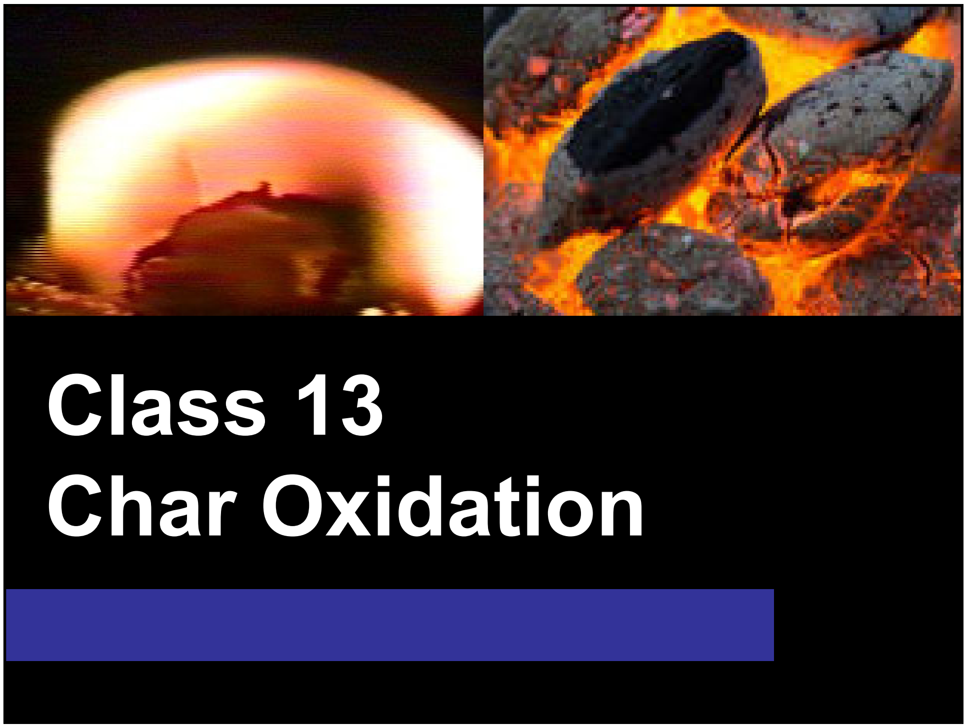


Class 13
Char Oxidation

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

Order of Presentation

1. Basic concepts (film diffusion, surface reaction), d_p & T dependence, CO/CO_2 ratio, α, n^{th} order, χ, 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 (1^{st} order rate expression)
  - surface rxn = diffusion rate through film
  - Units must match (grams of C reacted/$m^2 \cdot s$)

	Temperature*	Rxn controlled by	What happens to the particle
Zone 1	Low (ca. 1100 - 1300K)	Intrinsic rxn rate inside pores	Particle burns from inside. Particle density decreases while particle size remains the same.
Zone 2	Medium (ca. 1300 – 1600K)	Both diffusion & reaction kinetics. Consumption of the reactant gas exceeds the rate of internal diffusion. The reactant is consumed before it reaches the particle core.	Particle burns from both inside and outside. Particle size and density both decrease.
Zone 3	High (ca.1600 – 2000K and up)**	Film diffusion controls. Reactant gas does not have time to diffuse into the particle before it reacts at the particle surface.	Particle burns from outside. Particle diameter decreases and reactivity/porosity remain constant.

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

- $C(s) + \frac{1}{2} O_2 \rightarrow CO$ $\Delta H_c = -26.4$ kcal/mol of C
- $C(s) + O_2 \rightarrow CO_2$ $\Delta H_c = -94.052$ kcal/mol of C

EXOTHERMIC!!

- $CO + \frac{1}{2}O_2 \rightarrow CO_2$ $\Delta H_c = -67.7$ kcal/mol of C

- In other words,
  - ⅓ of heat for C → CO
  - ⅔ of heat for $CO \rightarrow CO_2$

Should the heat of reaction for char be the same as graphite?

The χ Factor

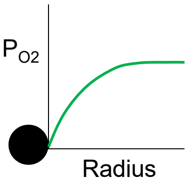
- Definition: $\chi = \dot{r}_p / \dot{r}_{p,\max}$

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

- Useful to know how close you are to the diffusion limit
  - χ ==> 1 when at the diffusion limit
  - χ << 1 when controlled by surface reaction

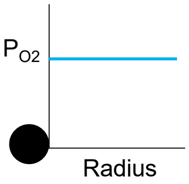
Radial Profiles of O_2 Near Particle Surface

Film Diffusion Control



Note: $P_{O2,surf} \rightarrow 0$

Surface Reaction Control



Note: $P_{O2,surf} \rightarrow P_{O2,bulk\ gas}$

Case 1: T_p specified

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

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

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

$$\rho_{os} = density\ at\ surface = \frac{\mathrm{P_{os}} \cdot \mathrm{MW_{os}}}{R \cdot T_s}$$

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)

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

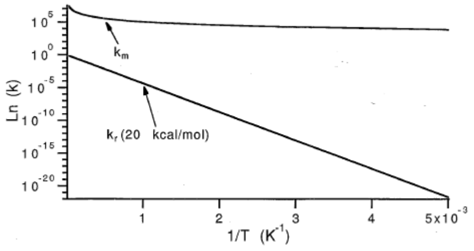
$$\chi = \frac{k_{diff}\left(\rho_{og} - \rho_{os}\right)}{k_{diff,T_{\max}}\left(\rho_{og}\right)}$$

What is the temperature dependence of the film diffusion limited rate?

$$\dot{r}''_{O2} = k_m \rho_{O2,g} = \frac{2D_{O2}}{d_p}\rho_{O2,g}$$

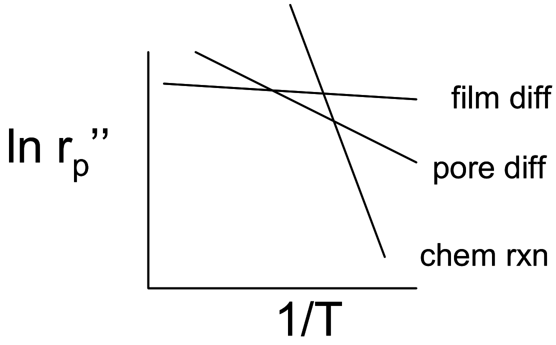
$$D_{O2} \sim T^{1.67}$$

$$\rho_{O2,g} \sim \frac{1}{T}$$



Char Combustion Zones

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

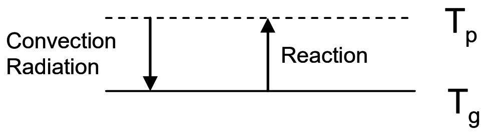


Particle Energy Balance

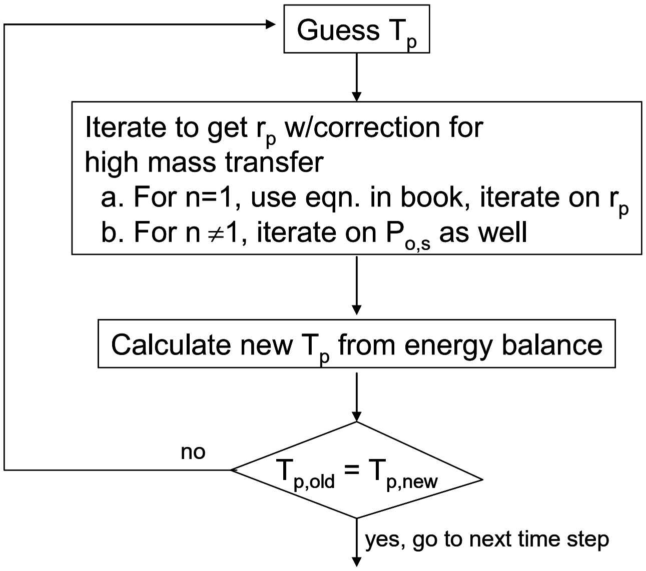
$$m_p C_p \frac{dT_p}{dt} = hA_p\left(T_g - T_p\right) + \sigma\varepsilon_p A_p\left(T_w^4 - T_p^4\right) + \sum r_{p,i}\Delta H_{rxn,i}$$

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

Driving forces:



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 ≠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
  - – $Sh = k_{diff}\, d_p / \mathscr{D}_{ox}$ (= 2.0 for small particles)
- How do you get $\mathscr{D}_{ox}$?
  - – Chapman-Enskog
  - – Really $\mathscr{D}_{ox,m}$, but perhaps $\mathscr{D}_{ox,N2}$ might work

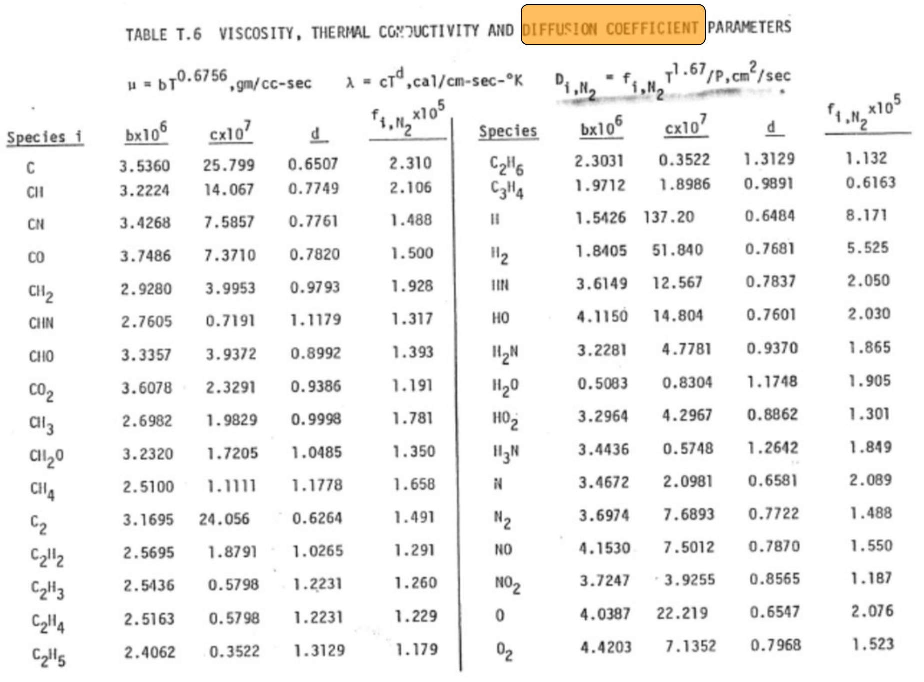


TABLE T.6 VISCOSITY, THERMAL CONDUCTIVITY AND DIFFUSION COEFFICIENT PARAMETERS

$\mu = bT^{0.6756}$, gm/cc-sec $\lambda = cT^{d}$, cal/cm-sec-°K $D_{i,N_2} = f_{i,N_2} T^{1.67}/P$, cm²/sec

Species i	$b \times 10^6$	$c \times 10^7$	d	$f_{i,N_2} \times 10^5$	Species	$b \times 10^6$	$c \times 10^7$	d	$f_{i,N_2} \times 10^5$
C	3.5360	25.799	0.6507	2.310	C_2H_6	2.3031	0.3522	1.3129	1.132
CH	3.2224	14.067	0.7749	2.106	C_3H_4	1.9712	1.8986	0.9891	0.6163
CN	3.4268	7.5857	0.7761	1.488	H	1.5426	137.20	0.6484	8.171
CO	3.7486	7.3710	0.7820	1.500	H_2	1.8405	51.840	0.7681	5.525
CH_2	2.9280	3.9953	0.9793	1.928	HN	3.6149	12.567	0.7837	2.050
CHN	2.7605	0.7191	1.1179	1.317	HO	4.1150	14.804	0.7601	2.030
CHO	3.3357	3.9372	0.8992	1.393	H_2N	3.2281	4.7781	0.9370	1.865
CO_2	3.6078	2.3291	0.9386	1.191	H_2O	0.5083	0.8304	1.1748	1.905
CH_3	2.6982	1.9829	0.9998	1.781	HO_2	3.2964	4.2967	0.8862	1.301
CH_2O	3.2320	1.7205	1.0485	1.350	H_3N	3.4436	0.5748	1.2642	1.849
CH_4	2.5100	1.1111	1.1778	1.658	N	3.4672	2.0981	0.6581	2.089
C_2	3.1695	24.056	0.6264	1.491	N_2	3.6974	7.6893	0.7722	1.488
C_2H_2	2.5695	1.8791	1.0265	1.291	NO	4.1530	7.5012	0.7870	1.550
C_2H_3	2.5436	0.5798	1.2231	1.260	NO_2	3.7247	3.9255	0.8565	1.187
C_2H_4	2.5163	0.5798	1.2231	1.229	O	4.0387	22.219	0.6547	2.076
C_2H_5	2.4062	0.3522	1.3129	1.179	O_2	4.4203	7.1352	0.7968	1.523

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 α as follows:

$$\frac{\rho}{\rho_0} = \left(\frac{m}{m_0}\right)^\alpha$$

Diameter vs Density (cont)

- α 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

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

Bob Hurt Model (CBK)

(Question 7)

CO/CO_2 ratio

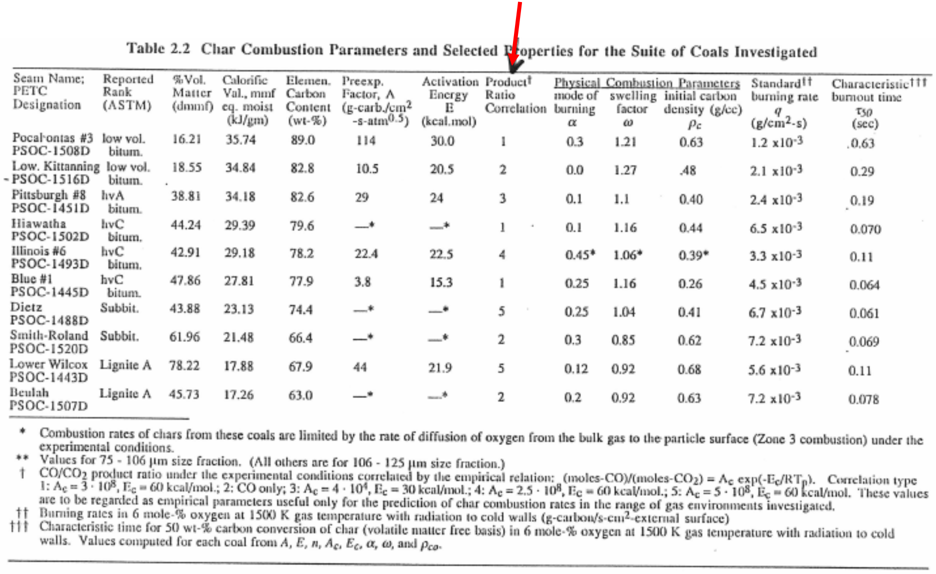


Table 2.2 Char Combustion Parameters and Selected Properties for the Suite of Coals Investigated

Seam Name; PETC Designation	Reported Rank (ASTM)	%Vol. Matter (dmmf)	Calorific Val., mmf eq. moist (kJ/gm)	Elemen. Carbon Content (wt-%)	Preexp. Factor, A (g-carb./cm^2-s-$atm^{0.5}$)	Activation Energy E (kcal.mol)	Product† Ratio Correlation	Physical Combustion Parameters			Standard†† burning rate q (g/cm^2-s)	Characteristic††† burnout time τ_{50} (sec)
								mode of burning α	swelling factor ω	initial carbon density (g/cc) ρ_c		
Pocahontas #3 PSOC-1508D	low vol. bitum.	16.21	35.74	89.0	114	30.0	1	0.3	1.21	0.63	1.2×10^{-3}	0.63
Low. Kittanning PSOC-1516D	low vol. bitum.	18.55	34.84	82.8	10.5	20.5	2	0.0	1.27	.48	2.1×10^{-3}	0.29
Pittsburgh #8 PSOC-1451D	hvA bitum.	38.81	34.18	82.6	29	24	3	0.1	1.1	0.40	2.4×10^{-3}	0.19
Hiawatha PSOC-1502D	hvC bitum.	44.24	29.39	79.6	—*	—*	1	0.1	1.16	0.44	6.5×10^{-3}	0.070
Illinois #6 PSOC-1493D	hvC bitum.	42.91	29.18	78.2	22.4	22.5	4	0.45*	1.06*	0.39*	3.3×10^{-3}	0.11
Blue #1 PSOC-1445D	hvC bitum.	47.86	27.81	77.9	3.8	15.3	1	0.25	1.16	0.26	4.5×10^{-3}	0.064
Dietz PSOC-1488D	Subbit.	43.88	23.13	74.4	—*	—*	5	0.25	1.04	0.41	6.7×10^{-3}	0.061
Smith-Roland PSOC-1520D	Subbit.	61.96	21.48	66.4	—*	—*	2	0.3	0.85	0.62	7.2×10^{-3}	0.069
Lower Wilcox PSOC-1443D	Lignite A	78.22	17.88	67.9	44	21.9	5	0.12	0.92	0.68	5.6×10^{-3}	0.11
Beulah PSOC-1507D	Lignite A	45.73	17.26	63.0	—*	—*	2	0.2	0.92	0.63	7.2×10^{-3}	0.078

* 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.)

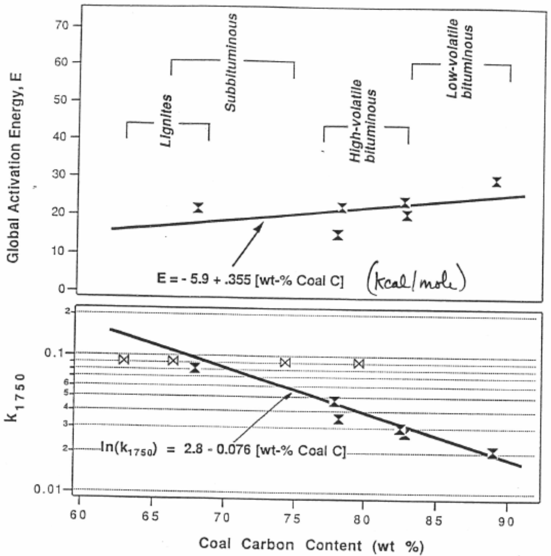
† CO/CO_2 product ratio under the experimental conditions correlated by the empirical relation: (moles-CO)/(moles-CO_2) = $A_c \exp(-E_c/RT_p)$. Correlation type 1: $A_c = 3 \cdot 10^8$, $E_c = 60$ kcal/mol.; 2: CO only; 3: $A_c = 4 \cdot 10^4$, $E_c = 30$ kcal/mol.; 4: $A_c = 2.5 \cdot 10^8$, $E_c = 60$ kcal/mol.; 5: $A_c = 5 \cdot 10^8$, $E_c = 60$ 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-cm^2-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 A, E, n, A_c, E_c, α, ω, and ρ_{co}.

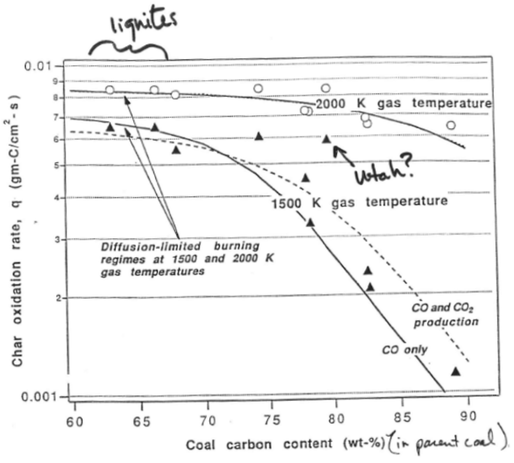
From Hurt and Mitchell, 1992

Question 7



1/2 order, $\frac{g}{cm^2 s}$ and atm, K $\ln(A) = \ln k_{1750} + \frac{E/R}{1750}$

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.



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.

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).

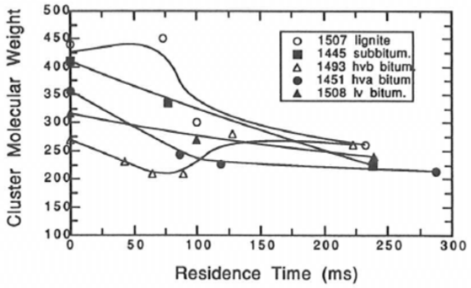
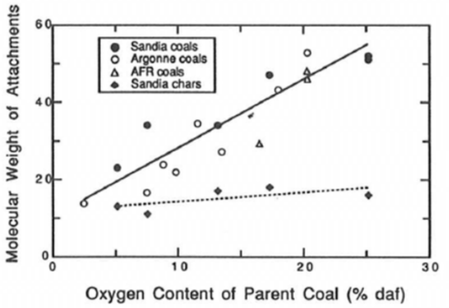
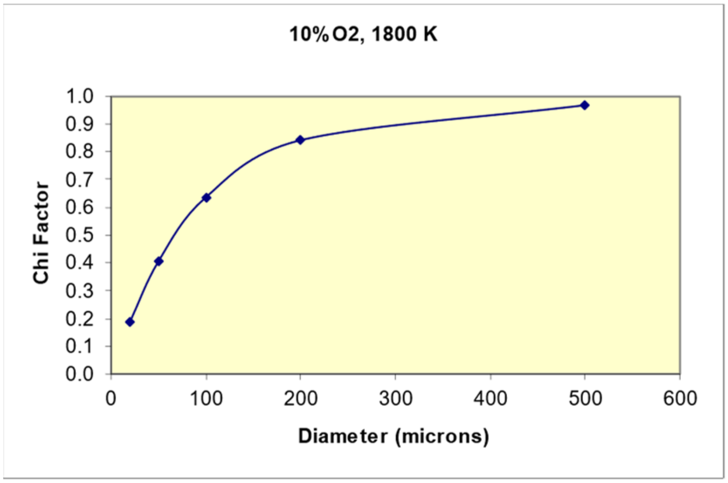


Figure 114. Average molecular weight of attachments to aromatic clusters in unreacted and fully devolatilized coals as a function of coal type. Data for non-Sandia coals are taken from Solum *et al.* (1989a). Fully devolatilized chars are from the longest residence time (~250 ms) in the 1250 K gas condition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



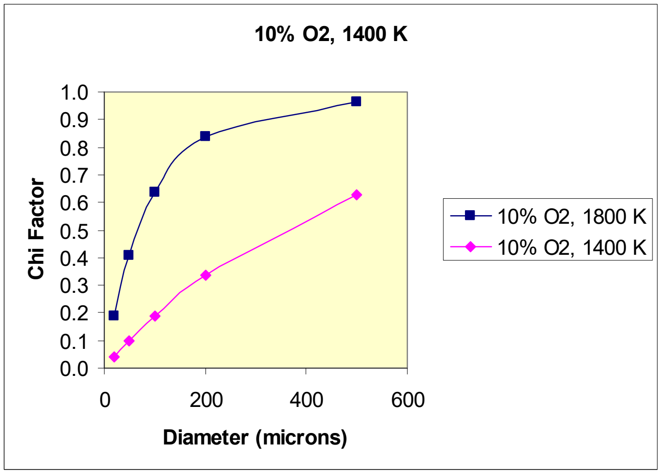
Question 8

(1800 K, 10 mol% O_2)



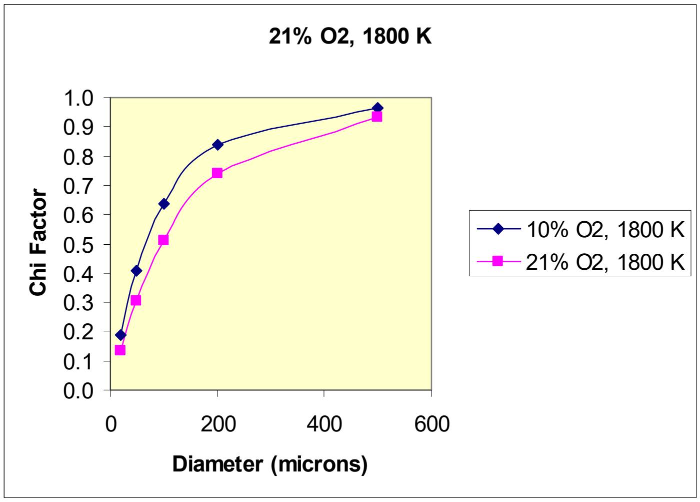
- **What is the point?**

Question 9a



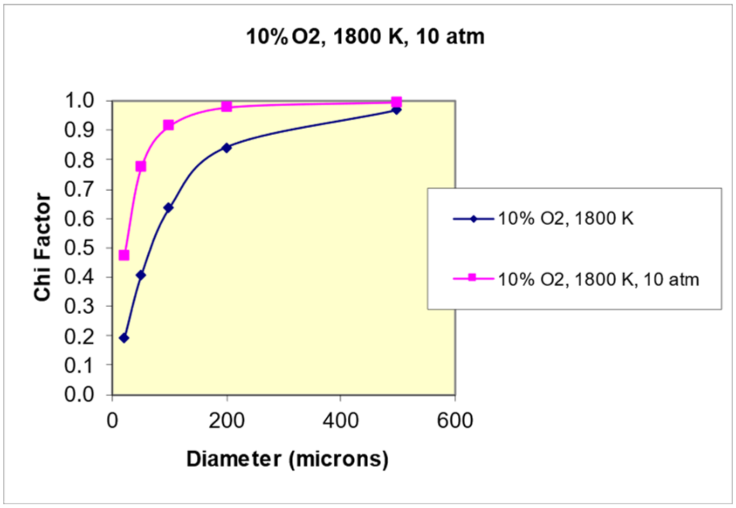
- What is the point?

Question 9b



- What is the point?

Question 9c



- What is the point?

Problem 10