

ARTICLE

Electronic Supplemental Information (ESI)

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Predicting thermal excursions during *in-situ* oxidative regeneration of packed bed catalytic fast pyrolysis catalyst

Bruce D. Adkins,^{a*} Zach Mills,^a James Parks II,^a M. Brennan Pecha,^b Peter N. Ciesielski,^b Kristiina Iisa,^b Calvin Mukarakate,^b David J. Robichaud,^b Kristin Smith,^b Katherine Gaston,^b Michael B. Griffin^b and Joshua A. Schaidle^b

GradientCheck Reports

Tables S1 and S2 show the full reports from the GradientCheck web tool for the nominal 2FBR and TCPDU cases summarized in Tables 3 and 4 in the main body of the paper. While this analysis is useful, it is not strictly applicable for the reasons mentioned before:

1. Carbon in coke is a fixed, non-diffusing reactant.
2. The regeneration process is transient, not steady state.
3. For most practical combustion rates, the reaction is confined to a combustion zone which is generally much smaller than the entire reactor.

2FBR Modelled Temperatures at the Outlet Face Center Point

Figure S1 shows the modelled 2FBR temperature profiles using the center point of the outlet face, for the four effective conductivities. The profiles based on the lowest, most realistic values of 0.25 W/(m.K) and 0.675 W/(m.K) do not match measured temperatures with any value of wall heat transfer coefficient. The 1.725 W/(m.K) profile does not match the shape of the measured profile very well. While the highest (bulk) value of 11.9 W/(m.K) gives a reasonable match, a very low wall heat transfer coefficient of 30 W/(m².K) is required. While not definitive, these results point to the average modelled outlet temperature as the better choice for this study.

Tube Wall Heat Flow Profiles for TCPDU Parametric Sweep

For reference, Figure S2 shows the tube wall heat flow profiles corresponding to the outlet temperature curves in Figure 14. The spread between the heat transfer parameter pairs increases with reduced N₂ flow and increased cooling air flow. Integrating these curves over the entire regeneration produced the values regressed in Figure 15.

^a Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830

^b National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO 80401

* Corresponding author email adkinsbd@ornl.gov

Table S1. GradientCheck analysis of 2FBR-PBR catalyst bed and operating conditions

Gradient/ (GradientCheck) for Heterogeneous Catalysts

By using this tool you agree to the terms of the license.

2FBR at 0.55% O₂ like 27r.json

Reaction Phase:

Gas Phase

Temperature (T₀ & T_{amb}):

663 / K

Pressure (P):

0.965 / bar

Reactor Radius (R_p):

0.0174 / m

Bed Length (L_{bed}):

0.1168 / m

Catalyst Particle Shape:

Spheres

Particle Radius (R_p):

2.545e-4 / m

Observed Reaction Rate (r_{obs}):

6.42e-4 / moles of A × kg cat⁻¹ × s⁻¹

Enthalpy of Reaction (ΔH_{rxn}):

3.94e5 / J × mole⁻¹

Reaction Order (n):

1

Activation Energy (E_{app}):

5e4 / J × mole⁻¹

Conversion (X_R):

1 / unitless (0 to 1)

Catalyst Bulk Density (ρ_{cat}):

900 / kg × m⁻³ (usually 500-1500)

Catalyst Void Fraction (ε):

0.437 / (0 to 1) (often 0.35-0.45 (default 0.4))

Catalyst Thermal Conductivity (k_p):

0.25 / W × m⁻¹ × K⁻¹ (often 0.13-0.25)

Catalyst Surface Area (S_{cat}):

54 / m² × g⁻¹

Catalyst Pore Volume (V_{por}):

0.37e-6 / m³ × g⁻¹

Catalyst Pore Tortuosity (τ):

4 / unitless (often 3-7 for porous catalysts)

Number of Reactants:

One

Main Reactant A:

0.0055

Product B:

0

Diluent C:

0.9945

Number of Products:

One

Inlet Mole Fractions:

0.0055

Fluid Viscosity (μ):

3.2e-5 / kg × m⁻¹ × s⁻¹

Heat Capacity (C_p):

1100 / J × kg⁻¹ × K⁻¹

Thermal Conductivity (k_f):

5e-2 / W × m⁻¹ × K⁻¹

Diffusion Volume (Σ_v):

12.2 / g × mol⁻¹

Molecular Weight (MW):

32

Notes:

Advanced Option

Output Filename: 2FBR at 0.55% O₂ like 27r

json

Calculated Properties

Reactant A:

0.544

Reactant B:

0.476

Diluent C:

0.965

Ideal Gas Density:

0.544

mol × m⁻³

Inlet Concentration of A:

0.965

mol × m⁻³

Validation Tests

Is the observed reaction rate realistic?

yes

Do the mole fractions add to one?

yes

Is the void fraction within typical range?

yes

Is the particle conductivity within typical range?

yes

Is the porosity within typical range?

yes

Is the tortuosity within typical range?

yes

Is the Prandtl number within typical range for a gas?

yes

Is the Reynolds number within the valid range for j-factor correlations?

yes

Are multiple steady states possible?

no

Does external diffusion limit reaction rate?

no

Does external diffusion control reaction rate?

no

Is the external temperature gradient significant?

no

Is the internal temperature gradient significant?

no

Does pore diffusion limit reaction rate?

yes

Does pore diffusion strongly affect reaction rate?

yes

ΔP > 0.2P

no

Does axial dispersion have a large effect upon rate?

yes

Does axial dispersion have a large effect upon rate?

yes

Do broad radial velocity profiles negatively effect the reactant RTD?

no

Does a radial interparticle heat transport limitation indicate a nonisothermal reactor?

yes

Gradient Plots

Plot Gradient

Temperature / K

Concentration of A / mol × m⁻³

Position in Catalyst Normalized to Radius / nondimensional

2 | J. Name., 2012, 00, 1-3

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Table S2. GradientCheck analysis of conceptual TCPD U-PBR catalyst bed (with no cooling tubes) and operating conditions

Please

GradientCheck (GradientCheck) for Heterogeneous Catalysis

By using this tool you agree to the terms of the license.

Inputs Section

Open JSON Input File TCPDU at 0.6% O₂ like Bu-jon

Reaction Phase:

Temperature (T₀ & T_{ad}): K

Pressure (P): bar

Reactor Radius (R_r): m [m - Accepts scientific notation e.g. 1e-3]

Bed Length (L_b): m

Catalyst Particle Shape:

Particle Radius (R_p): m

Observed Reaction Rate (r_{obs}): mol/m³s [moles of A × kg cat⁻¹ × s⁻¹]

Enthalpy of Reaction (ΔH_{rxn}): J/mol

Reaction Order (n):

Activation Energy (E_{app}): J/mol

Conversion (X_r):

Catalyst Bulk Density (ρ_{cat}): kg/m³ [usually 500-1500]

Catalyst Void Fraction (ε): [(0 to 1) [often 0.35-0.45 (default 0.41)]]

Catalyst Thermal Conductivity (k_p): W/m·K [W × m⁻¹ × K⁻¹ [often 0.13-0.25]]

Catalyst Surface Area (S_{cat}): m²/g [m² × g⁻¹]

Catalyst Pore Volume (V_{por}): m³/g [m³ × g⁻¹]

Catalyst Pore Tortuosity (τ):

Number of Reactants:

Reactant A	Product B	Diluent C
Inlet Mole Fractions: 0.0055	0	0.9945
Fluid Viscosity (μ): 3.2e-5	3.2e-5	3.2e-5
Heat Capacity (C _p): 1100	1100	1100
Thermal Conductivity (k _f): 5e-2	5e-2	5e-2
Diffusion Volume (V _{diff}): 12.2	9	9
Molecular Weight (MW): 32	28	28

Notes:

Validation Tests

Test	Result
Is the observed reaction rate realistic? (r _{obs} < r _{max})	yes
Do the mole fractions add to one? (Σ y _i = 1)	yes
Is the void fraction within typical range? (0.25 < ε < 0.55)	yes
Is the particle conductivity within typical range? (0.1 < k _p < 1)	yes
Is the porosity within typical range? (ε _p < 0.7)	yes
Is the tortuosity within typical range? (2 < τ < 6)	yes
Is the Péclet number within the valid range? (0.5 < Pe < 1.5)	yes
Is the Reynolds number within the valid range? (Re _{cat} > 0.01 or Re _{cat} > 1)	yes
Are multiple steady states possible? (β > 0.3)	no
Does external diffusion limit reaction rate? (C _p - C _p /C _p > 5%)	no
Does internal diffusion limit reaction rate? (C _p - C _p /C _p > 50%)	no
Is the external temperature gradient significant? (T _{fs} - T _{cd} > 1 K)	no
Is the internal temperature gradient significant? (T _{fs} - T _{cd} > 1 K)	yes
Does pore diffusion limit reaction rate? (η < 0.5)	yes
Does pore diffusion strongly affect reaction rate? (ΔP > 0.2P)	no
Is the bed pressure drop greater than 20% of inlet pressure? (ΔP > 0.2P)	yes
Does axial dispersion have a large effect upon the reaction rate? (Do axial dispersion have a large effect upon the reaction rate?)	yes
Does radial velocity profile negatively effect the reaction rate? (Do radial velocity profile negatively effect the reaction rate?)	no
Does a radial interparticle heat transport limit the reaction rate? (Does a radial interparticle heat transport limit the reaction rate?)	yes

Gradient Plots

Bed Scale Gradients

Bed Average	Bed Inlet	Bed Outlet
Weisz-Prater Modulus (M _{wp}): 0.47	0.47	0.47
Thiele Modulus (M _t): 3.6	3.6	3.6
Effectiveness Factor (η): 0.24	0.24	0.24
External Concentration Gradient: 3.37	3.37	3.37
External Temperature Gradient: 0.0781	0.0781	0.0781
Internal Temperature Gradient: 0.00321	0.00321	0.00321
Prater Number (β): 4.97e 6	4.97e 6	4.97e 6
Intrinsic (1 st Order) Rate Constant (k _{int}): 1.09	1.09	1.09
Max Possible Diffusion Limited Rate (r _{max}): 0.699	0.699	0.699

Notes:

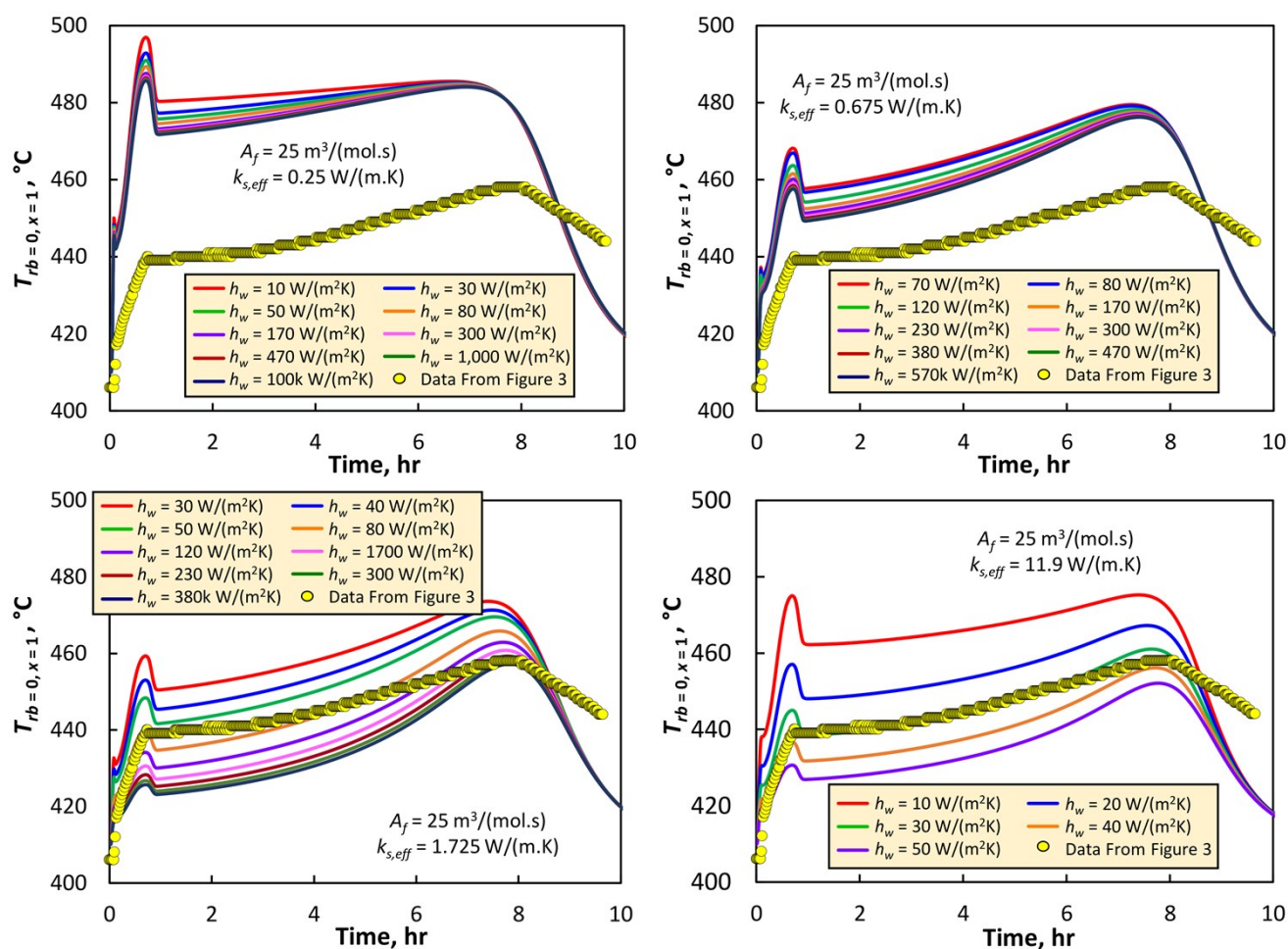
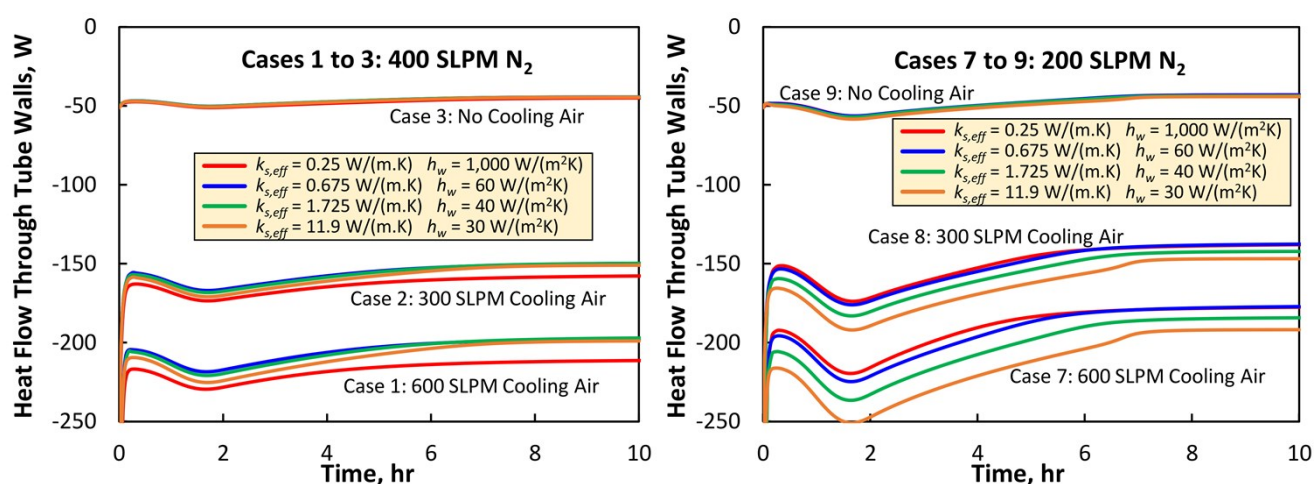
Figure S1. 2FBR modelled temperature profiles at center point of outlet ($r_b = 0, x = 1$) compared to data from Figure 3.

Figure S2. Tube wall heat flow profiles for TCPDU model, for process N2 flows of 400 SLPM (left) and 200 SLPM (right).