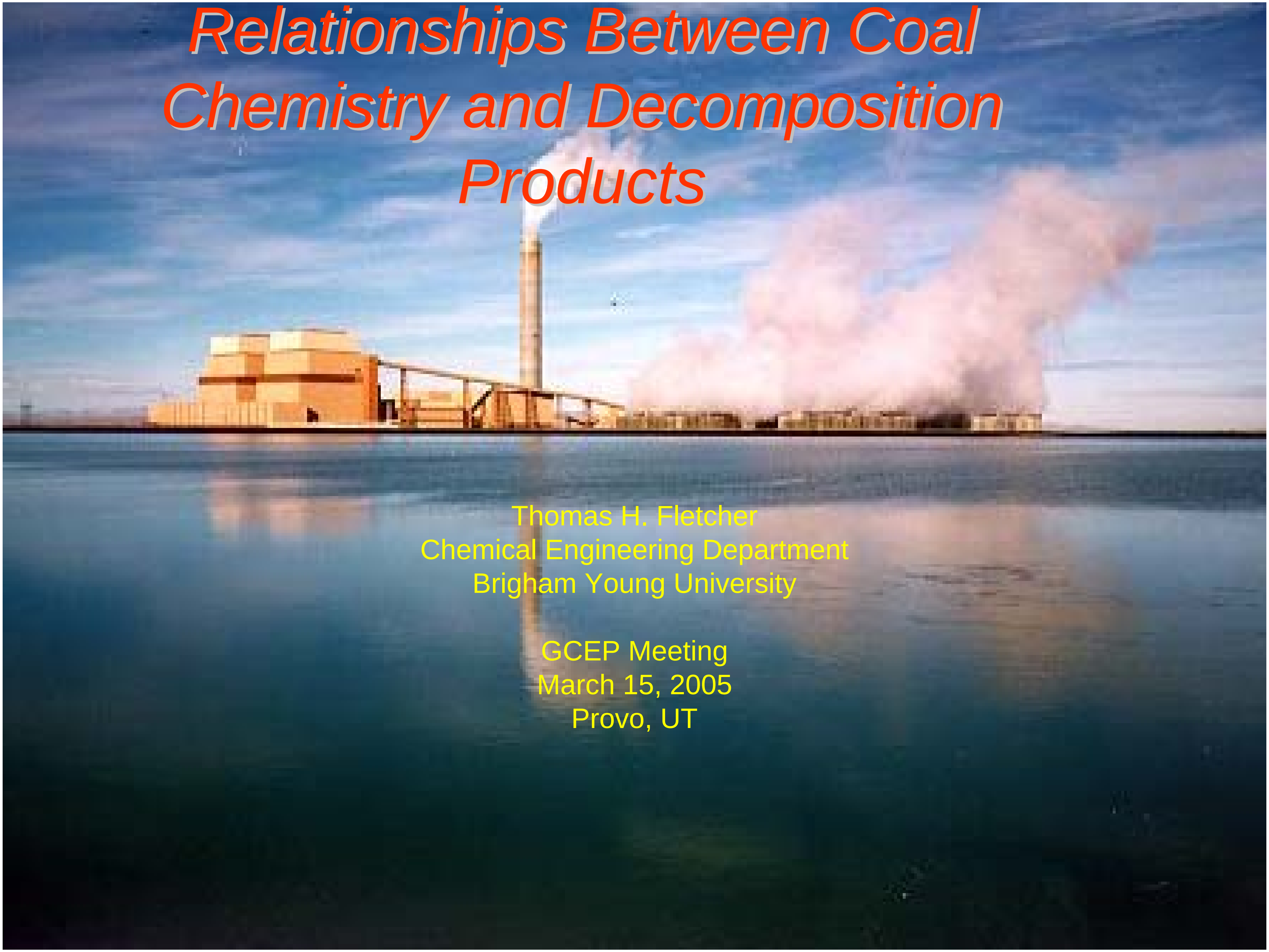

Relationships Between Coal Chemistry and Decomposition Products

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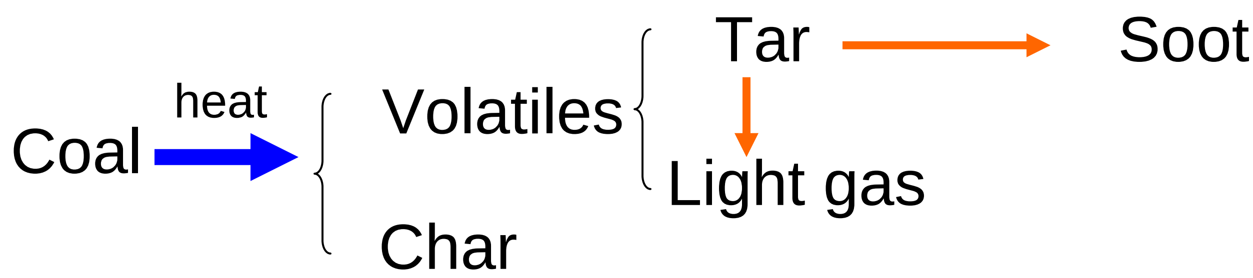
Brigham Young University

GCEP Meeting
March 15, 2005
Provo, UT

Outline

- What is coal?
- Simple descriptions of coal reaction
- Coal chemistry
- Lattice models
- Secondary reactions
- Light gas
- Nitrogen evolution

Coal Decomposition

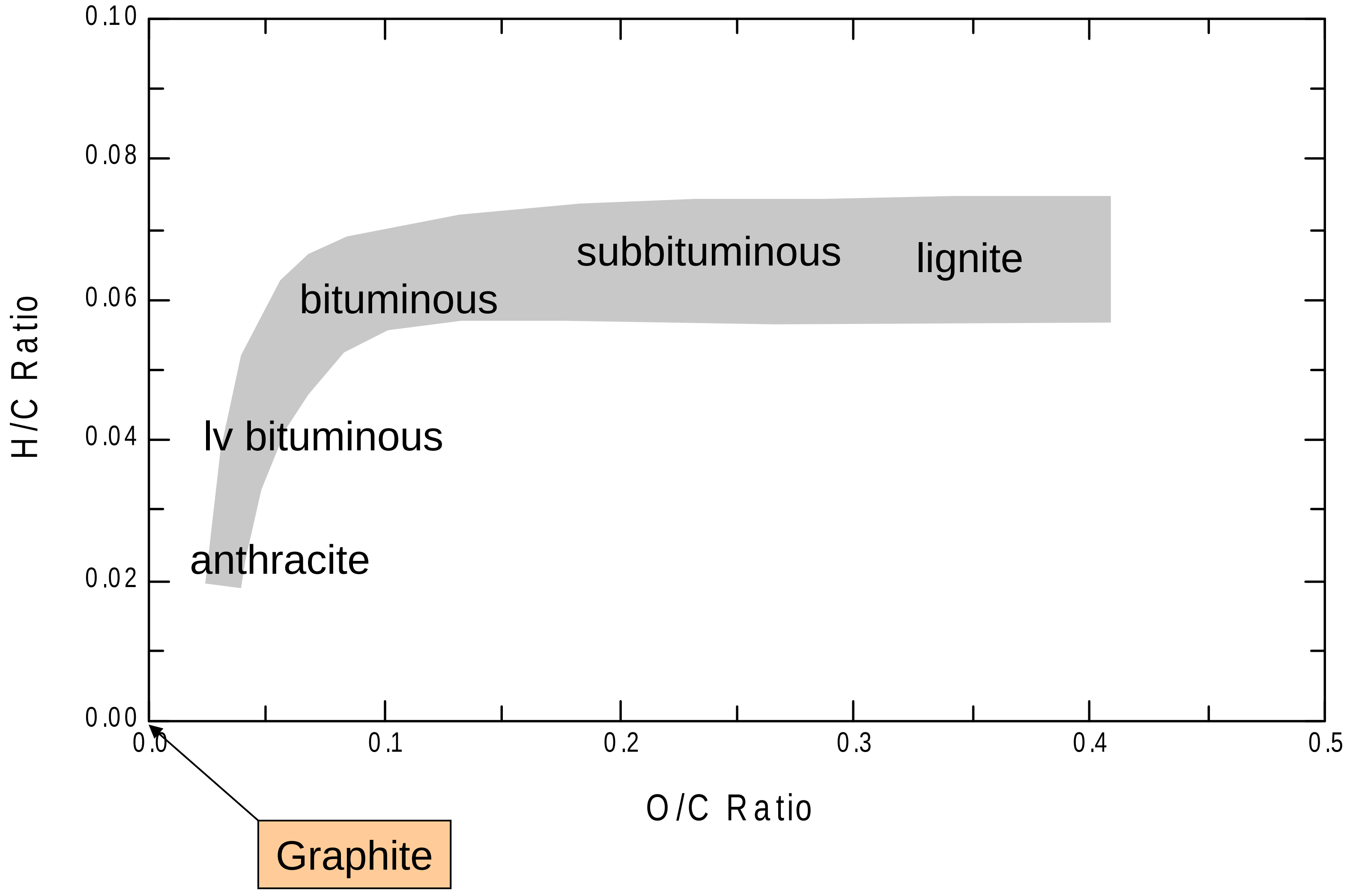


Primary Devolatilization

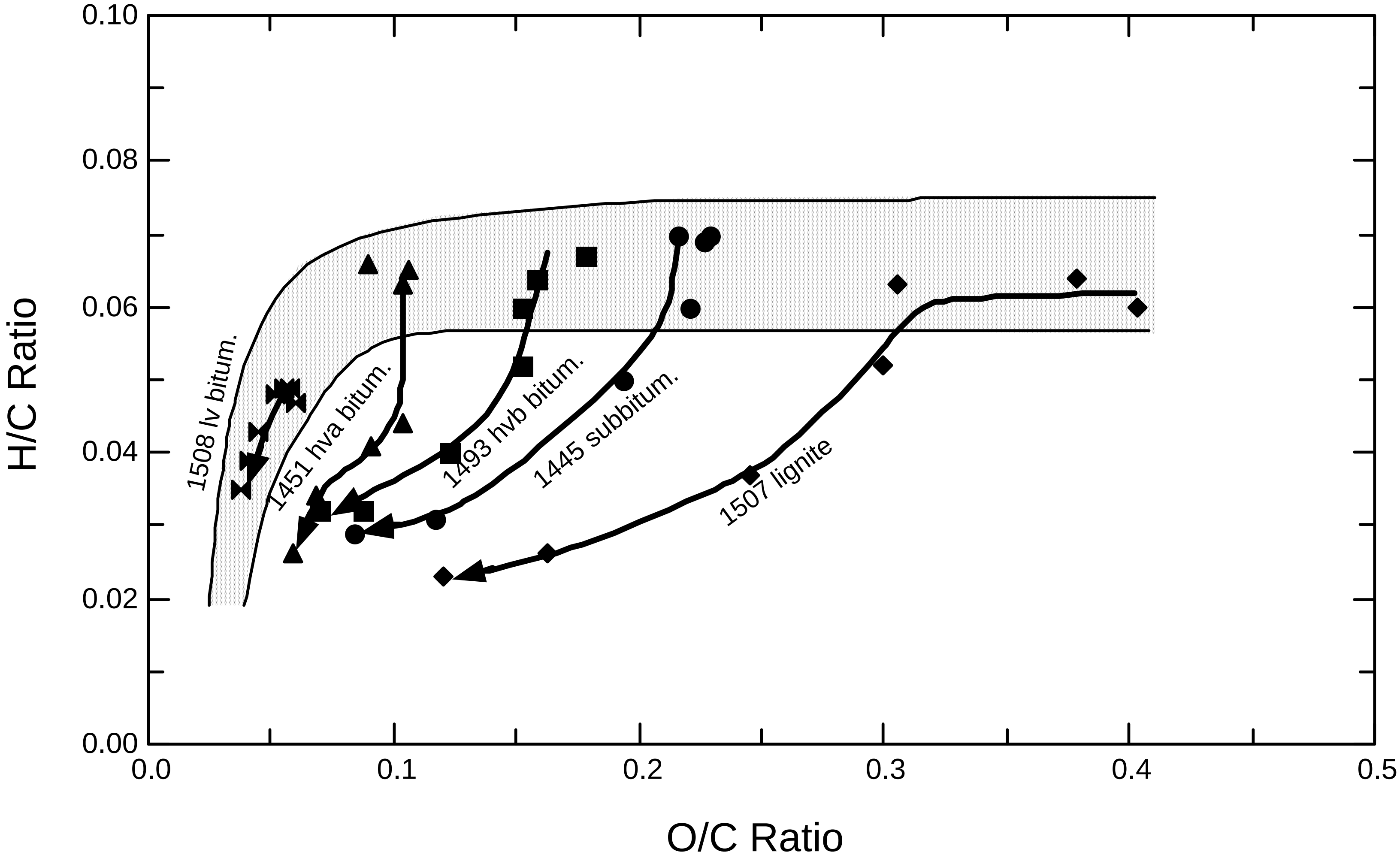
Secondary Devolatilization

Definition: Tar = Volatiles that condense at room T and P

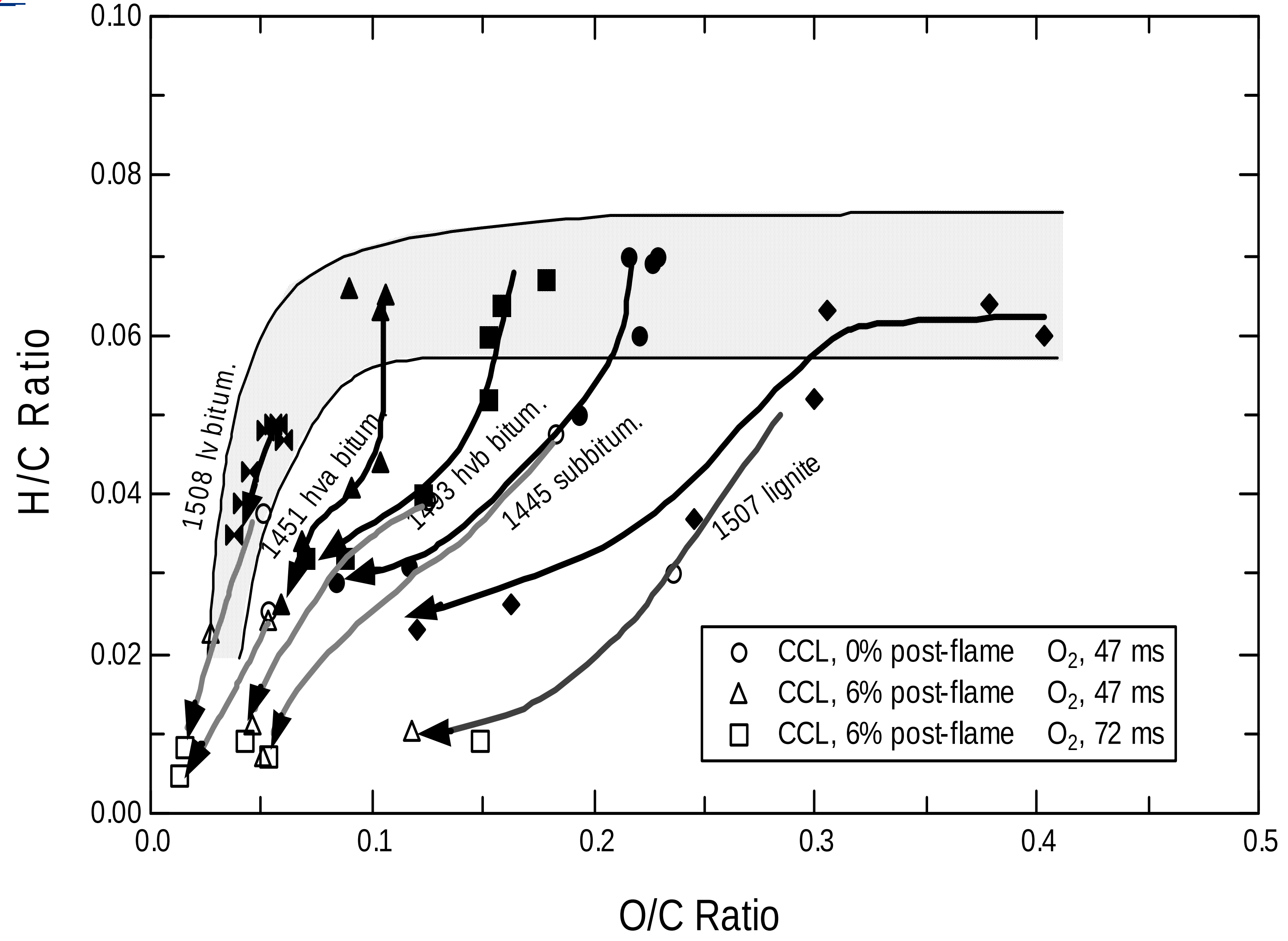
Coalification



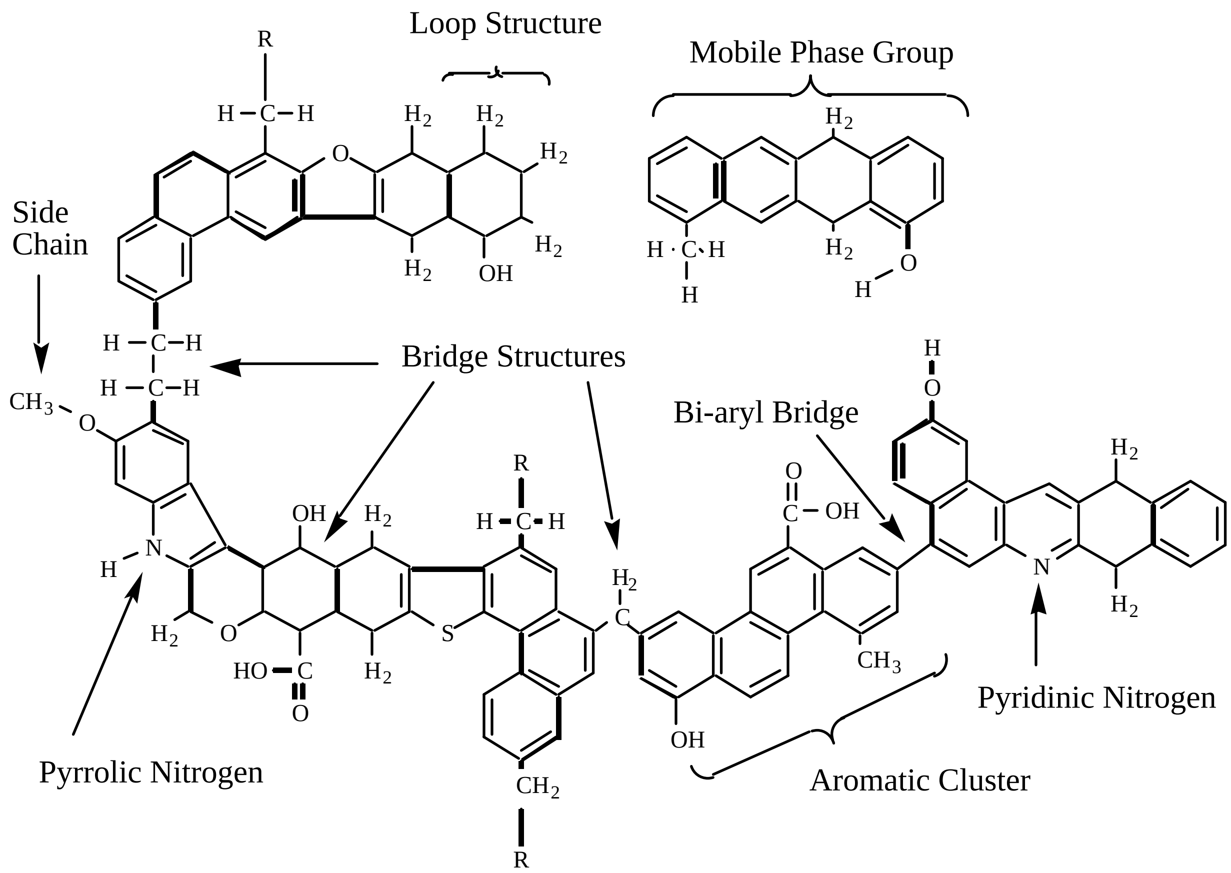
Moderate Temperature Pyrolysis



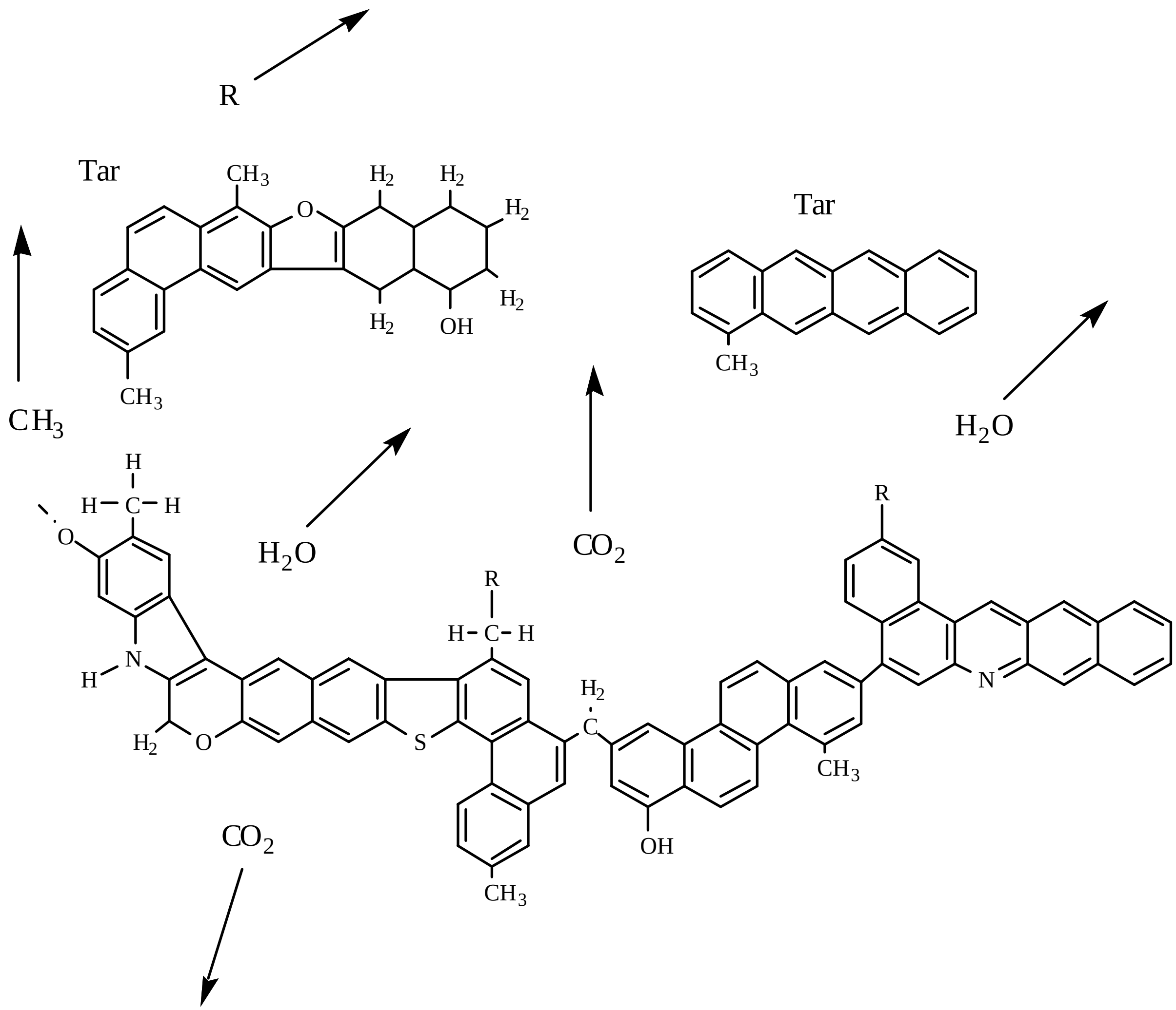
Early Char Combustion



Coal Structure



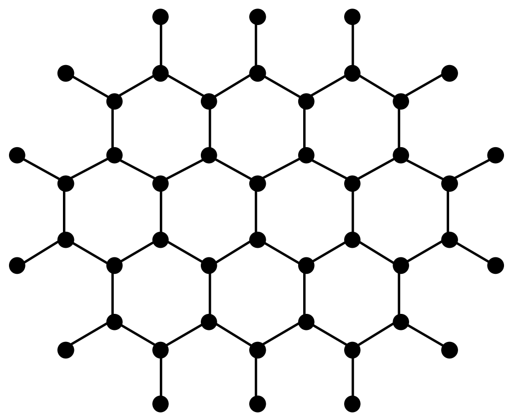
Primary Coal Pyrolysis



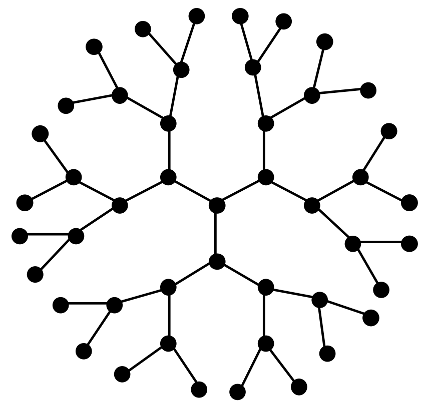
Lattice Devolatilization Models

- Coal molecule description
  - ^{13}C NMR spectroscopy
- Rates of bridge breaking
  - Aromatic clusters remain intact
  - Kinetics are coal independent
- Lattice statistics
  - Amount of liberated fragments
- Vapor-liquid equilibrium
  - Light fragments vaporize
- Crosslinking
  - Stable bridges form, making char

Types of Lattices



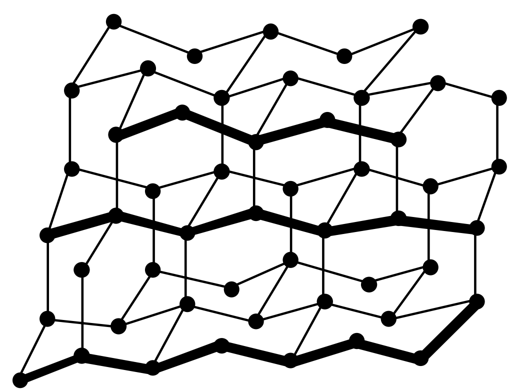
HONEYCOMB LATTICE



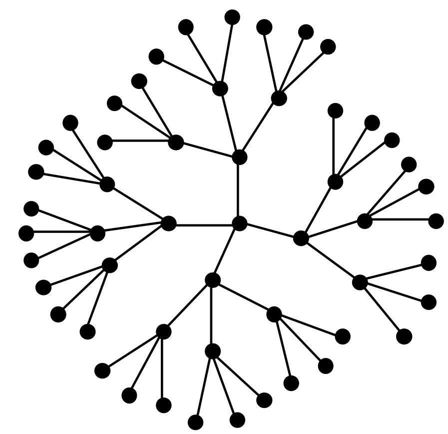
TRIGONAL BETHE LATTICE

A. Coordination number = 3

B. Coordination number = 4

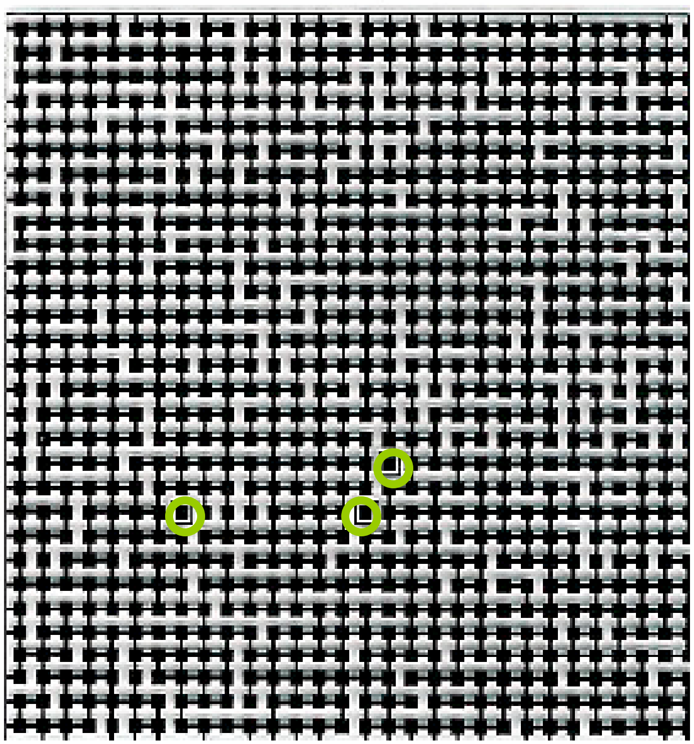


DIAMOND LATTICE

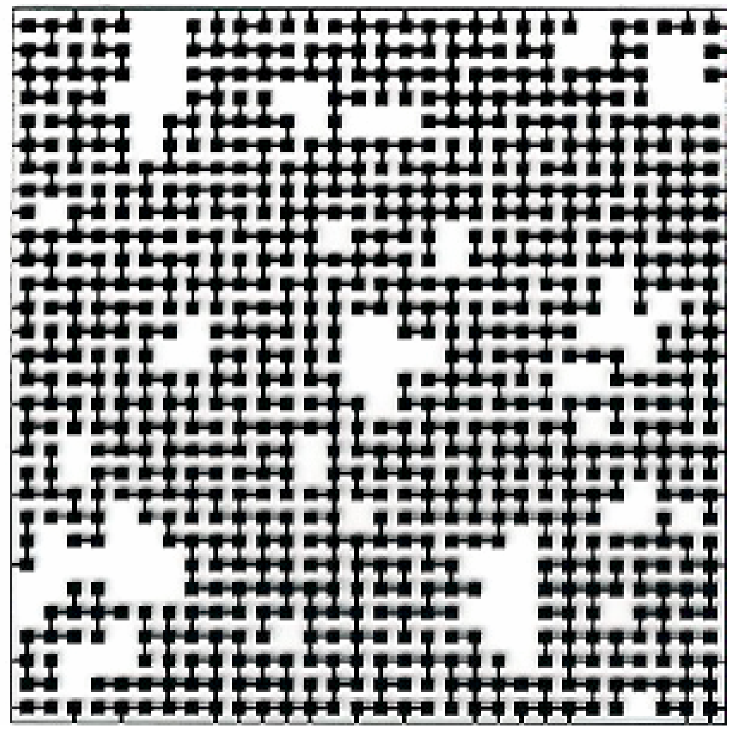


TETRAGONAL BETHE LATTICE

Lattice Statistics

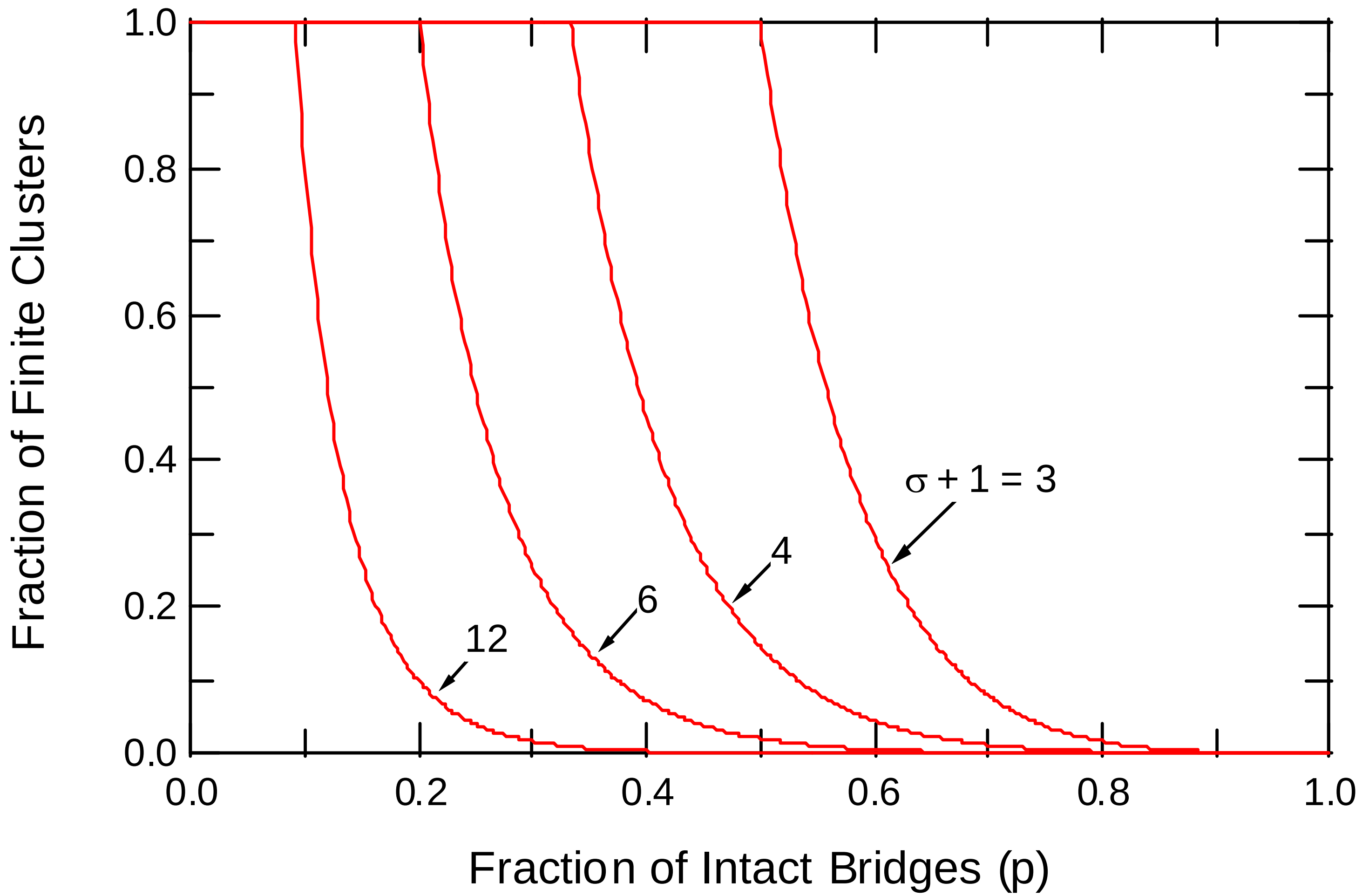


- 20% bridges broken,
- 0.3% fragments liberated

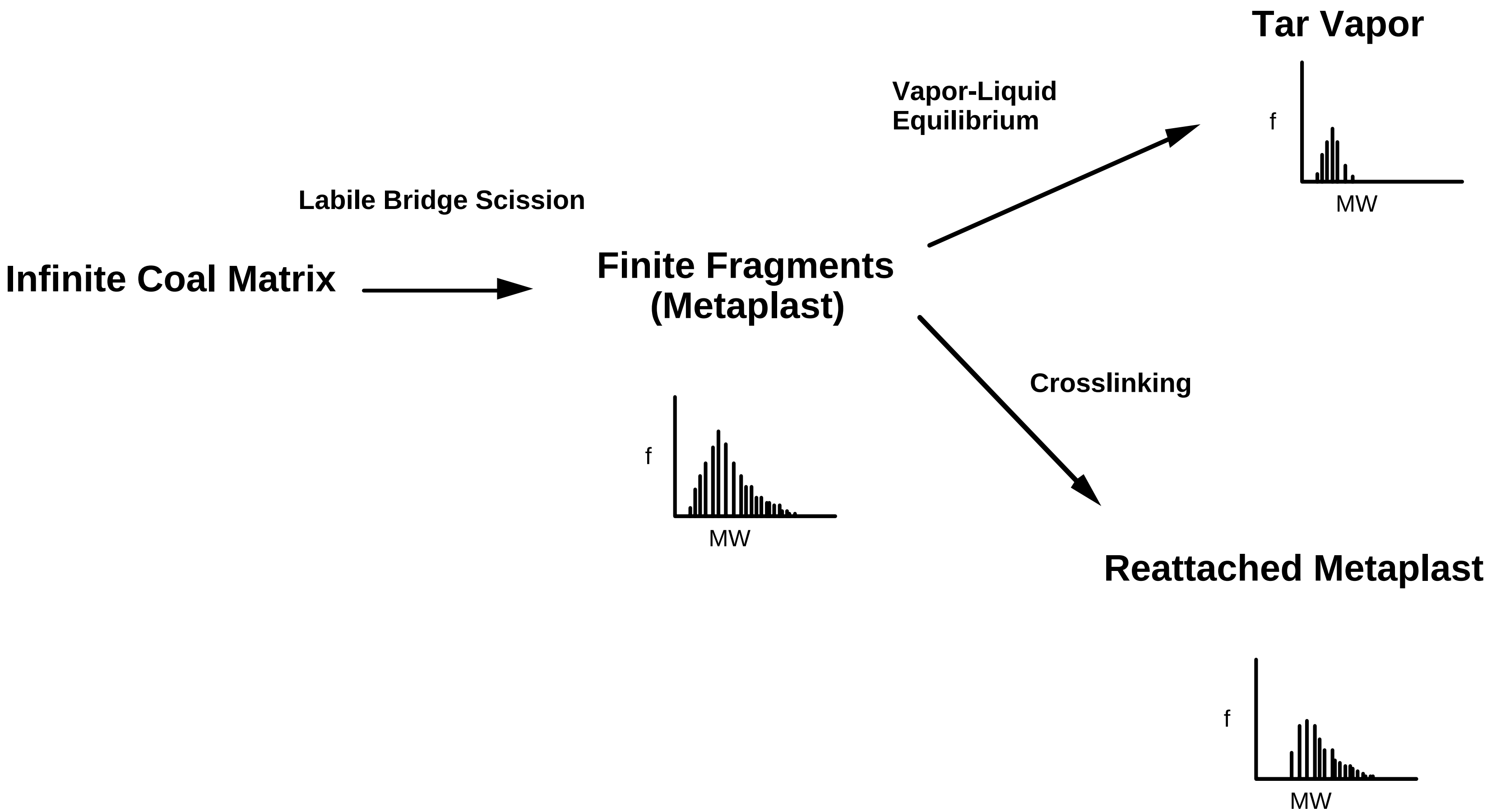


- 45% bridges broken,
- ~10% fragments liberated
- Fragments include monomers, dimers, trimers, etc.

Closed-Form Solution of Percolation Lattice Statistics

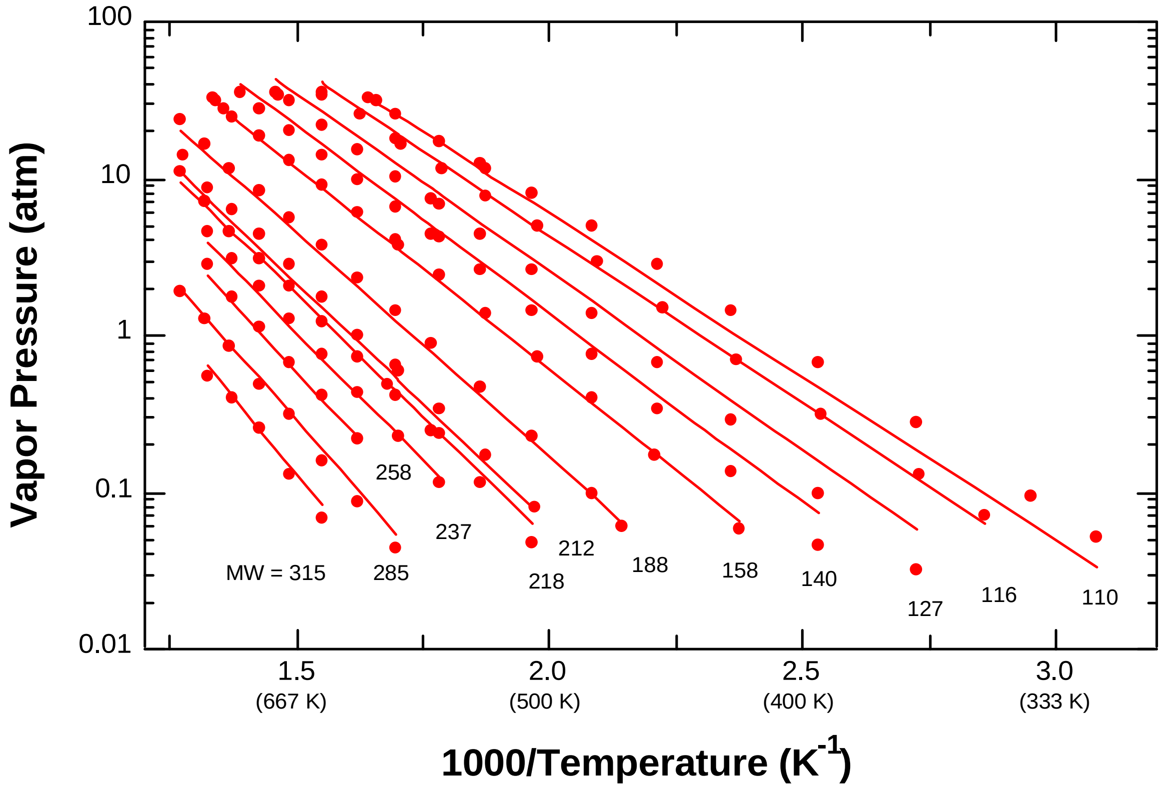


Vapor-Liquid Equilibrium and Crosslinking



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

Input Parameters Required by the CPD Model

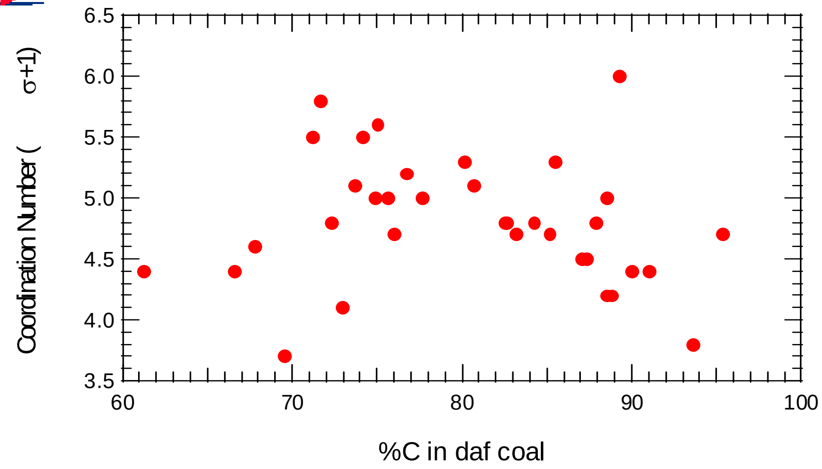
- Number of attachments per cluster (σ+1)
  (i.e., coordination number)
- Fraction of attachments that are bridges (p_0)
  (bridges/bridges+side chains)
- Molecular weight per aromatic cluster (M_{cl})
- Molecular weight per side chain (M_δ)

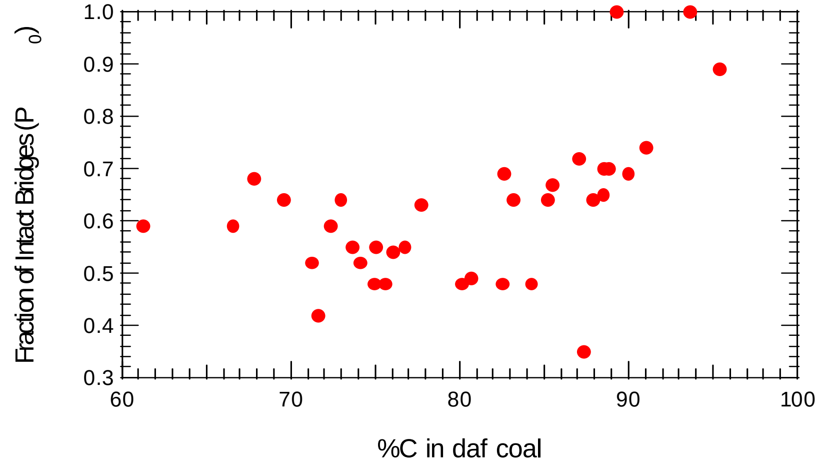
Measured with ^{13}C NMR Spectoscopy

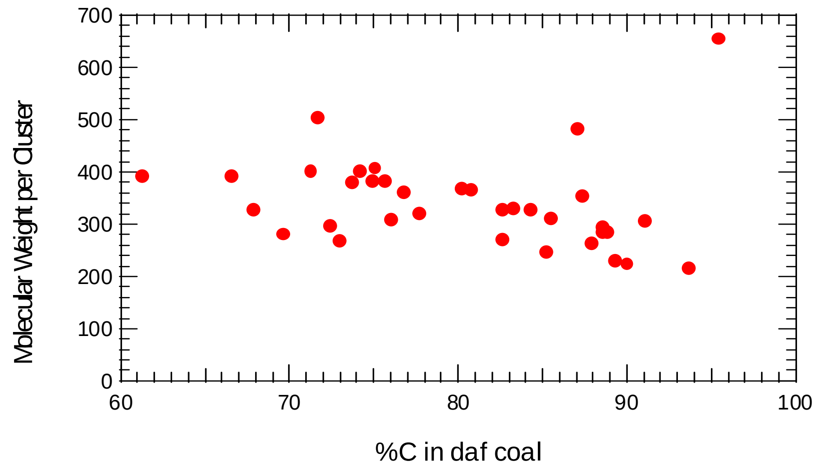
- Fraction of bridges that are stable (c_0)

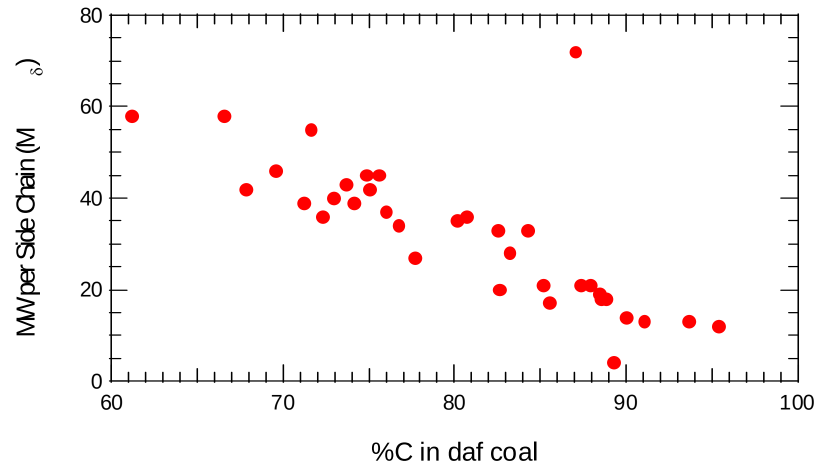
Not measured

Do Structure Parameters Correlate?









Lattice Model Capabilities

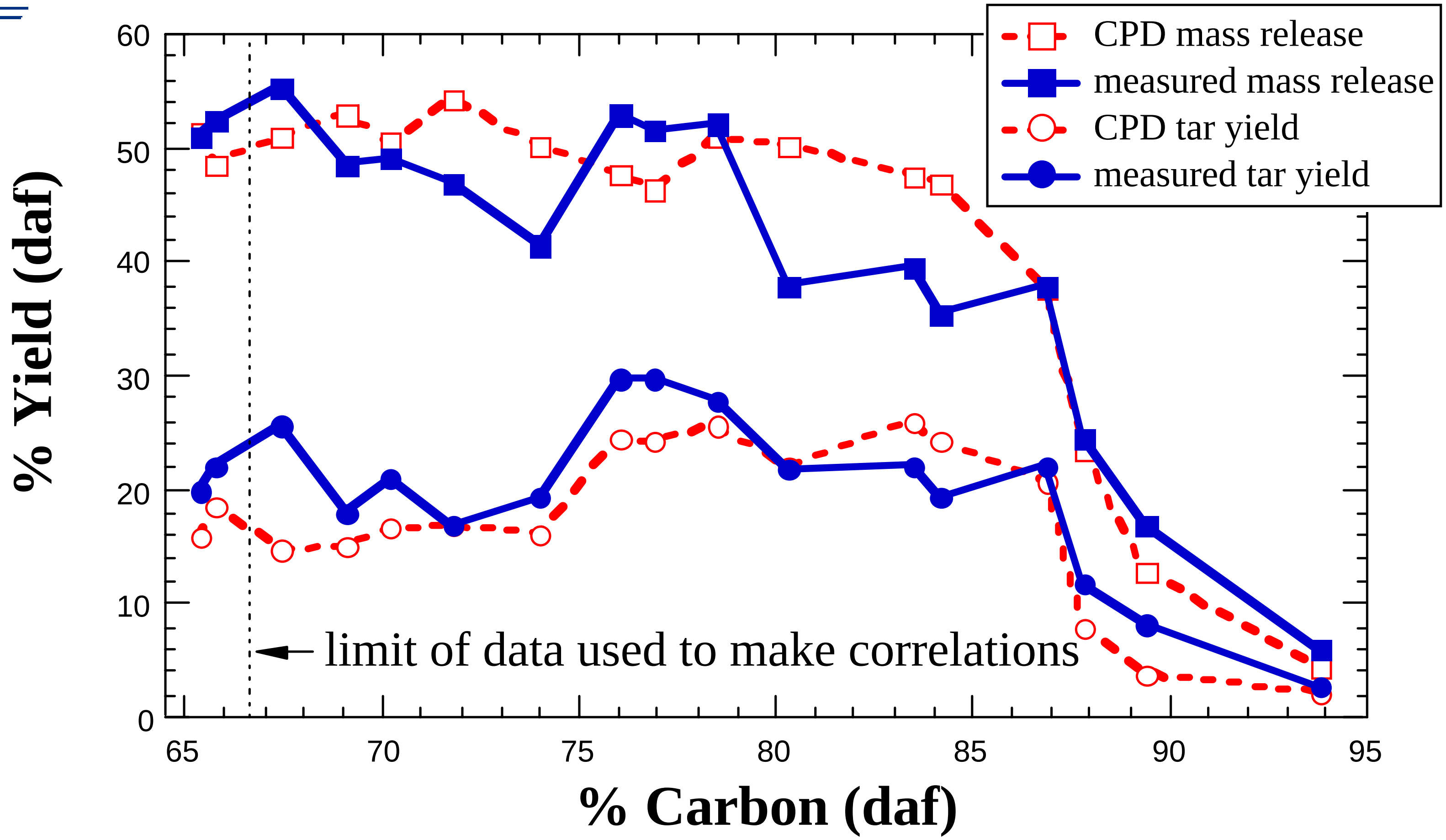
Can Predict:

- Tar yield
  - MW distribution
- Light gas yield
  - Speciation
- Char yield
  - Elemental composition

As a Function of:

- Coal type
  - Coal structure
- Residence time
  - Kinetic rates
- Particle heating rate
  - Distributed activation energies
  - Competing reactions
- Temperature
  - Kinetic rates
- Pressure
  - Vapor-liquid equilibrium

Using Correlations for Coal Structure Parameters



17 non - U.S. coals, 3000 K/s to 1037 K, (Xu & Tomita)

No ^{13}C NMR data available, from Genetti et al., E&F 1999

Light Gas Speciation is Empirical

19 species, needing yield factors and rate coefficients!

Table II. Kinetic Rate Coefficients and Species Composition Parameters for FG Subroutine

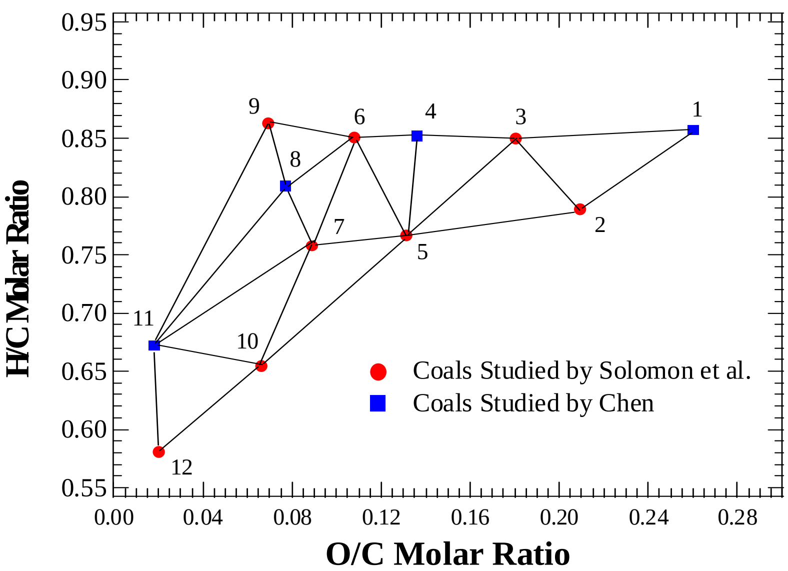
composition params	gas	primary functional group source	rate eq[a]	Pittsburgh No. 8 bituminous coal	North Dakota Zap lignite
C				0.821	0.665
H				0.056	0.048
N				0.017	0.011
S(org)				0.024	0.011
O				0.082	0.265
total				1.000	1.000
Y_1^0	CO_2 extra loose	carboxyl	$k_1 = 0.81E+13 \exp(-(22500 \pm 1500)/T)$	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 tight		$k_3 = 0.11E+16 \exp(-(38315 \pm 2000)/T)$	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	methane extra loose	methoxy	$k_{12} = 0.84E+15 \exp(-(30000 \pm 1500)/T)$	0.000	0.000
Y_{13}^0	methane loose	methyl	$k_{13} = 0.75E+14 \exp(-(30000 \pm 2000)/T)$	0.020	0.017
Y_{14}^0	methane 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
total				1.000	1.000
X^0	tar		$k_B = k_T = 0.86E+15 \exp(-(27700 \pm 1500)/T)$		

From Solomon et al., E&F, 1988.

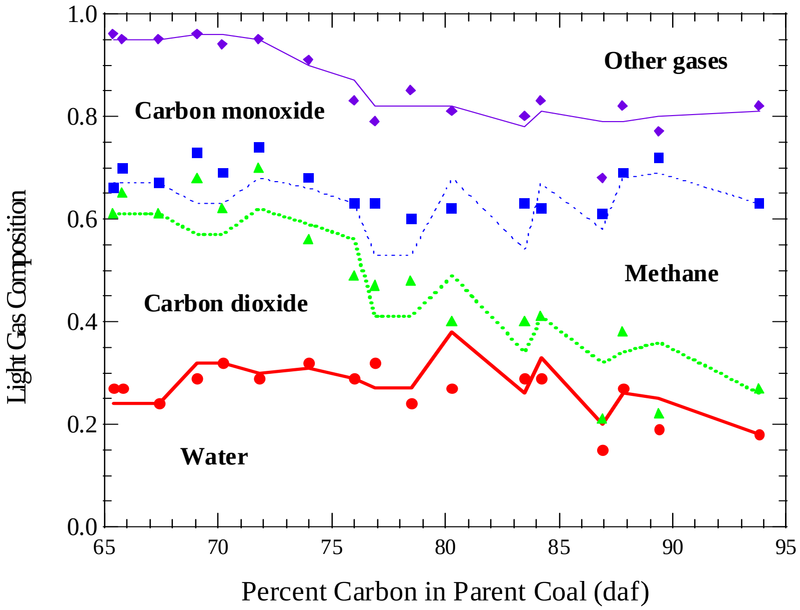
All E's are distributed!

Sample Predictions of Gas Species

From Genetti et al., E&F (1999)

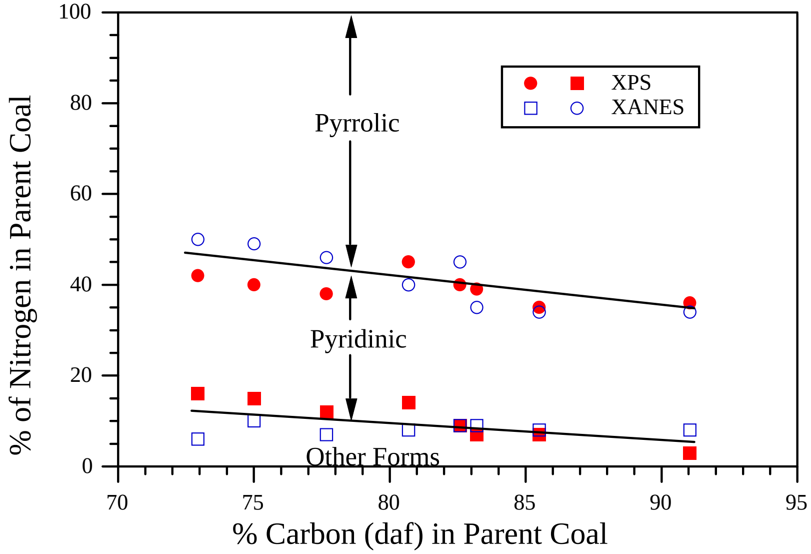


Interpolation matrix for gas species (based on coalification diagram)



Application to Xu and Tomita data (non-U.S. coals)

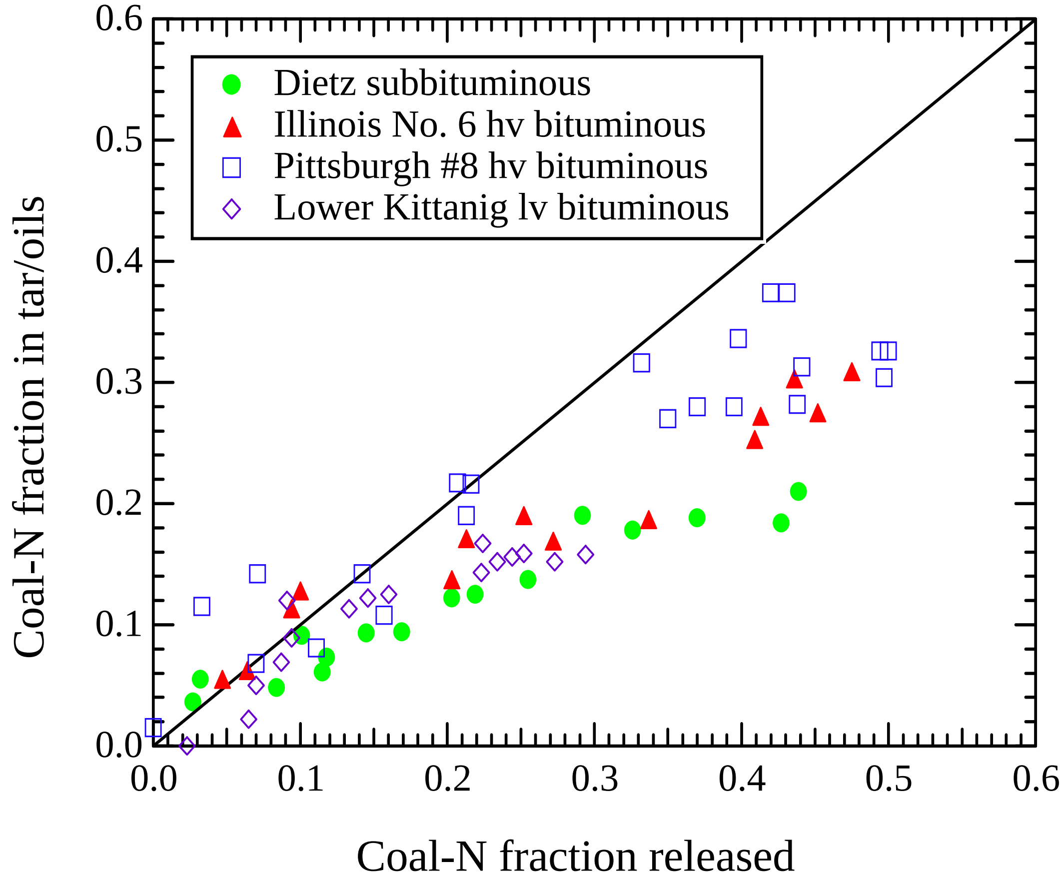
Nitrogen Release



- All nitrogen in coal is contained in the aromatic structure
  - Pyridinic, pyrrolic, and quartenary
- Nitrogen release highly dependent on tar release

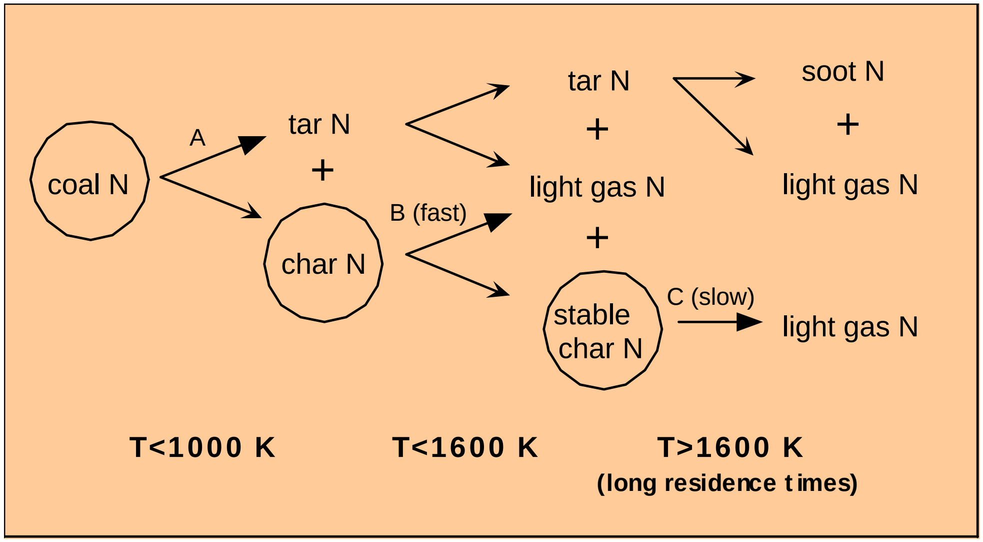
Argonne Premium Coals, XPS data from Kelemen et al. (1993), XANES data from Mitra-Kirtley et al. (1993)

Tar Does Not Contain All Pyrolyzed Nitrogen, Especially for Low Rank Coals



Pulverized coal particles in a radiant drop tube reactor (Chen, Stanford University, 1991)

Nitrogen Release Models



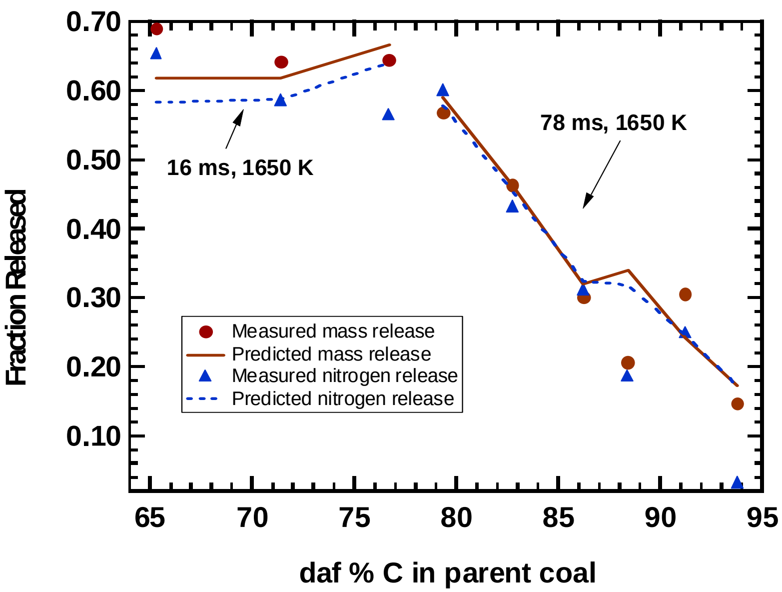
From S. Perry, PhD Dissertation, BYU, 1999

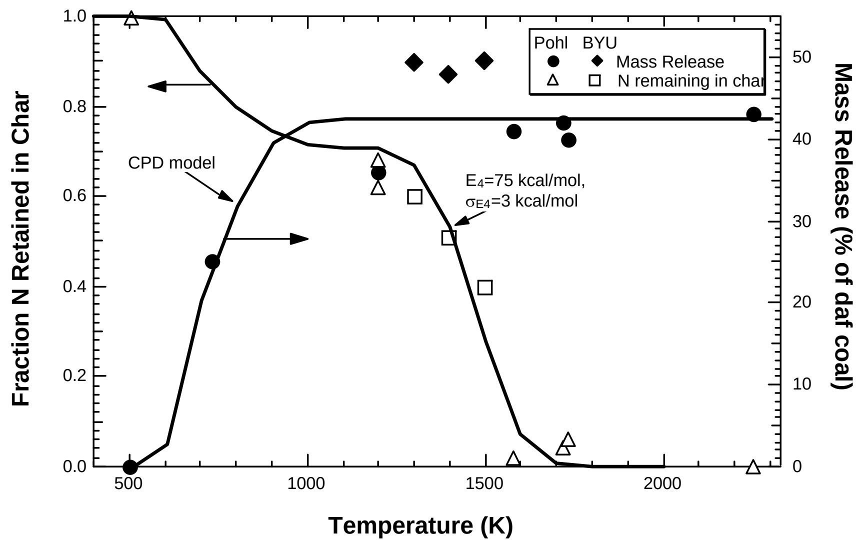
- Initial N release w/tar
- Subsequent N release from char as HCN at higher T
- Secondary tar reactions
  - Soot formation from tar
  - Light gas formation (HCN and then NH_3)
- Additional N release at extremely high T's
  - 100% nitrogen release possible!

Sample Nitrogen Release Predictions

^{13}C NMR data used for coal structure parameters

(from Perry et al., E&F, 2000)



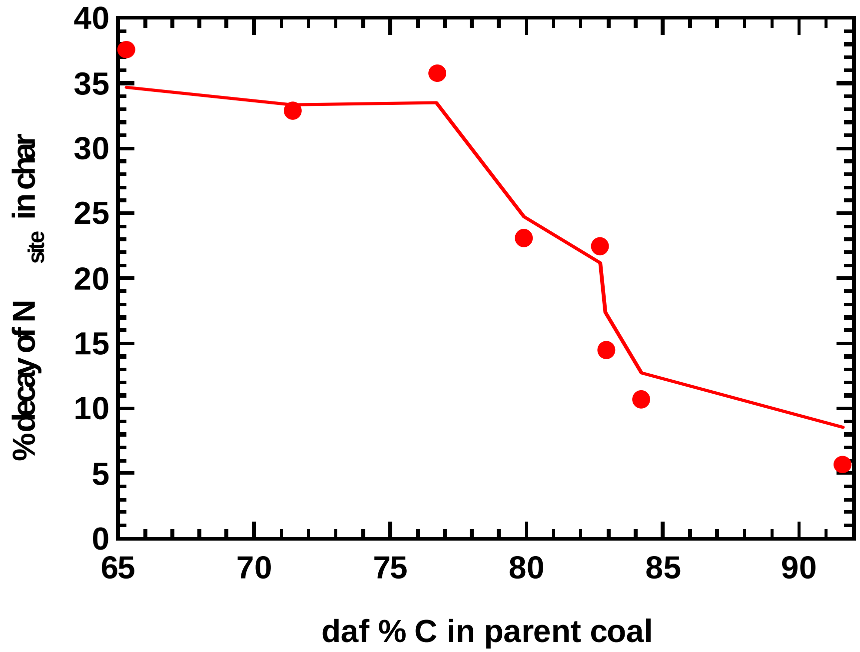


A. Flat-flame burner (high T and dT/dt)
- matches volatiles yield and
- nitrogen release)

B. High temperature crucible data
- volatiles reaches constant value
- nitrogen is totally released!

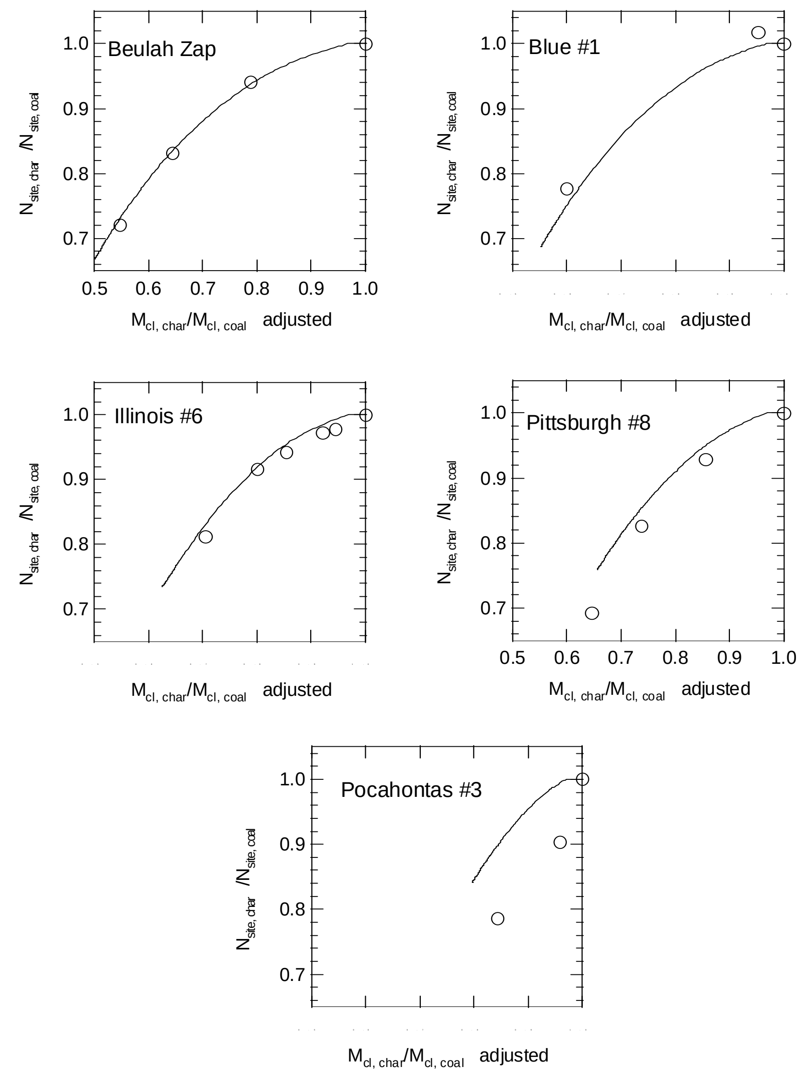
Nitrogen Structural Parameters Modeled Correctly!

(from Perry et al., E&F, 2000)

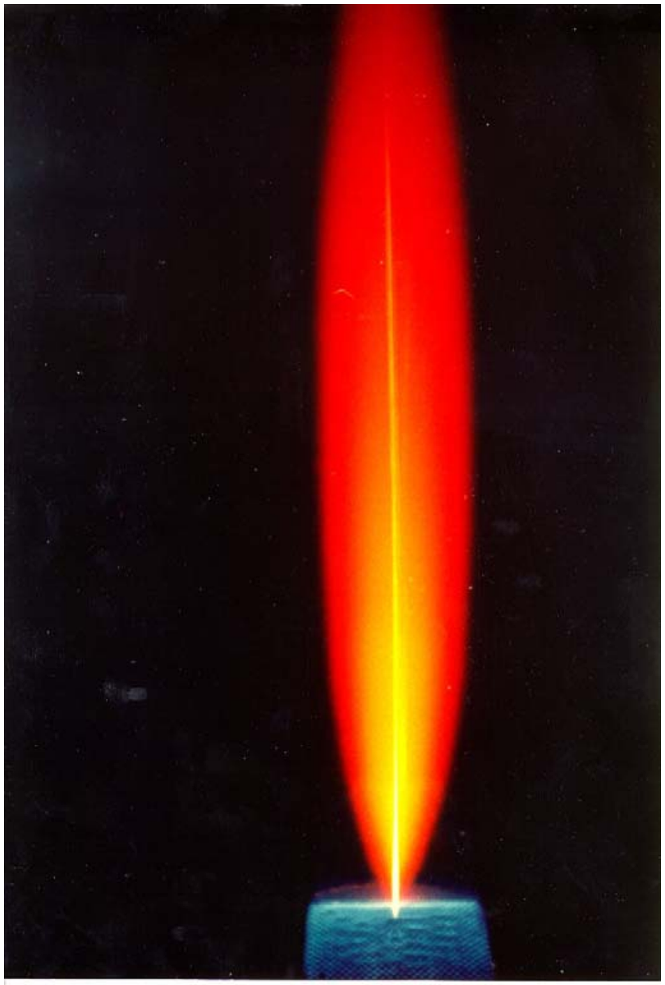


- Australian, Japanese, and American coals
- Pyrolyzed at 1100 K in N_2 (drop tube)
- Based on ^{13}C NMR analysis and elemental composition

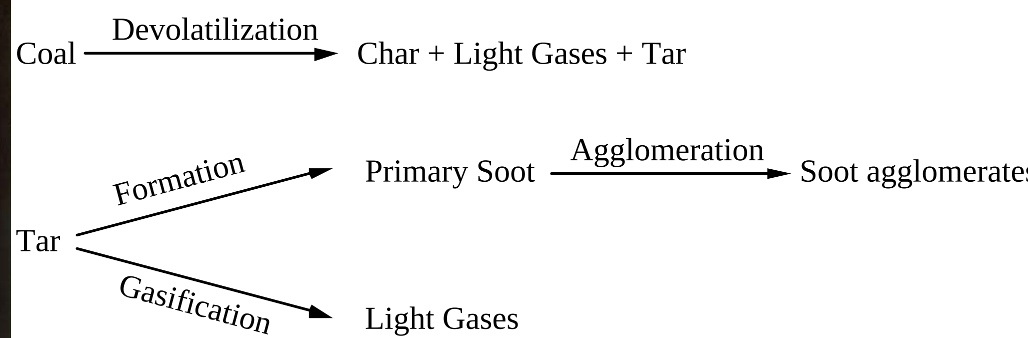
Structural N parameter as reaction proceeds



Soot Formation



- Soot forms from coal tar, not acetylene



- Soot model developed and implemented
  – Uses predicted tar from CPD model
  – Soot formation, oxidation, and growth included
  – Predicts up to 300 K lower near-burner temperature in CFD model

Conclusions

- A lot of good scientific research performed on coal pyrolysis
- Lattice models capture much of the chemistry
- Models tuned to match existing data
  - Mass release vs. t, T, dT/dt, P_{tot}, coal type
  - Tar yield (and MW, composition)
  - Gas species
  - Nitrogen release
  - Soot formation
- **These models are good tools to explore new concepts!**