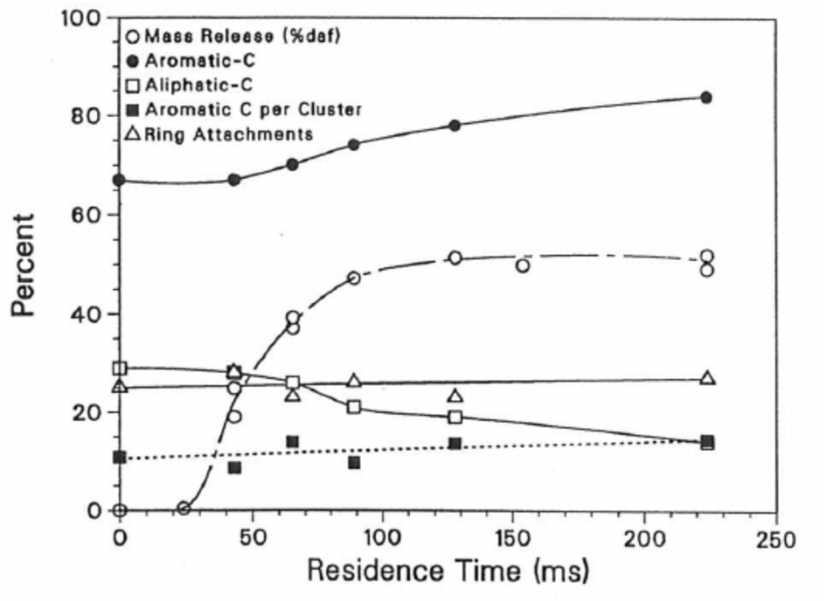
Network Devolatilization Models

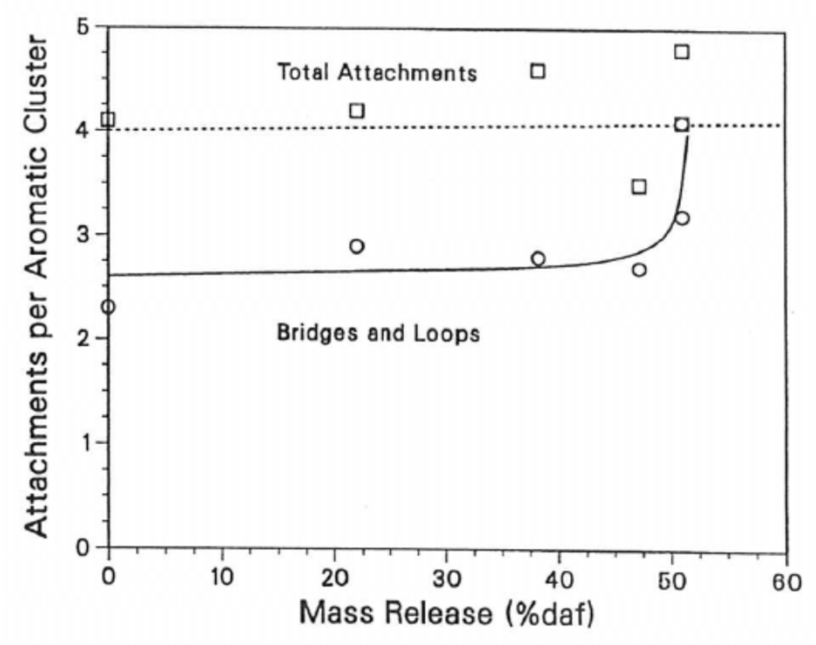
Class 8

Questions

1. Read the paper by Fletcher et al., 23rd Combustion Institute (1990) and comment on the main conclusions that would apply to network models.
2. Please review the main features of the network models. Discuss why you might want to use a network model instead of a simpler model (1-step, 2-step, etc.).
3. How does a flash calculation (used in CPD and FLASHCHAIN) differ from just using the vapor pressure as a cutoff value (like in FG-DVC)?
4. Compare the maximum MW vaporized at 1 atm at 550 K for the three models, assuming that everything with vapor pressure > ambient pressure vaporizes.
5. Please discuss the coal-dependent input parameters used by the three models, and how they pertain to macromolecular structure.
6. Using the flash program provided, or one of your own choosing, calculate
   (1) the average molecular weight of tar vapor and of tar liquid
   (2) the molecular weight distribution (fraction of tar vapor at each molecular weight)
7. Please run the base case for the cpd model at 3 different pressures (1, 20, and 50 atm) and plot the tar and total volatiles yields as a function of temperature for each pressure. You will need the fortran and input files. Zip files for the CPD Heat model in Matlab and Fortran are located http://www.et.byu.edu/~tom/classes/733/cpd/.

NMR Data on Char



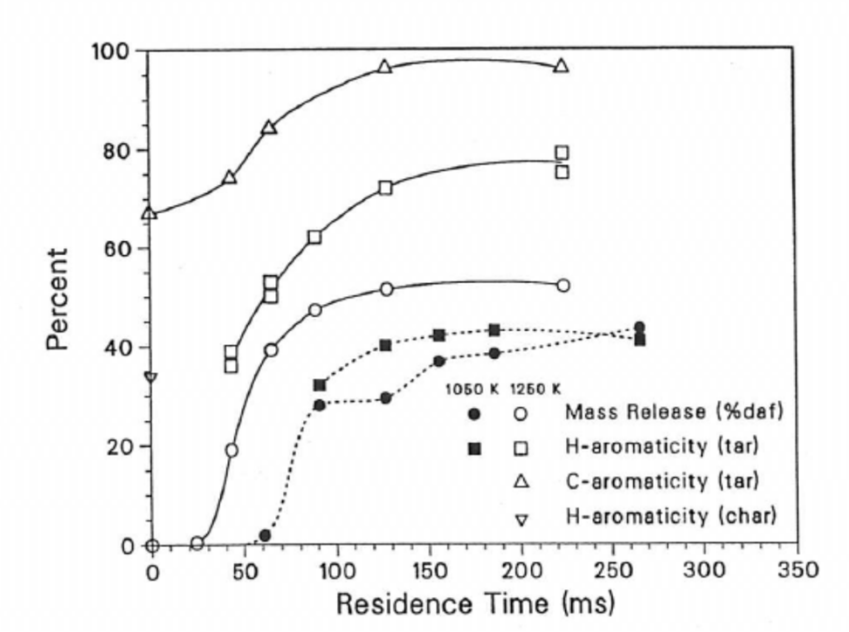


- Aromatic C/Cluster increases slightly
- Char aromaticity increases to 90%
  - Aliphatic C decreases
- Attachments constant

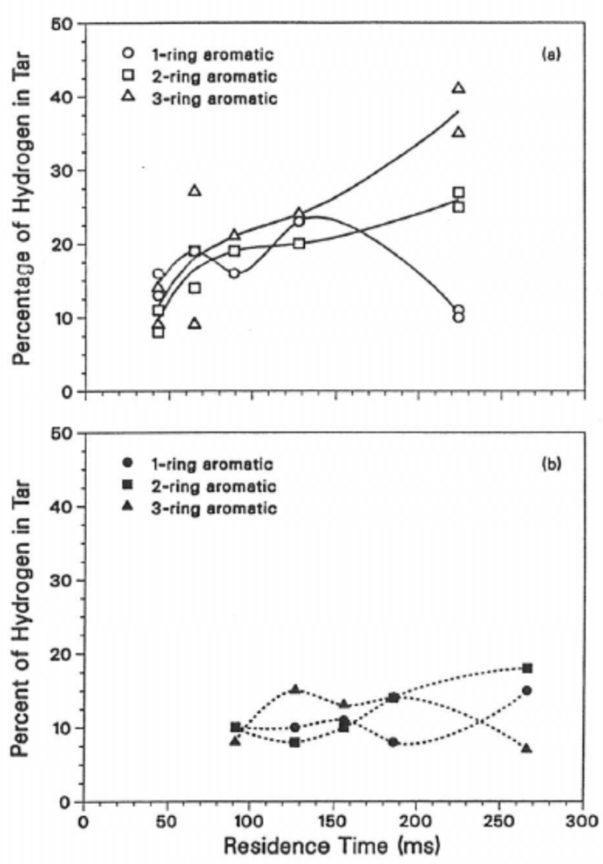
- Attachments per cluster constant
- Bridges and loops increases at end of devolatilization
  - Crosslinking!

(from Fletcher et al., 23rd Combustion Symposium, 1990)

NMR Data on Tar



- Tar C aromaticity increases to 95% at 1250 K
- Not as much H aromaticity increase at 1050 K



- Decrease in 1-ring compounds in tar at 1250 K
  - Increase in 3+ ring compounds
- Minimal change at 1050 K

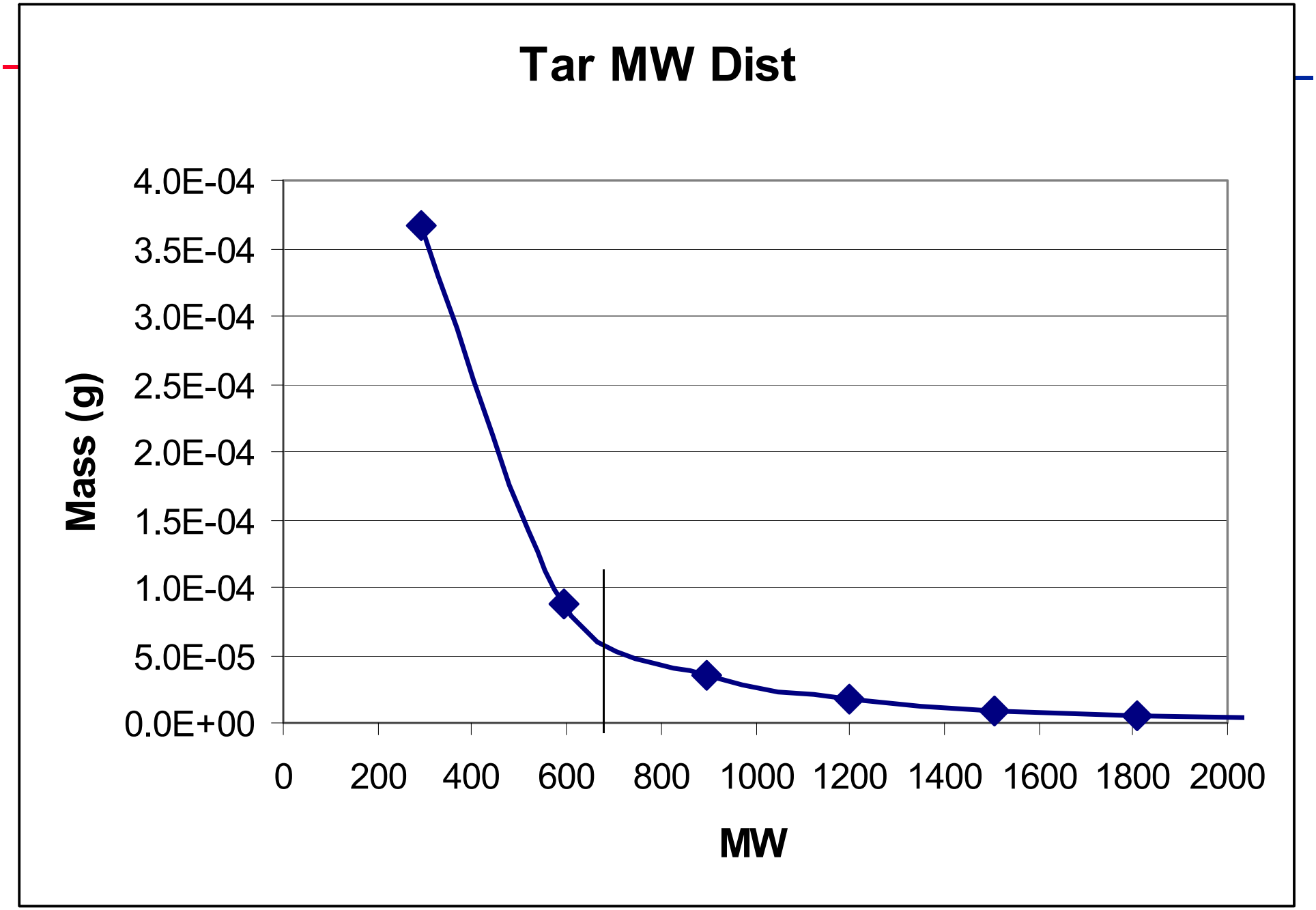
(from Fletcher et al., 23rd Combustion Symposium, 1990)

Questions

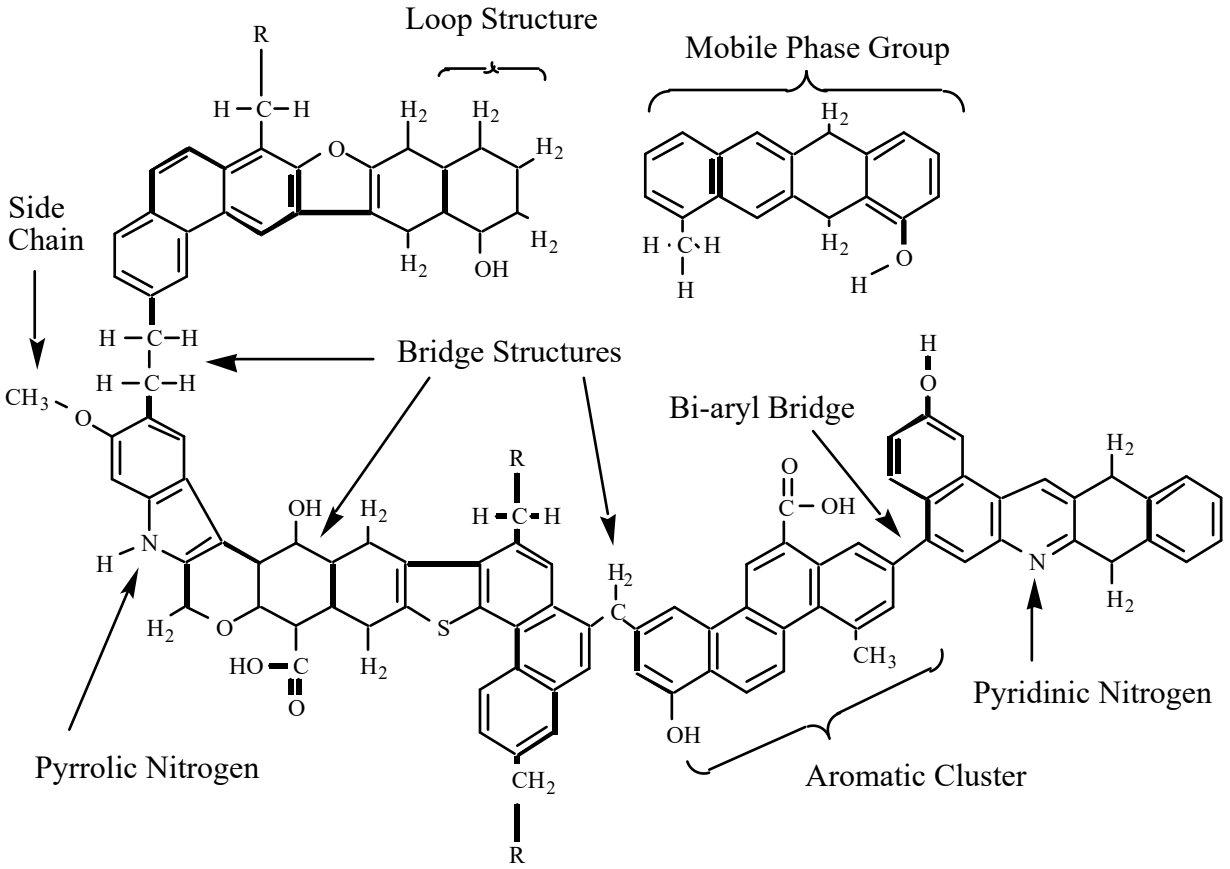
- A copy of this fortran program can be obtained from the ChE 733 web page followed by /flash (http://www.et.byu.edu/~tom/classes/733/flash)
- This is a Fortran 77 file. I recommend using the FORCE fortran compiler. Please click here for some background on how this program works.

	Mol. Wt.	Moles of feed
Light gas	30.	2.603E-03
Tar precursor (feed metaplast)	292.	3.674E-04
	595.	8.835E-05
	898.	3.431E-05
	1201.	1.667E-05
	1504.	9.226E-06
	1807.	5.566E-06
	2111.	3.570E-06
	2414.	2.396E-06
	2717.	1.666E-06
	3020.	1.191E-06
	3323.	8.717E-07
	3626.	6.502E-07
	3929.	4.929E-07
	4233.	3.789E-07
	4536.	2.948E-07
	4839.	2.317E-07
	5142.	1.839E-07
	5445.	1.471E-07
	5748.	1.185E-07
	6051.	9.618E-08

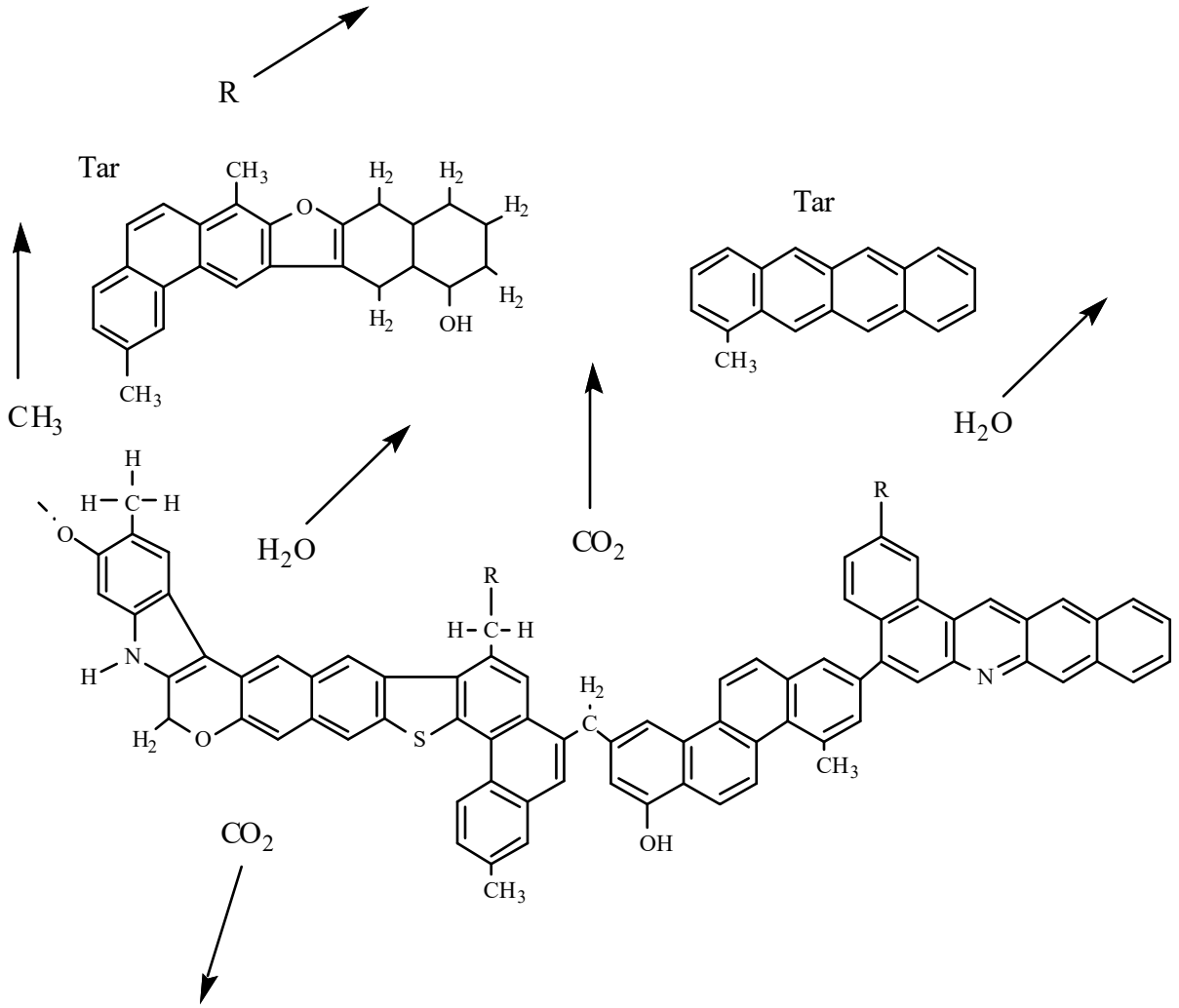
7. Please run the base case for the cpd model at 3 different pressures (1, 20, and 50 atm) and plot the tar and total volatiles yields as a function of temperature for each pressure. You will need the fortran and input files. The CPD Heat model is located http://www.et.byu.edu/~tom/cpd/cpdheat/cpd_heatfiles.html.


Tar MW Dist
Mass (g)
4.0E-04
3.5E-04
3.0E-04
2.5E-04
2.0E-04
1.5E-04
1.0E-04
5.0E-05
0.0E+00
0
200
400
600
800
1000
1200
1400
1600
1800
2000
MW

Coal Structure



Primary Coal Pyrolysis



Network Devolatilization Models

- FG-DVC, FLASHCHAIN, CPD Models
- Parent coal structure
- Statistical network model
- First order rate expressions with distributed activation energies
- Correlation of vapor pressure with tar molecular weight
- Crosslinking

FG-DVC

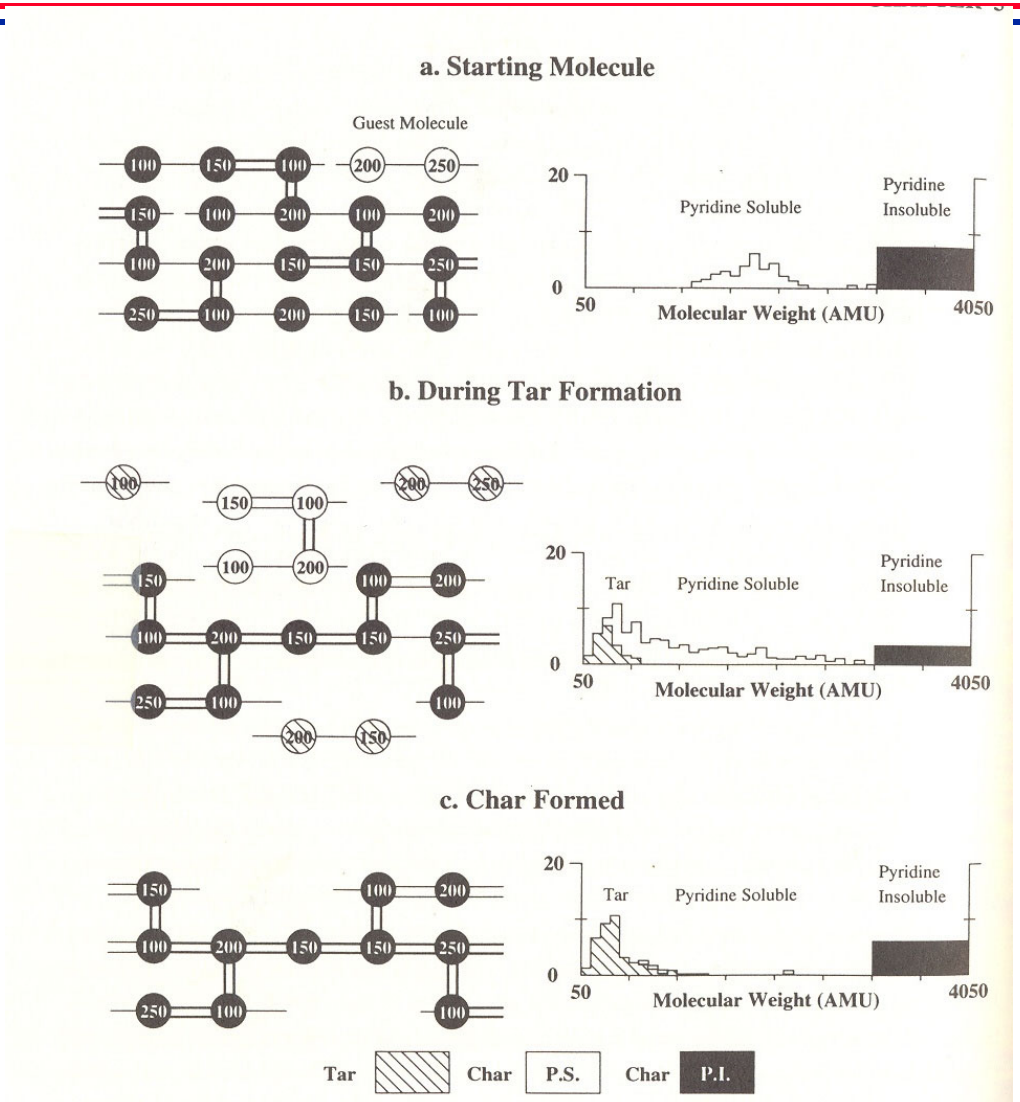


Figure 95. Representation of coal molecules in the DVC simulation with corresponding molecular-weight distributions. Circles represent monomers with the molecular weights shown including ring clusters and peripheral groups. Single-line bridges are breakable bridges and donate hydrogen while double-lined bridges are unbreakable (Solomon *et al.*, 1988a).

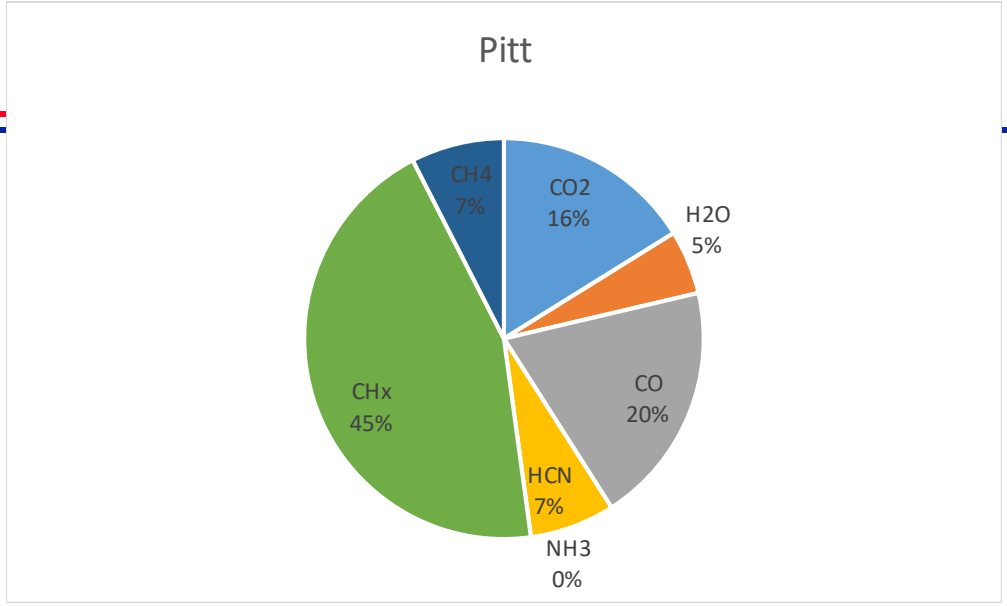
FG-DVC

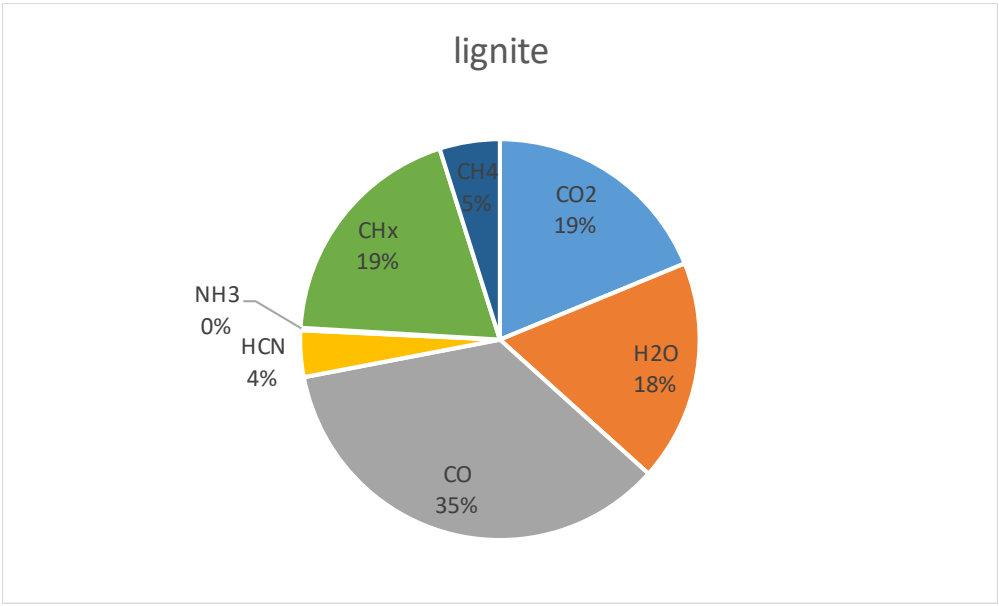
TABLE 59. Rank-Independent Rate Coefficients and Composition Parameters for the FG Submodel

Composition parameters	Gas	Functional group source	Rate equation[a]	Pittsburgh hvAb coal[b]	Beulah–Zap lignite[b]
Y_1^0	CO_2 extra loose	Carboxyl	$k_1 = 0.81E + 13 \exp(-(22500 \pm 1500)/T)$	0.000	0.065
Y_2^0	CO_2 loose	Carboxyl	$k_2 = 0.65E + 17 \exp(-(33850 \pm 1500)/T)$	0.007	0.030
Y_3^0	CO_2 light		$k_3 = 0.11E + 16 \exp(-(38315 \pm 2000)/T)$	0.005	0.005
Y_4^0	H_2O loose	Hydroxyl	$k_4 = 0.22E + 19 \exp(-(30000 \pm 1500)/T)$	0.012	0.062
Y_5^0	H_2O tight	Hydroxyl	$k_5 = 0.17E + 14 \exp(-(32700 \pm 1500)/T)$	0.012	0.033
Y_6^0	CO ether loose		$k_6 = 0.14E + 19 \exp(-(40000 \pm 6000)/T)$	0.050	0.060
Y_7^0	CO ether tight	Ether O	$k_7 = 0.15E + 16 \exp(-(40500 \pm 1500)/T)$	0.021	0.038
Y_8^0	HCN loose		$k_8 = 0.17E + 14 \exp(-(30000 \pm 1500)/T)$	0.009	0.007
Y_9^0	HCN tight		$k_9 = 0.69E + 13 \exp(-(42500 \pm 4750)/T)$	0.023	0.013
Y_{10}^0	NH_3		$k_{10} = 0.12E + 13 \exp(-(27300 \pm 3000)/T)$	0.000	0.001
Y_{11}^0	CH_x aliphatic	H (al)	$k_{11} = 0.84E + 15 \exp(-(30000 \pm 1500)/T)$	0.207	0.102
Y_{12}^0	CH_4 extra loose	Methoxy	$k_{12} = 0.84E + 15 \exp(-(30000 \pm 1500)/T)$	0.000	0.000
Y_{13}^0	CH_4 loose	Methyl	$k_{13} = 0.75E + 14 \exp(-(30000 \pm 2000)/T)$	0.020	0.017
Y_{14}^0	CH_4 tight	Methyl	$k_{14} = 0.34E + 12 \exp(-(30000 \pm 2000)/T)$	0.015	0.009
Y_{15}^0	H aromatic	H (ar)	$k_{15} = 0.10E + 15 \exp(-(40500 \pm 6000)/T)$	0.013	0.017
Y_{16}^0	Methanol		$k_{16} = 0$	0.000	0.000
Y_{17}^0	CO extra tight	Ether O	$k_{17} = 0.20E + 14 \exp(-(45500 \pm 1500)/T)$	0.020	0.090
Y_{18}^0	C nonvolatile	C (ar)	$k_{18} = 0$	0.562	0.440
Y_{19}^0	S organic			0.024	0.011
X^0	Tar		$k_B = k_T = 0.86E + 15 \exp(-(27700 \pm 1500)/T)$		

[a] Rate equation $k_n = k_0 \exp(-E/R \pm \sigma/R)/T)$. k_0 in s^{-1}, E/R and σ/R in K. σ designates the spread in activation energies in a Gaussian distribution.
[b] Initial fraction of component in parent coal; sum equals 1.
Source: Solomon *et al.* (1988a).

Light gas yields (Solomon model)





Flashchain

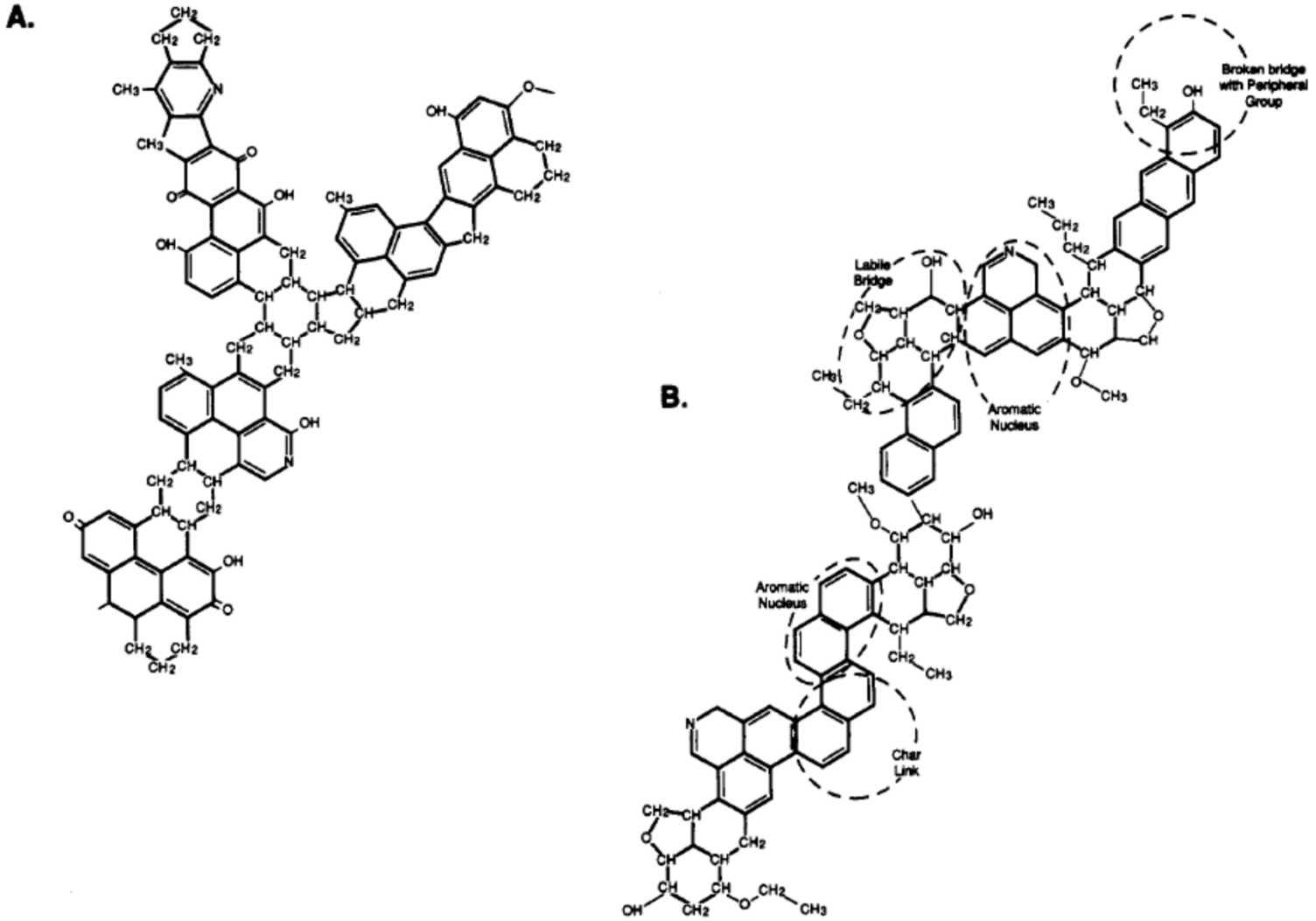


Figure 1. Ladner's proposed molecular model of an 82% C vitrinite (A) with H/C = 0.77, O/C = 0.09, and N/C = 0.02. Carbon and proton aromaticities are 0.62 and 0.17, respectively. Its analogue in FLASHCHAIN (B) maintains these characteristics, and also has C_A = 12 carbons, $p(0)$ = 0.91, and $F^b(0)$ = 0.63, so that β = 0.056. These latter values are consistent with this rank, as seen in part 3.

Niksa & Kerstein, Energy & Fuels, 5, 647 (1991)

Flashchain

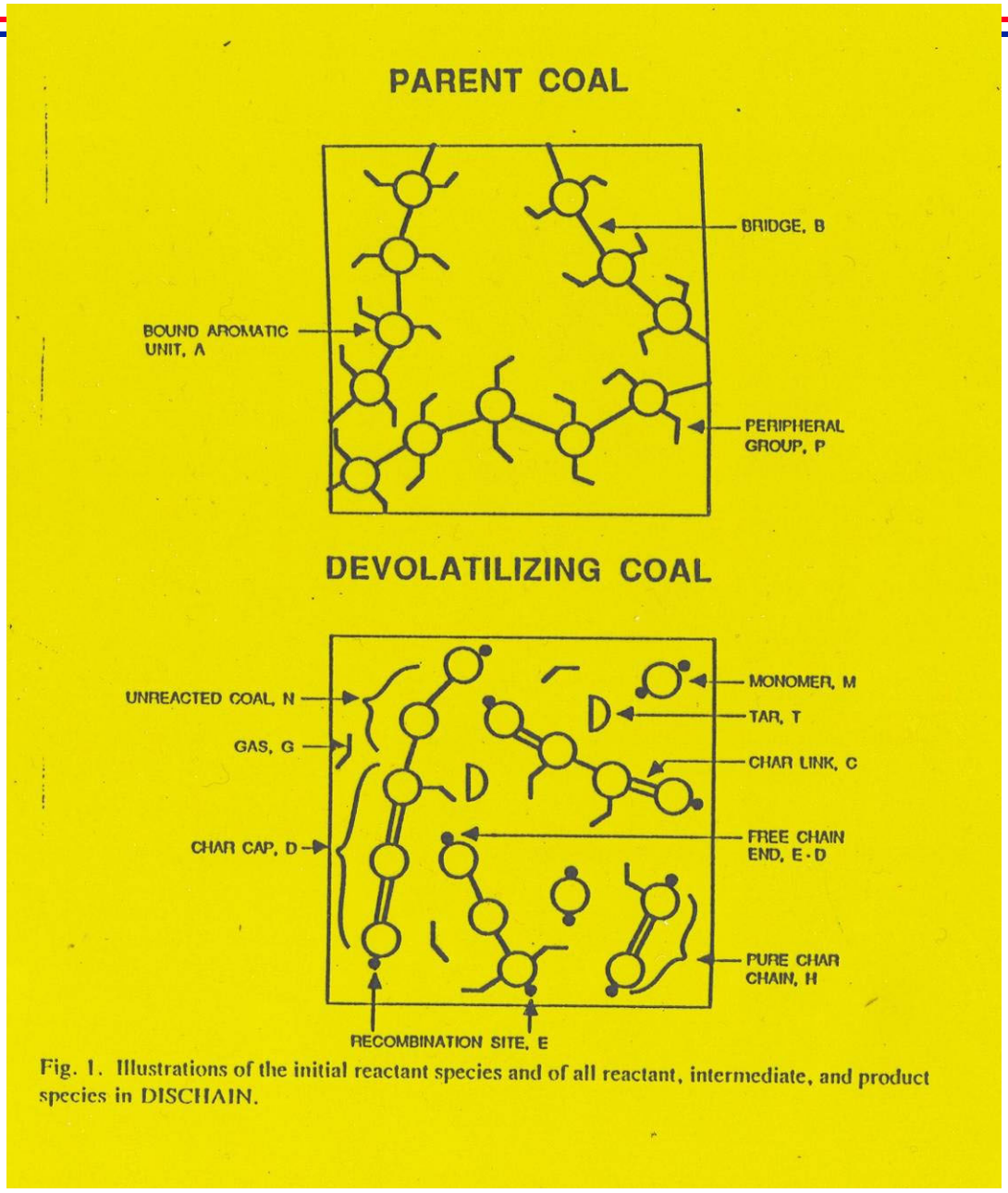


Fig. 1. Illustrations of the initial reactant species and of all reactant, intermediate, and product species in DISCHAIN.

Chemical Percolation Devolatilization (CPD) Model

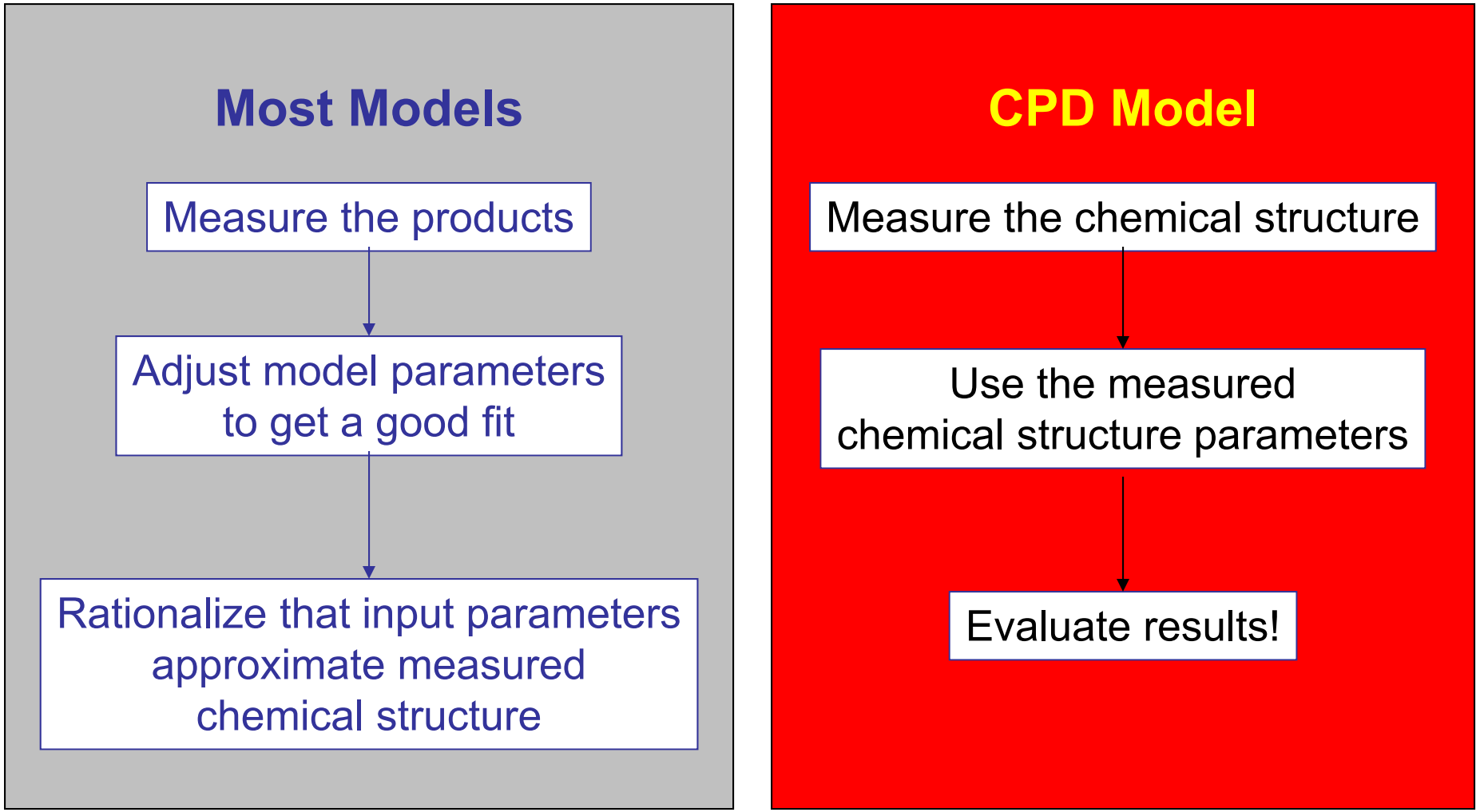
Joint research effort

Sandia National Labs

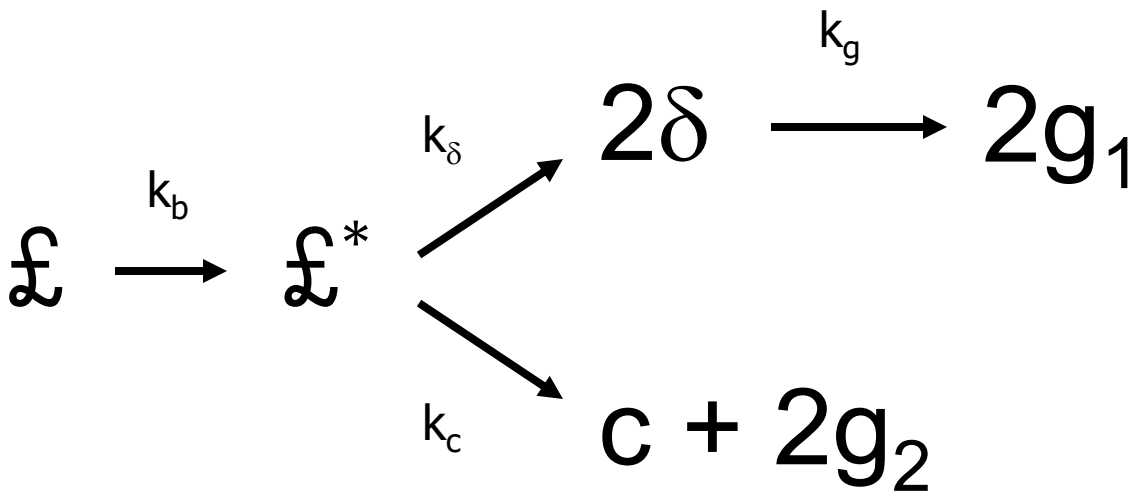
University of Utah

Brigham Young University

Philosophies Used in Pyrolysis Models



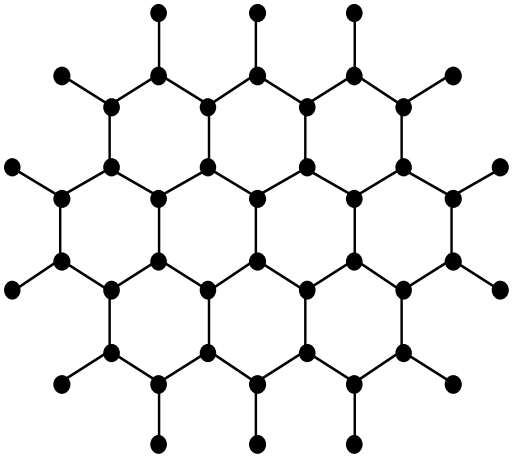
Bridge Scission Mechanism



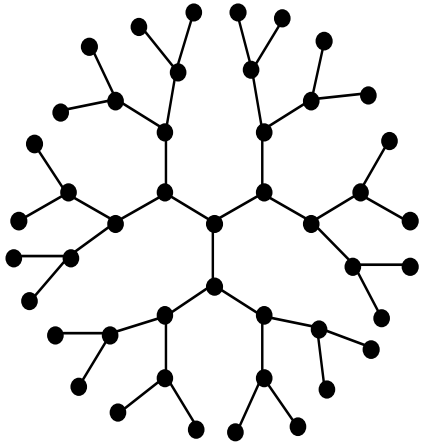
How Does Bridge-Breaking Relate to Mass Release?

⇨ Lattice structure (also called network)

Types of Lattices

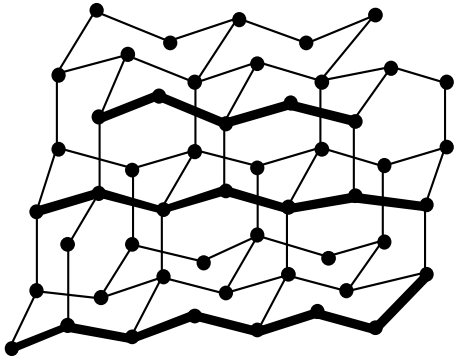


HONEYCOMB LATTICE

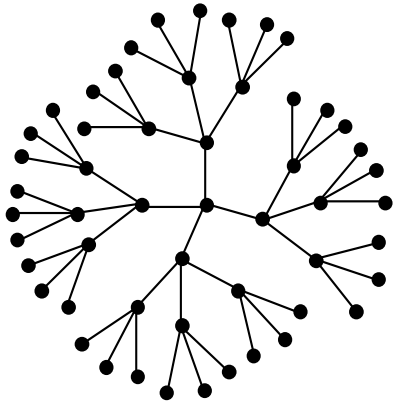


A. Coordination number = 3

B. Coordination number = 4

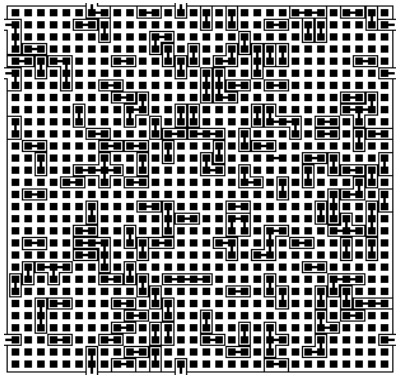


DIAMOND LATTICE

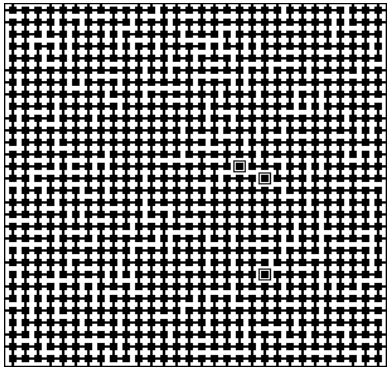


TETRAGONAL BETHE LATTICE

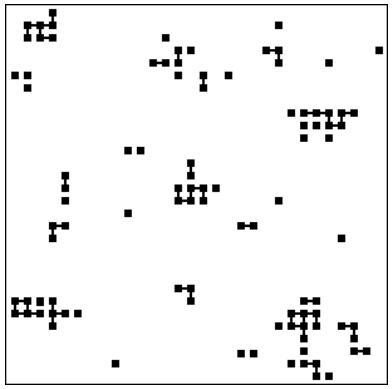
Relationship Between Broken Bridges and Finite Clusters



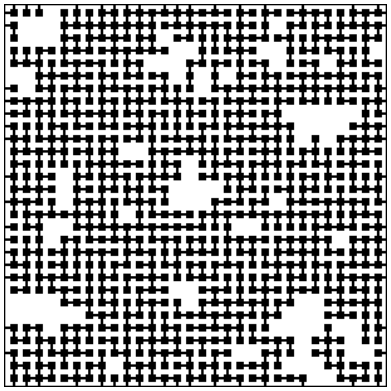
a. p = 0.1



b. p = 0.8

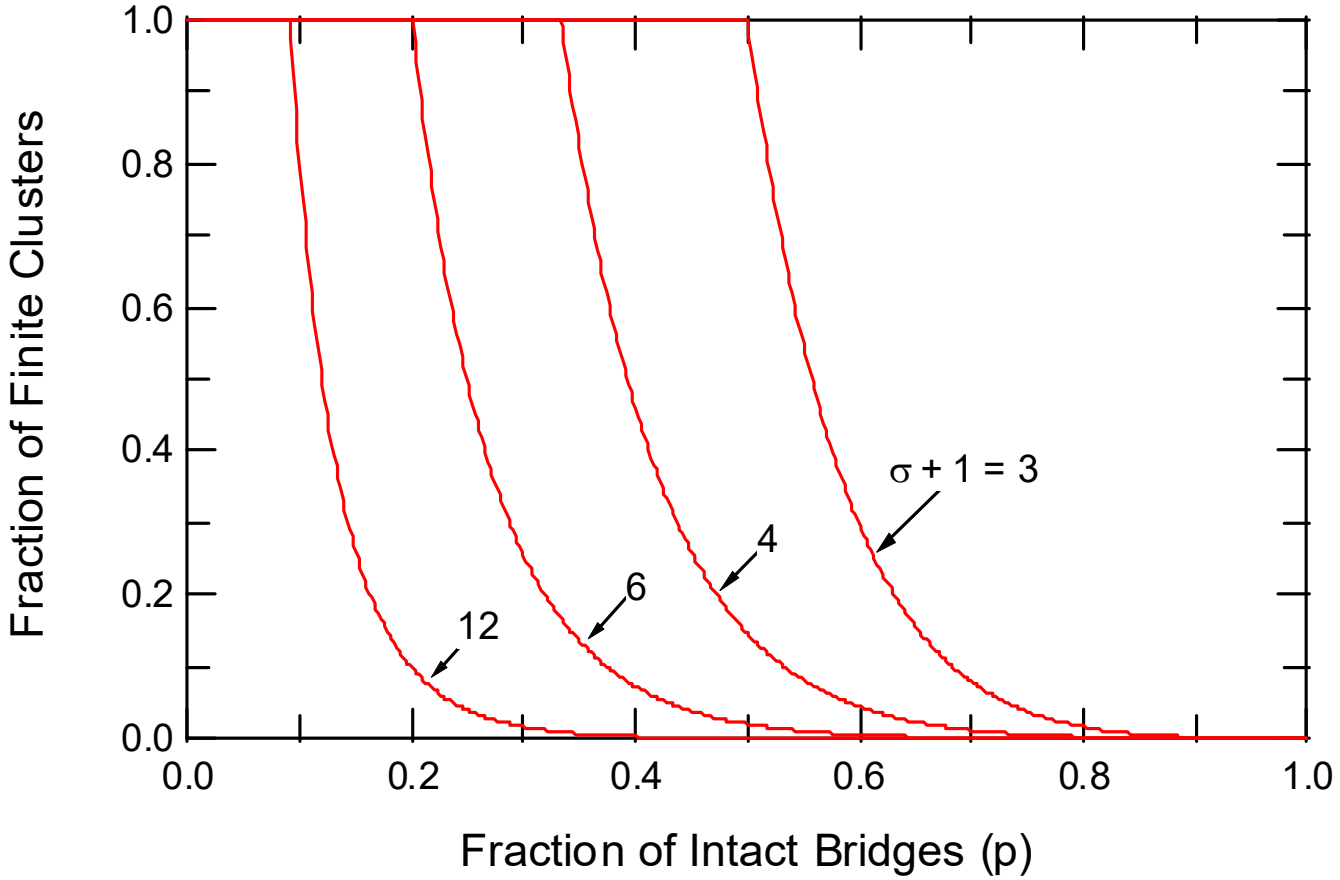


c. p = 0.55, finite fragments



d. p = 0.55, infinite lattice

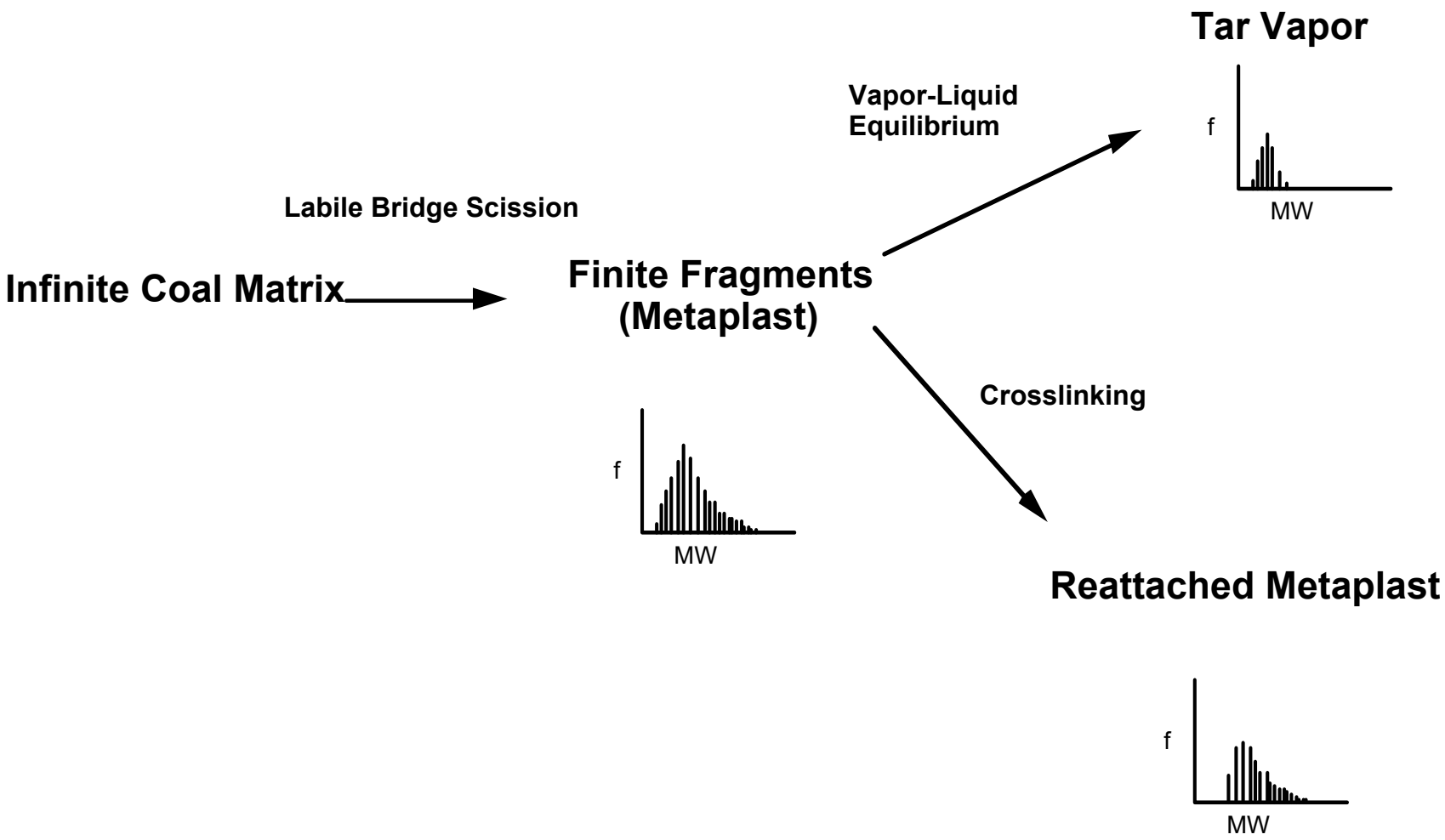
Closed-Form Solution of Percolation Lattice Statistics



$$F(p) = \left(\frac{1-p}{1-p^*} \right)^{\sigma+1}$$

where p* is the solution to $p^*(1-p^*)^{\sigma-1} = p(1-p)^{\sigma-1}$

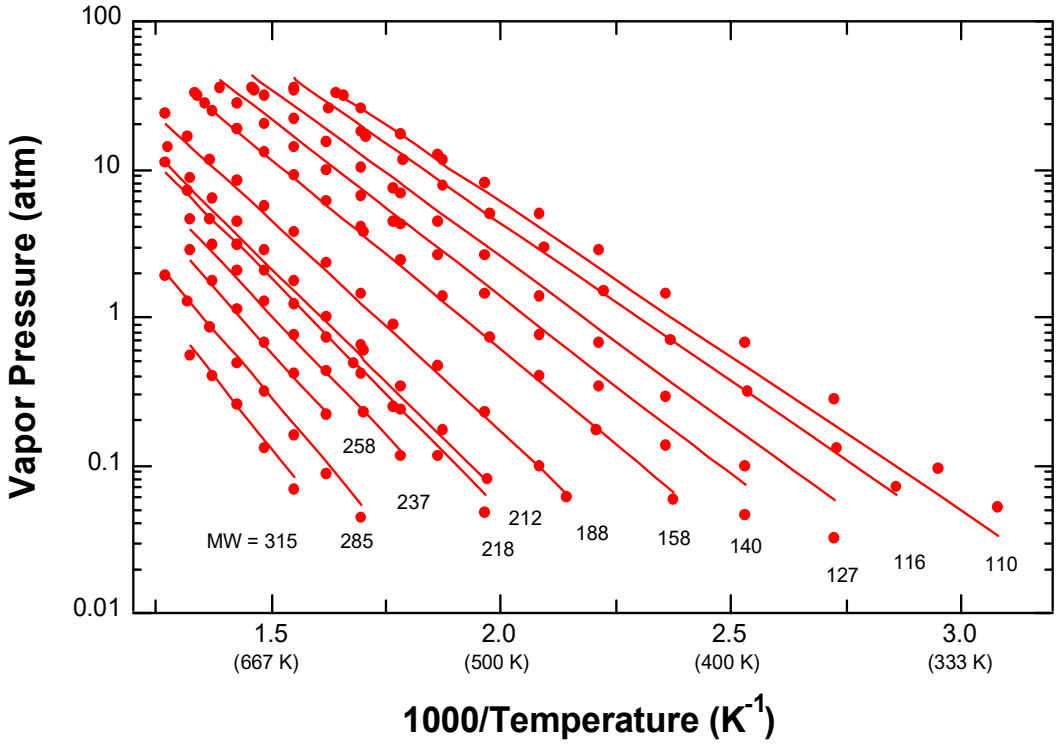
Vapor-Liquid Equilibrium and Crosslinking



How Do You Treat Vapor Pressures of Coal Fragments?

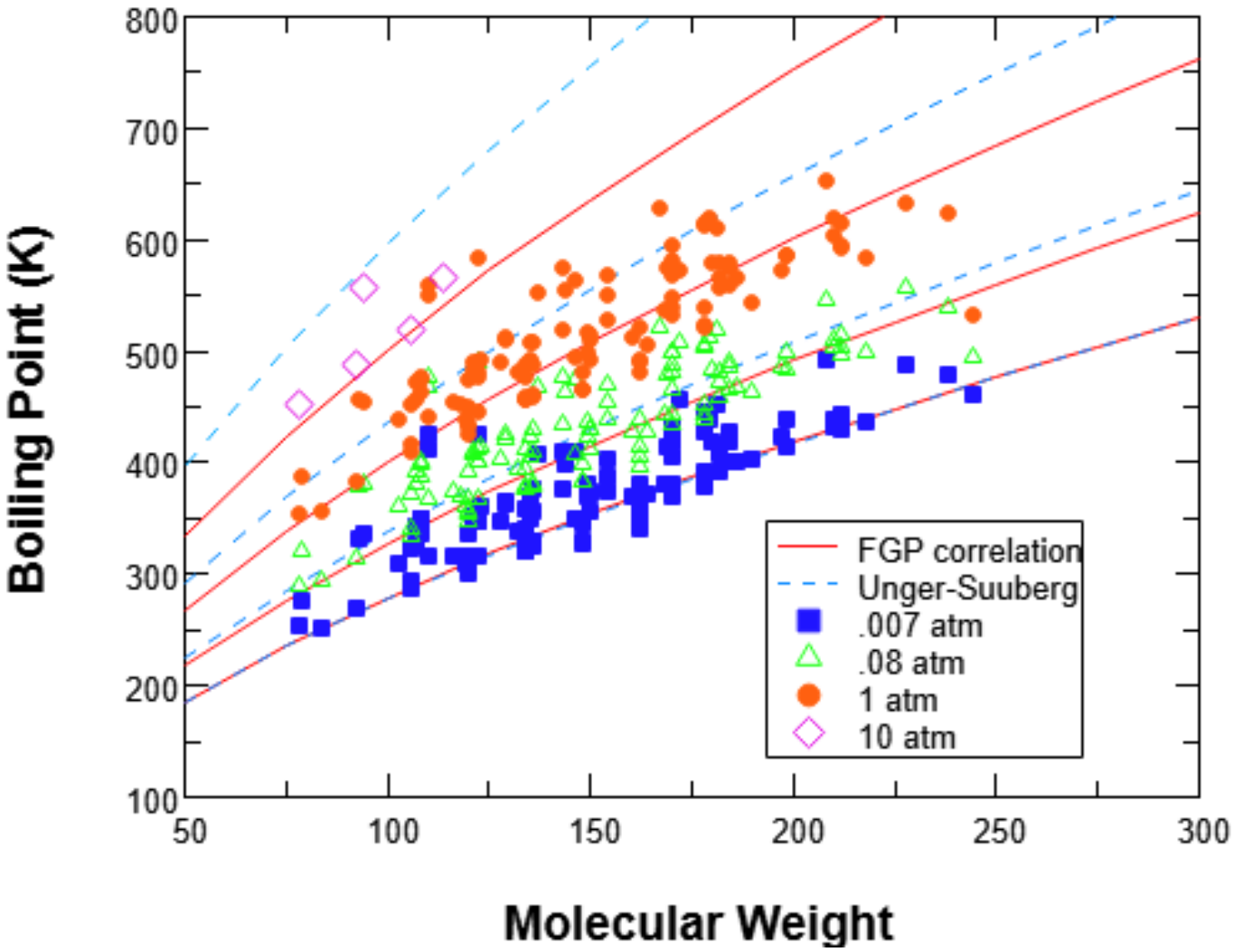
Generalized Hydrocarbon Vapor Pressure Correlation for the CPD Model

$$P_i^{vap} = c_1 \exp\left(-c_2 MW_i^{c_3} / T\right)$$



Data taken from Gray et al. (Ind. Eng. Chem. Process Des. Dev., 1985) for 12 narrow boiling point fractions of coal liquids from a Pittsburgh seam coal

Vapor Pressure Model Compares Well with Pure Component Data



Input Parameters Required by the CPD Model

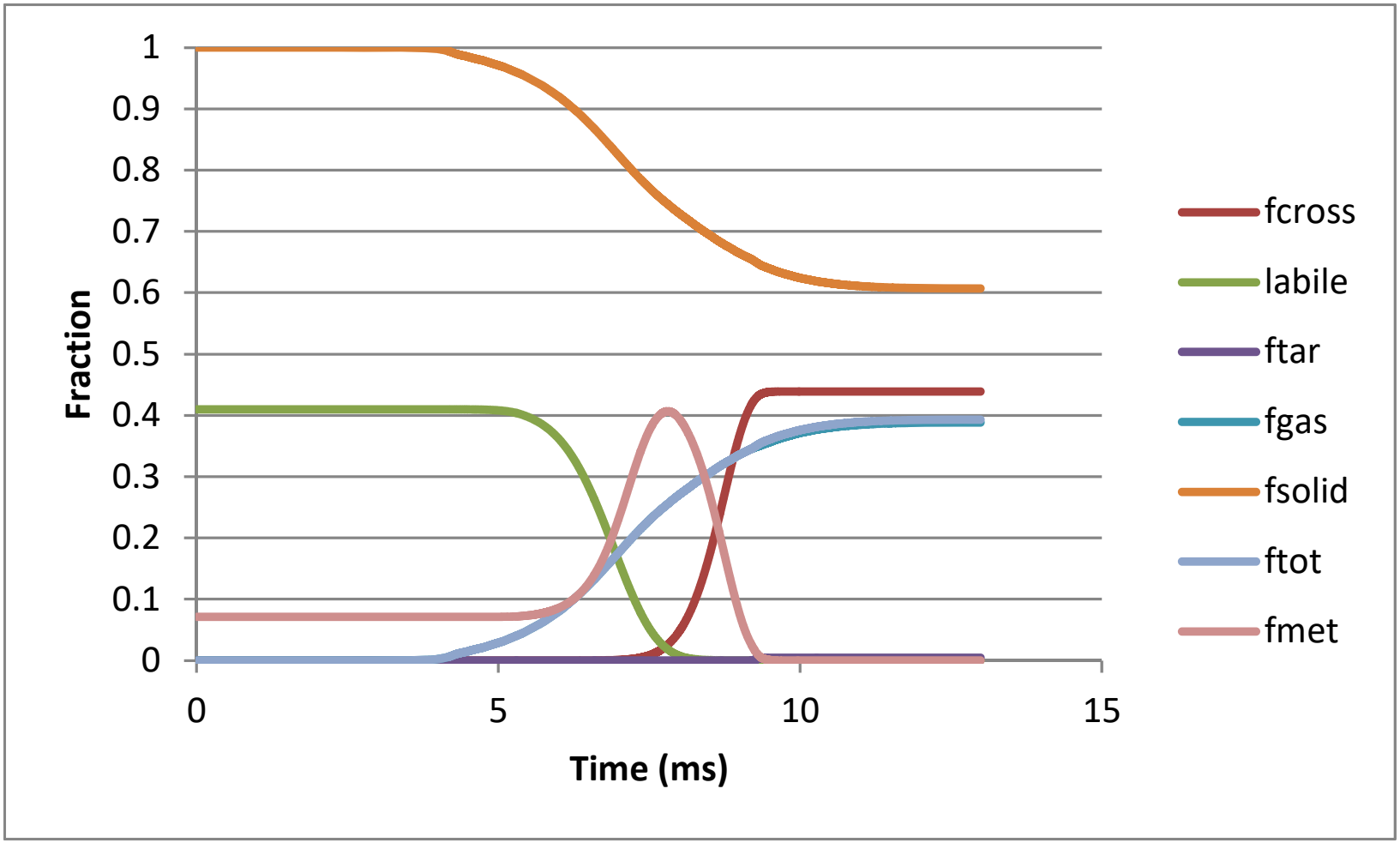
- Number of attachments per cluster ($\sigma+1$) (i.e., coordination number)
- Fraction of attachments that are bridges (p_0) (bridges/bridges+side chains)
- Molecular weight per aromatic cluster (M_{cl})
- Molecular weight per side chain (M_δ)

- Fraction of bridges that are stable (c_0)

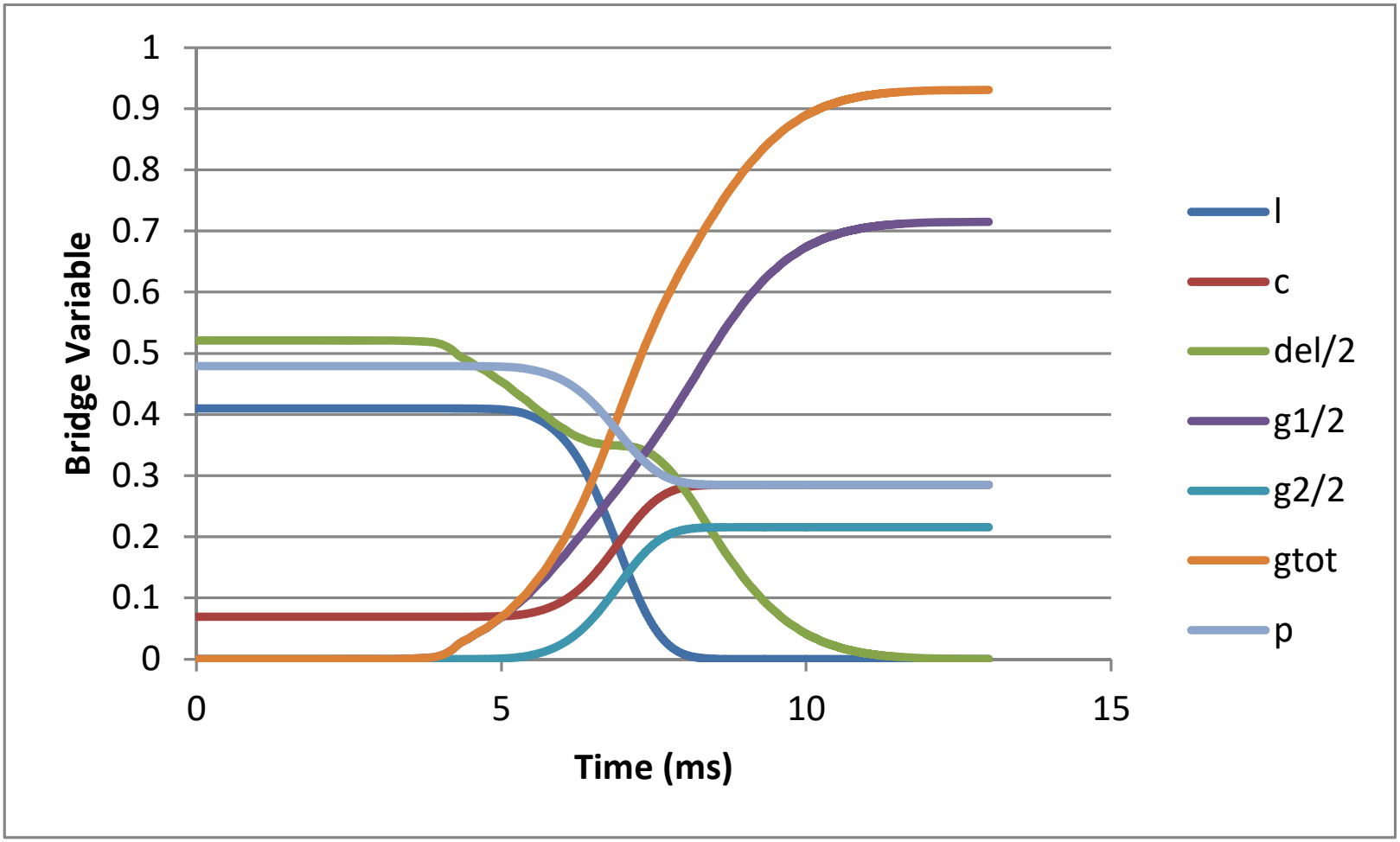
Other Parameters
(not usually adjusted)

- Rate coefficients
  - Assumed to be coal-independent
  - Set based on extensive comparisons with data
  - Uses sequential (not parallel) distributed activation energy
  - Kinetic Coefficients
    - A_b, E_b, σ_b (bridge breaking)
    - A_g, E_g, σ_g (side chain release)
    - A_{cr}, E_{cr} (crosslinking)
    - ρ (ratio of 2 A's for bridge breaking and bridge collapse)
- Vapor pressure coefficients
  - Assumed to be coal-independent

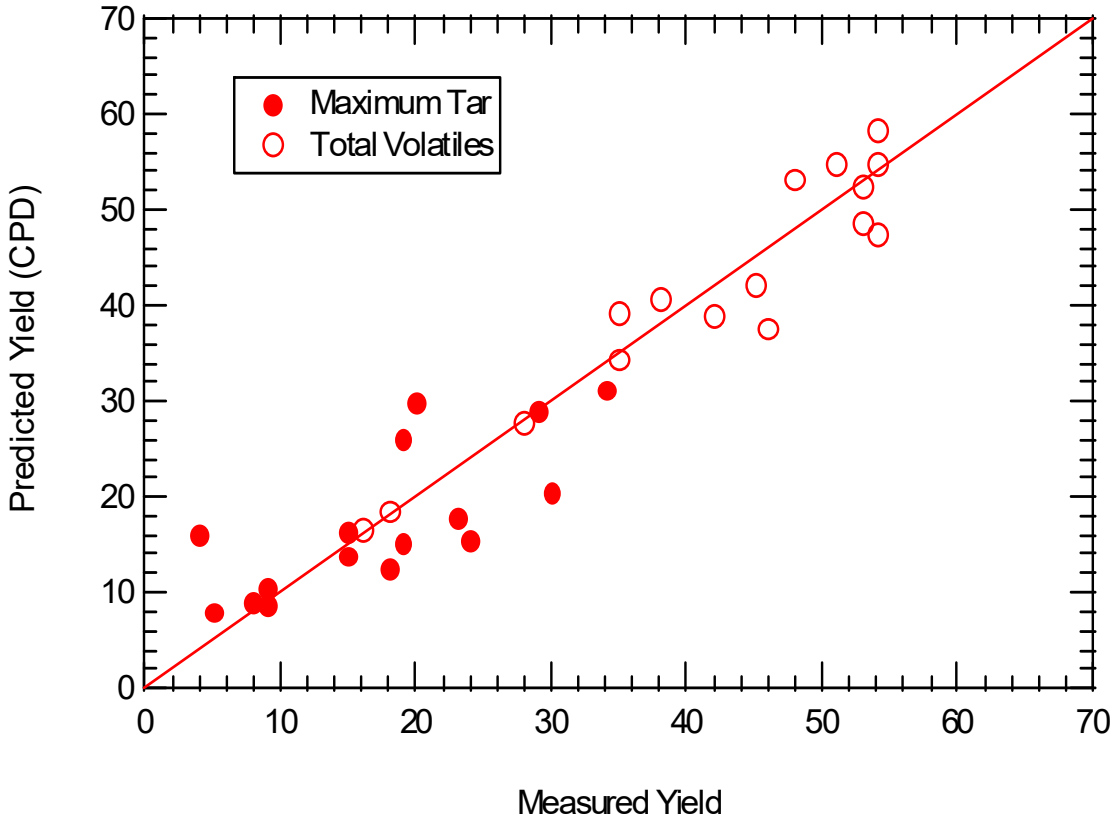
Sample CPD Prediction



Bridge Variables

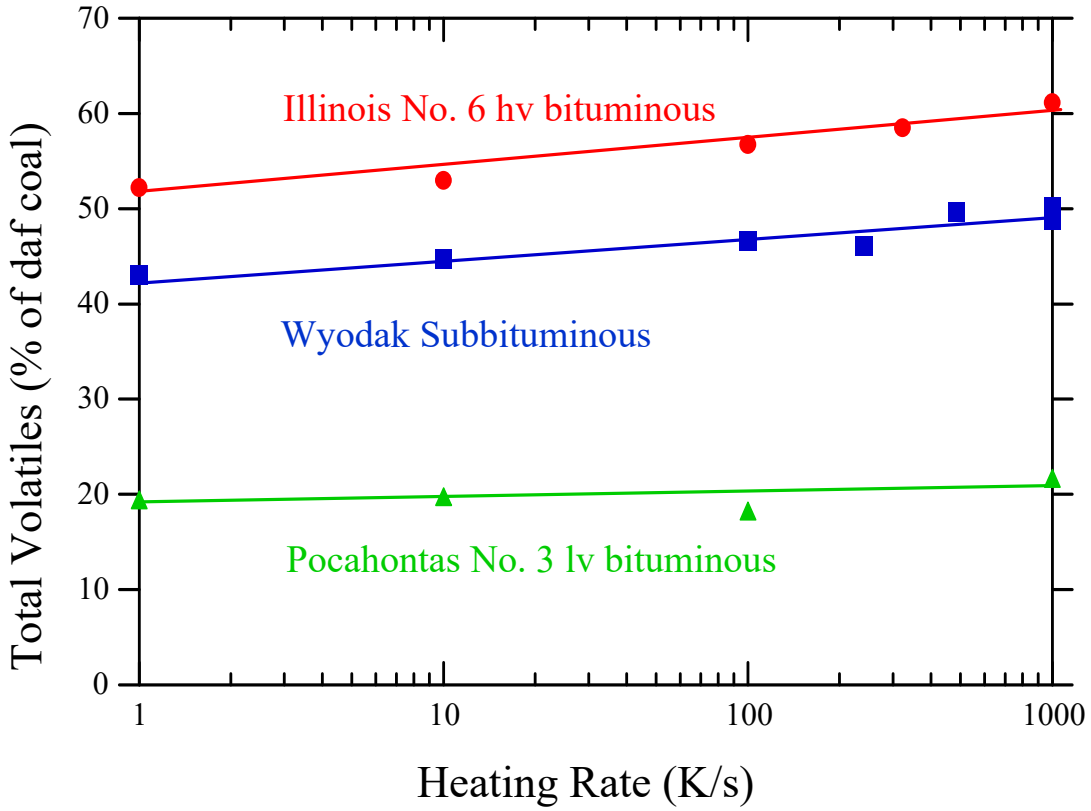


Good Agreement with Tar and Total Volatile Yields



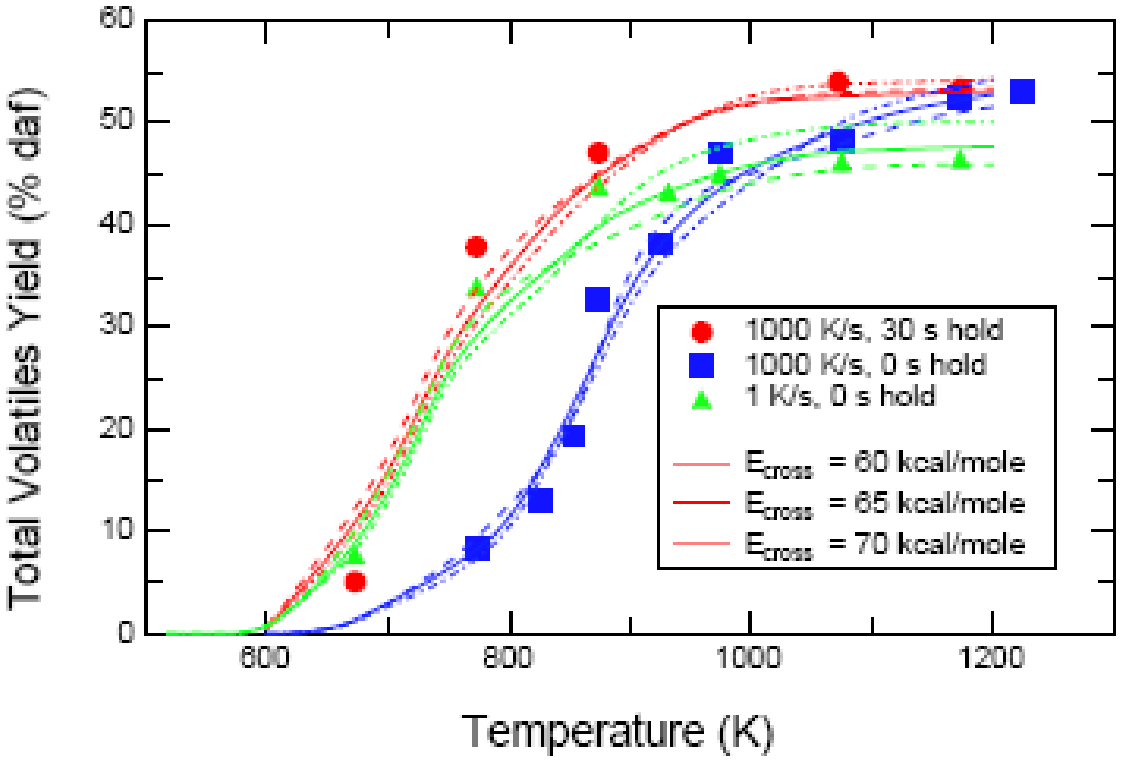
Coal-dependent input coefficients taken directly from NMR data for 16 coals (0.5 to 1000 K/s, 1000 to 1300 K)

Total Volatile Yield Increases with Increasing Heating Rate



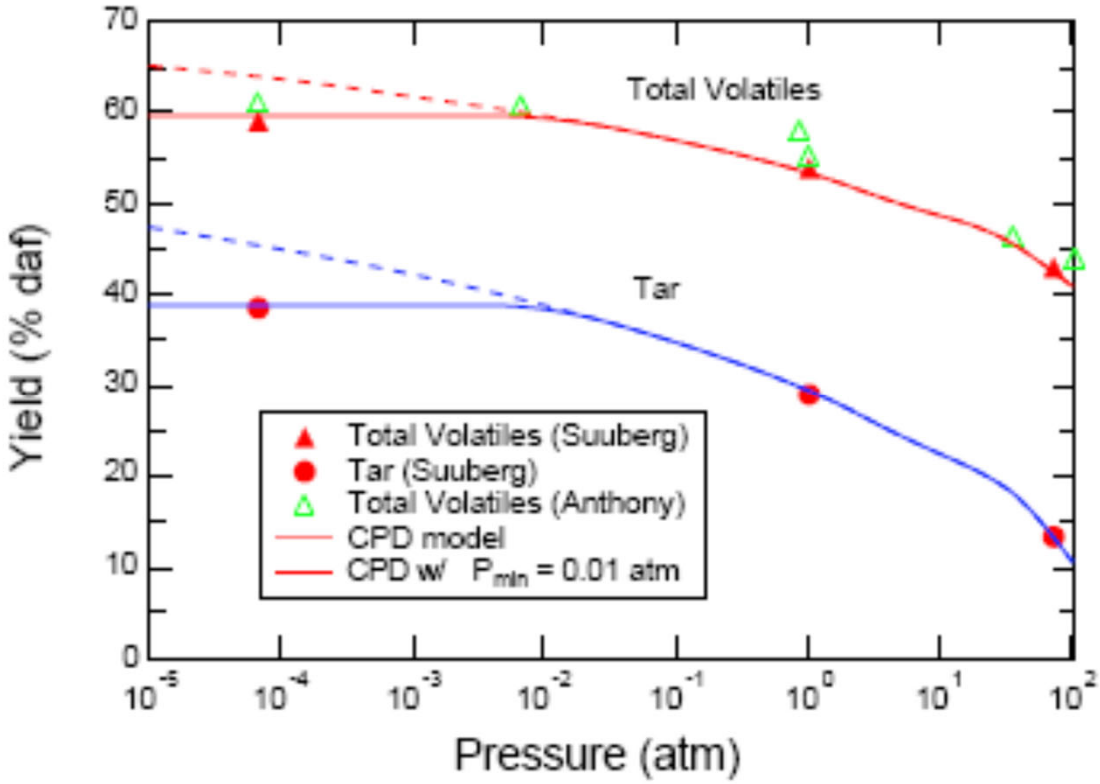
Argonne Premium coals heated to 700 °C in helium with 30 s hold (Gibbins and Kandiyoti, Energy & Fuels, 1989)

Reaction Temperature Increases with Increasing Heating Rate



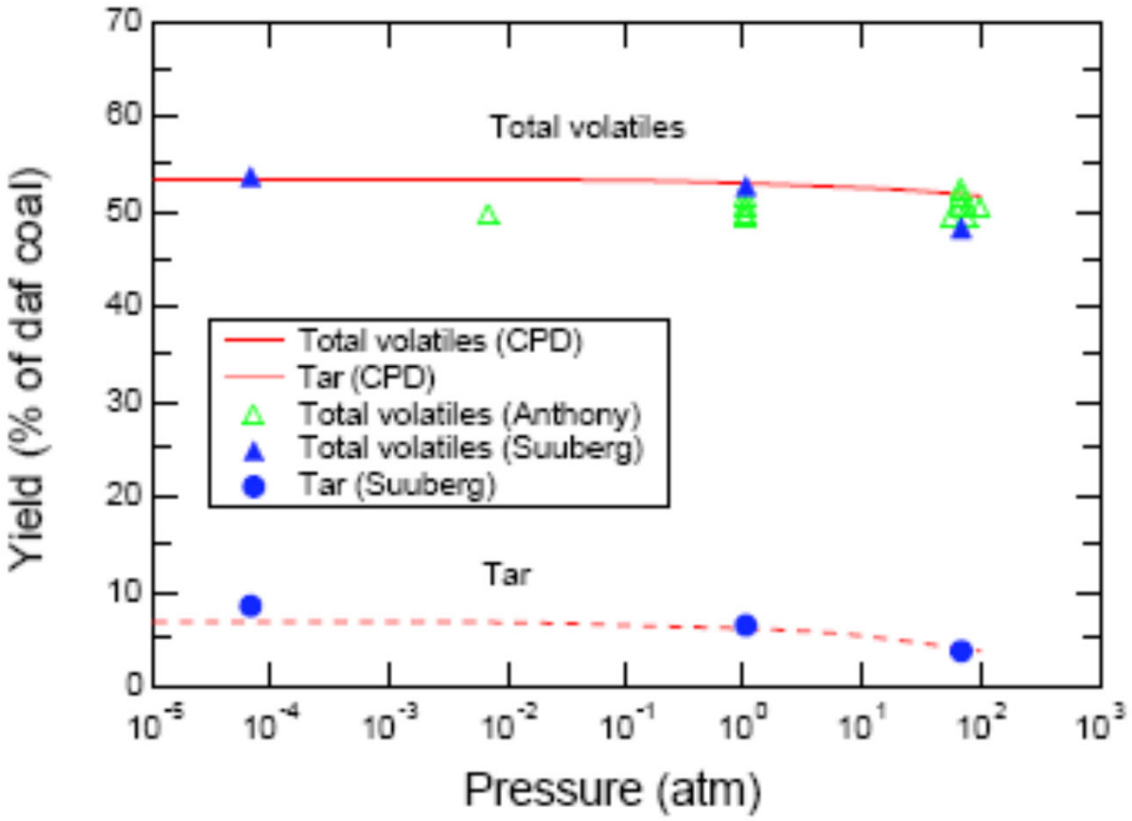
Pittsburgh No. 8 hv bituminous coal in Helium (Gibbins and Kandiyoti, E&F, 1989). Lines are CPD model predictions (Fletcher, et al., E&F 1992)

Total Volatile and Tar Yields Decrease with Increasing Pressure for hv Bituminous Coals



Pittsburgh hv bituminous coal data from heated grid experiments, Anthony (1974) and Suuberg (1977), 1000 K/s to 1000 °C. CPD model predictions from Fletcher, et al. (1992)

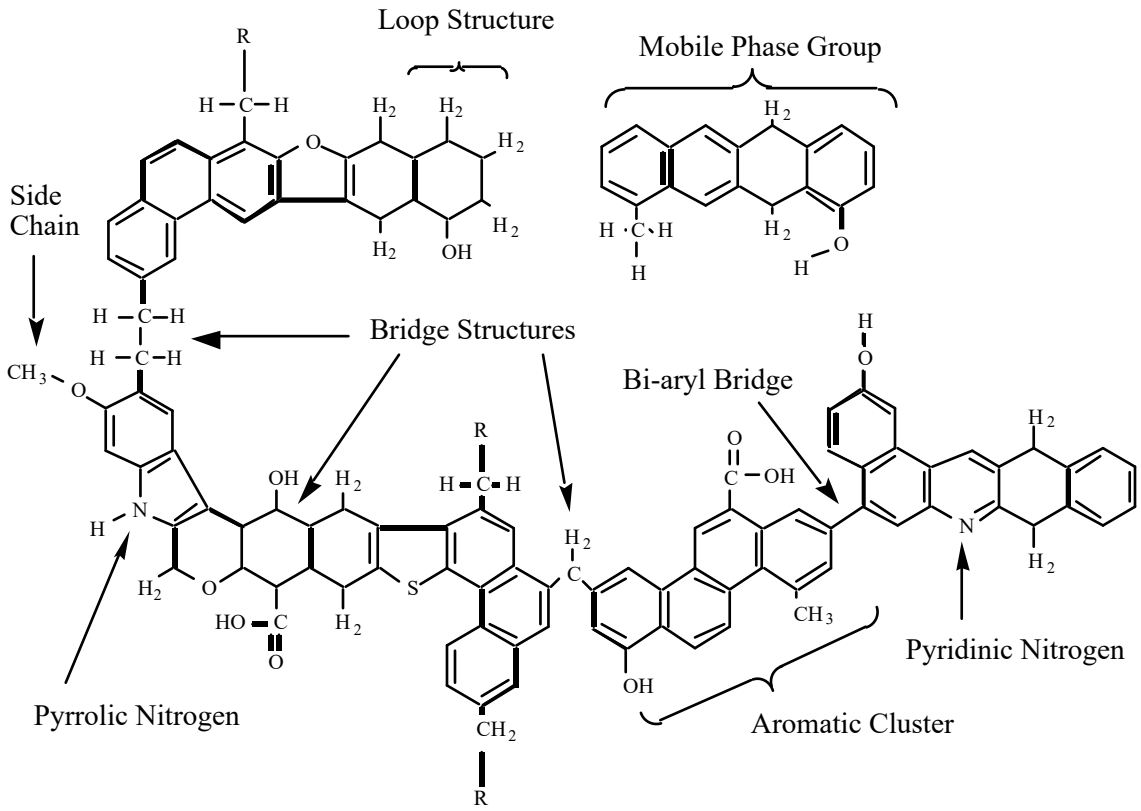
Effect of Pressure on Low Rank Coal Devolatilization is Small



Zap lignite data from heated grid experiments, Anthony (1974) and Suuberg (1977), 1000 K/s to 1000 ^{o}C. CPD model predictions from Fletcher, et al. (1992)

What if the NMR parameters are not measured for your coal?

Description of Parent Coal Structure



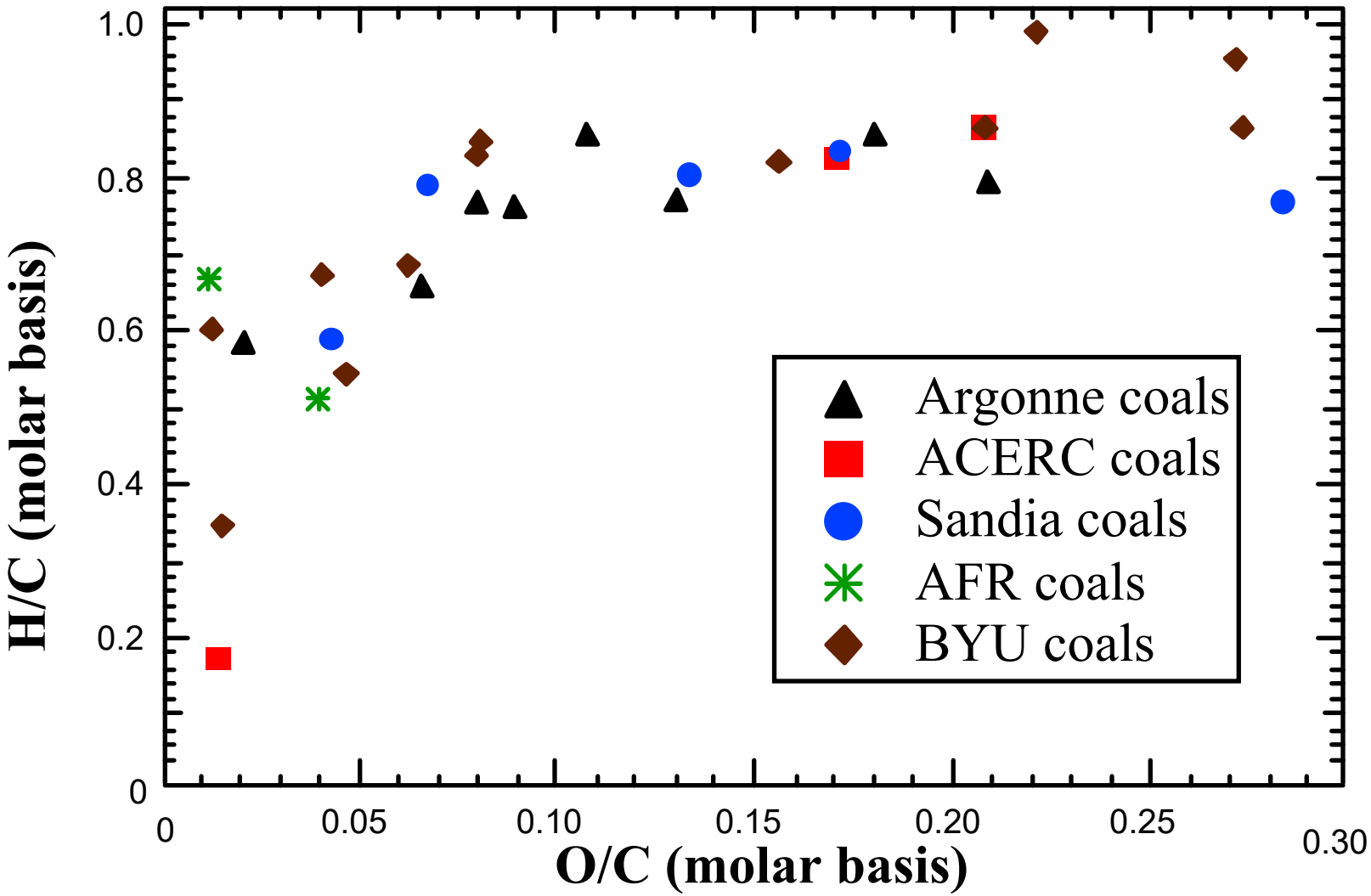
M_{cl} = average molecular weight per cluster

M_{δ} = average side chain molecular weight

$\sigma + 1$ = average number of attachments per cluster

p_0 = fraction of attachments that are bridges

NMR Data for Coals



#	Source	Seam	M_δ	M_{cl}	p_0	$\sigma+_1$	c_0
1	PSOC 1507 (AR)	Beulah-Zap	42	326	0.60	5.0	0.11
2	PSOC-1520 (AR)	Wyodak	41	357	0.54	5.0	0.08
3	PSOC-1502 (AR)	Blind Canyon	36	386	0.46	5.0	0.00
4	PSOC-1493 (AR)	Illinois #6	37	334	0.54	5.2	0.01
5	PSOC-1451 (AR)	Pittsburgh #8	31	330	0.53	4.9	0.00
6	ANL (AR)	Stockton	31	329	0.55	5.0	0.00
7	ANL (AR)	Upper Freeport	25	277	0.63	4.8	0.00
8	PSOC-1508 (AR)	Pocahontas #3	16	230	0.75	4.1	0.36
9	PSOC-1443 (ACERC)	Lower Wilcox	36	281	0.61	4.8	0.11
10	PSOC-1488 (ACERC)	Dietz	40	347	0.55	5.0	0.07
11	PSOC-1468 (ACERC)	Buck Mountain	14	616	0.90	4.6	0.36
12	PSOC-1445D (Sandia)	Blue #1	40	348	0.54	5.0	0.07
13	PSOC-1451D (Sandia)	Pittsburg #8	30	353	0.51	4.8	0.00
14	PSOC-1493D (Sandia)	Illinois #6	42	383	0.51	5.2	0.01
15	PSOC-1507D (Sandia)	Beulah-Zap	50	348	0.66	4.4	0.15
16	PSOC-1508D (Sandia)	Pocahontas #3	18	242	0.76	4.4	0.36
17	Goudey A (AFR)	not named	21	276	0.66	5.1	0.27
18	Goudey B (AFR)	not named	17	299	0.67	4.8	0.34
19	DECS-1 (BYU)	Bottom	50	436	0.48	4.5	0.12
20	DECS-7 (BYU)	Adaville #1	44	365	0.56	4.8	0.11
21	DECS-11 (BYU)	Beulah-Zap	46	320	0.63	4.5	0.15
22	DECS-13 (BYU)	Sewell	26	288	0.61	4.8	0.00
23	DECS-18 (BYU)	Kentucky #9	36	416	0.44	5.3	0.00
24	DECS-20 (BYU)	Elkhorn #3	33	387	0.48	4.9	0.00
25	DECS-21 (BYU)	Lykens Valley #2	9	321	0.94	4.0	0.36
26	DECS-27 (BYU)	Deadman	39	357	0.55	5.0	0.05
27	PSOC-1515 (BYU)	Penna. Semian. C	16	251	0.82	4.6	0.33
28	PSOC-1516 (BYU)	Lower Kittanning	21	301	0.66	4.9	0.08
29	PSOC-1520 (BYU)	Smith-Roland	52	386	0.56	4.2	0.15
30	PSOC-1521 (BYU)	Lower Hartshorne	16	237	0.71	4.1	0.36

NMR Database for coal

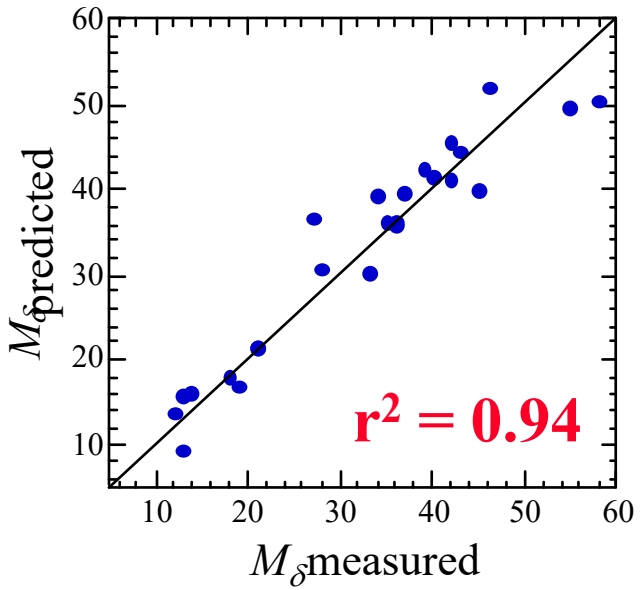
Correlation Procedure

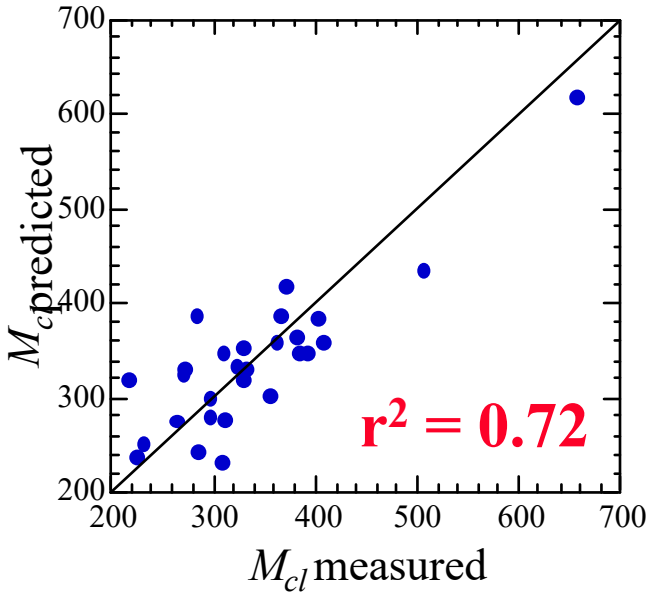
- Linear Correlations evaluated and ruled out
- Various non-linear equation forms examined

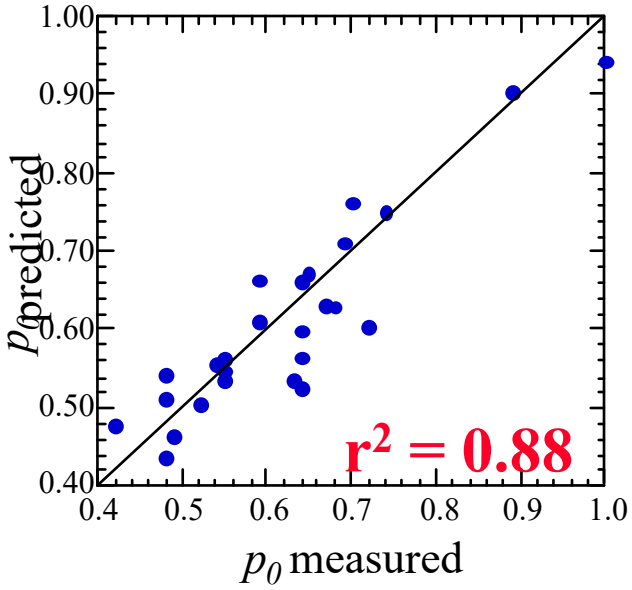
$$y = c_1 + c_2X_C + c_3X_C^2 + c_4X_H + c_5X_H^2 + c_6X_O + c_7X_O^2 + c_8X_{VM} + c_9X_{VM}^2$$

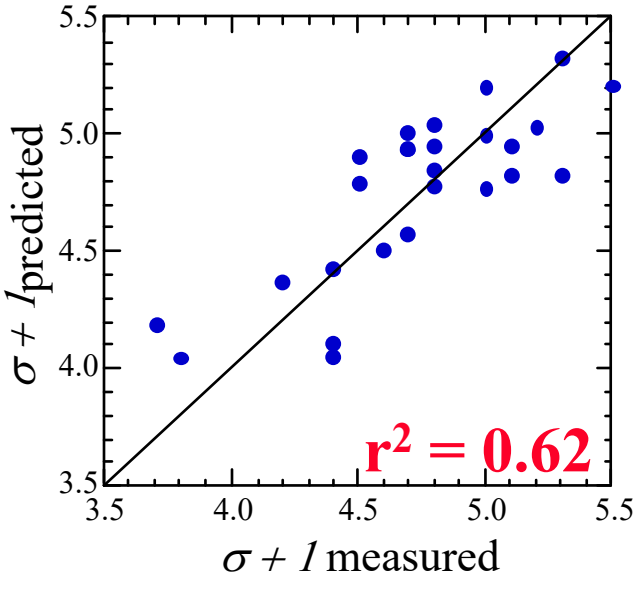
- NCSS used to examine data
- NCSS also used to regress constants

Correlation Results





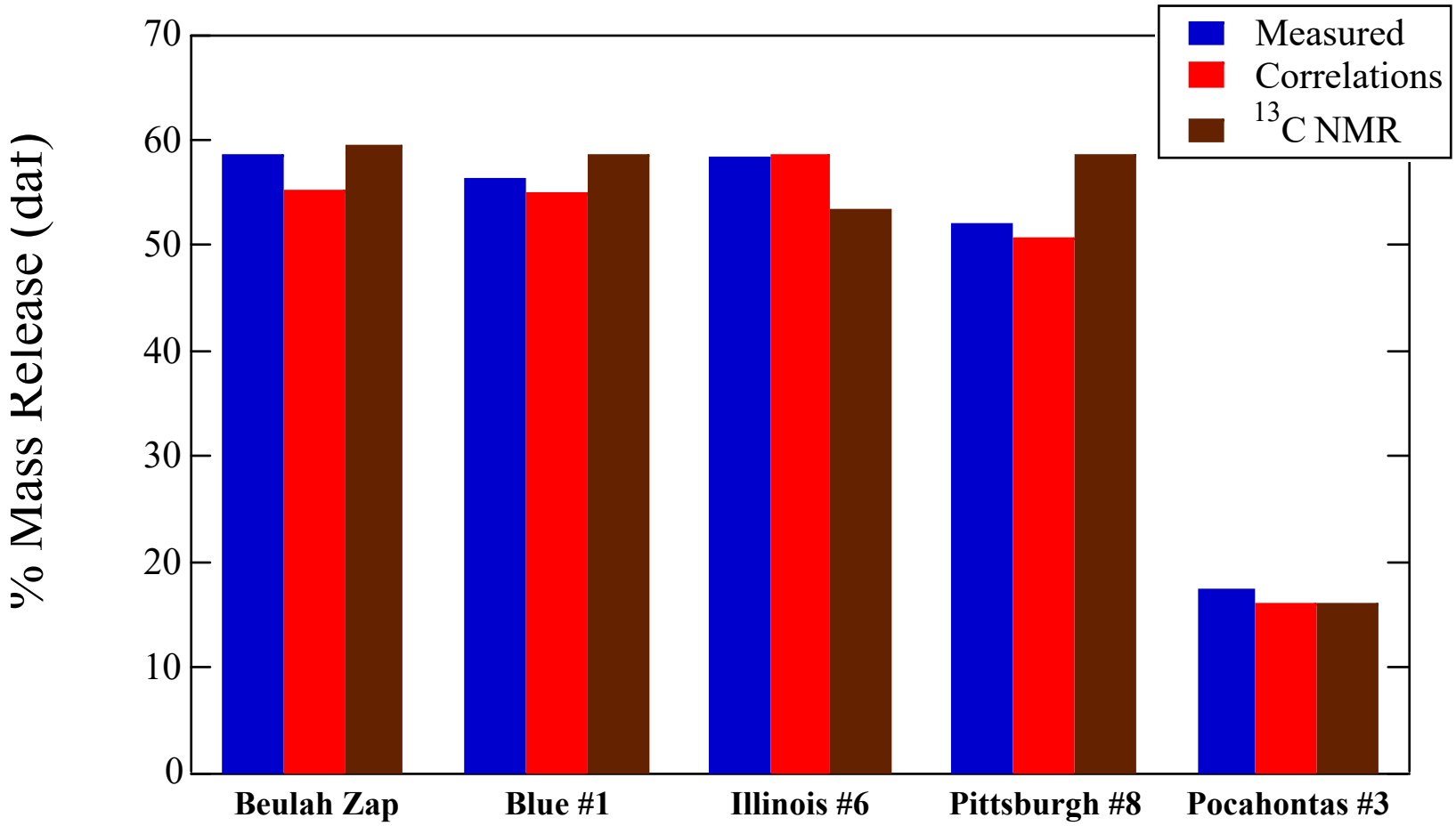




Empirical Correlation for C_0

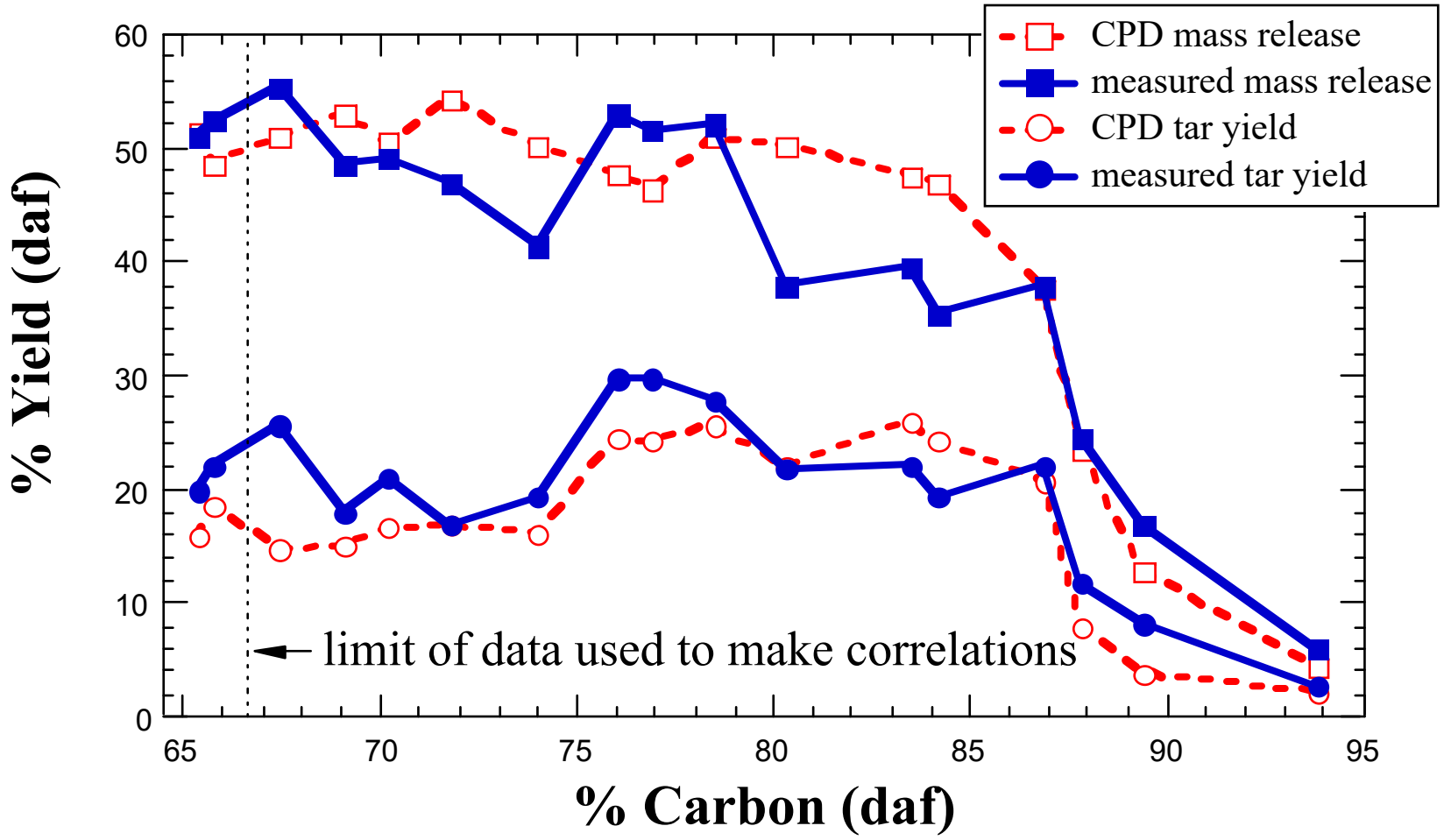
- Stable bridges in high rank coals
  - Correlated vs. %C (for C > 86% daf)
  - Based on CPD prediction of lv bit coals
- Early crosslinking in low rank coals
  - Correlated vs. %O (for O > 12% daf)
  - Based on CPD predictions of lignites

Application in CPD Model (Sandia)



10^5 K/s, 0% post flame O_2, ^{13}C NMR data available

Application in CPD Model (Xu and Tomita)



17 non - U.S. coals, 3000 K/s to 1037 K,

No ^{13}C NMR data available

Summary of NMR Correlation

- **Correlations work well for most coals**
- Not an adequate replacement for detailed ^{13}C NMR analysis
- Reasonable predictions of tar and light gas release may be expected when using correlated chemical structure parameters

CPD Calculations (RQ 6)