Modeling Particulate Emissions

Med Colket

Technical Session 2C

Impact of Particulate Emissions from Gas Turbine Powered Aircraft

Partners in Environmental Technology Technical Symposium
November 29 – December 1, 2011
Atmospheric levels of PM2.5 particulate matter near airports are increased by solid carbonaceous soot and condensable gaseous species emitted by military and commercial gas turbine aircraft engines. Carbonaceous materials are formed in the main combustor at elevated pressures and temperatures due to nucleation, surface growth, coalescence, aggregation and oxidation. Condensable materials nucleate in the engine exhaust plume at lower temperatures and at ambient pressures, followed by mass growth, and vaporization. Such gases may also condense onto existing soot emissions collocated in the plume. This presentation will review models developed to describe the formation of these two types of particulates and will compare and contrast the physics/chemistry associated with these processes and their interrelationships. Complicating the understanding the physics of formation for both the solid and volatile particles are sampling artifacts. A discussion of such issues will also be discussed briefly.
MODELING OF PARTICULATE EMISSIONS

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Objectives and Outline

**Objectives:**
- Compare/contrast physical models/processes of gas turbine generated particulate emissions

**Outline:**
- Overview
- Contrast physical processes in particulate formation
- Soot Formation in combustors (non-volatile particulates)
  - Observations of soot formation in combustors
  - Physical/chemical models
  - Soot summary
- Volatile particulate formation
  - $\text{H}_2\text{O} + \text{H}_2\text{SO}_4/\text{SO}_3$
  - Hydrocarbons/oxygenates
- Extensions to volatile condensation on non-volatile particulates
- Summary
Aircraft Emissions - Produced by Combustion of Fuel and Air

Modeling Particulate Emissions

Combustion Products

- Carbon Dioxide - CO2
- Water Vapor - H2O
- Nitrogen Oxides - NOx
- Carbon Monoxide - CO
- Unburned Hydrocarbons - UBHC
- Smoke
- Particulates
- Hazardous Air Pollutants- HAPs
Impact Of Aircraft Emissions is Altitude Dependent

*More than a local concern*

**Ozone Layer Depletion - Not an Immediate Concern**
- \(H_2O\)
- \(NO_x\)  
  Ozone Depletion (ice formation)  
  \(33,000-58,000\) ft

**Global Warming - An Emerging Concern**
- Traffic Growth
  - \(CO_2^*\)
  - \(NO_x\)  
  - \(O_3^*\)
  - \(NO_x\) Reduces CH\(_4\)
  - \(H_2O\) Vapor*
  - Particulates
  - \(SO_x\)

  Cloud Formation

  - Global Warming
  - Troposphere

* - Greenhouse Gases

**Local Air Quality - A Continuing Concern**
- Traffic Growth
  - \(NO_x\)
  - UHC
  - CO
  - Particulates
  - HAPs

  Ozone & Smog Formation

  Local Air Quality

  Health Effects

  Ground Level

Modeling Particulate Emissions
Complexities of Particulate Evolution

Combustor (chemical processor)

Turbine (quench)

Smoke No. and emissions of carbonaceous particulates (PM-2.5)

Near field (quench, nucleation)

Far field (absorption, Condensation, vaporization)

Plume evolution and growth

Upper and lower atmosphere (absorption, evaporation, chemistry)

Modeling Particulate Emissions

- Fuel → PAH, soot (f_v, d)
- Fuel S → SO, SO_2
- SO_2 → SO_3
- NOx ??
- Soot PAH → condensed particulates
- Soot → CCN
- SootPAH => condensed particulates
- HC droplets (+ oxygenates)
- H_2O
- SO → SO_3
- SO_3 → H_2SO_4
- Mixed volatile/non-volatile particulates
- Mixed particulates
- Volatile particulates
- Unburned HCs
- Radiation budget, pollution
### Formation Processes for Various Particulates
*Arise from Multiple Chemicals, Locations and Conditions*

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<thead>
<tr>
<th>Classification</th>
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Formation Processes for Various Particulates Arise from Multiple Chemicals, Locations and Conditions

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Modeling Particulate Emissions
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Video of soot formation at 10 atmospheres

Gas Turbine combustor
Courtesy of M. Roquemore, AFRL – 20,000 FPS)
Soot Particle Evolution in Laminar Premixed Flame

Transition from nucleation mode to coagulation/growth – The Beginning

Particle Size distributions in Laminar, premixed flame using Dilution probe and mobility particle sizer, with corrections for probe perturbations in modeling

Courtesy of H. Wang and co-workers
TEM photographs of soot from gas turbine (80% power)

Exhaust Particulates – *The End*

Gas Turbine combustor
Courtesy of Randy Vander Wal, PSU

Modeling Particulate Emissions
TEM photographs of soot from gas turbine (80% power)
Physics for Treatment of Soot/Particle Emissions

Physical Processes in Soot Formation

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)
Soot Formation Kinetics

**Inception:** Dimerization of pyrene (and other 202 amu species), after Appel, et al, 2000. (Full detailed kinetics required!)

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

**Condensation:**
Mass growth due to collision with PAH, followed by dehydrogenation

- \(C_{16}H_{10} + C(s) \rightarrow C(s)-C_{16}H_{10}\)
- \(C(s)-C_{16}H_{10} \rightarrow C'(s) + 5H_2\)

**Surface Growth:**
Mass growth (via acetylene addition) assumed proportional to particle surface area

- \(H + C(s) \leftrightarrow \dot{C}(s) + H_2\)
- \(H + \dot{C}(s) \leftrightarrow C(s)\)
- \(\dot{C}(s) \leftrightarrow C_2H_2 + \text{products}\)
- \(C_2H_2 + \dot{C}(s) \leftrightarrow C(s)CHCH\)
- \(C(s)CHCH \leftrightarrow C'(s) + H\)
Sectional Modeling of Soot Growth

Discrete particle size (logarithmic scale)

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

\[
\frac{dN_i}{dt} = J_i + C_{i-1}N_{i-1} - C_iN_i + \frac{1}{2} \sum_{j+k=i} \beta_{jk}N_kN_j - N_i \sum_j \beta_{ij}N_j
\]

Sectional Conservation Equation

Agglomeration simulated with peak size for surface growth

Modeling Particulate Emissions
Soot Kinetics
Based on OH, O₂ and available particle surface area


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

Oxidation by OH dominates!!

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

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

- Formation occurs at phi>1.5, and oxidizes at 0.7<phi<1.5
- 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 quenched below phi of 0.7

Exit plane distributions

Predicting trends
Predicted vs. Measured SN

Modeling Particulate Emissions
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Effects of Different Levels of Fuel Sulfur


<table>
<thead>
<tr>
<th>ppm sulfur</th>
<th>ppm sulfur</th>
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</thead>
<tbody>
<tr>
<td>170</td>
<td>5500</td>
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</table>

Increased sulfur causes sooner onset of contrail formation and a 25-50% increase in number of particulates.

Rolls-Royce/SNECMA M45H MK501 turbofan engines. Bypass 3:1 and 32.4 KN takeoff thrust

<table>
<thead>
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<th>% thrust</th>
<th>SN</th>
</tr>
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<tr>
<td>7</td>
<td>2.7</td>
</tr>
<tr>
<td>30</td>
<td>10.9</td>
</tr>
<tr>
<td>85</td>
<td>46.3</td>
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Modeling Particulate Emissions
Formation of Aqueous (Volatile) Particulates

\( H_2SO_4 / SO_3 \) is key to plume formation

Source of sulfur –

- Fuel sulfur \( \Rightarrow \) SO\(_2\) (~1 g/kg fuel at exit of burner) \( \Rightarrow \)
- SO\(_3\) (few percent of SO\(_2\)) \( \Rightarrow \) H\(_2\)SO\(_4\)

Nucleation rates

\[ J \sim \exp \left(-\Delta G^*/RT\right), \text{where } \Delta G^* \text{ is critical energy to form embryo } \]

\[ \Delta G^* = fn \left( (\mu_{\text{liquid}} - \mu_{\text{gas}}), \text{surface tension} \right) \]

Surface tension for water is very high….hard to form small (pure water) droplets!

Condensation rates

\[ \frac{dm}{dt} \sim (P_i - P_i^{\text{saturation}}) \]

Sulfur affinity for water

- 1 ppm nucleates water at 50% RH (Roth, et al, 1994)
Calculations of Homogeneous Nucleation  
*Dominated by $H_2SO_4/H_2O$ clusters*  

Calculations by Hsi-Wu Wong  
(Aerodyne)

Sulfuric acid-water and hydrocarbon embryo concentration from binary sulfuric acid-water nucleation and (pure) hydrocarbon nucleation, respectively.
Non-Volatile – Volatile Interactions

Changing Fate of Carbonaceous Particulates (soot):

Combustor Exit  Engine Exit  Exhaust Plume
100% hydrophobic  99% hydrophobic  ~70% hydrophobic
1% hydrophilic  ~ 30% hydrophilic

Hydrophobic particle + hydrocarbon (or oxygenate) = Non-aqueous HC coat on soot particle

Activation

+ H_2SO_4 = Hydrophilic particle  + H_2O/H_2SO_4 = Aqueous coat on soot particle

+ oxygenate = Hydrophilic particle  + H_2O/H_2SO_4 = Aqueous coat on soot particle
### Non-Volatile – Volatile Interactions

**Changing Fate of Carbonaceous Particulates (soot):**

<table>
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<tr>
<th>Location</th>
<th>Hydrophobic</th>
<th>Hydrophilic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustor Exit</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>Engine Exit</td>
<td>99%</td>
<td>1%</td>
</tr>
<tr>
<td>Exhaust Plume</td>
<td>70%</td>
<td>30%</td>
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Hydrophobic particle + hydrocarbon (or oxygenate) = HC coat on soot particle (non-aqueous)

\[ \text{Hydrophobic particle} + \text{hydrocarbon (or oxygenate)} = \text{HC coat on soot particle} (\text{non-aqueous}) \]

\[ + \text{H}_2\text{SO}_4 = \text{Hydrophilic particle} \]

\[ + \text{H}_2\text{O}/\text{H}_2\text{SO}_4 = \text{Aqueous coat on soot particle} \]

\[ + \text{oxygenate} = \text{Hydrophilic particle} \]

\[ + \text{H}_2\text{O}/\text{H}_2\text{SO}_4 = \text{Aqueous coat on soot particle} \]
Example Predictions for Sample Case

*Water/sulfuric acid and Unburned HCs contribute to both soot coating and volatile aerosols*

**Mass fractions on Soot**

Aerosol model allows for co-condensation of aqueous and non-aqueous materials

**Mass fractions in Aerosol**

Total condensed (volatile material) is continuing increasing

Calculations by Hsi-Wu Wong (Aerodyne)

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Modeling Particulate Emissions
Summary

- Very similar processes controlling volatile/non-volatile particulates – but different species and conditions govern rates
- Soot inception/nucleation is poorly defined
- Hydrocarbon nucleation/condensation negligible, except perhaps for idle conditions and in the case of lube oil emissions
- Volatile/non-volatile particulate interactions remains active area of research
  - Activation processes/rates
THANK YOU!

- Dave Liscinsky (UTRC)
- Bob Hall (UTRC, retired)
- Heidi Hollick (UTRC)
- Rick Miake-Lye (Aerodyne)
- Hsi-Wu Wong (Aerodyne)
- Mel Roquemore (AFRL)

SERDP: WP1577, WP1625
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

Species
\[ \dot{m}(Y_k - Y_k^*) - (\dot{\omega}_k^g + \dot{\omega}_k^s)W_k V = 0, \quad k = 1,2,...,K \]

Sectional
\[ \dot{m}(Y_k - Y_k^*) - \dot{Q}_k V = 0, \quad k = K+1,K+2,...,K+M \]

Energy
\[ \dot{m} \sum_{k=1}^{K} (Y_k h_k - Y_k^* h_k^*) + Q = 0 \]
\[ \dot{m} \sum_{k=1}^{M} (Y_k h_k - Y_k^* h_k^*) + Q = 0 \]

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

Fuel injector/swirler

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

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

Network Reactor Simulation

Fuel-spray shear layer Quench zones Burn-out zones

Recirculation 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
- $T_3 = 811K$ (1000F)
- $P_3: 16.3$ atm
General Formation Characteristics

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

**Dependence of Soot Processes on Equivalence Ratio**

- Oxidation
- Growth dominates
- Oxidation quenched
- Growth slow

**Rates**

- \( S_1 \) (growth)
- \( S_2 \) (oxid by O2)
- \( S_3 \) (oxid by OH)

**Phi**

(Fuel/Air Equivalence Ratio)

Modeling Particulate Emissions
Particle Formation in Fuel Spray Shear Layer

*Number density increase dramatically with position*

Particle Evolution in Fuel Spray Shear Layer

Particle Number Density

- **TAUs ~ 0.3 millisec**

Diameter (nm)

- **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 

TAUs ~ 0.7-1.7 msec
Particle Evolution Through Quench Zone

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

Particle Number Density

TAUs ~ 0.02-0.05 msec

Diameter (nm)

Particle Evolution Through Quench Zone (phi)

10a (2.45)
11a (2.06)
12a (1.78)
13a (1.56)
14a (1.39)
15a (1.25)
16a (1.13)
17a (1.04)
18a (0.955)
19a (0.887)
Particle Oxidation in Burn-Out Zone

Oxidation reduces number density and size (and mass)

Particle Oxidation in Burn-Out Zone

Particle Number Density

(#/cc)

Diameter (nm)

TAUs ~ 0.2 msec

20 (0.66)
21 (0.621)
22 (0.587)
23 (0.557)
24 (0.529)
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