Chemical Engineering 633

Combustion Processes

Soot Formation

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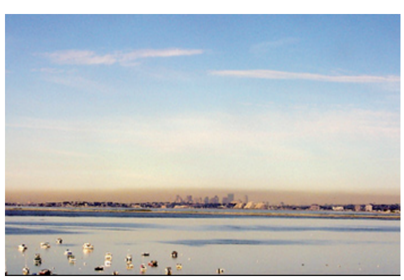
Outline

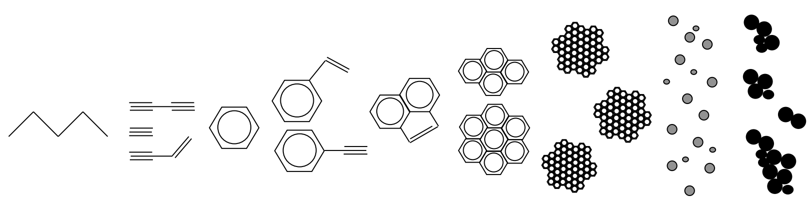
- Soot overview
  - Properties
  - Mechanisms
  - Fuel dependence
- Research results
  - Soot in unsteady flames
    - Laminar
    - 2D turbulent
    - 3D turbulent



Soot Overview

- Soot forms in nonpremixed and rich premixed flames, but is most important in nonpremixed flames.
- Soot is a small carbonacious particulate species
- Soot forms on the rich side of nonpremixed flames as gaseous fuels are pyrolysed.
- Soot particles consist of agglomerates of nominally round primary particles.
- Primary particle sizes are around 50 nm.
- Soot volume fractions are around 1-2 ppmv (up to 10-20).
- Soot forms at temperatures between 1300 and 1600 K.
- Formation mechanisms are highly complex and an important area of current research.
- Concentrations increase with pressure (engines)

Soot Growth Process



- Soot forms as a progression:
  - Small molecules → ring structures
  - These rings grow by acetelyne addition to form sheets
  - These sheets bend and collide to form primary particles
  - Primary particles agglomorate
  - Particle oxidation may or may not occur

Smoke Point

- Emperical measure of sooting propensity
- Laminar flames
- Increase flow rate until smoke escapes flame tip
  - Recall flame length depends on flow rate alone.

Fuel		$\dot{m}_{sp}$ (mg/s)	$f_{v,m} \times 10^6$	Y_s (%)
Acetylene	C_2H_2	0.51	15.3	23
Ethylene	C_2H_4	3.84	5.9	12
Propylene	C_3H_6	1.12	10.0	16
Propane	C_3H_8	7.87	3.7	9
Butane	C_4H_{10}	7.00	4.2	10
Cyclohexane	C_6H_{12}	2.23	7.8	19
n-Heptane	C_7H_{16}	5.13	4.6	12
Cyclooctane	C_8H_{16}	2.07	10.1	20
Isooctane	C_8H_{18}	1.57	9.9	27
Decalin	$C_{10}H_{18}$	0.77	15.4	31
4-Methylcyclohexene	C_7H_{12}	1.00	13.3	22
1-Octene	C_8H_{16}	1.73	9.2	25
1-Decene	$C_{10}H_{20}$	1.77	9.9	27
1-Hexadecene	$C_{16}H_{32}$	1.93	9.2	22
1-Heptyne	C_7H_{12}	0.65	14.7	30
1-Decyne	$C_{10}H_{18}$	0.80	14.7	30
Toluene	C_7H_8	0.27	19.1	38
Styrene	C_8H_8	0.22	17.9	40
o-Xylene	C_8H_{10}	0.28	20.0	37
1-Phenyl-1-propyne	C_9H_8	0.15	24.8	42
Indene	C_9H_8	0.18	20.5	33
n-Butylbenzene	$C_{10}H_{14}$	0.27	14.5	29
1-Methylnaphthalene	$C_{11}H_{10}$	0.17	22.1	41

Soot Mechanisms

- Many mechanisms of varying complexity exist:
  - Emperical mechanisms (Correlate directly to fuel or mixture fraction)
  - Semi-empirical mechanisms (Assume global steps for important processes)
    - Leung and Lindstead
  - Detailed mechanisms (Attempt to directly model the detailed chemistry)
    - HACA mechanism
- Four-step process
  1. Nucleation: **$C_2H_2 \rightarrow 2C(s) + H_2$**
  2. Growth: **$C_n(s) + C_2H_2 \rightarrow C_{n+2}(s) + H_2$**
  3. Oxidation: **$C(s) + 1/2\ O_2 \rightarrow CO$**
  4. Coagulation: **$C_n(s) + C_n(s) \rightarrow C_{2n}(s)$**
- The first three use common (global) reaction rates, and the last is written in terms of particle collision theories.
- Soot is treated as a particle phase with source/sink coupling to the gas phase.

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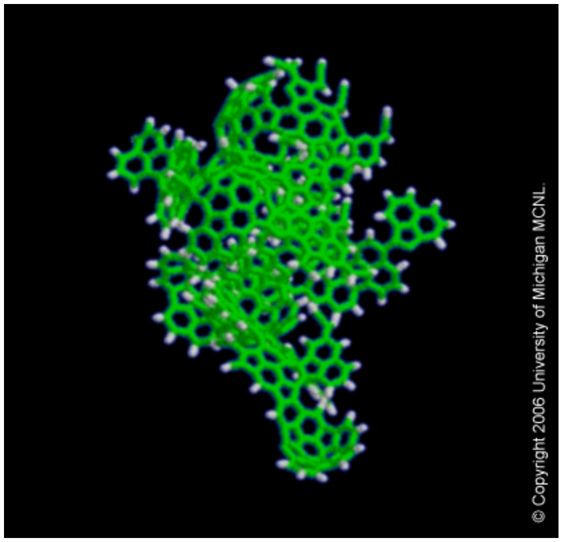

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Transport

- Soot transport via
  - Convection
  - Diffusion
  - Thermophoresis
- Soot diffusivity varies inversely with square of particle diameter.
- Le = 9500 for 1 ppmv, $n=1\times10^{17}\ m^{-3}$, 1500 K.
- Thermophoresis dominates diffusion and acts to push soot away from a flame.

$$\frac{\partial(\rho Y_s)}{\partial t} = -\nabla\cdot(\rho Y_s \boldsymbol{v}) - \nabla\cdot \boldsymbol{j}_s + S_{Y_s}$$

$$j_M = -\rho D_{p1}\nabla\left(\frac{1}{Le_s}\frac{M}{\rho}\right) - 0.556 M\frac{\nu}{T}\nabla T,$$

$$D_{p,k} \propto k^{-2/3} \qquad D_{p,k} = D_{p,1}k^{-2/3}$$

$$Le_s = k^{2/3} = (\rho Y_s/n m_1)^{2/3}$$

Here, M is either ρY_s or number density (#/m^3)

Particle Size Distribution

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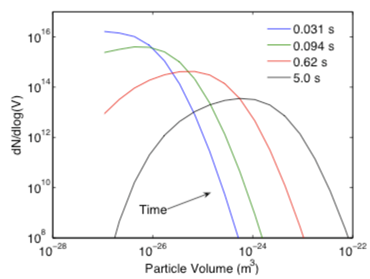
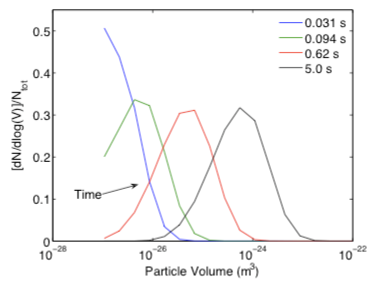
- To treat soot, one needs:
  - Detailed gas mechanism
  - Soot chemical mechanism
  - Description of soot particle size distribution.
- How to represent the PSD?
  - Direct representation
  - Sectional methods
  - Method of moments
- Assume spherical particles
- Particles increase in size and decrease in number with time, but reach a so-called self preserving size distribution.





Method of Moments

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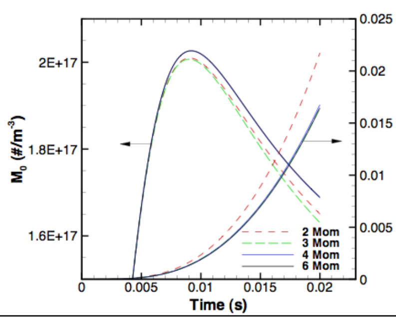
- Detailed and sectional models are expensive
- Instead, solve for statistical moments of the PSD.
- Closure problems arise.
  - Fractional moments.
  - Other unclosed moments
- Closure approaches
  - Interpolation/extrapolation
  - Assumed shape distributions
    - Monodispersed: 2 Moments
    - Lognormal: 3 Moments
  - Quadrature (QMOM, DQMOM)

$$\frac{\partial n_j}{\partial t} + \nabla \cdot (\vec{v} n_j) = \nabla \cdot \left(0.556 \nu n_j \frac{\nabla T}{T}\right) + \dot{n}_j$$

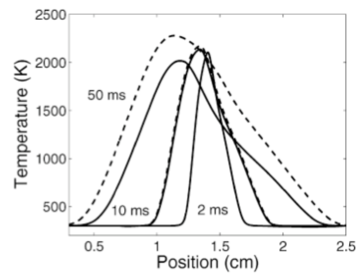
$$M_r = \sum_{j=1}^{\infty} j^r n_j, \quad r = 0, \infty$$

$$\frac{\partial M_r}{\partial t} + \nabla \cdot (\vec{v} M_r) = \nabla \cdot \left(0.556 \nu M_r \frac{\nabla T}{T}\right) + S_{M_r}$$

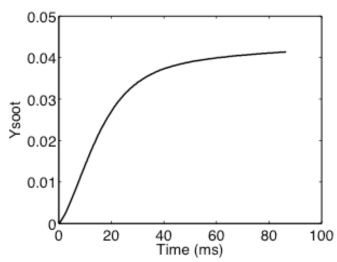


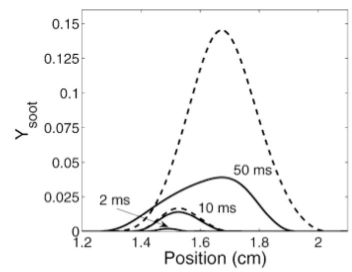
1-D Soot Formation

- Consider a relaxing diffusion flame
  - Just give a tanh mixture fraction profile and initialized with a burning flame solution.
- Watch evolution of soot in time.
- Soot timescale is O(30 ms).
- Similar for radiation.
- Recall χ_q = 1907 s^{-1}



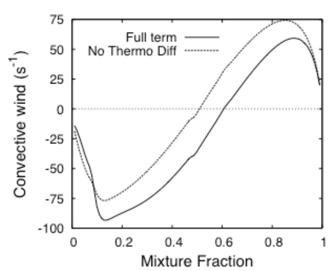
Dashed lines = no radiation

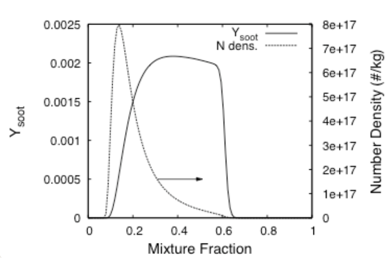


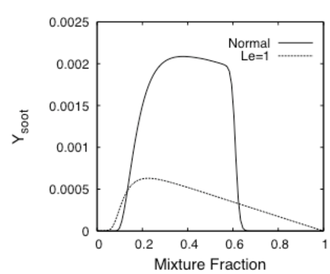


Soot Flamelets

- Solve the flamelet equations for soot with proper transport.
- Stagnation plane (SP) at mixf=0.5
- Soot convected to SP, and pushed past by thermophoresis.
- Normal gaseous diffusion is qualitatively different.

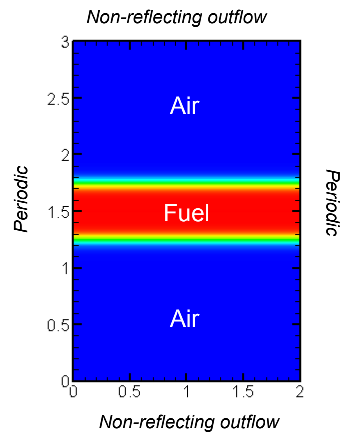






2D Decaying Turbulence Simulation

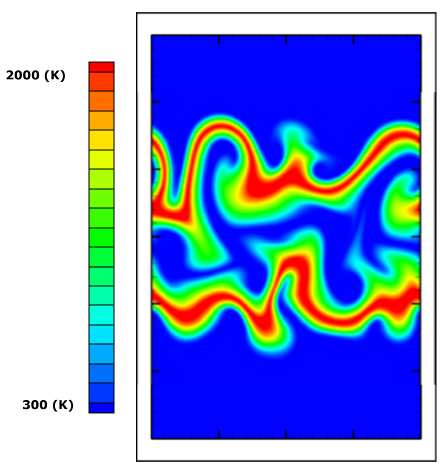
- 2D, open domain
- Nonpremixed, pure ethylene stripe surrounded by air
  - 300 K, 1 atm
- Periodic and nonreflecting outflow BCs
- Flame initialized with burning laminar flamelet solution
- Overlay velocity spectrum
  - Decays
  - Initially filtered near boundary
- Initial velocity field wrinkles flame



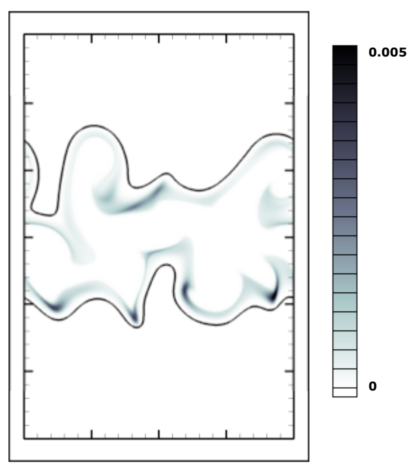
Parameter		Parameter		Timescale (ms)	
L_x (cm)	2	δ_ξ (cm)	0.11	Turbulence	1.25
L_y (cm)	3	# cells	960,000	Soot reaction	10
L_{11} (cm)	0.188	# timesteps	325,000	Soot diffusion	6
u' (cm/s)	150	Run time (ms)	5	Flame dissipation (ms)	13
H_ξ (cm)	0.5	Sim. Cost. (cpuh)	32,500		

2D Temperature and Soot

Temperature

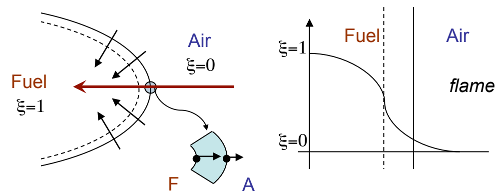


Soot Mass Fraction



Flame Curvature and Motion

- Curvature complicates flame dynamics
  - Curvature works with or against normal diffusion
- Quantify with isosurface velocity relative to flow.
  - Stoichiometric mixture fraction

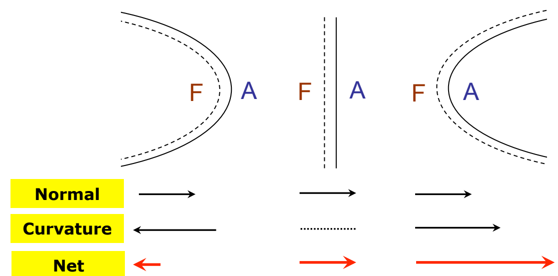


$$v_\xi = -\frac{D_\xi \nabla^2 \xi}{|\nabla \xi|}$$

$$v_\xi = -D_\xi \kappa - \frac{D_\xi}{|\nabla \xi|}\frac{\partial^2 \xi}{\partial \eta^2}$$

$$\kappa = \nabla \cdot \vec{n}$$

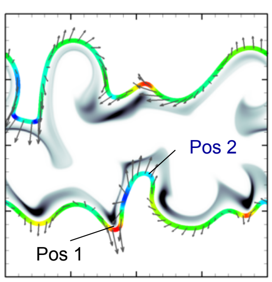
$$v_\xi = -D_\xi \kappa - \frac{D_\xi}{2}\frac{\partial}{\partial \eta}\ln(\rho^2 D_\xi \chi)$$

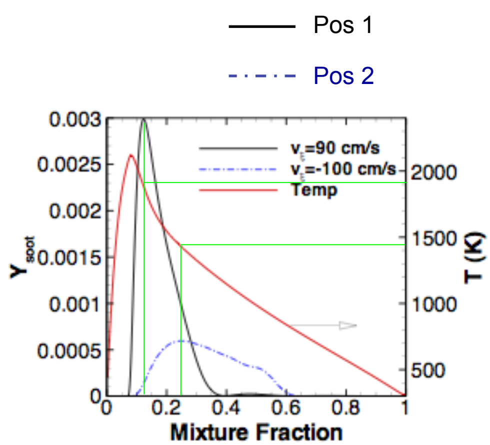


*Gibson, Phys. Of Fluids 11 (11): 2305-2315, 1968,
*Pope, Int. J. Engng. Sci. 26 (5): 445-469, 1988

2 Flame Normals - Soot

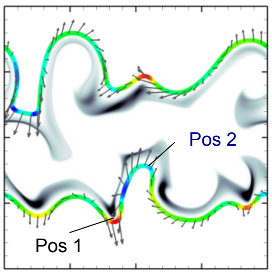
- Examine flame normal profiles
- 2 positions, nearly equal χ
- Soot shifted towards flame for $+v_\xi$
  - Higher T, rates
- Low T scatter suggests thermal focusing is not responsible for increased soot.

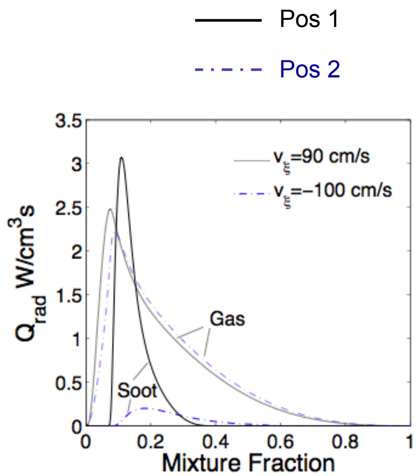




2 Flame Normals - Radiation

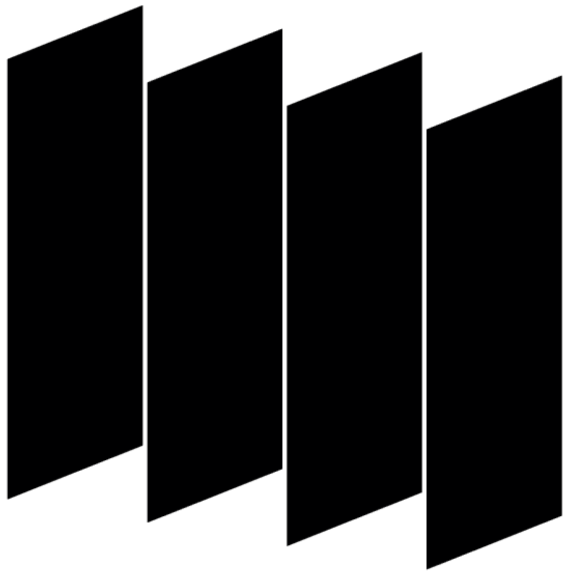
- The position of the soot relative to the flame strongly impacts radiation rates.
- Soot radiation at 90 cm/s is 10 times that at position -100 cm/s
- Overall radiation at position 90 cm/s is twice that at -100 cm/s





3D Jet with Soot

3D Jet with Soot



3D Jet Temperature