Char Oxidation Concepts

1. χ
2. CO/CO_2 ratio
3. n^{th} 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

1

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?
  - Constant diameter vs. constant density
- How does the surface product of char oxidation change with temperature?
- What is the χ factor, and how does it change with temperature?

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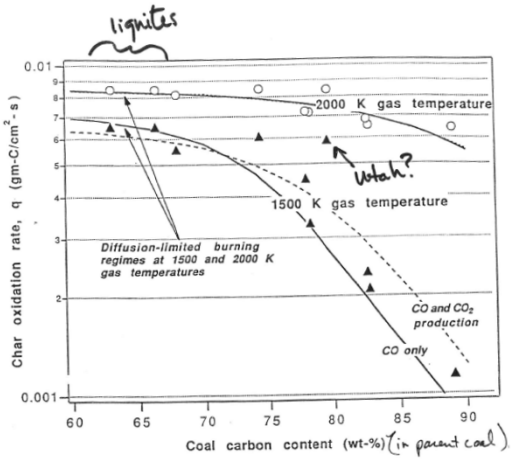

Figure 1. Char combustion rates in selected gas environments as a function of parent coal carbon content. *Points:* rates calculated from global kinetic parameters reported in Table 1, Δ – 1500 K gas temperature, O - 2000 K gas temperature. *Curves:* rates calculated from the correlation proposed in Eq. 6. Solid curve: CO assumed to be sole heterogeneous product. Dashed curve: limited CO_2 production assumed in accordance with Eq. 3 with A_c = $3 \cdot 10^8$ and E_c = 60 kcal/mol.

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Review (cont.)

- If the surface reaction rate is:

$$r''_{rxn} = k_{rxn} P^n_{O_2,s}$$

and the film diffusion rate is:

$$r''_{diff,O_2} = k_m \left(P_{O_2,g} - P_{O_2,s}\right)$$

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?

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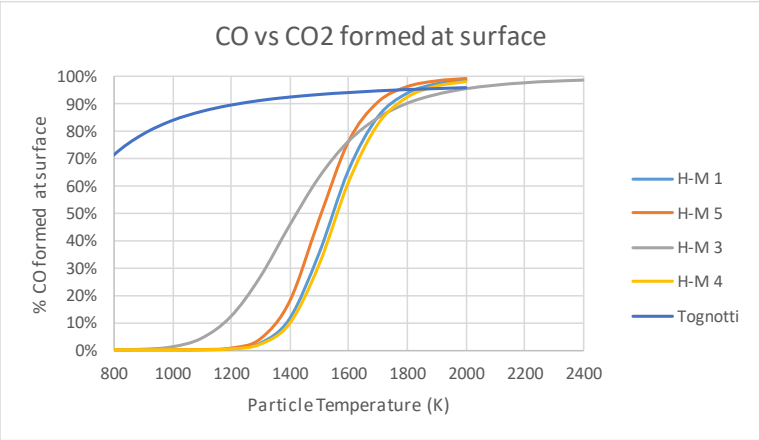
Q1. Different CO/CO_2 Correlations from (a) Hurt and Mitchell (H-M), (b)Tognotti



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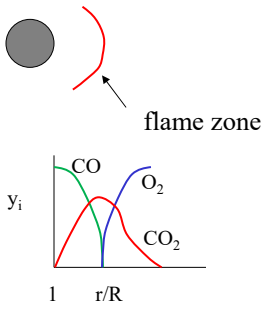
2-film Model of Char Oxidation

- 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 $CO + ½\ O_2 \rightarrow CO_2$
- CO_2 diffuses back to the particle surface and away from the flame to the bulk gas

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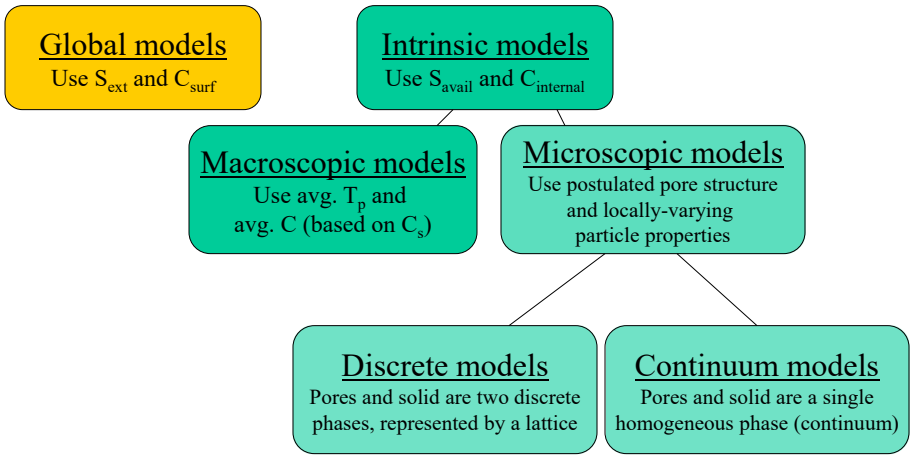
Classification of Char Oxidation Models



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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

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Global Models

(cont.)

Example:

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

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)

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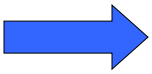
Intrinsic Models

(motivation)

TGA Rate Measurements
- cheap
- fast
- repeatable



High Temperature Reaction Behavior
- expensive
- time-consuming
- data scatter

$$r'''_{p,intrinsic} = k'''_{rxn} A_{active} C_{oxidizer}^{m}$$

- Use a pore structure model to approximate A_{active}
  - A_{active} may vary with conversion and radius
- Model local concentrations within the pore structure
- Macroscopic vs. microscopic approaches

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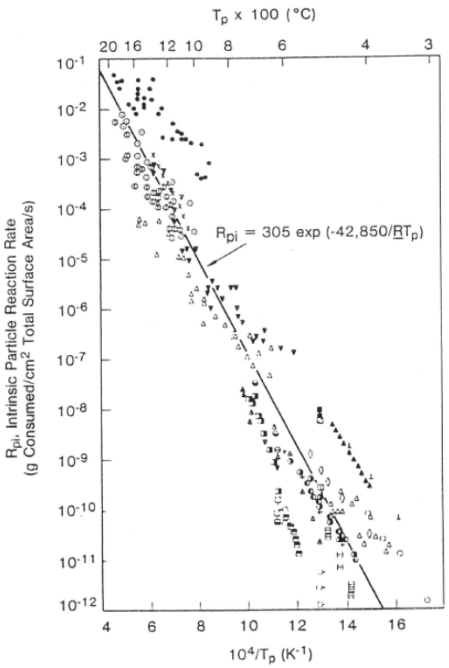

igure 4.10. Intrinsic reactivity of several porous carbonaceous solids in oxygen [at an oxygen ressure of 0.1 mPa (1 atm)]. (Figure used with permission from Smith, 1982.)

Ian Smith Correlation

Idea:
All intrinsic char reactivities are the same

From Smoot & Smith, p. 101

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Reading Question 2: Key features of intrinsic models

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Features of Intrinsic Char Oxidation Models

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

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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

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Reading Question 3:

Thiele Modulus

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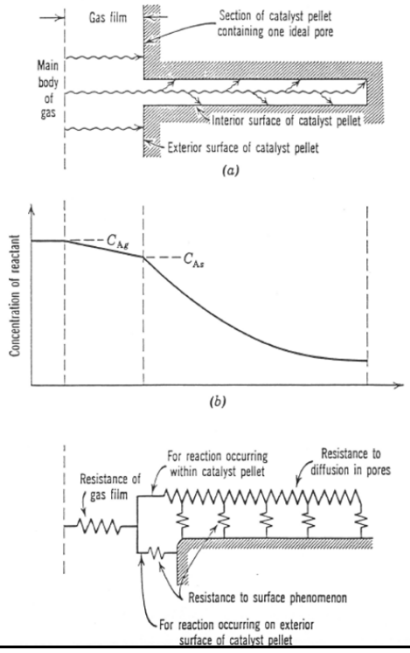
Pore Diffusion



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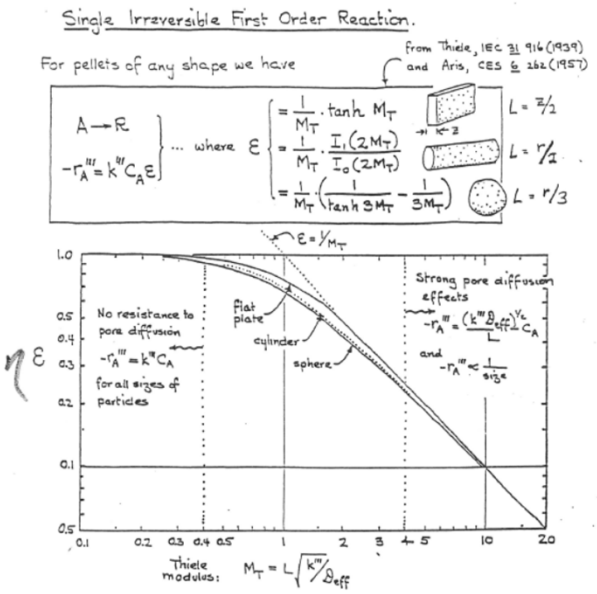
Effectiveness Factor



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Intrinsic Kinetics (macroscopic)

1. Determine rate per external surface area from kinetic expression

$$\dot{r}_C''' = \eta k''' C_{O_2,s}$$

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
   - η = 1 means no pore diffusion resistance (C_{O2} = constant in particle interior)
   - η < 1 means some pore diffusion resistance ($C_{O2,avg} < C_{O2,surface}$)
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

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

A. Langmuir - Hinshelwood: Reaction of two adsorbed species

$A + S \leftrightarrow A\text{-}S$ (quasi equilibrium)

$B + S \leftrightarrow B\text{-}S$ (quasi equilibrium)

$A\text{-}S + B\text{-}S \rightarrow$ products

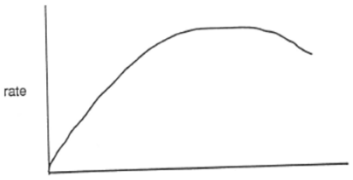
If both A and B compete for the same surface sites

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}$$

$$r = k\theta_A\theta_B$$

$$r = \frac{kK_AK_BP_AP_B}{(1 + K_AP_A + K_BP_B)^2}$$ (note denominator squared)



Decreases at high pressure (negative order) because more strongly adsorbed species replaces other on the surface. e.g. CO in CO oxidation
Maximum occurs at $K_AP_A = K_BP_B$; hence, K_A/K_B can be calculated at the maximum rate

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Reading Question 4:

Thiele Modulus vs. Microscopic Intrinsic Models

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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

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Microscopic Continuum Models

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

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

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

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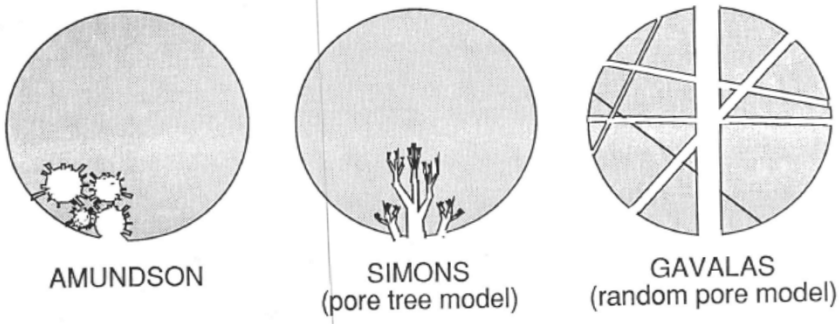
PORE STRUCTURE REPRESENTATIONS IN THREE MICROSCOPIC INTRINSIC MODELS



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Microscopic Discrete Models

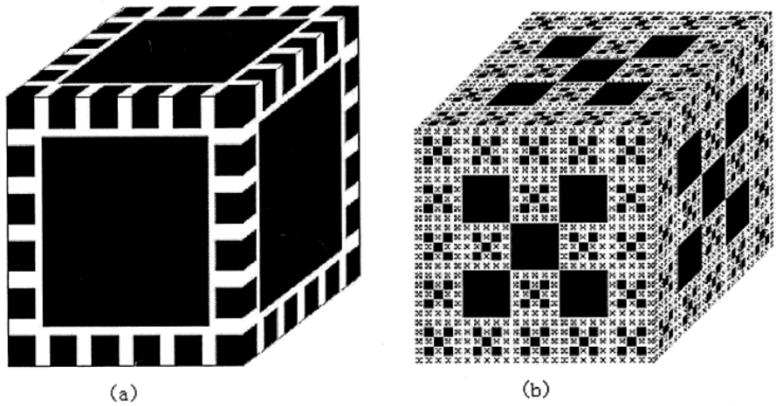

Figure 2. Fractal models. Models a and b corresponding to coal particle and char particle with 39.53% burnoff level, respectively.

Song, et al.

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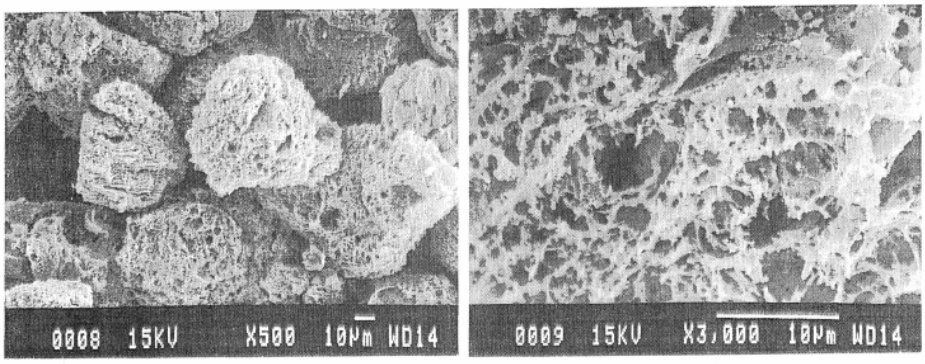
EXTERNAL vs. AVAILABLE (TOTAL ?) SURFACE AREA



ext. SA (m^2/g)	total SA (m^2/g) $[N_2]$	$[CO_2]$
0.17	136	559

Partially-oxidized (1620 K, 3% O_2) Zap lignite char

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Reading Question 5:

Limitations of intrinsic models in large simulations

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Problem with Intrinsic Models

- What surface area do you use?
  - N_2 BET surface area? (mesopores)
  - CO_2 surface area (micropores)
  - O_2 surface area (active surface area)

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

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Q6. 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.

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Q7. Method of Solomon et al.
(semi-empirical)

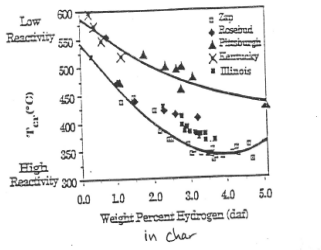

Figure 6.29 Comparison of reactivity for chars from five coals as a function of hydrogen content in the char. Upper line is a best fit of Pittsburgh and Kentucky #9 bituminous chars and the lower line is a best fit of Beulah-Zap lignite chars. The Zap, Pittsburgh and Illinois coal chars are coals from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

- Measure T_{crit}
  - 30 K/min
  - 15% O_2
  - 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

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