Char Oxidation
Char Oxidation Concepts

1. $\chi$
2. CO/CO$_2$ ratio
3. $n^{th}$ order
4. $\alpha$
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
Order of Presentation

1. Basic concepts (film diffusion, surface reaction), $d_p$ & $T$ dependence, CO/CO$_2$ ratio, $\alpha$, $n^{th}$ order, $\chi$, Bob Hurt parameters

2. Intrinsic reactivities, Thiele modulus, Reade-Hecker approach

3. Catalytic effects, pressure effects, correlations vs elemental composition, late burnout
Concepts

• Question 1 (definitions)
  – film diffusion
  – surface reaction
  – pore diffusion

• Question 2 (rate expressions)
  – pure film diffusion control
  – pure surface reaction control

• Question 3 (1st order rate expression)
  – surface rxn = diffusion rate through film
  – Units must match (grams of C reacted/m²·s)
<table>
<thead>
<tr>
<th>Zone</th>
<th>Temperature*</th>
<th>Rxn controlled by</th>
<th>What happens to the particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>Low (ca. 1100 - 1300K)</td>
<td>Intrinsic rxn rate inside pores</td>
<td>Particle burns from inside. Particle density decreases while particle size remains the same.</td>
</tr>
<tr>
<td>Zone 2</td>
<td>Medium (ca. 1300 – 1600K)</td>
<td>Both diffusion &amp; reaction kinetics. Consumption of the reactant gas exceeds the rate of internal diffusion. The reactant is consumed before it reaches the particle core.</td>
<td>Particle burns from both inside and outside. Particle size and density both decrease.</td>
</tr>
<tr>
<td>Zone 3</td>
<td>High (ca.1600 – 2000K and up)**</td>
<td>Film diffusion controls. Reactant gas does not have time to diffuse into the particle before it reacts at the particle surface.</td>
<td>Particle burns from outside. Particle diameter decreases and reactivity/porosity remain constant.</td>
</tr>
</tbody>
</table>
Questions 3-4

3. Derivation of Eq. 6.19

4. What if $n \neq 1$
5. Effects of CO$_2$ Formation at Surface

C + O$_2$ $\rightarrow$ CO$_2$

• Affects the consumption rate of O$_2$
  – More O$_2$ is used per C consumed

• Net heat of reaction increases as CO$_2$ production increases

• CO$_2$ a possibly a gasification agent
Heats of Reaction

- C(s) + ½ O₂ → CO  \( \Delta H_c = -26.4 \text{ kcal/mol of C} \)
- C(s) + O₂ → CO₂  \( \Delta H_c = -94.052 \text{ kcal/mol of C} \)
  EXOTHERMIC!!
- CO + ½O₂ → CO₂  \( \Delta H_c = -67.7 \text{ kcal/mol of C} \)

- In other words,
  - ⅓ of heat for C → CO
  - ⅔ of heat for CO → CO₂
The $\chi$ Factor

• Definition: $\chi = \frac{\dot{r}_p}{\dot{r}_{p,\text{max}}}$

where $\dot{r}_{p,\text{max}}$ is the maximum rate defined by film diffusion limitations

• Useful to know how close you are to the diffusion limit
  – $\chi \implies 1$ when at the diffusion limit
  – $\chi \ll 1$ when controlled by surface reaction
Radial Profiles of $O_2$ Near Particle Surface

Film Diffusion Control

- $P_{O_2}$ vs. Radius
- Note: $P_{O_2,\text{surf}} \rightarrow 0$

Surface Reaction Control

- $P_{O_2}$ vs. Radius
- Note: $P_{O_2,\text{surf}} \rightarrow P_{O_2,\text{bulk gas}}$
Case 1: $T_p$ specified

$$\dot{r}''_p = k_{\text{diff}} \left( \rho_{og} - \rho_{os} \right)$$

$$\dot{r}''_{p,\text{max}} = k_{\text{diff}} \left( \rho_{og} \right)$$

$$\therefore \chi = \frac{k_{\text{diff}} \left( \rho_{og} - \rho_{os} \right)}{k_{\text{diff}} \left( \rho_{og} \right)} = 1 - \frac{\rho_{os}}{\rho_{og}} = 1 - \frac{P_{os} / T_s}{P_{og} / T_g}$$
Case 2: $T_g$ specified

- Constant $T_g$, but $T_p$ changes with $\dot{r}_p''$
- The energy equation becomes:

$$0 = q_c + q_{rad} + \dot{r}_p'' \Delta H_{rxn}$$

- so as $\dot{r}_p''$ increases, the particle temperature increases (at constant $T_g$)

$$\therefore \dot{r}_p', \max = k_{diff} \bigg|_{T_{\max}} \rho_{og}$$

$$\chi = \frac{k_{diff} \left( \rho_{og} - \rho_{os} \right)}{k_{diff',T_{\max}} \left( \rho_{og} \right)}$$
What is the temperature dependence of the film diffusion limited rate?

\[ \dot{r}'' = k_m \rho_{O_2,g} = \frac{2D_{O_2}}{d_p} \rho_{O_2,g} \]

\[ D_{O_2} \sim T^{1.67} \]

\[ \rho_{O_2,g} \sim \frac{1}{T} \]
Char Combustion Zones

- As $\chi \to 1$, Zone III
- As $\chi \to 0$, Zone I
- Everywhere else, Zone II
Particle Energy Balance

\[ m_p C_p \frac{dT_p}{dt} = hA_p \left(T_g - T_p\right) + \sigma \varepsilon_p A_p \left(T_w^4 - T_p^4\right) + \sum r_{p,i} \Delta H_{rxn,i} \]

- We usually assume steady-state for simple problems, so \( \frac{dT_p}{dt} = 0 \)

Driving forces:

Convection  \[ \rightarrow \]  Reaction

\[ T_p \]

\[ T_g \]
Solution Strategy

Guess $T_p$

Iterate to get $r_p$ w/ correction for high mass transfer
  a. For $n=1$, use eqn. in book, iterate on $r_p$
  b. For $n \neq 1$, iterate on $P_{o,s}$ as well

Calculate new $T_p$ from energy balance

$T_{p,old} = T_{p,new}$

no

yes, go to next time step
Shortcuts

• Diffusion coefficients
  – \( \text{Sh} = \frac{k_{\text{diff}} \, d_p}{D_{\text{ox}}} \) ( = 2.0 for small particles)

• How do you get \( D_{\text{ox}} \)?
  – Chapman-Enskog
  – Really \( D_{\text{ox},m} \), but perhaps \( D_{\text{ox},N2} \) might work
TABLE T.6 VISCOSITY, THERMAL CONDUCTIVITY AND DIFFUSION COEFFICIENT PARAMETERS

\[ \nu = b T^{0.6756}, \text{gm/cc-sec} \]
\[ \lambda = c T^{d}, \text{cal/cm-sec-oK} \]
\[ D_i N_2 = f_i N_2 T^{1.67}/P, \text{cm}^2/\text{sec} \]

<table>
<thead>
<tr>
<th>Species ( i )</th>
<th>( b \times 10^6 )</th>
<th>( c \times 10^7 )</th>
<th>( d )</th>
<th>( f_i N_2 \times 10^5 )</th>
<th>Species</th>
<th>( b \times 10^6 )</th>
<th>( c \times 10^7 )</th>
<th>( d )</th>
<th>( f_i N_2 \times 10^5 )</th>
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<tbody>
<tr>
<td>C</td>
<td>3.5360</td>
<td>25.799</td>
<td>0.6507</td>
<td>2.310</td>
<td>C(_2)H(_6)</td>
<td>2.3031</td>
<td>0.3522</td>
<td>1.3129</td>
<td>1.132</td>
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<td>CH</td>
<td>3.2224</td>
<td>14.067</td>
<td>0.7749</td>
<td>2.106</td>
<td>C(_3)H(_4)</td>
<td>1.9712</td>
<td>1.8986</td>
<td>0.9891</td>
<td>0.6163</td>
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<tr>
<td>CN</td>
<td>3.4268</td>
<td>7.5857</td>
<td>0.7761</td>
<td>1.488</td>
<td>H(_2)</td>
<td>1.5426</td>
<td>137.20</td>
<td>0.6484</td>
<td>8.171</td>
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<tr>
<td>CO</td>
<td>3.7486</td>
<td>7.3710</td>
<td>0.7820</td>
<td>1.500</td>
<td>H(_2)(_2)</td>
<td>1.8405</td>
<td>51.840</td>
<td>0.7681</td>
<td>5.525</td>
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<tr>
<td>CH(_2)</td>
<td>2.9280</td>
<td>3.9953</td>
<td>0.9793</td>
<td>1.928</td>
<td>H(_2)N</td>
<td>3.6149</td>
<td>12.567</td>
<td>0.7837</td>
<td>2.050</td>
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<td>CIH(_4)</td>
<td>2.3705</td>
<td>0.7191</td>
<td>1.1179</td>
<td>1.317</td>
<td>H(_2)O</td>
<td>4.1150</td>
<td>14.804</td>
<td>0.7601</td>
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<td>C(_2)I(_2)</td>
<td>3.3357</td>
<td>3.9372</td>
<td>0.8992</td>
<td>1.393</td>
<td>H(_2)N</td>
<td>3.2281</td>
<td>4.7781</td>
<td>0.9370</td>
<td>1.865</td>
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<tr>
<td>CO(_2)</td>
<td>3.6078</td>
<td>2.3291</td>
<td>0.9386</td>
<td>1.191</td>
<td>H(_2)O</td>
<td>0.5083</td>
<td>0.8304</td>
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<td>C(_2)I(_3)</td>
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<td>1.9829</td>
<td>0.9998</td>
<td>1.781</td>
<td>H(_3)N</td>
<td>3.4436</td>
<td>0.5748</td>
<td>1.2642</td>
<td>1.849</td>
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<tr>
<td>C(_2)I(_4)</td>
<td>2.5100</td>
<td>1.1111</td>
<td>1.1778</td>
<td>1.658</td>
<td>N</td>
<td>3.4672</td>
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<td>0.6581</td>
<td>2.089</td>
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<td>C(_2)</td>
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<td>1.1111</td>
<td>1.1778</td>
<td>1.658</td>
<td>N(_2)</td>
<td>3.6974</td>
<td>7.6893</td>
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<td>1.488</td>
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<tr>
<td>C(_2)H(_2)</td>
<td>2.5100</td>
<td>1.1111</td>
<td>1.1778</td>
<td>1.658</td>
<td>NO</td>
<td>4.1530</td>
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<td>0.7870</td>
<td>1.550</td>
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<td>C(_2)H(_3)</td>
<td>2.5436</td>
<td>0.5798</td>
<td>1.2231</td>
<td>1.260</td>
<td>NO(_2)</td>
<td>3.7247</td>
<td>3.9255</td>
<td>0.8565</td>
<td>1.187</td>
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<td>C(_2)H(_4)</td>
<td>2.5163</td>
<td>0.5798</td>
<td>1.2231</td>
<td>1.229</td>
<td>O</td>
<td>4.0387</td>
<td>22.219</td>
<td>0.6547</td>
<td>2.076</td>
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<tr>
<td>C(_2)H(_5)</td>
<td>2.4062</td>
<td>0.3522</td>
<td>1.3129</td>
<td>1.179</td>
<td>O(_2)</td>
<td>4.4203</td>
<td>7.1352</td>
<td>0.7968</td>
<td>1.523</td>
</tr>
</tbody>
</table>
Diameter & Density Changes

\[
\frac{m}{m_0} = \frac{\rho}{\rho_0} \left( \frac{d}{d_0} \right)^3
\]

- We get \( m/m_0 \) from the rate equation, but this does not tell us whether we have:
  - constant density burning
  - constant diameter burning
  - some combination

- Let’s define a variable called \( \alpha \) as follows:

\[
\frac{\rho}{\rho_0} = \left( \frac{m}{m_0} \right)^\alpha
\]
Diameter vs Density (cont)

- $\alpha$ is the burning mode parameter
  - For constant density, $\alpha = 0$
  - For constant diameter, $\alpha = 1$

- Combining definitions,
  
  $$\frac{m}{m_0} = \left(\frac{m}{m_0}\right)^{\alpha} \left(\frac{d}{d_0}\right)^3$$

  which simplifies to:

  $$\left(\frac{m}{m_0}\right)^{1-\alpha} = \left(\frac{d}{d_0}\right)^3$$

  and then

  $$\frac{d}{d_0} = \left(\frac{m}{m_0}\right)^{\frac{1-\alpha}{3}}$$
Bob Hurt Model (CBK)

(Question 7)
Table 2.2 Char Combustion Parameters and Selected Properties for the Suite of Coals Investigated

<table>
<thead>
<tr>
<th>Seam Name; PETC Designation</th>
<th>Reporte d Rank (ASTM)</th>
<th>% Vol. Matter (dmmf)</th>
<th>Calorific Val. mmf eq. moist (kJ/gm)</th>
<th>Elemen. Carbon Content (wt-%)</th>
<th>Preexp. Factor, A (g-carb./cm²-s-atm0.5)</th>
<th>Activation Energy E (kcal/mol)</th>
<th>Product Ratio Correlation</th>
<th>Physical mode of burning θ</th>
<th>Combustion Parameters θ</th>
<th>Characteristics θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pocahontas #3</td>
<td>low vol. bitum.</td>
<td>16.21</td>
<td>35.74</td>
<td>89.0</td>
<td>114</td>
<td>30.0</td>
<td>1</td>
<td>0.3</td>
<td>1.21</td>
<td>0.63</td>
</tr>
<tr>
<td>Low. Kittanning</td>
<td>low vol. bitum.</td>
<td>18.55</td>
<td>34.84</td>
<td>82.8</td>
<td>10.5</td>
<td>20.5</td>
<td>2</td>
<td>0.0</td>
<td>1.27</td>
<td>0.48</td>
</tr>
<tr>
<td>Pittsburgh #8</td>
<td>hvA bitum.</td>
<td>38.81</td>
<td>34.18</td>
<td>82.6</td>
<td>29</td>
<td>24</td>
<td>3</td>
<td>0.1</td>
<td>1.1</td>
<td>0.40</td>
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<tr>
<td>Hiawatha</td>
<td>hvC bitum.</td>
<td>44.24</td>
<td>29.39</td>
<td>79.6</td>
<td>*</td>
<td>*</td>
<td>1</td>
<td>0.1</td>
<td>1.16</td>
<td>0.44</td>
</tr>
<tr>
<td>Illinois #6</td>
<td>hvC bitum.</td>
<td>42.91</td>
<td>29.18</td>
<td>78.2</td>
<td>22.4</td>
<td>22.5</td>
<td>4</td>
<td>0.45*</td>
<td>1.06*</td>
<td>0.39*</td>
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<tr>
<td>Blue #1</td>
<td>hvC bitum.</td>
<td>47.86</td>
<td>27.81</td>
<td>77.9</td>
<td>3.8</td>
<td>15.3</td>
<td>1</td>
<td>0.25</td>
<td>1.16</td>
<td>0.26</td>
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<tr>
<td>Dietz</td>
<td>Subbit.</td>
<td>43.88</td>
<td>23.13</td>
<td>74.4</td>
<td>*</td>
<td>*</td>
<td>5</td>
<td>0.25</td>
<td>1.04</td>
<td>0.41</td>
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<tr>
<td>Smith-Roland</td>
<td>Subbit.</td>
<td>61.96</td>
<td>21.48</td>
<td>66.4</td>
<td>*</td>
<td>*</td>
<td>2</td>
<td>0.3</td>
<td>0.85</td>
<td>0.62</td>
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<tr>
<td>Lower Wilcox</td>
<td>Lignite A</td>
<td>78.22</td>
<td>17.88</td>
<td>67.9</td>
<td>44</td>
<td>21.9</td>
<td>5</td>
<td>0.12</td>
<td>0.92</td>
<td>0.68</td>
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<tr>
<td>Beulah</td>
<td>Lignite A</td>
<td>45.73</td>
<td>17.26</td>
<td>63.0</td>
<td>*</td>
<td>*</td>
<td>2</td>
<td>0.2</td>
<td>0.92</td>
<td>0.63</td>
</tr>
</tbody>
</table>

* Combustion rates of chars from these coals are limited by the rate of diffusion of oxygen from the bulk gas to the particle surface (Zone 3 combustion) under the experimental conditions.
** Values for 75 - 106 μm size fraction. (All others are for 106 - 125 μm size fraction.)
† CO/CO₂ product ratio under the experimental conditions correlated by the empirical relation: (moles-CO)/(moles-CO₂) = Aₑ exp(-Eₑ/RTₚ). Correlation type 1: Aₑ = 3 x 10⁸, Eₑ = 60 kcal/mol; 2: CO only; 3: Aₑ = 4 x 10⁵, Eₑ = 30 kcal/mol; 4: Aₑ = 2.5 x 10⁸, Eₑ = 60 kcal/mol; 5: Aₑ = 5 x 10⁸, Eₑ = 60 kcal/mol. These values are to be regarded as empirical parameters useful only for the prediction of char combustion rates in the range of gas environments investigated.
†† Burning rates in 6 mole-% oxygen at 1500 K gas temperature with radiation to cold walls (g-carbon/s-cm²-external surface)
††† Characteristic time for 50 wt-% carbon conversion of char (volatile matter free basis) in 6 mole-% oxygen at 1500 K gas temperature with radiation to cold walls. Values computed for each coal from Aₑ, n, A₉, Eₑ, α, ω, and ρₑ₀.

From Hurt and Mitchell, 1992
Figure 2. The Sandia Coal Char Reactivity Correlation. *Closed symbols:* measured values of $k_{1750}$ and $E$; *Open symbols:* lower limits on $k_{1750}$ determined for those chars reacting at diffusion-limited rates during kinetic experiments.
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. △ - 1500 K gas temperature, ○ - 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 \( A_{\text{c}} = 3 \times 10^8 \) and \( E_{\text{c}} = 60 \text{ kcal/mol} \).
Figure 113. Average cluster molecular weights in coals and chars collected in the 1250 K gas condition in the Sandia Coal Devolatilization Laboratory (CDL), determined from $^{13}$C NMR analyses. Parent coals are represented at 0-ms residence time (Fletcher et al., 1992b; Fletcher and Hardesty, 1992). Four-digit numbers refer to PSOC number (Penn State Data Base) (Fletcher et al., 1992b).

Figure 114. Average molecular weight of attachments to aromatic clusters in unreacted and fully devolatilized coals as a function of coal type. Data for non-Sandia coals are taken from Solum et al. (1989a). Fully devolatilized chars are from the longest residence time ($\sim 250$ ms) in the 1250 K gas condition in the Sandia CDL (Fletcher et al., 1992b; Fletcher and Hardesty, 1992).
Question 8
(1800 K, 10 mol% O₂)

What is the point?
Question 9a

What is the point?
Question 9a

What is the point?
Question 9a

What is the point?
Problem 10

10% O₂, T₉=1800 K

Chi Factor vs Diameter (microns)

Particle Temperature (K) vs Diameter (microns)