Business

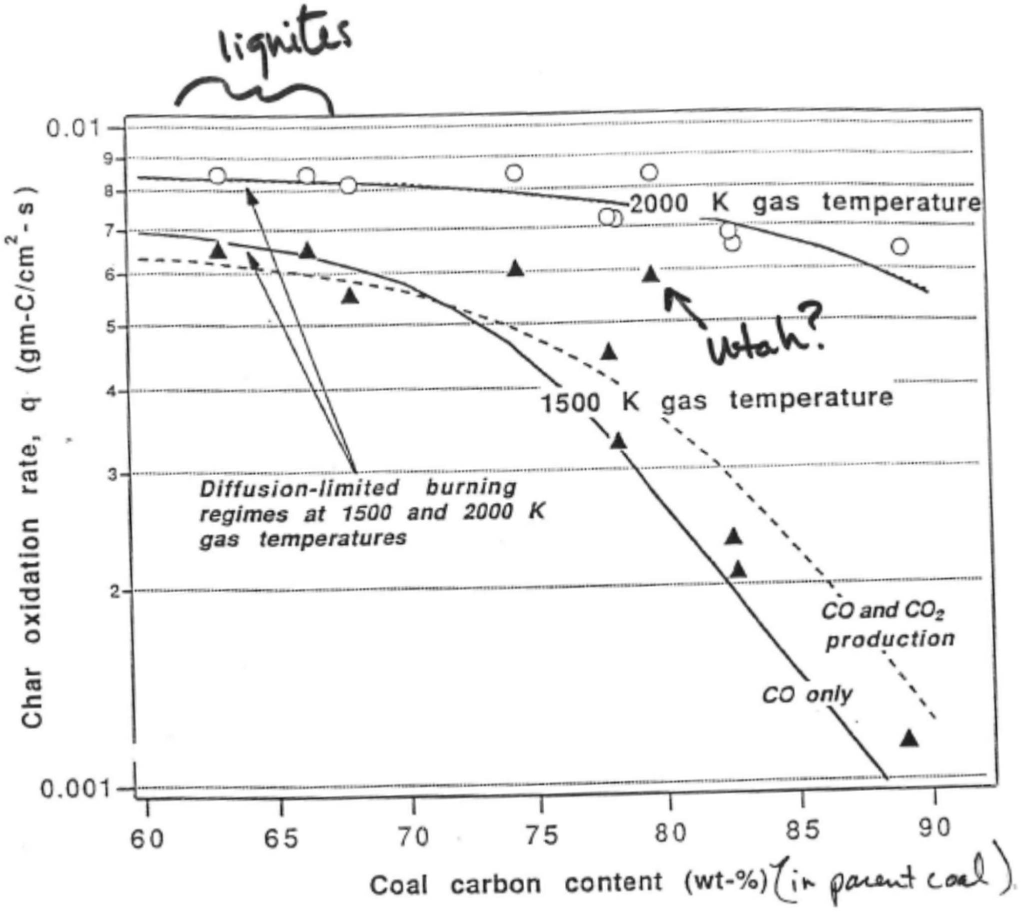
- IPP Trip
  - Trip report due Friday
  - Discussion
- How many people are going to the Clearwater Coal Conference?
  - Schedule change?

Char Oxidation Concepts

1. χ
2. CO/CO_2 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

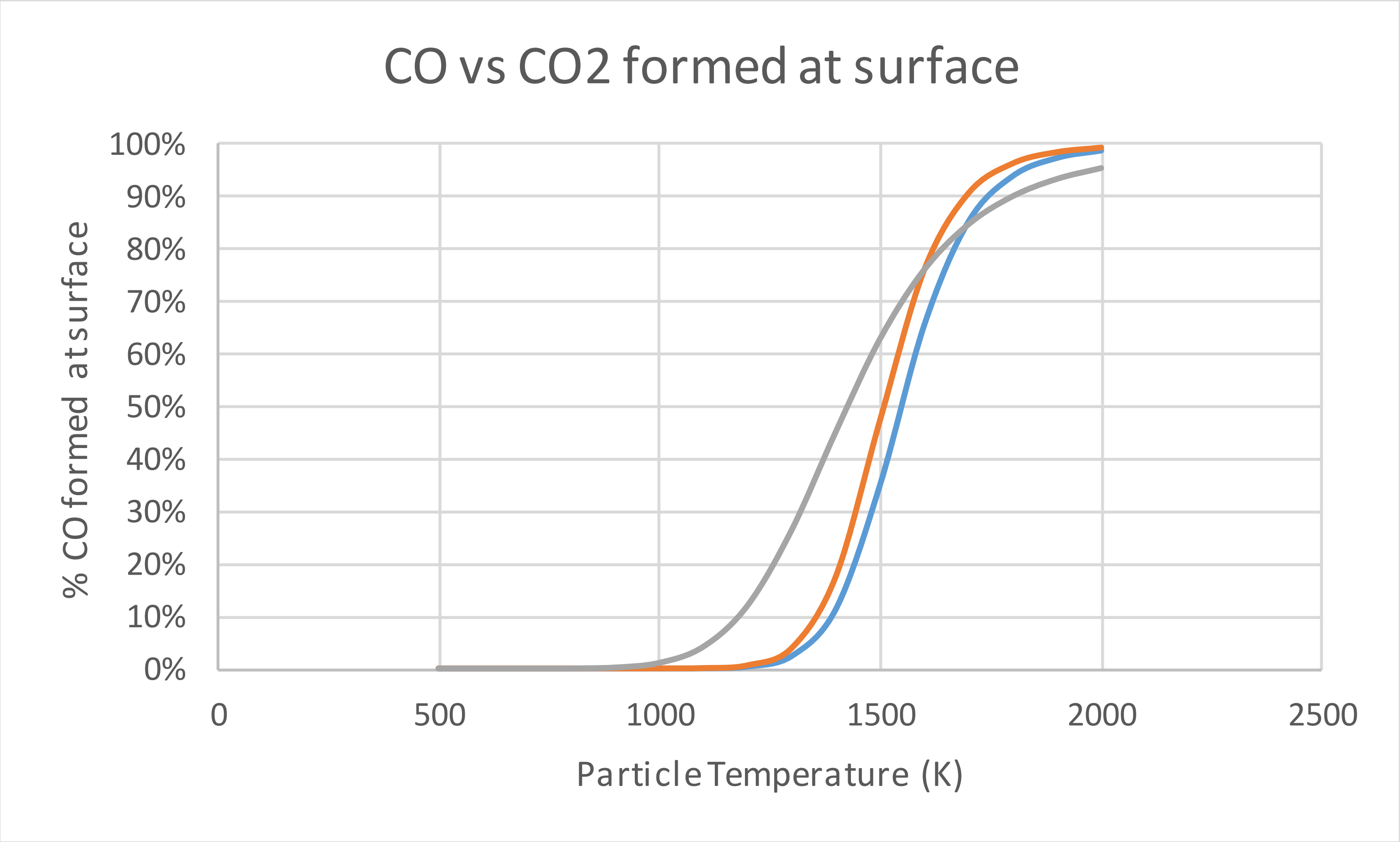
- How does char oxidation rate vary with coal type?
  - How much more reactive is lignite than low volatile bituminous coal (at 1500 K)
- What are the three zones of char oxidation?
- How does the surface product of char oxidation change with temperature?
- What is the χ factor, and how does it change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



Trend: reactivity ↓ as X_c° ↑

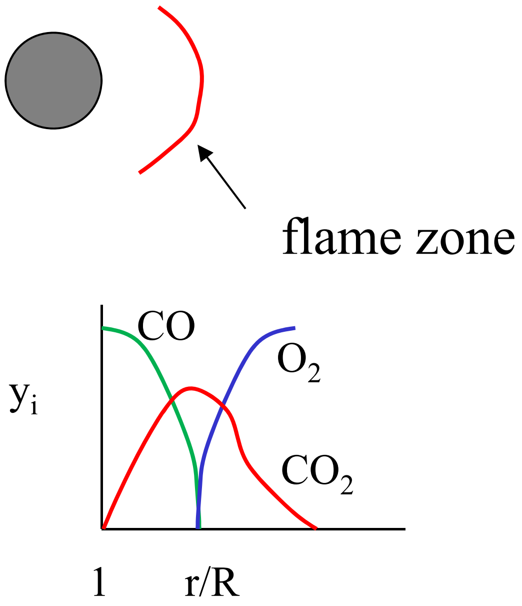
Figure 1. Char combustion rates in selected gas environments as a function of parent coal carbon content. *Points:* rates calculated from global kinetic parameters reported in Table 1, Δ – 1500 K gas temperature, O - 2000 K gas temperature. *Curves:* rates calculated from the correlation proposed in 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.

Different Correlations from Hurt and Mitchell (1992)



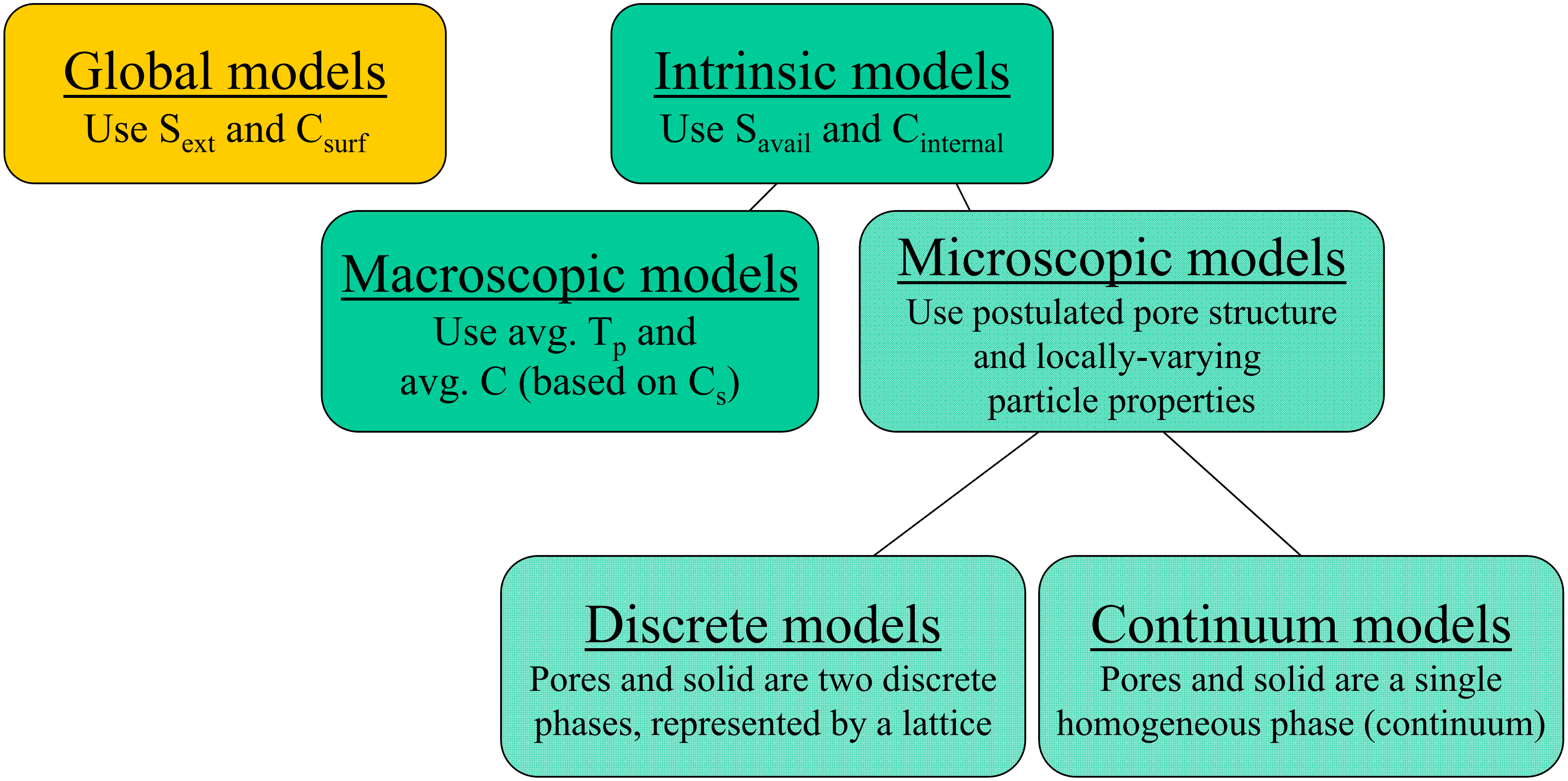
2-film Model of Char Oxidation

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

Classification of Char Oxidation Models



Global models

Use S_{ext} and C_{surf}

Intrinsic models

Use S_{avail} and $C_{internal}$

Macroscopic models

Use avg. T_p and
avg. C (based on C_s)

Microscopic models

Use postulated pore structure
and locally-varying
particle properties

Discrete models

Pores and solid are two discrete
phases, represented by a lattice

Continuum models

Pores and solid are a single
homogeneous phase (continuum)

Global Models

(motivation)

- Hard to scale up from TGA measurments
- 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:

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

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

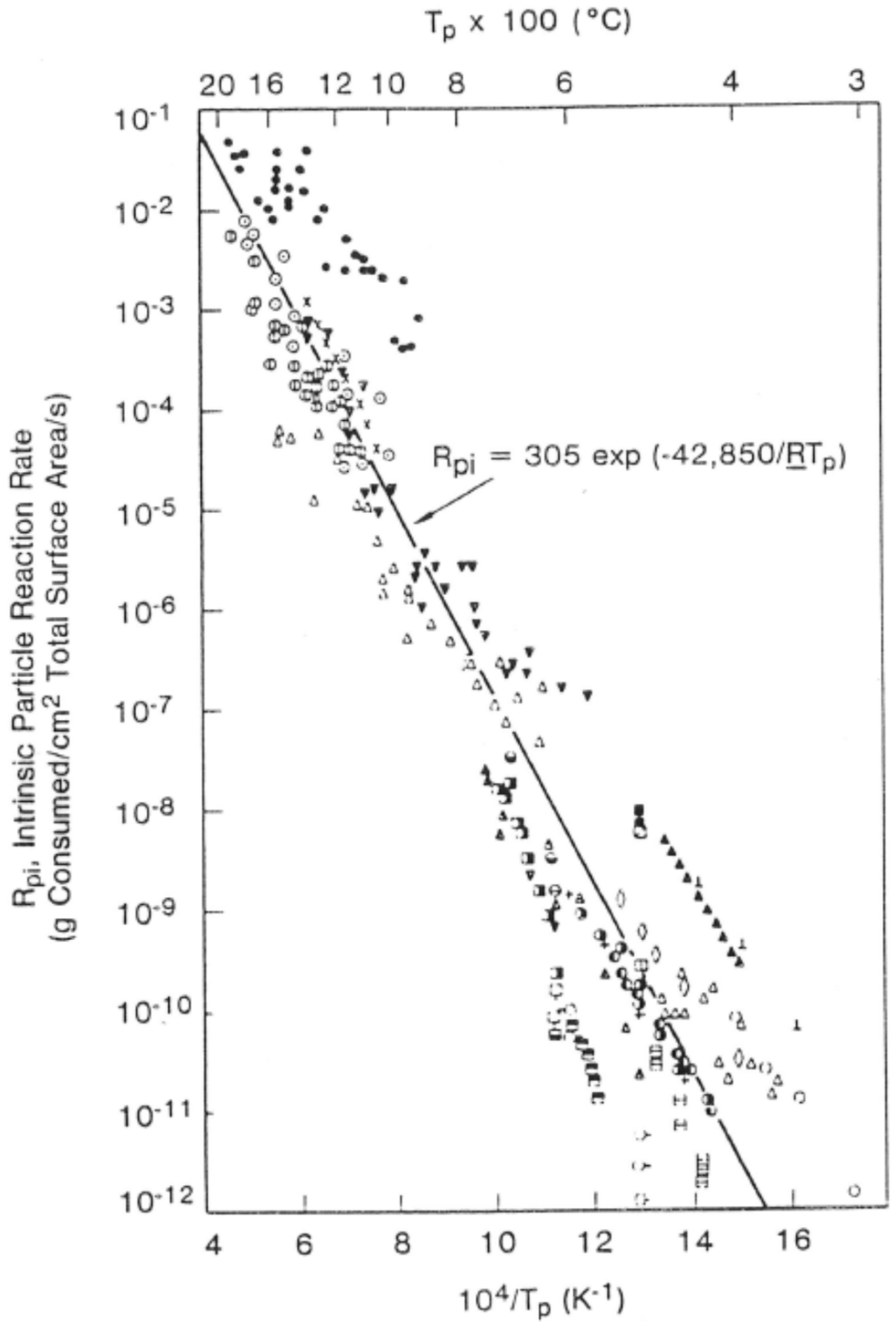
$$r_{pi} = k_i A_a C_o^m$$

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



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.)

From Smoot & Smith, p. 101

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

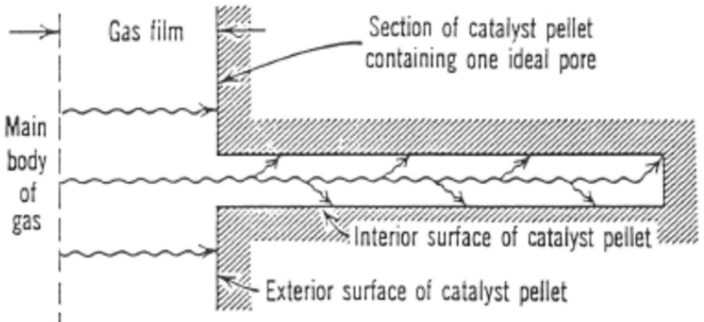
(like Thiele modulus approach)

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

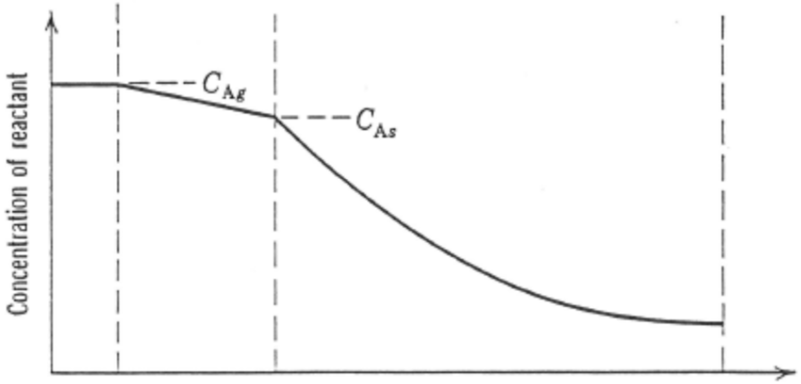
Reading Question 2:

Thiele Modulus

Pore Diffusion



(a)



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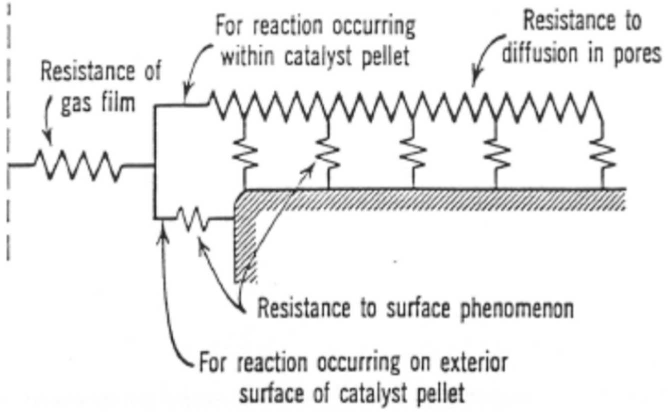


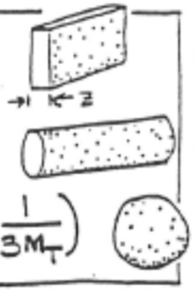
Effectiveness Factor

Single Irreversible First Order Reaction.

For pellets of any shape we have

from Thiele, IEC 31 916 (1939)
and Aris, CES 6 262 (1957)

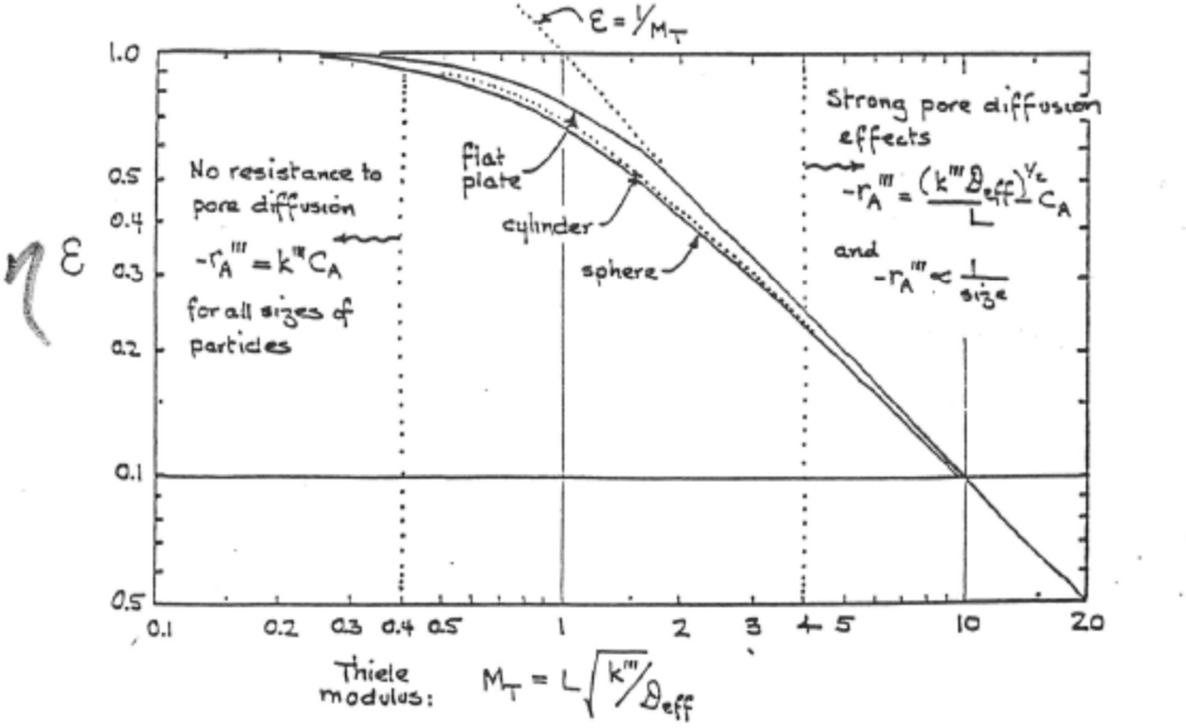
$$\left.\begin{array}{l} A \rightarrow R \\ -r_A''' = k''' C_A \mathcal{E} \end{array}\right\} \dots \text{ where } \mathcal{E} \begin{cases} = \dfrac{1}{M_T}\cdot \tanh M_T \\ = \dfrac{1}{M_T}\cdot \dfrac{I_1(2M_T)}{I_0(2M_T)} \\ = \dfrac{1}{M_T}\cdot\left(\dfrac{1}{\tanh 3M_T} - \dfrac{1}{3M_T}\right) \end{cases}$$



$L = z/2$

$L = r/2$

$L = r/3$



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 $\left(\eta = \dfrac{C_{O_2,average}}{C_{O_2,surface}} \right)$.

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 control
      (C_{O2} = constant in particle interior)
   $\eta < 1$ means some pore diffusion resistance
      ($C_{O2,\ avg} < C_{O2,\ surface}$)

4. Since the D_e term contains some temperature dependence, the overall "apparent" activation energy turns out to be $E_a = E_t / 2$

5. η is therefore a function of T_p, d_p, and pore size.

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

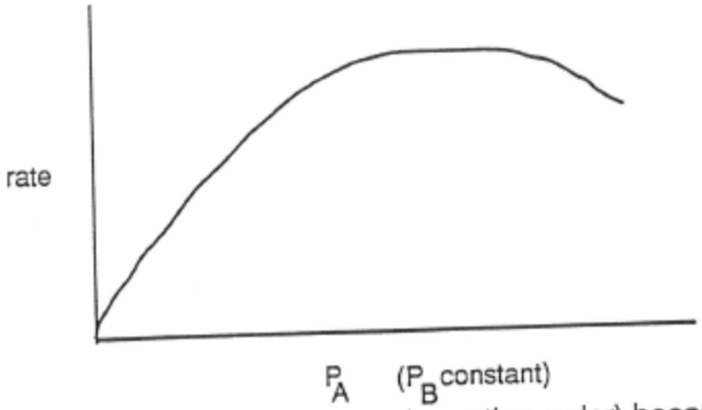
If both A and B compete for the same surface sites

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

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

$$r = k\theta_A\theta_B$$

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

Reading Question 3:

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

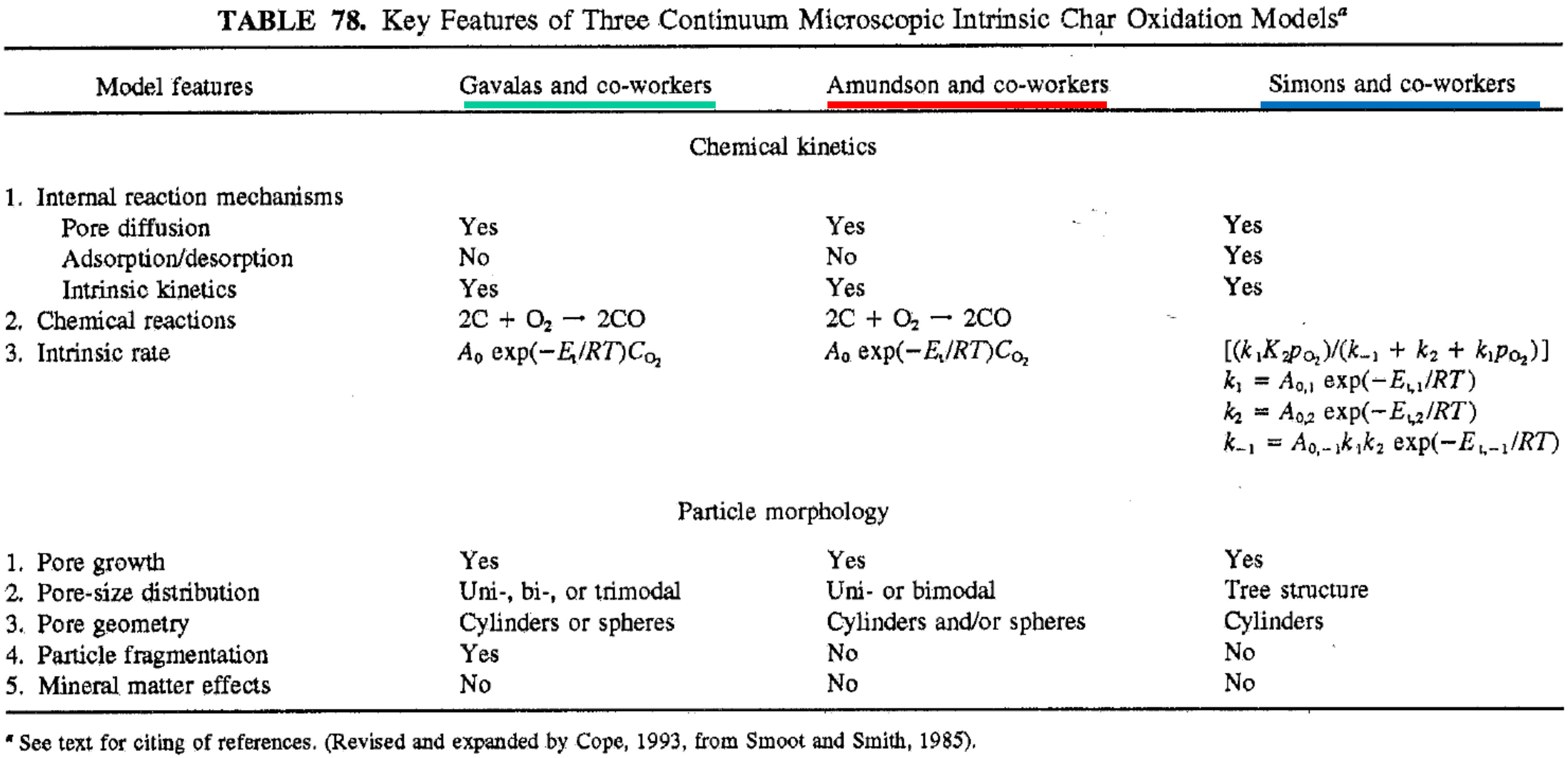
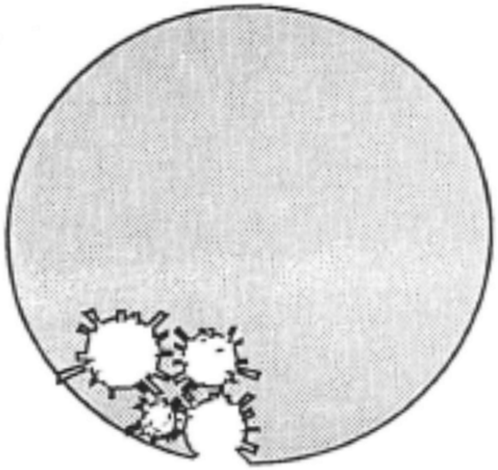


TABLE 78. Key Features of Three Continuum Microscopic Intrinsic Char Oxidation Models[a]

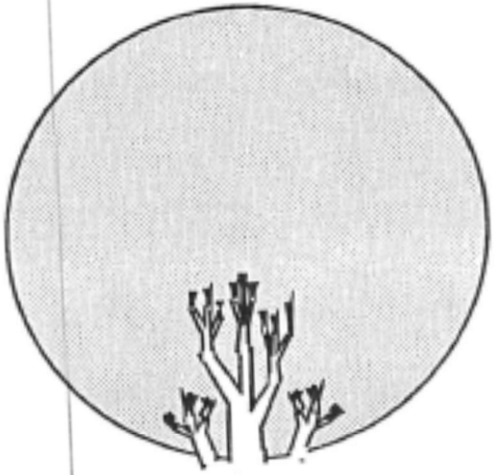
Model features	Gavalas and co-workers	Amundson and co-workers	Simons and co-workers
		Chemical kinetics	
1. Internal reaction mechanisms			
Pore diffusion	Yes	Yes	Yes
Adsorption/desorption	No	No	Yes
Intrinsic kinetics	Yes	Yes	Yes
2. Chemical reactions	$2C + O_2 \rightarrow 2CO$	$2C + O_2 \rightarrow 2CO$	
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).

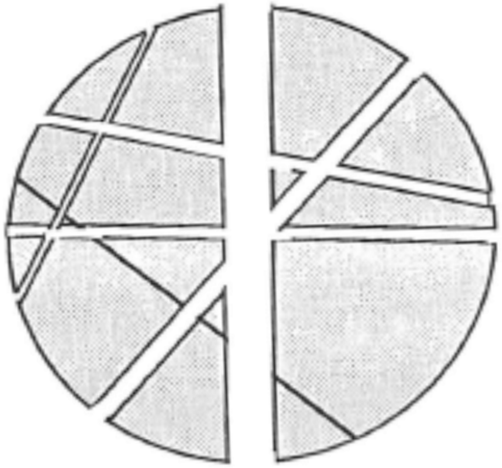
PORE STRUCTURE REPRESENTATIONS IN THREE MICROSCOPIC INTRINSIC MODELS



AMUNDSON



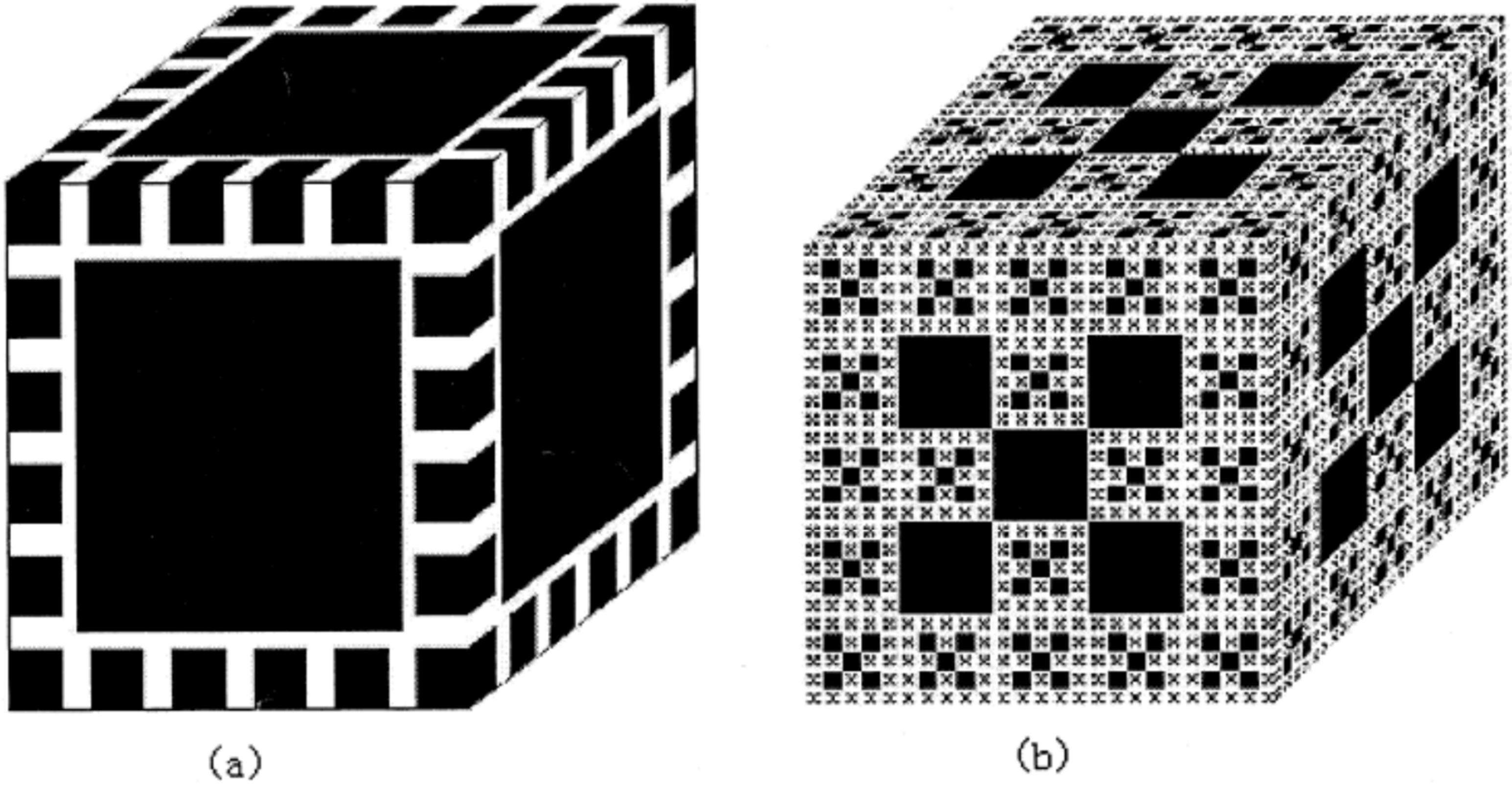
SIMONS
(pore tree model)



GAVALAS
(random pore model)

Microscopic Discrete Models

Fractal Structure of Coal Char *Energy & Fuels, Vol. 16, No. 5, 2002* **1131**

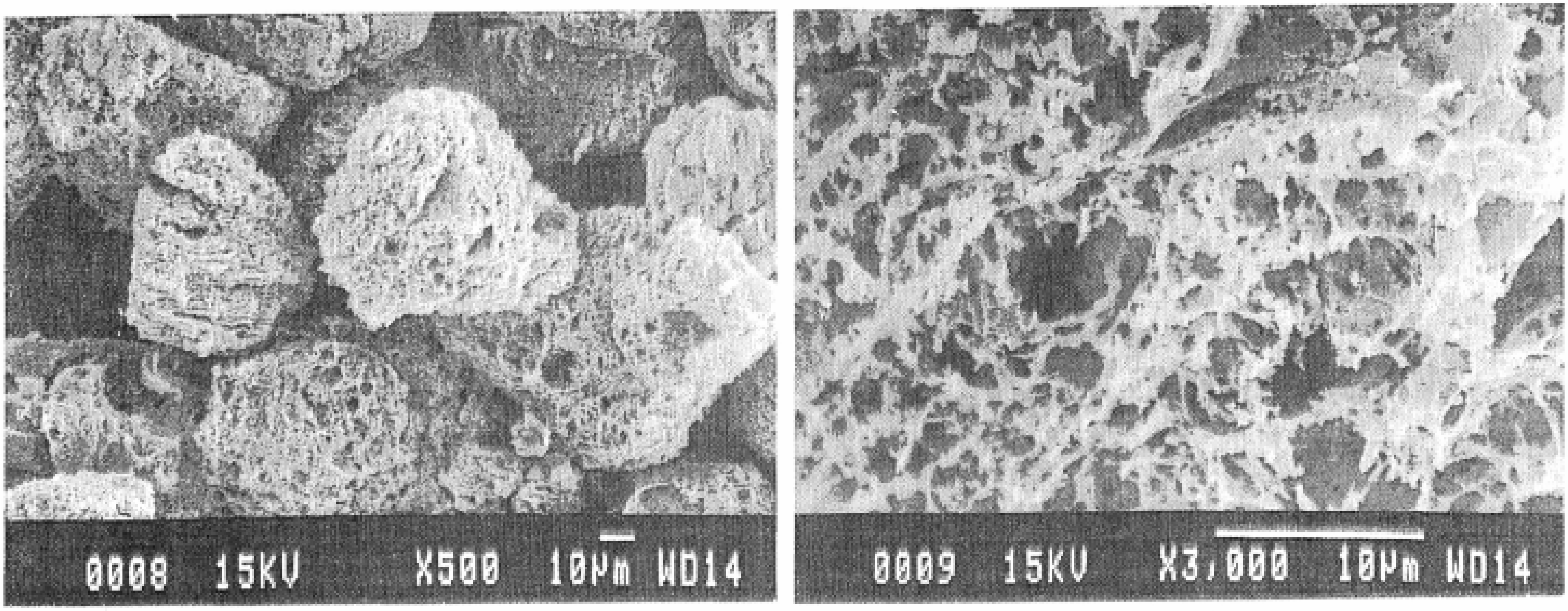


(a) (b)

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

Song, et al.

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

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)
  - CO_2 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)

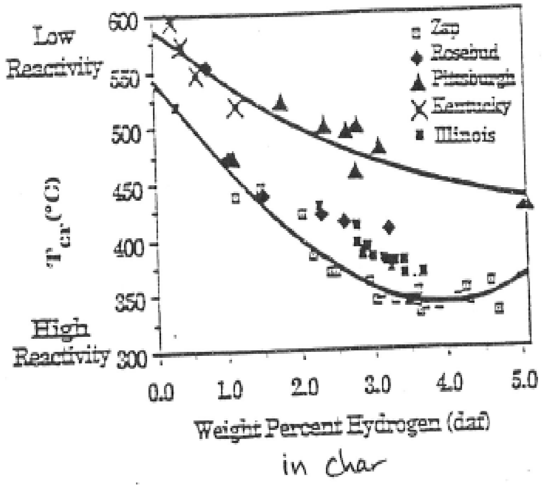


Figure 6.29 Comparison of reactivity for chars from five coals as a function of hydrogen content in the char. Upper line is a best fit of Pittsburgh and Kentucky #9 bituminous chars and the lower line is a best fit of Beulah-Zap lignite chars. The Zap, Pittsburgh and Illinois coal chars are coals from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