Properties of jet engine combustion particles during the PartEmis experiment: Particle size spectra (d > 15 nm) and volatility

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[1] Size distributions (d > 15 nm) and volatile properties of combustion particles were measured during test-rig experiments on a jet engine, consisting of a combustor and three simulated turbine stages (HES). The combustor was operated to simulate legacy (inlet temperature 300°C) and contemporary (500°C) cruise conditions, using kerosene with three different fuel sulfur contents (FSC; 50, 400 and 1300 μg g^{-1}). Measurements found that contemporary cruise conditions resulted in lower number emission indices (EI_{N15}) and higher geometric mean particle diameter (d_G) than for legacy conditions. Increasing FSC resulted in an overall increase in EI_{N15} and decrease in d_G. The HES stages or fuel additive (APA101) had little influence on EI_{N15} or d_G, however, this is uncertain due to the measurement variability. EI_{N15} for non-volatile particles was largely independent of all examined conditions. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305). **Citation:** Nyeki, S., M. Gysel, E. Weingartner, U. Baltensperger, R. Hitzenberger, A. Petzold, and C. W. Wilson (2004), Properties of jet engine combustion particles during the PartEmis experiment: Particle size spectra (d > 15 nm) and volatility, *Geophys. Res. Lett.*, *31*, L18105, doi:10.1029/2004GL020569.

1. Introduction

[2] Ground and in-flight studies have observed that aircraft exhaust emissions contain both primary emitted soot particles as well as volatile particles, formed by nucleation [*Anderson et al.*, 1998; *Petzold et al.*, 1999; *Schröder et al.*, 2000]. High concentrations of nucleation mode (d < 10 nm) volatile particles are believed to be composed of H_2SO_4 and unburned/partially oxidized non-methane hydrocarbons (NMHCs). Despite progress on microphysical models [*Vancassel et al.*, 2004], the effect of jet engine operating conditions on aerosol properties still needs to be further characterized.

[3] The PartEmis project (Measurement and Prediction of Emissions of Aerosols and Gaseous Precursors from Gas Turbine Engines) was initiated to extend current knowledge of jet engine emissions. An overview of all measured parameters and test-rig technical aspects is given in *Wilson et al.* [2004, and references therein]. The present study deals with measurements of particle size spectra and their volatile properties.

2. Methods

[4] Two test-rig campaigns were conducted at the QinetiQ facilities in Farnborough, UK. The first campaign (Jan.–Feb. 2001) focused on characterizing emissions from a jet engine combustor (previously used during AEROTRACE [see *Wilson et al.*, 2004]) and the second (March 2002) focused on the same combustor, integrated to a so-called Hot End Simulator (HES) unit. The HES passively simulated thermodynamic conditions at three pressure stages within a turbine (high, intermediate, low; hp, ip, lp; ~3.7, 2.5, 1.1 bar). Combustor operating conditions were chosen to simulate legacy (referred to as Old) and contemporary (Modern) aircraft cruise conditions at 33,000 ft (~11000 m) altitude for which inlet temperatures were 300 and 500°C, respectively. These conditions conformed to the ICAO (International Civil Aviation Organization) engine emissions smoke standard. Jet fuel kerosene with fuel sulfur contents 50, 400 and 1300 μg g^{-1} (low, mid and high FSC) was used where 400 μg g^{-1} FSC approximates the contemporary fleet average. A Shell additive (APA101) was used in the kerosene in a second round of tests at concentrations of 256 and 1280 μg g^{-1}. APA101 has recently been shown to result in lower particle concentrations amongst other beneficial properties [e.g., *Corporan et al.*, 2002]. Emissions were sampled using a 5-hole equal area water-cooled gas sampling probe to map the lateral distribution at 11 positions across the combustor exit plane. However, average combustor properties are only presented due to a lack of data. After exit from the combustor, exhaust emissions were cooled to ~150°C using a water jacket, diluted by a factor of ~65, and then allowed to cool naturally to 20–25°C in the sample line (length ~38 m, tube diameter ~21 mm. Dilution factors were determined from CO_2 mixing ratios, and temperature and pressure sensors which were distributed throughout the system. Aerosol losses (C. Hurley, internal report) were estimated to total 20% but were not modeled as a function of particle diameter (d). In the absence of size-resolved correction factors, data have not been corrected here. Particle size spectra were measured using two standard TSI 3071 DMAs (differential mobility analyzer) and a TSI CPC 3022 (condensation particle counter). The instrument was operated in two modes: i) SMPS (scanning mobility particle sizer) mode for polydisperse particles, or ii) TDMA (tandem DMA)

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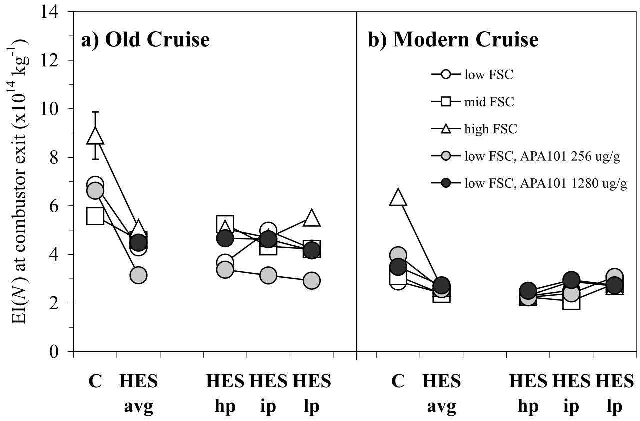

Figure 1. Summary of Combustor and Combustor-HES results. Comparison of EI_{N15} for a) Old and b) Modern conditions at the combustor exit (C) and HES stages (HES average, high, intermediate and low pressure = hp, ip, lp, respectively). Only single error bar (measurement variability; ±1 stdev.) shown for clarity.

mode to select and measure monodisperse particles. The addition of a custom-built thermodesorber [*Burtscher et al.*, 2001] allowed particle volatile properties to be measured at temperatures $T = 25$, 120 and 300°C. The ranges, i) $T = 25$–120 (T_{25-120}), ii) 120–300 ($T_{120-300}$), and iii) >300°C ($T_{>300}$) are commonly attributed to the following aerosol components, respectively: i) H_2SO_4, ii) (bi)sulfate, and iii) elemental carbon (EC) or soot, mineral dust and sea salt. Category iii) is commonly referred to as refractory or (NV) non-volatile aerosol, and is composed almost entirely of EC in our case. It should be noted that NMHCs may result in a positive artifact at all temperatures, and is discussed later. Size-dependent corrections for thermodesorber losses were applied. The effect of particle-bound water on particle size determination was considered negligible due to the low sample line RH (<10%). Polydisperse size spectra were measured with a 3–5 minute resolution per thermodesorber channel to give the number concentration N_{15} over the range d = 15–550 nm. Monodisperse particles were measured at 11 nominal diameters d_o = 15–100 nm. The ratio d^3/d_o^3 therefore gives the volume shrinkage factor where $1 - d^3/d_o^3$ equals the volume fraction of volatile material assuming particle sphericity. Emitted particle concentrations (number integral of SMPS spectra) are reported as number emission indices per kg burned fuel (EI_{N15}). As the measurement variability was larger than the uncertainty, standard deviations for the former are given.

3. Combustor Measurements

[5] An overview of EI_{N15} and geometric mean diameter d_G at the combustor exit as a function of FSC and cruise conditions is given in Figures 1 and 2, respectively. Combustor-HES results are also shown and are discussed in Section 4. The largest difference lies in the grand average of EI_{N15} for Old versus Modern conditions which gave 7.0 ± 1.4 and 4.0 ± 1.4 × 10^{14} kg^{-1}, respectively. Corresponding values of d_G were 41.0 ± 1.6 and 43.4 ± 1.8 nm. FSC resulted in higher EI_{N15} for the high FSC case, while a decrease in d_G was observed on average with increasing FSC. The differences between high and mid or low FSC were significant at the 95% level (Students T-test) in most cases. The effect of APA101 additive on EI_{N15} and d_G on the other hand was uncertain when considering the measurement variability.

[6] An interesting observation during both campaigns was that only monomodal size spectra were observed. The geometric standard deviation during the combustor campaign was $\sigma_G = 1.67 \pm 0.05$. However, a nucleation mode at d_G = 4–7 nm for high FSC cases was observed for $d <$ 15 nm in other simultaneous measurements [*Petzold et al.*, 2003]. A distinct minimum in particle concentration at $d \sim$ 10 nm occurred between the nucleation mode and the lower tail of the Aitken mode (d = 10–100 nm). The above results are similar to previous in-flight studies where EI in the range 0.1–1 × 10^{15} kg^{-1} and d_G = 30–60 nm were found [*Anderson et al.*, 1998; *Hagen et al.*, 1998; *Petzold et al.*, 1999; *Schröder et al.*, 2000]. The decrease in EI_{N15} and increase in d_G with increase in combustor inlet temperature (i.e., Old to Modern conditions here) is consistent with other studies [e.g., *Petzold et al.*, 2003]. This reflects the fleet-average trend of civilian aircraft towards a reduction in particulate emissions.

[7] Measurements of particle volatility on monodisperse particles gave similar results for both cruise conditions. Figures 3 and 4 illustrate d^3/d_o^3 (Modern conditions) at both thermodesorber temperatures without and with APA101 additive, respectively. Particles tend to exhibit greater shrinkage (i.e., increasing volatility) with decreasing d_o except for the low FSC case. In addition, mid and high FSC curves also appear to illustrate greater shrinkage. Although each data point consists of 3–6 size scans, the measurement variability does not allow any clear conclusions to be drawn. Hence, polynomial fits are illustrated as solid curves in both figures (see captions for details). In Figure 3, small particles (d_o < 20 nm) exhibited volatile volume fractions ~10 and ~5% for the T_{25-120} and $T_{130-300}$ fractions, respectively, which decreased to <3% for $d_o \geq 50$ nm particles. Particle volatility for d_o < 30 nm is therefore mainly due to the T_{25-120} fraction, and is most probably due to H_2SO_4/NMHCs. Above this size, volatility appears to be independent of FSC and cruise conditions. The above observations are supported in part by NMHC

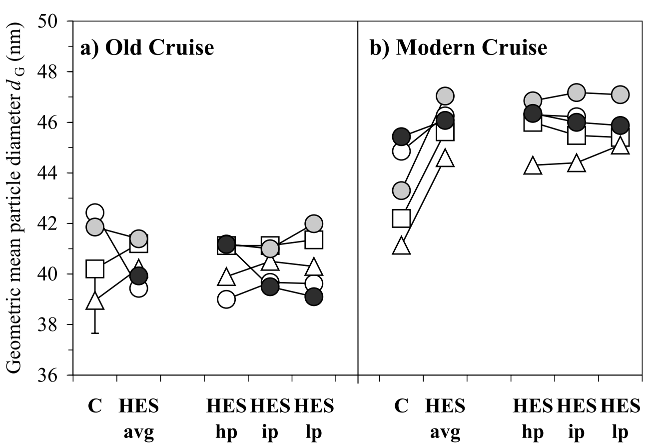

Figure 2. Comparison of d_G, otherwise same as for Figure 1.

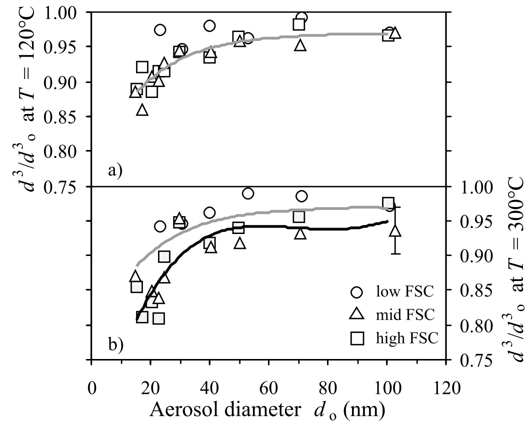

Figure 3. Combustor results, modern cruise conditions. Volume shrinkage factor (d^3/d_o^3) for monodisperse particles at thermodesorber temperatures: a) T = 120, and b) 300°C. Solid curves depict a polynomial fit with respect to mid/high FSC results. The gray curve in a) is repeated in b) for comparison.

desorption measurements on particulate samples. Only 0.4 wt% of NMHCs were found to desorb at T < 130°C, whereas 99.6 wt% desorbed at T = 130 to 350°C (H. Puxbaum, personal communication, 2004). These results are not size-resolved but do suggest that the T_{25-120} fraction is mainly H_2SO_4 and $T_{130-300}$ is composed of NMHCs and not just (bi)sulfate. In Figure 4, the absence of particle shrinkage for d_o < 30 nm is obvious when compared to the mid and high FSC results in Figure 3, again suggesting that H_2SO_4 is responsible for the T_{25-120} fraction. The influence of APA101 appears to be negligible, if any. Only low FSC was chosen for tests with APA101 as it represents future FSC trends in fuel kerosene.

4. Combustor-HES Measurements

[8] Particles were sampled at all three pressure stages of the HES. An inter-comparison of HES stages suggests little effect on EI_{N15} for constant FSC or APA 101 additive. A similar conclusion is reached for d_G in Figure 2. In order to increase the statistical significance, results averaged over all HES stages are also shown in Figures 1 and 2. A clear difference is evident between HES Old and Modern conditions which gave EI_{N15} = 4.3 ± 0.7 and 2.5 ± 0.2 × 10^{14} kg^{-1}, and d_G = 40.4 ± 0.8 and 45.9 ± 0.9 nm.

[9] When comparing Combustor with Combustor-HES measurements, only one conclusive trend is apparent. Lower EI_{N15} concentrations are observed in the HES for both Old and Modern conditions, while d_G is slightly higher only under Modern conditions. Cloud condensation nuclei concentrations during the Combustor-HES campaign were also significantly lower than during Combustor measurements (unpublished data). Particle coagulation between the combustor exit and HES entrance was examined as a possible reason for lower EI_{N15}. The geometric standard deviation for Combustor-HES measurements was 1.78 ± 0.03, and compares with 1.67 ± 0.05 for the Combustor campaign. However, if σ_G values from the 11 probe positions at the combustor exit are weighted with the appropriate gas density then a value 1.74 is found. Hence, the observed broadening between combustor exit and HES exit can be explained by mixing effects rather than coagulation. In conclusion, the most likely explanation for the difference in EI_{N15} is differences in nominal combustor settings resulted from Combustor and Combustor-HES campaigns not being back-to-back.

[10] The volatile properties of monodisperse particles during Combustor-HES measurements (not shown) were largely similar to those for the Combustor campaign. However, due to the increased measurement variability (due to fewer size scans) no clear conclusions can be drawn concerning the effect of FSC or APA101.

5. Discussion and Conclusions

[11] An important aspect of PartEmis was not only to characterize the physical but also chemical properties of particles. Our measurements are only able to suggest but not conclusively determine the composition of the T_{25-120} and $T_{130-300}$ fractions. Further evidence comes from PartEmis measurements of nucleation mode EI_N [*Petzold et al.*, 2003] which not only suggest the presence of H_2SO_4, but also demonstrate a clear effect with high FSC. More direct measurements with size-selected impactor samples and ion chromatography analysis [*Puxbaum et al.*, 2003], and a chemical ionization mass spectrometer [*Katragkou et al.*, 2004] conclusively confirm sulfur species to be present. In-flight studies also indicate H_2SO_4 particles as being a component of exhaust emissions. Nucleation mode EI_N have been found to increase with FSC, and is attributed to H_2SO_4 droplets [e.g., *Petzold et al.*, 1999; *Schröder et al.*, 2000]. An inter-mode minimum at $d \sim 10$ nm separates a mostly volatile nucleation mode from a non-volatile Aitken mode in young exhaust plumes. Such volatile particles nucleate in cooling exhaust gases up to 1–2 s after emission. In our case, nucleation primarily occurred after dilution in the main sampling line [*Wilson et al.*, 2004]. However, volatile particle EI_N are apparently not linearly related to FSC. For instance, *Schröder et al.* [2000] reported little effect when FSC was decreased below 100 $\mu g\ g^{-1}$.

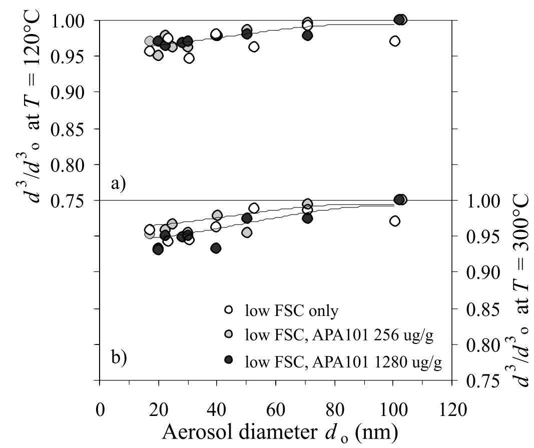

Figure 4. Combustor results, modern cruise conditions. Influence of APA101 on monodisperse particles with low FSC fuel. Solid curves depict a polynomial fit with respect to all FSC/APA101 results. The gray curve in a) is repeated in b) for comparison.

Modeling studies suggest that NMHCs may substantially contribute to the T_{25-120} fraction [e.g., *Kärcher et al.*, 2000]. The increase in monodisperse aerosol volatility for $d < 30$ nm (Figure 3) may therefore be due to: 1) a thicker coating of volatile material, and/or 2) external H_2SO_4/NMHC particles belonging to the upper tail of the nucleation mode. The former is in agreement with hygroscopicity TDMA results which also suggest an increasingly thick coating with decreasing d_G and increasing FSC [*Gysel et al.*, 2003].

[12] Previous studies on APA101 indicate a decrease in d, and EI_N by 20–35%, although the mechanism of action, whether chemical, physical or other, is at present poorly understood [see *Corporan et al.*, 2002, and references therein]. It is unclear why similar effects were not observed here. APA101 appears to have a greater influence on fuels with high aromatic and sulfur content (P. Bogers, personal communication, 2004). APA101 was only tested here with low FSC having a low aromatic content (18.1% v/v), and may partly explain the lack of a reduction in EI_{N15} and d_G. In addition, our back-to-back measurements with and without APA101 additive may not be comparable with other studies where tests were first conducted 50–100 hours after the addition of APA101. The maintenance of clean engine components is believed to result in optimum fuel combustion conditions (i.e., fuel spray distribution etc) and hence in reduced emissions [*Corporan et al.*, 2002]. The lack of an observable effect therefore suggests the above mechanism to be more probable than either chemical or physical mechanisms, which may be expected to cause an immediate reduction in EI_N.

[13] Several in-flight studies have observed that non-volatile EI_N are relatively unaffected by FSC level [*Hagen et al.*, 1998; *Petzold et al.*, 1999]. PartEmis measurements of non-volatile emission indices ($EI_{N15,NV}$) reflected the trends for EI_{N15} in Figures 1 and 2. For instance, $EI_{N15,NV}$ for Old and Modern conditions during the Combustor campaign were $\sim 4.8 \pm 1.5$ and $2.4 \pm 1.3 \times 10^{14}$ kg^{-1} (average over all FSC), respectively, and compare with EI_{N15} of 7.0 ± 1.4 and $4.0 \pm 1.4 \times 10^{14}$ kg^{-1}. High FSC resulted in a higher EI_{N15} only for Old conditions ($6.9 \pm 0.1 \times 10^{14}$ kg^{-1}. $EI_{N15,NV}$ may thus be insensitive to FSC level and APA101 additive, although the measurement variability should be taken into account.

[14] In summary, this study investigated the size spectra and volatile properties of particle emissions from a jet engine combustor and turbine simulation stage. As the dataset is multi-dimensional (polydisperse and monodisperse aerosol properties with respect to aerosol volatility, combustor conditions, FSC, and APA101 additive) definite trends were somewhat difficult to ascertain. Nevertheless, certain trends were discernible: 1) Modern versus Old conditions resulted in lower EI_{N15} and higher d_G; 2) high FSC versus mid or low FSC led to increased EI_{N15} and a decrease in d_G; 3) EI_{N15} and d_G were unaffected by APA101 additive, however, this cannot be stated with any certainty due to the measurement variability; 4) monodisperse particles (d_o = 15–30 nm) exhibited increasing volatility with decreasing d_o and also with increasing FSC.

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