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The Effect of Oxygen Penetration on Apparent Pulverized Coal Char Combustion Kinetics

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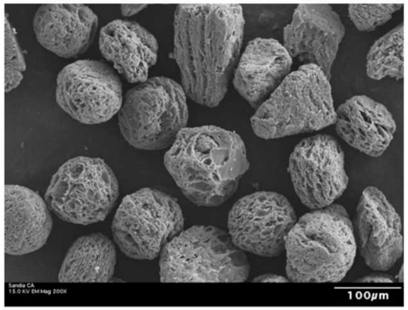

Western States Section of the Combustion Institute
Bend, Oregon
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Motivation

- Due to uncertainties in internal structure of char particles and a lack of an ability to readily measure oxygen penetration during high temperature combustion, char kinetic rates are most frequently expressed on an apparent kinetics basis

$$q = k_s p_{O_2,s}^{n} \qquad k_s = Aexp\left({}^{-E}/_{RT_p}\right)$$

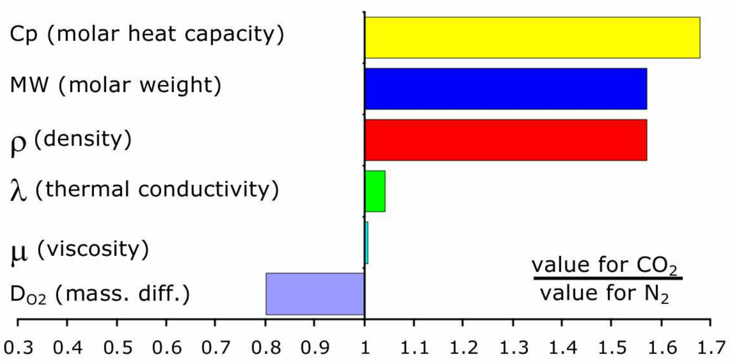
surface-specific reaction rate, gmol/cm^2-s

- This approach treats everything that happens inside the particle as a "black box"

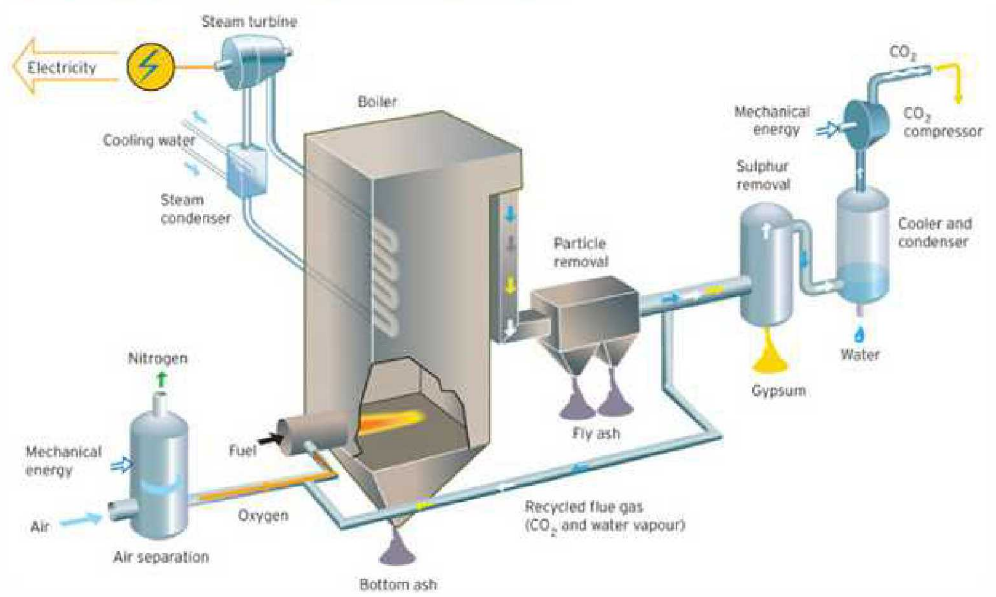
- Begs the question of what is effect of having different O_2 diffusivities in gas (both in bath gas and as local gas composition in particle changes)

Motivation II

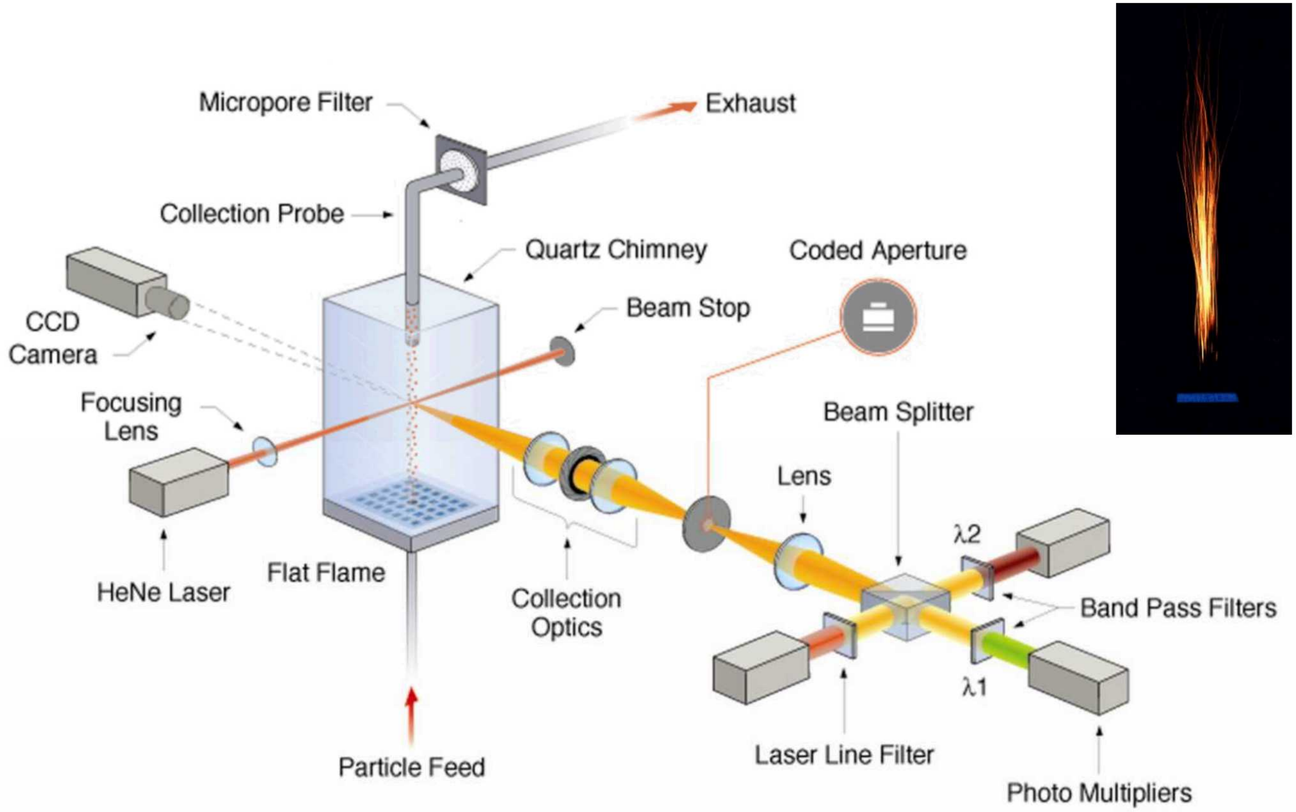
- Specific question: how to transfer char oxidation rates measured in N_2-dominant environments to CO_2-dominant environments characteristic of oxy-fuel combustion?



Oxyfuel (O_2/CO_2 recycle) combustion capture



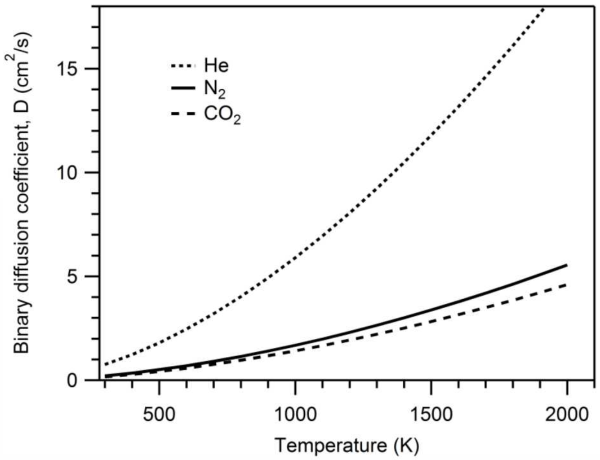
Experimental Measurements: Char Combustion Particle Temperatures and Burnout

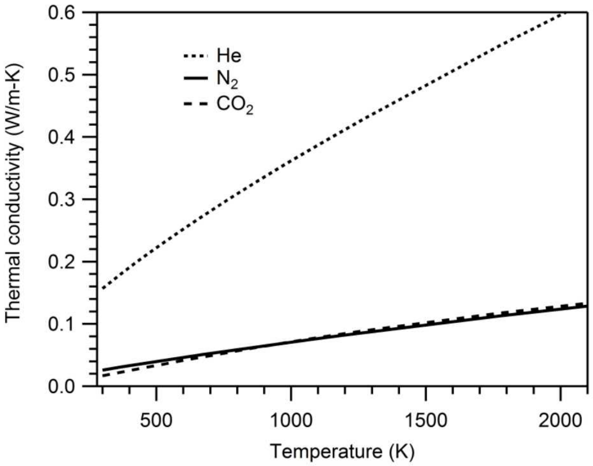


- 5 cm X 5 cm cross-section
- 1 atm
- laminar furnace flow from compact, diffusion-flamelet (Hencken) burner
- sieved char particles slowly introduced along centerline
- quartz chimney
- N_2 or He diluent with matched $[O_2]$, $[H_2O]$, and gas T
- particle T from calibrated 2-color pyrometry

Flow Reactor Operation with He

- Helium has high diffusivity and thermal conductivity

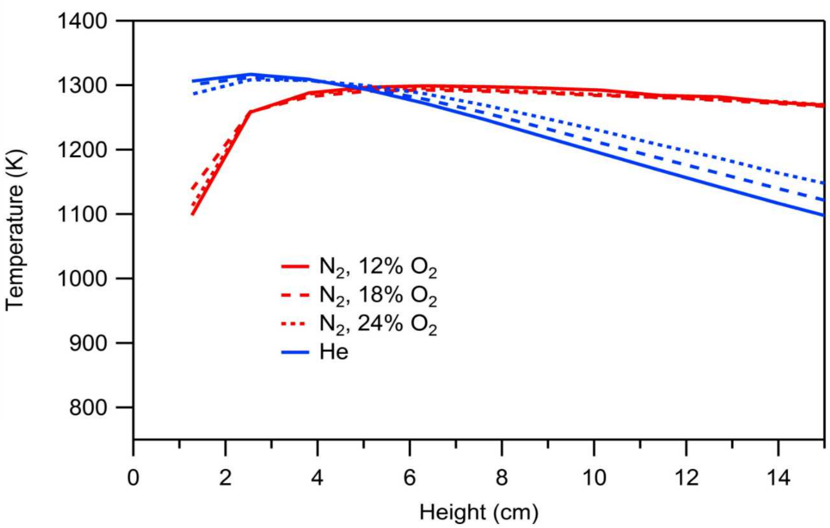




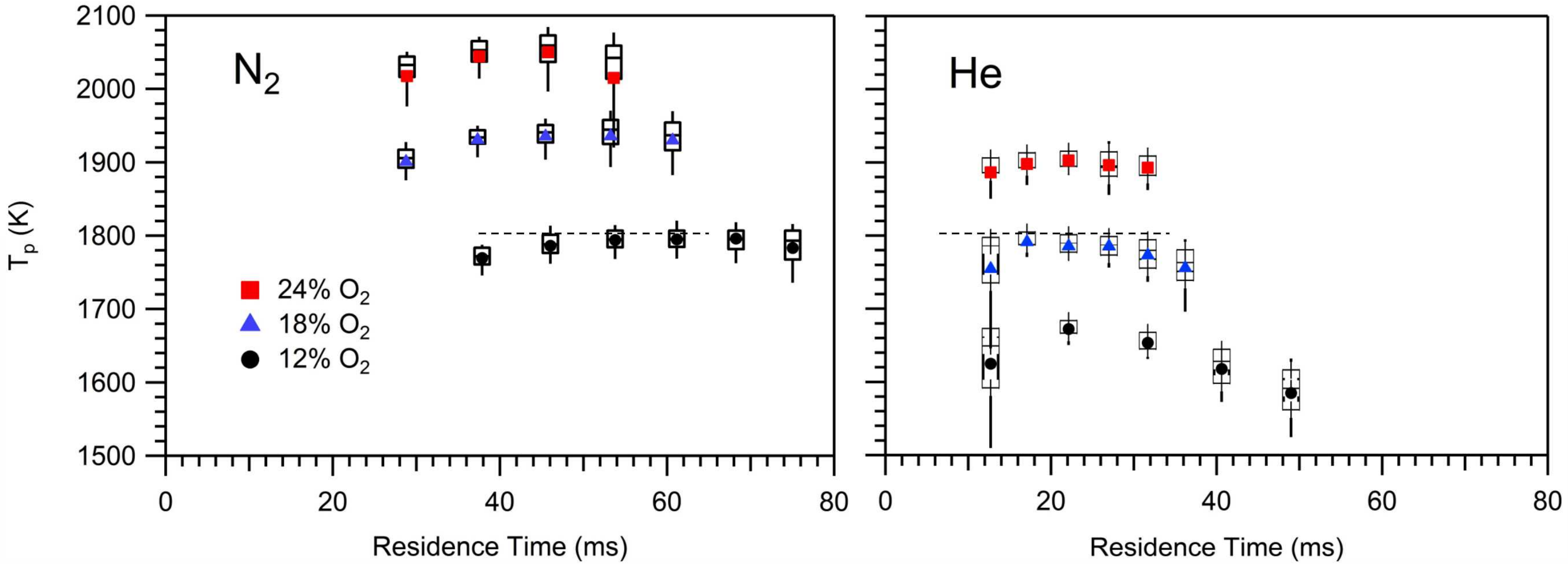
- For particle combustion, higher diffusivity increases particle burning rate (and combustion temperature), whereas high thermal conductivity tends to cool the particle, reducing the burning rate

Flow Reactor Operation

- High heating rate 63-75 μm Black Thunder char particles pre-formed by feeding sieved coal into turbulent N_2 flow at 1200 deg C (250 ms)
- Relatively low gas T chosen to minimize CO-CO_2 conversion near particle surface and influence of CO_2 gasification reaction, which complicate interpretation of results
- Heat loss to walls is strong with He flow, so gas temperatures were approximately matched in region where char combustion data were collected



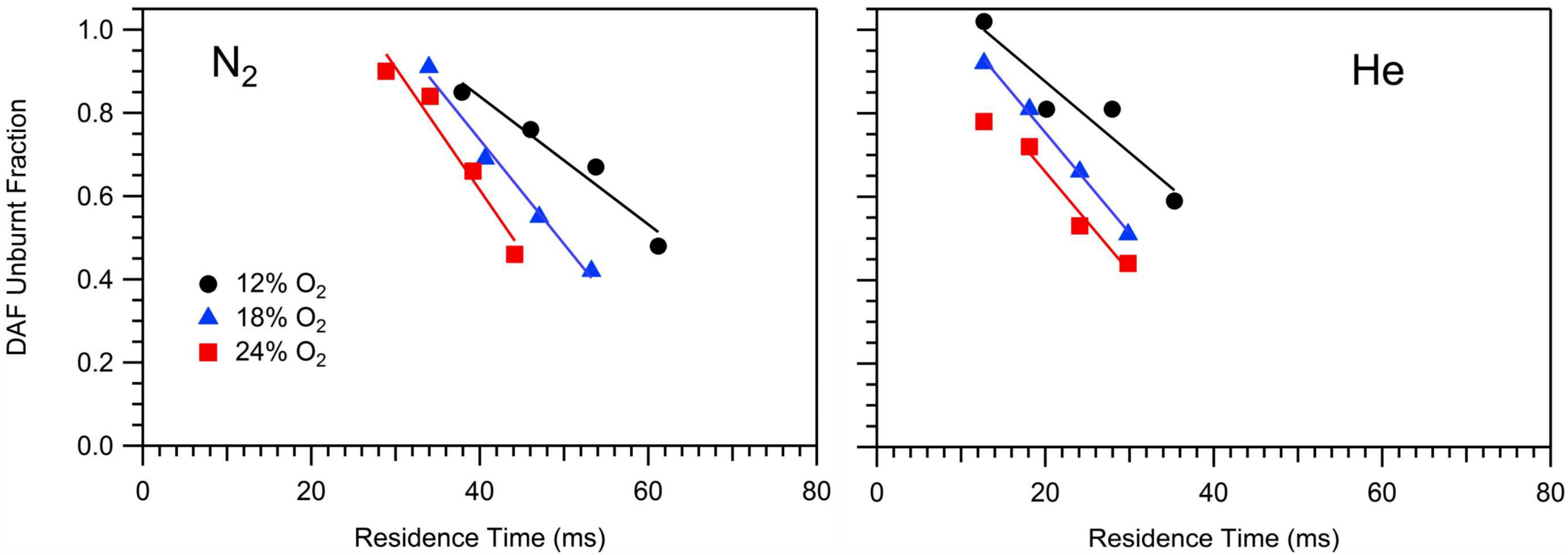
Experimental Results: Char Particle Temperatures



- Earlier particle ignition in He
- Somewhat cooler particle temperatures in He
- Tp ~ 1800 K for combustion in 12% O_2 in N_2 *and* for 18% O_2 in He

Experimental Results: Char Particle Burnout

Ash tracer technique – averaged from ICP-OES analysis of Si, Al, Ti



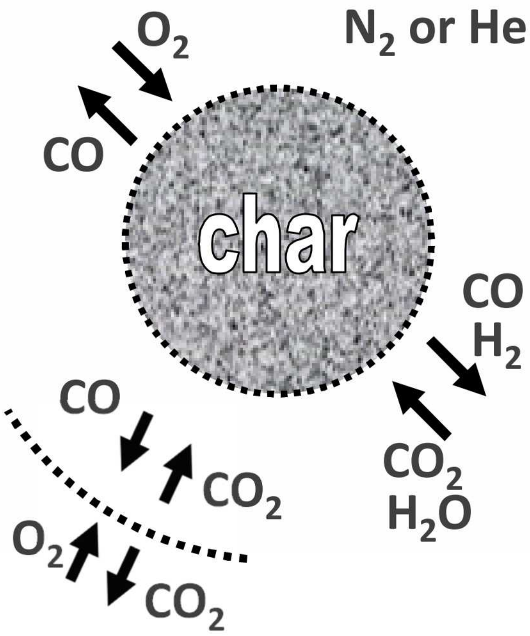
Diluent Gas	Oxygen Concentration	Burning Rate (1/s)
N_2	**12.0 vol-%**	**15.4**
	18.0 vol-%	25.1
	24.0 vol-%	29.4
He	12.4 vol-%	17.0
	18.4 vol-%	**24.1**
	24.6 vol-%	24.0

Detailed Char Particle Oxidation Modeling

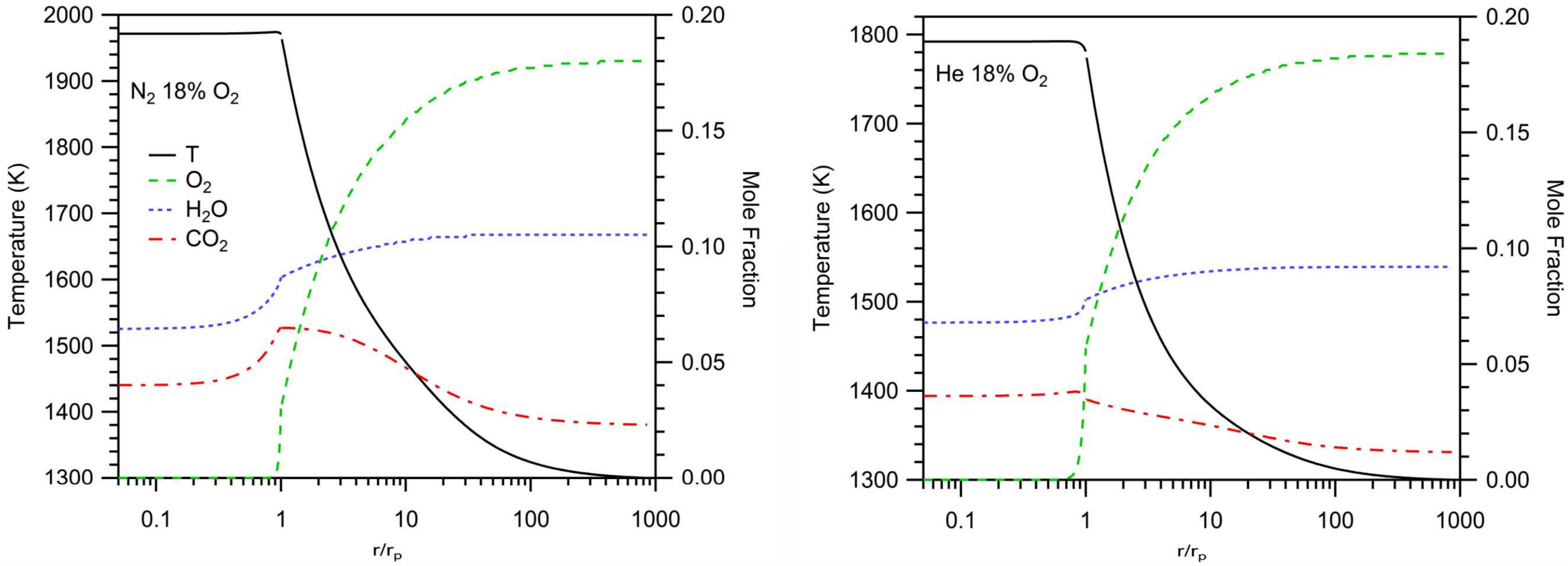
SKIPPY (Surface Kinetics in Porous Particles) – Brian Haynes, U. Sydney

- 1D steady-state model of spherical porous char particle
- Detailed surface kinetics and gas-phase kinetics provided through links to CHEMKIN II
- Heterogeneous mechanism, char properties, and combustion environment specified by user
- Use GRI-MECH 3.0 (w/o NO chemistry) to describe CO oxidation

Reaction	*A* (g/cm^2 s)	*E* (kJ/mol)
Heterogeneous oxidation:		
(R1) $C\_s + O_2 \Rightarrow CO + O\_s$	3.3E+15	167.4
(R2) $O\_s + 2C(b) \Rightarrow CO + C\_s$	1.0E+08	0.
(R3) $C\_s + O_2 \Rightarrow O_{2}\_s + C(b)$	9.5E+13	142.3
(R4) $O_{2}\_s + 2C(b) \Rightarrow C\_s + CO_2$	1.0E+08	0.
Char gasification:		
(R5) $C\_s + CO_2 \Rightarrow CO + O\_s$	1.8E+15	251.0
(R6) $C\_s + H_2O \Rightarrow H_2 + O\_s$	2.2E+14	222.0

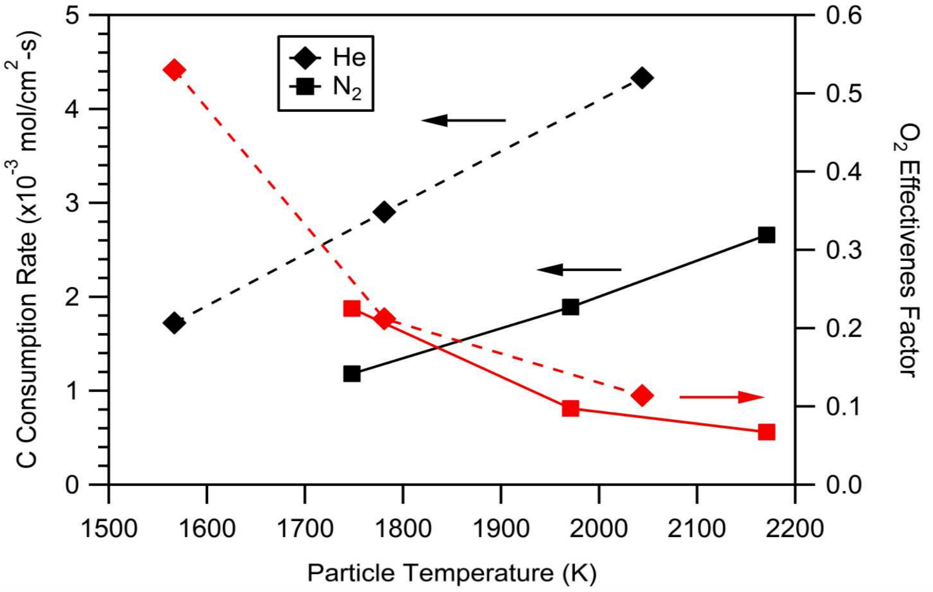


Modeling Results:
Char Particle Temperatures and Gas Species Profiles



- CO_2 and H_2O show minimal consumption in particle (esp. for He)
- Some CO_2 produced near surface in N_2 environment (higher local T)
- Significantly greater O_2 penetration of char in He

Modeling Results:
Carbon Consumption Rates and Effectiveness Factors



- Difficult to untangle effects of different surface oxygen concentrations and char T's on burning rates
- Common profile of effectiveness factor vs. char T (regardless of diluent) – is this a coincidence?
- Burning rate in He is 1.6x that in N_2, for a given char T (ref. data)

Theory of Reacting Porous Particles

- Diffusivity through porous particle is proportional to gas-phase diffusivity

$$D_{eff} = \frac{\varepsilon}{\tau} D$$

ε = porosity
τ = tortuosity

- Reactivity is characterized by Thiele modulus

$$\phi_n^2 = \frac{reaction\ flux}{diffusion\ flux}$$

$\phi_n \rightarrow 0$ in kinetic limit
$\phi_n \rightarrow \infty$ in diffusion limit

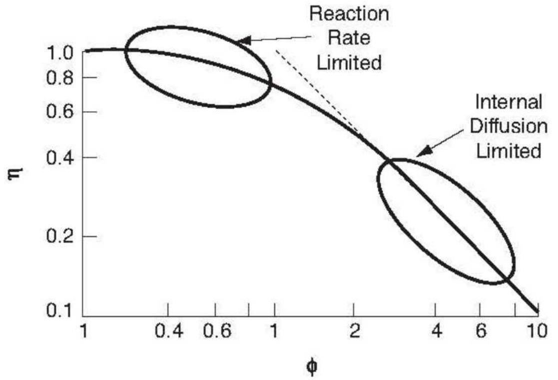
- For a spherical particle, Thiele modulus is expressed as

$$\phi_n^2 = \frac{kR^2[O_{2,s}]^n}{D_{eff}}$$

- All else being equal, Thiele modulus in He should be lower than in N_2 by factor of sqrt(3.5) = 1.9

Theory of Reacting Porous Particles

- Effectiveness factor (burning rate) decreases with increasing Thiele modulus



R. Aris, Introduction to the Analysis of Chemical Reactors, 1965

- For high Thiele modulus (approaching diffusion limit)

$$\eta \sim {}^{1}/_{\phi}$$

- Therefore, as approach diffusion limit, expect 1.9x higher burning rate in He

- Observed factor of 1.6x higher burning rate is consistent with this

Summary

- Combustion of pc char particles in He diluent resulted in lower char particle temperatures than in equivalent N_2 environments
- Measured char burning rates are ~ 1.6x greater in He when particles are burning at same T as in N_2
- Detailed porous particle modeling revealed
  - significantly greater O_2 penetration for combustion in He, for a given reaction environment
  - a 1.6x greater burning rate in He, for a given char particle T
- Classic porous particle reaction theory shows that the maximum possible enhancement in burning rate in He is a factor of 1.9, in the diffusion limit
- For application to oxy-fuel combustion, the char oxidation rate should be lower, but by at most 9% (in the diffusion limit)

Acknowledgment

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- Prof. Brian Haynes (U. Sydney) provided SKIPPY code

Questions?