COMSOL Model for Optimizing Regeneration of CFP Catalyst in Packed-Bed Reactors

COMSOL Meeting 2019

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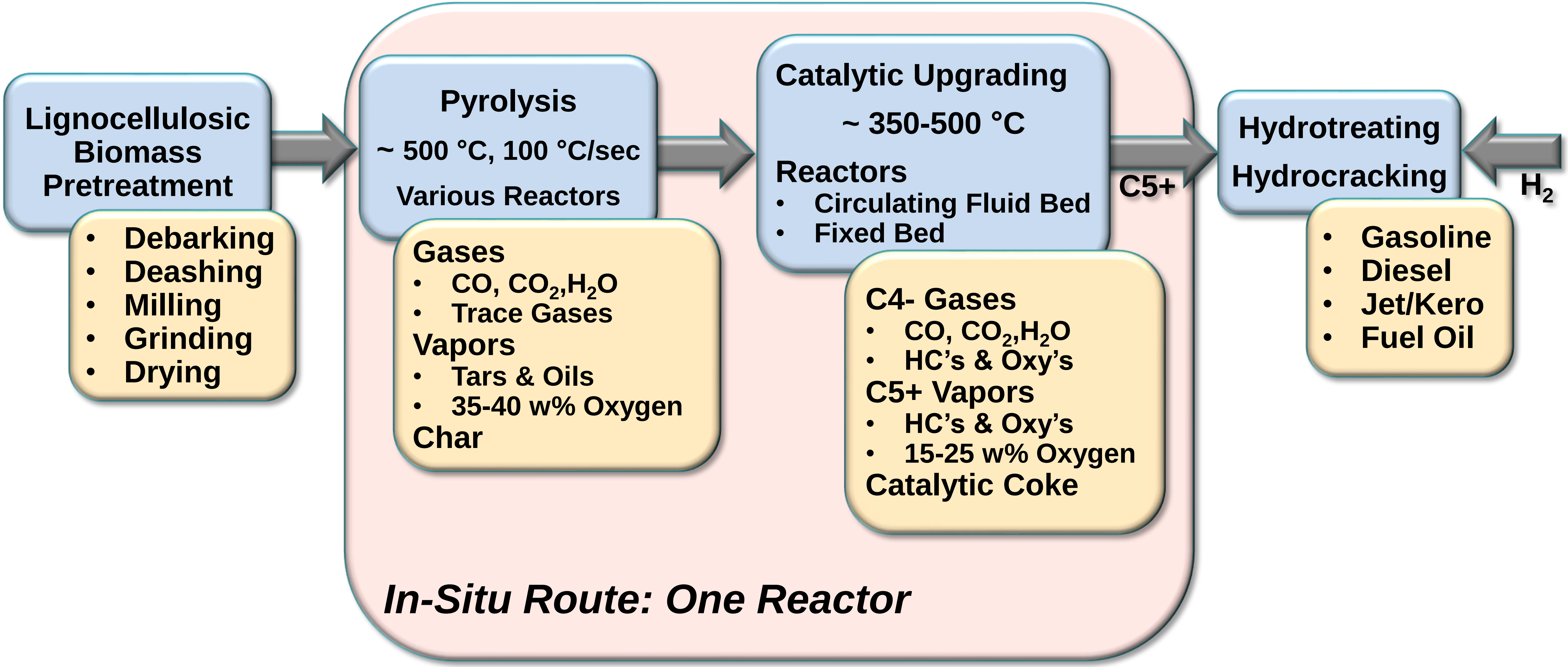
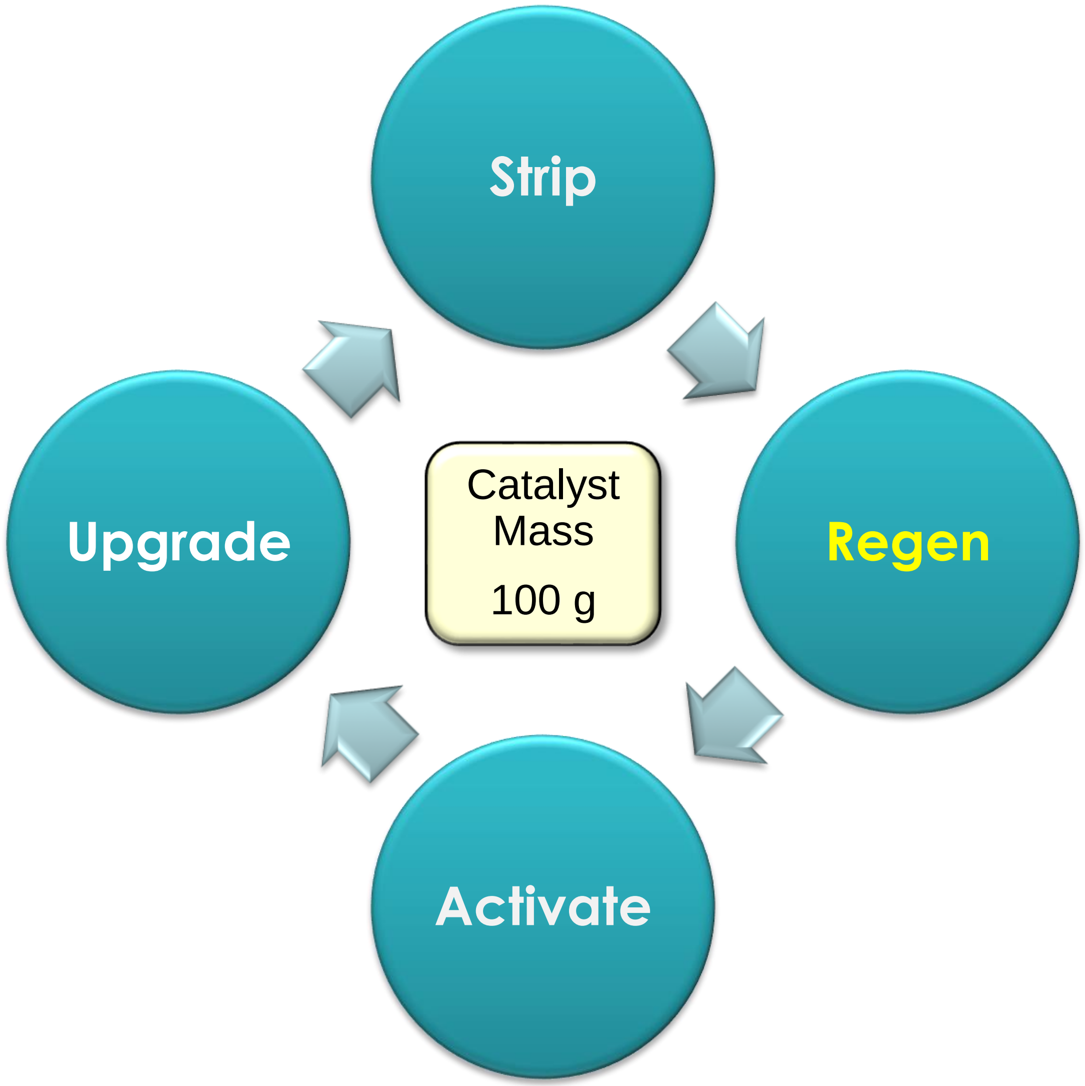
Catalytic Fast Pyrolysis (CFP)

Ex-situ Route



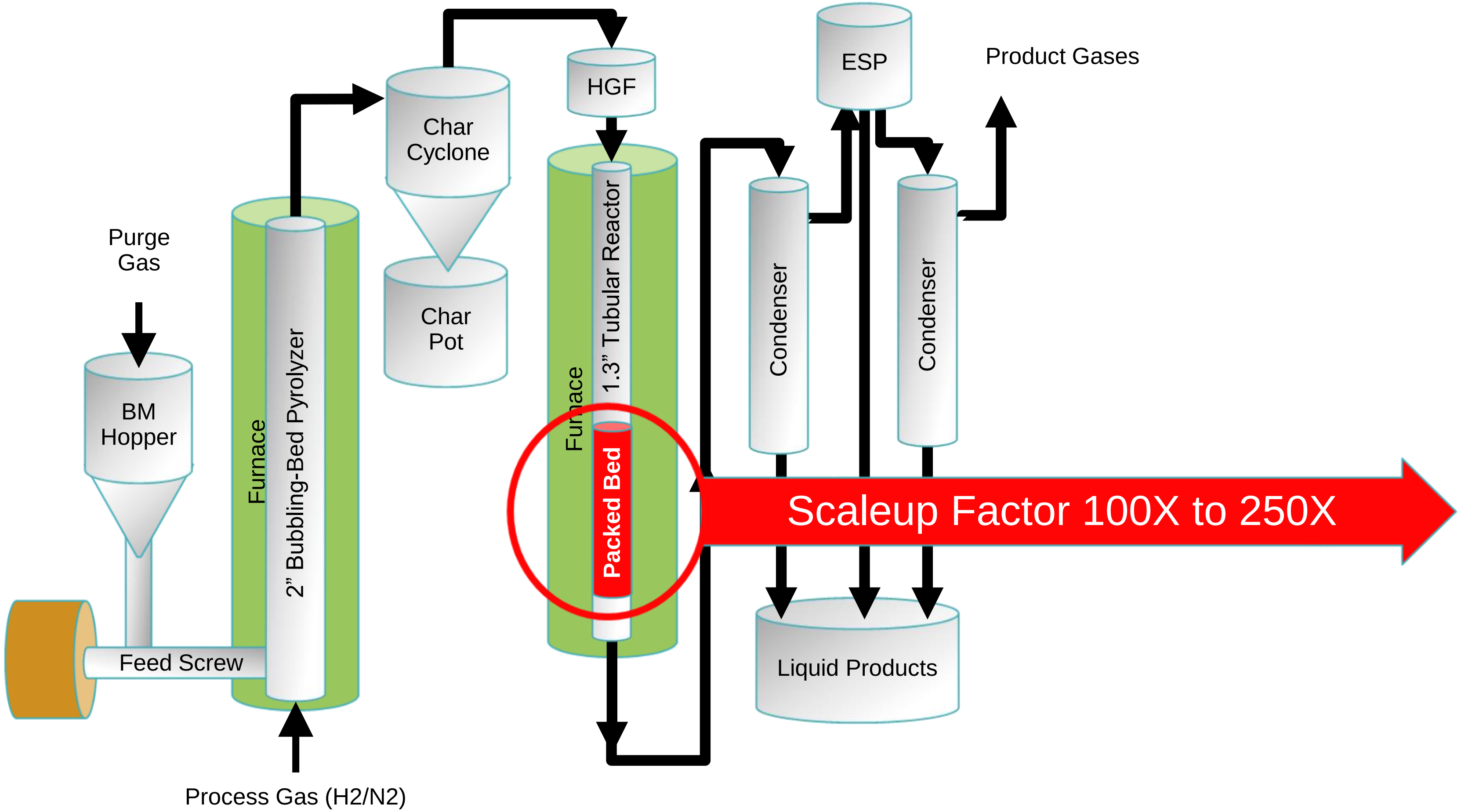
"2FBR" Packed-Bed Reactor (PBR): Typical Operating Conditions

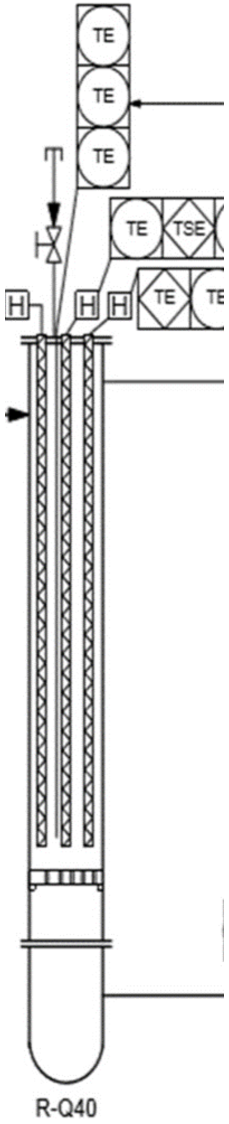
Upgrading	
Biomass Feedrate, g/hr	150
Char, wt%	15
Pressure, Pa	110,000
Temperature, °C	450
H2 Flowrate, SLPM	13.5
N2 Flowrate, SLPM	2.4
WHSV, hr^{-1}	1.35
Duration, hr	2-8

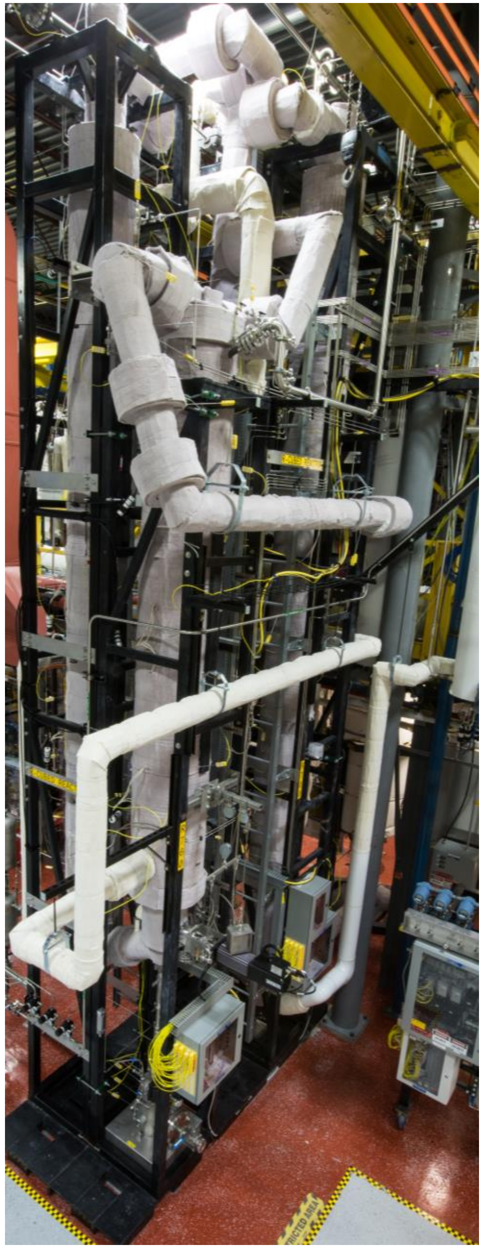


Regeneration	
Bed Inlet Temp, °C	380
Bed Outlet Temp, °C	450
N2 Flowrate, SLPM	14.0
Air Flowrate, SLPM	0.4-0.7
Duration, hr	1-6

Scaling Up from 2FBR to TCPDU

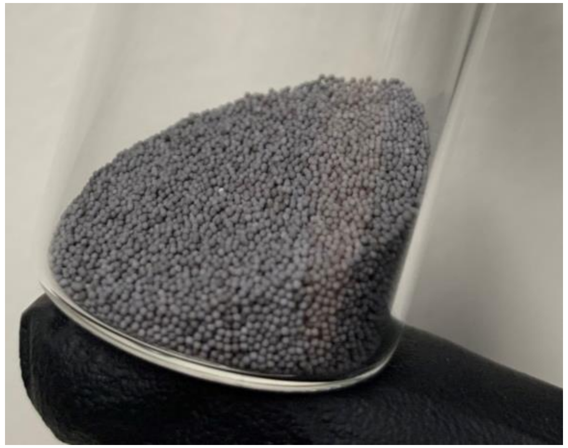




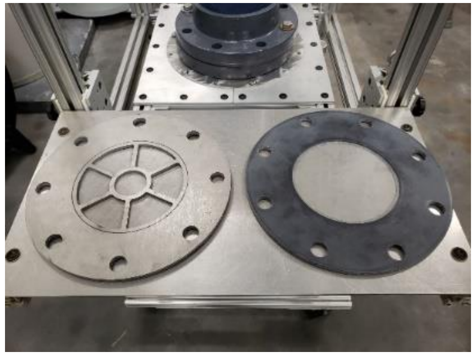


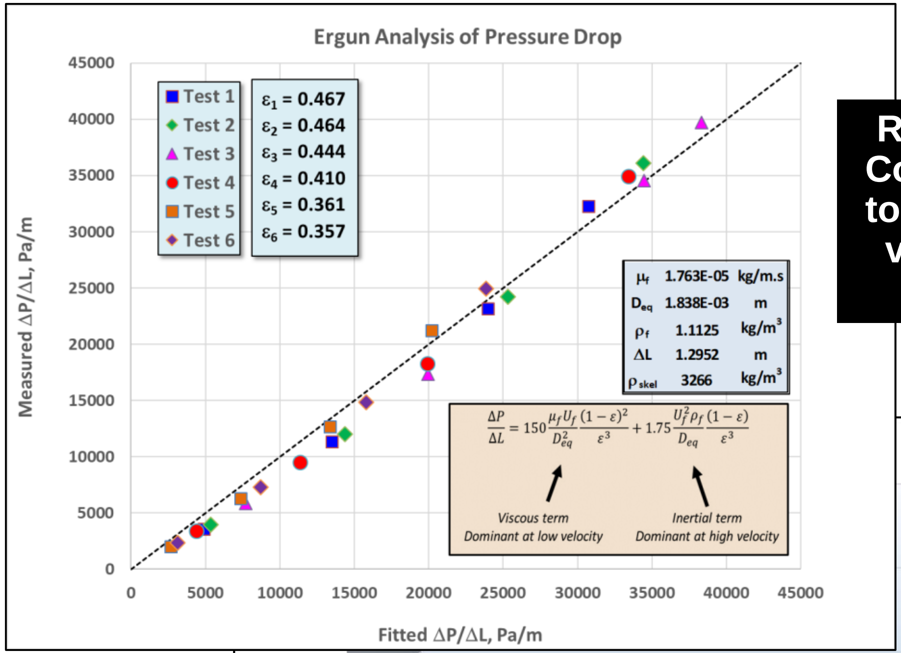
Pt/TiO_2 Catalysts

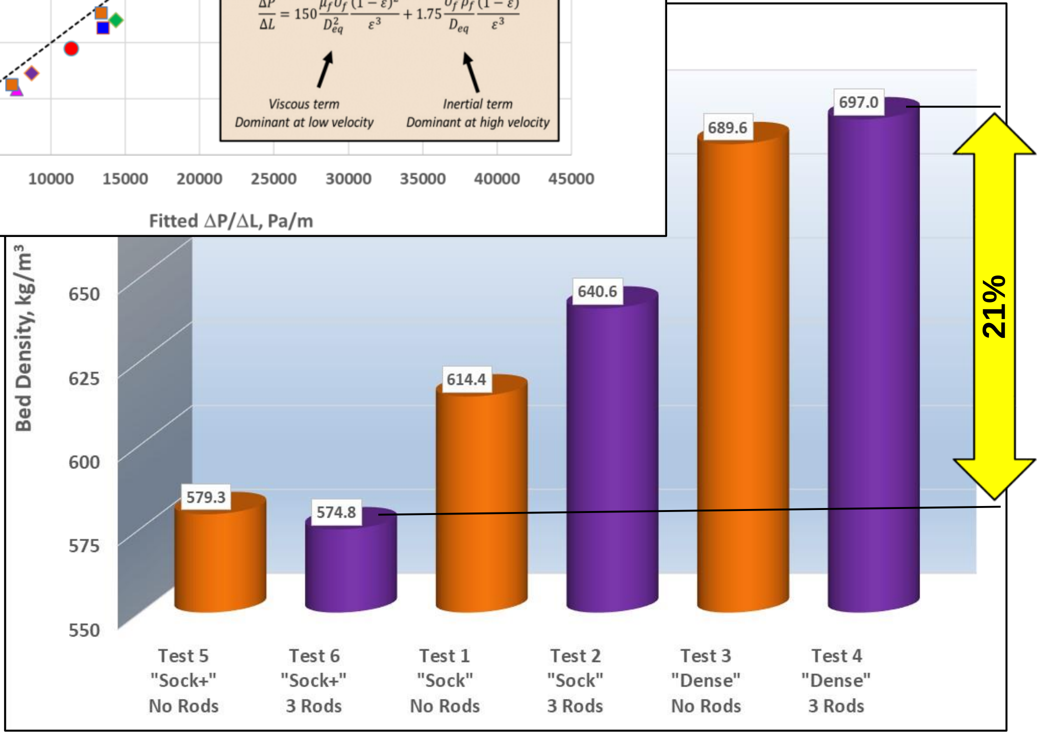
Catalyst	A	B
Shape	Cylinder	Sphere
D_{avg}, mm	1.65	0.5
L_{avg}, mm	4.5	-
Bulk Density, kg/m^3	1050	900
Loading Factor	0.9	1
Bed Depth, cm	13.36	14.02
Bed Voidage	0.41	0.44
Est. Particle Count	6,500	950,000
Ergun ΔP, Pa	602	6,641
Performance @ Biomass:Catalyst = 3, 450°C		
Oxygen in Oil, wt%db	19%	11%



Catalyst Load Testing at National Energy Technology Lab (NETL)







Range of Densities Compares Very Well to Commercial Sock vs Dense Loading Methods

Model Deliverables

1. Regeneration
   - **Temperature distribution during coke combustion is critical information**
     - Large rapid swings in temperature can physically damage catalysts
       - ➢ Particle confinement stress

$$\sigma_{pcs} = E_{bm}\alpha_{tc}\Delta T$$

- E_{bm} = bulk modulus of compressibility, Pa
- α_{tc} = thermal expansion coefficient, K^{-1}

       - ➢ Variations in heating rates
     - High temperatures can accelerate deactivation (Ostwald ripening)

CURRENT

FOCUS

2. Upgrading
   - Flow (mal)distribution
   - Catalytic performance
   - Deactivation by coke & contaminants
3. Full cycle
   - Optimize individual steps and overall cycle
   - Predict long term performance
   - Scale-up to commercial scale

COMSOL Model Elements

Geometry
- Full 3D *OR* 2D Axisymmetric
- Mesh

Solvers
- Time Depend. BDF
  - Rel. Tolerance?
- Segregated vs. Fully Coupled
- Direct vs. Iterative

Heat Transfer Module
- N2 & Air Thermal Properties
- Heat Source
- Reactor Thermal Properties
- Particle Thermal Properties

Laminar Flow Module
- Bulk Convection N2 & Air Properties
- Porous Bed Kozeney-Carman Permeability
- Free Convection Furnace Cavities

Transport of Dilute Species Module

Reactive Pellet Bed
- Reactions
- Heat Release
- Intraparticle Diffusion D_p = ? m^2/s
- Film Resistance?
- Discretization of Xtra Dim.
- Particle Properties
  - Surface Area = ? m^2/g
  - Pore Volume = ? cm^3/g
  - Skeletal Density = ? kg/m^3
  - Therm Conduct = ? W/m.K
  - Heat Capacity = ? J/kg.K
- Bed Properties
  - Particle Shape & Dimensions
  - Bed Porosity = ?

Bulk Diffusion
D = ? m^2/s

Chemistry Module

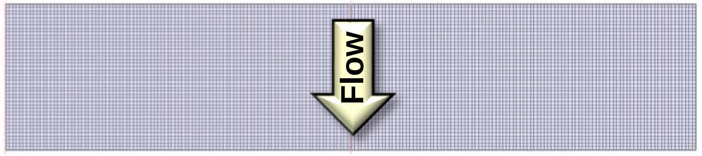
Coke Combustion
- $C + O_2 \rightarrow CO_2$, $\Delta H = 3.94\times10^5$ J/mol
- $H_2 + ½O_2 \rightarrow H_2O$, $\Delta H = 2.40\times10^5$ J/mol
- Surface Species *OR* Nondiffusive Volume Species
- **E_a = ? J/mol**
  A_f = ? $m^3/mol.s$

N2 as Solvent

Kinetic Constants for Petroleum Cokes

Coke Type	E_a, J/mol	A_f, s^{-1}
Soft	60,964	598
Medium	72,680	223
Hard	130,798	71,870

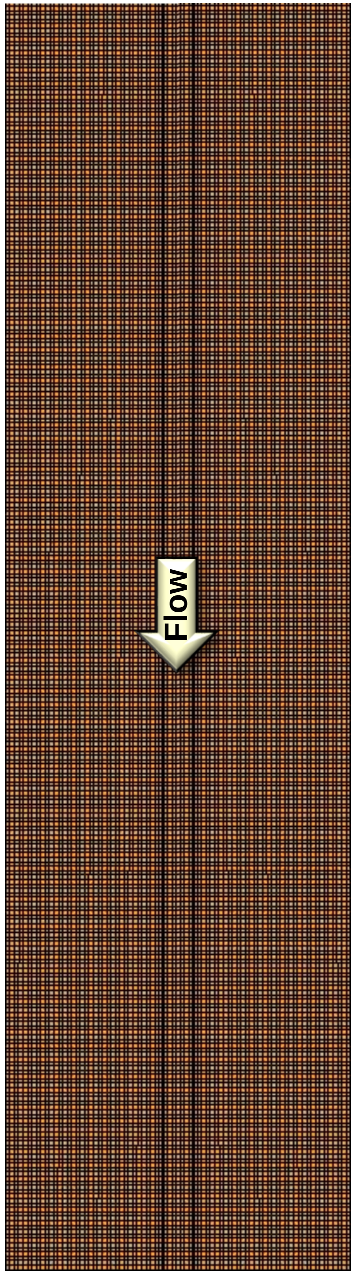
Different Versions for Different Needs

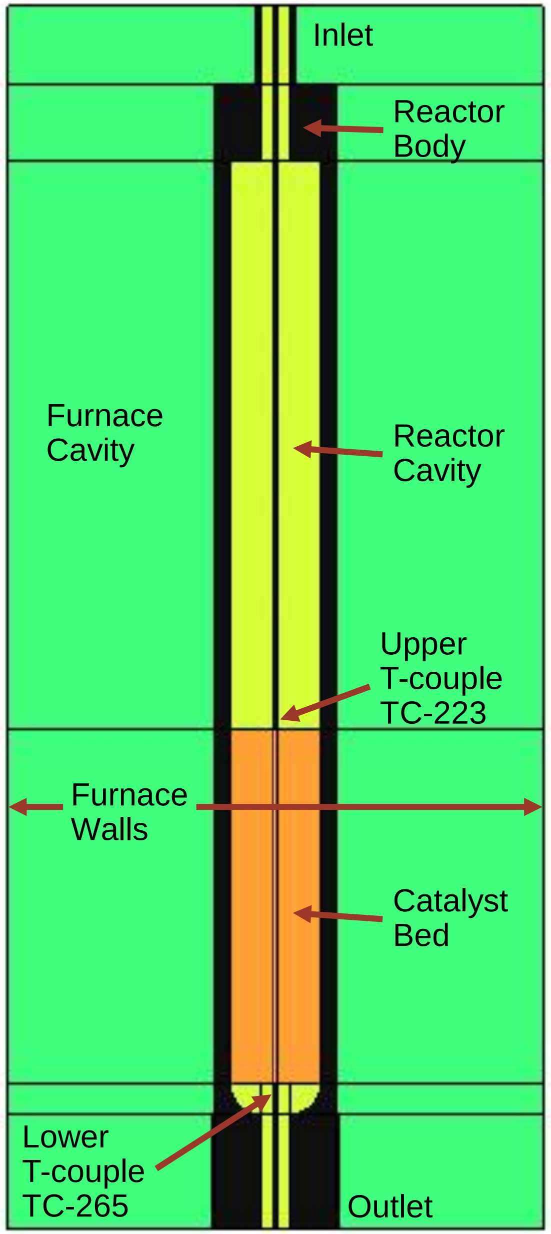


Bed Slice: 1-5 g Catalyst
Discretization Studies

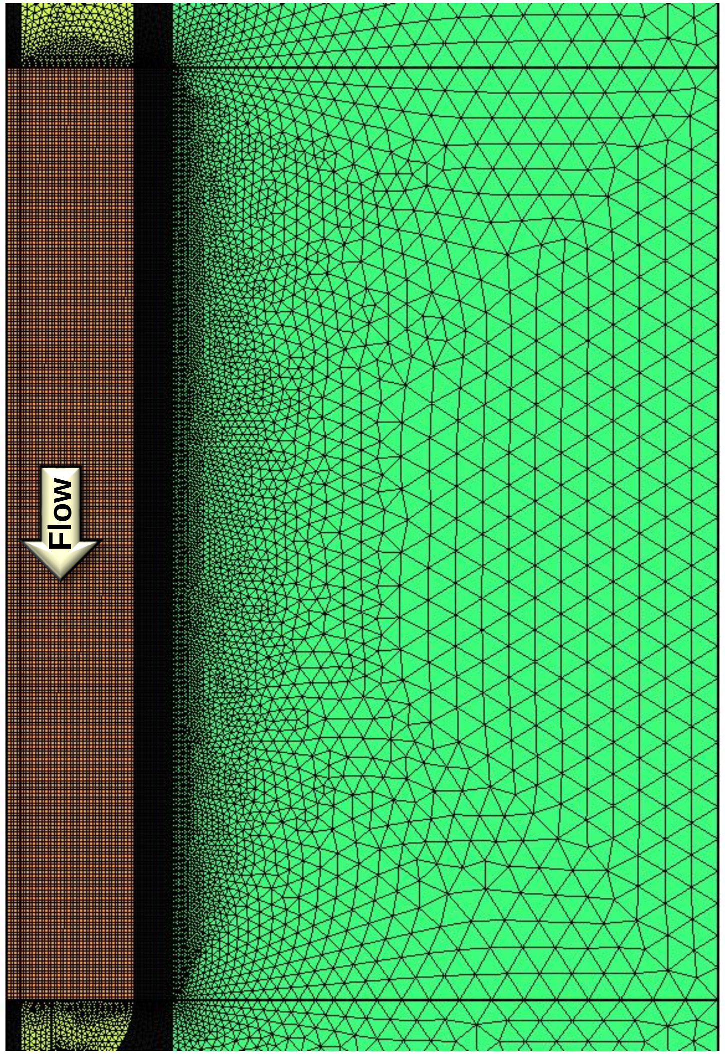
2D Axisymmetric Models
Also 3D Models
21 Versions to Date

Full Bed: 100 g Catalyst
Initial Validation Studies



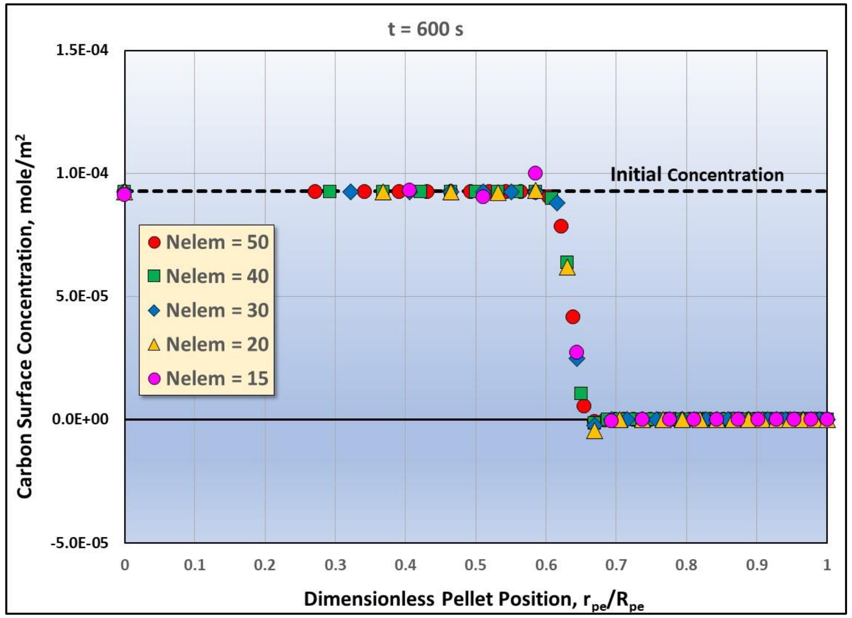


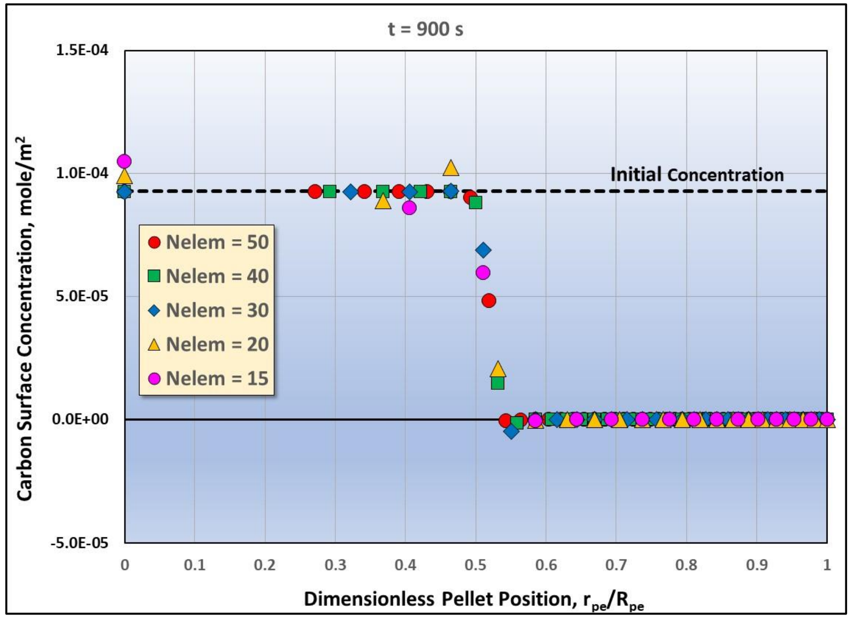
Complete System
Full Validation Studies



Oak Ridge National Laboratory

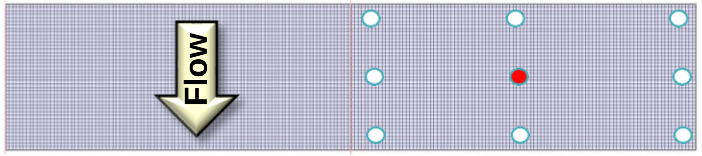
Discretization of Extra Dimension in Reactive Pellet Bed Model





atxd2(r,z,tds.rpb1.cpes_cC_surf)

Bed Slice



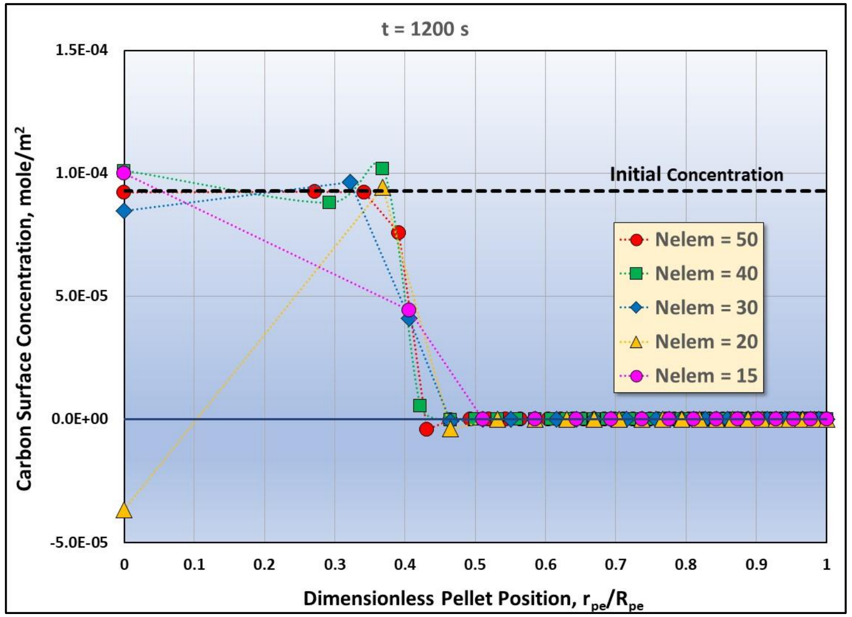
1,050 cells λ_{avg} = 1.32 mm

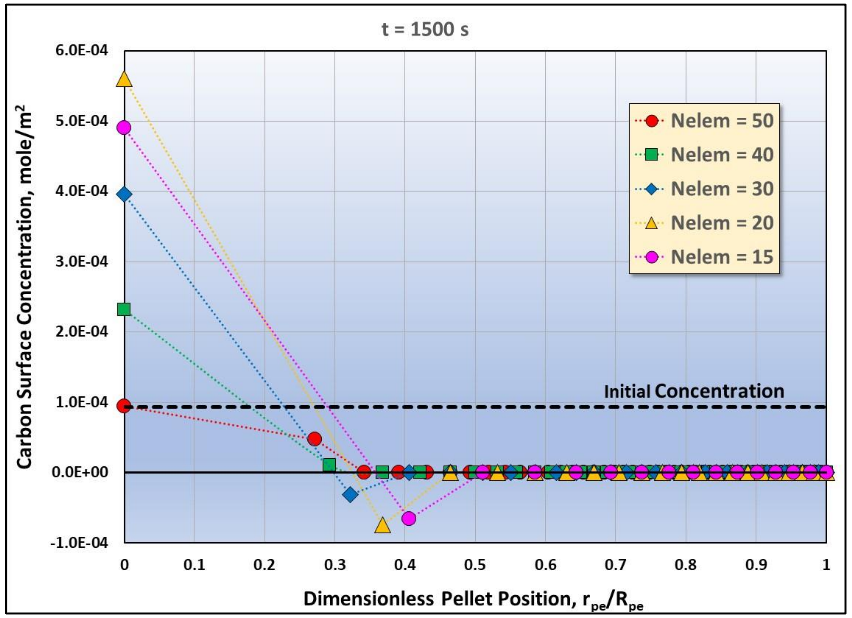
Catalyst A

$E_a = 5 \times 10^4$ J/mol

$A_f = 5 \times 10^4$ m³/mol.s

$D_p = 1 \times 10^{-5}$ m²/s





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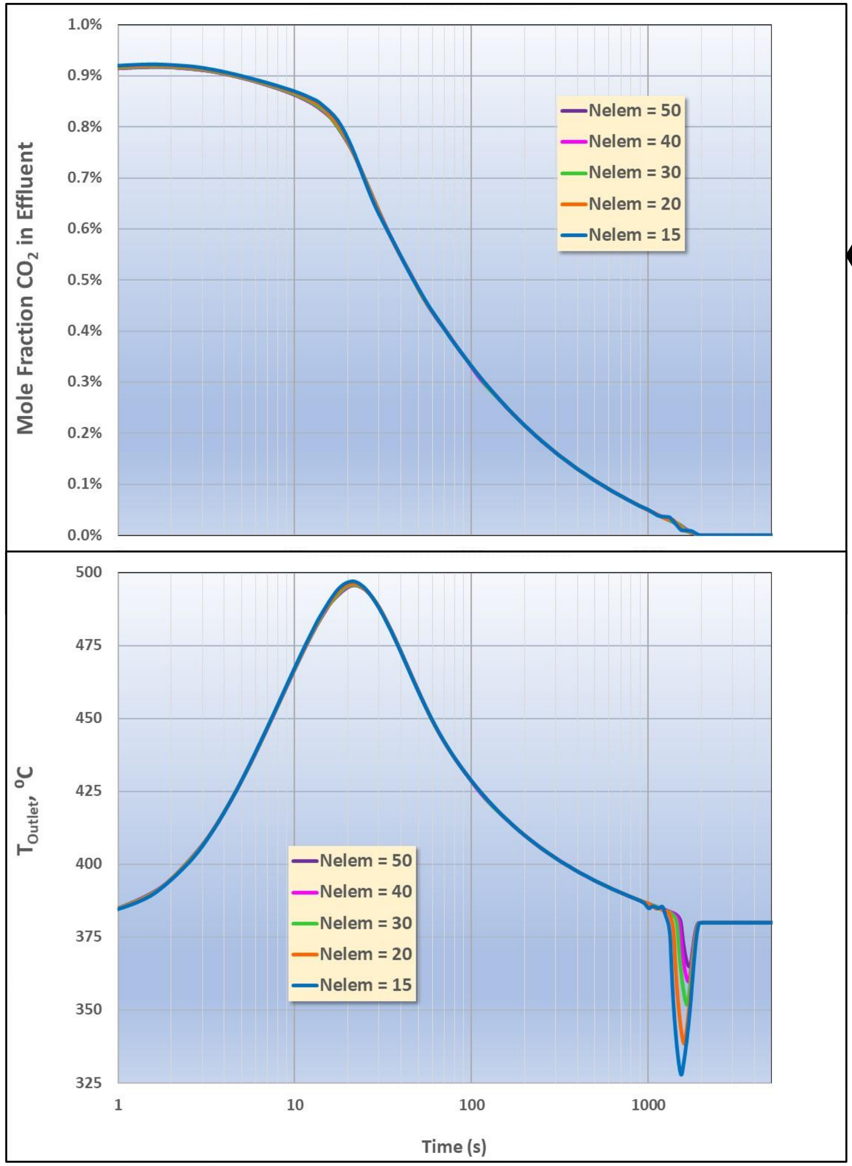


Catalyst A

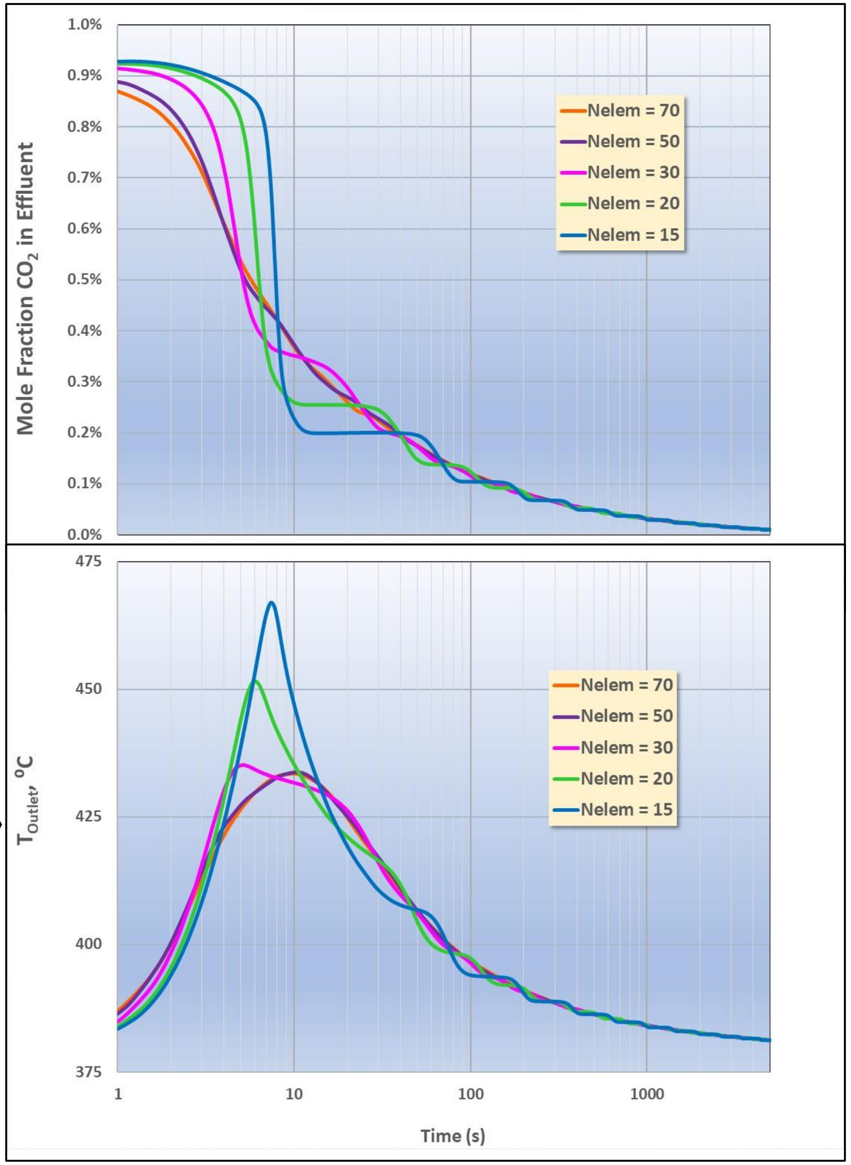
E_a = 5x10^4 J/mol

A_f = 5x10^4 m^3/mol.s

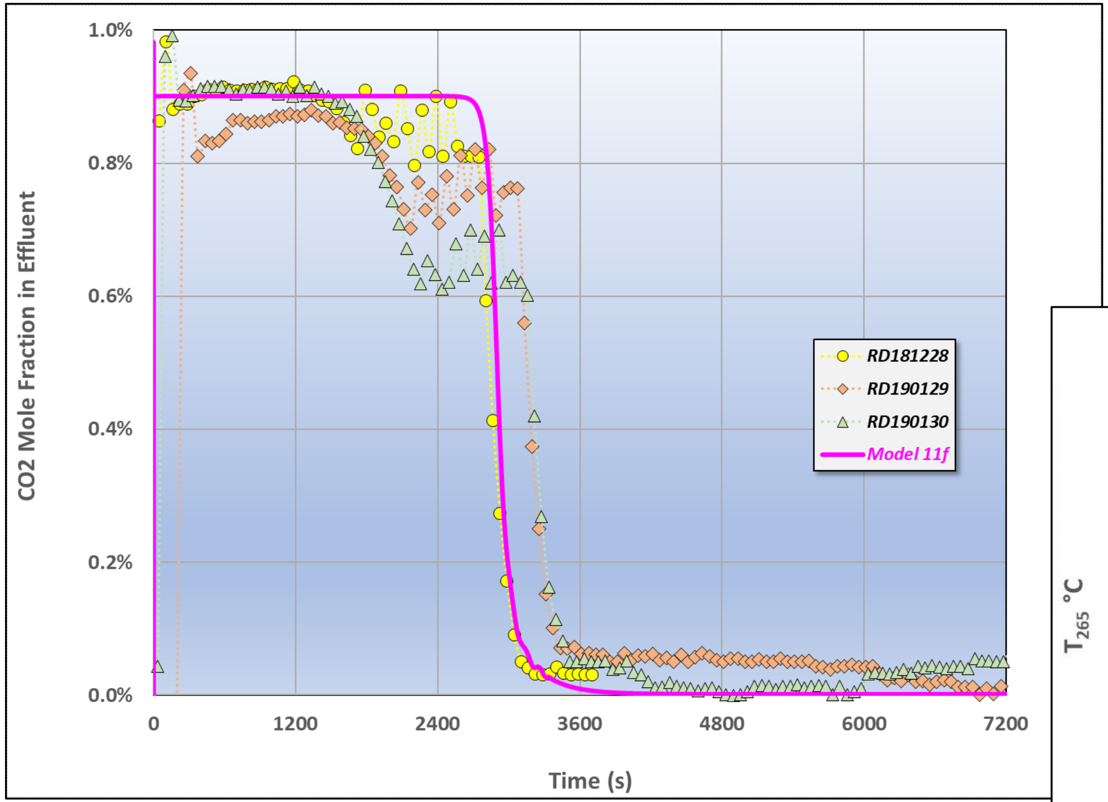
D_p = 1x10^{-5} m^2/s

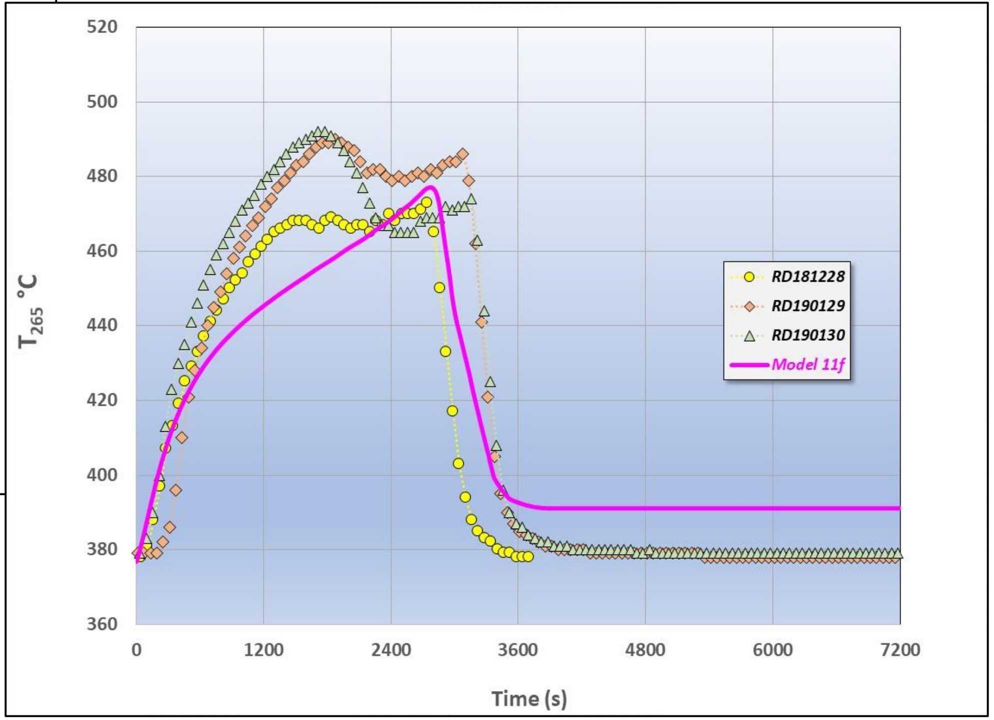
A_f = 2x10^5 m^3/mol.s

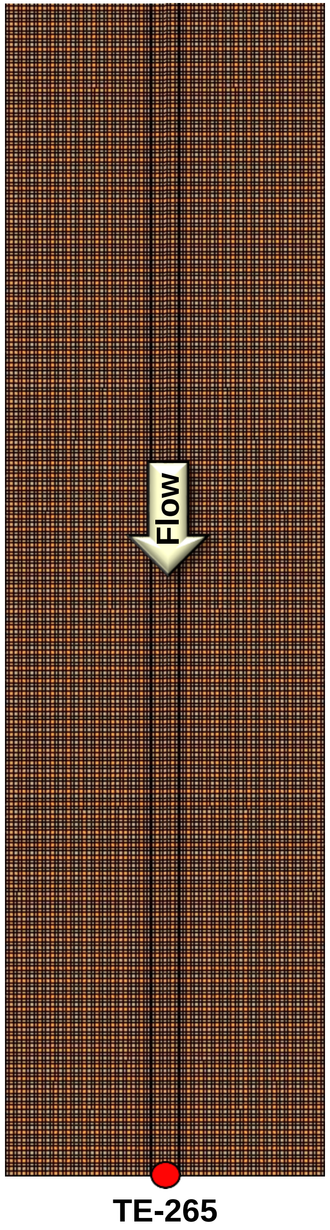
D_p = 1x10^{-6} m^2/s



Partial Validation with Full Bed Model





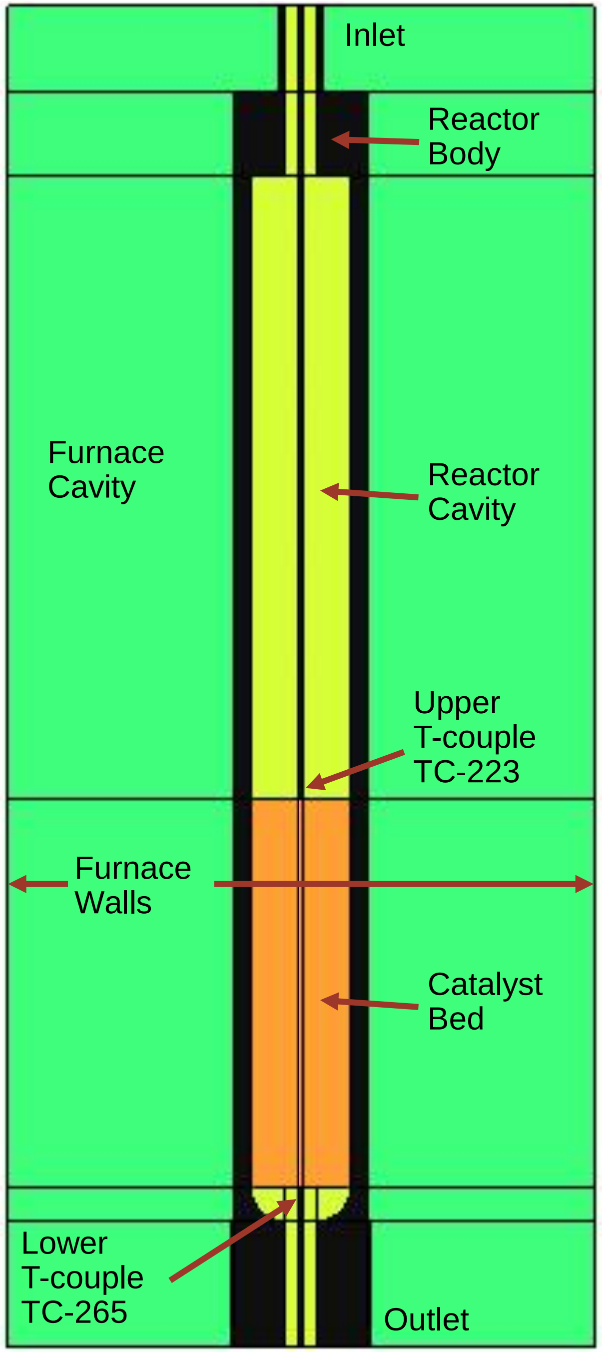


Catalyst A

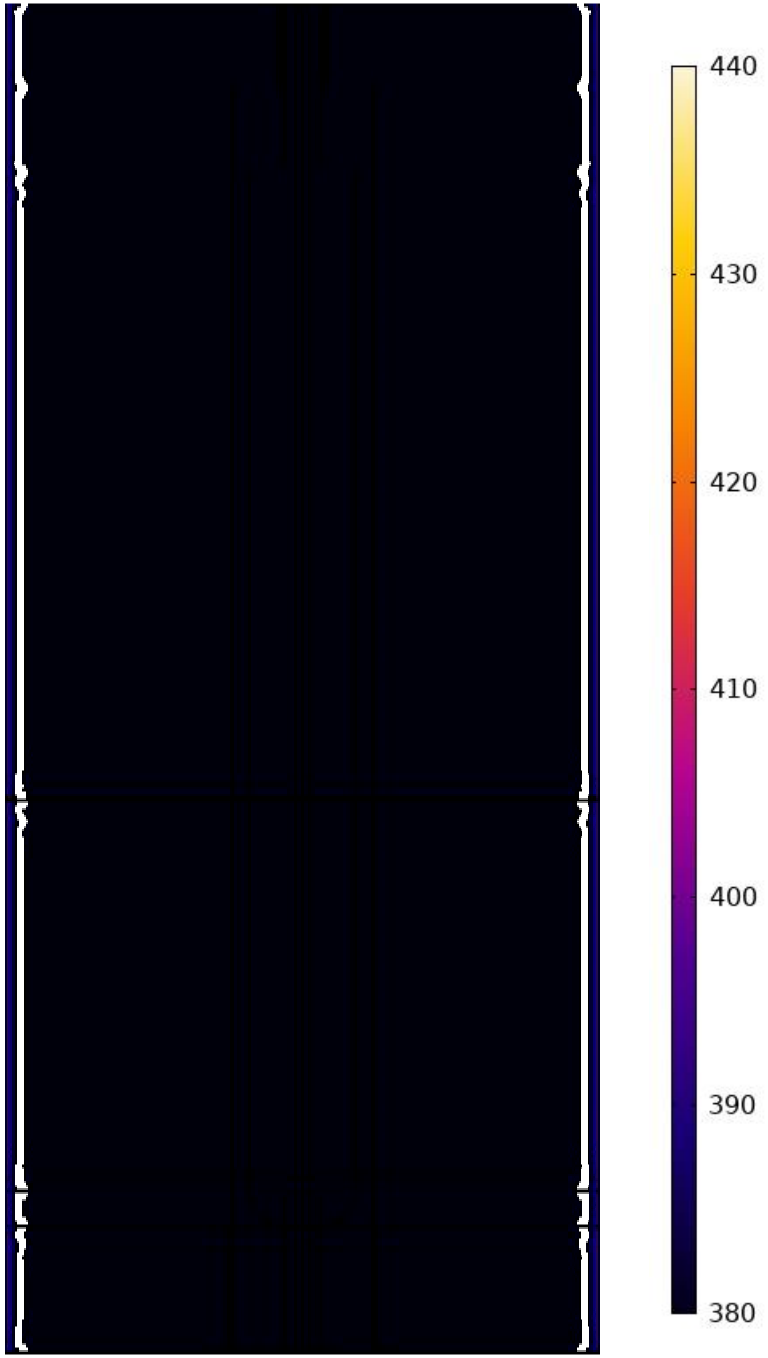
$E_a = 5x10^4$ J/mol

$A_f = 1x10^5$ m^3/mol.s

$D_p = 1x10^{-5}$ m^2/s



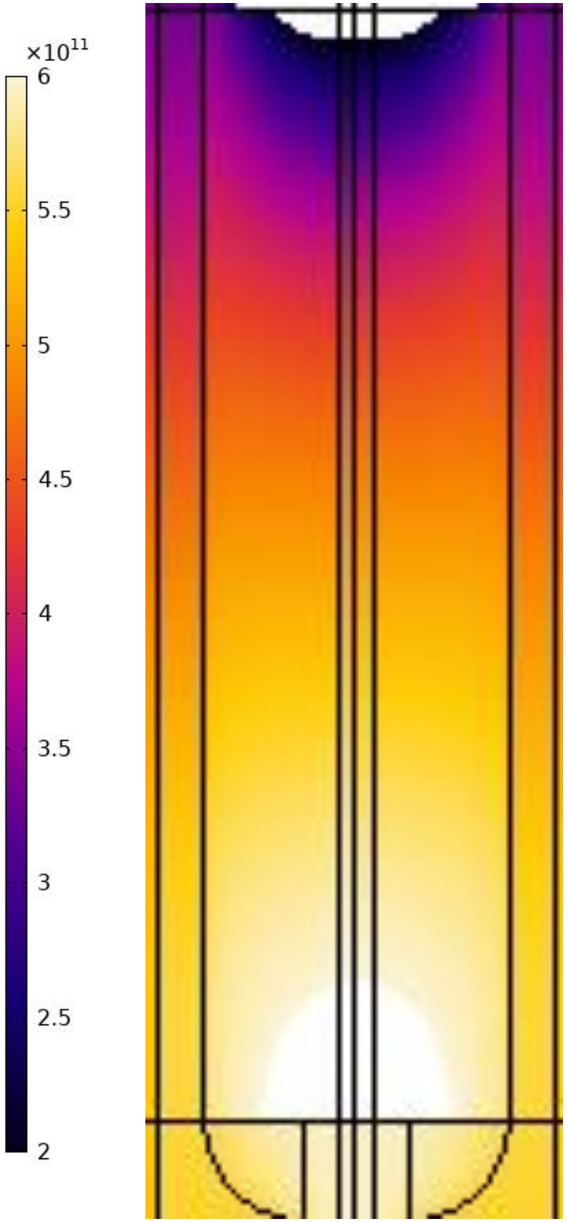
Complete System Model



Cumulative Particle Confinement Stress – One Regeneration Cycle

σ_{pcs}

Pa.s



$$\sigma_{pcs} = \int_0^{t_{regen}} E_{bm} * \alpha_{tc} * (T - T_{init})\,\partial t$$

Anatase TiO_2

$E_{bm} = 300 \times 10^9$ Pa

$\alpha_{tc} = 12 \times 10^{-6}$ K^{-1}

Summary

1. COMSOL has been used to build a computational model of a packed bed CFP reactor in regeneration mode. A key ingredient is the Reactive Pellet Bed (RPB)

2. Coke combustion in this system exhibits classical "cigar burn" behavior, and the kinetic model is a stiff system of equations. Non-physical results, mass closure errors and rapid divergence can result from excessively coarse discretization
   - It is important to thoroughly test the effects of:
     - discretization in the pellet extra dimension in RPB, and
     - meshing in the bed

     for each combination of:
     - intrapellet diffusion rate
     - reaction rate
     - pellet geometry, and
     - bed geometry
   - Time stepping relative tolerance is also important to numerical stability. Typical value is 0.001

3. The model is still being tuned at 100 gram scale with cylindrical catalyst

4. Extensions of the model to 0.5 mm spherical catalyst and 10+ kg scale are in progress

Acknowledgements

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