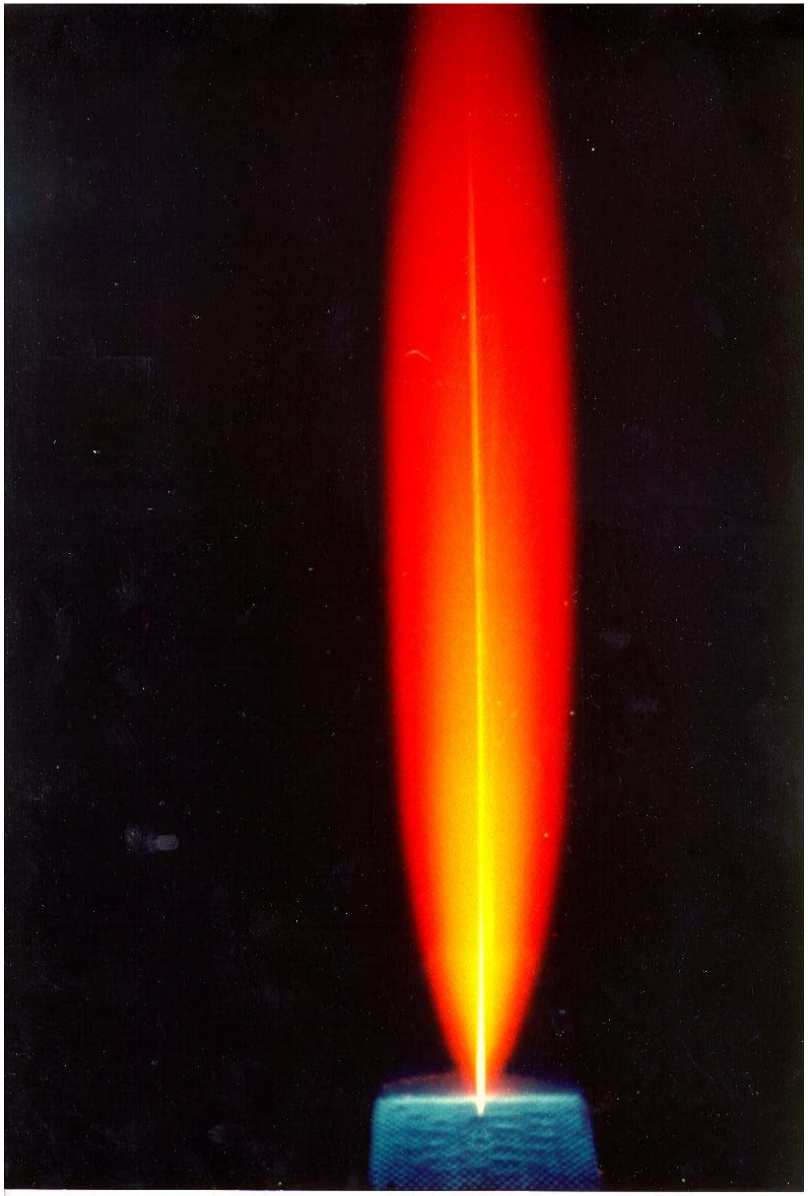


Class 8

Secondary Pyrolysis, Soot Formation from Coal Tar

Thanks to:

Jinliang Ma

Alex Brown

Soot

Soot from HC Gas

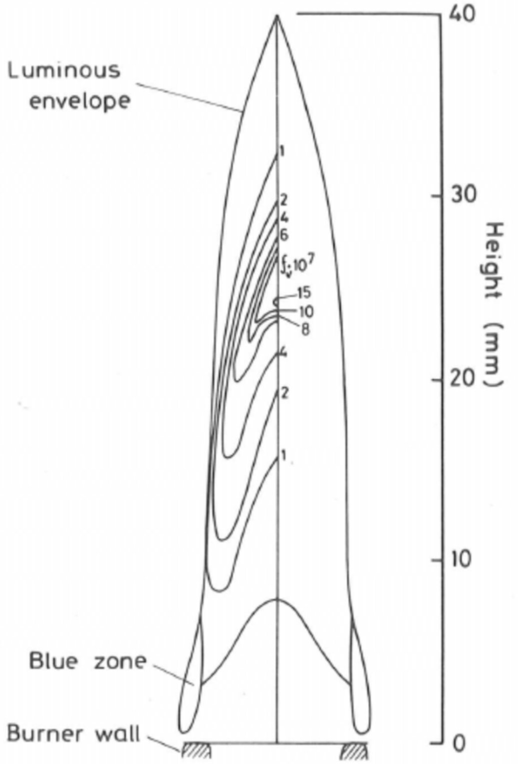


FIGURE 22. Distribution of soot volume fraction in the *n*-hexane diffusion flame of Figures 8 and 9. Redrawn from Spengler and Kern,[74] with permission from the publisher.

- HACA mechanism
  - – Hydrogen abstraction
  - – Carbon (acetylene) addition
- 3 acetylenes make a benzene ring
- 2 more acetylenes make a 2-ring structure (naphthalene)
- Soot volume fraction on the order of 5×10^{-7}

from Fossil Fuel Combustion, ed. Bartok & Sarofim, Wiley, p 314 (1991).

Soot from Coal

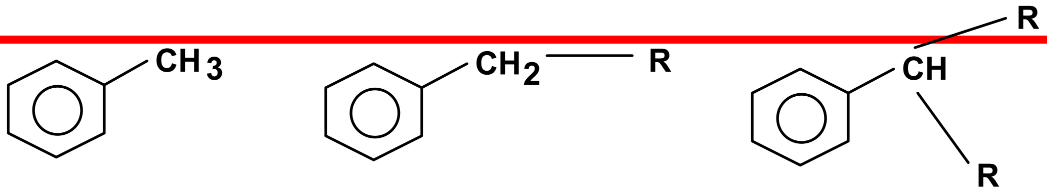
- Comes from coal tar
- Coal tar has avg MW of 350 at 1 atm
- Coal tar does not break down to C_2H_2 and then reform aromatic rings
- Coal tar already has 3-4 rings, plus attachments

What Is Secondary Pyrolysis and Why Is It Important?

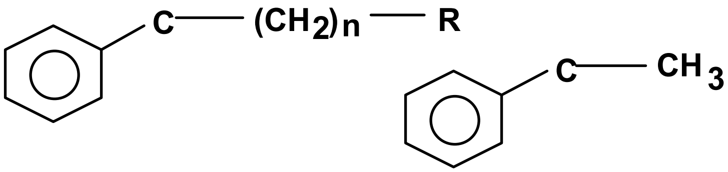
primary tar $\xrightarrow{\text{heat}}$ **light gas**
higher molecular weight tar
soot

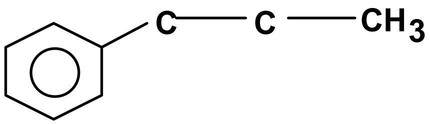
- Soot in flame regions can radiate significant amount of heat away from flame
- Accurate calculation of gas temperatures in flames is critical to predictions of NO_x
- Soot is harder to burn than light gases
- Some fuel nitrogen ends up in the soot

Definitions



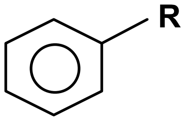
α-hydrogens



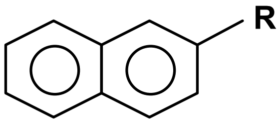


β hydrogens

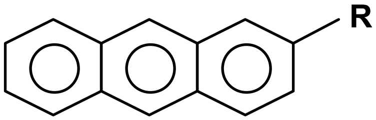
γ hydrogens



1-Ring

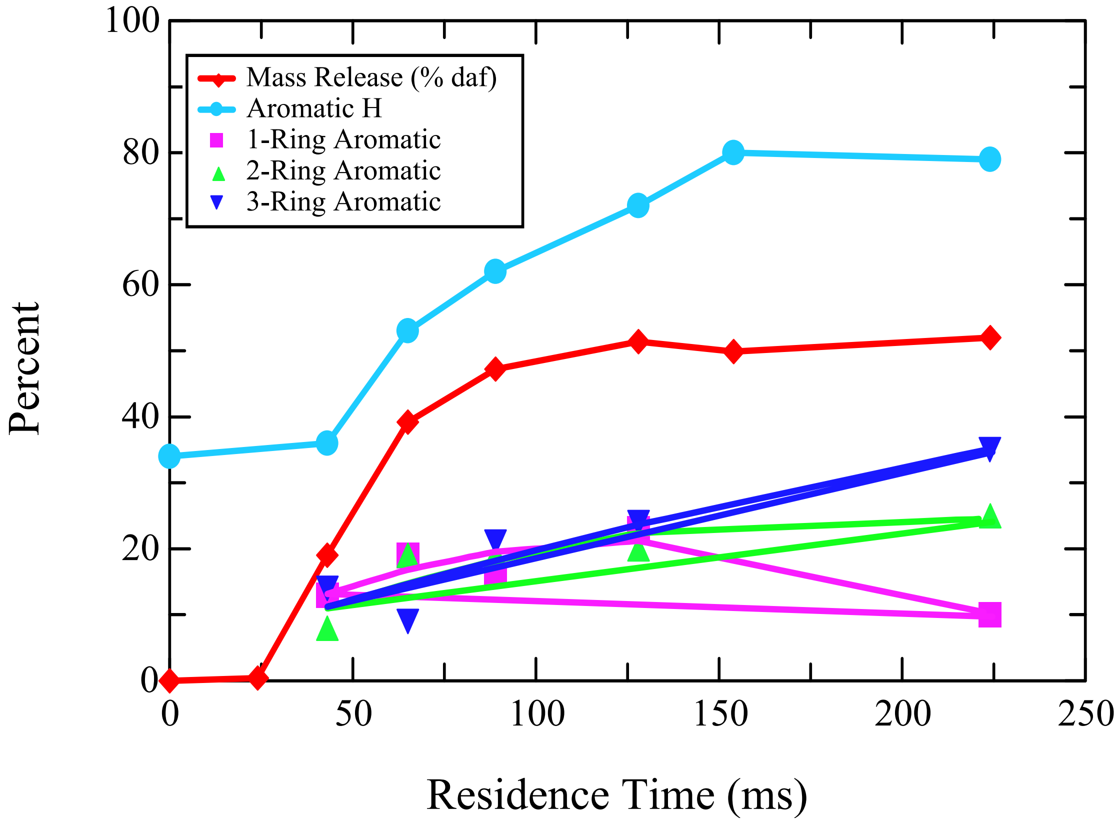


2-Ring



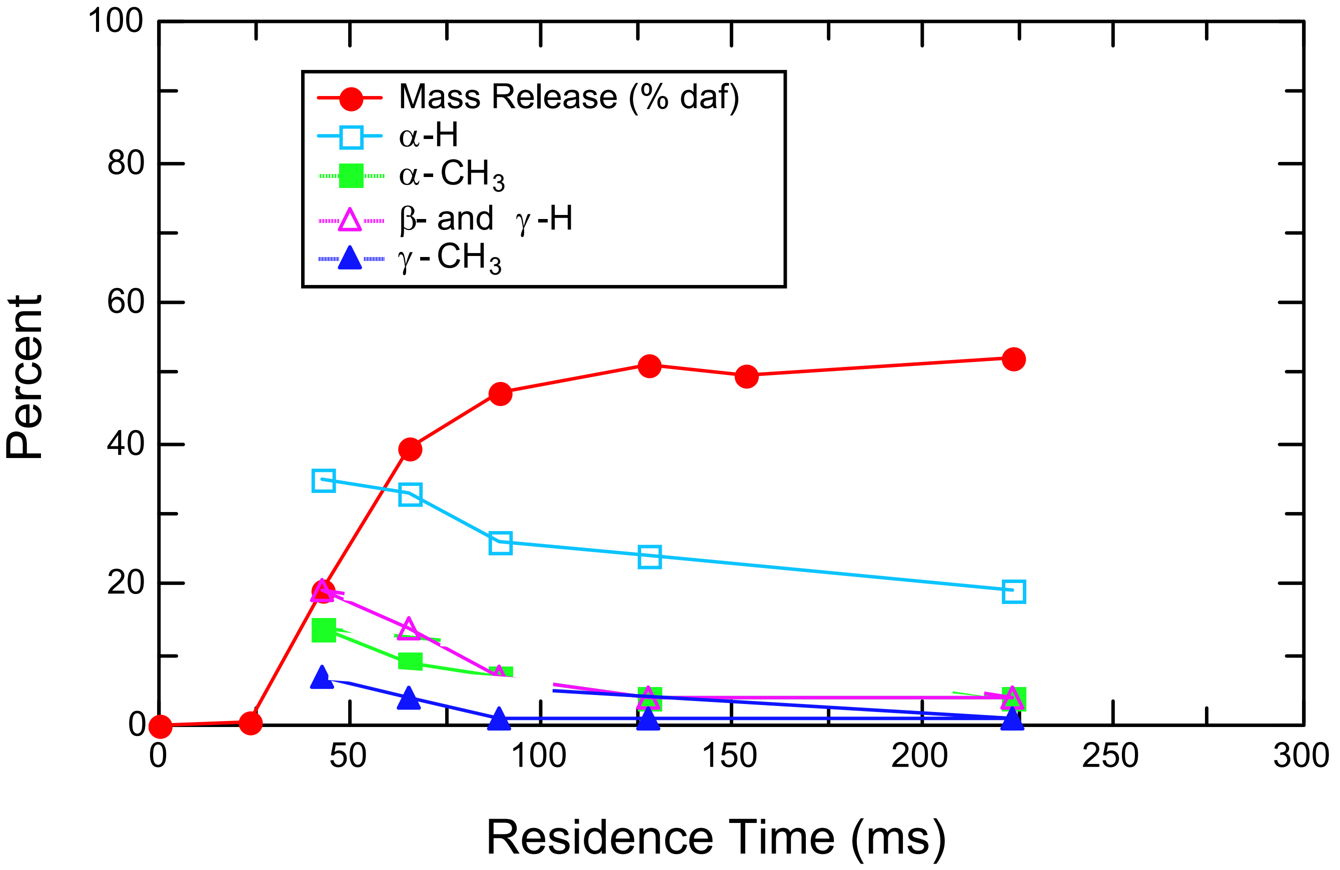
3-Ring

Change in Ring Structure, Aromaticity (Fletcher/Pugmire)



Illinois No. 6 hv bituminous coal, 10^4 K/s to 1250 K in a drop tube reactor (Fletcher, et al., 23rd Symp., 1990)

Changes to Attachments



Percentage of hydrogen contained in aliphatic structures in Illinois No. 6 coal tars, with hydrogen in the α, β, or γ position relative to the aromatic ring, vs. residence time in the 1250 K gas condition.

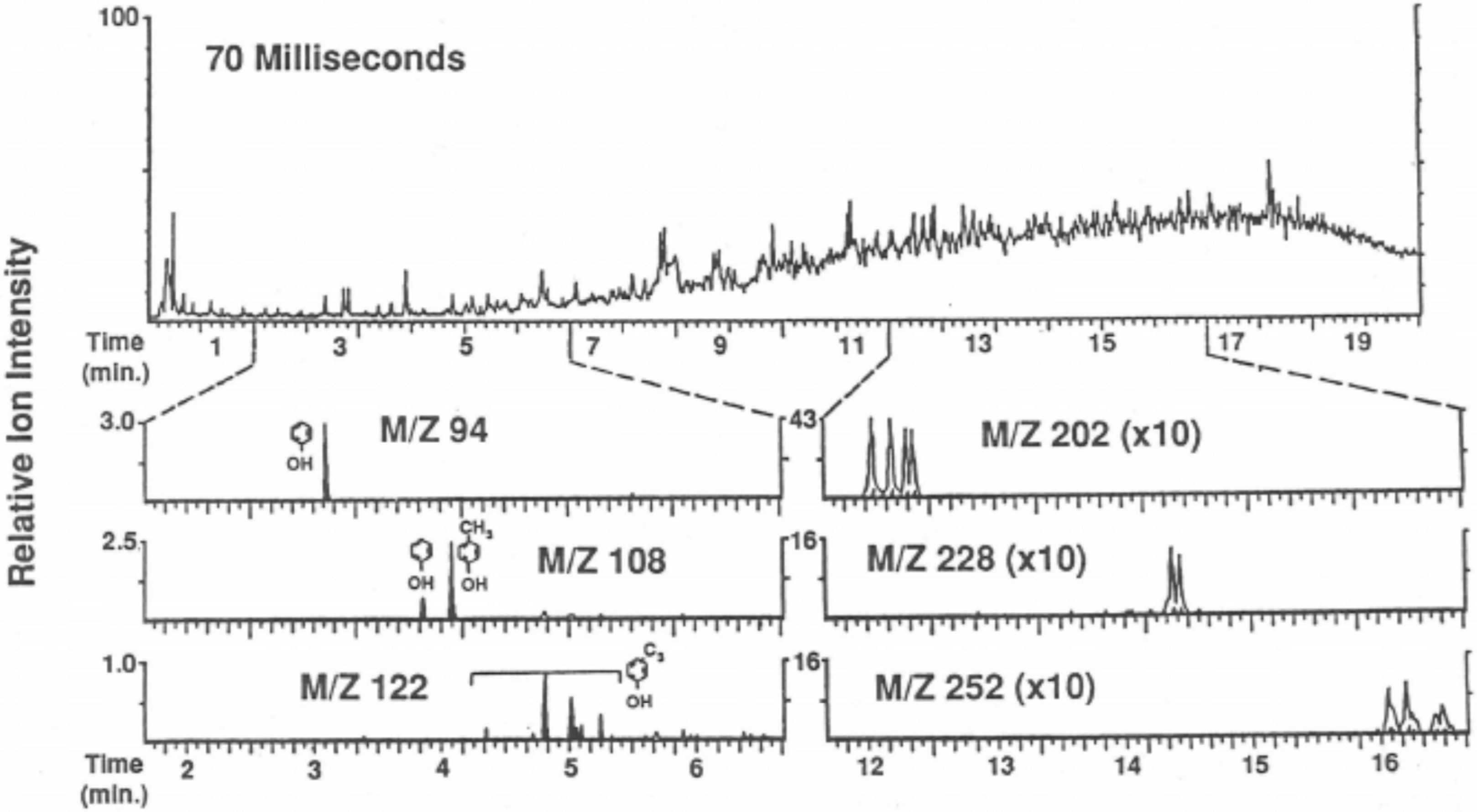


Figure 5.59 Curie-point desorption GC/MS profiles of Illinois #6 tar obtained at 1250 K after 70 ms. Total ion chromatogram (upper profile) and selected ion chromatograms (lower profiles) show relative abundance of (alkyl) phenols vs. pyrenes, perylenes, and picenes.

From Fletcher & Hardesty, Compilation of Sandia Coal Devolatilization Data, Milestone report (1992)

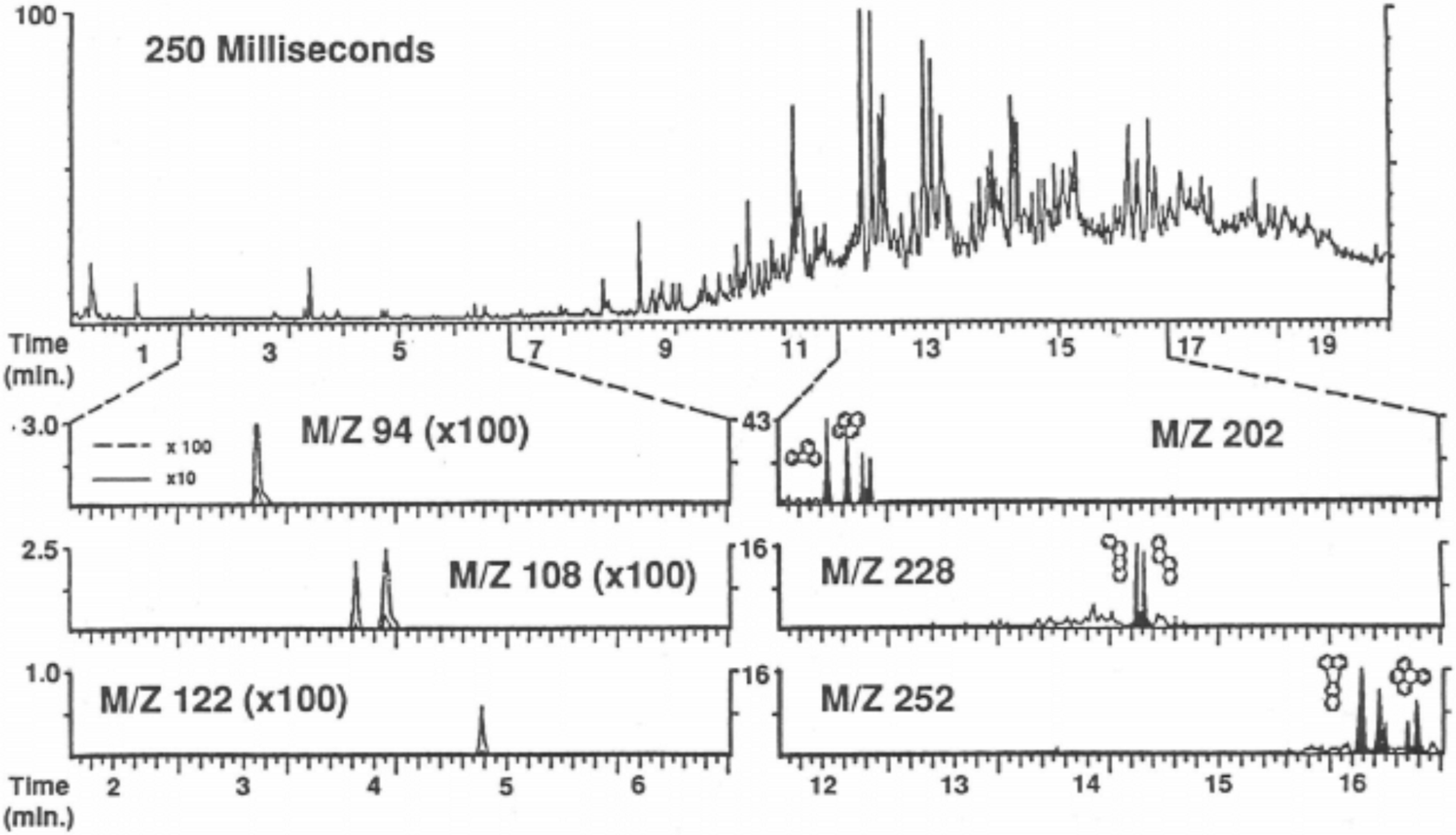
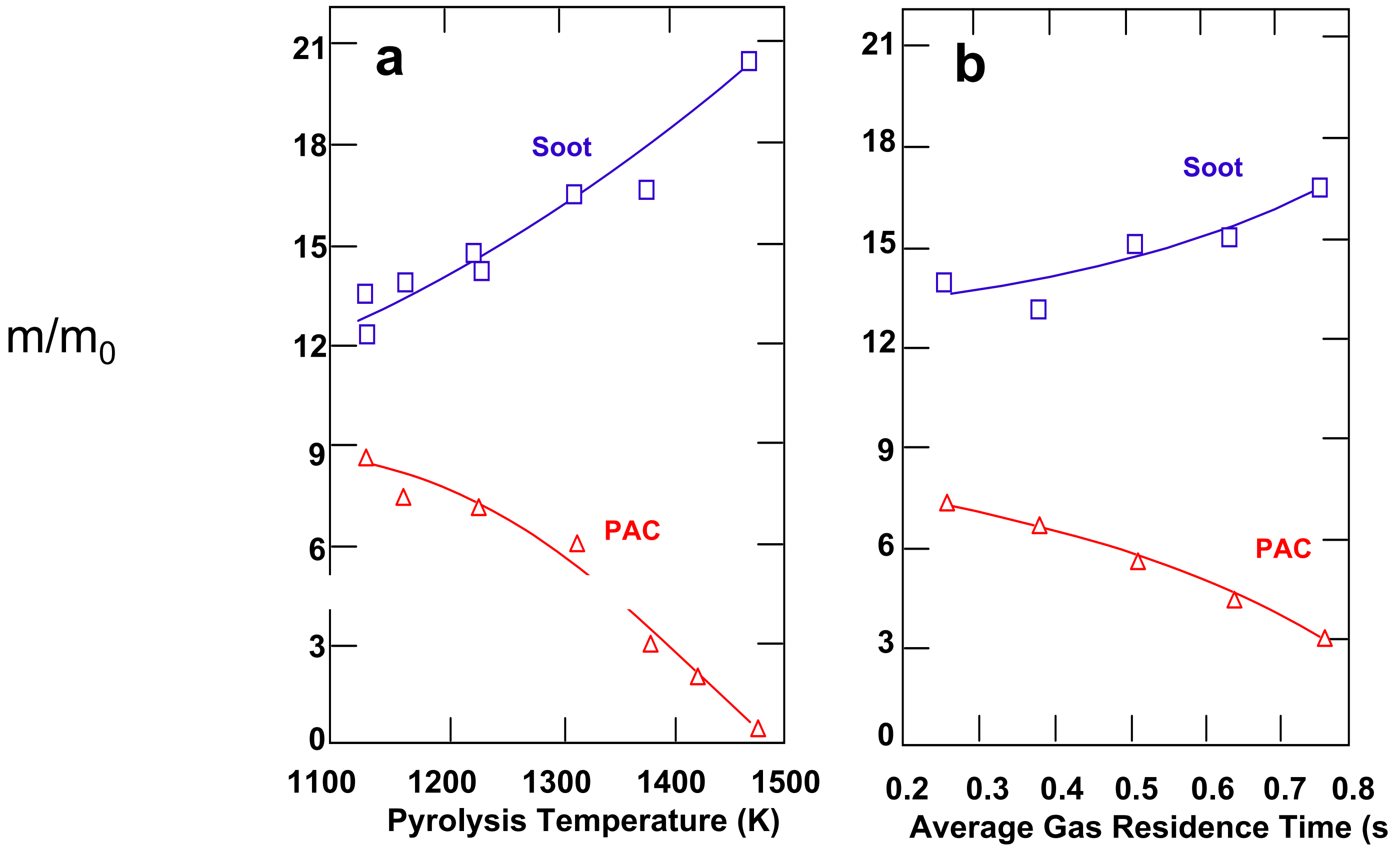


Figure 5.60 Same as Fig. 5.59 but obtained after 250 ms. Note 100-fold decrease in (alkyl) phenol as opposed to 10-fold increase in polynuclear aromatic hydrocarbons.

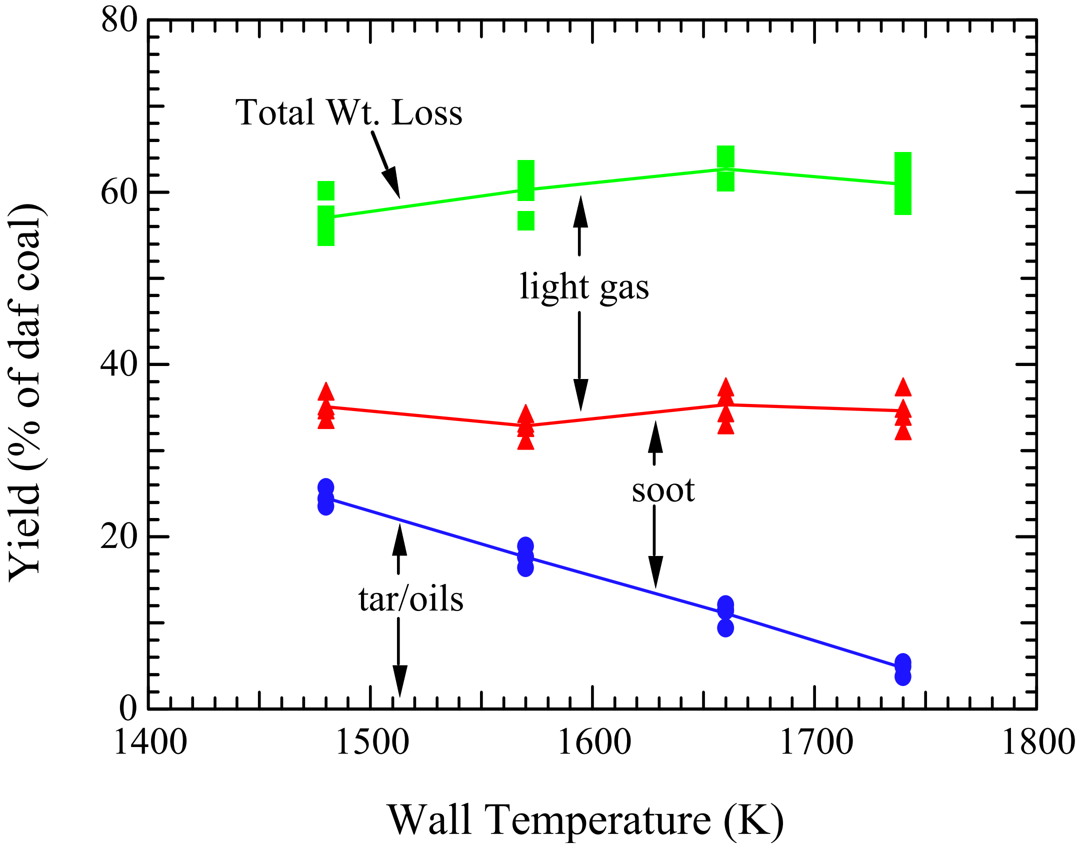
Concentration of m/z > 200 has increased significantly (10×) after 250 ms, and concentration of m/z < 125 has decreased significantly (~100×)!

Soot Yields Increase With Both Temperature And Residence Time



Pittsburgh seam coal in drop tube, rapid heating rate, (a) vs temperature at 0.75 s, and (b) vs residence time at 1375 K (Wornat, et al., Energy & Fuels, 1987)

Additional Data Supporting Tar + Soot = Constant



Pittsburgh No. 8 hv bituminous coal in radiant drop tube, rapid heating, particle temperature lower than wall temperature (Chen and Niksa, 1992). Similar results for Dietz subbitumninous coal.

Previous Coal-Derived Soot Models

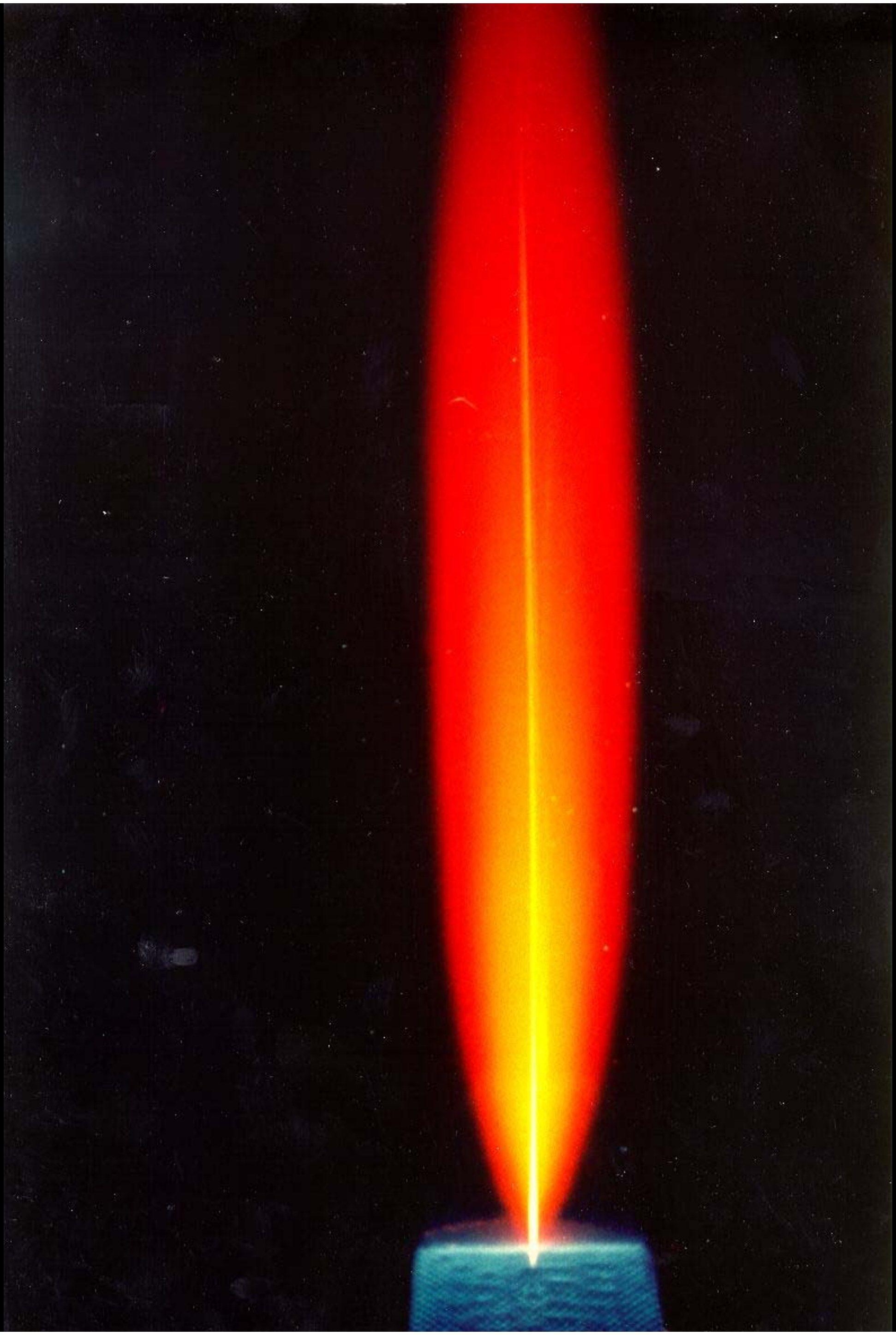
- Ubhayakar et al. (1976)
  - Empirical relation based on mole fraction CO
- Adams and Smith (1995)
  - Empirical relation based on mixture fraction

$$f_{v,C} = \frac{C_1 C_2 \beta_C M_C}{\rho_C}$$

where $C_1 = 0.1$ (i.e., assumed fraction of volatile carbon going to soot),

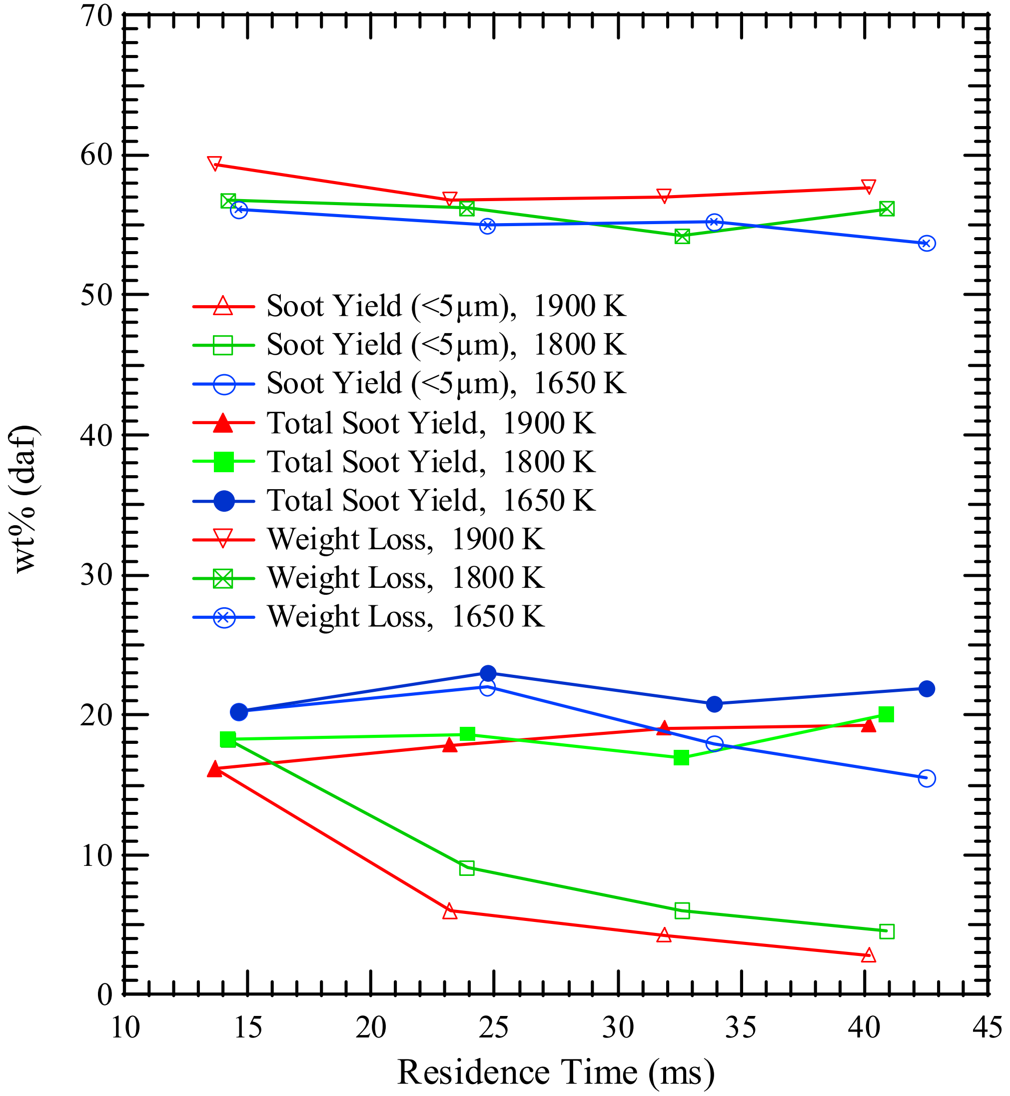
C_2 = empirical function of equivalence ratio,

$\beta_C = f(f,\eta)$, i.e., function of mixture fractions

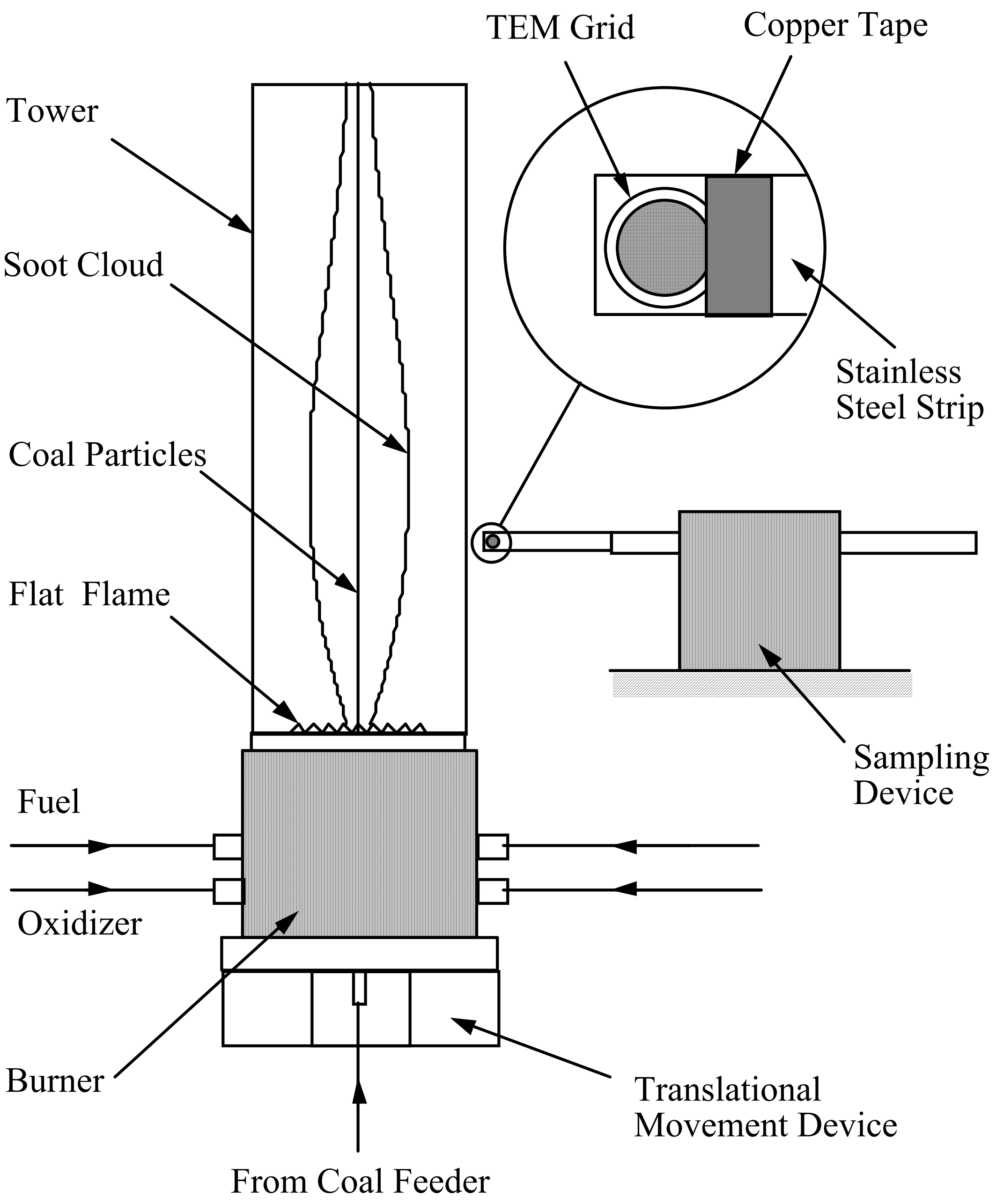


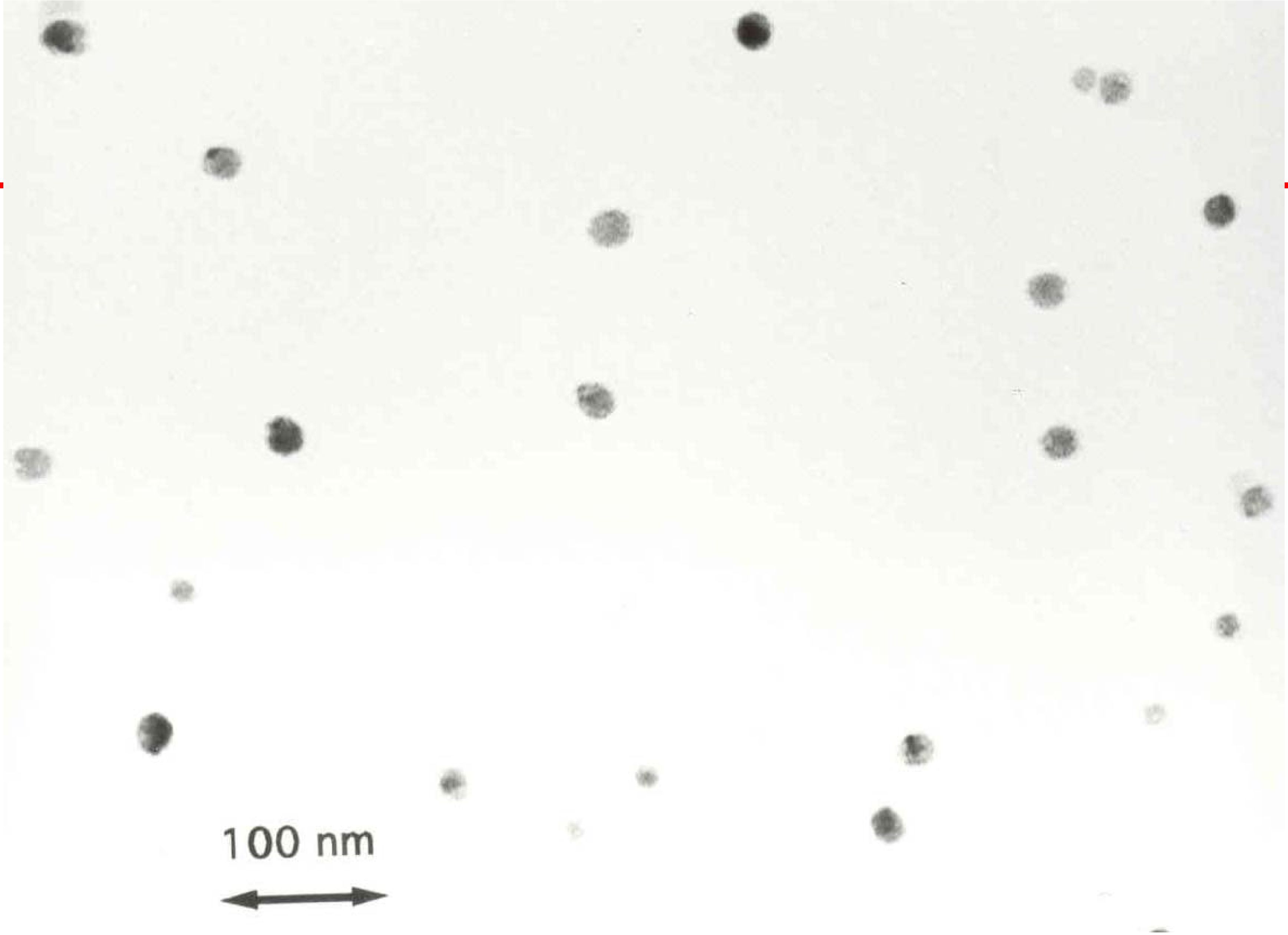
FFB Data for Pitt#8 Coal

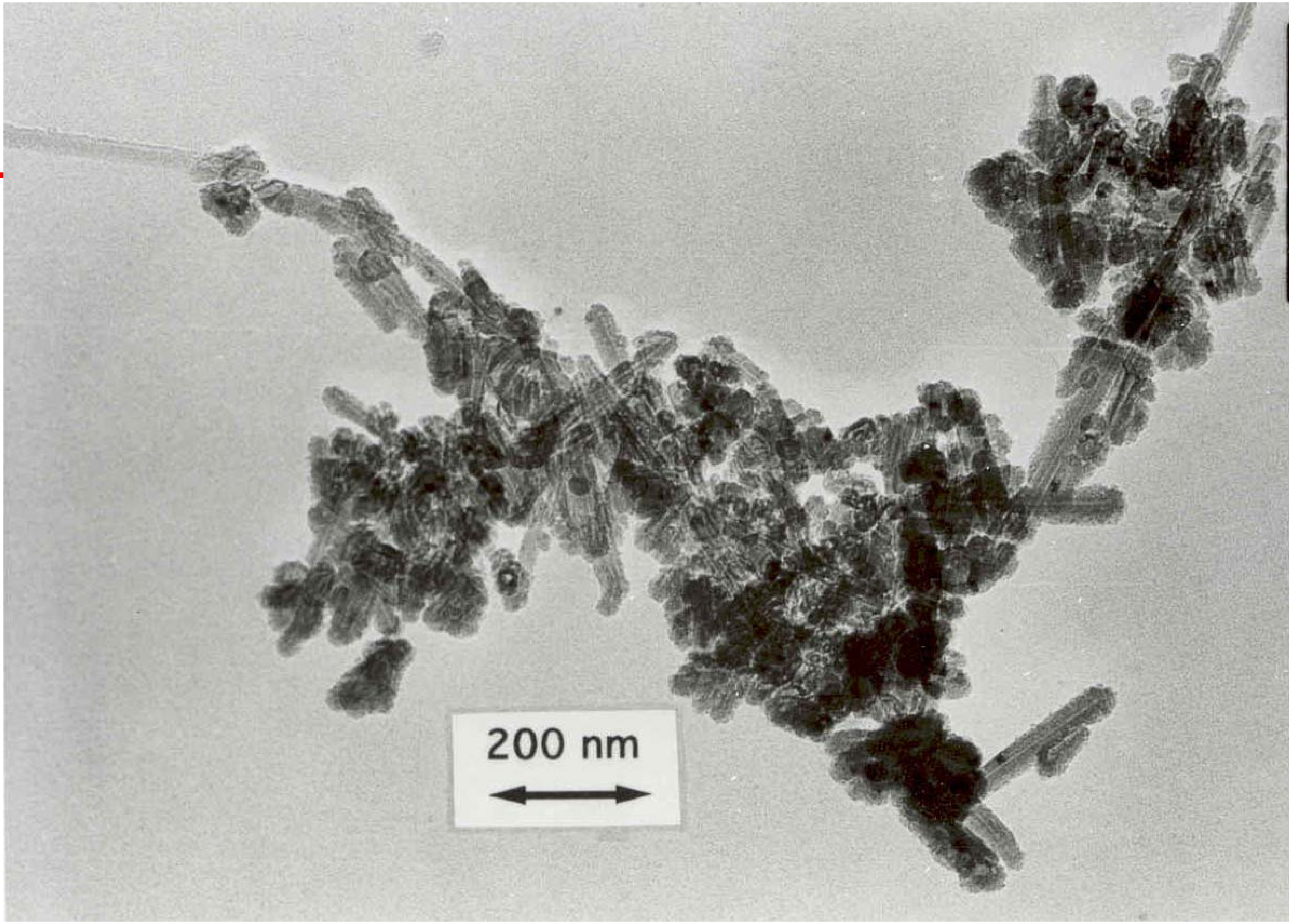
(Ma, 1996)



Thermophoretic Sampling System for FFB




100 nm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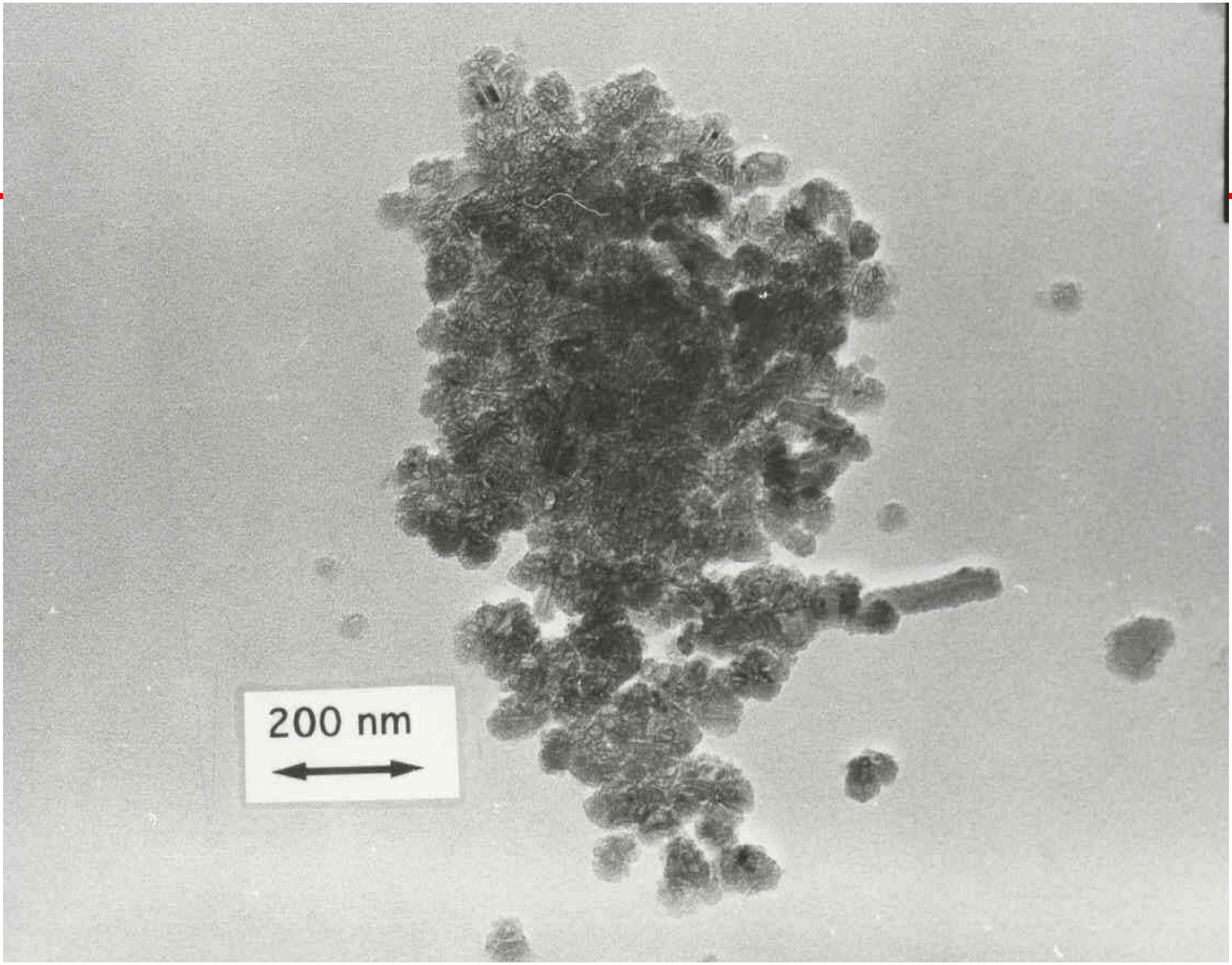
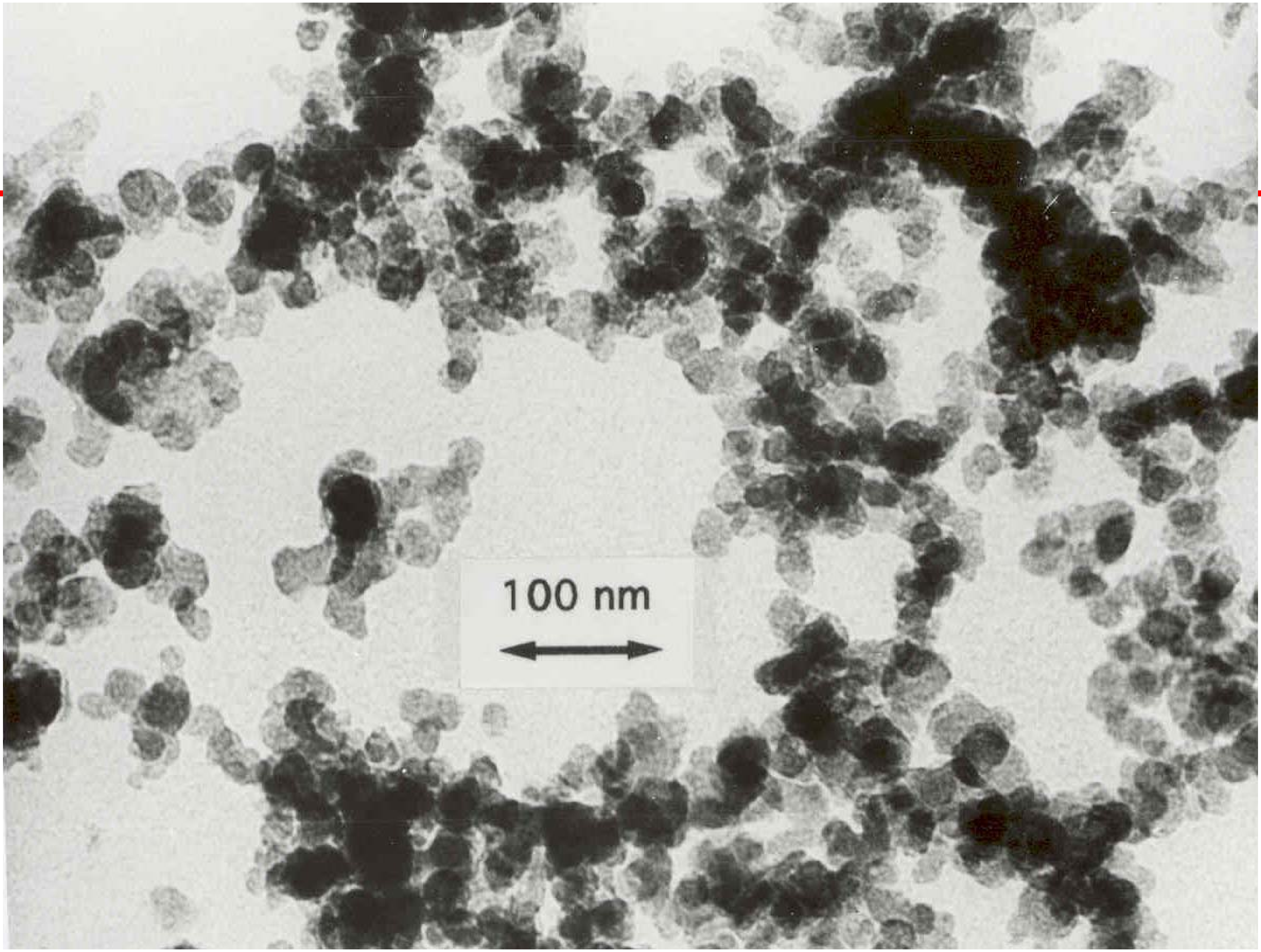
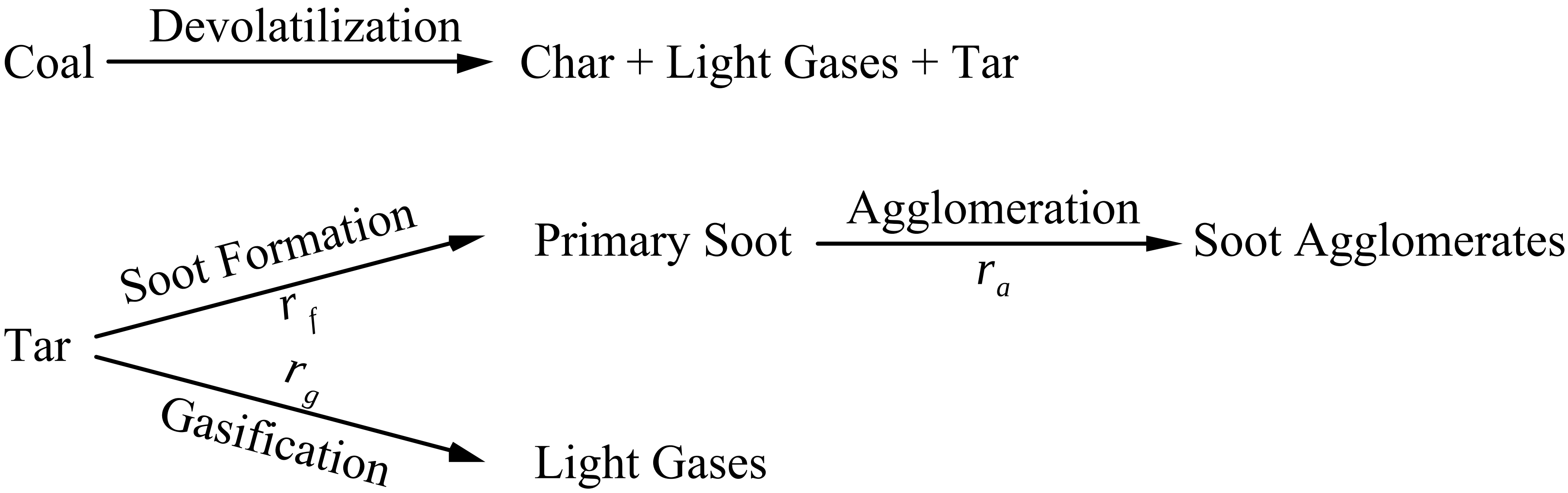

200 nm


100 nm

Presumed Pathway for Soot Formation (Ma, 1996)



$$\text{Coal} \xrightarrow{\text{Devolatilization}} \text{Char + Light Gases + Tar}$$

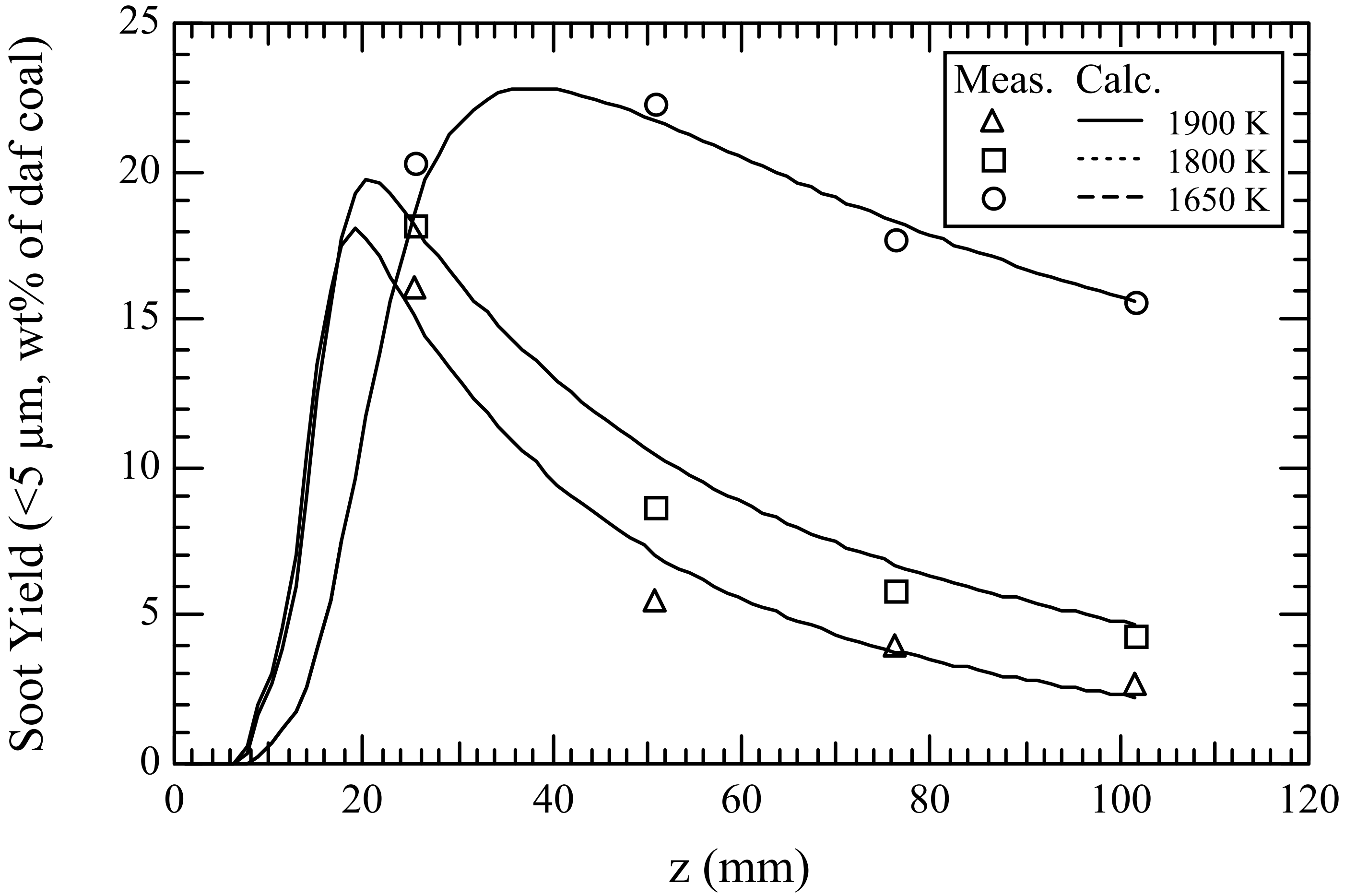
$$\text{Tar} \xrightarrow[r_f]{\text{Soot Formation}} \text{Primary Soot} \xrightarrow[r_a]{\text{Agglomeration}} \text{Soot Agglomerates}$$

$$\text{Tar} \xrightarrow[\text{Gasification}]{r_g} \text{Light Gases}$$

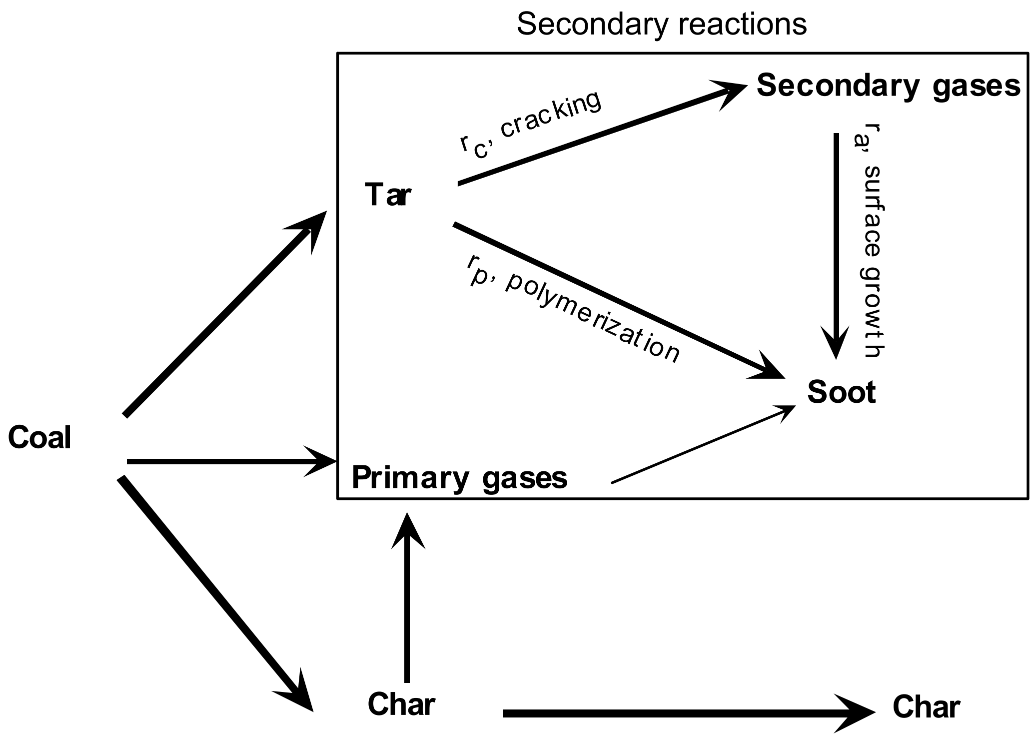
Derived Kinetic Coefficients

Soot formation	E_f (kJ/mol)	198.9
	A_f (s^{-1})	5.02×10^8
Tar gasification	E_g (kJ/mol)	286.9
	A_g (s^{-1})	9.77×10^{10}
Soot agglomeration	E_a (kJ/mol)	129.9
	A_a (s^{-1})	3.10×10^5

Modeling Soot from Pitt #8 coal



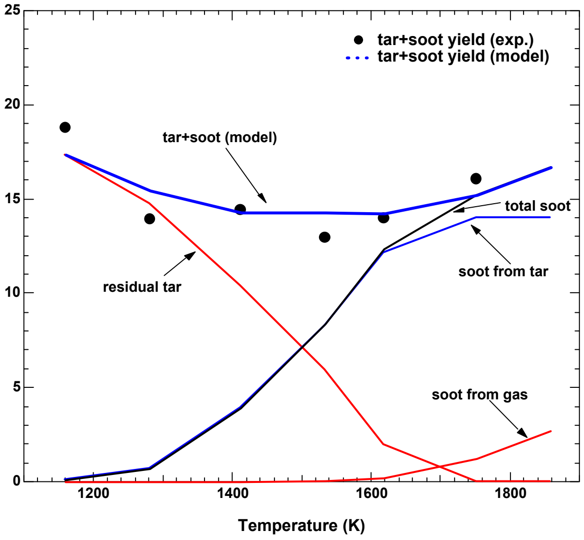
Proposed Mechanism for Secondary Pyrolysis (Zhang, 2001)



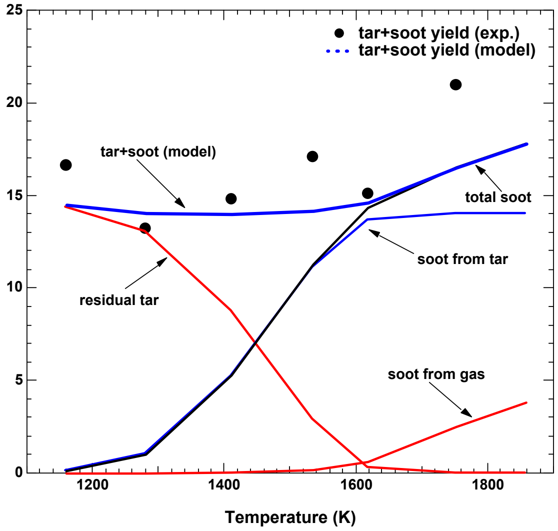
- Two competitive reactions are assumed for tar
  - Thermal cracking (dominant below 1300 K)
  - Polymerization (dominant above 1400 K)
- Fraction of primary tar that can be directly converted to soot is rank dependent
- Additional soot growth from hydrocarbons in gas

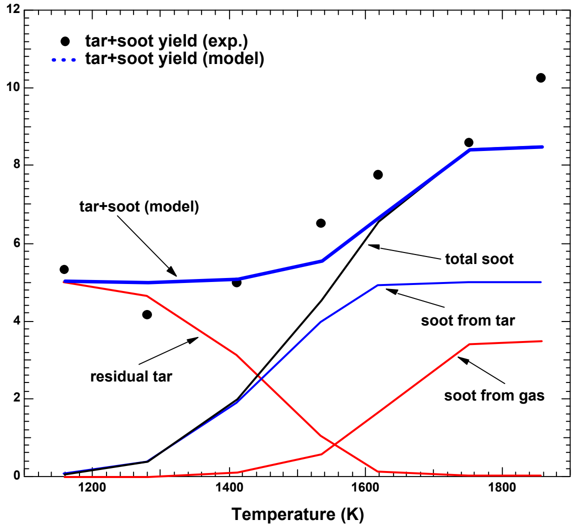
Comparison of Experimental Data and Model Prediction (Zhang, 2001)

Illinois #6

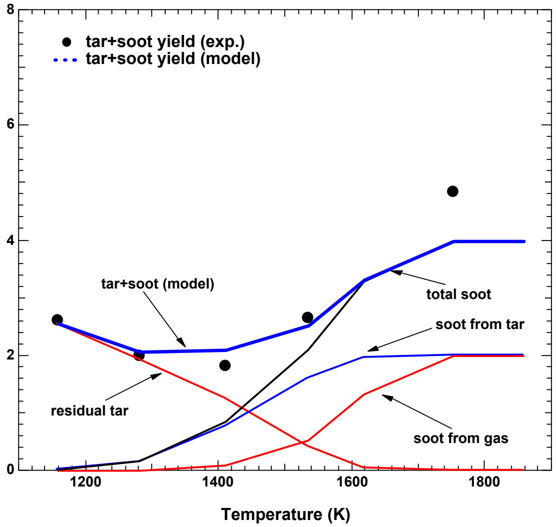


Utah





Black Thunder



Knife River

Application to CFD Model

(Brown, 1997)

A. Sole source of soot is coal tar

Definitions:

Soot mass fraction (Y_C)

Tar mass fraction (Y_T)

Soot particles per unit mass (N_C)

Theory (cont.)

A. Tar Mass $\nabla(\rho u_i Y_T) = \nabla\left(\frac{\mu}{\sigma}\nabla Y_T\right) + \rho S_{Y_T}$

$$S_{Y_T} = Formation_T - Formation_C - Gasification_T - Oxidation_T$$

B. Soot Mass $\nabla(\rho u_i Y_C) = \nabla\left(\frac{\mu}{\sigma}\nabla Y_C\right) + \rho S_{Y_C}$

$$S_{Y_C} = Formation_C - Oxidation_C$$

C. Soot Number $\nabla(\rho u_i N_C) = \nabla\left(\frac{\mu}{\sigma}\nabla N_C\right) + \rho S_{N_C}$

$$S_{N_C} = \frac{N_a}{M_C C_{\min}} Formation_C - Agglomeration_N$$

Source Terms

$$Formation_T = SP_{tar}$$

$$Oxidation_T = \rho_g [c_T][c_{O2}] A_{OT} e^{-E_{OT}/RT}$$

$$Gasification_T = [c_T] A_{GT} e^{-E_{GT}/RT}$$

$$Formation_C = [c_T] A e_{FC}^{-E_{FC}/RT}$$

$$Oxidation_C = SA_{v,C} \frac{p_{O2}}{T^{1/2}} A_{OC} e^{-E_{OC}/RT}$$

$$SA_{v,C} = \frac{6^{2/3} \pi^{1/3} (\rho_g N_C)^{1/3} Y_C^{2/3} \rho_g^{2/3}}{\rho_C^{2/3}}$$

A description of source term constants with literature sources.

Term	*A*	*E (kJ/g-mol)*	*Source*
$Formation_T$	N/A	N/A	Particle Phase Calculations
$Oxidation_T$	6.77×10^5 (1/s)	52.3	Shaw et al. (1990)
$Gasification_T$	9.77×10^{10} (1/s)	286.9	Ma (1996)
$Formation_C$	5.02×10^8 (1/s)	198.9	Ma (1996)
$Oxidation_C$	1.09×10^4 ($K^{1/2}$/s)	164.5	Lee et al. (1962)
A_o	N/A	N/A	Kennedy et al. (1990)
$Agglomeration_N$	N/A	N/A	Fairweather et al. (1992)

Features of the New Soot Model

- Tar formation is based on CPD predictions.
- Tar and soot equations are coupled.
- Empirical volatiles combustion model (from Essenhigh) uncoupled with mixture fraction approach
- Empirical soot oxidation rate from literature
- Tar gasification and soot agglomeration rates from data of Ma (BYU, 1996)

Volatiles Combustion

Approaches to Volatiles Combustion

- Detailed elementary step reaction mechanisms
- Global reactions
  - Hydrocarbons → CO, followed by
  - $CO \rightarrow CO_2$
- Overall burning rates
  - Volatiles → CO_2, H_2O, etc.
- Local chemical equilibrium

Volatiles Combustion

- What output variables are important for your problem?
  - Individual particles combustion vs group combustion
  - Laminar flow vs turbulent flow
  - Scale of the system
    - Does it all happen in one computation cell?
- How well do you know the input variables?
  - Volatiles composition
  - Reaction rate coefficients
  - Heats of reaction

Simplified CH_4 oxidation

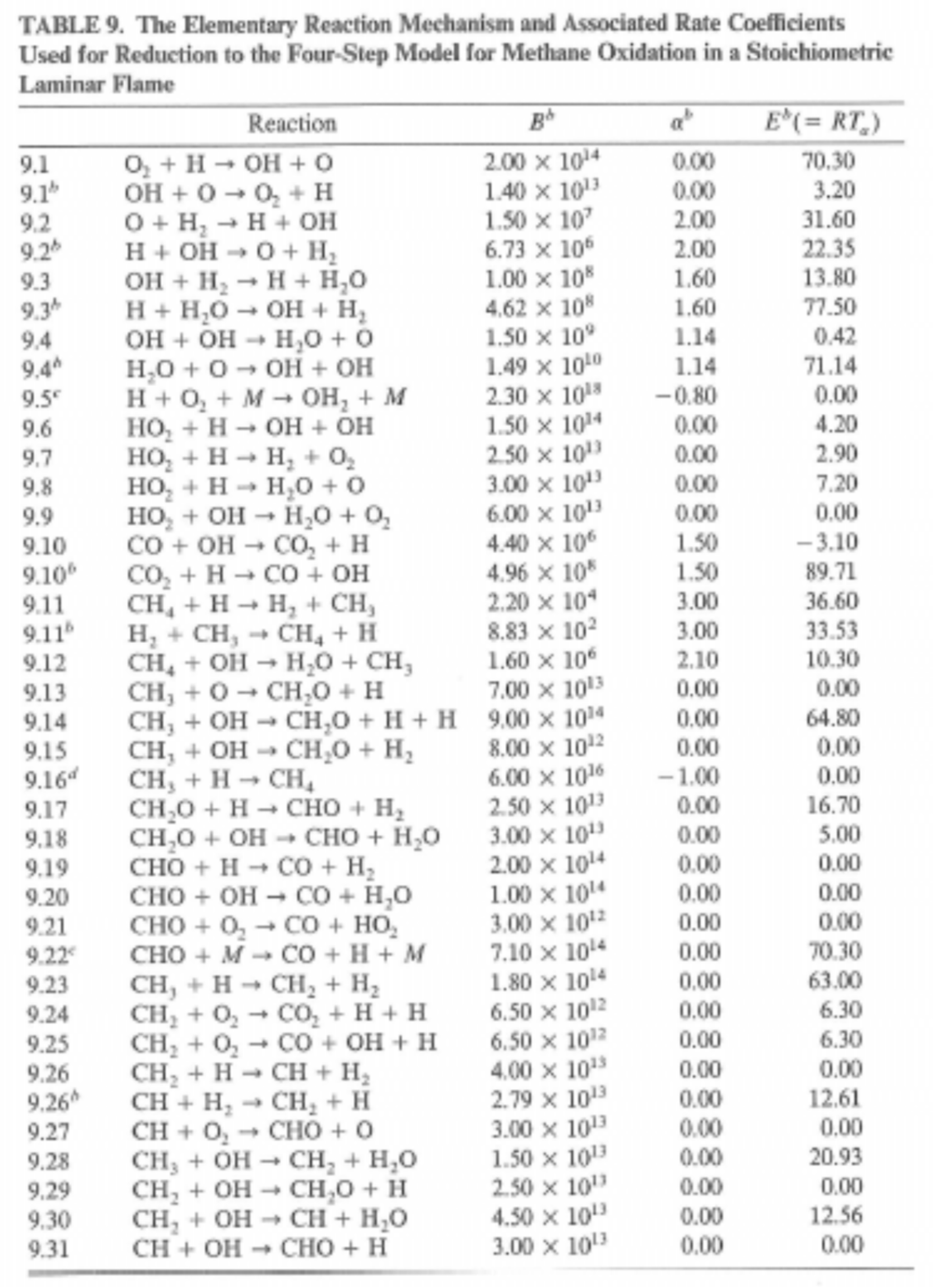


TABLE 9. The Elementary Reaction Mechanism and Associated Rate Coefficients Used for Reduction to the Four-Step Model for Methane Oxidation in a Stoichiometric Laminar Flame

	Reaction	B^b	α^b	$E^b(=RT_\alpha)$
9.1	$O_2 + H \rightarrow OH + O$	2.00×10^{14}	0.00	70.30
9.1[b]	$OH + O \rightarrow O_2 + H$	1.40×10^{13}	0.00	3.20
9.2	$O + H_2 \rightarrow H + OH$	1.50×10^{7}	2.00	31.60
9.2[b]	$H + OH \rightarrow O + H_2$	6.73×10^{6}	2.00	22.35
9.3	$OH + H_2 \rightarrow H + H_2O$	1.00×10^{8}	1.60	13.80
9.3[b]	$H + H_2O \rightarrow OH + H_2$	4.62×10^{8}	1.60	77.50
9.4	$OH + OH \rightarrow H_2O + O$	1.50×10^{9}	1.14	0.42
9.4[b]	$H_2O + O \rightarrow OH + OH$	1.49×10^{10}	1.14	71.14
9.5[c]	$H + O_2 + M \rightarrow OH_2 + M$	2.30×10^{18}	−0.80	0.00
9.6	$HO_2 + H \rightarrow OH + OH$	1.50×10^{14}	0.00	4.20
9.7	$HO_2 + H \rightarrow H_2 + O_2$	2.50×10^{13}	0.00	2.90
9.8	$HO_2 + H \rightarrow H_2O + O$	3.00×10^{13}	0.00	7.20
9.9	$HO_2 + OH \rightarrow H_2O + O_2$	6.00×10^{13}	0.00	0.00
9.10	$CO + OH \rightarrow CO_2 + H$	4.40×10^{6}	1.50	−3.10
9.10[b]	$CO_2 + H \rightarrow CO + OH$	4.96×10^{8}	1.50	89.71
9.11	$CH_4 + H \rightarrow H_2 + CH_3$	2.20×10^{4}	3.00	36.60
9.11[b]	$H_2 + CH_3 \rightarrow CH_4 + H$	8.83×10^{2}	3.00	33.53
9.12	$CH_4 + OH \rightarrow H_2O + CH_3$	1.60×10^{6}	2.10	10.30
9.13	$CH_3 + O \rightarrow CH_2O + H$	7.00×10^{13}	0.00	0.00
9.14	$CH_3 + OH \rightarrow CH_2O + H + H$	9.00×10^{14}	0.00	64.80
9.15	$CH_3 + OH \rightarrow CH_2O + H_2$	8.00×10^{12}	0.00	0.00
9.16[d]	$CH_3 + H \rightarrow CH_4$	6.00×10^{16}	−1.00	0.00
9.17	$CH_2O + H \rightarrow CHO + H_2$	2.50×10^{13}	0.00	16.70
9.18	$CH_2O + OH \rightarrow CHO + H_2O$	3.00×10^{13}	0.00	5.00
9.19	$CHO + H \rightarrow CO + H_2$	2.00×10^{14}	0.00	0.00
9.20	$CHO + OH \rightarrow CO + H_2O$	1.00×10^{14}	0.00	0.00
9.21	$CHO + O_2 \rightarrow CO + HO_2$	3.00×10^{12}	0.00	0.00
9.22[c]	$CHO + M \rightarrow CO + H + M$	7.10×10^{14}	0.00	70.30
9.23	$CH_3 + H \rightarrow CH_2 + H_2$	1.80×10^{14}	0.00	63.00
9.24	$CH_2 + O_2 \rightarrow CO_2 + H + H$	6.50×10^{12}	0.00	6.30
9.25	$CH_2 + O_2 \rightarrow CO + OH + H$	6.50×10^{12}	0.00	6.30
9.26	$CH_2 + H \rightarrow CH + H_2$	4.00×10^{13}	0.00	0.00
9.26[b]	$CH + H_2 \rightarrow CH_2 + H$	2.79×10^{13}	0.00	12.61
9.27	$CH + O_2 \rightarrow CHO + O$	3.00×10^{13}	0.00	0.00
9.28	$CH_3 + OH \rightarrow CH_2 + H_2O$	1.50×10^{13}	0.00	20.93
9.29	$CH_2 + OH \rightarrow CH_2O + H$	2.50×10^{13}	0.00	0.00
9.30	$CH_2 + OH \rightarrow CH + H_2O$	4.50×10^{13}	0.00	12.56
9.31	$CH + OH \rightarrow CHO + H$	3.00×10^{13}	0.00	0.00

from Fossil Fuel Combustion, ed. Bartok & Sarofim,
Wiley, p 199 (1991).

Simpler Mechanisms

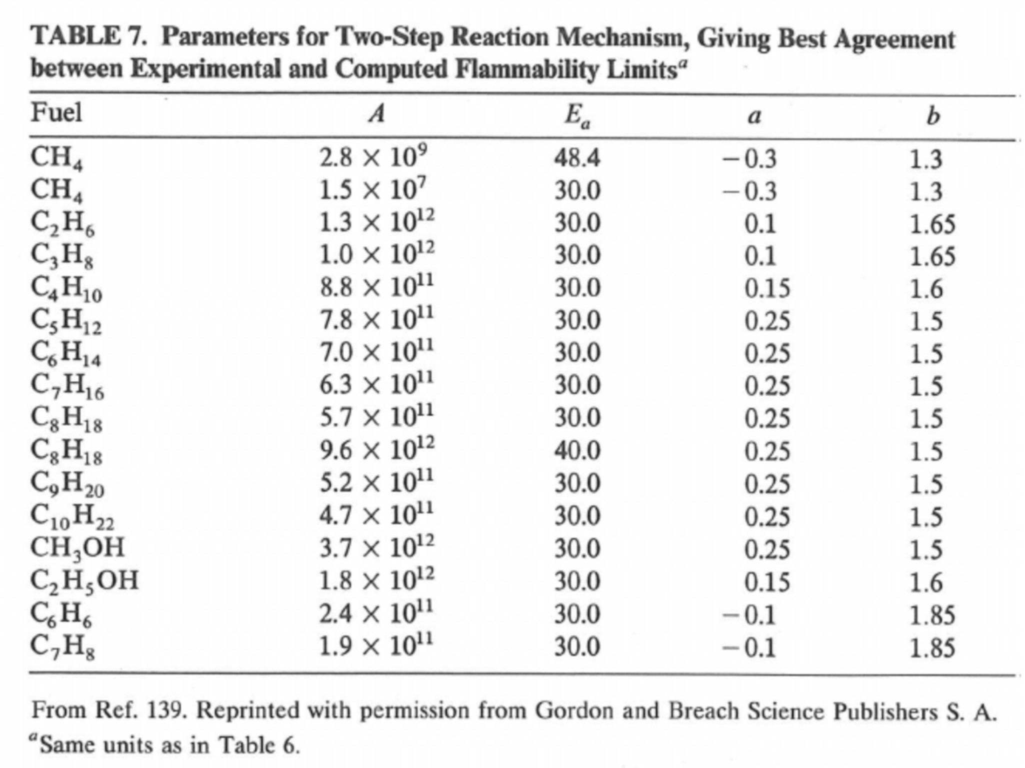


TABLE 7. Parameters for Two-Step Reaction Mechanism, Giving Best Agreement between Experimental and Computed Flammability Limits[a]

Fuel	A	E_a	a	b
CH_4	2.8×10^9	48.4	−0.3	1.3
CH_4	1.5×10^7	30.0	−0.3	1.3
C_2H_6	1.3×10^{12}	30.0	0.1	1.65
C_3H_8	1.0×10^{12}	30.0	0.1	1.65
C_4H_{10}	8.8×10^{11}	30.0	0.15	1.6
C_5H_{12}	7.8×10^{11}	30.0	0.25	1.5
C_6H_{14}	7.0×10^{11}	30.0	0.25	1.5
C_7H_{16}	6.3×10^{11}	30.0	0.25	1.5
C_8H_{18}	5.7×10^{11}	30.0	0.25	1.5
C_8H_{18}	9.6×10^{12}	40.0	0.25	1.5
C_9H_{20}	5.2×10^{11}	30.0	0.25	1.5
$C_{10}H_{22}$	4.7×10^{11}	30.0	0.25	1.5
CH_3OH	3.7×10^{12}	30.0	0.25	1.5
C_2H_5OH	1.8×10^{12}	30.0	0.15	1.6
C_6H_6	2.4×10^{11}	30.0	−0.1	1.85
C_7H_8	1.9×10^{11}	30.0	−0.1	1.85

From Ref. 139. Reprinted with permission from Gordon and Breach Science Publishers S. A.

[a] Same units as in Table 6.

Step One

$$C_nH_{2(n+1)} + \frac{2(n+1)}{2}O_2 \rightarrow (n+1)H_2O + nCO$$

$$\frac{d[fuel]}{dt} = A\exp\left(-\frac{E_a}{RT}\right)[fuel]^a[O_2]^b$$

Step Two

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$\frac{d[CO_2]}{dt} = 10^{14.6}\exp\left(-\frac{40{,}000}{RT}\right)[CO]\,[O_2]^{0.25}[H_2O]^{0.5}$$

from Fossil Fuel Combustion, ed. Bartok & Sarofim, Wiley, pp 182-189 (1991).

Volatiles Combustion

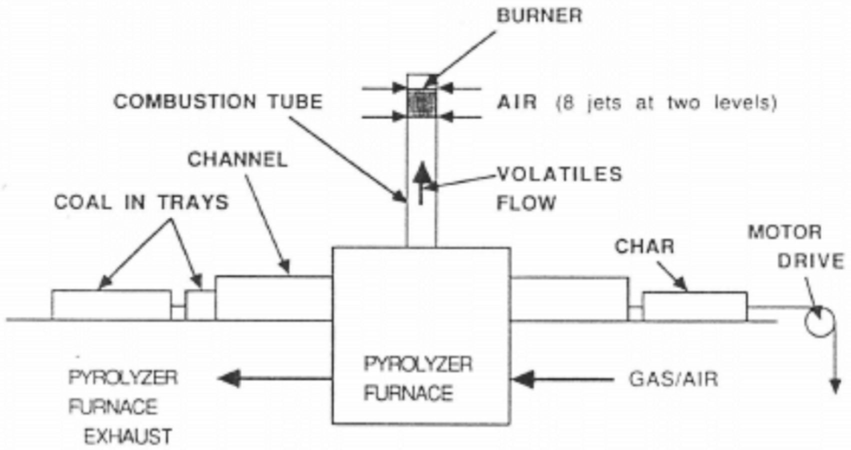


FIG. 1. Schematic of Pyrolyzer and Volatile Combustor. Trays carrying coal are linked, and pulled through gas heated pyrolyzer by motor drive. Volatiles are burned in a counter-vortex mixing section at top of combustion tube. [Note: Pyrolyzer is a muffle furnace so that pyrolyzer exhaust is separate from pyrolysis products].

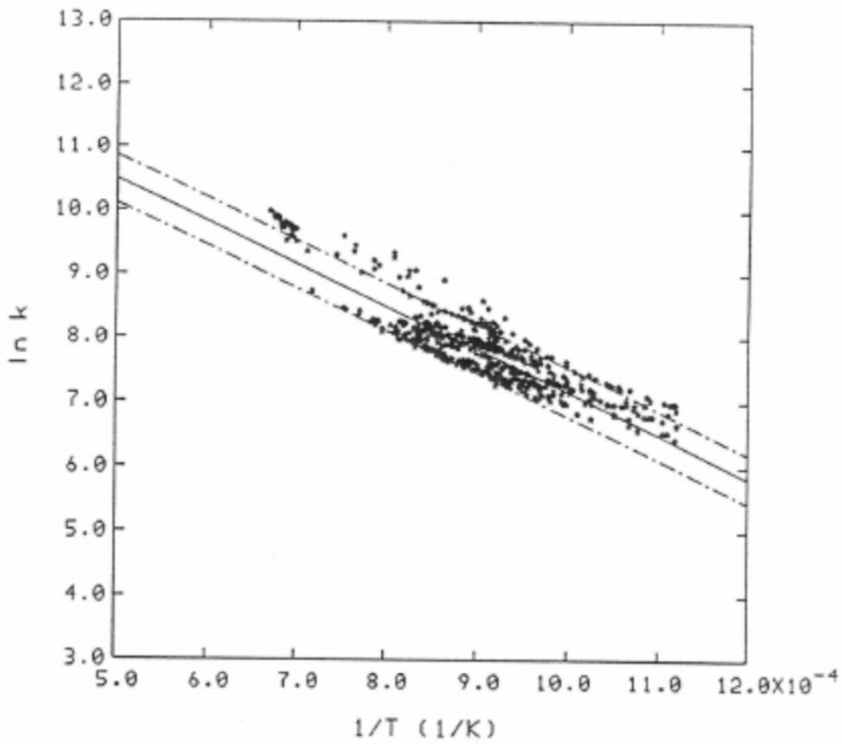


FIG. 4. Arrhenius plot of experimentally determined values of rate constant for combustion of volatiles from 14 coals. Solid line is the best linear fit and the two dotted lines give the range determined by 2 X (std. deviation). Total number of points: 541

from Shaw et al., 23rd Symp on Combustion (1990) (Essenhigh's group)

Light Gas Combustion

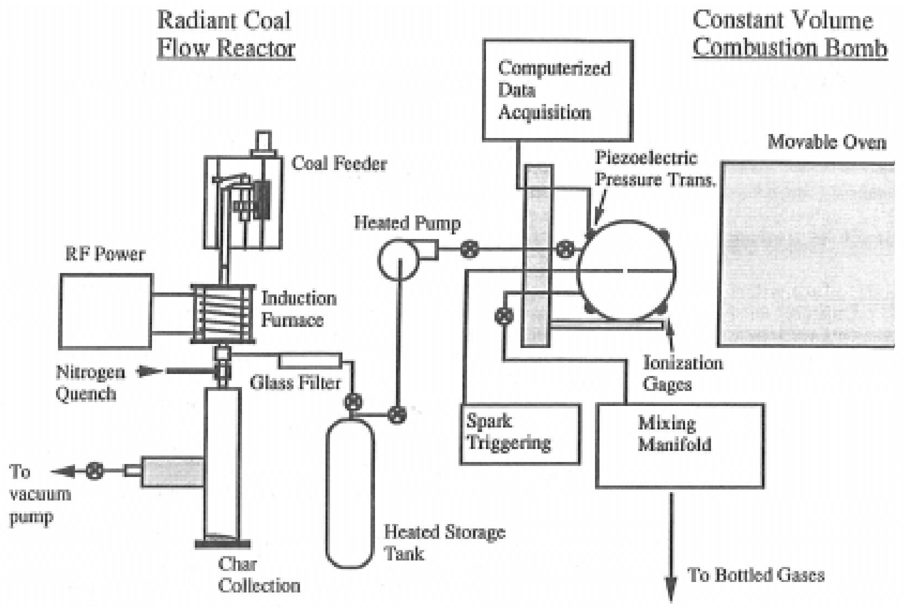


FIG. 1. Schematic of the radiant coal pyrolyzer, the heated handling system for volatiles, and the constant-volume combustion bomb.

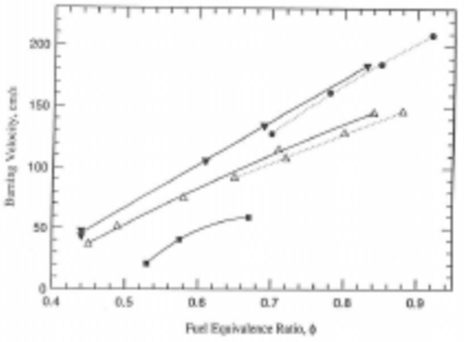


FIG. 3. Laminar burning velocities of the noncondensible fuel mixtures from Ill. #6 coal generated in the furnace at 1635 (■), 1715 (△), 1770 (●), and 1800 K (▼). In all cases values indicate the flame speed when the combustible mixture was compressed to atmospheric pressure and heated to about 430 K. The molar dilution ratio of $N_2/H_2O/CO_2$:O_2 is 3.8.

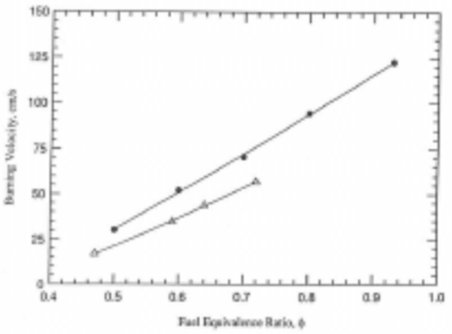


FIG. 4. Laminar burning velocities of the noncondensible fuel mixtures from Dietz subbituminous coal generated in the furnace at 1715 (△), and 1770 K (●). In all cases values indicate the flame speed when the combustible mixture was compressed to atmospheric pressure and heated to about 430 K. The molar dilution ratio of $N_2/H_2O/CO_2$:O_2 is 3.8.

- Tar filtered from volatiles
- Light gases stored until ready
- Combustion bomb experiments on light gases

from Marlow et al., 24th Symp on Combustion, pp 1251-1258 (1992) (Niksa's group)

Equilibrium Considerations

- In some instances, chemical reactions are fast compared to other time scales
  - mixing, fluid dynamics
- Chemical equilibrium routines (based on Gibbs free energy minimization) compute fully combusted conditions
  - Temperature
  - Species concentrations
- Input required
  - Initial T (energy level)
  - Initial elemental composition
  - Pressure
  - Energy level of products (adiabatic?)

Single Particle Combustion

Photo of Volatiles Combustion and Char Oxidation in Sandia FFB

Single Particle Combustion

Backlit Image of Single Particle Volatiles Combustion

McLean et al., 18th Symposium on Combustion, 1239-1248 (1981)

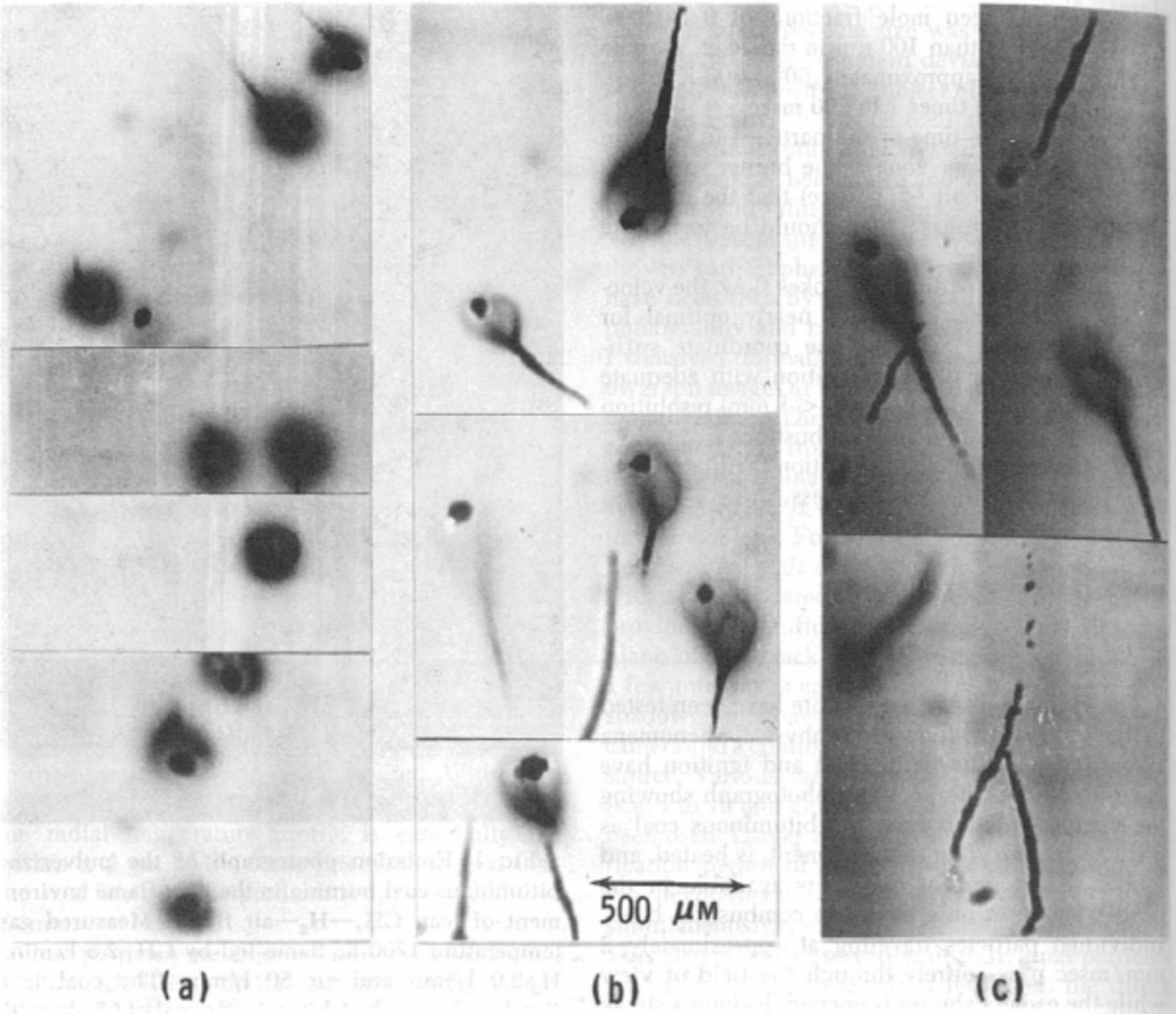
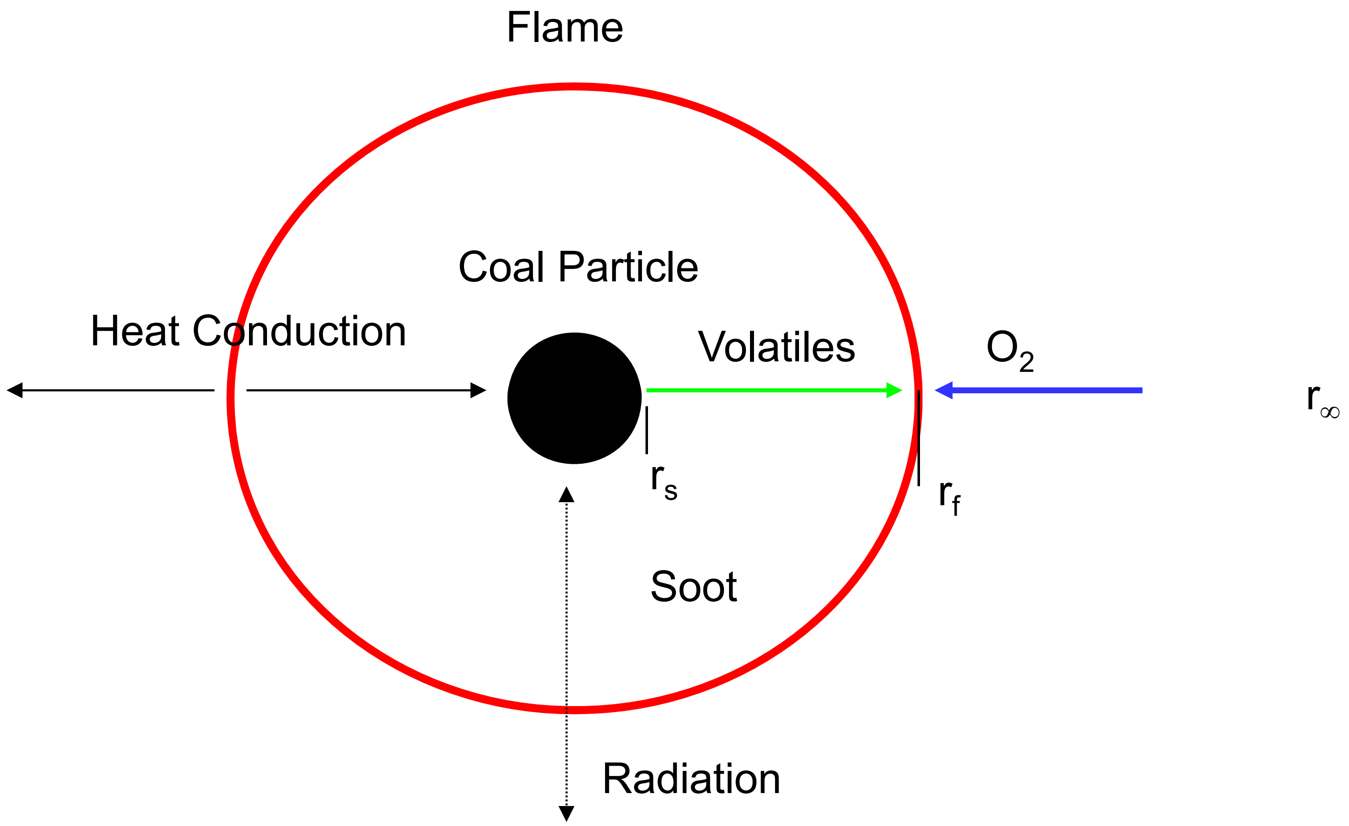


FIG. 2. Shadowgraphs showing bituminous coal particles during the early stages of combustion; (a) near ignition, (b) several msec after ignition, (c) approximately 10 msec after ignition; gas flow upward.

Principles of Single Particle Combustion



Principles of Single Particle Combustion

- Volatiles release is transient
  - Flame moves with time
- Reaction zone is not infinitely thin
- Presence of volatiles flame enhances heating rate of coal particle
- Flow around particle is not a 1-D problem
- Where is the soot?
  - Between particle and flame?
  - Thin film in near-flame region?
  - Soot tails
- Computationally intensive
  - How badly do you want to know this?

Group Combustion Concepts

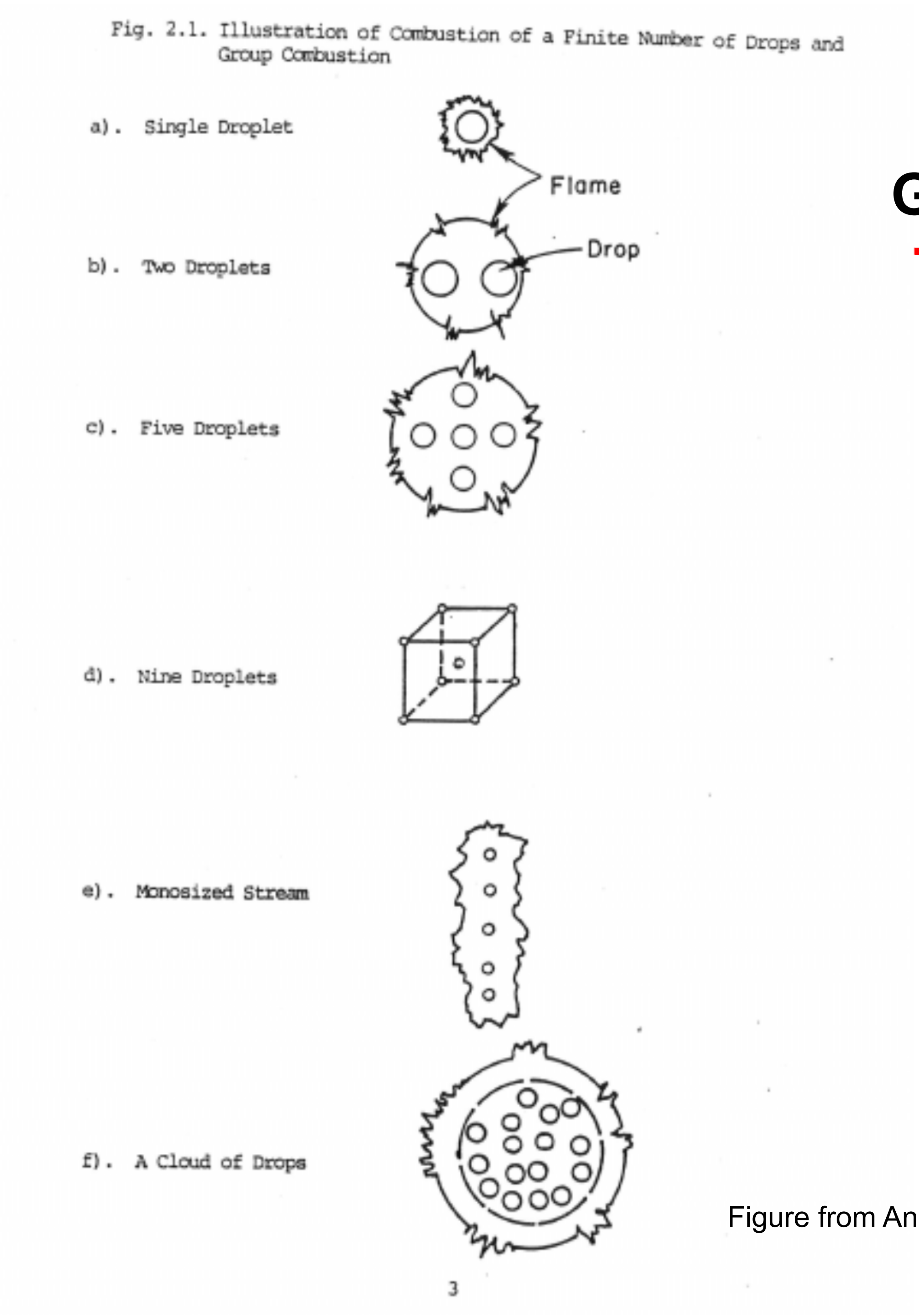


Fig. 2.1. Illustration of Combustion of a Finite Number of Drops and Group Combustion

When does single particle behavior end?

When does group combustion start?

- Particle diameter
- Particle spacing
- Turbulence

Figure from Annamalai et al., Annual Report, DE-FG 22-85 PC 80528 (1986)