

Business

- Wednesday – Andrew will have review for exam
- Thursday – exam
- Friday – no class
- Monday – Memorial Day holiday (no class)

Midterm Exam

- ~30 minutes
- Oral
- Closed book, closed notes
- Have some paper and a pencil
- No calculator needed

8:30 am Kamron

9:15 am Maisy

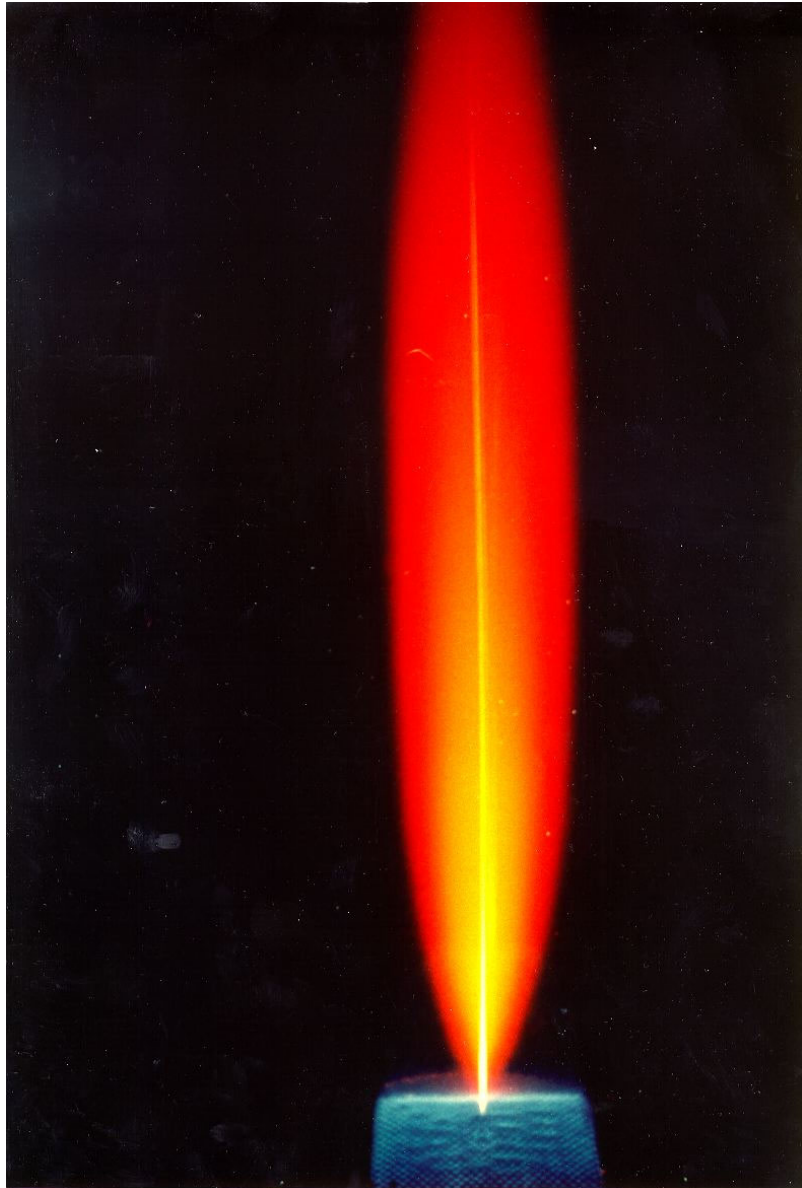
10 am Mahsa

10:45 am Raj

11:30 am Keane

3 pm Don

3:45 pm Scott



Class 9

Secondary Pyrolysis, Soot Formation from Coal Tar

Thanks to:
Jinliang Ma
Alex Brown

Soot





Soot from HC Gas

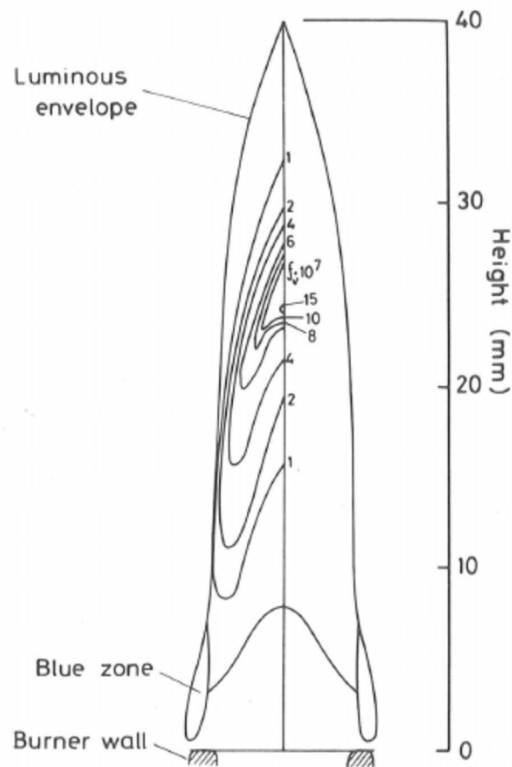


FIGURE 22. Distribution of soot volume fraction in the *n*-hexane diffusion flame of Figures 8 and 9. Redrawn from Spengler and Kern,⁷⁴ with permission from the publisher.

- 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}

Soot from Coal

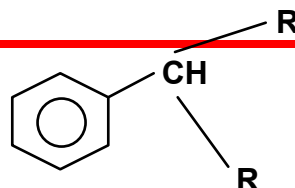
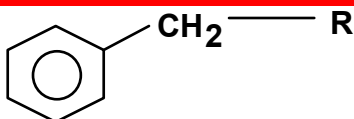
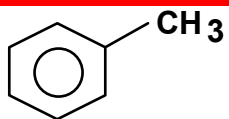
- Comes from coal tar
- Coal tar has avg MW of 350 at 1 atm
- Coal tar does not break down to C_2H_2 and then reform aromatic rings
- Coal tar already has 3-4 rings, plus attachments

What Is Secondary Pyrolysis and Why Is It Important?

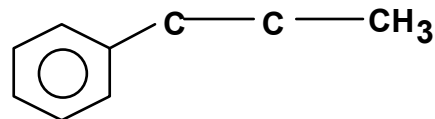
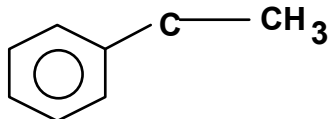
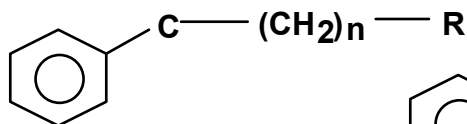


- Soot in flame regions can radiate significant amount of heat away from flame
- Accurate calculation of gas temperatures in flames is critical to predictions of NO_x
- Soot is harder to burn than light gases
- Some fuel nitrogen ends up in the soot

Definitions

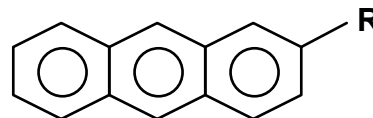
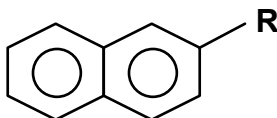
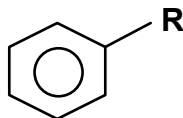


α -hydrogens



β hydrogens

γ hydrogens

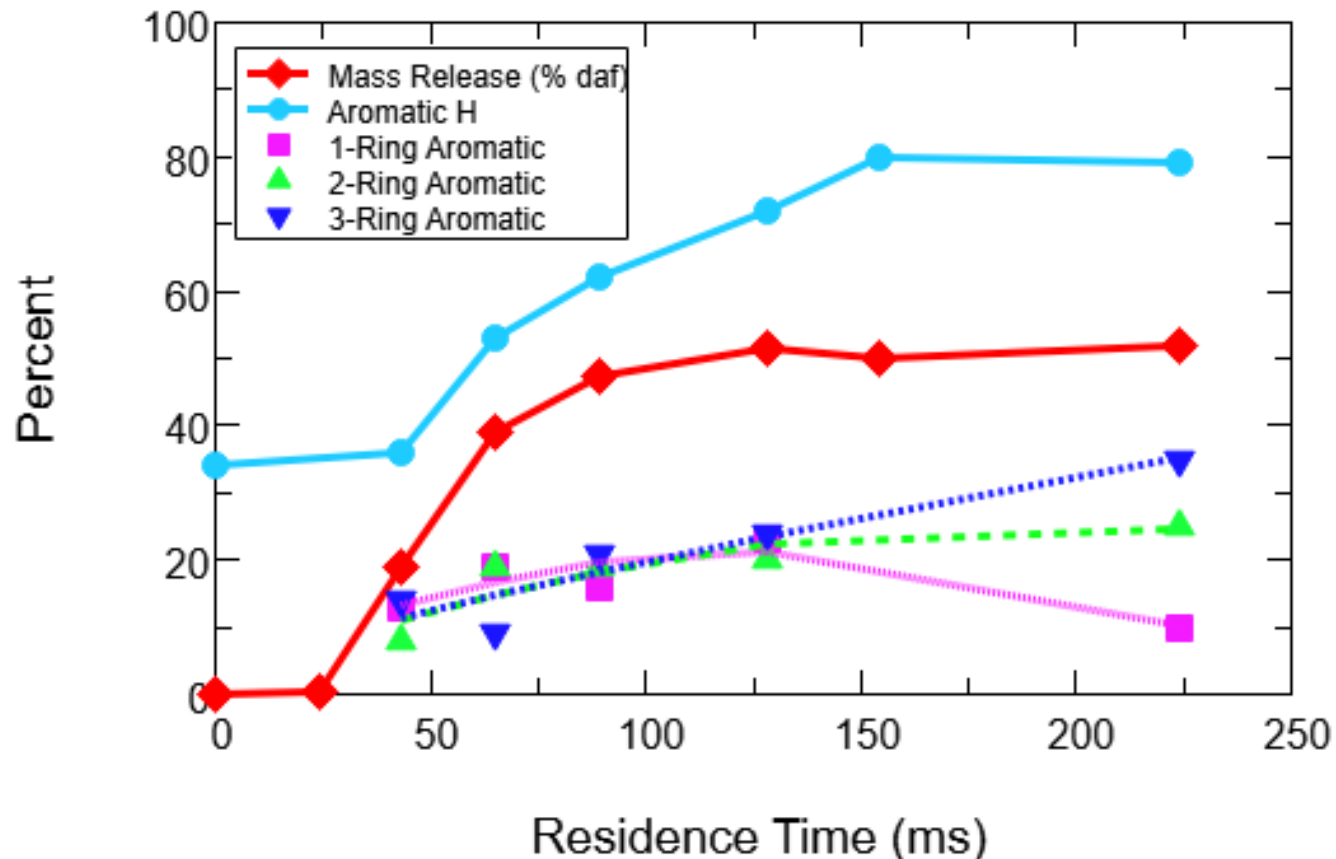


1-Ring

2-Ring

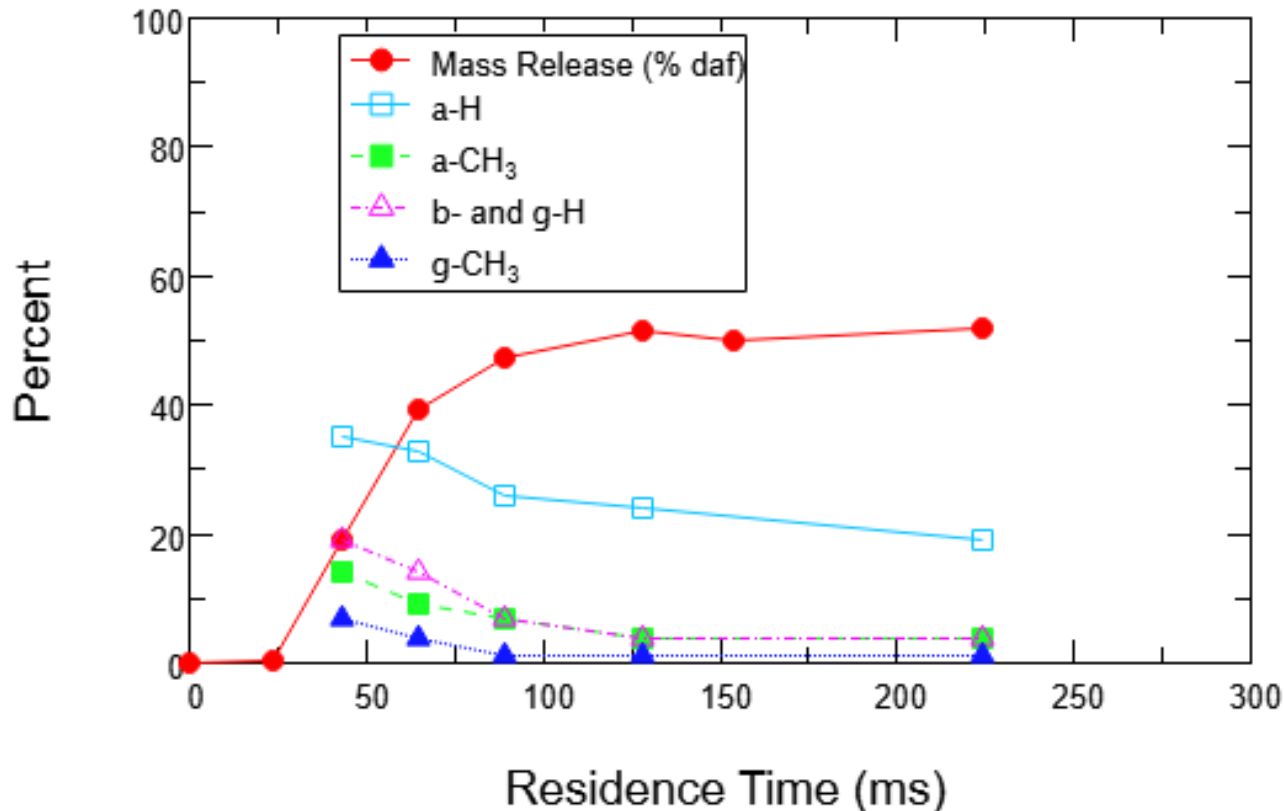
3-Ring

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.

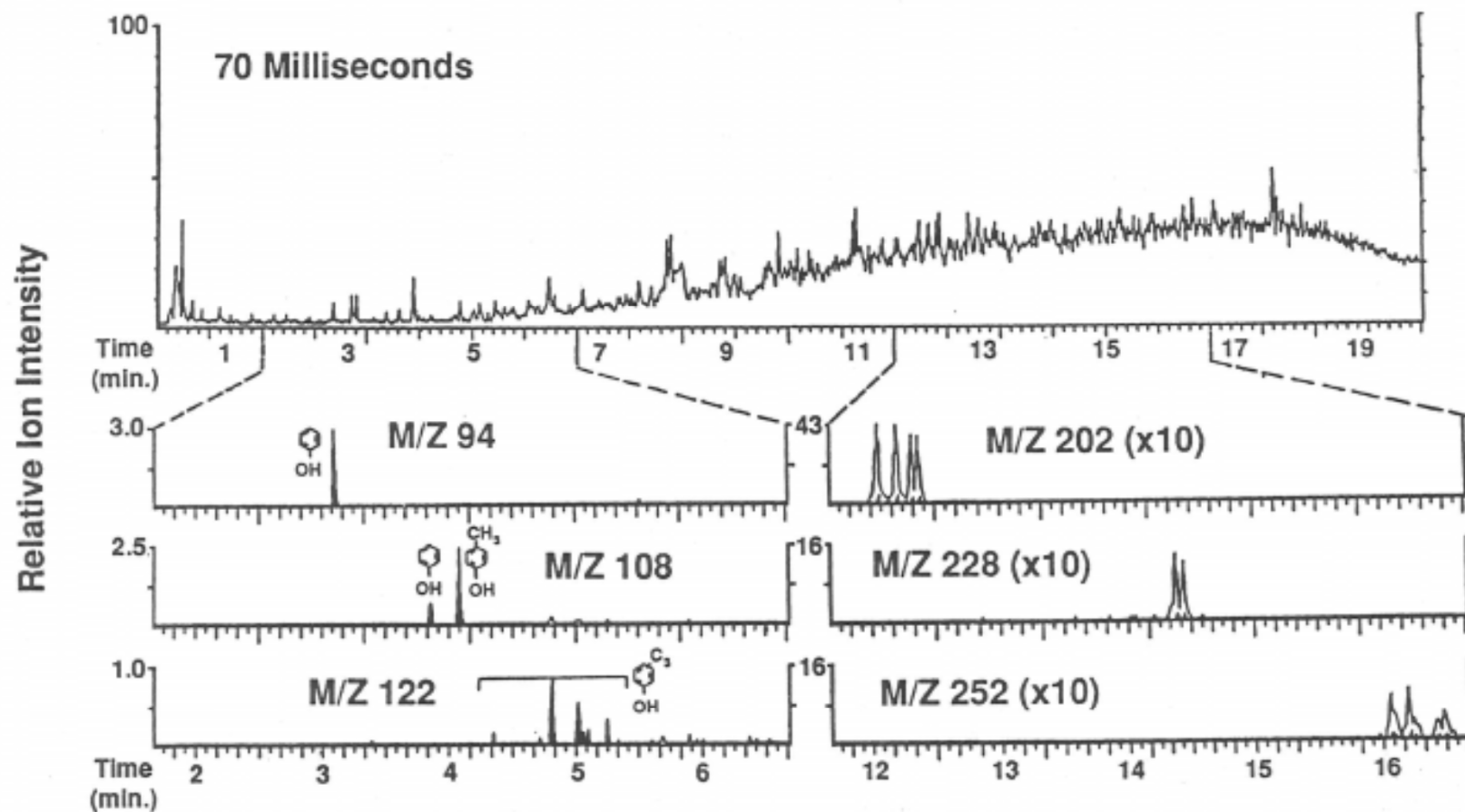


Figure 5.59 Curie-point desorption GC/MS profiles of Illinois #6 tar obtained at 1250 K after 70 ms. Total ion chromatogram (upper profile) and selected ion chromatograms (lower profiles) show relative abundance of (alkyl) phenols vs. pyrenes, perylenes, and picones.

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

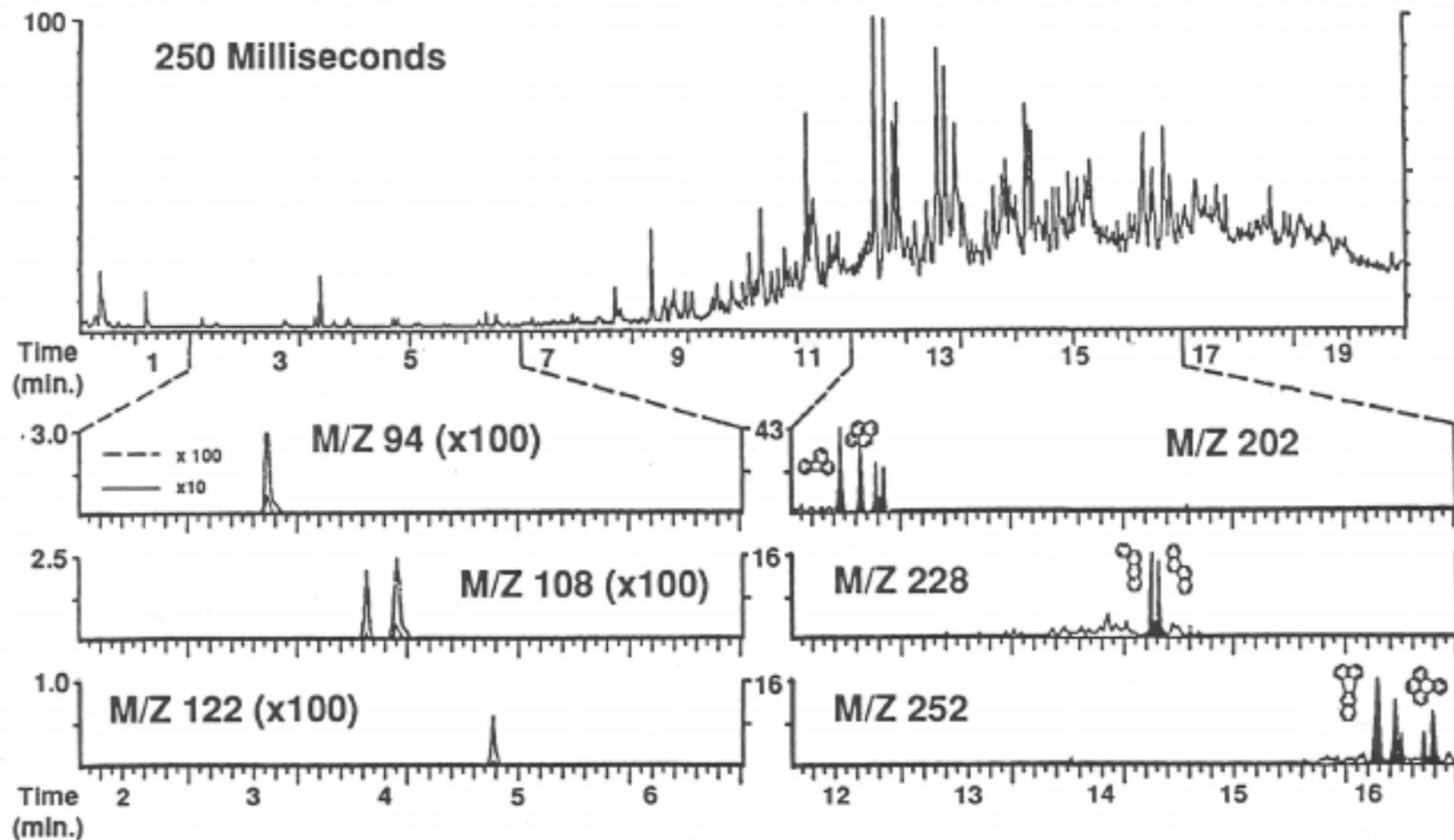
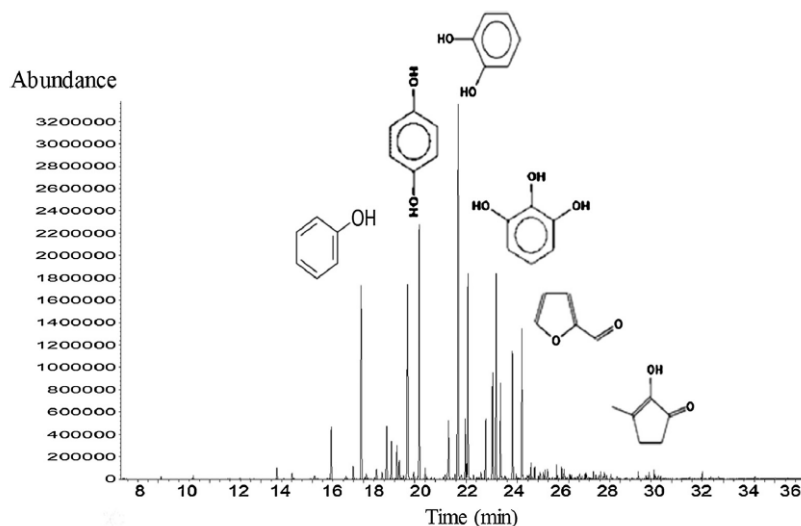


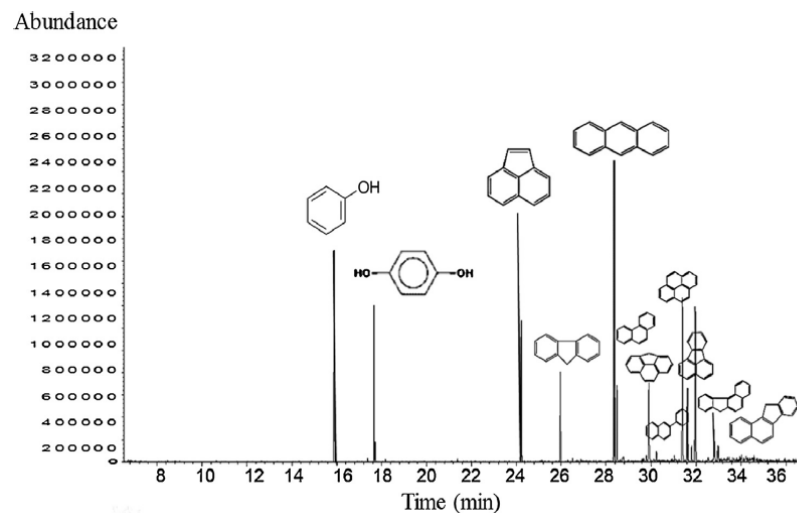
Figure 5.60 Same as Fig. 5.59 but obtained after 250 ms. Note 100-fold decrease in (alkyl) phenol as opposed to 10-fold increase in polynuclear aromatic hydrocarbons.

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

Secondary Reactions in Tar from Live Vegetation



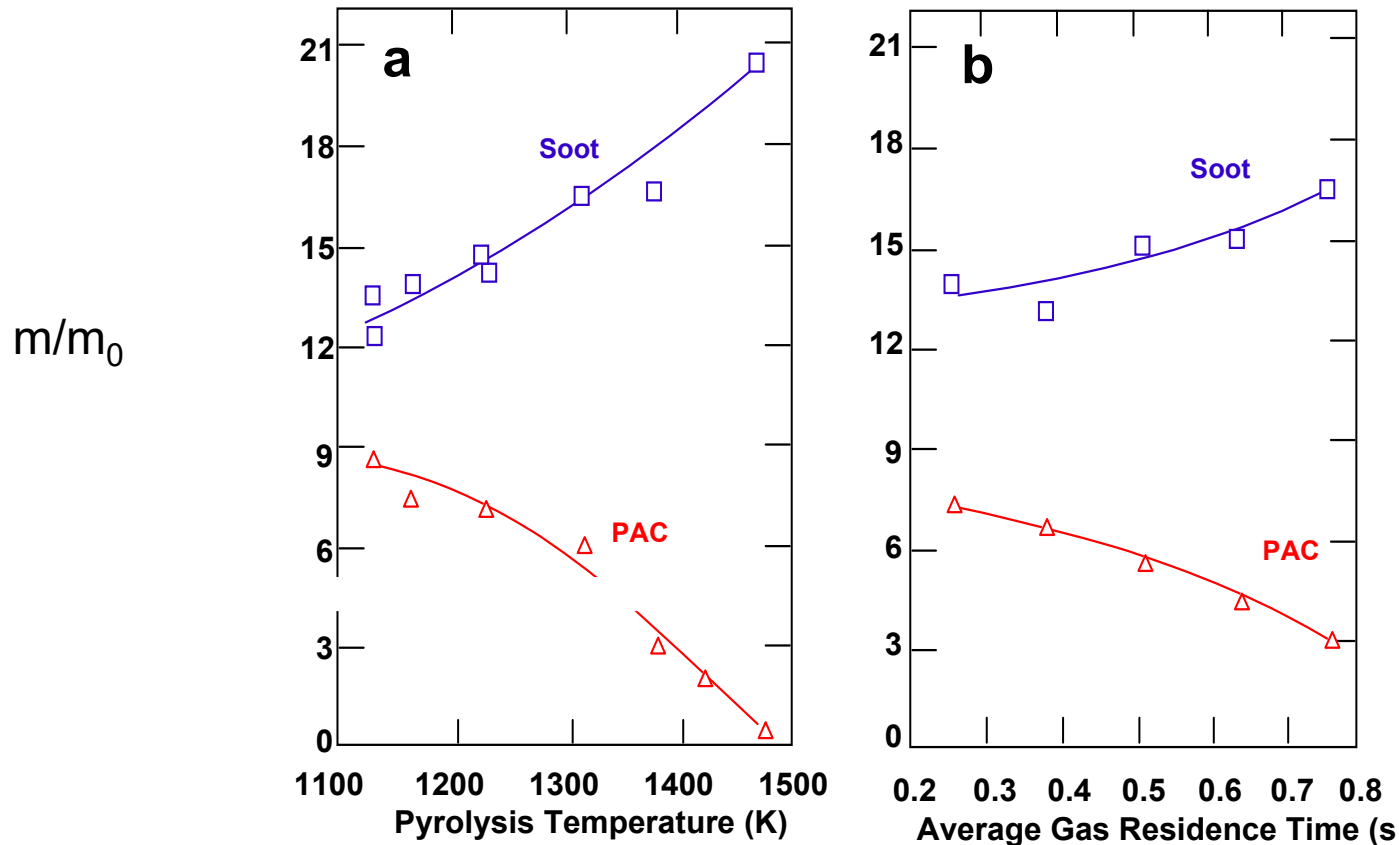
0.5°C/s to 500°C



180°C/s to 750°C

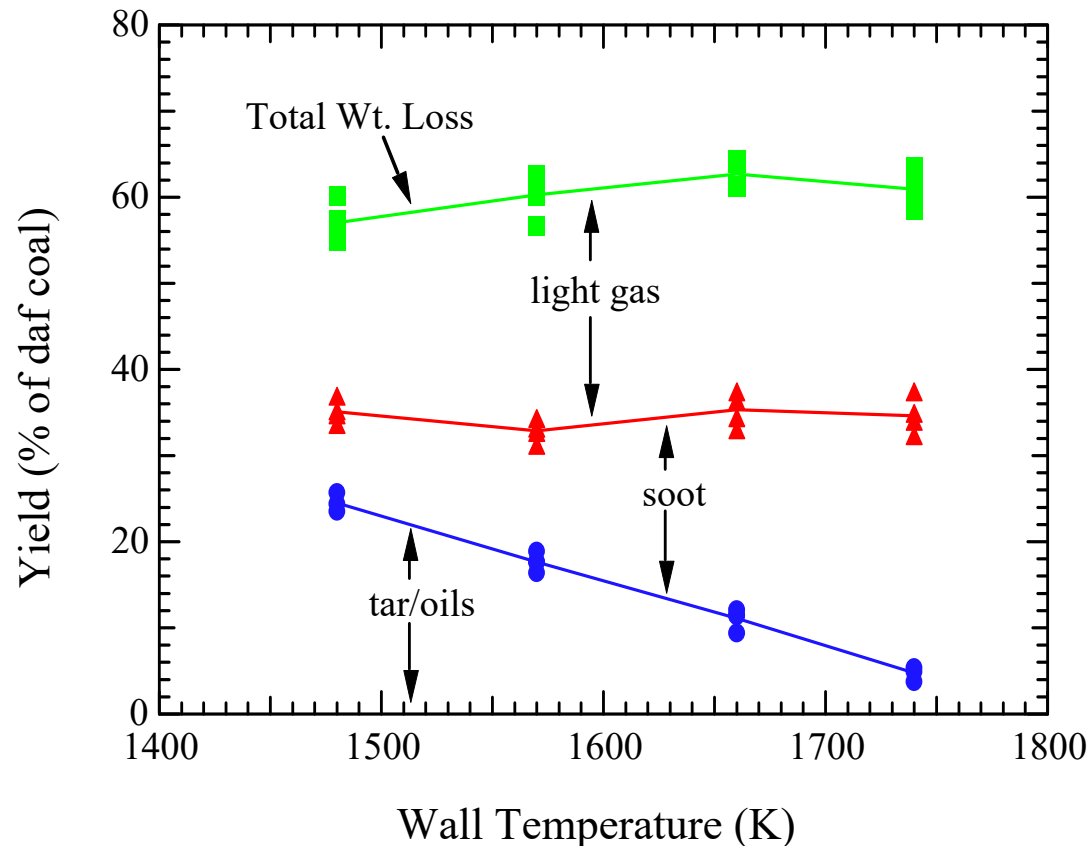
Safdari, M-S., E. Amini, D. R. Weise, and T. H. Fletcher, "Heating Rate and Temperature Effects on Pyrolysis Products from Live Wildland Fuels," *Fuel*, **242**, 295-304 (2019).

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



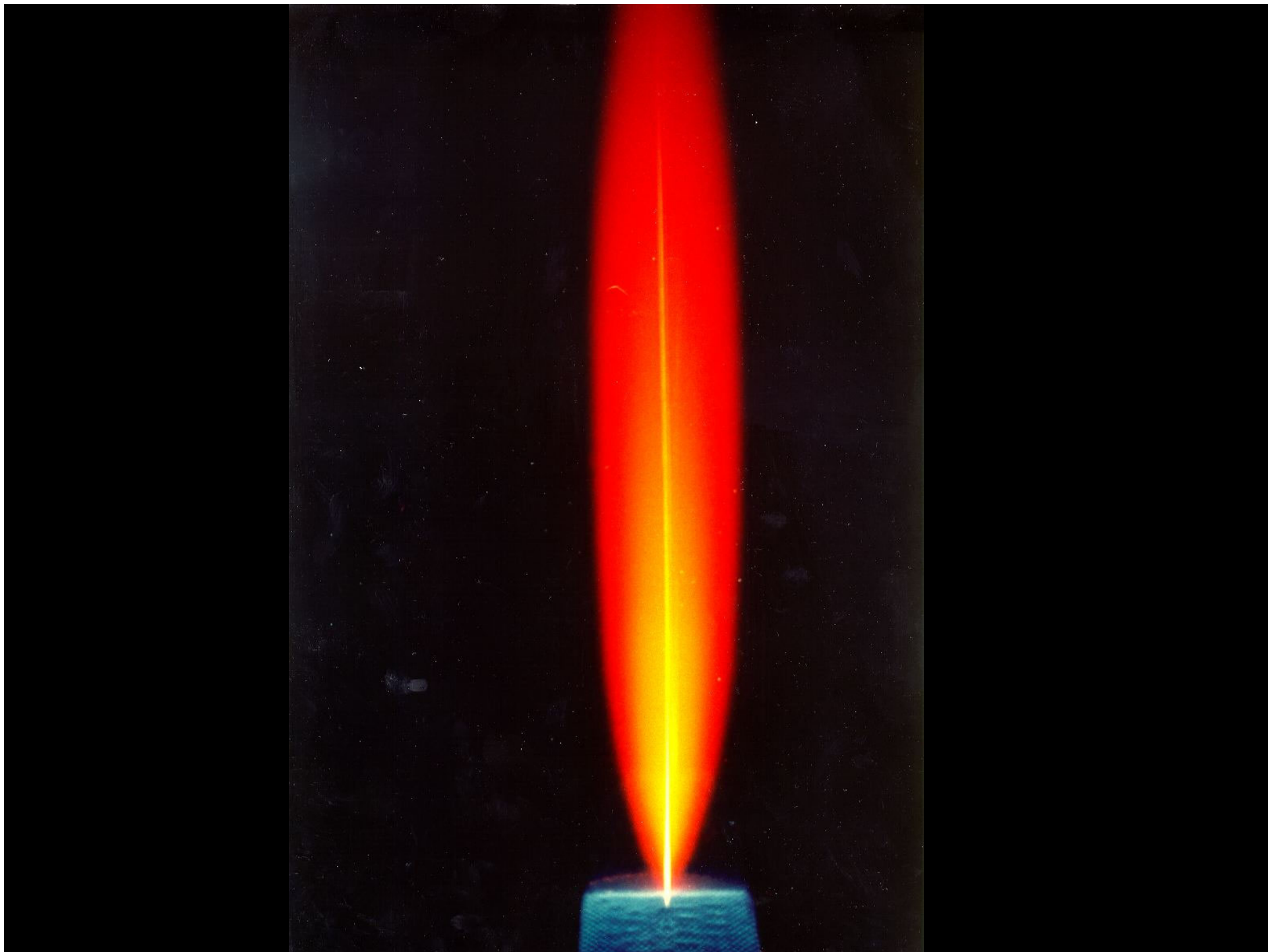
Pittsburgh No. 8 hv bituminous coal in radiant drop tube, rapid heating, particle temperature lower than wall temperature (Chen and Niksa, 1992). Similar results for Dietz subbituminous coal.

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

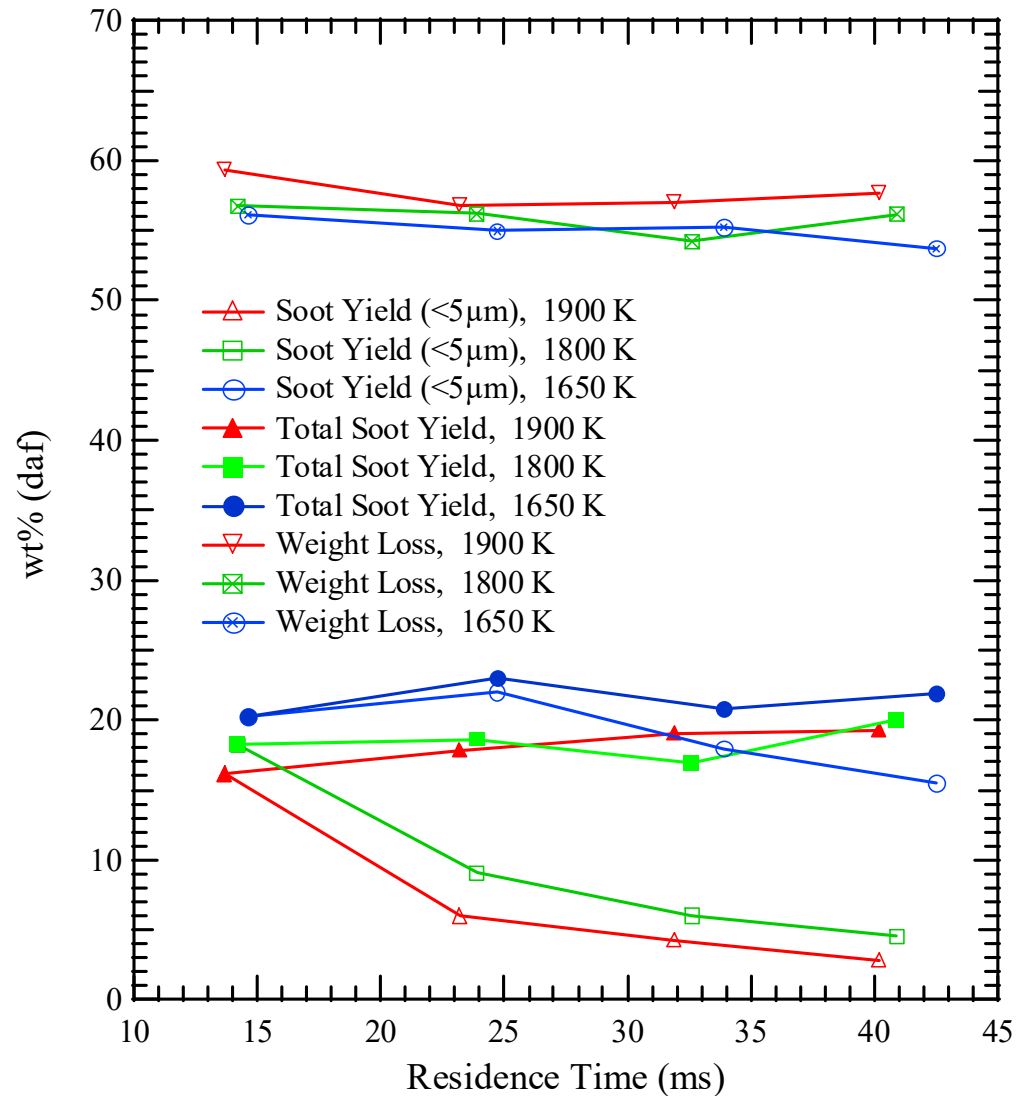
$$f_{v,C} = \frac{C_1 C_2 \beta_C M_C}{\rho_C}$$

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

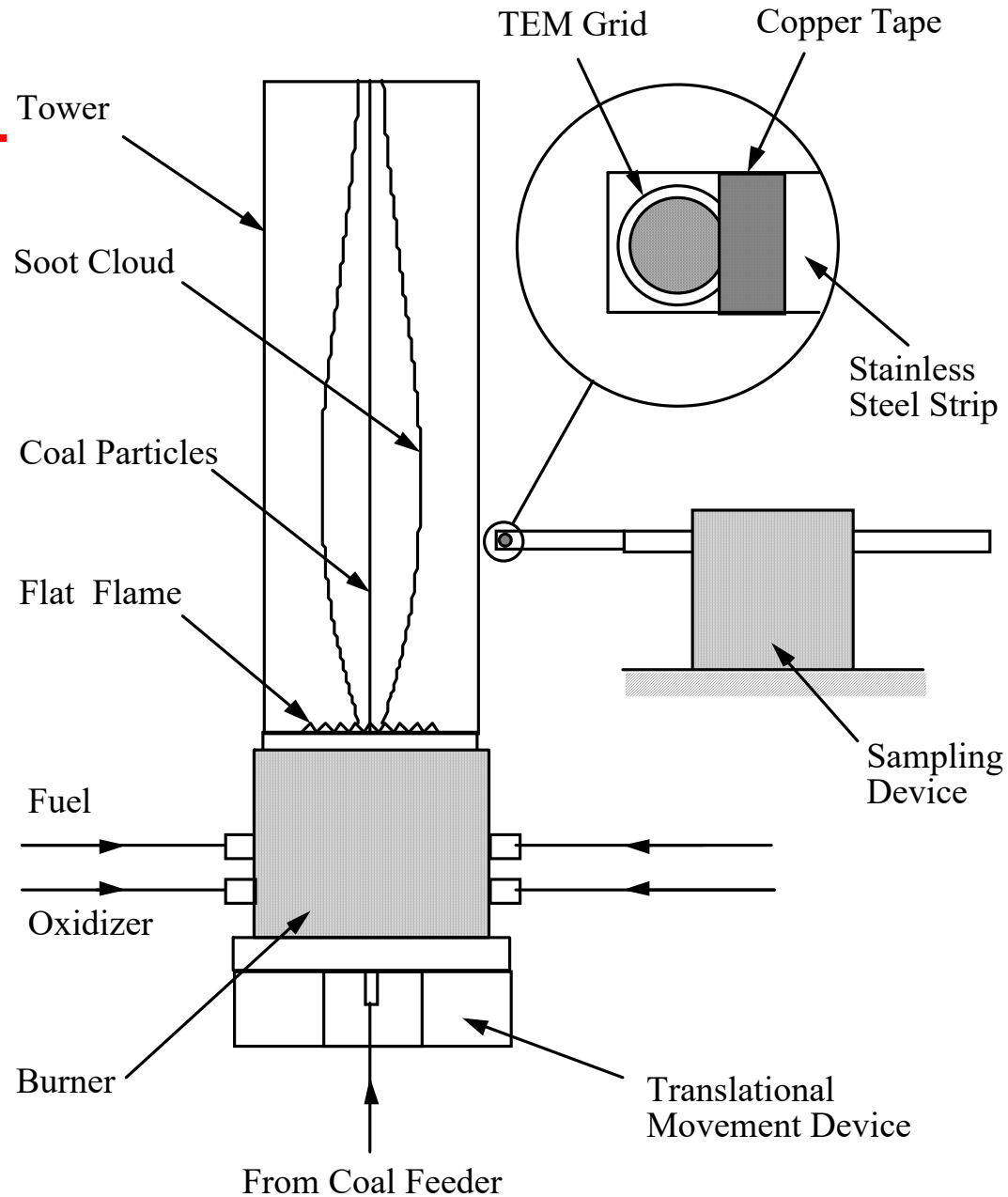


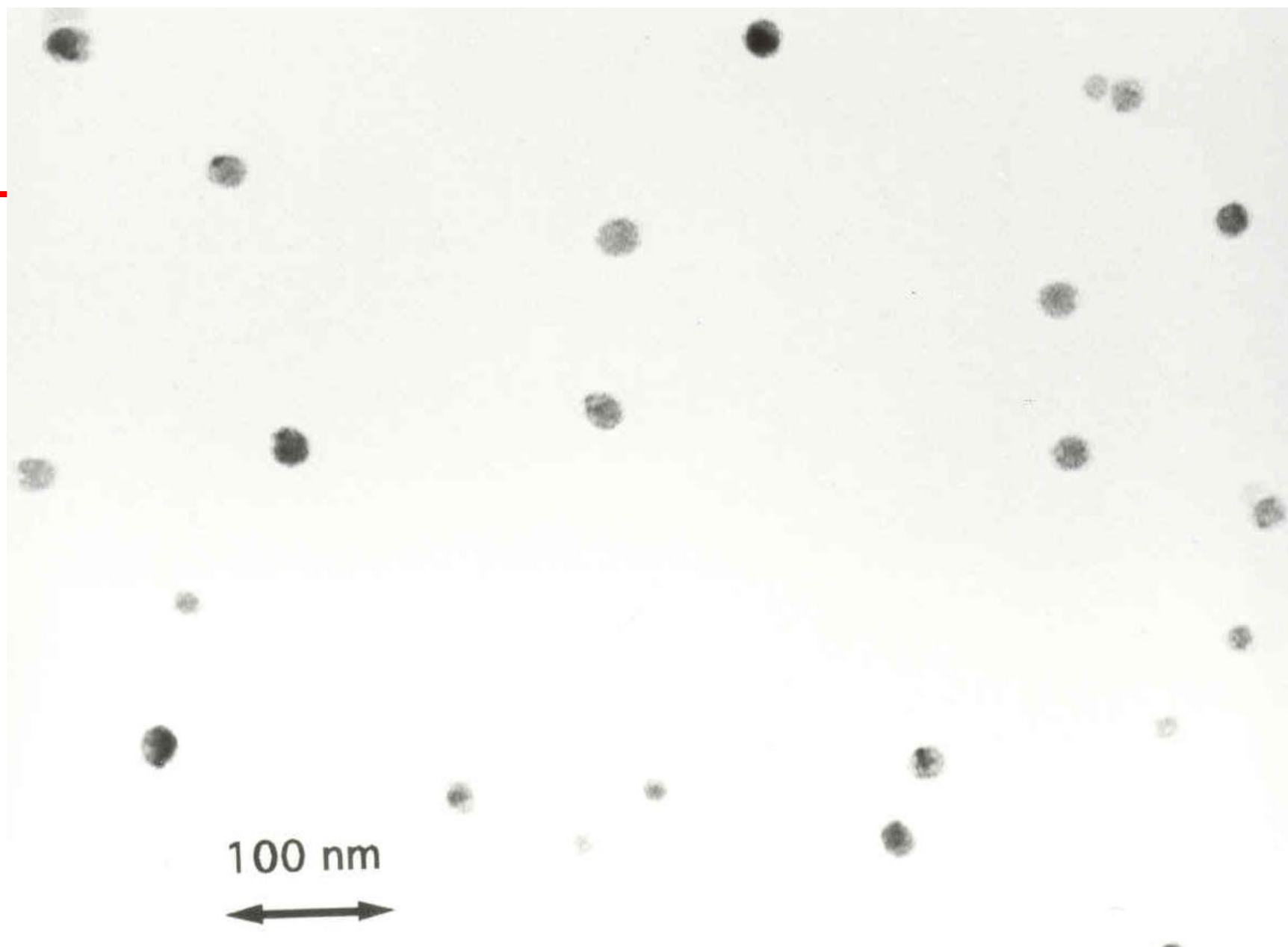
FFB Data for Pitt#8 Coal

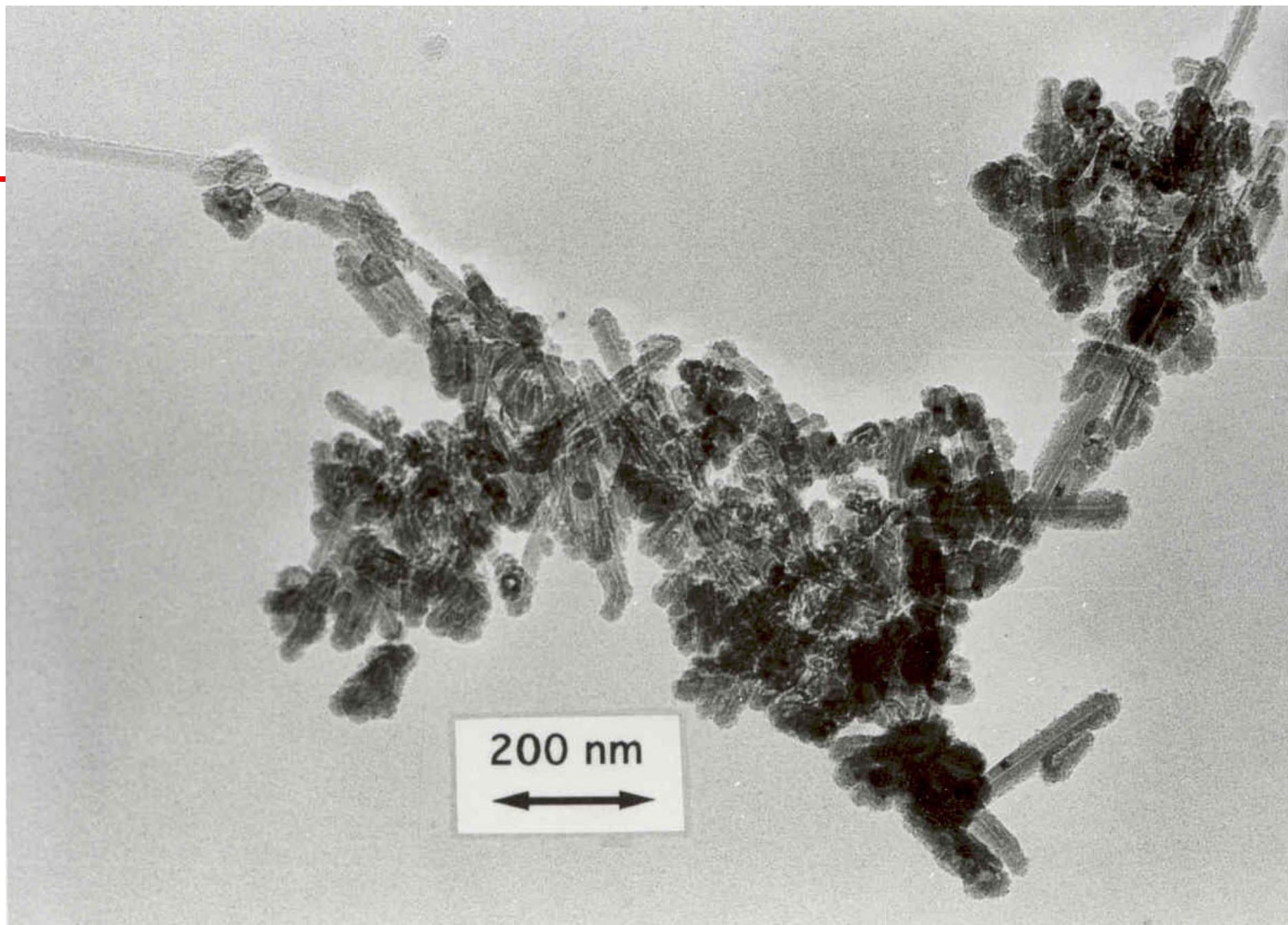
(Ma, 1996)

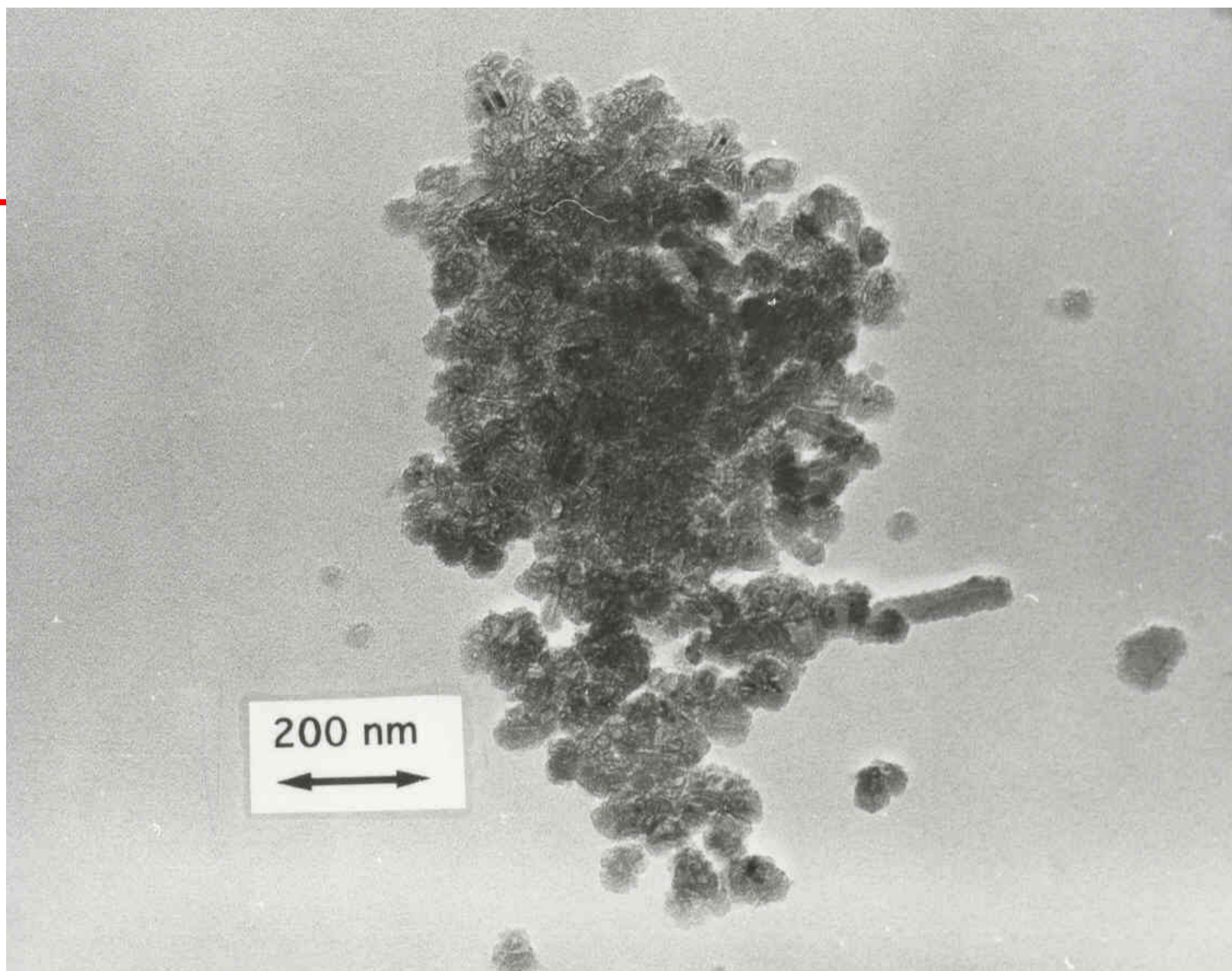


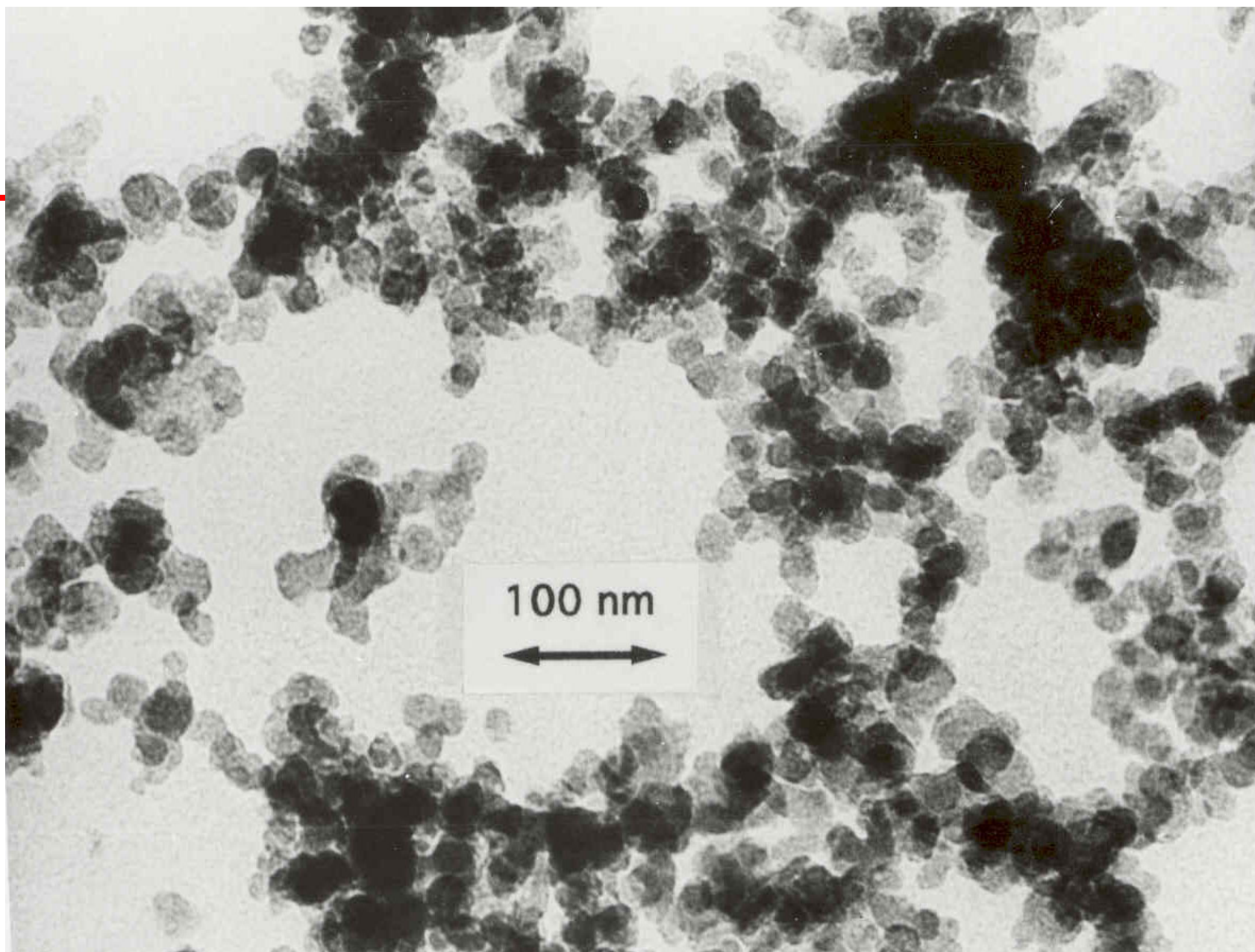
Thermophoretic Sampling System for FFB



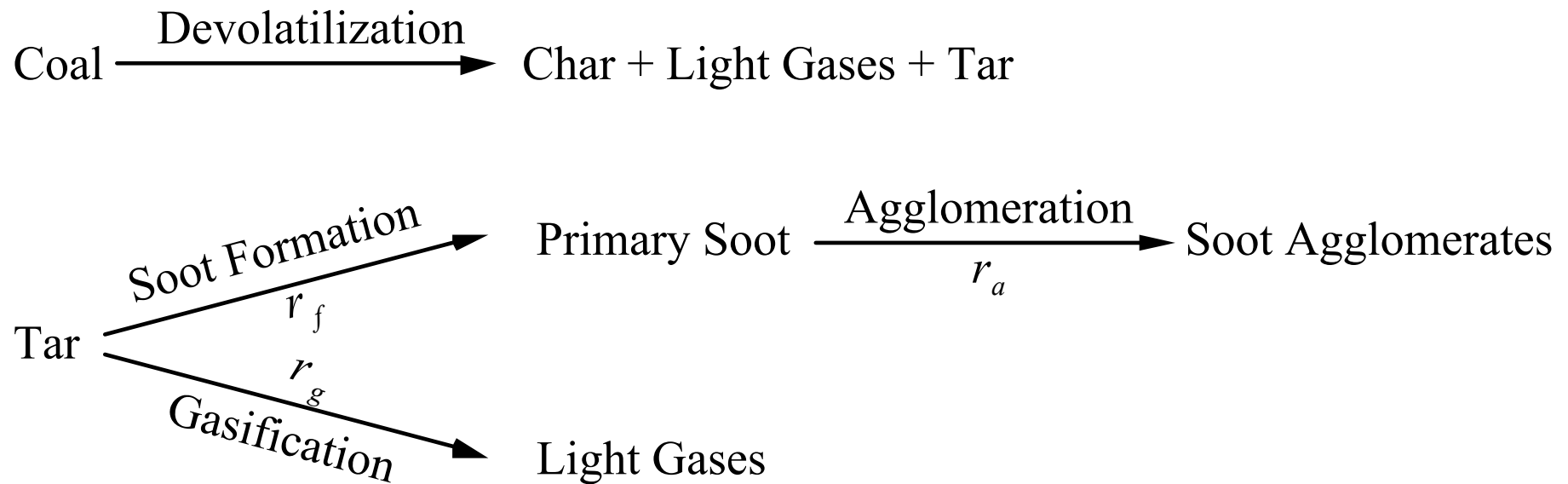








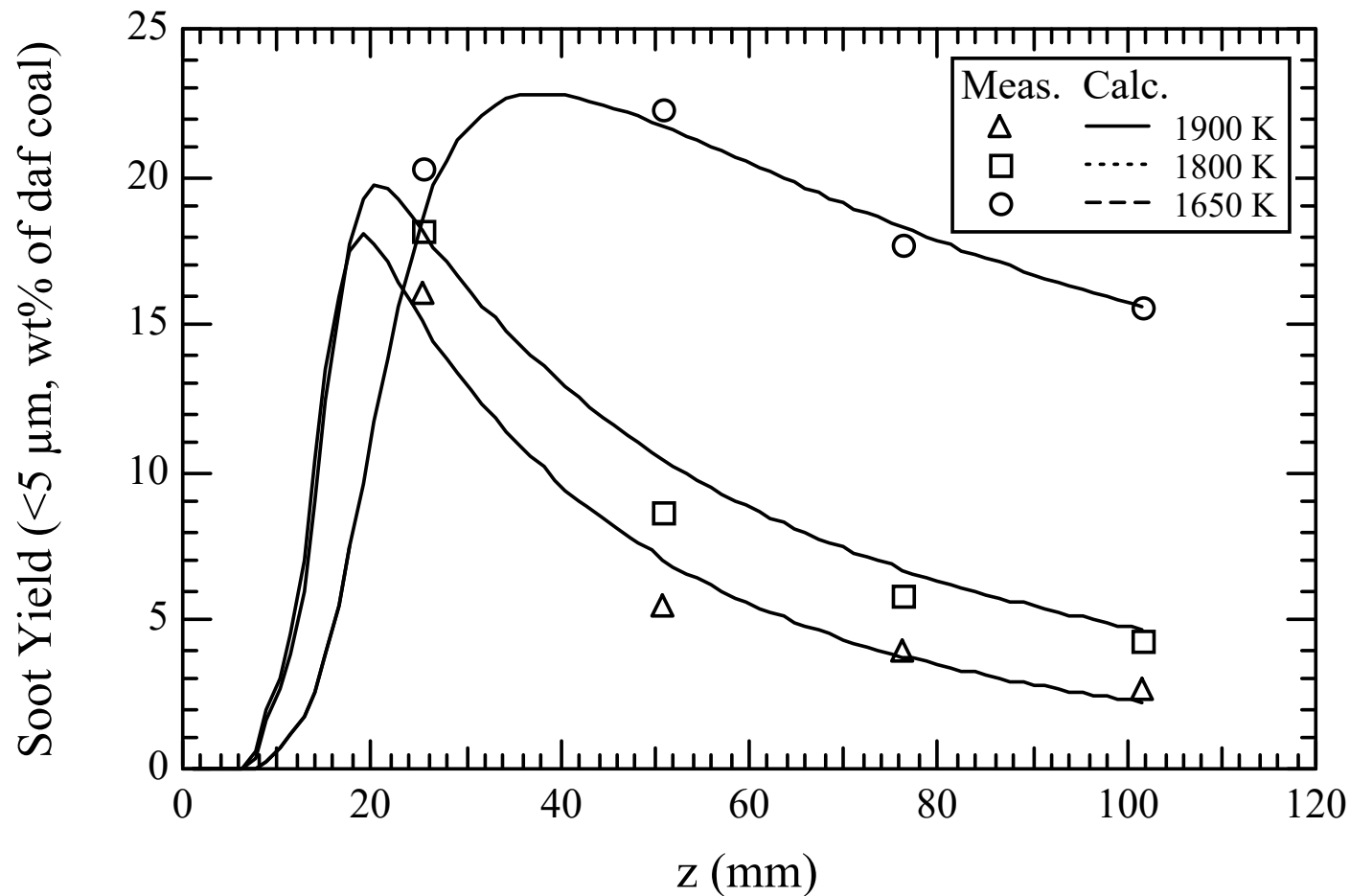
Presumed Pathway for Soot Formation (Ma, 1996)



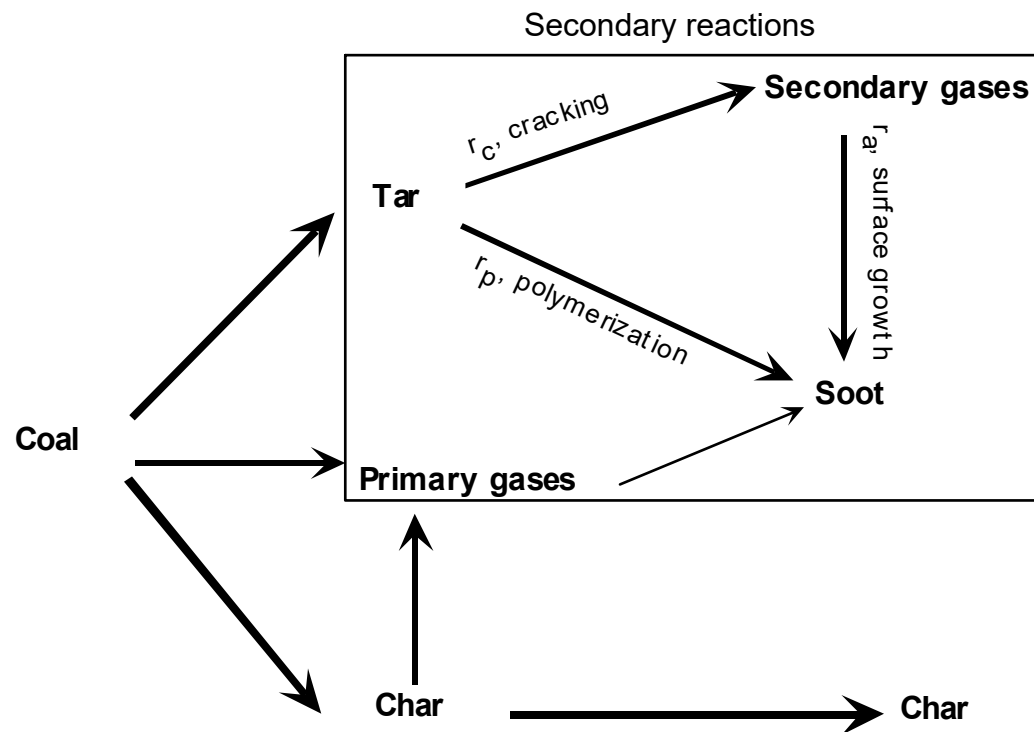
Derived Kinetic Coefficients

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



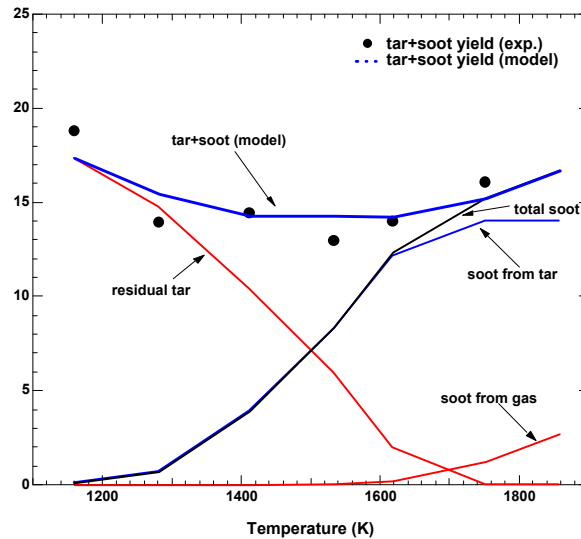
Proposed Mechanism for Secondary Pyrolysis (Zhang, 2001)



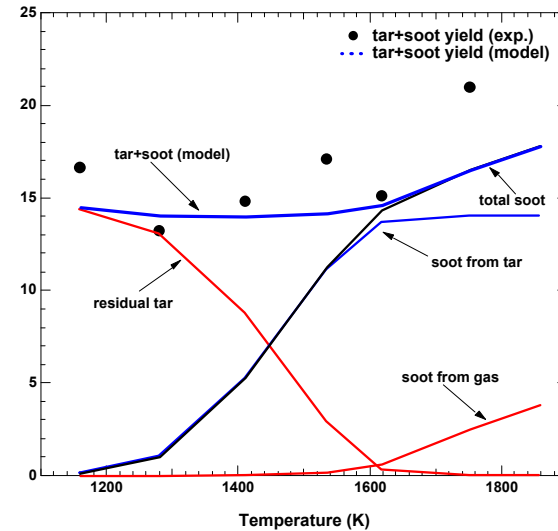
- Two competitive reactions are assumed for tar
 - Thermal cracking (dominant below 1300 K)
 - Polymerization (dominant above 1400 K)
- Fraction of primary tar that can be directly converted to soot is rank dependent
- Additional soot growth from hydrocarbons in gas

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

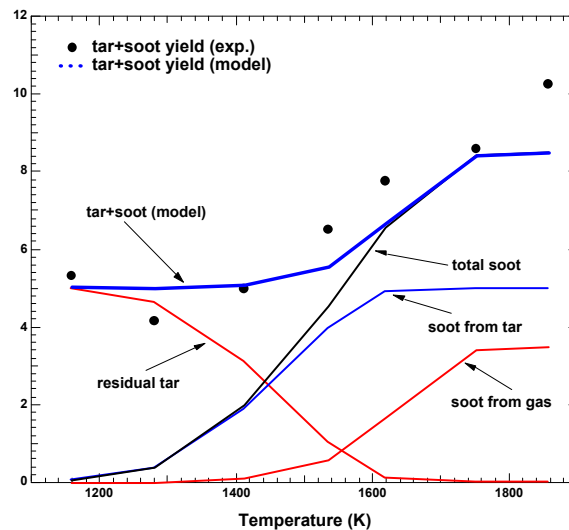
Illinois #6



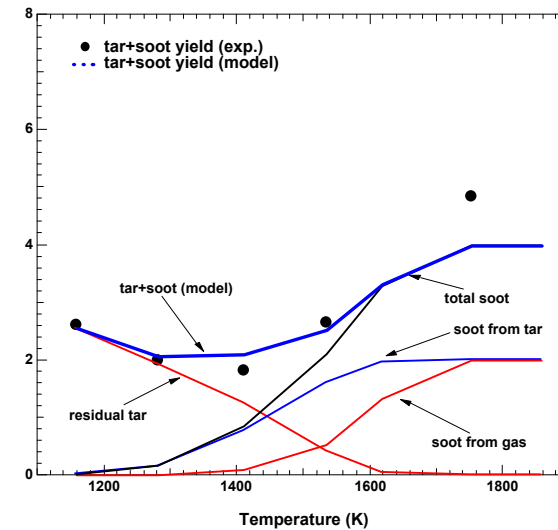
Utah



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

$$S_{Y_T} = \text{Formation}_T - \text{Formation}_C - \text{Gasification}_T - \text{Oxidation}_T$$

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

$$S_{Y_C} = \text{Formation}_C - \text{Oxidation}_C$$

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

$$S_{N_C} = \frac{N_a}{M_C C_{\min}} \text{Formation}_C - \text{Agglomeration}_N$$

Source Terms

$$Formation_T = SP_{tar}$$

$$Oxidation_T = \rho_g [c_T] [c_{O_2}] A_{OT} e^{-E_{OT} / RT}$$

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

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

$$Oxidation_C = SA_{v,C} \frac{p_{O_2}}{T^{1/2}} A_{OC} e^{-E_{OC} / RT}$$

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

A description of source term constants with literature sources.

<i>Term</i>	<i>A</i>	<i>E (kJ/g-mol)</i>	<i>Source</i>
Formation _T	N/A	N/A	Particle Phase Calculations
Oxidation _T	6.77x10 ⁵ (1/s)	52.3	Shaw et al. (1990)
Gasification _T	9.77x10 ¹⁰ (1/s)	286.9	Ma (1996)
Formation _C	5.02x10 ⁸ (1/s)	198.9	Ma (1996)
Oxidation _C	1.09x10 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 \rightarrow CO, followed by
 - $\text{CO} \rightarrow \text{CO}_2$
- Overall burning rates
 - Volatiles \rightarrow 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

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	$E^b (= RT_a)$
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

Simplified CH₄ oxidation

Simpler Mechanisms

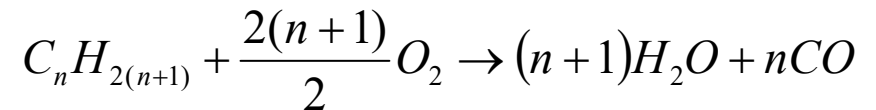
TABLE 7. Parameters for Two-Step Reaction Mechanism, Giving Best Agreement between Experimental and Computed Flammability Limits^a

Fuel	<i>A</i>	<i>E_a</i>	<i>a</i>	<i>b</i>
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 ₂ H ₆	1.3 × 10 ¹²	30.0	0.1	1.65
C ₃ H ₈	1.0 × 10 ¹²	30.0	0.1	1.65
C ₄ H ₁₀	8.8 × 10 ¹¹	30.0	0.15	1.6
C ₅ H ₁₂	7.8 × 10 ¹¹	30.0	0.25	1.5
C ₆ H ₁₄	7.0 × 10 ¹¹	30.0	0.25	1.5
C ₇ H ₁₆	6.3 × 10 ¹¹	30.0	0.25	1.5
C ₈ H ₁₈	5.7 × 10 ¹¹	30.0	0.25	1.5
C ₈ H ₁₈	9.6 × 10 ¹²	40.0	0.25	1.5
C ₉ H 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 ₃ OH	3.7 × 10 ¹²	30.0	0.25	1.5
C ₂ H ₅ OH	1.8 × 10 ¹²	30.0	0.15	1.6
C ₆ H ₆	2.4 × 10 ¹¹	30.0	-0.1	1.85
C ₇ H ₈	1.9 × 10 ¹¹	30.0	-0.1	1.85

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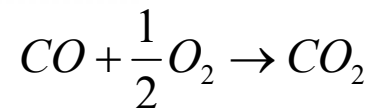
^aSame units as in Table 6.

Step One



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

Step Two



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

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

Volatiles Combustion

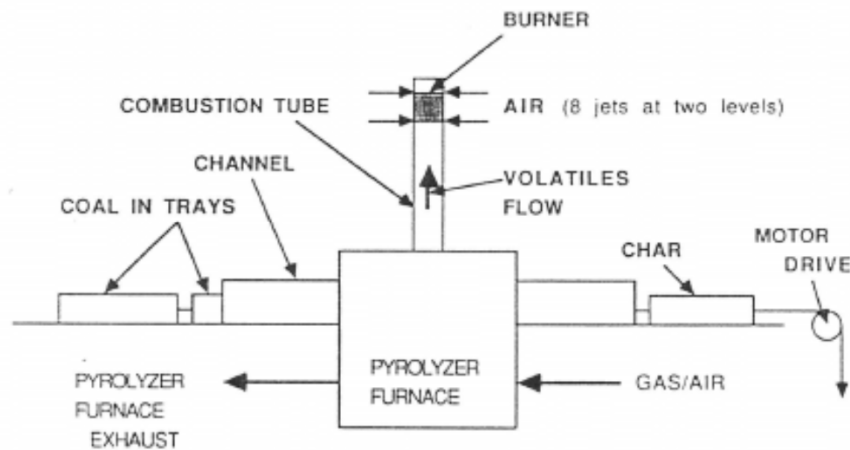


FIG. 1. Schematic of Pyrolyzer and Volatile Combustor. Trays carrying coal are linked, and pulled through gas heated pyrolyzer by motor drive. Volatiles are burned in a counter-vortex mixing section at top of combustion tube. [Note: Pyrolyzer is a muffle furnace so that pyrolyzer exhaust is separate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

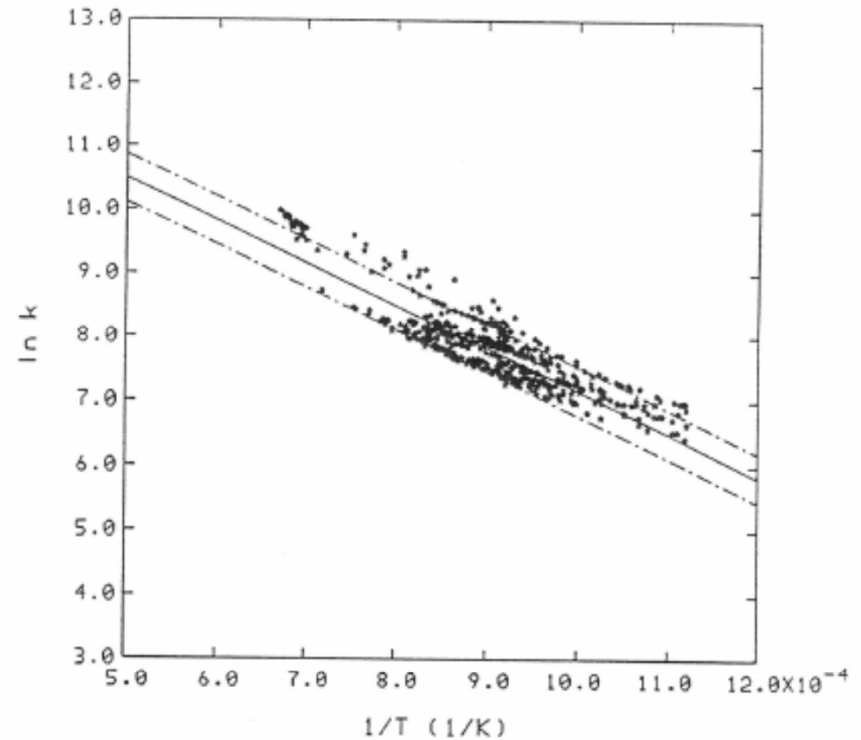


FIG. 4. Arrhenius plot of experimentally determined values of rate constant for combustion of volatiles from 14 coals. Solid line is the best linear fit and the two dotted lines give the range determined by $2 \times$ (std. deviation). Total number of points: 541

Light Gas Combustion

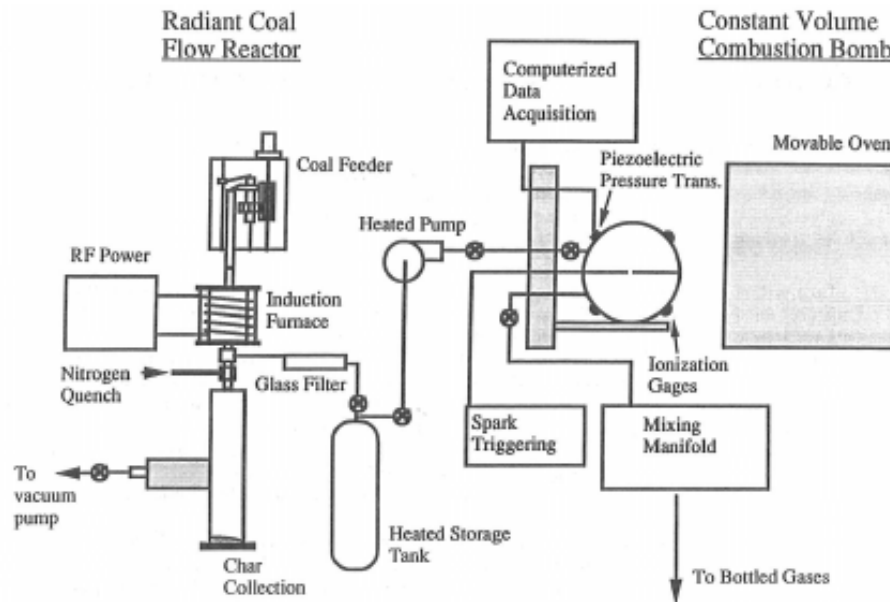


FIG. 1. Schematic of the radiant coal pyrolyzer, the heated handling system for volatiles, and the constant-volume combustion bomb.

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

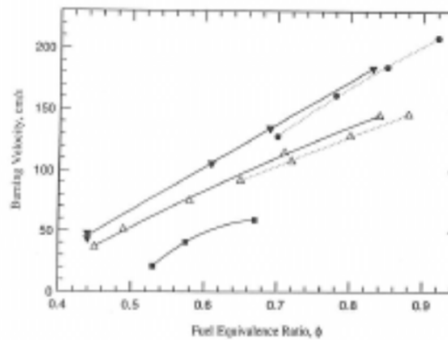


FIG. 3. Laminar burning velocities of the non-condensable fuel mixtures from Ill. #6 coal generated in the furnace at 1635 (■), 1715 (△), 1770 (●), and 1800 K (▼). In all cases values indicate the flame speed when the combustible mixture was compressed to atmospheric pressure and heated to about 430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

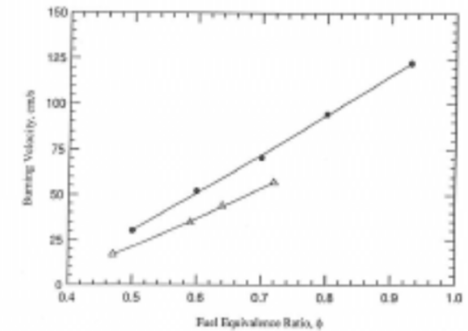


FIG. 4. Laminar burning velocities of the non-condensable fuel mixtures from Dietz subbituminous coal generated in the furnace at 1715 (△), and 1770 K (●). In all cases values indicate the flame speed when the combustible mixture was compressed to atmospheric pressure and heated to about 430 K. The molar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

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)

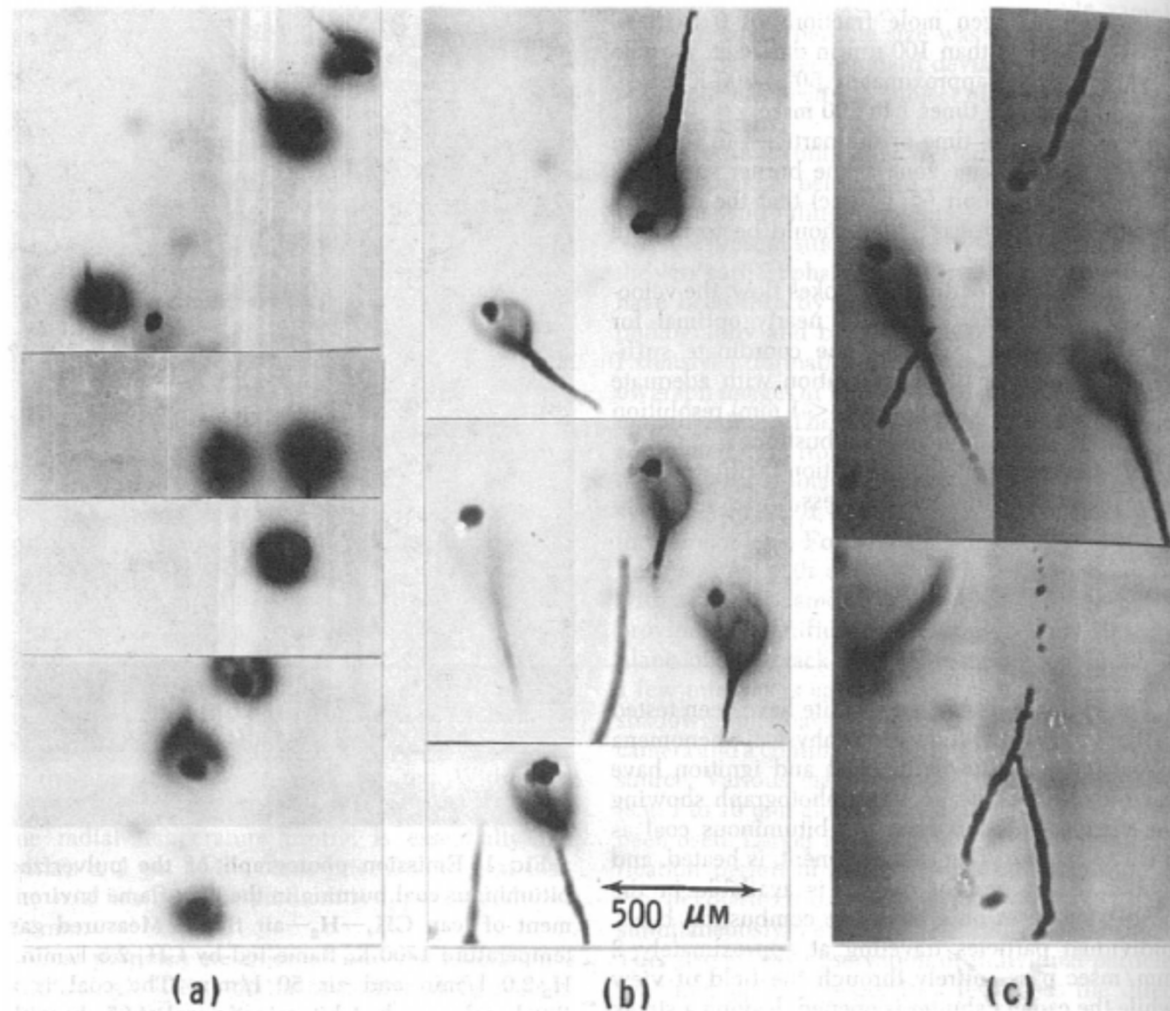
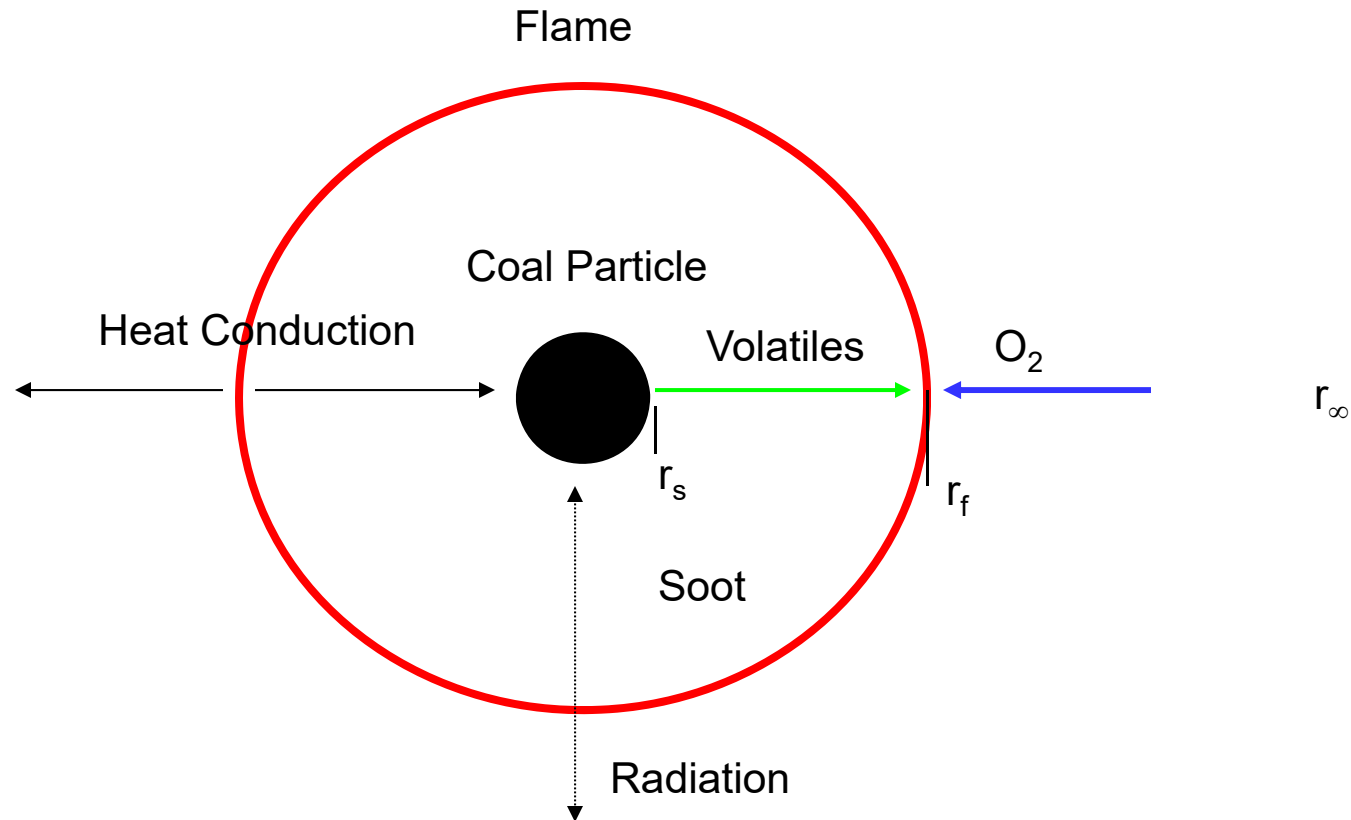


FIG. 2. Shadowgraphs showing bituminous coal particles during the early stages of combustion; (a) near ignition, (b) several msec after ignition, (c) approximately 10 msec after ignition; gas flow upward.

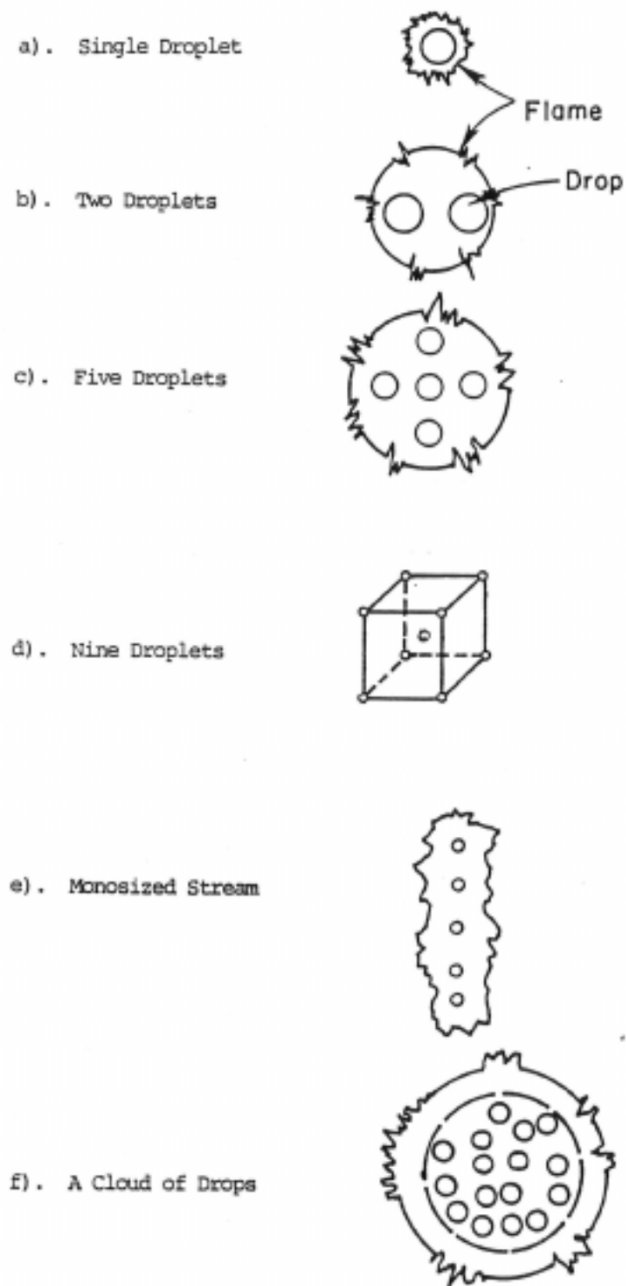
Principles of Single Particle Combustion



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?

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



Group Combustion Concepts

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)