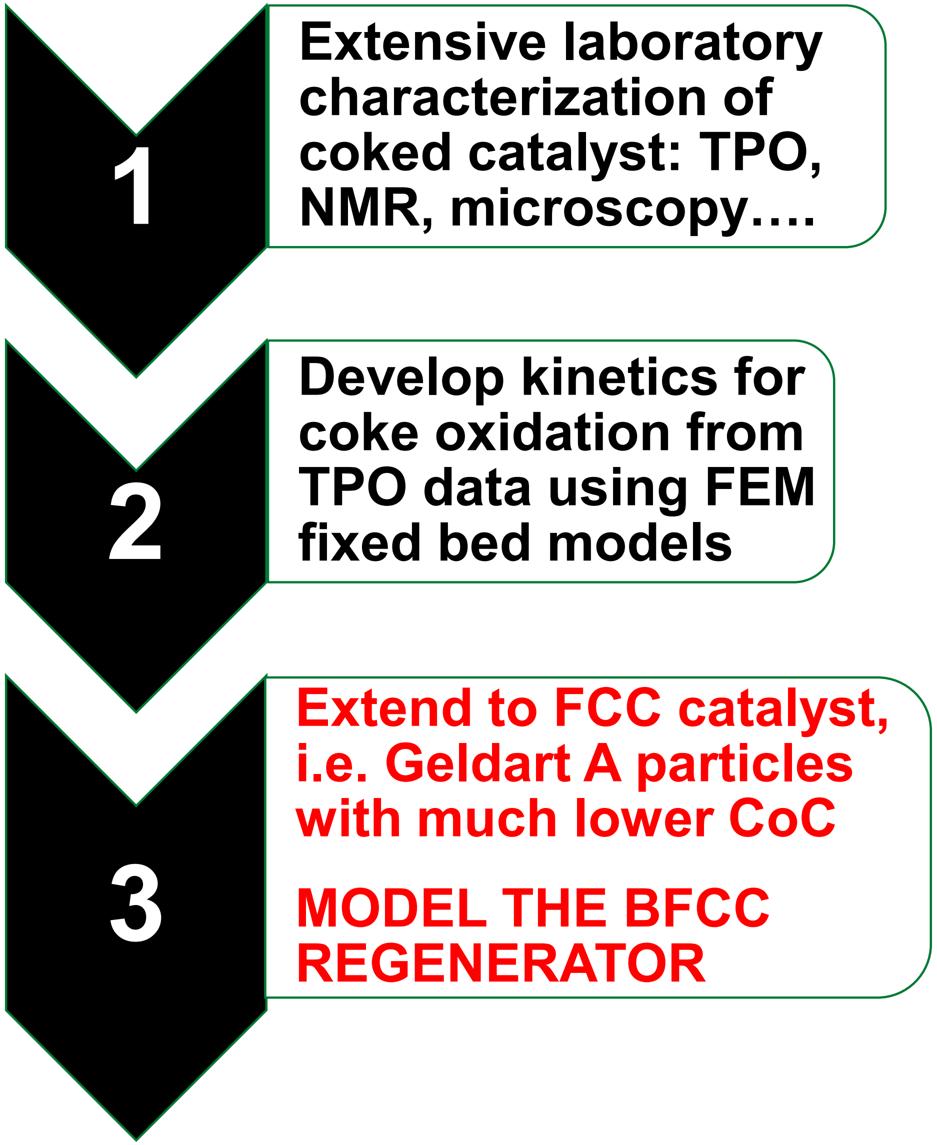
ZSM-5 Based Catalysts Used in 2FBR Bubbling-Bed Upgrader

80% ZSM-5
20% Alumina

+/- P-promotion
(2.5 wt%)

Geldart B
Dp = 500 – 800 μm

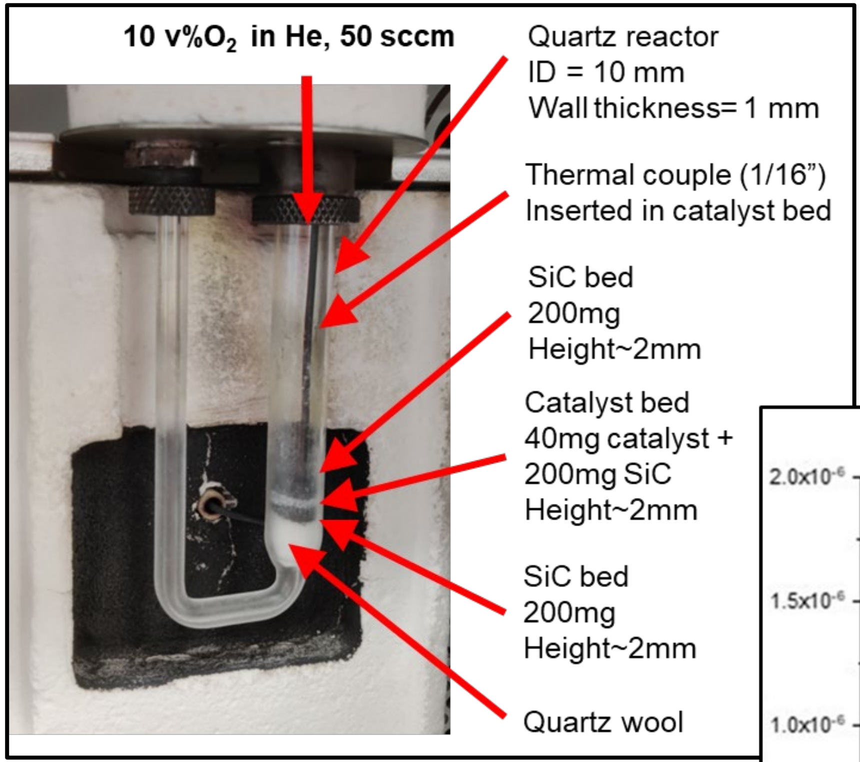
Spent Catalyst:
9-13 wt% CoC
(Coke on Catalyst)



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 THE BFCC REGENERATOR

Coke Characterization and Combustion Behavior



10 v%O_2 in He, 50 sccm

Quartz reactor
ID = 10 mm
Wall thickness= 1 mm

Thermal couple (1/16")
Inserted in catalyst bed

SiC bed
200mg
Height~2mm

Catalyst bed
40mg catalyst +
200mg SiC
Height~2mm

SiC bed
200mg
Height~2mm

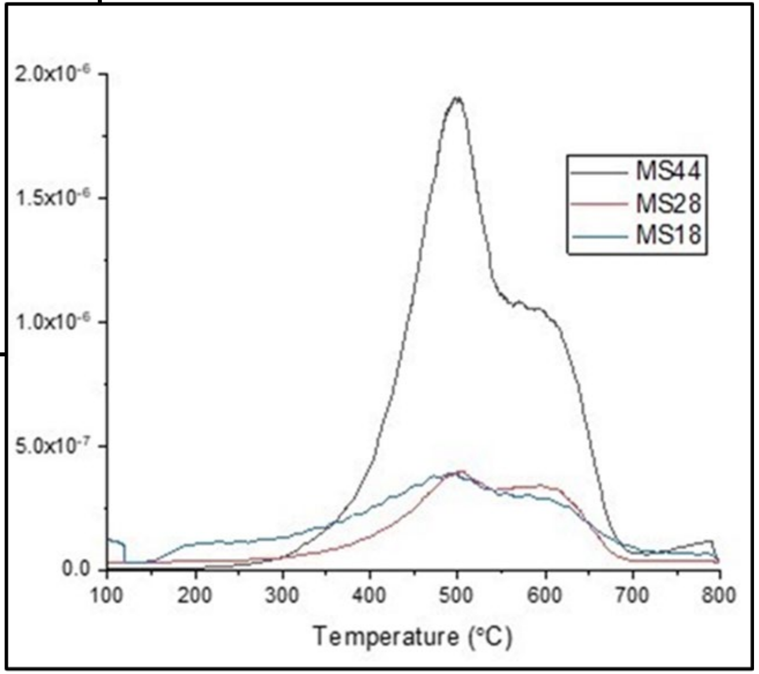
Quartz wool

Temperature Programmed Oxidation (TPO):

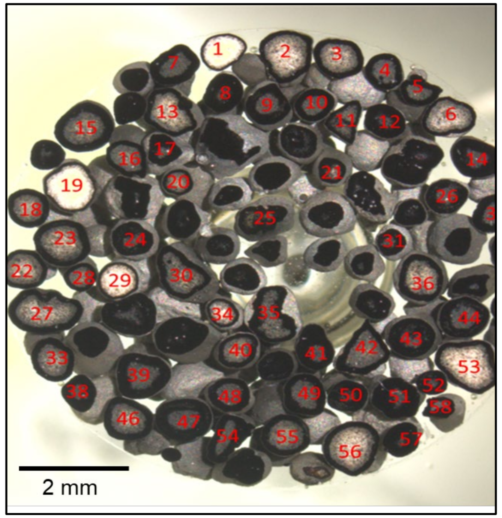
"Low" and "High" Temperature Carbon

Whole Pellets (~600 μm)

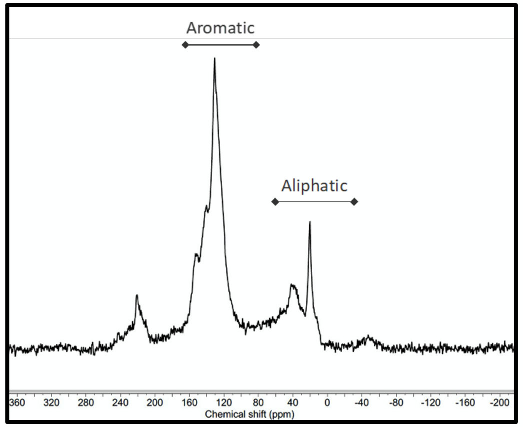
vs Crushed (< 100 mesh)



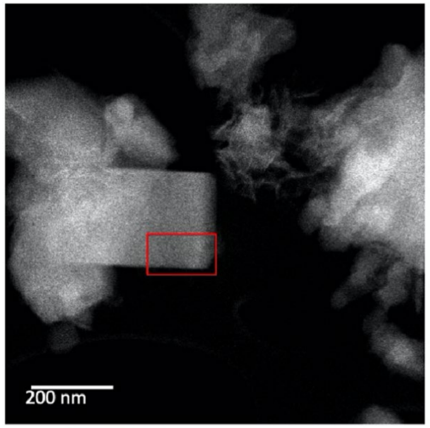
Microscopy



^{13}C-NMR



STEM-EELS

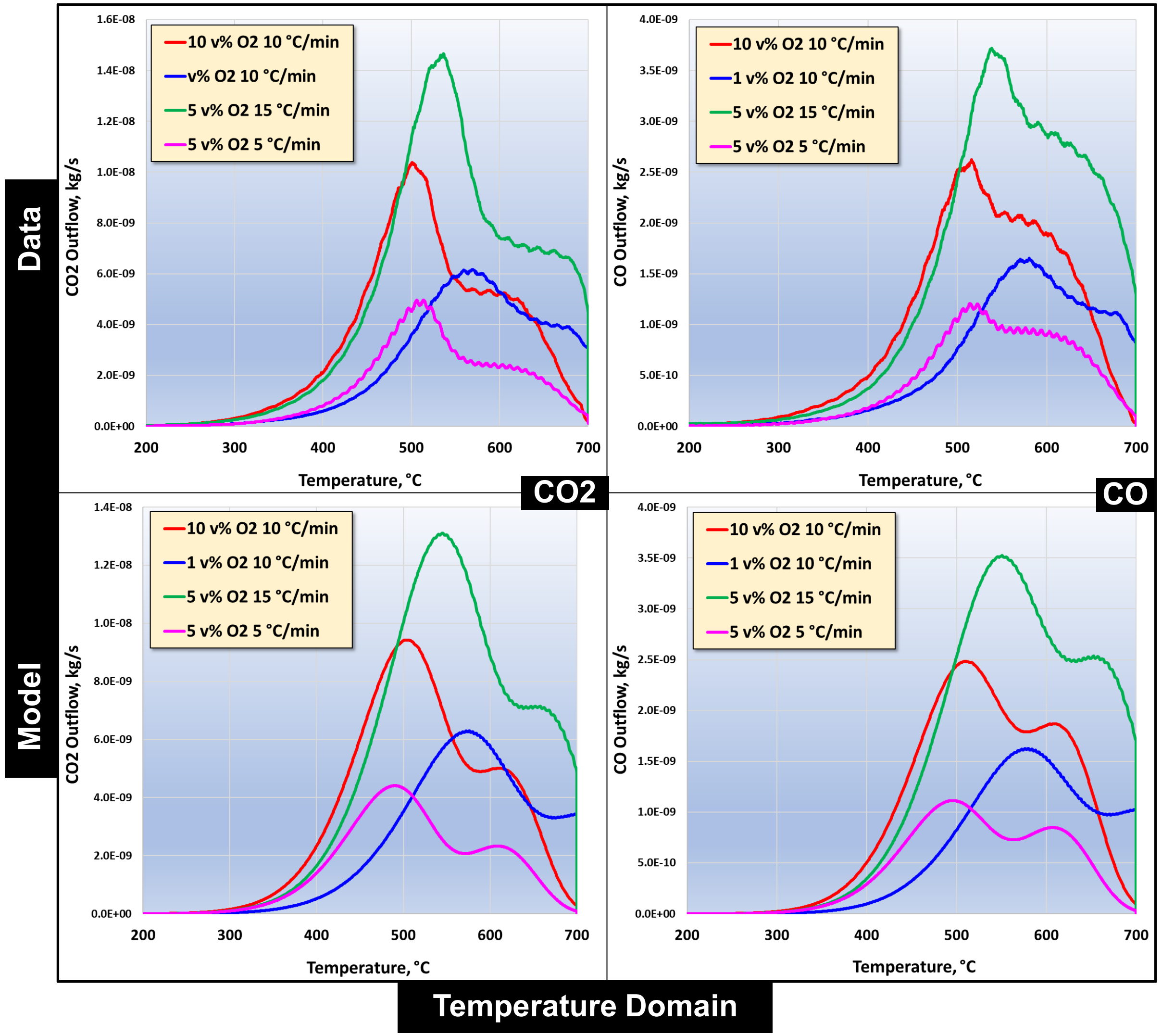


Consortia Acknowledgements:

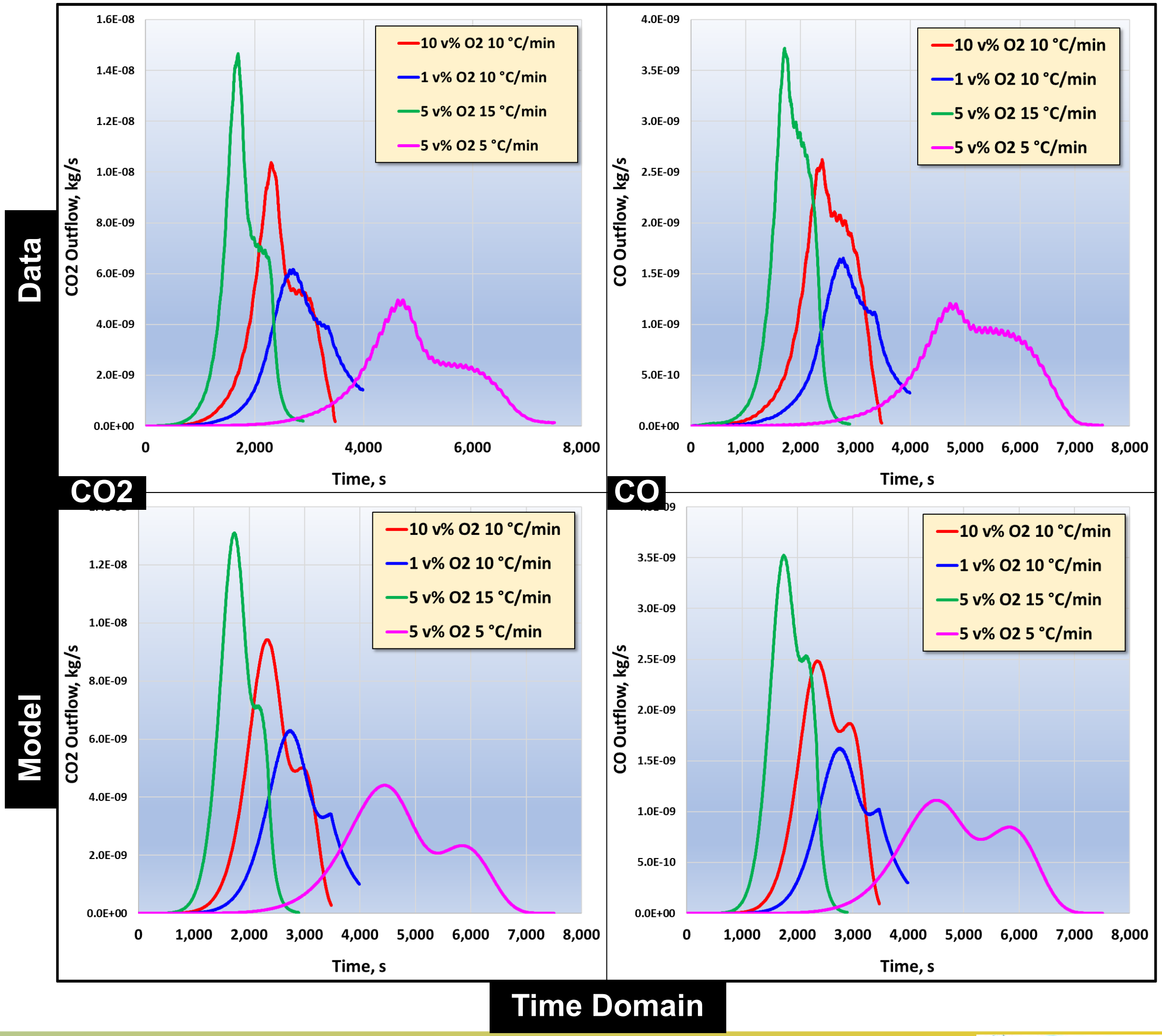
CDM: Catalyst Deactivation Mitigation

ACSC: Advanced Catalyst Synthesis and Characterization

Quality of Fit: Four TPO Runs



Crushed -100 Mesh



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 and heat transfer effects in catalyst particles and in bed*

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

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

   - The 80% ZSM-5, 20% Al2O3 formulation is too high in Z/M (too many active sites and too low in mesoporosity, i.e.Thiele number is too high). This very likely leads to the core-shell coke profile. **WE EXPECT A LOWER Z/M FOR BFCC CATALYSTS.**

2. Convert reaction expressions to volume concentrations (mass/volume) instead of surface concentrations (mass/area)

Parameter	Units	COMSOL	Barracuda
a_{CO_CO2}	m³/(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	
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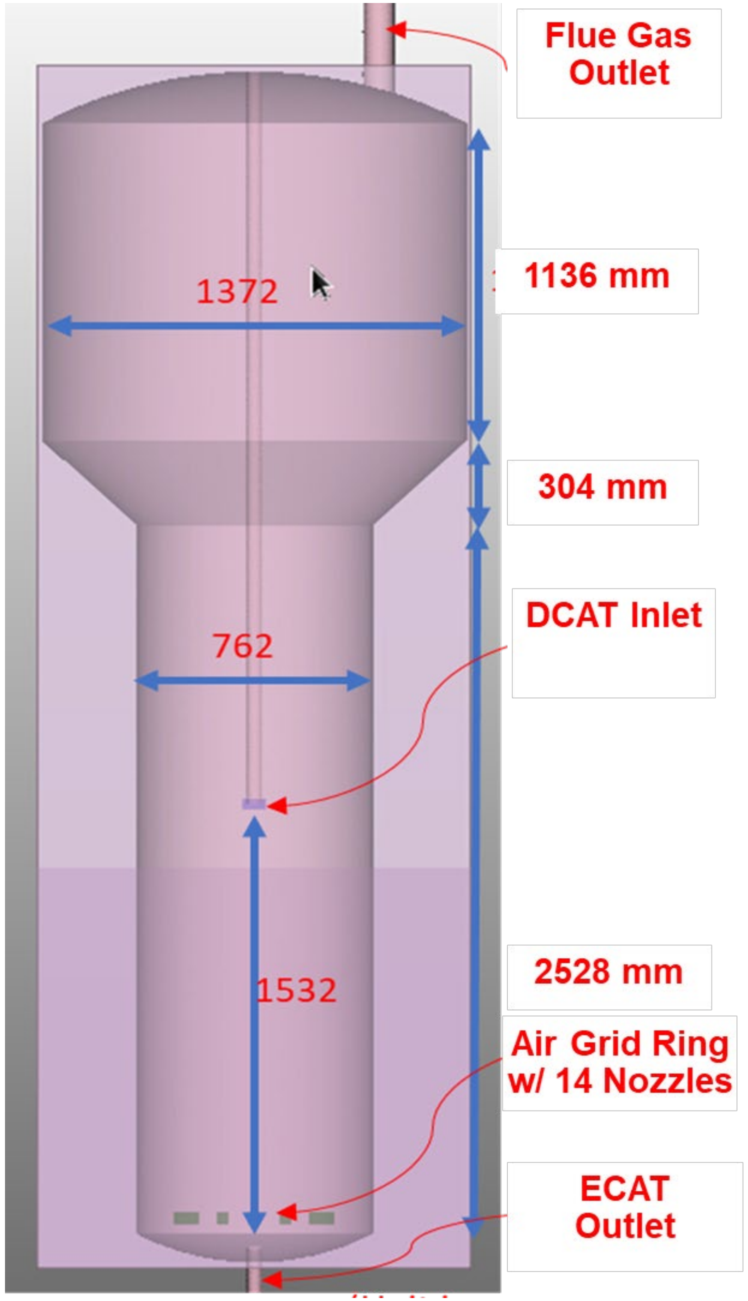
Ea_{CO_low}		109,677	
Ea_{CO_hi}		143,340	

BFCC Regenerator Case Study:
5 metric ton/day (mTPD) Demo Unit



Flue Gas Outlet

1136 mm

304 mm

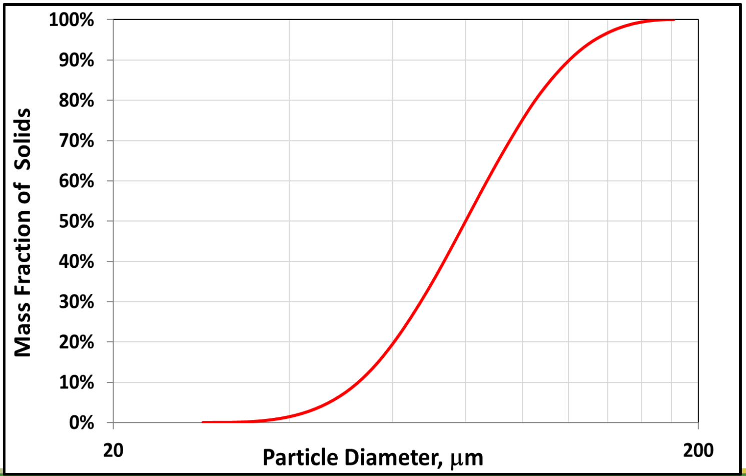
DCAT Inlet

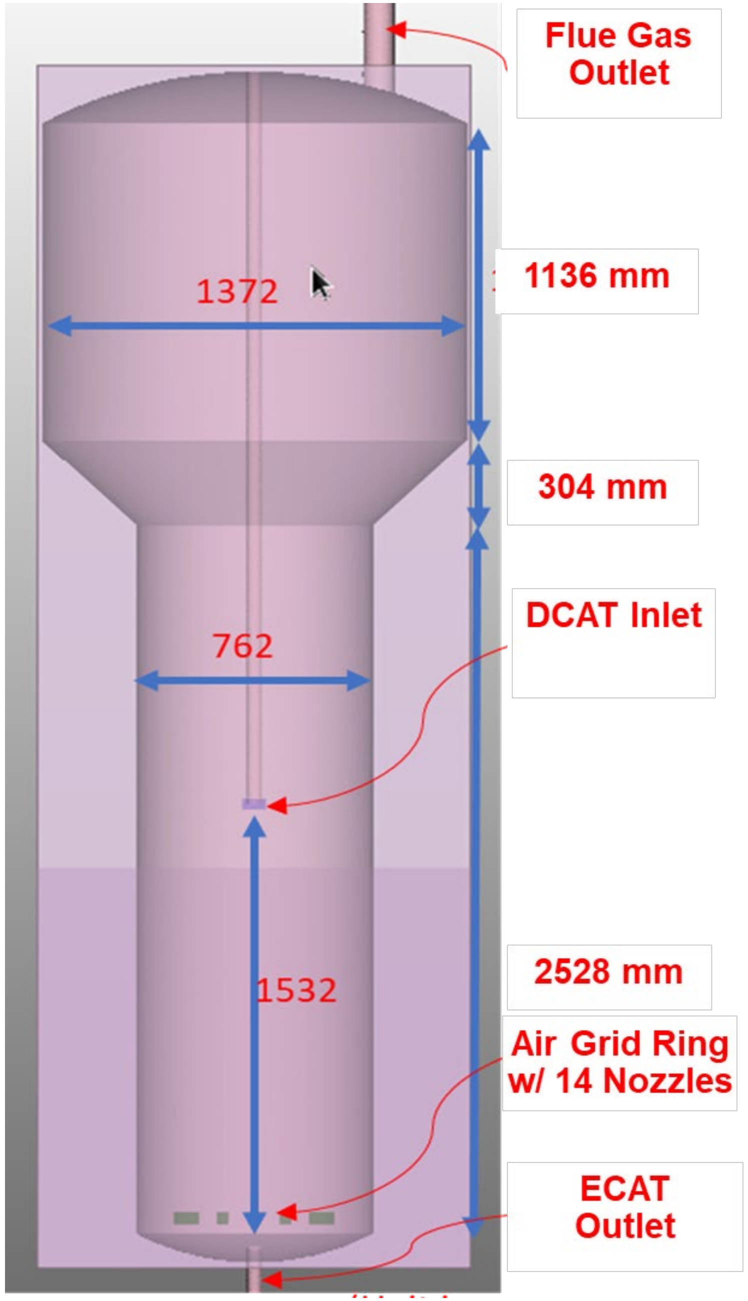
2528 mm

Air Grid Ring w/ 14 Nozzles

ECAT Outlet

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





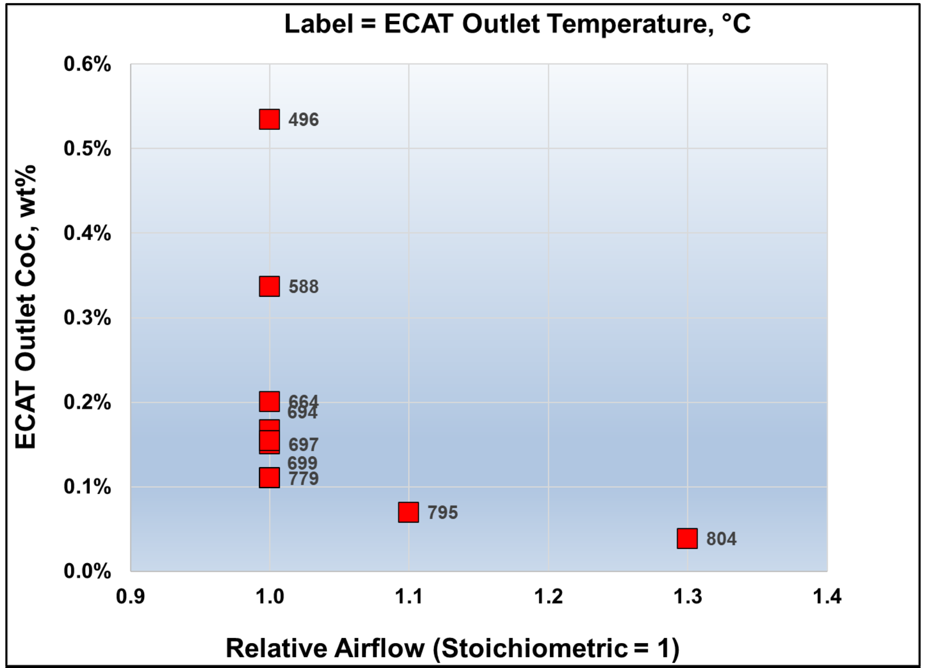
Variables Studied

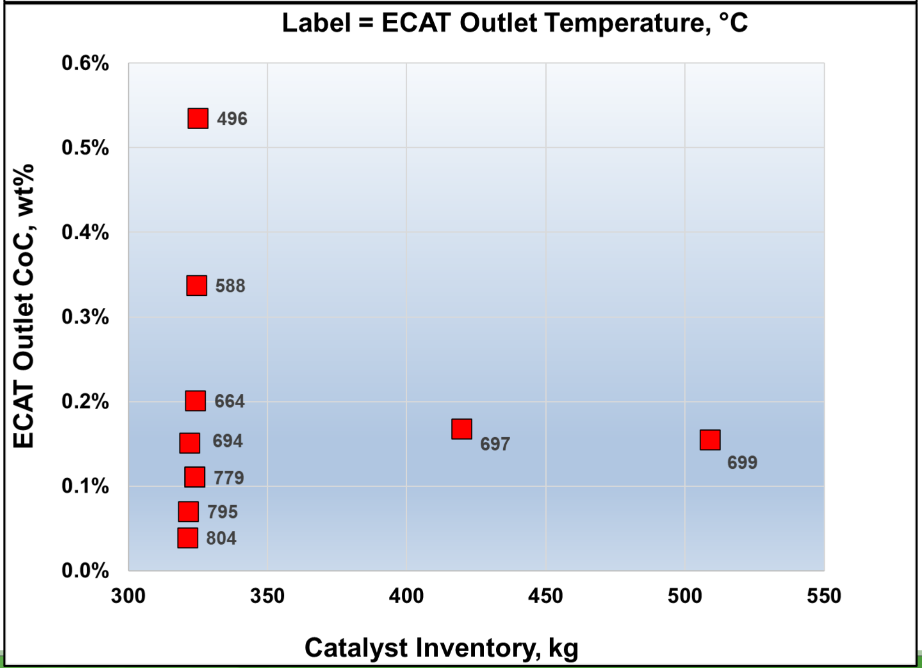
Variables	Units	Range
Relative Airflow (Stoichiometric = 1)	-	1.0 -1.3
Catalyst Inventory, kg		1.0 - 1.6
DCAT Temperature *Effect of Riser Outlet Temp (ROT) and/or catalyst cooler*	°C	450 - 550

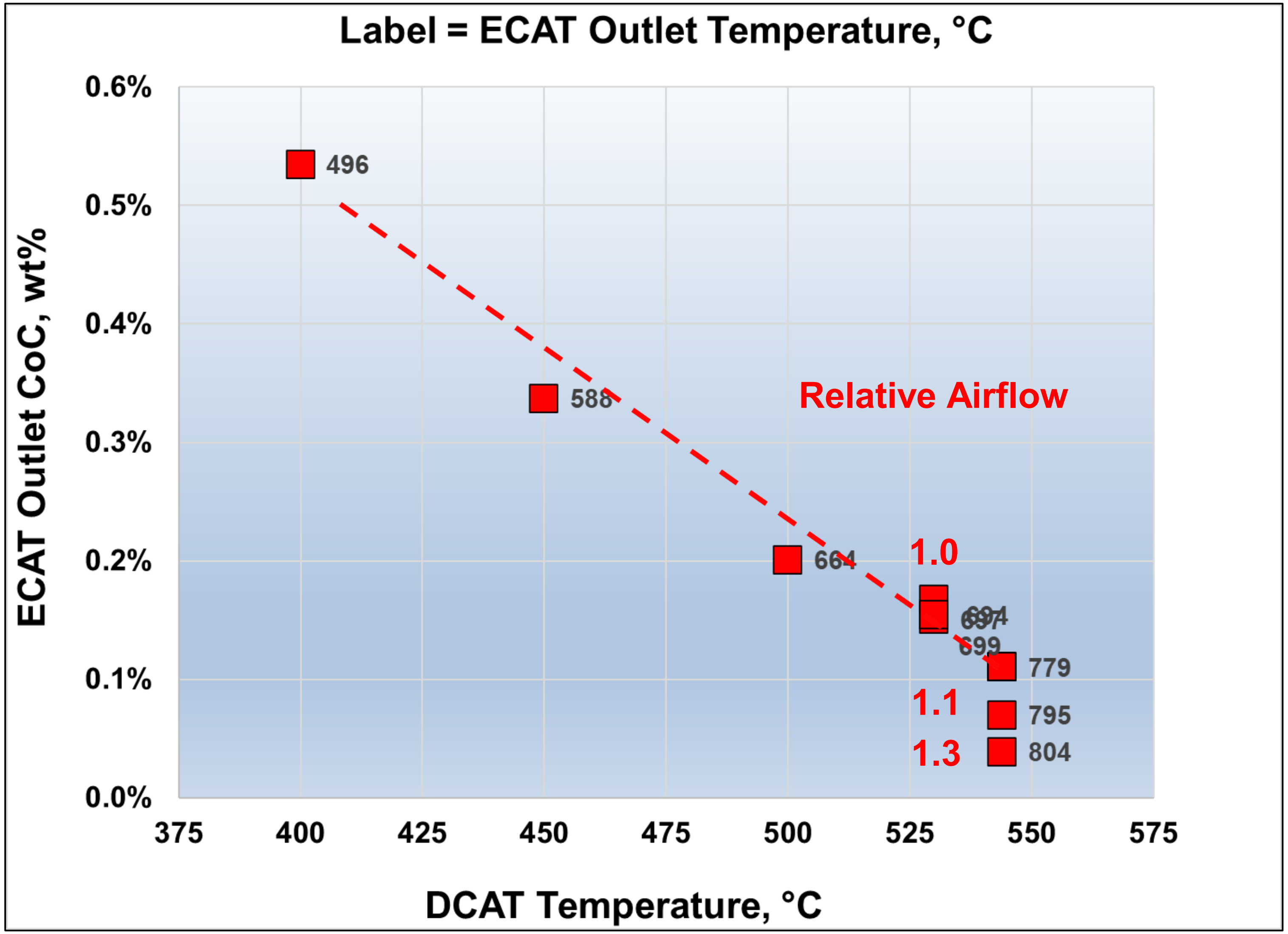
Important Outputs

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)

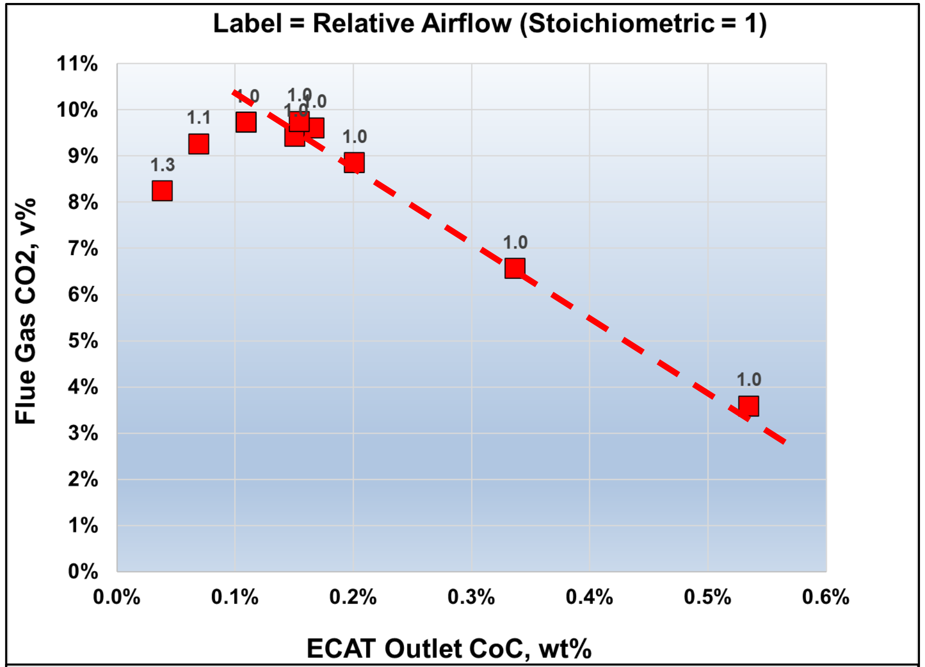
Regenerated ECAT Carbon on Catalyst (CoC)

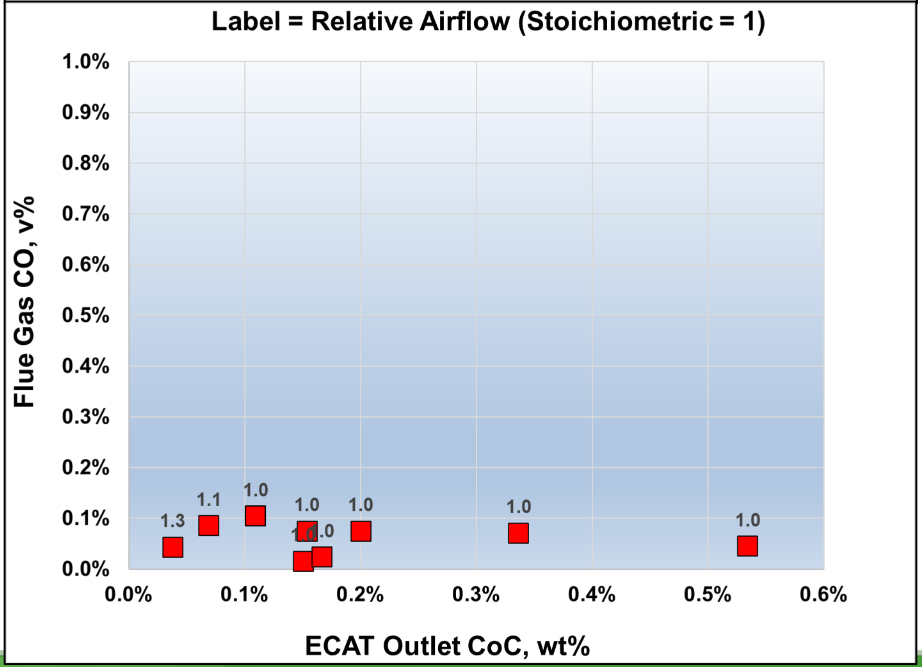


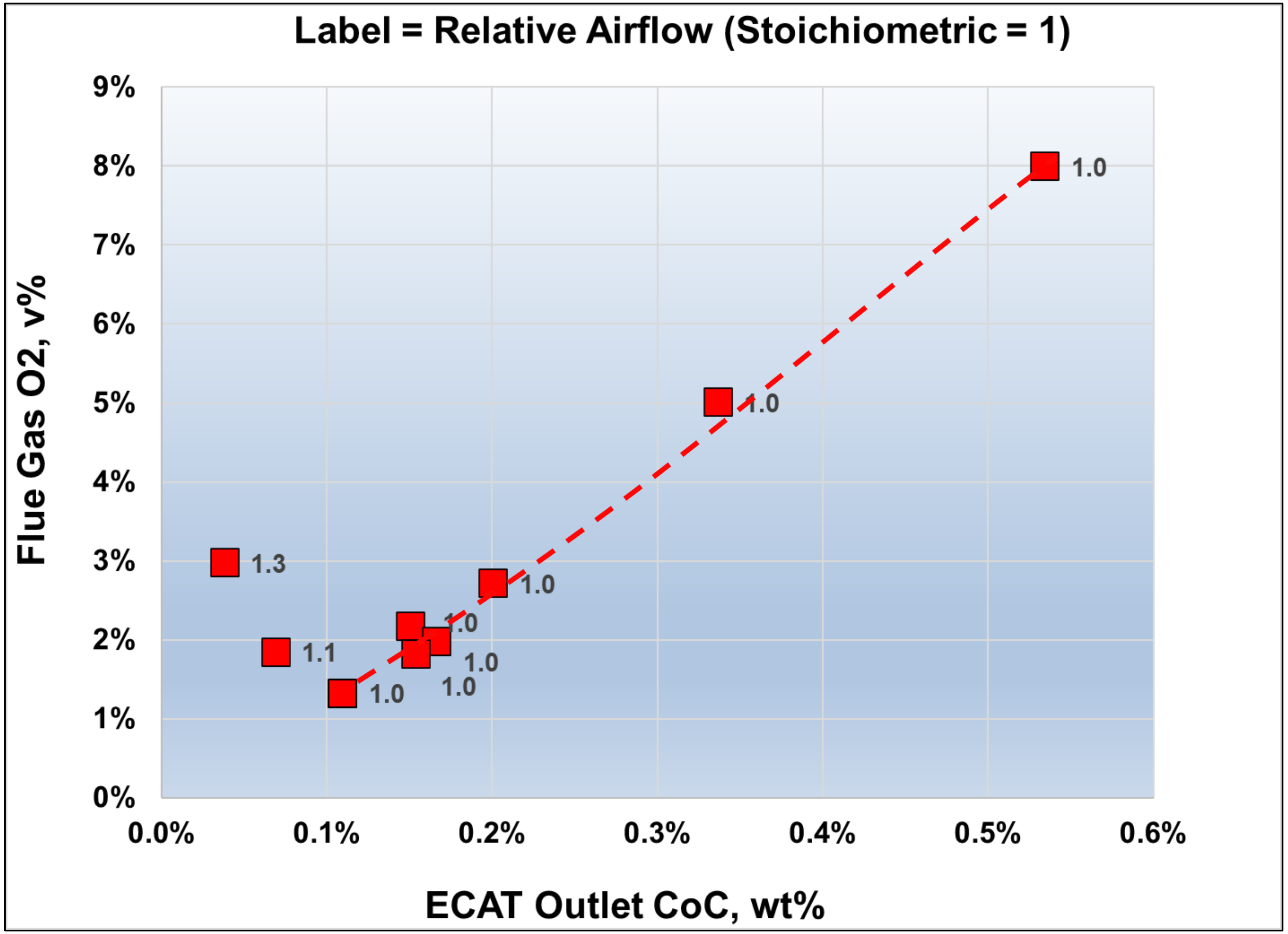




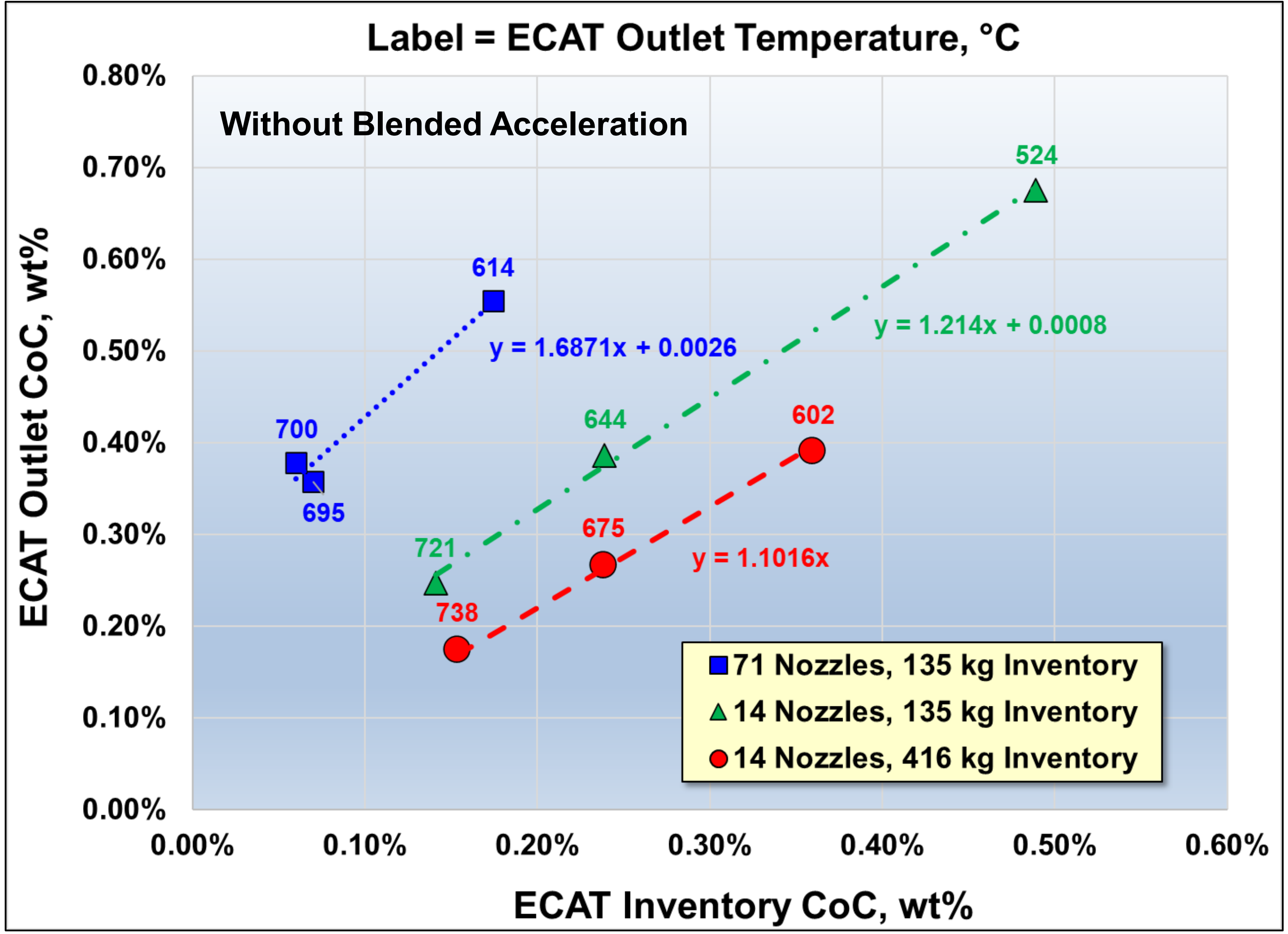
Flue Gas Composition







Catalyst Flow Segregation



The Blended Acceleration Model

P. J. O'Rourke and D. M. Snider. A new blended acceleration model for the particle contact forces induced by an interstitial fluid in dense particle/fluid flows. Powder Technology, 256(): 39–51, 2014

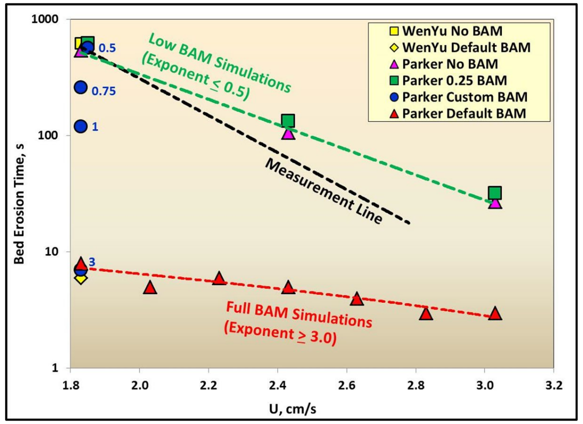
Weighting parameter for blending the MP-PIC and average particle accelerations:

$$wt_{frac} = 1 - (1 - \theta_p/\theta_{p,cp})^n$$

Default value is n = 6

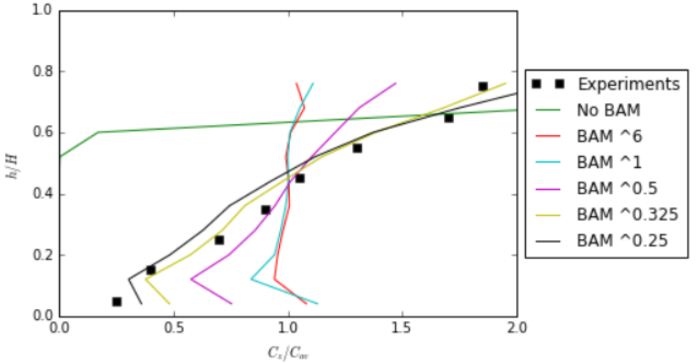
Mixing of Biomass and FCC Catalyst

Adkins and Kapur, Barracuda Users Conference (2015)



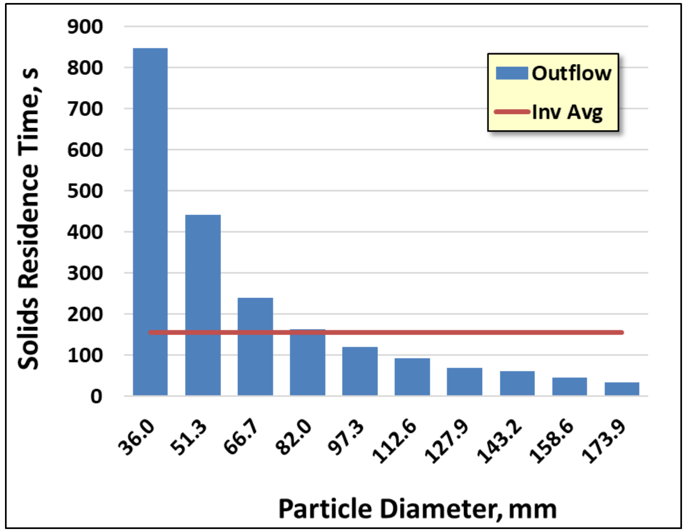
Mixing of Coal Char and Sand

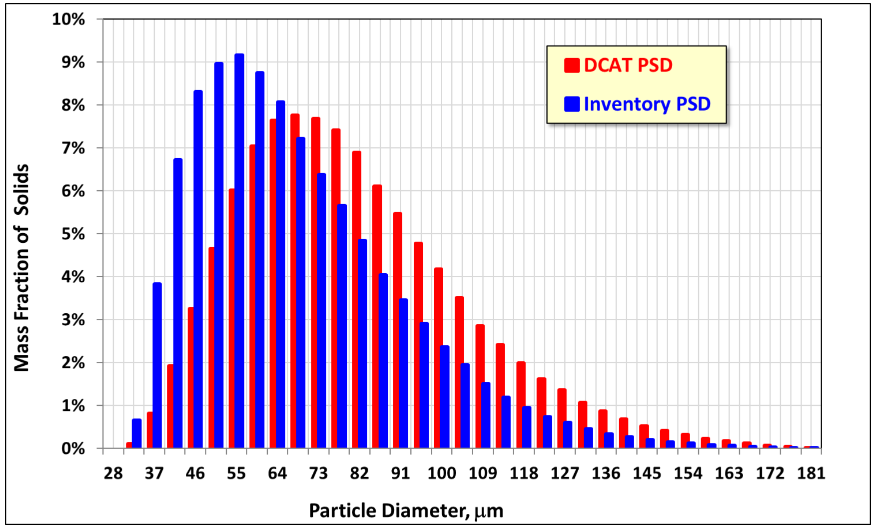
Zhang et.al, Powder Technology, 228(): 206-209, 2012

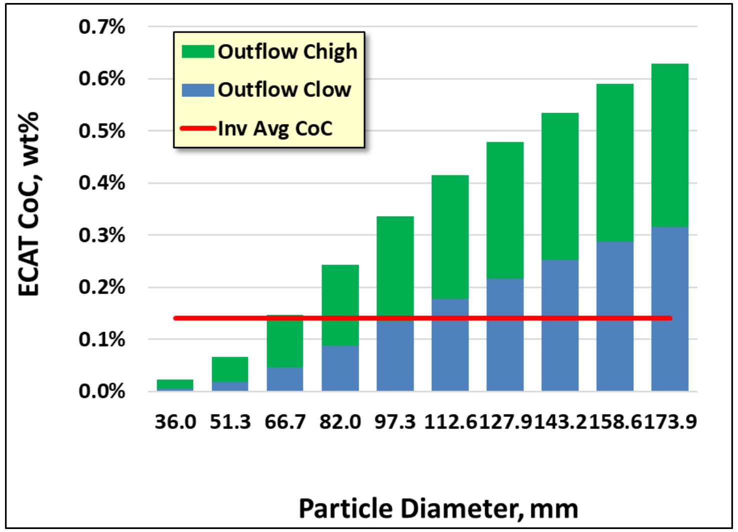


Effect of Blended Acceleration (n = 6)

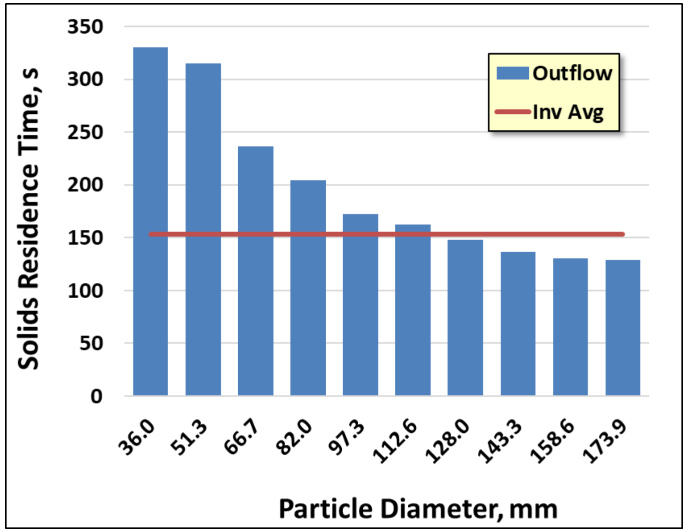
No Blended Acceleration

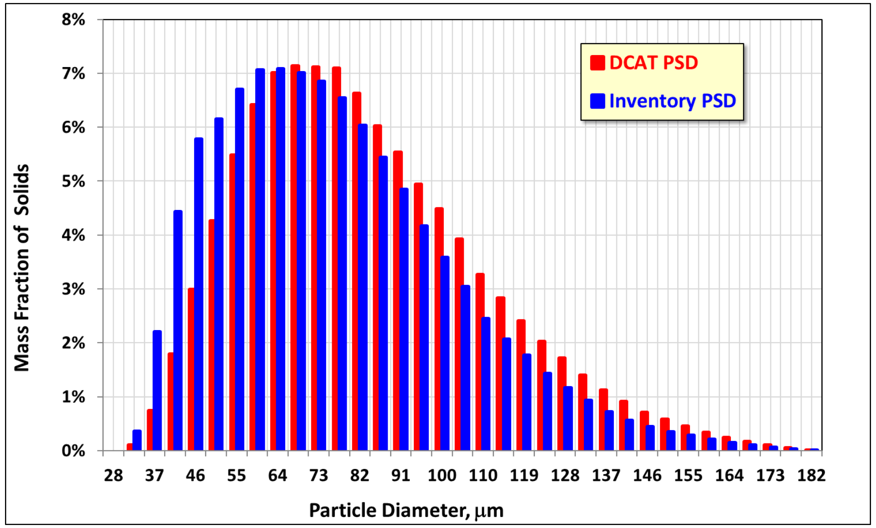


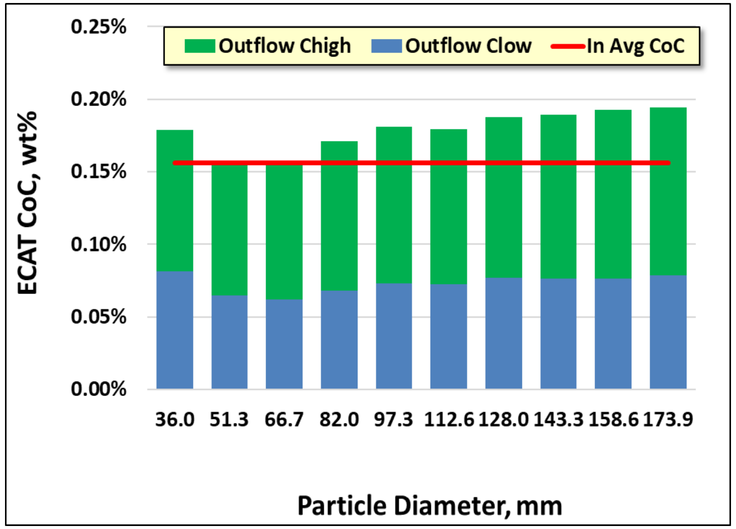




Blended Acceleration (n = 6)

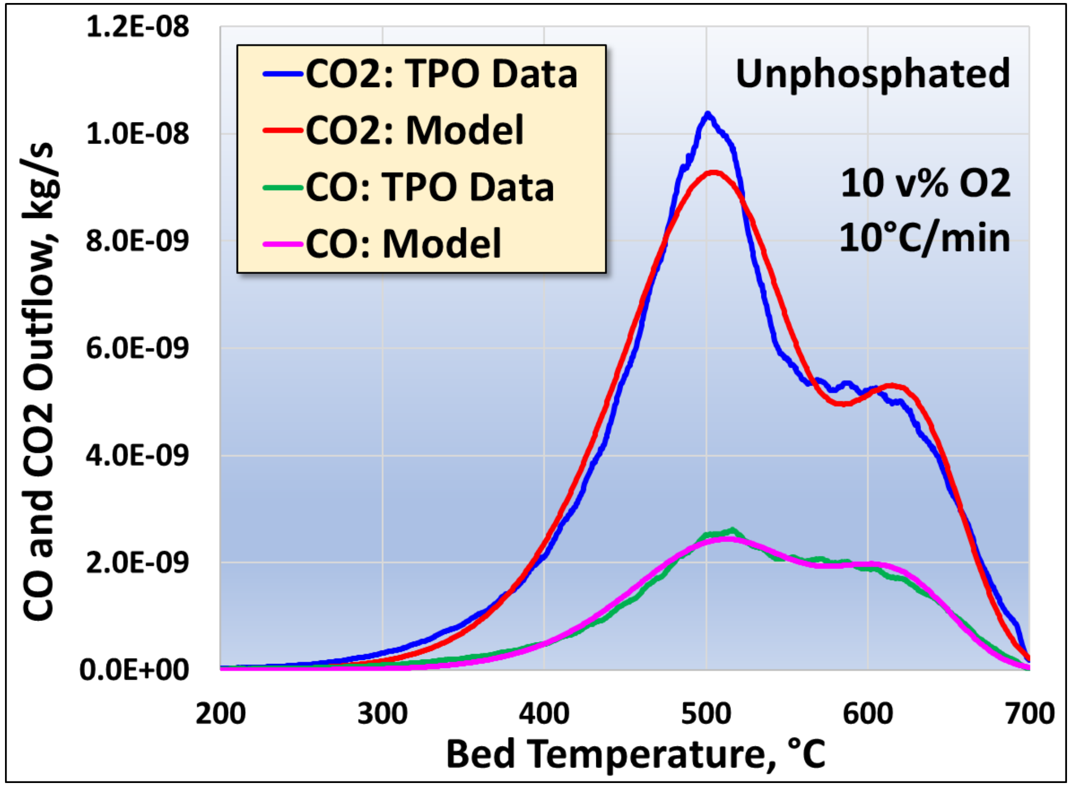


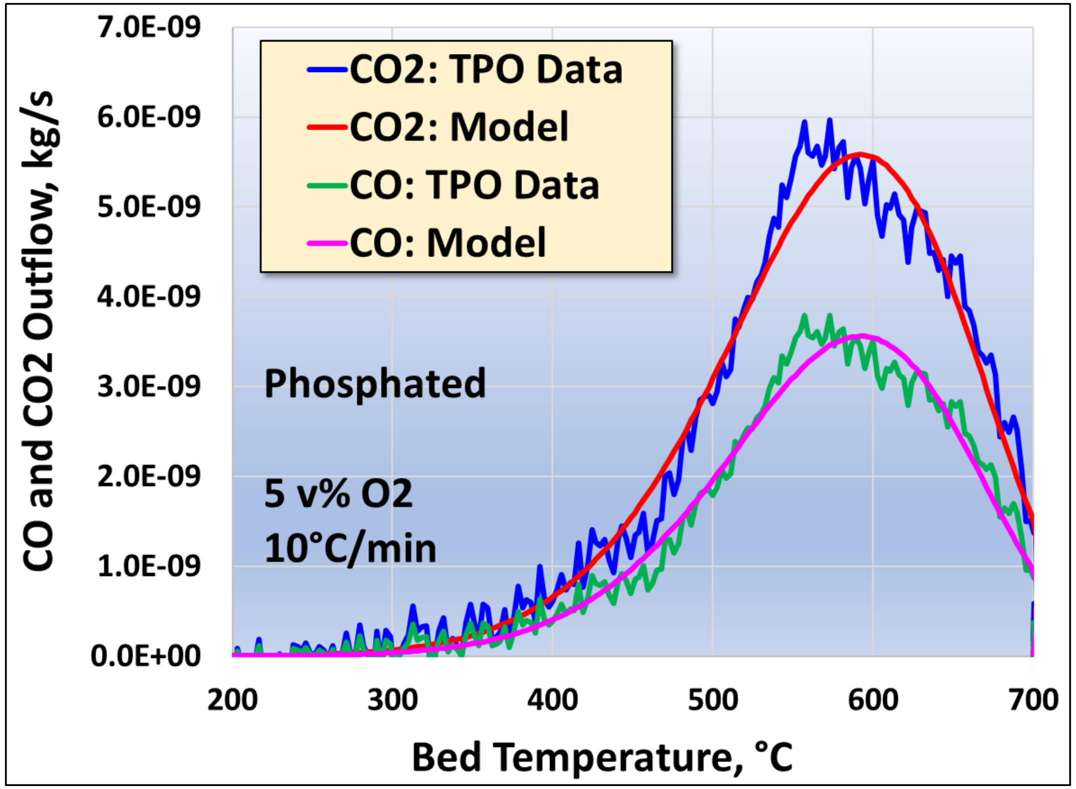




Effect of Phosphation

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

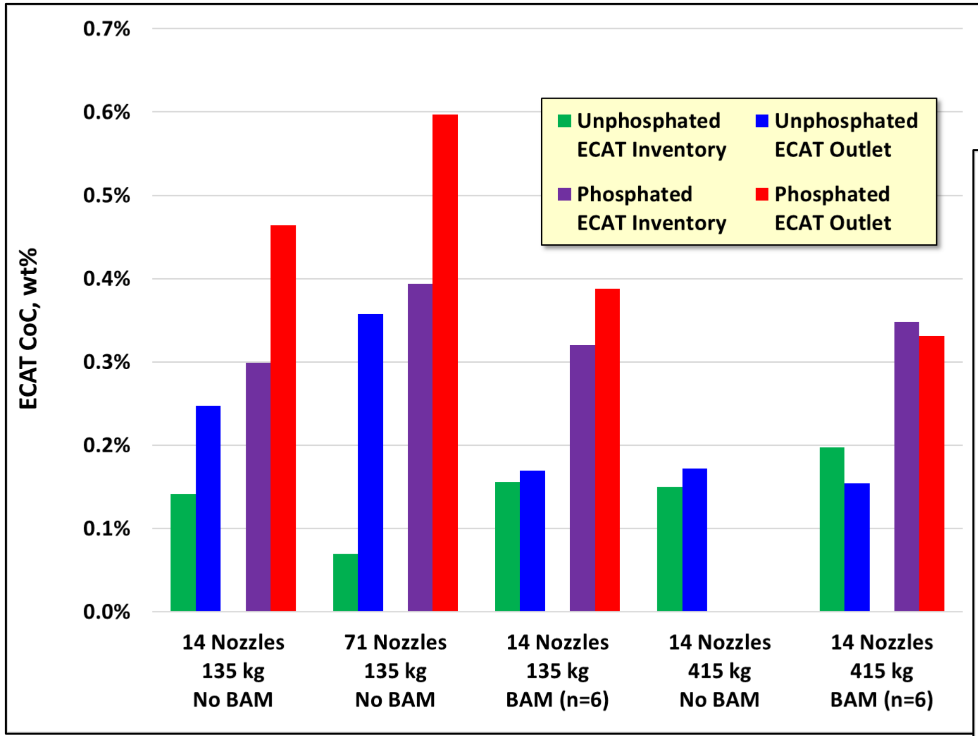


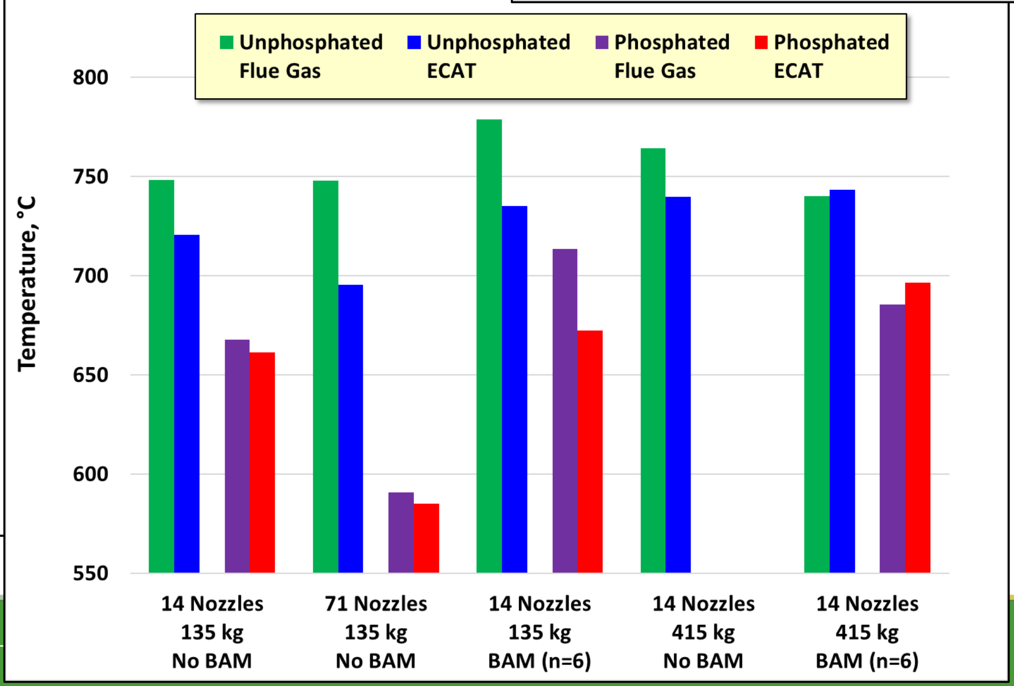


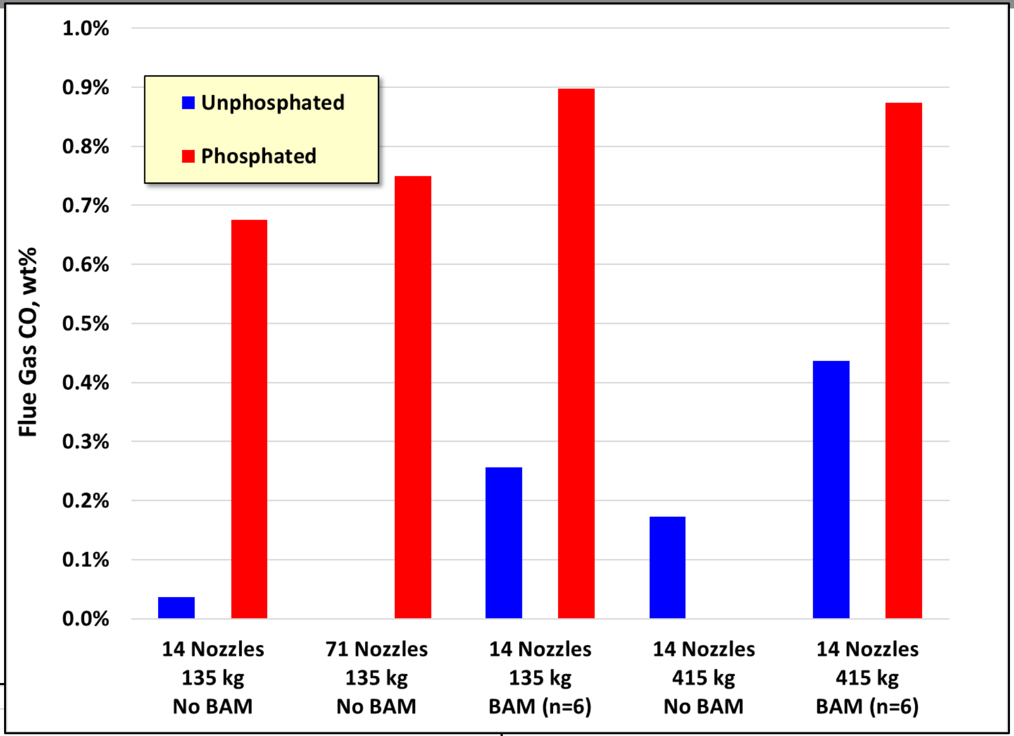
Second Study

Phophated vs Unphosphated

DCAT Temperature = 580°C   Airflow = Stoichiometric







Conclusions

- **Computational models based on bio-coked zeolite catalyst for Catalytic Fast Pyrolysis indicate catalyst regeneration in Fluid Catalytic Cracker type reactors is feasible and manageable with proper operating parameters**
  - **Unphosphated catalyst**
    - Initial results indicate that excessively high 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)
    - At demo scale (5 mTPD) risk of afterburn is low
      - Need to consider commercial scale
  - **Phosphated catalyst**
    - Combustion behavior is different! Higher CO/CO2 ratio, lower regenerator temperatures, higher ECAT CoC → Needs higher DCAT temperature
    - More TPO data needed at other O2 levels
  - **Segregating Flow**
    - Segregating flow is very important to regenerator performance
    - Data needed!