Soot Formation and Oxidation at Elevated Pressures

Med Colket

Workshop on Techniques for High Pressure Combustion
Argonne National Laboratories, Chicago, Ill
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Background

- Global Warming:
  - Studies suggesting that soot and related particulates contribute significantly to global warming
  - Changes in fuels has large 1st order effect on particulate emissions
- Health:
  - Increased understanding of health risks associated with ultrafine particles
- Regulation:
  - Enactment of EPA PM2.5 ambient standards (mass of particles below 2.5 microns)
  - Concern that local site implementation plans may limit commercial airline traffic or introduction of new engines/planes
- Durability:
  - Impact of soot radiation on combustor liners and related hardware
  - Soot deposition on surfaces
- Challenges:
  - Predicting or measuring time- and spatially-dependent soot fields (even at atmospheric pressure factor of two is best achievable)
Objectives and Outline

Objectives:
- Review challenges in modeling and measurements of soot at elevated pressures

Outline:
- Observations of soot formation in combustors
  - Laboratory
  - Gas Turbine Combustor
  - Diesel spray
- Soot fundamentals
- Modeling
  - Approach
  - Simulation of pressure dependence
  - Simulation soot evolution in RQL combustor
- Conclusions/Recommendations
Images and LII Signals from Coflow Diffusion Flames

CoFlow C2H4 diluted flame
Courtesy of Bob Santoro, PSU

Photographs

Laser Induced Incandescence

Computed soot volume fractions ($f_v$) with height

Soot Formation and Oxidation
Images and LII Signals from Coflow Diffusion Flames

CoFlow C2H4 diluted flame with 5% m-xylene
Courtesy of Bob Santoro, PSU

Photographs
Temperature and OH profiles also available

Laser Induced Incandescence

PLIF images of large PAH

Soot Formation and Oxidation
Soot in Turbulent Surrogate JP-8 Jet Flame (1 atm)

Instantaneous, mean, and rms soot volume fractions ($f_v$) measured by LII imaging. The mean and rms statistics are computed from 1000 instantaneous images taken at each height.

Courtesy of Shaddix and Pickett, Sandia Re no. ~ 20,000

Photograph of flame base

Soot Formation and Oxidation
Soot, OH, PAH in turbulent ‘JP-8’ jet (Re ~ 20,000)

LIF from OH• and PAH (in interior regions, particularly low in flame)

Soot LII, with boundaries of OH• in white

Courtesy of Chris Shaddix and Lyle Pickett, Sandia

1 atm

Soot Formation and Oxidation
High speed video of Soot Formation (1 atm) - lean

Gas Turbine combustion
(Courtesy of M. Roquemore, AFRL)
Video of soot formation at 10 atmospheres – less lean

Gas Turbine combustor
Courtesy of M. Roquemore, AFRL – 20,000 FPS
TEM photographs of soot from gas turbine (80% power)

Gas Turbine combustor
Courtesy of Randy Vander Wal, PSU

[Soot Formation and Oxidation]
TEM photographs of soot from gas turbine (80% power)
Soot Formation Following Ignition (at 40 atmospheres)

Ignition and soot formation in diesel fuel spray (JP-8)
Courtesy of Lyle Pickett and Chris Shaddix (Sandia)
Soot sampling from sprays within high-temperature, high-pressure combustion vessel

TEM probe within the combustion vessel

TEM grid:

- 3 mm diameter
- TEM grid: copper mesh covered by an amorphous carbon film

TEM grid held within the probe to protect it from excessive heating

Restrictive passage quenches reaction and protects the TEM grid.

Soot-laden gas skims past the probe, enters through a 1-mm diameter hole, and deposits on the TEM grid.

From Kook and Pickett, PROCI, 33, 2011

TEM image of soot particles

Soot Formation and Oxidation

United Technologies Research Center
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‘Sooting’ PSR Based upon established particle physics

Processes all occur simultaneously in well-mixed systems (stirred reactor)

Calcote 1982 – described by Wang 2003

aggregation

mass growth

soot inception

PAH formation

flame

burner

CO, H₂, CO₂, H₂O, C₂H₂

Soot Formation and Oxidation
Sooting NETPSR code includes detailed treatment of particle inception, surface growth, surface oxidation, aerosol particle dynamics (sectional) to predict particle size distribution through reactor network (simulated combustor)
Gas-Phase Kinetics

Combustor*

- Detailed reaction mechanism from Babushok and Tsang (2004) – heptane
- Includes PAH formation, truncated above 202 amu
- Total mechanism: ~240 species and ~1500 reactions
Soot Kinetics

*Inception and Growth based upon prior work*


\[
\frac{dS_1}{dt} = k[C_{16}H_{10}]^2
\]

Surface Growth: Mass growth onto any particle is assumed be proportional to particle surface area, after Colket and Hall, 1994 (MODFW)

\[
\begin{align*}
H + C(s) & \rightleftharpoons \dot{C}(s) + H2 \\
H + \dot{C}(s) & \rightleftharpoons C(s) \\
\dot{C}(s) & \rightleftharpoons C2H2 + \text{products} \\
C2H2 + \dot{C}(s) & \rightleftharpoons C(s)CHCH \\
C(s)CHCH & \rightleftharpoons C'(s) + H
\end{align*}
\]
Soot Kinetics

Based on OH, O₂ and available particle surface area


\[ R_{OH} = (0.13) N_{OH} \sqrt{\frac{R_{gas} T}{2\pi W_{OH}}} \frac{12}{N_A} \text{ gm/sec/cm}^2 \]

Oxidation by O₂ – Nagle and Strickland-Constable (1963)

\[ R_{O_2} = 12 \left( \frac{K_a P_{O_2} \chi'}{1 + K_z P_{O_2}} \right) + K_b P_{O_2} \left( 1 - \chi' \right) \text{ gm/sec/cm}^2 \]
Sectional Modeling of Soot Growth in PSR Code

Discrete particle size (logarithmic scale)

Surface growth and coalescence* – based on free molecular form (Kn > 1)

* Follows development by Gelbard and coworkers (see Hall, et al, 1997)
Simulation of Pressure Dependence

Pressure dependence decreases rapidly for counter-flow diffusion flames

Calculations by M. Smooke

\[ f_v \sim P^n \]

- High Pres
- Old Model

P in atm

Soot Formation and Oxidation
Modeling Approach (single Perfectly Stirred Reactor)

Modify Sandia PSR (CHEMKIN) model by adding sectional soot equations

Conservation equations modified to add sectional equations* to model soot particles, with source terms in species equations to account for scrubbing

\[
\begin{align*}
\dot{m}(Y_k - Y^*_k) - \omega^s_k W_k V &= 0, \quad k = 1, 2, \ldots, K \\
\sum_{k=1}^{K} (Y_k h_k - Y^*_k h^*_k) + Q &= 0 \\
\dot{m}(Y_k - Y^*_k) - (\omega^s_k + \omega^s_k) W_k V &= 0, \quad k = 1, 2, \ldots, K \\
\sum_{k=K+1}^{K+M} (Y_k h_k - Y^*_k h^*_k) + Q &= 0
\end{align*}
\]

* Sectional equations allow predictions of particle size distributions. Size classes divided by logarithmic scale.
Idealized Rich-Quench-Lean (RQL) Combustor

Fuel injector/swirler

Full set of reaction kinetics and soot equations solved for each reactor volume

Network Reactor Simulation

Fuel-rich front end Quench Zone Lean, Burn-Out Zone

Fuel-spray shear layer Recirculation zones Quench zones Burn-out zones

Reactor flux, volumes, back-mixing, etc. determined by geometry, flow splits, and empirical tuning to NOx, CO emissions
Simulation Results

General characteristics of soot formation, growth and oxidation

- Plotted as function of local equivalence ratio (phi)

Computations of typical particle size distribution and its evolution through combustor

- Fuel-shear layer
- Outer recirculation zone
- Quench zone
- Burn-out zone

Burner conditions:
- Rig simulated Take-off
- T3 = 811K (1000F)
- P3: 16.3 atm
**General Formation Characteristics**

**Soot Formed at phi > 1.5, oxidized 0.7<phi<1.5 (by OH)**

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**Dependence of Soot Processes on Equivalence Ratio**

- Oxidation
- Growth dominates
- Oxidation quenched
- Growth slow

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**Rates**

- Red: S1 (growth)
- Blue: S2 (oxid by O2)
- Green: S3 (oxid by OH)

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**Fuel Lean** → **Phi** → **Fuel Rich**

(Fuel/Air Equivalence Ratio)

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Soot Formation and Oxidation
Particle Formation in Fuel Spray Shear Layer

Number density increase dramatically with position

Particle Evolution in Fuel Spray Shear Layer

Particle Number Density

Diameter (nm)

Particle Number Density (#/cc)

TAUs ~ 0.3 millisec

(phi)

1 (0.95)

2 (1.50)

3 (1.87)

4 (1.91)

5 (2.08)
Particle Formation in Outer Recirculation Zone

*Number density saturates due to long residence times* (phi)

Particle Number Density (#/cc)

Diameter (nm)

TAUs ~ 0.7-1.7 msec

Soot Formation and Oxidation
Particle Evolution Through Quench Zone

Particles first increase and then decrease: fastest changes in small particles

Particle Number Density (#/cc)

TAUs ~ 0.02-0.05 msec

Diameter (nm)

Soot Formation and Oxidation
Particle Oxidation in Burn-Out Zone

**Oxidation reduces number density and size (and mass)**

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**Particle Oxidation in Burn-Out Zone**

- **Particle Number Density** (#/cc)
  - 1.E+05
  - 1.E+06
  - 1.E+07
  - 1.E+08
  - 1.E+09

- **Diameter (nm)**
  - 0
  - 50
  - 100

- **TAUs ~ 0.2 msec**

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**Research Center**

Soot Formation and Oxidation
Simulations of Soot at Combustor Exit Plane

Peak soot mass fractions decreases by 4 orders of magnitude from front end (of RQL burner) to exit plane.

Number density decreases by two orders of magnitude

Numbers in agreement with experimental data (~30% mass and size)

Reduced-order soot model employed

© Courtesy of PW
Summary/Conclusions

- Formation occurs at phi>1.5, and oxidizes at 0.7<phi<1.5
- Particle evolution depicts rapid growth in #/cc, size and mass in fuel-rich front end
- Particle formation saturates in long residence time, fuel-rich recirculation zones
- Formation continues into leading edge of quench zone
- Particle oxidation limited by quenching to below phi of 0.7
Recommendations: Research Needs

- Spray and fuel distribution is critical
- Validated detailed reaction models for fuels of interest
  - Particularly for fuel-rich chemistry, PAH formation
- Reduced chemistry with soot precursor modeling
- Simultaneous information on T, [OH], f/a, soot mass and diameters (ideally PSD) – in heavy soot laden flows
- Optical thickness
- CFD models that can incorporate detailed reaction chemistry, including PAH, soot equations, mass scrubbing, PSD, oxidation, and radiation effects
- Probe sampling effects (loss of small particles to walls)
- Soot physics: inception (liquid-like particles), agglomeration, PSD
- Fuel effects
THANK YOU!
Experiments were performed in an optically-accessible high-temperature/high-pressure combustion vessel.

**Operating Conditions**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Ambient Gas O₂</td>
<td>15%</td>
</tr>
<tr>
<td>Ambient Gas Temperature</td>
<td>1000 K</td>
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<tr>
<td>Ambient Gas Density</td>
<td>22.8 kg/m³</td>
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<tr>
<td>Ambient Gas Pressure</td>
<td>6.7 MPa</td>
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<tr>
<td>Injection Pressure</td>
<td>150 MPa</td>
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<tr>
<td>Injection Duration</td>
<td>7 ms</td>
</tr>
<tr>
<td>Fuels tested</td>
<td>WA, SR</td>
</tr>
</tbody>
</table>

**Fuels tested**: WA, SR

**Soot sampling probe**

- Integrating sphere
- Spherical Lens (f = 200 mm)
- HeNe laser (633 nm)
  - 1 mm diameter
  - 15 mW
- Divergence Aperture
- Exit Aperture

**Nd:YAG laser** (532 nm)
- 80 mm wide sheet
- 100 mJ per pulse

**Transmission Electron Microscope Grid**