Char Oxidation Concepts

- 1. χ
- 2. CO/CO₂ ratio
- 3. nth order
- 4. α
- 5. T dependence
- 6. d_p dependence
- 7. $CO \rightarrow CO_2$ in boundary layer (2-film model)
- 8. energy balance / iteration

- 9. Thiele modulus
- 10. Ian Smith reactivity correlation
- 11. TGA rate vs high T rate
- 12. Catalytic effects at low T
- 13. Pressure effects
- 14. Correlations vs. chemistry
- 15. Late burnout ideas
- 16. N-release during char oxidation

Review

- How does char oxidation rate vary with coal type?
 - How much more reactive is lignite than low volatile bituminous coal (at 1500 K)
- What are the three zones of char oxidation?
- How does the surface product of char oxidation change with temperature?
- What is the χ factor, and how does it change with temperature?



Figure 1. Char combustion rates in selected gas environments as a function of parent coal carbon content. *Points:* rates calculated from global kinetic parameters reported in Table 1, Δ – 1500 K gas temperature, O - 2000 K gas temperature. *Curves:* rates calculated from the correlation proposed in Eq. 6. Solid curve: CO assumed to be sole heterogeneous product, Dashed curve: limited CO₂ production assumed in accordance with Eq. 3 with A_c = 3 ·10⁸ and E_c = 60 kcal/mol.

Review (cont.)

• If the surface reaction rate is:

$$r_{rxn}^{\prime\prime} = k_{rxn} P_{O_2,s}^n$$

and the film diffusion rate is: $r_{diff,O_2}^{\prime\prime} = k_m (P_{O_2,g} - P_{O_2,s})$

How do you calculate the reaction rate of the char?

• How do you calculate the char oxidation rate when you need to solve the particle energy equation as well?

Different CO/CO₂ Correlations from (a) Hurt and Mitchell (H-M), (b)Tognotti



2-film Model of Char Oxidation

 For large particles, where the boundary layer is large enough (200 μm or higher?)



- Actual surface reaction is C + $CO_2 \rightarrow 2CO$
- The "flame" is from $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- CO₂ diffuses back to the particle surface <u>and</u> away from the flame to the bulk gas

Classification of Char Oxidation Models



Global Models

(motivation)

- Hard to scale up from TGA measurements
- Char properties and reactivity are functions of T, dT/dt , and P_{tot}

- Measure reactivity at conditions representative of industrial environment (T, dT/dt, P, d_p, etc.)
- Use global correlation that accounts for pore diffusion effects, etc.

Problem: These measurements are extremely challenging and expensive

Global Models (cont.)

Example:

$$\dot{r}'' = k'' P_{O_2,sur}^n$$

Features:

- Mathematically simple (used in comprehensive codes)
- External surface area
- Oxidizer concentration at the external surface
 - Need to solve for $P_{O2,surf}$

Things not treated:

- Temporally changing porosity and surface area
- Particle fragmentation
- Mineral matter effects (diffusion or reaction)

Intrinsic Models

(motivation)

- TGA Rate Measurements
 - cheap
 - fast
 - repeatable

High Temperature Reaction Behavior

- expensive
- time-consuming
- data scatter

$$r_{pi} = k_i A_a C_o^m$$

Use a pore structure model to approximate available or active surface area, and possibly even local oxidizer concentrations within the particle pores

Intrinsic models can be further classified as macroscopic or microscopic intrinsic char oxidation models



Ian Smith Correlation

Idea:

All intrinsic char reactivities are the same



Figure 4.10. Intrinsic reactivity of several porous carbonaceous solids in oxygen [at an oxygen pressure of 0.1 mPa (1 atm)]. (Figure used with permission from Smith, 1982.)

Reading Question 1: Key features of intrinsic models

Features of Intrinsic Char Oxidation Models

Chemical Kinetics

- 1. Internal reaction including:
 - Pore diffusion
 - Adsorption/desorption
 - Intrinsic chemical reaction
 - Mineral matter catalysis
- 2. Chemical reactions considered
 - Heterogeneous/homogeneous
- 3. Particle heating

Particle Morphology

- 1. Postulated pore geometry
 - Total or active surface area
- 2. Degree of pore branching
- 3. Evolution of pore structure
- 4. Particle fragmentation
- 5. Mineral matter blockage effects

Macroscopic Intrinsic Models (like Thiele modulus approach)

- Variations of shrinking core and progressive conversion models
- **Strength:** Numerically efficient
- Weaknesses:
 - Empirical effective diffusivity & effectiveness factor
 - Average macroscopic properties
 - Porosity
 - Tortuosity

Reading Question 2: Thiele Modulus

Pore Diffusion



Effectiveness Factor



Intrinsic Kinetics (macroscopic)

1. Determine rate per external surface area from kinetic expression

$$\dot{r}_C^{\prime\prime\prime} = \eta k^{\prime\prime\prime} C_{O_2,S}$$

where η is a "fudge factor" to correct for pore diffusion effects

$$\eta = \frac{C_{O_2,average}}{C_{O_2,surface}}$$

- 2. Determine value of η from the effective diffusivity (D_e), the tortuosity, etc.
- 3. The η is called the effectiveness factor
 - $\eta = 1$ means no pore diffusion resistance (C₀₂ = constant in particle interior)
 - $\eta < 1$ means some pore diffusion resistance (C_{02,avg} < C_{02,surface})
- 4. Since the η terms contains some temperature dependence, the overall "apparent" activation energy turns out to be $E_{app} = E_{true}/2$
- 5. The η is therefore a function of reaction rate (k'''), T_p, d_p, and pore size

IV. Bimolecular Surface Reactions $A + B \rightarrow$ Products

- A. <u>Langmuir Hinshelwood</u>: Reaction of two adsorbed species
 - $A + S \leftrightarrow A S$ (quasi equilibrium) $B + S \leftrightarrow B S$ (quasi equilibrium) $A S + B S \rightarrow$ products

If both A and B compete for the same surface sites



 $\mathbf{r} = \mathbf{k} \theta_A \theta_B$



Reading Question 4:

Thiele Modulus vs. Microscopic Intrinsic Models

Microscopic Intrinsic Models

- More complex pore model
- Model local diffusivity and pore structure
 - No empirically-determined effective diffusivity
- Strength: Promise of better fundamental understanding
- Weakness: Numerically cumbersome

– Not for use in boiler simulation codes

Microscopic Continuum Models

Model features	Gavalas and co-workers	Amundson and co-workers	Simons and co-workers
	Chemi	cal kinetics	
 Internal reaction mechanisms Pore diffusion Adsorption/desorption Intrinsic kinetics Chemical reactions Intrinsic rate 	Yes No Yes $2C + O_2 \rightarrow 2CO$ $A_0 \exp(-E_1/RT)C_{O_2}$	Yes No Yes $2C + O_2 \rightarrow 2CO$ $A_0 \exp(-E_t/RT)C_{O_2}$	Yes Yes Yes $[(k_1K_2p_{0_2})/(k_{-1} + k_2 + k_1p_{0_2})]$ $k_1 = A_{0,1} \exp(-E_{1,1}/RT)$ $k_2 = A_{0,2} \exp(-E_{1,2}/RT)$ $k_{-1} = A_{0,-1}k_1k_2 \exp(-E_{1,-1}/RT)$
	Particle	morphology	
 Pore growth Pore-size distribution Pore geometry Particle fragmentation Mineral matter effects 	Yes Uni-, bi-, or trimodal Cylinders or spheres Yes No	Yes Uni- or bimodal Cylinders and/or spheres No No	Yes Tree structure Cylinders No No

TABLE 78. Key Features of Three Continuum Microscopic Intrinsic Char Oxidation Models^a

* See text for citing of references. (Revised and expanded by Cope, 1993, from Smoot and Smith, 1985).

PORE STRUCTURE REPRESENTATIONS IN THREE MICROSCOPIC INTRINSIC MODELS



AMUNDSON



SIMONS (pore tree model)





GAVALAS (random pore model)

Microscopic Discrete Models

Fractal Structure of Coal Char

Energy & Fuels, Vol. 16, No. 5, 2002 1131



Figure 2. Fractal models. Models a and b corresponding to coal particle and char particle with 39.53% burnoff level, respectively.

EXTERNAL vs. AVAILABLE (TOTAL ?) SURFACE AREA



ext. SA	total S/	4 (m²/g)
(m²/g)	[N ₂]	[CO ₂]
0.17	136	559

Partially-oxidized (1620 K, 3% O₂) Zap lignite char

Reading Question 4:

Limitations of intrinsic models in large simulations

Problem with Intrinsic Models

- What surface area do you use?
 - $-N_2$ BET surface area? (mesopores)
 - CO₂ surface area (micropores)
 - $-O_2$ surface area (active surface area)

NONE of the above S_{int} seem to work correctly!

Reade and Hecker Idea

Walter Reade and Dr. Hecker have developed a different kind of intrinsic model, using the following steps:

(1) generate a high temperature char experimentally,

(2) perform TGA experiments to obtain TGA rates as a function of burnout for that starting char, and

(3) use the TGA rates with an intrinsic model to calculate the high temperature rates as a function of burnout.

Please comment on potential advantages and disadvantages of this approach.

Method of Solomon et al. (semi-empirical)



Figure 6.29 Comparison of reactivity for chars from five coals as a function of hydrogen content in the char. Upper line is a best fit of Pittsburgh and Kentucky #9 bituminous chars and the lower line is a best fit of Beulah-Zap lignite chars. The Zap, Pittsburgh and Illinois coal chars are coals from the coal suite. Source: Best <u>et al.</u> (1987).

- Measure T_{crit}
 - 30 K/min
 - 15% O₂
 - When mass loss rate reaches 6.5%/min
- As T_{crit} increases, reactivity decreases
 - High reactivity occurs at low T_{crit}
- Intrinsic reactivity correlated with %H, O, and Ca in char
 - Thiele modulus approach used