**Aircraft soot from conventional fuels and biofuels during ground idle and
climb-out conditions: electron microscopy and X-ray micro-spectroscopy**

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Abstract

Aircraft soot has a significant impact on global and local air pollution and is of particular concern for the population working at airports and living nearby. The morphology and chemistry of soot are related to its reactivity and depend mainly on engine operating conditions and fuel-type. We investigated the morphology (by transmission electron microscopy) and chemistry (by X-ray micro-spectroscopy) of soot from the exhaust of a CFM 56-7B26 turbofan engine, currently the most common engine in aviation fleet, operated in the test cell of SR Technics, Zurich airport. Standard kerosene (Jet A-1) and an alternative fuel blend (Jet A-1 with 32% HEFA) were used at ground idle and climb-out engine thrust, as these conditions highly influence air quality at airport areas. The results indicate that soot reactivity decreases from ground idle to climb-out conditions for both fuel types. Nearly one third of the primary soot particles generated by the blended fuel at climb-out engine thrust bear an outer amorphous shell implying higher reactivity. This characteristic referring to soot reactivity needs to be taken into account when evaluating the advantage of HEFA blending at high engine thrust. The soot type that is most prone to react with its surrounding is generated by Jet A-1 fuel at ground idle. Alternative fuel blending slightly lowers soot reactivity at ground idle but does the opposite at climb-out conditions. As far as soot reactivity is concerned, alternative fuels can prove beneficial for airports where ground idle is a common situation; the benefit of alternative fuels for climb-out conditions is uncertain.

Keywords

Aircraft emissions; soot; TEM nanostructure; HEFA; biofuel

Capsule

Conventional kerosene (Jet A-1) at ground idle produces the most reactive soot; alternative fuel can prove beneficial for ground idle; its advantage for climb-out is uncertain.

1. Introduction

Aviation affects global and local air quality, and influences climate, the environment and human health. Air traffic has a global annual growth of ~5% [1] and is expected to rise in the future thus increasing the environmental and human health concerns and posing new challenges for further research on aircraft emissions. Aircraft emissions include gaseous components such as CO₂, NO_x, CO and SO_x, volatile organic compounds, as well as solid particulate matter (PM). Solid PM comprises mainly soot and to a small extent ash (metal particles). Soot generated by road transport is known to have adverse effects on human health while studies concerning the health impacts of jet exhaust soot are limited [2].

Introduction of biofuels in road transport has proven successful for soot reduction (e.g., [3-5]). Biofuels have been tested recently also in aviation in form of blends with standard aviation fuel. Note that aviation fuels contain only trace levels of oxygen [6] but the use of oxygenated biofuels in aviation is a topic of scientific discussion [7]. Common biofuels with beneficial environmental potential are hydro-processed esters and fatty acids (HEFA), as well as those produced by a Fischer-Tropsch synthesis (FT) [8]. The few studies dealing with aircraft engine exhaust characterization with biofuel blends [8-10] conclude that biofuel blending reduces soot emissions.

A key issue that can elucidate the impact of soot on health and the environment is the knowledge of physical and chemical properties in the micro- and nano-scale. Physical properties refer to the morphology of soot particles (size and internal nano-structure, i.e. degree of atomic order). These properties vary depending on type of the fuel used and the engine operating conditions, i.e. the fuel / air ratio during combustion, as well as flame temperature and residence time of the particles in the flame [10-15]. Soot morphology and chemistry reflect its reactivity, important for determining the oxidation capacity of soot and/or its capacity to react with the surrounding, in general. The formation of ice clouds from soot

has also been related to soot morphology and chemical composition [16, 17]. Moreover, the hydrophilic character of soot, in combination with the active particle number (particles serving as condensation nuclei versus total particles) are properties used in recent models on contrail and cirrus formation [18].

A series of studies have been devoted to the oxidation reactivity of soot in road transport and showed that soot with small particle size (large surface to volume ratio) and amorphous internal nano-structure (low thermodynamic stability) favor oxidation reactivity, in contrast to large particle sizes and well-ordered nanostructures (e.g. [19, 20]). Whether the size weighs more than the internal nano-structure in determining the degree of soot reactivity is unclear but there are indications that the size is rather the more important parameter [21]. Regarding the chemical composition of soot versus oxidation reactivity, different studies [22-24] arrive at different conclusions but show a trend for high reactivity when soot has high oxygen content. Although not adequately researched and established, soot reactivity can be considered, in a more general sense, as referring to the availability of atoms on the particle surface and bulk for reaction, not strictly with oxygen only.

Soot particles resulting from different fuel types, engine operating conditions and/or ambient temperatures have comparable but not identical morphologies. The primary particle constituents of the agglomerates all share a nearly spherical shape and consist of generally concentric, carbon-dominated layers (approaching the graphene structure) of variable length, separation distances and periodicity. The nano-structure of soot is well demonstrated on high resolution transmission electron microscopy (HRTEM) images. With increasing degree of structural order, carbon lamellae length increases (less edge atoms are exposed), separation distances between carbon lamellae decreases and reactivity is reduced. In addition to the primary particle morphology, the morphological characteristics of soot agglomerates may also influence reactivity.

While numerous studies use TEM to determine morphological characteristics of soot generated in road-traffic, only few publications are available on aircraft soot morphology. Popovicheva et al. [25] studied nano-structural parameters of soot and report significant water adsorption on soot generated by a typical aircraft engine compared to non-polar gases. Detailed TEM characterization of aircraft soot was presented by [15] and [26] reporting a clear variation in the degree of soot crystallinity with engine thrust level, the lower thrust soot exhibiting a lower structural order than at high thrust. The same conclusion was reached in a more general study on aircraft PM emissions including TEM characterization [27]. In addition, Vander Wal et al. [15] reported significant oxygen content on soot surfaces which may influence the hydrophilic properties of soot.

Regarding biofuel use in road transport, soot morphology shows a lower degree of structural order, and thus higher reactivity, than diesel soot [21, 23, 24, 28, 29]. To our knowledge, TEM studies on soot from alternative fuels in aviation are lacking.

The chemical composition of soot can also provide important information on the degree of reactivity. Carbonyl or carboxyl groups, for instance, can increase soot reactivity with respect to pure carbon since the energy needed to remove oxygen is lower than the one needed to remove elemental carbon. A previous study reported that surface bound carboxyl functional groups tend to decarboxylate in the presence of ozone, sunlight and adsorbed water [30]. Soot in the ambient atmosphere has been extensively characterized using scanning transmission X-ray microscopy coupled to near edge X-Ray absorption fine structure (STXM/NEXAFS) spectroscopy [31-33]. STXM/NEXAFS yields X-ray absorption peaks at particular X-ray energies quantifying the molecular bonding environment of carbon atoms. Ground based particle sampling shows that soot is typically found at the center of particles mixed with organic and inorganic matter as its atmospheric residence time increases [32, 33]. To date, only a single study using NEXAFS (in electron yield mode, as opposed to transmission mode

in STXM) spectroscopy on soot from an aircraft engine using conventional fuel is available and revealed that soot surfaces can be more oxidized than the soot core, on average [26]. Within the framework of the present paper, the morphology (by TEM) and chemistry (by NEXAFS spectroscopy) of soot generated by a CFM 56-7B26 turbofan engine, currently the most common engine in aviation fleet, operated with standard aviation conventional kerosene (Jet A-1) and an alternative fuel (HEFA) blend at ground idle and climb-out conditions were investigated. These engine thrust conditions were chosen as they are crucial for the population working at airports and leaving in the surrounding. The turbofan engine was operated in the test cell of SR Technics, Zurich airport. The aim of the paper was to investigate and inter-compare the morphological and chemical characteristics of soot generated by the different fuel types and thrust levels, evaluate soot reactivity for each condition and examine the environmental benefits from the use of alternative fuels from the soot reactivity point of view.

2. Experimental

2.1 Sampling Setup and Procedures

The experiments were carried out in the engine test cell of SR Technics at Zurich airport, within the framework of the project EMPAIREX. An in-service CFM 56-7B26 hi-bypass turbofan engine was used, popular in the current aircraft fleet and used on the Boeing 737 short- to medium-range twinjet narrow-body airliner. This particular engine had 15'200 flight cycles (32'000 h wing time) and a stable performance during the entire campaign. The engine thrust levels were controlled according to the engine combustor inlet temperature (T3, proprietary value) for which the corresponding thrust levels are known for standard atmospheric conditions (15 °C, 1013.25 hPa). Idling thrust is affected by ambient conditions. In this work it corresponded to 3-4% of the maximum sea level thrust output. During the experiments two different fuel types were used: i) Jet A-1 and ii) a blend consisting of Jet A-1

with 32% HEFA (Supplementary Table S2). HEFA fuel has many of the properties of petroleum derived jet fuels the main difference from Jet A-1 being the lower total aromatics and the sulfur contents (18.1% v/v and 490 ppm for Jet A-1, respectively and 11.3% v/v and 350 ppm for the HEFA- Jet A-1 blend, respectively).

PM was collected during climb-out (~85% engine thrust; P85) and ground idle conditions, directly on TEM grids (for soot morphology) and on silicon nitride (Si_3N_4) membranes (for NEXAFS analyses). For each engine thrust condition, both Jet A-1 and HEFA blend were used. An additional experiment applying Jet-A1 fuel doped with 4% HEFA at nearly 100% thrust conditions ('Maximum Continuous') was conducted and used in STXM/NEXAFS analysis. Supplementary Table S1 summarizes the conditions during sampling, including online measurements. Details on the sampling setup and procedure and a schematic of the sampling equipment are given in the supplementary information (section S1).

2.2. Transmission electron microscopy – Image processing

TEM studies were performed with a JEOL 2200FS TEM/STEM microscope equipped with an Omega filter, a Schottky field emission gun at 200 kV, and a point to point resolution of 0.23 nm (Electron Microscopy Center of Empa). The TEM instrument is equipped with an EDX detector (JEOL EDX detector: EX-24065JGT) for elemental analysis. Images were taken in bright field (BF) and dark field (DF) STEM mode, as well as in TEM and HRTEM mode. For optimum contrast and distinction of nano-structural features, particles located in holes of the carbon film were chosen.

Image processing of five representative soot particles per thrust condition and fuel type was carried out in order to quantify and compare the fringe length. For the quantification of the fringe length we used MATLAB following a procedure suggested in different recent papers (e.g. [23, 38]) including the following steps: image cropping, negative transformation, image

181 histogram equalization, Gaussian low-pass filter; top hat transformation, binarization and
182 skeletonization. Removal of artifacts (branch points removal) was most efficient by marking
183 the fringes by hand onto the HRTEM image of the soot particles. The binary image was
184 processed using MATLAB by applying the built-in skeletonization function. The analysis was
185 then automated and standardized.

187 2.3. *X-Ray Micro-spectroscopy (NEXAFS)*

189 Carbon functionalities in single particles were investigated with STXM/NEXAFS. A detailed
190 overview of this technique can be found in [34]. Focused single energy X-rays irradiated
191 particles deposited either on silicon nitride, Si₃N₄, membranes or TEM grids as sample
192 substrates. Substrates were transported under a N₂ atmosphere to the PolLux beamline
193 (X07DA) of the Swiss Light Source at the Paul Scherrer Institute. STXM/NEXAFS analysis
194 was conducted on a total of 44 particles and classified as either soot (10 particles), mixtures of
195 organic and soot (13 particles) or organic only (21 particles). Scanning X-ray energies were
196 278–320 eV; absorption was measured with a high spatial resolution of 35x35 nm to observe
197 carbon bonding. This energy range covers electron binding energies for ground state electron
198 orbitals of the carbon atom (carbon K-edge). Absorption spectra were converted to optical
199 density (OD) over the 2-D projected particle area as a function of X-ray energy where
200 $OD = -\ln(I/I_0)$, and I and I_0 are the transmitted and initial X-ray light intensities, respectively.
201 Energy calibration was performed by comparing the measured lowest energy peak of
202 polystyrene with its literature value [35]. Series of particle OD images at closely spaced
203 energy steps were taken and processed with publically available software for automated X-ray
204 image analysis [36]. Spectra reported here were background subtracted by the OD at the
205 carbon pre-edge (278-280 eV) and normalized to the spectral area at the carbon post-edge
206 (305-320 eV) [37].

3. TEM Results

3.1. Size of agglomerates and primary particles

The size of soot agglomerates and their primary particle constituents was determined from TEM images using the measuring tool of the software ‘Digital Micrograph’. The size of the agglomerates is taken here as their maximum length, that of the nearly spherical primary particles by the diameter of their circular projection. For the measurements we took into consideration isolated, freestanding agglomerates. Thus the agglomerate size expressed as maximum length would be a representative and consistent figure allowing comparison between different thrust conditions. We have no indication for agglomeration on the TEM grid during sampling. The geometric mean diameters of the agglomerates, as obtained by simultaneous online measurements are also listed in supplementary Table 1.

Based on 300-400 measurements, ground idle conditions result in significantly smaller agglomerates than climb-out. We determined a modal size range of soot agglomerates and primary particles. For both Jet A-1 and HEFA blend fuel types, ~80% of soot agglomerates generated at ground idle conditions fall within the size mode <40 nm (Fig. 1a). At 85% engine load, a modal size of 40-80nm was observed accounting for ~35% of the particles, while another ~20% were between 80-120nm. Inside the smallest size range (<40nm), idle Jet A-1 agglomerates are considerably smaller than idle HEFA blend ones (Fig. 1b; Jet A1: ~45% are <20nm versus HEFA blend: only ~15% are <20nm). The increasing trend from low to high thrust level identified for agglomerates is also observed for the primary soot particles (Fig. 1c): the big majority (~75-85%) at ground idle conditions for both fuel types was between 5-10nm; at P85 the maximum (~30%) lies between 15-20nm; ~60% of them are 10-25nm in diameter (Fig. 1c). HEFA blend at idle conditions produces the highest percentage of the smallest primary particles (~20% are 3-5nm large in contrast to 2% of the Jet A-1 ones).

The TEM images of Fig. 2 depict a representative view of the size and relative amount of soot agglomerates under P85 and ground idle conditions. The described differences between low and high thrust conditions were also found in a previous TEM study of aircraft soot emissions [27], where ~60% of the primary particle sizes during taxiing (~7% thrust) were 10-15nm (mode 13nm) and ~60% of primary particles under full thrust (~100 % thrust) were 10-25nm (mode 24nm). Moreover, the results of simultaneous online measurements of the size of soot agglomerates show the same trend as the TEM results (supplementary Table S1). Taking into account only the size of soot agglomerates and primary particles, i.e. not considering internal nanostructures and internal arrangement of primary particles within the agglomerate, our results indicate higher reactivity for ground idle particles of both fuel types compared to P85 particles. It is reminded that small primary soot particles and small agglomerates tend to be more reactive than large ones (see earlier, Introduction).

Fig. 1: Size distribution of soot agglomerates (a, b) and primary particles (c) for ground idle and P85 thrust conditions with Jet A-1 and HEFA blend showing significantly lower sizes for idle conditions.

Fig. 2: TEM images demonstrating the higher abundance and larger agglomerate sizes of P85 (left panel) versus ground idle conditions (right panel). The P85 image was taken with a 10'000 magnification, the ground idle one with 20'000x to make particles distinguishable. The images are representative for both fuel types.

3.2. *Internal nano-structure of primary soot particles*

Primary soot particles from both investigated fuel types and engine thrust conditions consist of discontinuous carbon lamellae (fringes) (Fig. 3). Discontinuities in carbon lamellae are marked by grey areas on the images where no fringes can be distinguished and correspond to regions of highly disordered arrangements, likely due to irregular and episodic incorporation of organic compounds during particle growth.

Representative HRTEM images are given in Fig. 3. Amorphous cores usually constitute a very small part of the particle volume; particles with strongly bent carbon lamellae are observed almost to the particle's center. Abundance of curved lamellae at particle interiors indicates a relatively high functionality and therefore high reactivity of soot at this stage of particle development. More or less planar, slightly deformed lamellae of various length form packages of different thickness and orientation overlying the particle interior and resulting in an approximately concentric arrangement.

A peculiarity in soot nanostructure is identified for the P85 soot of the HEFA blend: a considerable part of the examined particles show a highly disordered, nearly amorphous outer shell 2-8nm thick (Fig. 3C). We estimate the percentage of the particles bearing this type of

amorphous shell to about 30-40% of the totally observed particles. Note that this observation requires high resolution imaging which cannot go along with solid statistics. Thus the 30-40% estimation is only a rough approximation. Note also that no expansion and, in general, no deformation of this amorphous shell was observed under the electron beam. The outer shell described above has been identified also in P85 soot generated with HEFA-doped fuel (4% HEFA), but was not observed in soot produced with Jet A-1. An amorphous outer shell has been reported by La Roca et al. [38] for primary particles of soot from engine oil of a modern direct injection gasoline engine. In our case, an origin of this soot type from engine oil cannot be completely excluded but the fact that it has been found only when using HEFA fuel and only at high thrust conditions favors its formation in connection with the use of HEFA fuel type. Finally, in a few P85 soot particles produced by both Jet A-1 fuel and HEFA blend ash particles are observed either inside the particle or attached on it (Fig. 3D). It is recalled that ash (or metal PM), represents the non-carbonaceous inorganic fraction of solid PM at the aircraft exhaust originating mainly from lubricating oil and to a small degree from fuel additives. Depending on the saturation level, ash may occur as separate particles attached onto soot or inside soot particles. Ash may also include fragments detached from various engine components (engine wear).

Fig. 3: HRTEM images of soot particles depicting their internal nanostructure. (A) ground idle conditions; (B): P85 thrust; (C) P85 thrust with HEFA blend showing an amorphous

external shell (greyish) around the carbon lamellae-bearing part. Black squares in (A) and (B) mark examples of crystallites: Images (A and B) are representative for both fuel types.

3.2.1. Carbon lamellae (fringe) length - Image processing

HRTEM images of primary soot particles qualitatively reveal that ground idle particles (Fig. 3A) have a lower degree of order with respect to carbon lamella length and arrangement than the P85 particles (Fig. 3B). Carbon lamella length is the continuous linear distance of an atomic carbon layer plane uninterrupted by any amorphous interference.

Fig. 4 shows histograms of fringe length frequency. It is noteworthy that each individual soot particle used for the quantification of the fringe length gave consistent results for each thrust condition and fuel type examined. Data is presented for the same engine thrust with different fuel types (Fig. 4a and b), and again for the same fuel type and different engine thrust (Fig. 4c, d). It is noted that Fig. 4e comparing P85 soot particles with and without the outer amorphous shell was determined by excluding the amorphous shell. The results indicate that soot particles with the shortest graphene lamellae, which are the most reactive, are produced by Jet A-1 fuel at ground idle conditions (Fig. 4a). The second most reactive particle type in terms of graphene length is idle soot generated by HEFA blend. The least reactive soot, i.e. the one with the highest amount of long graphene lamellae is the one produced by HEFA blend at P85 conditions. However, taking into account that around 30-40% of P85 HEFA blend soot particles are enveloped by a ~2-8nm thick amorphous (highly reactive) shell (Fig. 3C), it is quite likely that P85 HEFA blend soot is overall more reactive than P85 Jet A-1-soot. Moreover, the P85 HEFA blend particles with an outer amorphous shell have more abundant short fringes in the inner (non-amorphous) part than the particles without this shell. Finally, differences in fringe length distribution between the two fuel types are less pronounced for ground idle particles.

Fig. 4: Distribution of graphene sheet length of primary soot particles generated under idle and P85 engine thrust with Jet A-1 and HEFA blend fuel types. Bin size is 0.3nm. AR: amorphous rim.

3.2.2. Separation distances (d_{002}) and periodicity of carbon lamellae

The separation distance between adjacent carbon lamellae, d_{002} is equivalent to the distance between individual graphene planes in the crystal lattice of graphite. As a result of randomly folded carbon lamellae slipped out of alignment, known as turbostratic stacking, irregular separation distances are common in soot particles, also in the examined ones. The carbon lamellae pattern of soot particles imaged on the HRTEM images is an interference pattern between non-diffracted and diffracted electrons in the beam and is depicted in form of different degrees of brightness. For a quantification of the separation distances between carbon lamellae, the profile line plot of Digital Micrograph was applied. This tool can depict variations of the brightness across successive carbon lamellae and can be transformed to numerical data thus providing the spacing between dark and bright fringes, as well as the

periodicity. Various fields of view were selected on HRTEM images where adjacent carbon lamellae were nearly straight and formed crystallites (see earlier, section 3.2). d_{002} was measured from totally 155 to 180 carbon lamellae per particle type.

Fig. 5 presents histograms of d_{002} comparing the different fuel types (Fig. 5a and b) and engine thrust levels (Fig. 5c and d). Panel e) shows d_{002} for HEFA blend soot with and without the amorphous shell (section 3.2; Fig. 3C). The particles with the highest d_{002} percentage deviating most from that of graphite (0.335nm), i.e. the most reactive ones, are those generated at ground idle conditions using Jet A-1 fuel. At P85 (Fig. 5b), the HEFA blend soot produced particles with d_{002} closer to that of graphite compared to Jet A-1 fuel. In general, both fuel types at P85 thrust produce soot with d_{002} closer to graphite than at ground idle. This difference is more pronounced for the HEFA blend (compare Figs. 5c and d). The HEFA blend P85 soot particles show comparable d_{002} distribution patterns irrespective of the presence of an outermost amorphous shell (Fig. 5e). In Fig. 5f, the mean d_{002} values (with the standard deviation), as well as the median values have been plotted, indicating a tendency of increasing crystallinity (decreasing d_{002}) from ground idle to P85 conditions for both fuel-types, as well as from Jet A-1 soot to HEFA blend soot. As for the periodicity, maximum values of 4 and 5 were measured for idle and P85 soot, respectively, for both fuel types. The width and amount of the crystallites is higher for P85 soot than for idle one, for both fuels.

Fig. 5: (a-e): distribution of separation distances d_{002} between carbon lamellae measured from crystallites of primary soot particles generated at ground idle and P85 engine thrust with Jet A-1 and HEFA blend fuel types. Bin size is 0.025nm; (f) mean/median d_{002} values vs. thrust level / fuel type exhibiting decrease of crystallinity from ground idle to P85 and from Jet-A1 to HEFA blend. AR: amorphous rim.

Conclusively, d_{002} values and periodicity indicate a trend of increasing crystallinity from ground idle to 85% engine thrust and from Jet A-1 fuel to HEFA blend. The presence of an amorphous rim in HEFA blend P85 particles may, however, inverse this trend for the P85 conditions, possibly rendering the HEFA blend P85 soot overall more reactive than the Jet A-1 P85 one. Table 1 summarizes the morphological features of soot for the different engine thrust levels and fuel types.

Table 1: Summary of morphological characteristics of soot

	Ground idle		P85		P100
	<i>Jet A-1</i>	<i>HEFA blend</i>	<i>Jet A-1</i>	<i>HEFA blend</i>	<i>4% HEFA doping</i>
Agglomerate size (nm)	9-40 (80%)	10-40 (80%)	40-80 (35%) 80-120 (20%)	40-80 (35%) 80-120 (20%)	-
Primary particle size (nm)	5-10 (75-85%)	5-10 (75-85%)	10-25 (60%)	10-25 (60%)	-
Fringe length (nm)	0.7-1 (~45%)	0.7-1 (~40%)	0.7-1 (~35%)	0.7-1 (~20%)	-
Inter-fringe distance d_{002} mean $\pm$ std dev. / median	0.387 $\pm$ 0.033 / 0.394	0.373 $\pm$ 0.028 / 0.375	0.380 $\pm$ 0.033 / 0.376	0.364 $\pm$ 0.022 / 0.362	-
Periodicity (max)	4	4	5	5	-
Degree of graphitization (based on NEXAFS)	0.62	-	-	0.76	0.71

3.3. X-Ray Micro-spectroscopy (NEXAFS)

NEXAFS spectroscopy was applied on a series of samples collected under the following engine thrust and fuel types: (i) ground idle with Jet A-1, (ii) 85% with Jet A-1, (iii) 85% with Jet A-1/32% HEFA blend and (iv) ~100% engine thrust with 4% HEFA doped Jet A-1 fuel.

Figure 6 shows average NEXAFS spectra of analyzed material. Those which are ascribed exclusively to soot are shown in Fig. 6a and have a characteristic X-ray absorption peak at about 285.4 eV corresponding to carbon-carbon double bonding with a similar OD compared with the carbon post-edge between 305-320 eV [39]. These spectra were additionally identified as soot, based on the observed OD at 288.6 eV being less than or equal to the peak at 285.4 eV. The peak position and height found in the analyzed spectra are qualitatively in agreement with previous literature [11, 26, 36]. Parent et al. [26] investigated soot generated

from an aircraft engine operating with common kerosene fuel at 85% load using electron yield NEXAFS spectroscopy (black dashed line in Fig. 6a). The spectrum from bulk primary soot particles is similar to the ones obtained here for HEFA blend soot and for soot doped with 4% HEFA at high thrust and shown as the red and green lines, respectively. Similar spectra of soot in atmospheric samples depicting carbon-carbon double bonding peak position (285.4 eV) are reported by [36].

In addition to soot, organic matter was also found on some of the analyzed particles from all run conditions and fuel-types indicated by a peak at 288.6 eV corresponding to the carboxyl functionality (Fig 6b; [36]). We suggest that this organic matter is mixed with soot, as both 285.4 (carbon-carbon double bonding) and 288.6 eV peaks are always observed together. Most peak positions for organic matter are found at 288.6 eV with one exception at 286.0 eV seen for ~100% engine load with 4% HEFA-doped fuel, indicating phenolic (C-OH) bonding [39]. We do not report on precise proportions of particles that are either soot or organic-type using NEXAFS, as this would require investigation of a very large amount of particles and is beyond the scope of our work. The exact organic-type could not be clearly identified using STXM/NEXAFS. Some theoretical possibilities include deposited particles of engine lubrication oil or particles nucleated from semi-volatile organics in the exhaust as it cools after leaving the engine or condensation of organic vapor to buildup organic matter on the substrate during impaction. However, we do not consider these possibilities as likely because we never observed spherical shaped particles (droplets) indicative of condensation on a substrate. Furthermore, the sampling strategy (heating and prompt dilution) minimizes the potential for homogenous nucleation. It is also unlikely, that the signal is from uniform condensation of organic matter because NEXAFS spectra are normalized to the substrate signal exactly adjacent to particles. Organic matter with a characteristic peak at 288.6 eV has been observed to be always associated with ambient soot [32, 36, 39-42]. Diesel soot [11] also

has both carbon-carbon double bonding and organic matter, however, peak positions differ slightly from ours and other previous literature.

Figure 6: NEXAFS spectra of soot (a) and soot with organic matter (b) on substrates for particles collected under different engine thrust conditions and fuel combinations. Spectra from previous studies on soot and associated organic matter (if present) are shown vertically shifted downwards for clarity for 85% engine thrust with unblended fuel (black) [26], ambient soot particles (dark grey) [36] and diesel exhaust (light grey) [11]. The black horizontal lines above the spectra mark energy ranges from 284.9-285.5 eV, 286.7-287.3 eV, 287.0-288.5 eV, 288.3-290.0 eV and 290.0-290.7 eV corresponding to functionalities R(C=C)R, R(C-OH), R(C=O)R, R(C=O)OH and CO₃, respectively.

Braun et al. [43] investigated how X-ray exposure can chemically transform or damage organic matter associated with diesel soot and observed that increasing X-ray exposure would decrease absorption at 288.6 eV while increasing absorption at 290.2 eV attributable to CO₃ production. We did investigate damage due to X-ray exposure of the samples collected at 85% load with a 32% HEFA blend and found that even doubling the X-ray dose does not alter X-ray absorption spectra (Fig. S3). Furthermore, all spectra did not have clearly discernable peaks at 290.2 eV with the exception of a single particle from samples collected at ~100% engine load doped with 4% HEFA fuel (Fig S2). Therefore, we claim the vast majority of particles may not have been susceptible to the beam damage as observed by Braun et al. implying a different organic composition despite a qualitatively similar spectral appearance.

Finally, we investigated oxygen NEXAFS spectroscopy on organic matter from the same sample and found similar spectra compared to organic matter associated with soot from Moffet et al. [39] (Fig. S2). We note that quantification of soot in atmospheric aerosol particles and how they are mixed with organic and inorganic material has proved highly useful, especially for predictions of direct radiative effects [32, 44]. We conclude that those particles emitted from aircraft engine run on both conventional and alternative fuels can be identified using existing methods.

The degree of graphitization in soot particles is an indicator of soot reactivity, i.e. the more graphite-like particles tend to have less reactivity (e.g. [19, 20]). In terms of NEXAFS related observables, the degree of graphitization in carbonaceous material can be defined as the ratio, $r = OD_{C=C} / OD_{C_{edge}}$, where $OD_{C=C}$ and $OD_{C_{edge}}$ is the pre-edge subtracted OD at the carbon-carbon double bonding peak (285.3 eV) and the C-edge step at 292 eV [31, 45, 46]. Compared to graphite in which $r = 1.55$ [45], our soot samples (Fig. 6a) have $r = 0.76$, 0.71 and 0.62 when the engine was operated with 85% load and HEFA blend, ~100% load and 4% HEFA-doped Jet A-1 fuel and ground idle with Jet A-1 fuel, respectively (Table 1). We note that [26] using 85% load and conventional fuel had $r = 0.74$. This implies that the HEFA blend used in our study at climb-out conditions has almost no impact on the degree of graphitization expressed in the NEXAFS spectra. It is important to note the spatial scale of the STXM/NEXAFS technique is not capable of resolving amorphous carbon layers at soot surfaces with a thickness of a few nanometers, as seen on the HRTEM images (Fig. 3). Thus, we cannot claim this amorphous rim was not an organic carbon coating on the surface of primary soot particles.

4. Discussion

The smaller size of ground idle soot agglomerates and primary particles compared to that of P85 soot, for both fuel types investigated implies that ground idle soot is the more reactive one in this respect. The smaller size of ground idle primary particles can be attributed to soot inception and oxidation mechanisms in the engine combustor, which depend on air to fuel ratio, temperature and residence time. However, the exact formation mechanisms of soot are highly complex and it is hard to distinguish which parameter(s) are responsible for the observed differences. More research is needed to clarify these issues.

The lower degree of crystallinity of ground idle soot compared to P85 soot implies also higher reactivity and indicates that idle particles are richer in organic carbon relative to elemental carbon. This inference is in line with the findings of [47] and [10], who reported that the elemental carbon to organic carbon ratio increases with engine thrust level. An increase in the degree of crystallinity of soot with engine power is reported also by [15], in a TEM study of soot generated by a CFM-56-3 engine aboard a DC-8 aircraft fueled by a kerosene fuel type JP-8. On the other hand, Parent et al. [26], who studied the nanostructure of soot produced by a different engine (PowerJet, SaM146-1S17) burning Jet A-1 fuel and operated on a test facility (SNECMA, Villaroche, France) found no significant variations in soot nanostructure with engine operating regimes. The above authors comment that different engines and fuels complicate a direct comparison of soot generated under similar engine operating regimes and that the engine technology probably influences the combustion conditions and the soot characteristics.

As already mentioned in the Introduction, one parameter that can influence the degree of crystallinity is temperature. Temperature which favors graphitization (de-hydrogenation) increases with engine thrust level. This would explain our results as to why the P85 soot is more crystalline than the idle one. In this respect, Vander Wal et al. [15] suggest that the change in soot nanostructure from idle (more disordered) to P85 (better ordered) is driven by

changing species contributing to soot surface growth (PAHs, likely fuel-borne at low temperature and acetylene at higher temperatures).

A trend towards increasing degree of soot crystallinity was observed in the present study for ground idle conditions when Jet A-1 was blended with HEFA fuel. At 85% thrust, the situation becomes more complicated due to the presence of a disordered 2-8nm broad outermost particle shell in a considerable part of soot particles studied. The fraction of P85 HEFA blend soot without the amorphous outermost shell shows a slightly more graphitized nanostructure than P85 Jet A-1 soot. Moreover, the inner (crystalline) part of the P85 HEFA blend particles with the amorphous shell have shorter fringe length (indicating lower crystallinity) but slightly lower inter-fringe distances (indicating higher crystallinity) than the HEFA blend soot particles without this shell. It cannot be judged which of the above opposing characteristics (fringe length or inter-fringe distance) weighs more for ascribing a net result on the degree of crystallinity.

The experiments of the present study indicate that the addition of HEFA favors the formation of slightly more graphitized soot. In this case, temperature can be considered as an influencing factor promoting graphitization of HEFA blend soot, as there are indications that the addition of purely aliphatic species, such as HEFA fuel, increases slightly the local flame temperature in the rich section of the combustor. The pure HEFA component used in this study had a slightly higher specific energy content of 44.2 MJ/kg versus Jet A-1 used which had 43.3 MJ/kg). However, considering the partial and relatively extended (30-40%) presence of soot with a nearly amorphous shell when using P85 HEFA blended (and 4% HEFA-doped) Jet A-1 fuel, the soot generated with HEFA (blending and doping) at high thrust is overall less crystalline, i.e. more reactive than the Jet A-1 one. Moore et al. [48] investigated HEFA blended Jet A-1 fuel (50/50) at in-flight cruise conditions and mention that the greatest effect of the HEFA blend on emissions is associated with a reduction in black-carbon-equivalent mass. The finding of these authors is in line with the overall less crystalline P85 HEFA blend

soot particles identified in the present study. The crystalline part of the soot particles generated by burning HEFA blend can be ascribed to dehydrogenation (graphitization) and reactions related to fuel pyrolysis (mainly production of C_2H_2 species) of Jet A-1 components of the blend, possibly promoted by HEFA-induced higher temperatures. As a result, C=C chains are formed leading to a graphitized structure of soot particles. The amorphous shell of soot particles could potentially be attributed to an insufficient quenching and oxidation of soot precursors within the combustor which is probably favored for the HEFA blend. Further research is needed to understand the precise mechanism (or mechanisms) involved in the formation of such an amorphous shell at the outermost part of soot particles.

As stated in the Introduction, studies on soot reactivity refer strictly to its oxidation capacity. However, it is plausible to hypothesize that soot reactivity cannot be limited to its capacity for oxidation only, but refers generally to the presence of atoms on the particle surface and bulk available for reaction. Such reactions may occur when soot comes into contact with its surrounding, i.e. atmospheric components or cells. Aircraft soot emissions generated at ground level (ground idle) and close to ground level (climb out) contribute to an increase of local air pollution and bear the risk to cause health damage. On the other hand, soot at altitude has an effect mainly on tropospheric chemistry and global warming. The generation of aircraft soot with high reactivity at and close to ground level can be considered as having both benefits and disadvantages: the beneficial part is related to the stage of soot formation in the engine where it can still react with oxygen and be partly or totally eliminated, i.e. before reaching the exhaust. As soon as it reaches the ambient air and can be inhaled, highly reactive soot can prove more harmful than less reactive one, as it has a higher capacity to react with its surrounding, also with cells. The results of the present study indicate that the soot type with the highest reactivity and thus the most prone to react with oxygen and probably also when it comes into contact with cells is the one generated at ground idle conditions with the Jet-A-1 fuel, due to the small particle size and defected nanostructure. This finding is of high

significance for the people working at airports and/or living in the surrounding areas as these conditions at airports are prevalent. The HEFA blend ground idle (small size), as well as the P85 soot (amorphous shell) can be also considered as highly reactive. Whether the particle size or the presence of the amorphous shell is the more decisive parameter for rendering soot more reactive cannot be evaluated at this stage of research. Thus it cannot be predicted, based on soot morphology, which soot type shows higher reactivity. It is also not known how soot chemistry influences cell dysfunction and damage. Despite these shortcomings, ample work has shown that soot can generate reactive oxygen species (ROS) in lung epithelial cells [49] which is known to cause adverse health effects in humans [50]. To our knowledge, any link between an amorphous rim on primary soot particles and generation of ROS species has not been investigated in previous literature. The lack of crystallinity may allow for greater reaction pathways and generation of more ROS exacerbating any health impacts of soot exposure beyond what is already expected. Interestingly, a study on health effects of aircraft exhaust carried out within the framework of the same research project revealed that among ground idle and P85 soot with Jet A-1 and HEFA blend, ground idle soot with Jet A-1 is the one with the highest impact on bronchial cells (Jonsdottir et al., Nature Comm. Biology; in revision). These results are in line with the detailed soot morphology results obtained here, as the idle Jet A-1 soot was shown to possess a combination of morphological characteristics indicating very high reactivity. One should, however, consider that HEFA blend produces lower amounts of soot as compared to conventional, Jet A-1 kerosene (both particle number and mass; Table S1 in Supplementary Information). The net effect among the roles of soot reactivity versus soot amount with respect to potential health risk needs still to be evaluated and should be taken into consideration in order to assess the benefit of alternative fuels. From the environmental point of view, the apparent nano-structural defects of the ground idle soot, as well as the ones of the P85 soot from HEFA blend (or HEFA-doped Jet A-1) with the outermost amorphous shell imply the presence of numerous reactive sites at the soot surface,

such as unsaturated organics or hydroxyl groups, for instance. Indeed, oxygenated functional groups were always observed on all samples from STXM/NEXAFS analysis. These oxygenated groups have a variety of functional forms due to the various carbon K-edge absorption peaks (Fig. 6b). We also note that identified soot spectra in Fig. 6a further suggest reactive sites due to the observed oxygenated groups. Of course, the common and main feature in soot spectra is the C=C peak which occurs at a consistent X-ray energy (285.3 eV) in agreement with previous studies [26, 39]. These soot types with numerous defected sites may have a different behavior towards atmospheric components compared to more graphitized soot. The surface of the more defected particles may have, for instance, a higher ability to attract or repulse water favoring or not the formation of contrails but this effect is related to soot present at altitude and is beyond the goal of the present paper.

5. Conclusions

Based on both the physical and chemical characterization of aircraft soot, the following conclusions can be drawn from this study.

1. The soot type that shows the highest reactivity is the one produced with Jet A-1 fuel at ground idle conditions. Assuming that reactivity is related to the presence of atoms on the particle surface and bulk available for reaction, this soot type has the potential to react most with oxygen and be eliminated during and immediately after its generation. It is also the soot type that would be most prone to react with the atmospheric environment and probably also with cells, when inhaled.

2. At ground idle conditions, blending of HEFA with Jet A-1 fuel decreases slightly the reactivity of the generated soot. Thus, as far as health risks are concerned, mixing of Jet A-1 with HEFA could possibly prove beneficial at airport areas where ground idle conditions are prevalent.

3. At climb-out conditions the HEFA blend soot shows higher reactivity thus potentially bearing higher health risk compared to Jet A-1 produced soot at this thrust level. However, HEFA blending produces lower soot amounts than Jet A-1 and this needs to be taken into account besides soot reactivity, in order to obtain the net effect.

4. The reactivity of soot decreases with increasing engine thrust level (from ground idle to climb-out conditions). HEFA blending may result in a more moderate reactivity decrease at climb-out conditions, as inferred from the presence of a reactive outermost shell in nearly one third of the investigated soot particles.

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