OVERVIEW OF A FEW PM PROJECTS AT NVFEL
A Few Projects at NVFEL

• PM Generator
  – SwRI work (location of main research program)
  – NVFEL (beginning implementation here)

• PM number Initiative
  – Respond to current focus on PM number
  – Develop measurement method
    • Understand measurement complexities
    • Include all parts of PM that have human health impacts

• nvPM from turbine aircraft engines
  – Regulatory initiative under the United Nations International Civil Aviation Organization (ICAO)
  – Test procedure development under International Society of Automotive Engineers (SAE)
PM Generator Project

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Motivation

• Difficulty of measuring combustion PM
  – Instrument sensitivity to differing PM species
  – Sampling system design
  – Produce chemical thermodynamics in a controlled environment (vs. combustion engine source)

• Need some standard mechanism to produce combustion PM that is
  – stable
  – reproducible
  – can vary characteristics (i.e., size, chemistry, and mass) over a wide range in a simple manner (vs. engine source)
PM Generator Schematic (Housed at SwRI Nanoparticle Laboratory)
PM Generator  
(Housed in SwRI Nanoparticle Laboratory)

**Diagram Description**

- **Ia.** MC 
  Propane Flame Exhaust: $CO_2, CO, HC's, \ldots$ soot, soot+HC's

- **Ib.** CS 
  Catalytic Volatile Removal: $CO_2, H_2O, Soot$ (300°C)

- **Ic.** CC1 
  NaOH

- **Id.** A-CO$_2$
  CO$_2$ and H$_2$O removal: soot

- **II.** H$_2$OS
  SO$_3$S
  Mixing Chamber: Mixtures of soot, SO$_3$, H$_2$O, and C$_n$H$_{2n+2}$ (250°C)

- **III.** MC
  Filter collection soot+C$_n$H$_{2n+2}$ (250°C)

**Instrument Suite**

- A-CO$_2$
- A-TEM
- A-EC/OC
- A-MSS
- A-EEPS

**Abbreviations**

- MC: Minicast Combustion source
- CS: Catalytic Stripper
- CC1 & CC2: Cooling Coils
- NaOH: CO$_2$ absorber
- HCS: HydroCarbon Source
- SO$_3$S: SO$_3$ source
- H$_2$OS: H$_2$O source
- MC: Mixing Chamber
- FH1 thru FH3: Filter Holders
- A-CO$_2$: CO$_2$ analyzer
- A-TEM: transmission electron microscope
- A-EC/OC: semicontinuousEC/OC analyzer
- A-MSS: AVL photoacousticmicrosoot sensor
- A-EEPS: TSI scanning mobility particle analyzer

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Soot / Carbon Source

- Carbon source
  - Re-design
    - Jing mini-Cast Soot generator
      - With catalytic stripper (removes semi-volatile HC’s and converts them to CO₂)

- CO₂ scrubber:
  \[ \text{CO}_2 + \text{H}_2\text{O} \Rightarrow \text{H}_2\text{CO}_3 \]
  \[ \text{H}_2\text{CO}_3 + 2\text{NaOH} \Rightarrow \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \]
  \[ [\text{CO}_2 + 2\text{NaOH} \Rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}] \]

- Soot Output Characterization
  - Size distribution (SMPS, EEPS)
  - Concentration (AVL microsoot sensor, EC/OC analyzer)
  - Stability
  - Morphology (ORNL TEM studies)
  - CO₂ scrubber characterization
HC Sources

- HC sources
  - $C_{16}H_{34}$, $C_{19}H_{40}$, $C_{20}H_{42}$, $C_{26}H_{54}$, $C_{32}H_{66}$, $C_{36}H_{74}$, $C_{42}H_{86}$

- HC source characterization
  - Temperature dependence of HC concentrations
    - Mass measurements
    - Summed CO$_2$ mass from concentration measurements
  - Nucleation of individual species
  - Soot and HC mixing
  - Transport and modeling in a short section of tubing
SO$_3$ Source

1. SO$_2$ to SO$_3$ catalytic conversion
   i. SO$_2$ and O$_2$ bottled gases
   ii. Commercial diesel palladium/platinum oxidation catalyst
   iii. O$_2$ + 2SO$_2$ → 2SO$_3$

2. SO$_2$ to SO$_3$ conversion monitoring
   i. 1100°C oven (SO$_3$ to SO$_2$ decomposition)
   ii. SO$_2$ UV Fluorescence analyzer
Continuing Work

- **HC sources**
  - HC species production: evaporation and CO$_2$ detection
  - HC particulate nucleation
  - Transport studies begun
  - Stability and repeatability demonstrated

- **Soot source characterization**
  - Morphology of bare soot and HC – soot mixing
  - Stability and repeatability demonstrated
  - Fine tuning of miniCAST to get desired soot morphology

- **SO$_2$ source design**
  - SO$_3$ catalyzed from SO$_2$, O$_2$, and DOC catalyst
Continuing Work

• Conduct preliminary fundamental PM formation experiments

• Theoretical
  – PM and gas transport modeling to simulate losses
  – PM formation modeling

• Replicate Apparatus at NVFEL

• Modifications when needed
PM Number Initiative Overview

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U.S. EPA

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Motivation I

- Use of Solid Particle Number (SPN) as the primary metric for mobile source PM
  - Adoption in Europe for LDV SI-GDI and diesel
    - Still no PM or PN standard for SI-PFI
  - Under consideration in China
  - California is considering SPN with a conversion factor as a mass metric
Motivation II

• Stakeholder concerns
  – Environmental community often equates mobile source SPN with total PN and Ultrafine Particulate Matter (UFP, typically <100nm)
  – Ethanol lobby is pointing towards LDV/LDT SPN reduction as reason to adopt higher EtOH blends even though filter mass measurement often shows PM increases
    • Potential increase in SVOC due to fuel impingement into lubricating oil film on cylinder wall surfaces
Motivation III

• Current PMP-SPN measurement methods only measure “solids”
  – Significant (>40%) contributors to PM mass are not measured
    • Organic carbon PM (largely due to lubricating oil consumption)
    • Semi-volatile ions (nitrate and sulfate)
    • The majority contributors to particle number, nucleation aerosols and UFP are also not measured

• Components that are excluded from SPN measurement include mutagens and suspected carcinogens
  – Controls for SVOC components of PM (catalysts, cold-start improvements) generally reduce PM mutagenic activity

• “Conversion factors” from solid particle number measurements to PM mass as originally proposed by CARB for LEV III are problematic because the relationships are engine- and technology-specific
  – Conversion necessary for linkage to current PM-NAAQS
  – Relationship to mass changes with combustion technology (diesel, PFI, GDI, possibly EGR) and engine calibration
  – The increase in SPN emissions over a vehicle’s useful life is likely to be significantly less than increases in PM mass emissions
    • No measurement of lubricating oil contribution to PM – a significant contributor to PM near the end of useful life
  – Dropped from final LEV III regulation in part due to EPA concerns but likely to resurface within 2018 technology review

• There is risk that an SPN standard would be less constraining than stringent PM mass standards (at 1mg/mile)
  – Particularly near the end of useful life as consumption of lubricating oil increases
Guiding Thoughts on Implementation

- EU Number Regulations Do not consider Total PM
  - a negative and an opportunity to improve method
    - *Total PM* must be measured because of its negative impacts on human health and welfare
    - Realize the inclusion of volatiles adds a high degree of difficulty and will require more than a simple number measurement (size, probably some chemistry, and modeling)
Reference Method for PM Number (or Probably More Appropriately UFP)

– Start with the current PM sampling system configuration (40 CFR Parts 1065 & 1066)

– A “scalar” number measurement is not enough to address all health and welfare effects of PM
  • Size distributions will give information on the lung deposition
  • Chemical signatures are needed to address atmospheric chemistry (SOA and climate forcing) and future epidemiology

– Measure total PM, i.e., volatiles and soot
  • Volatiles are the major source of measurement difficulty
    – Careful attention must be paid to temperature, dilution, and flow
  • Modeling of sampling system can be used to help understand the relative importance of sampling system variables
    – Traceable PM chemistry/predictable system, i.e., using model, emissions (PM and chemical concentrations) measurements, sampling system thermodynamic and flow conditions the system chemistry should be definable
    – Uncertainties understood from the standpoint of model and testing
Current Status

- Laboratory modifications
- PM source and DAQ
  - NVFEL PM generator
- Finite element software tools
Emission Standard Development for Non-volatile PM Emissions from Commercial Aircraft Turbofan Engines

Participants:

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U.S. EPA

E31 – many others
International Aircraft Regulatory Scheme

- **International Civil Aviation Authority (ICAO)**
  - (http://www.icao.int/about-icao/Pages/default.aspx)
  - Agency of UN created in 1944
  - Sets standards and regulations for environmental protection, safety, security, efficiency, and regularity
  - Member states
- **Aircraft Engine Emissions**
  - **Volume II of ANNEX 16 to the Convention on International Civil Aviation**
  - **Committee on Aviation Environmental Protection (CAEP)**
    - Each formal meeting produces a report with specific recommendations for the consideration of the ICAO Council
    - Working Group (WG) 3 is subcommittee for PM
      - Member states and interested parties
    - SAE was assigned by WG 3 to update PM sampling and measurement method
      - SAE E31 standards committee to produce an Aircraft recommended practice (ARP) for nonvolatile PM
  - **Future**
    - Engines, APU’s, … < 27.6kN
    - Volatile PM
SAE E31 Work

• E31 (gaseous and) PM standards group
  – PM
    • Currently only nvPM
    • Only engines with thrust >27.6kN
    • Technical teams
      – Mass Team
      – Sample Team
      – Number Team
      – Calculation Team
  • Main participants
    – E.U. (EASA and FOCA), U.S. (EPA, FAA, and Airforce), Canada (TC and NRC), U.K. (C.A.A.)
    – Rolls Royce, G.E., Pratt and Whitney, Honeywell
    – instrument manufacturers
AAFEX Sampling stand and inlet rake used behind the left inboard engine; inset shows arrangement of gas (G) and particle (P) probes and sensors (thermocouple and pressure tap) in the water-cooled rake.
Volume size distributions \([\text{d}E/\text{d} \log D_p \text{ (mg/kg)}]\) as a function of sampling probe position and engine power for JP-8 fuel.

exhaust plane - particles are comprised of a single soot mode

downwind - nucleation mode appears, peaking at 15 to 25 nm in the volume (10 to 20 nm in number) distribution

low power - nucleation mode dominates the PSD in downstream samples

increasing power - nucleation mode decreases and the soot mode increases with the soot mode dominating at high power
Schematic of Particle Measurement System
Particle number measurement system

• Similar to E.U. PMP protocol for solid number
  – VPR (either thermal or catalytic stripper)
  – CPC particle penetration of 90% at 15nm
  – VPR
    – Particle Penetrations Specified
      | Particle size, $d_i$ | 15 nm | 30 nm | 50 nm | 100 nm |
      | Penetration, $Pen(d)$ | ≥30%  | ≥65%  | ≥70%  | ≥75%  |
  – Volatile removal efficiency specified (tetracontane)
  – Calibration
    • Similar to E.U. PMP
Mass measurement

• Instruments
  – Laser induced incandescence (LII)
  – Photoacoustic spectrometer
  – Calibration
    • NIOSH 5040
    • PM combustion source: diffusion flame
    • EC fraction ≥ 0.8 and soot concentrations of 0, 50, 100, 250, 500, and 1000 μg/m³
Loss Estimation Method

(A.) Use measured mass and number to determine a lognormal size distribution

\[ GMD = \left( \frac{6 \cdot M_{\text{meas}}}{\pi \rho N_{\text{meas}}} \right)^{1/3} \cdot e^{-3 \cdot s^2 / 2} \]

\[ s = \ln(\sigma_g), \quad \sigma_g = 1.77 \]

(B.) Apply sampling system penetration fraction functions to determine mass and number at engine exit

\[ C_N = \frac{N_{\text{exit plane}}}{N_{\text{measured}}} \]

\[ C_M = \frac{M_{\text{exit plane}}}{M_{\text{measured}}} \]
Thanks!