Class 4

Physical Properties of Coal

Reading Assignment:

a. **Lee Smith Book, 154-168**
b. **Article by Merrick (*Fuel*, 62, 540-546, 1983)**

1. Discuss Figure 4.50 in the Lee Smith book.
2. What is meant by porosity, true density, apparent density, and internal surface area? Why are these quantities important in coal combustion? How do they vary as a function of coal rank? How do the these properties vary between chars and coals?
3. Please use your group to find and discuss the model proposed by Merrick for heat capacity.
4. Please show the transient particle energy equation in terms of particle temperature, with appropriate terms for a single coal particle injected into a hot inert gas. Be prepared to describe all of the terms, including thermal radiation.
5. Please compute the number distribution (# vs. diameter in microns) for the following mass distribution:

Mesh Size (passing)	400	325	270	250	200	170	150
Weight (%)	5	10	20	30	20	10	5

6. Please compute the heat capacity in J/kg/K of the dried Argonne Premium Wyodak coal at temperatures from 300 K to 700 K.

Figure 4.50

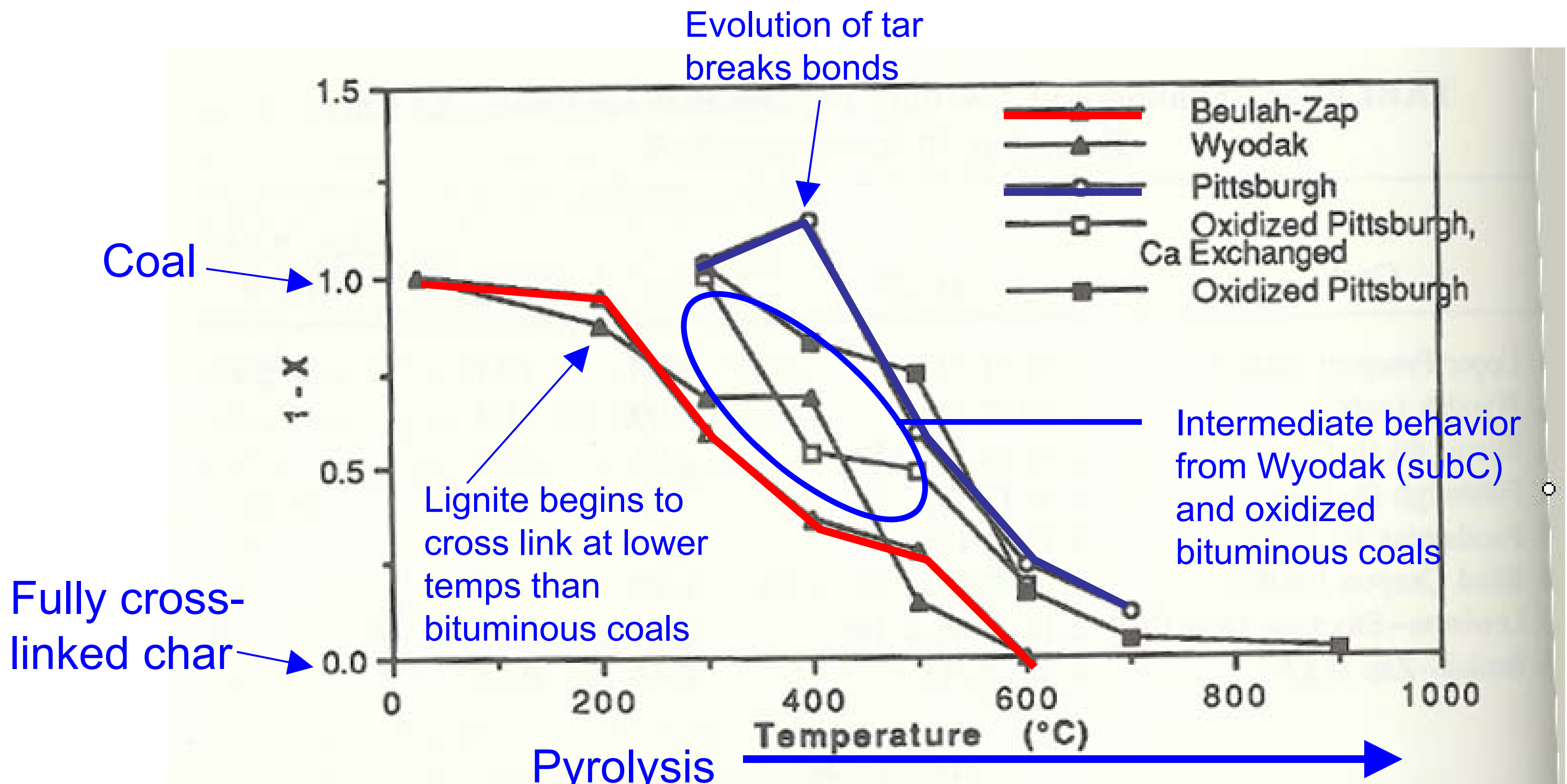


Figure 50. Comparison of solvent-swelling ratios for some Argonne premium coals at a series of pyrolysis final temperatures. Effects of oxidation and minerals on cross-linking behavior are shown for the Pittsburgh coal. The Beulah–Zap and Wyodak coals were pyrolyzed with a heating rate of 30 K/min while the Pittsburgh coal sample were pyrolyzed with a heating rate of 0.5 K/s (Solomon *et al.*, 1990).

Particle Densities

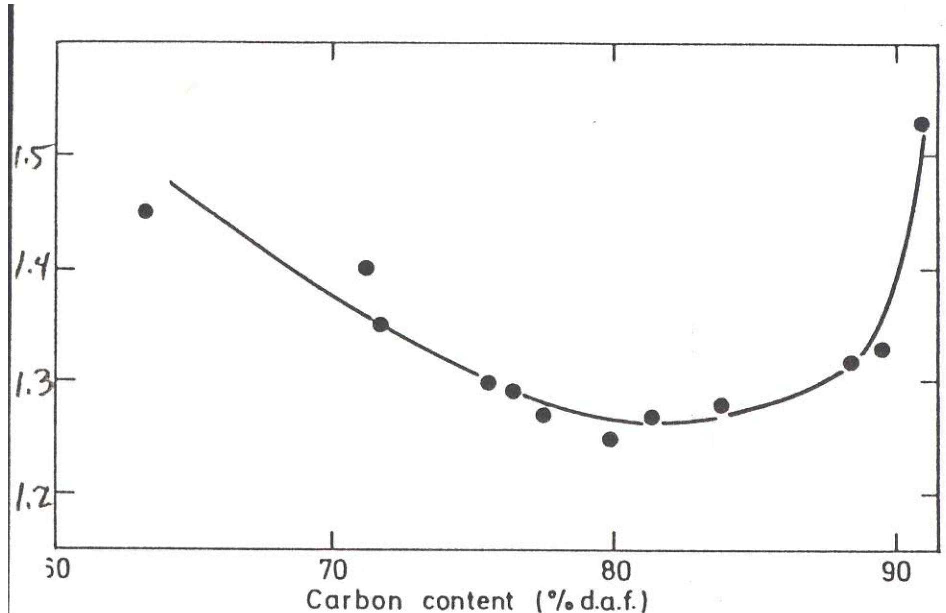
1. True Density
   (He pyncnometry)
   $$\frac{mass\ of\ \ solid}{volume\ of\ \ solid}$$

2. Apparent Density
   $$\frac{mass\ of\ \ solid}{volume\ of\ \ solid\ + volume\ of\ \ voids\ in\ solid}$$

3. Bulk Density
   $$\frac{mass\ of\ \ solid}{volume\ of\ \ bed}$$

   $V_{bed} = V_{solid} + V_{voids\ in\ solid} + V_{voids\ between\ particles}$

True Particle Densities



ıre 2 Variation of helium density of coals with carbon content

From Gan et al. Fuel, Vol. 51 (1972)

Apparent Densities

- Hg porosimetry
  - Measure change in Hg volume as pressure increases
  - Interpret volume change
- Tap density
  - Weigh particles
  - Place in graduated cylinder
  - Tap to settle particles
  - Assume packing factor
  - Ratio of bulk densities ($\rho_b / \rho_{b,0}$) equals ratio of apparent densities ($\rho_a / \rho_{a,0}$)

MICROMERITICS AUTO-PORE 9200 V2.03

New Mexico Blue Subbituminous

T.FLETCHER
REQ88423 COAL T103 PSOC 1445 HIGH TEMP
PNTR NUMBER +882 1250 K, 70 mm

LP 11:19:50 5/18/88
HP 15:6:54 5/18/88

PRESSURE PSIA	PORE DIAMETER MICRO-M	INTRUSION VOLUME CC/G	PORE SURFACE SQ-M/G	MEAN DIAMETER MICRO-M	DV
+1.4	+129.6650	+0.0000	+0.0000	+129.6650	+0.0000
+1.7	+107.5830	+0.0139	+0.0005	+118.6240	+0.0139
+2.0	+90.9093	+0.0510	+0.0020	+99.2459	+0.0371
+2.7	+67.4971	+0.1205	+0.0055	+79.2031	+0.0695
+4.0	+45.4547	+0.6439	+0.0425	+56.4758	+0.5234
+5.3	+34.3604	+1.2739	+0.1057	+39.9075	+0.6300
+7.9	+22.7483	+1.5055	+0.1381	+28.5543	+0.2316
+9.6	+18.8785	+1.5426	+0.1453	+20.8134	+0.0371
+11.9	+15.1051	+1.5704	+0.1518	+16.9918	+0.0278
+12.8	+14.0699	+1.5843	+0.1556	+14.5875	+0.0139
+13.9	+12.9734	+1.5936	+0.1584	+13.5216	+0.0093
+16.4	+11.0279	+1.6029	+0.1615	+12.0006	+0.0093
+20.8	+8.6932	+1.6215	+0.1690	+9.8605	+0.0186
+23.9	+7.5433	+1.6354	+0.1759	+8.1182	+0.0139
+25.7	+7.0333	+1.6354	+0.1759	+7.2883	+0.0000
+28.9	+6.2484	+1.6355	+0.1759	+6.6409	+0.0000
+33.5	+5.3881	+1.6402	+0.1791	+5.8183	+0.0047
+40.1	+4.5020	+1.6402	+0.1792	+4.9450	+0.0001
+45.6	+3.9596	+1.6450	+0.1836	+4.2308	+0.0047
+51.6	+3.4946	+1.6682	+0.2086	+3.7271	+0.0232
+60.8	+2.9693	+1.7007	+0.2489	+3.2320	+0.0325
+76.7	+2.3527	+1.7612	+0.3397	+2.6610	+0.0604
+93.9	+1.9222	+1.8124	+0.4355	+2.1375	+0.0512
+118.2	+1.5264	+1.8868	+0.6082	+1.7243	+0.0744
+140.6	+1.2834	+1.9334	+0.7409	+1.4049	+0.0466
+183.0	+0.9863	+2.0081	+1.0040	+1.1349	+0.0747
+232.6	+0.7760	+2.0782	+1.3222	+0.8812	+0.0701
+267.7	+0.6742	+2.1064	+1.4779	+0.7251	+0.0282
+334.2	+0.5400	+2.1627	+1.8492	+0.6071	+0.0564
+429.0	+0.4207	+2.2147	+2.2823	+0.4804	+0.0520
+530.5	+0.3402	+2.2621	+2.7805	+0.3805	+0.0474
+637.9	+0.2829	+2.2956	+3.2104	+0.3116	+0.0335
+800.1	+0.2256	+2.3295	+3.7440	+0.2543	+0.0339
+988.6	+0.1826	+2.3635	+4.4105	+0.2041	+0.0340
+1214.2	+0.1486	+2.3930	+5.1229	+0.1656	+0.0295
+1516.0	+0.1191	+2.4228	+6.0134	+0.1339	+0.0298
+1903.8	+0.0948	+2.4436	+6.7893	+0.1069	+0.0207
+2354.1	+0.0767	+2.4689	+7.9706	+0.0857	+0.0253
+2908.0	+0.0621	+2.4850	+8.8989	+0.0694	+0.0161
+3603.0	+0.0501	+2.5057	+10.3792	+0.0561	+0.0208
+4562.9	+0.0396	+2.5220	+11.8322	+0.0448	+0.0163
+5576.2	+0.0324	+2.5378	+13.5914	+0.0360	+0.0158
+6857.8	+0.0263	+2.5536	+15.7365	+0.0293	+0.0157
+8646.0	+0.0209	+2.5693	+18.4062	+0.0236	+0.0157
+10613.1	+0.0170	+2.5847	+21.6436	+0.0189	+0.0153
+13176.2	+0.0137	+2.5998	+25.6000	+0.0154	+0.0152
+16484.5	+0.0109	+2.6148	+30.4615	+0.0123	+0.0150
+20493.1	+0.0088	+2.6342	+38.2900	+0.0099	+0.0193

Interparticle ↑

Intraparticle ↓

from Sandia Report SAND88-8240, Coal Combustion Science Quarterly Progress Report, January – March, 1988

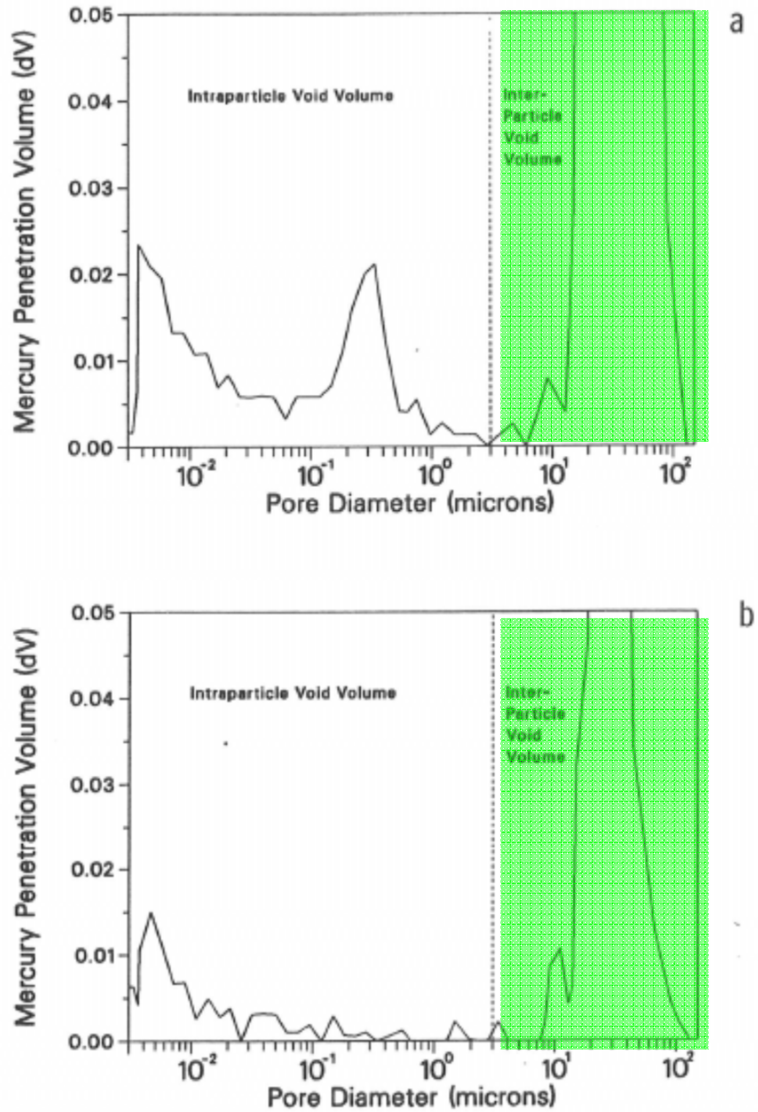
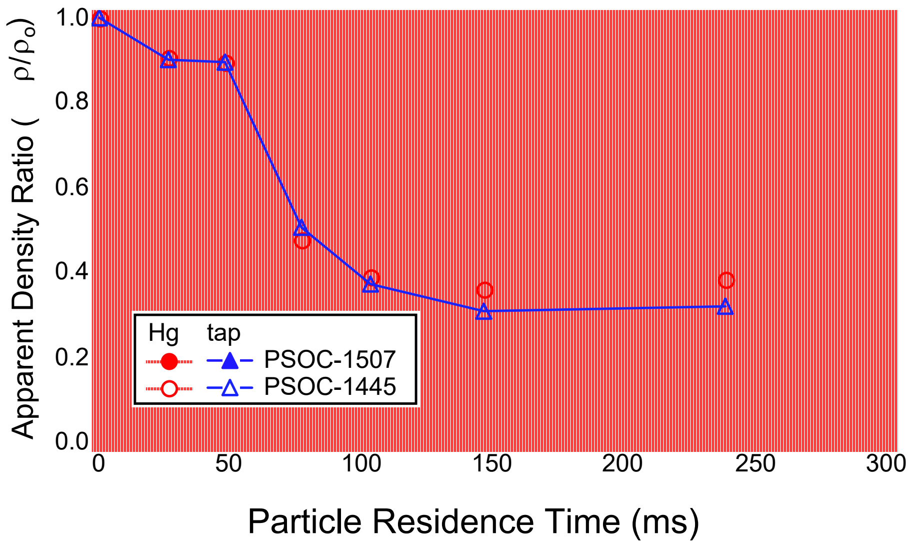
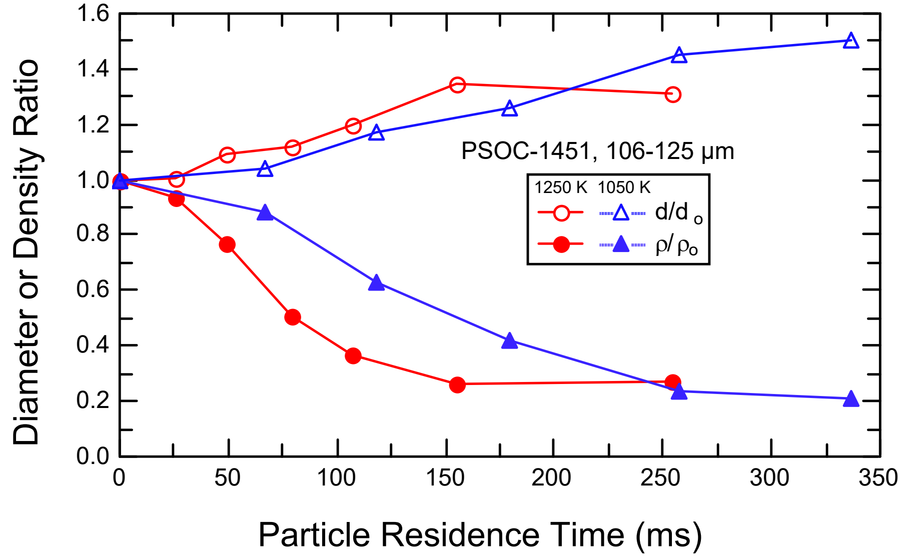


Figure 2. Incremental penetration volume from mercury porosimetry analysis of (a) Spherocarb particles (125 - 149 µm), and (b) PSOC 1415d Pittsburgh #8 high volatile bituminous coal particles (106-125 µm size fraction).

Apparent Particle Densities





From Fletcher Sandia Milestone Report

Heat Capacity of Coal

$$h = \int_{T_{ref}}^{T} C_p dT$$

C_p (particle) = x_{moist} $C_{p,\,moist}$ + x_{org} $C_{p,\,org}$ + x_{ash} $C_{p,\,ash}$

Note: C_p is a function of $T_{particle}$

Einstein's Formulation for C_p (from Merrick, 1983):

A. Simple

$$C_p = (3R/a)\ g_1\{1200/T\} J/kg/K$$

$$a = \left[\sum y_n / \mu_n\right]^{-1}$$

where a = mean coal atomic weight, y_n = mass fraction of element n, and μ = atomic weight of element n

g_1 is a function:

$$g_1\{z\} = \frac{\exp(z)}{[(\exp(z)-1)/z]^2}$$

R = universal gas constant (8314.3 N-m/K/kg-mol

B. 2-stage (along bedding plane and perpendicular to bedding plane)

$$C_p = (R/a)\ g_1\{380/T\} + 2g_1\{1800/T\}\ J/kg/K$$

Also note that enthalpy is calculated by Merrick as:

$$h = 3600(R/a)\ g_0\{1200/T\}\ J/kg \quad \text{or}$$
$$h = (R/a)\ [380g_0\{380/T\} + 3600g_0\{1800/T\}]\ J/kg$$

Where $g_0\{z\} = \dfrac{1}{\exp(z)-1}$

C. C_p for Ash

$C_{p,\,ash}$ = 754 + 0.586 T (J/kg/K where T is in °C) or
$C_{p,\,ash}$ = 593 + 0.586 T (J/kg/K where T is in K)

Merrick Heat Capacities

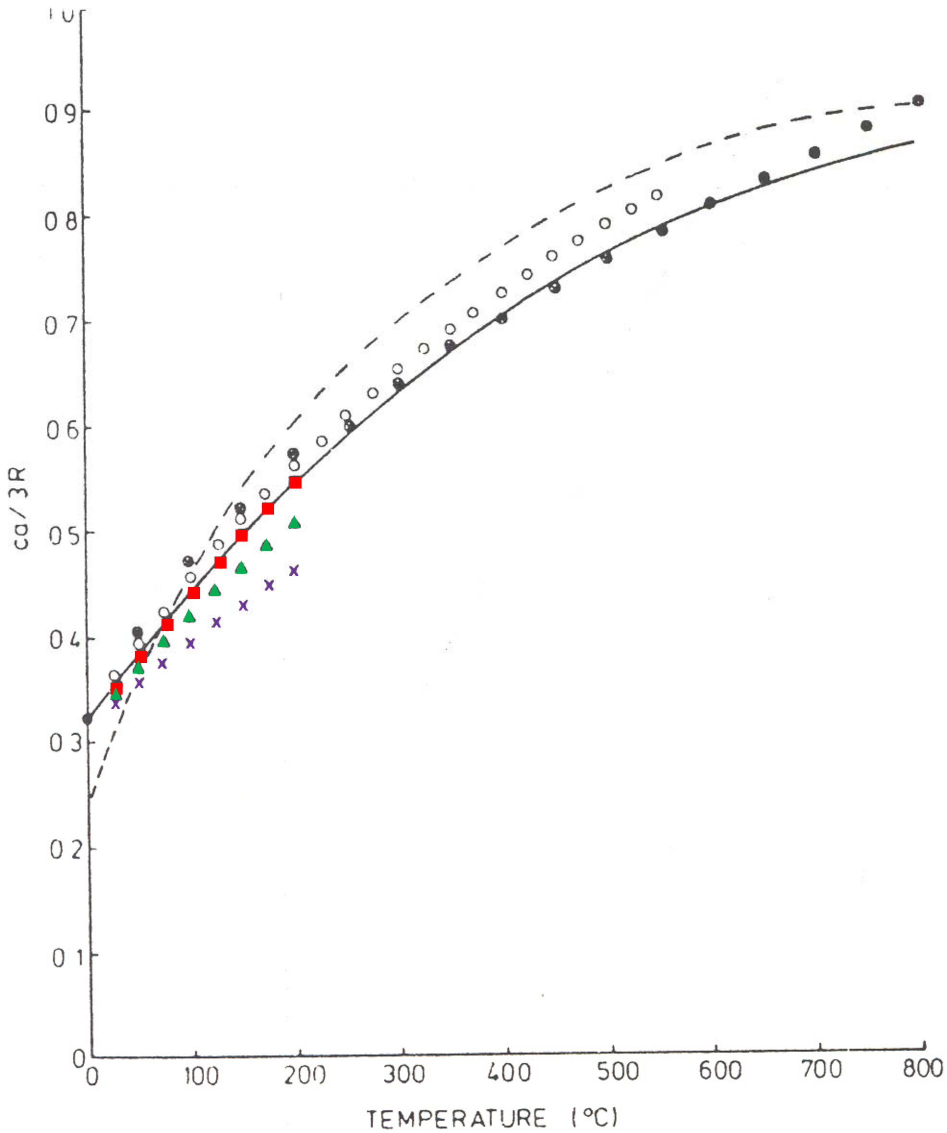
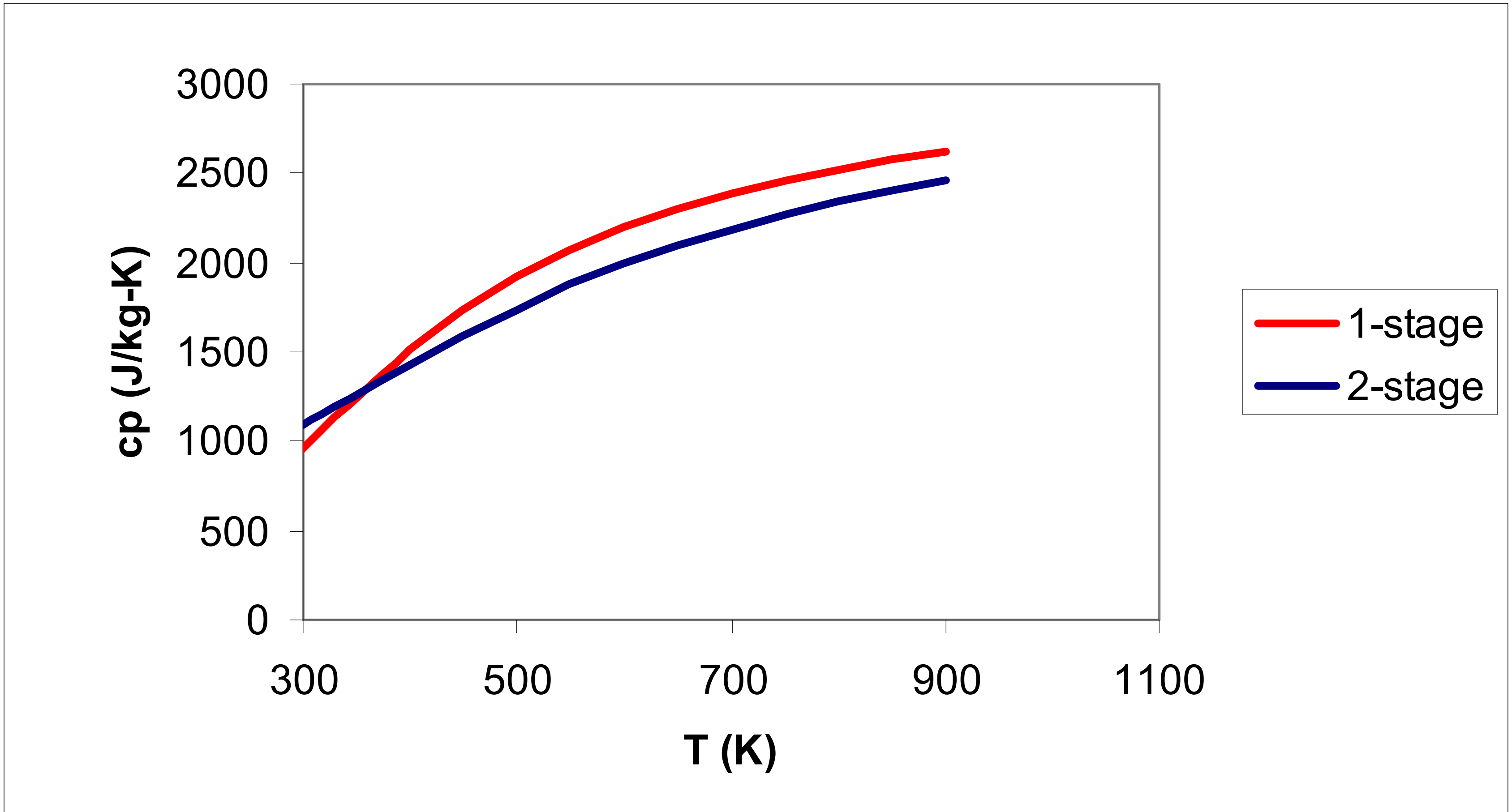


Figure 2 Variation of *ca*/3*R* with temperature. ---, Simple Einstein model; ———, Einstein model with two characteristic temperatures. ●, Graphite; ○, coke; □, 35 wt% VM; △, 25 wt% VM; ×, 15 wt% VM

Computed Heat Capacities

(Wyodak Coal)



Heat Capacities (Conclusions)

Cautions about the Merrick model:

- **Good for graphite and char (coke)**
- **Coal heat capacity data are limited**
- **Model does not fit data from different coal ranks very well!**
- **Coal data only extends to 200°C (573 K)**

In other words, keep a look out for better heat capacity data!

Thermal Conductivities

- Atkinson and Merrick (1983) report that the thermal conductivities *k* of coal, semi-cokes and cokes (W m-1 K-1) can be correlated as follows:

  $k = (\rho_t/4511)^{3.5}\ T^{0.5}$

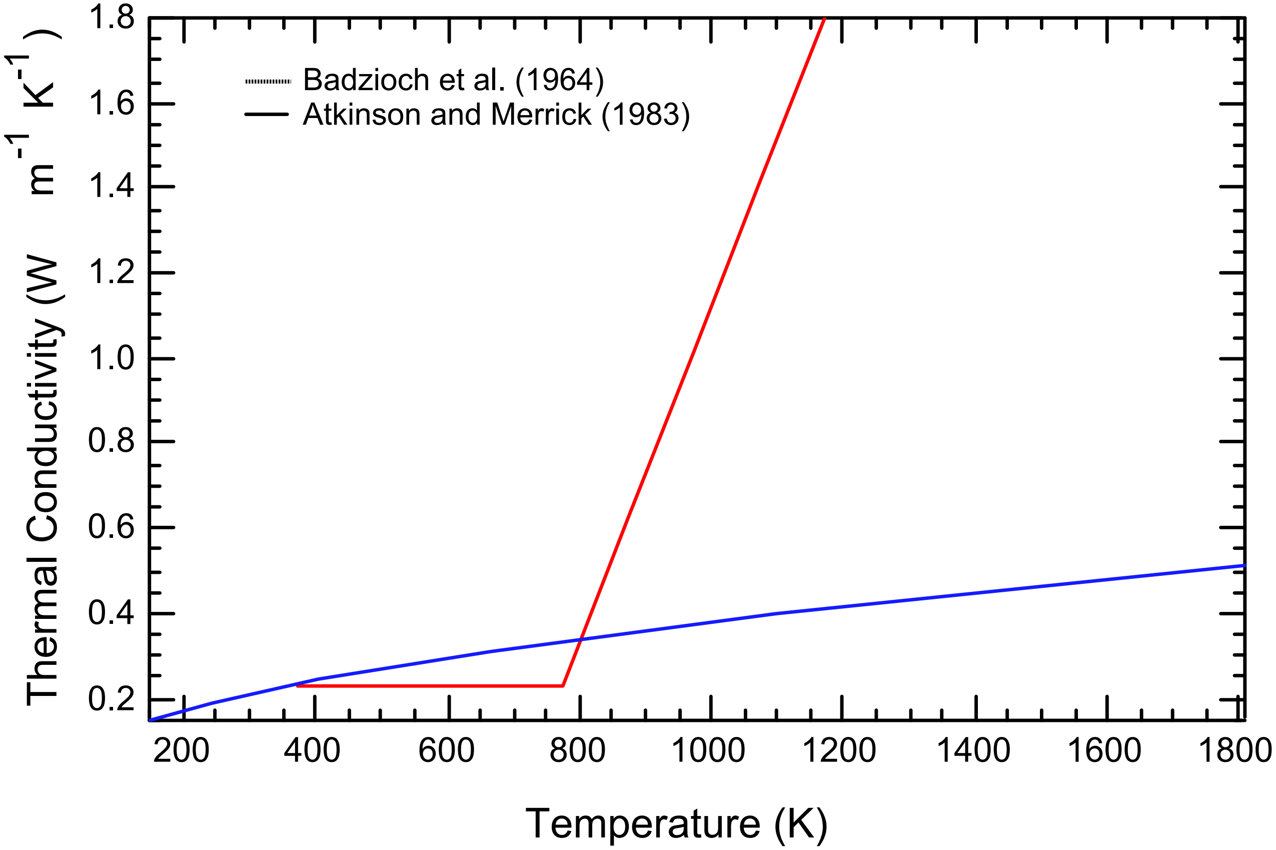
  where ρ_t is the true density of the material (2260 kg m^3 for amorphous carbon, 1279 kg m^3 for coal)
- The temperature dependence of this correlation does not agree well with the findings of Badzioch, et al. (1964), which are approximately correlated by the following expression:

$k = 0.23$	$300\ K < T < 773\ K$
$k = (T/255) – 2.8$	$773\ K < T < 1173\ K$

- The two expressions agree at temperatures below 800 K, but the data and correlation from Badzioch and coworkers indicate significantly higher thermal conductivities at temperatures greater than 800 K.

Recommendation

- Set the thermal conductivity to 0.25, which agrees with all of the data at temperatures below 800 K, and agrees somewhat with the correlation of Atkinson and Merrick at even higher temperatures.



Comparison of thermal conductivity correlations from Atkinson and Merrick (1983) and Badzioch et al. (1964).

Single Particle Energy Equation

- Temperature form

$$m_p C_p \frac{dT_p}{dt} = \theta h A_p \left(T_g - T_p\right) + \varepsilon \sigma A_p \left(T_w^4 - T_p^4\right) + \sum_i r_{pi} \, \Delta H_{rxn,i}$$

- Enthalpy form

$$\frac{d\left(m_p h_p\right)}{dt} = Q_{rp} + Q_{cp} - r_p h_{pg}$$

- where

$$h_{pg} = \frac{\sum r_{vol,i} h_{vol,i} + h_{char} \sum r_{char,i}}{r_{tot}}$$

Particle Size Distribution

- In general, means are defined as:

$$x_m = \frac{\int_a^b x\,df}{\int_a^b df} = \frac{\sum_{i=1}^{n} x_i f_i}{\sum_{i=1}^{n} f_i}$$

- Mass mean:

$$d_m = \sum_{i=1}^{n} d_i w_i, \qquad where \quad \sum_{i=1}^{n} w_i = 1$$

Particle Size Distributions (cont.)

- Mass per particle:

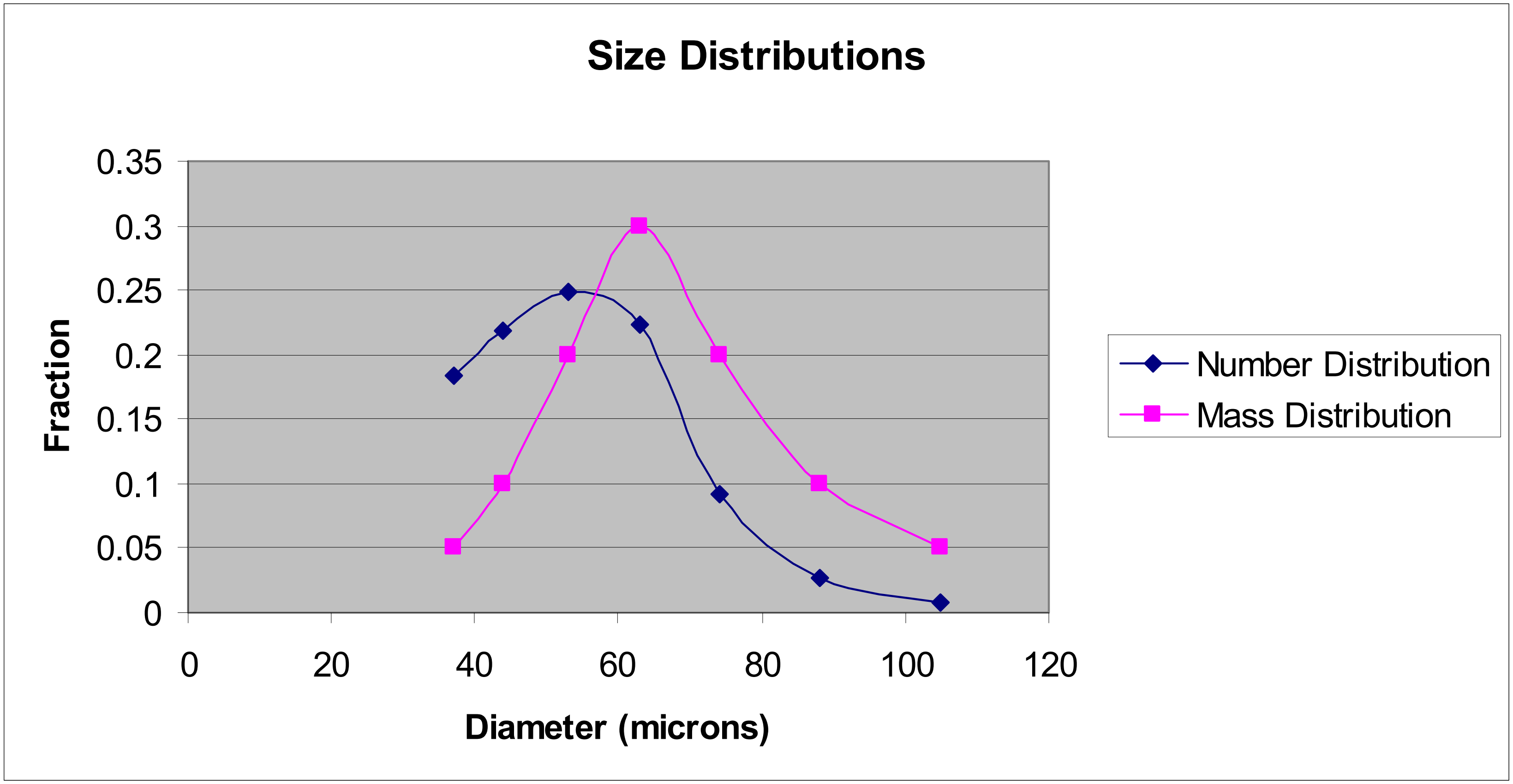
$$m_p = \rho \frac{4}{3} \pi r^3$$

- Number of particles = mass/(mass per particle)
- Number mean becomes:

$$d_n = \frac{\sum_{i=1}^{n} d_i \left(\frac{6 w_i}{\rho \pi d_i^3} \right)}{\sum_{i=1}^{n} \left(\frac{6 w_i}{\rho \pi d_i^3} \right)_i} = \frac{\sum_{i=1}^{n} d_i \left(\frac{w_i}{d_i^3} \right)}{\sum_{i=1}^{n} \left(\frac{w_i}{d_i^3} \right)_i}$$

Please compute the number distribution (# vs. diameter in microns) for the following mass distribution

Mesh Size (passing)	400	325	270	250	200	170	140
Weight (%)	5	10	20	30	20	10	5



Number mean = 53.6 μm
Mass mean = 64.6 μm

From Perry's Chemical Engineers' Handbook

Table 21-12. U.S. Sieve Series and Tyler Equivalents

(A.S.T.M.—E-11-61)

Sieve designation		Sieve opening		Nominal wire diam.		Tyler equivalent designation
Standard	Alternate	mm.	in. (approx. equivalents)	mm.	in. (approx. equivalents)	
107.6 mm.	4.24 in.	107.6	4.24	6.40	0.2520	
101.6 mm.	4 in.†	101.6	4.00	6.30	.2480	
90.5 mm.	3½ in.	90.5	3.50	6.08	.2394	
76.1 mm.	3 in.	76.1	3.00	5.80	.2283	
64.0 mm.	2½ in.	64.0	2.50	5.50	.2165	
53.8 mm.	2.12 in.	53.8	2.12	5.15	.2028	
50.8 mm.	2 in.†	50.8	2.00	5.05	.1988	
45.3 mm.	1¾ in.	45.3	1.75	4.85	.1909	
38.1 mm.	1½ in.	38.1	1.50	4.59	.1807	
32.0 mm.	1¼ in.	32.0	1.25	4.23	.1665	
26.9 mm.	1.06 in.	26.9	1.06	3.90	.1535	1.050 in.
25.4 mm.	1 in.†	25.4	1.00	3.80	.1496	
22.6 mm.*	⅞ in.	22.6	0.875	3.50	.1378	0.883 in.
19.0 mm.	¾ in.	19.0	.750	3.30	.1299	.742 in.
16.0 mm.*	⅝ in.	16.0	.625	3.00	.1181	.624 in.
13.5 mm.	0.530 in.	13.5	.530	2.75	.1083	.525 in.
12.7 mm.	½ in.†	12.7	.500	2.67	.1051	
11.2 mm.*	7/16 in.	11.2	.438	2.45	.0965	.441 in.
9.51 mm.	⅜ in.	9.51	.375	2.27	.0894	.371 in.
8.00 mm.*	5/16 in.	8.00	.312	2.07	.0815	2½ mesh
6.73 mm.	0.265 in.	6.73	.265	1.87	.0736	3 mesh
6.35 mm.	¼ in.†	6.35	.250	1.82	.0717	
5.66 mm.*	No. 3½	5.66	.223	1.68	.0661	3½ mesh
4.76 mm.	No. 4	4.76	.187	1.54	.0606	4 mesh
4.00 mm.*	No. 5	4.00	.157	1.37	.0539	5 mesh
3.36 mm.	No. 6	3.36	.132	1.23	.0484	6 mesh
2.83 mm.*	No. 7	2.83	.111	1.10	.0430	7 mesh
2.38 mm.	No. 8	2.38	.0937	1.00	.0394	8 mesh
2.00 mm.*	No. 10	2.00	.0787	0.900	.0354	9 mesh
1.68 mm.	No. 12	1.68	.0661	.810	.0319	10 mesh
1.41 mm.*	No. 14	1.41	.0555	.725	.0285	12 mesh
1.19 mm.	No. 16	1.19	.0469	.650	.0256	14 mesh
1.00 mm.*	No. 18	1.00	.0394	.580	.0228	16 mesh
841 micron	No. 20	0.841	.0331	.510	.0201	20 mesh
707 micron*	No. 25	.707	.0278	.450	.0177	24 mesh
595 micron	No. 30	.595	.0234	.390	.0154	28 mesh
500 micron*	No. 35	.500	.0197	.340	.0134	32 mesh
420 micron	No. 40	.420	.0165	.290	.0114	35 mesh
354 micron*	No. 45	.354	.0139	.247	.0097	42 mesh
297 micron	No. 50	.297	.0117	.215	.0085	48 mesh
250 micron*	No. 60	.250	.0098	.180	.0071	60 mesh
210 micron	No. 70	.210	.0083	.152	.0060	65 mesh
177 micron*	No. 80	.177	.0070	.131	.0052	80 mesh
149 micron	No. 100	.149	.0059	.110	.0043	100 mesh
125 micron*	No. 120	.125	.0049	.091	.0036	115 mesh
105 micron	No. 140	.105	.0041	.076	.0030	150 mesh
88 micron*	No. 170	.088	.0035	.064	.0025	170 mesh
74 micron	No. 200	.074	.0029	.053	.0021	200 mesh
63 micron*	No. 230	.063	.0025	.044	.0017	250 mesh
53 micron	No. 270	.053	.0021	.037	.0015	270 mesh
44 micron*	No. 325	.044	.0017	.030	.0012	325 mesh
37 micron	No. 400	.037	.0015	.025	.0010	400 mesh

follow some distribution, such as the **Rosin-Rammler-Bennett** [Rosin and Rammler, *J. Inst. Fuel*, 7, 29–36 (1933); Bennett, *ibid.*, **10**, 22–39 (1936)]:

$$Y = 1 - \left[\exp - \left(\frac{X}{X'}\right)^n\right] \tag{8-1}$$

or the **Gates-Gaudin-Schumann** distribution [Schumann, *A.I.M.E. Tech. Paper* 1189, *Mining Tech.* (1940)]:

$$Y = \left(\frac{X}{k}\right)^m \tag{8-2}$$

or the **logarithmic-probability** distribution [Hatch and Choate, *J. Franklin Inst.*, **207**, 369 (1929)]:

$$Y = \operatorname{erf}\left(\frac{\ln X/X'}{\sigma}\right) \tag{8-3}$$

or the **Gaudin-Meloy** distribution [Gaudin and Meloy, *Trans. A.I.M.E.*, **223**, 40–50 (1962)]:

$$Y = 1 - \left(1 - \frac{X}{X'}\right)^r \tag{8-4}$$

where Y = cumulative fraction by weight undersize; X = size; k, X' = parameters with dimension of size; m, n, r = dimensionless

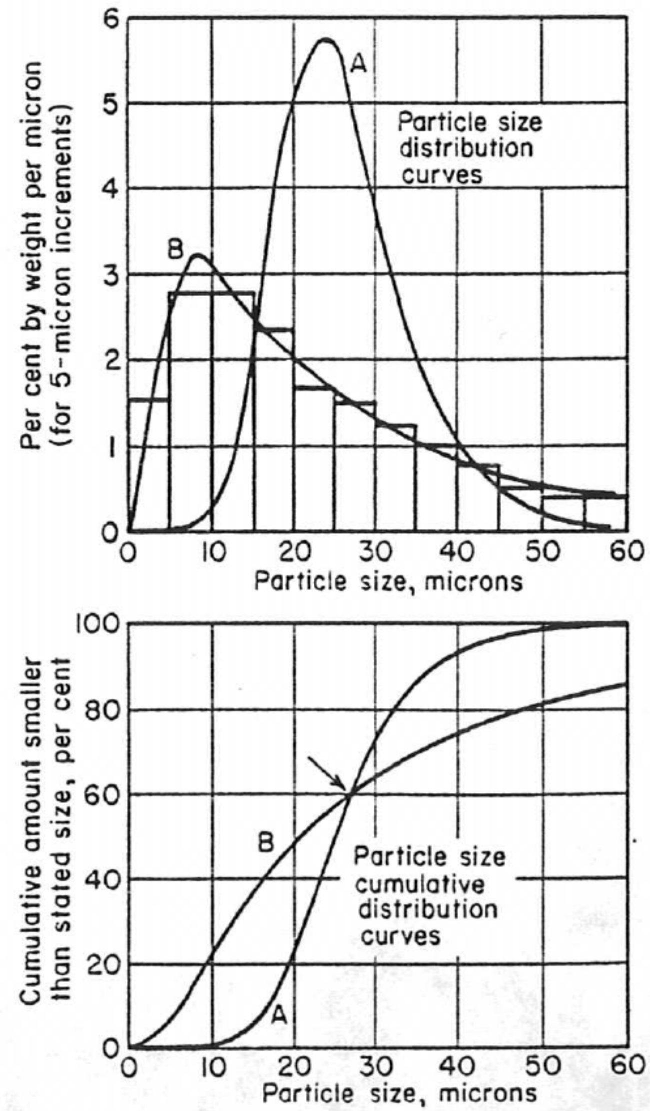


Fig. 8-1. Particle-size distribution curves for simple powders.

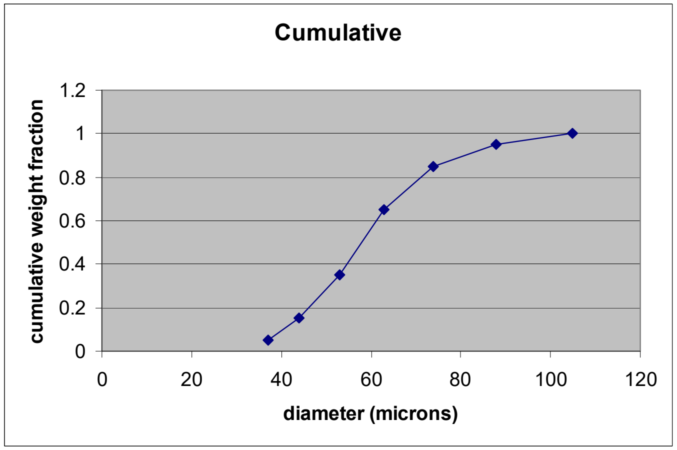
From Perry's Chemical Engineers' Handbook

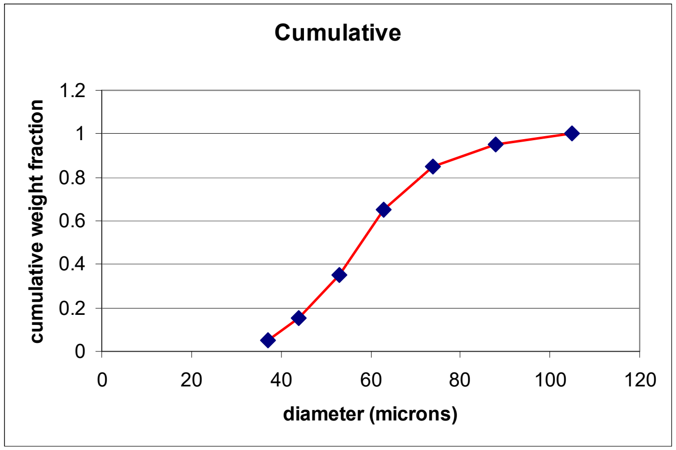
Rosin-Rammler Distribution

(similar to a Weibull distribution)

$$f = 1 - e^{-\left(\frac{d}{a}\right)^n}$$

where *f* is the cumulative weight fraction under size *d*, and *a* and *n* are fitting parameters.





Internal Surface Areas

- Internal surface areas are measured by adsorption of some gas (N_2, CO_2, O_2, Ar)
- Units are generally m^2/g
- Raw coal generally has less surface area than char (after devolatilization)
- CO_2 method generally gives larger internal surface area than N_2 method
- No method is accepted as standard

Internal Surface Area Data

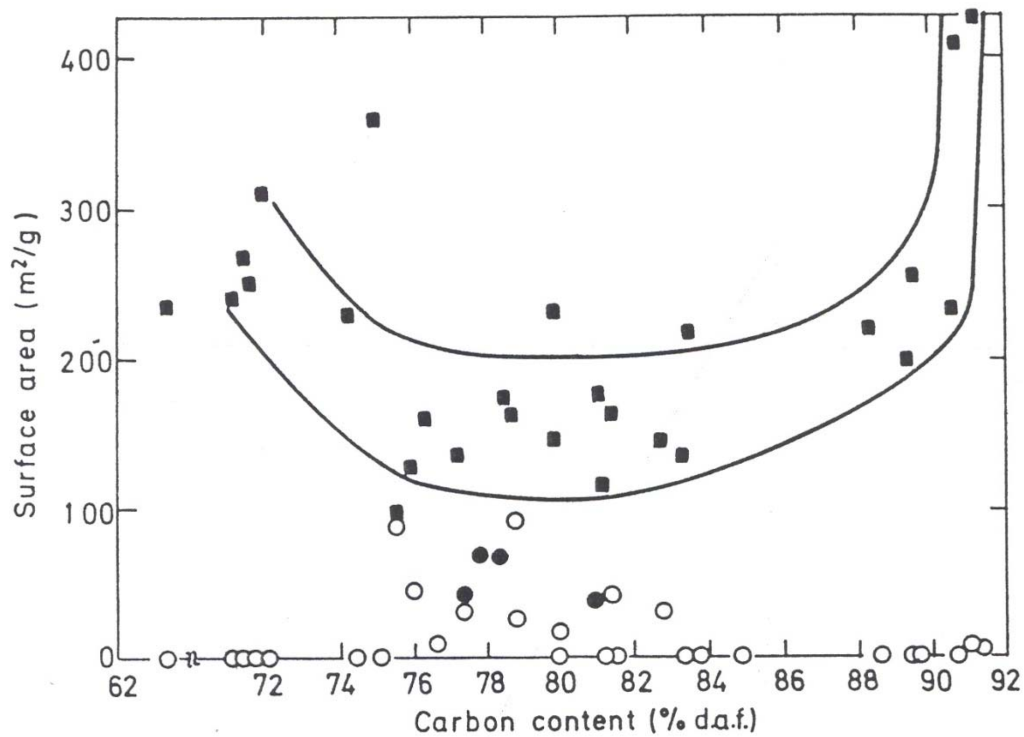
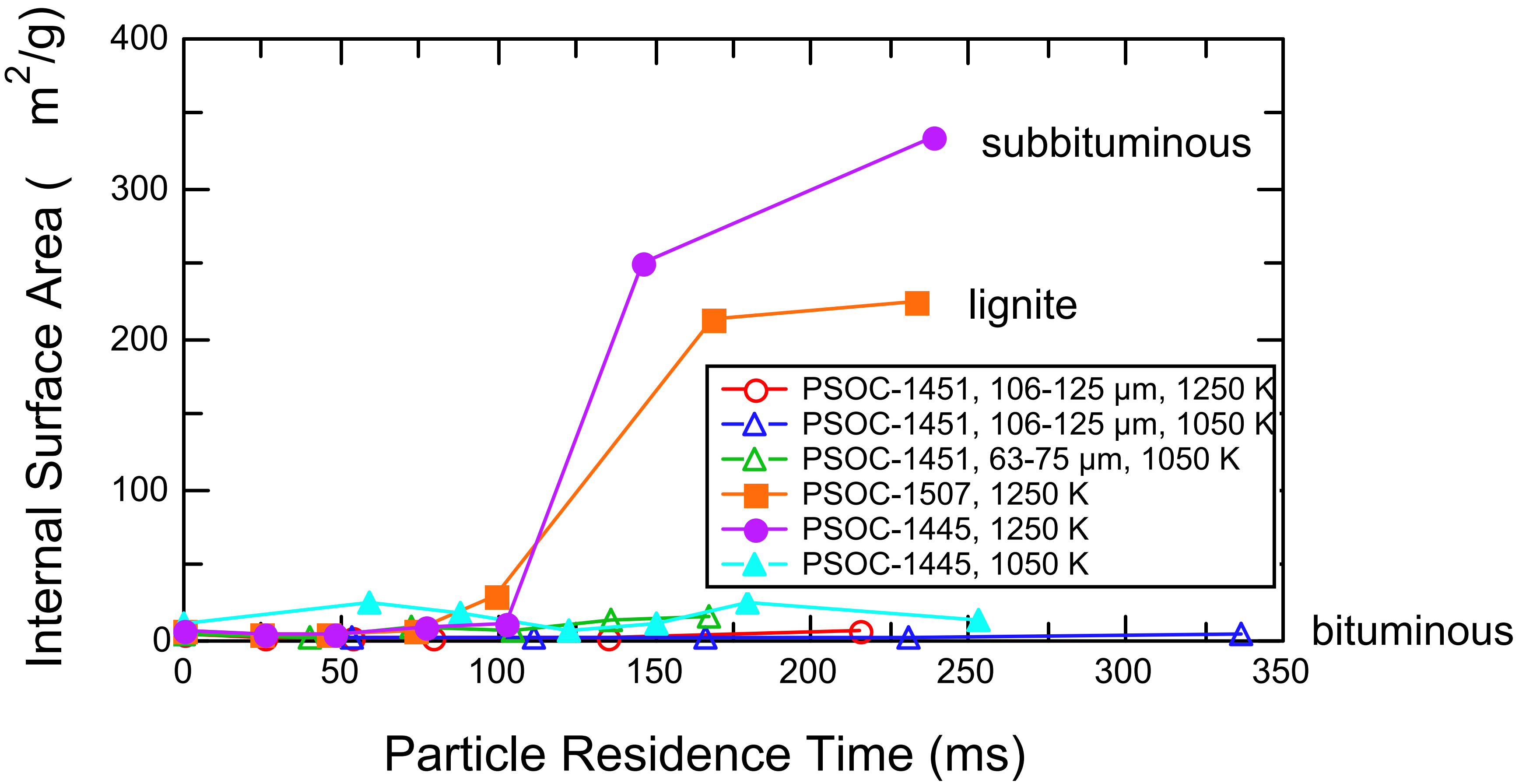


Figure 1 Variation of nitrogen and carbon dioxide surface areas of coals with carbon content
● N_2 (from reference 14), ○ N_2 (determined), ■ CO_2

From Gan et al. Fuel, Vol. 51 (1972)

N_2 Internal Surface Area Data



Internal surface areas of char particles from different coals as a function of residence time, as measured by the N_2 BET method.
From Fletcher Sandia Milestone Report

Heating Value

- A common terminology has been adopted in the United States regarding the heating value of coal. The term "high heating value" is defined to be the calorific value of coal, computed as if the water (H_2O) products of coal combustion end up in the liquid form.
- In other words,
- C ==> CO_2 (gas)
- H ==> H_2O (liquid)
- O ==> O_2 (gas), which helps burn the C, H, and S
- N ==> N_2 (gas)
- S ==> SO_2 (gas)

- Q_h = 145.44 (%C) + 620 [(%H) - (%O)/8] + 41(%S) (Btu/lb) (DuLong formula)
- $Q_l = Q_h$ - 92.7 (%H) (Btu/lb)

(daf compositions)

(Q_l and Q_h are positive when exothermic)

(from Perry's Chem. Eng. Handbook)

Heating Value (cont.)

Note:

- **If the high heating value of the coal is defined to have the hydrogen products end up as H_2O (liq.), then the latent heat of moisture evaporation is automatically removed from the problem.**

- **% moisture = %H2O (liq.) ==> H2O (liq.) ΔH_{react} = 0.0**

- **So:**

$$\frac{Q_h \left(Btu/lb\ of\ \ wet,\ ash-included\ \ coal\right)}{\left(1-x_{ash}-x_{moist}\right)} = Q_h \left(Btu/lb\ of\ \ daf\ \ coal\right)$$

Other Heating Value Correlations

$$Q_s = 338.3C + 1443\left(H - \frac{O}{8}\right) + 94.2S \quad (1)$$

$$Q_s = 340.6C + 14324H - 153.2O + 104.7S \quad (2)$$

$$Q_s = 339.1\left(C - \frac{3}{8}O\right) + 238.6\left(\frac{3}{8}O\right) + 1444\left(H - \frac{1}{16}O\right) + 104.7S \quad (3)$$

$$Q_s = 339.1C + 1433.7H + 93.1S - 127.3O \quad (4)$$

$$Q_s = 519C + 1625H + O^2 - 17870 \quad (5)$$

$$Q_s = 340.3C + 1243.2H + 62.8N + 190.9S - 98.4O \quad (6)$$

$$Q_s = 351.7C + 1162.6H + 104.7S - 111O \quad (7)$$

$$Q_s = 341.4C + 1444.5H - \frac{1000(N + O - 1)}{8} + 93S \quad (8)$$

$$Q_s = 341C + 1323H + 68.5 - 119.4(O + N) \quad (9)$$

$$Q_s = 349.1C + 1178{,}3H + 100.5S - 103.4O - 15N \quad (10)$$

$$Q_s = 339C + 1214\left(H - \frac{O}{8}\right) + 104S + 226H \quad (11)$$

[7] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051-63.

[8] Selvig WA, Gibson FH. Calorific value of coal. In: Lowry HH, editor. Chemistry of coal utilization , vol. 1, New York: Wiley; 1945, p. 139.

[9] Strache H, Lant R. Kohlenchemie. Leipzig: Akademische Verlagsgesellschaft; 1924.

[10] Steuer W.: Brennstoff-Chem, vol. 7, 1926, p. 344 according: Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051.

[11] D'Huart K.: Die Warme, vol. 53, 1930, p. 313 Chem Abstr., vol. 24, 1930, p. 5966 according: Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051.

[12] Seylor A.C.: Proc S Wales Inst Engrs., vol. 53, 1938, p. 254 according: Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051.

[13] Gumz W.: Feuerungstech, vol. 26, 1938, p. 322. Chem Abstr., vol. 33, 1939, p. 6556 according: Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051.

[14] Boie W.: Energietechnik, vol. 3, 1953, p. 309 according: Channiwala S.A., Parikh P.P.: A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81:1051.

[15] Grabosky M, Bain R. Properties of biomass relevant to gasification. In: Reed TB, editor. Biomass gasification – principles and technology, New Jersey: Noyes Data Corporation; 1981, p. 41.

[16] IGT. Coal Coversion Systems Technical Data Book, DOE Contract EX 76-C-01-2286. Springfield, VA: NTIS; 1978.

[17] Ocheduszko S. Termodynamika stosowana (in Polish). WNT Warszawa; 1967.

(from Sciazko, M., 2012)