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Impact of Biofuel Blends on Black Carbon Emissions from a Gas Turbine Engine

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Abstract

Presented here is an overview of non-volatile particulate matter (nvPM) emissions, i.e. “soot” as assessed by TEM analyses of samples collected after the exhaust of a J-85 turbojet fueled with Jet-A as well as with blends of Jet-A and Camelina biofuel. A unifying explanation is provided to illustrate the combustion dynamics of biofuel and Jet-A fuel. The variation of primary particle size, aggregate size and nanostructure are analyzed as a function of biofuel blend across a range of engine thrust levels. The postulate is based on where fuels start along the soot formation pathway. Increasing biofuel content lowers aromatic concentration while placing increasing dependence upon fuel pyrolysis reactions to form the requisite concentration of aromatics for particle inception and growth. The required “kinetic” time for pyrolysis reactions to produce benzene and multi-ring PAHs allows increased fuel-air mixing by turbulence, diluting the fuel-rich soot-forming regions, effectively lowering their equivalence ratio. With a lower precursor concentration, particle

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inception is slowed, the resulting concentration of primary particles is lowered and smaller aggregates were measured. The lower equivalence ratio also results in smaller primary particles because of the lower concentration of growth species.

Graphical Abstract

1. Introduction

The importance of biofuel in the aviation industry has been increasing due to their environmental benefit of mitigating greenhouse gas emissions and carbon footprints.^{1–5} Aviation related non-volatile particulate matter (nvPM) emission, referred to as elemental carbon (EC) in atmospheric or aerosol science or in combustion contexts as “soot” contributes to both local and global air pollution.^{6–10} The overall emission of CO₂ from fuel is expected to double by 2050 and the emission from global aviation increase by three to four fold compared to the 2000 levels.^{1, 11–12} Elemental carbon aerosols absorb solar radiation strongly and reduce the surface albedo which results in positive radiative forcing and profoundly increases the global warming.^{4, 13} Additionally, jet aircraft nvPM (soot) size range is well within the PM_{2.5} classification, often less than 100 nm with ability then to reach lung alveoli. Epidemiological studies conclude that inhalation of particulate matter such as soot has many negative impacts on human health, including respiratory and cardiovascular disease.^{14–19} Thus controlling elemental carbon emission is essential to reducing its direct impacts on public health and indirect impact on climate change. By 2050 the International Air Transport Association (IATA) is aiming to reduce the aviation related air pollution by 50% as compared to levels observed during the 2000 to 2005 period.^{1,11,12} The use of sustainable biofuels or its blends with jet fuel is critical to achieve this goal in addition to engineering advancements of increasing the engine efficiency.^{1, 20–22}

Biofuels derived from bio-feedstocks such as camelina, jatropha and algae are potential fuel source for the future aviation because of their ability to ameliorate the issues of fossil-based jet fuel.^{23–26} It is reported that 50% Camelina blended Jet-A fuel reduces the particulate number and mass emission by (50–70)% compared to pure Jet-A fuel.¹ Gas turbines have flexibility of running a wide variety of fuels which enable them to use biofuel without further modification of the current aircraft engine design or fuel distribution system.^{3, 20, 27–28} (Operational environments impose additional thermophysical property requirements). A number of studies have shown that the addition of 50% synthetic biofuel to conventional fuel is allowable without reducing the engine efficiency.^{29–30} Bio-based alternative aviation fuels consist of a mixture of long chain saturated hydrocarbons (C₈–C₁₆) with minimal aromatic content due to catalytic hydrotreatment whereas petroleum-based jet

fuels contain about 20% aromatics in addition to sulfur, and linear and cyclic paraffins.^{25, 31} Reduced nvPM mass emissions from bio-based fuels and their blends with petroleum based fuels^{1,4,10} has been captured by a predictive relation for emission index attributing the decrease to fuel hydrogen content. However, our understanding of biofuel impacts on combustion dynamics affecting this observed mass decrease and intertwined related soot characteristics is incomplete, requiring systematic, fuel-dependent studies.

Combustion-produced soot has complex chemical and physical properties which vary with formation environment and fuel chemistry. The measurement of mass, number and size distribution do not capture the physical scales of soot and additional techniques such as high-resolution transmission electron microscopy (HRTEM) are required.^{32–35} It has been shown that the aggregate size, morphology, concentration, and internal nanostructure of soot reflect the combustion dynamics and the soot formation process.³⁶ However, there are yet relatively few studies of these physical metrics for soot emitted by a gas turbine engine.

Nanostructure is key to understanding the chemical and thermal environment of soot formation processes.^{36–38} Our previous studies show that the two-dimensional curvature in nanostructure is directly related to the formation of the cyclopentadiene (C5) reflecting the local fuel/oxygen equivalence ratio(ϕ) for partial premixed combustion.^{37, 39–43} A recent study on the nanostructure of aircraft soot found crystalline structure to increase with increasing engine thrust.⁴⁴ Primary particle size and aggregate morphology study is additionally required for understanding the gas-turbine combustion of bio-jet fuels and related environmental impacts. Primary particle size governs the particulate surface area for interaction with other pollutants such as ozone^{45–46}, relevant to its atmospheric aging by surface reactions with these pollutants. Aggregate size and morphology govern light scattering and absorption properties, relevant to its atmospheric warming potential as soot is considered the second larger contributor to the greenhouse gas effect.^{47–48}

Here we report a systematic evaluation of particulate emissions from a J-85 turbojet engine for three different fuel compositions; Jet-A, 30% and 70% Camelina blended Jet-A at various engine output conditions to investigate the impacts of fuel composition on soot production. Aggregate morphology and soot nanostructure are analyzed by HRTEM to study the formation process. It is found that, the combustion dynamics of aromatic rich conventional Jet-A fuel is different from the biofuel blended Jet-A fuel and hence the size, concentration, morphology and internal structure of corresponding soot emissions are also different.

2. Experimental Approach

These tests were conducted in 2018 by the U.S. Environmental Protection Agency, in cooperation with Arnold Engineering and Development Complex (AEDC, U.S. Air Force), as part of a series of studies entitled VARIABLE Response in Aircraft nvPM Testing (VARIAnT) field campaigns. Tests were performed at the Arnold Engineering Development Center (AEDC) in Tennessee, elevation 325 m AMSL.

2.1 Sample Collection

Particulate emissions from the J-85 engine for each fuel and engine thrust were collected with a sampling system having temperature, pressure and dilution controls designed to minimize changes to the exhaust PM before being measured. Dilution factors ranged between 3 and 7. TEM grids were collected at the end of a ~30 m sampling system directly onto an ultrathin carbon grid with a Naneos Partector TEM sampler. Direct collection of particulate matter on TEM grid has benefit over filter-based collection which requires subsequent dispersal of particulate upon a TEM grid. This re-dispersal process may cause further incidental aggregation of particulate matter and the recognition of individual aggregate can then become challenging. However, for high magnification TEM measurements on nanostructure within individual primary particles, filter collected soot was transferred to lacey carbon grids using a dry transfer method. For mass-based emission indices of black carbon, filter collection was employed. Elemental versus organic carbon (EC/OC) split was determined using a Sunset Laboratory OC-EC aerosol analyzer, applying NIOSH method 5040. Samples were collected across a range of operating conditions for the three fuels tested.

2.2 Soot Characterization by HRTEM

High resolution transmission electron microscopy (HRTEM) images are taken using a FEI Talos F200X having 0.12 nm resolution. The instrument is operated at 200 kV and images are taken at various magnification ranging from 10k-650k. HRTEM images of soot particles collected on ultrathin carbon film was taken as received. The digital images are analyzed using the ImageJ software package to measure the size of aggregates and primary particles. Approximately 20–25 TEM images, each having a total of 150–200 aggregates, are analyzed to provide an accurate information on particle size and their distribution. Aggregate size is reported for circular equivalent area based on the 2D projected area as measured in ImageJ by outlining aggregates. Primary particle size is reported for similar size sampled measurements – with each particle being measured along two orthogonal axes and then averaged. For fringe analysis, digital images are processed using custom image processing algorithms written with MATLAB software.^{49–51} The obtained data on fringe tortuosity are further analyzed using the software program KaleidaGraph™. (Tortuosity is a measure of the curvature of the fringes). Figure 1 shows an example of primary particle and nanostructure of an aggregate produced by gas turbine engine while using Jet-A fuel at 100 % thrust.

2.3 Fuel Compositions

Neat (unmixed, pure) Jet-A, and two blends of Camelina with Jet-A fuel, with respectively 30 and 70-% Camelina were tested. The Camelina fuel, provided by the U. S. Air Force Research Laboratory at Wright Patterson Air Force Base, OH, was derived from *camelina sativa*, a low-input non-food oil seed plant. This type of fuel is manufactured by catalytic hydro-processing to produce primarily *n*-paraffins and iso-paraffins, which meets all applicable specifications established by ASTM Standard D7566 for alternative jet fuel.^{52–53} Typical properties of these fuels are provided in Table SI1 and fuel flow rate (gram per

minute, g/m) at corresponding thrust values are tabulated in Table SI2 in the supporting information.

3. Result and Discussion

3.1 Soot Formation Pathway & Fuel Dependence

Soot begins with fuel pyrolysis producing acetylene, benzene, buildup of multi-ring aromatics, leading to particle inception.^{54–56} Thereafter particle growth and coalescence produces aggregates. Though considered as separate steps for modeling purposes, these steps overlap spatially and temporally.^{57–58} Given the essential reactive role played by aromatics in particle inception – a requisite concentration is required – whether supplied by fuel or produced by pyrolysis, as the operative postulate. With high aromatic content, Jet-A can begin soot formation early – meaning that particle inception and growth can occur earlier than for a fuel without aromatic content for which pyrolysis processes are first required, which imposes a kinetic time delay (for the required pyrolysis and aromatic buildup reactions to occur).^{59–60} Effectively Jet-A fuel can start along the soot formation pathway (see Figure 2) at a higher (more progressed) point along the process than a neat paraffinic biofuel or its blends. These latter fuels start at the beginning of the formation pathway, due to their lower (or absent) aromatic content. Pyrolysis reactions must first occur to produce aromatics at sufficient concentrations for the subsequent stage of particle inception. As for the biofuel, the other paraffinic fuel components in Jet-A are less active in contributing to soot formation – requiring all the same pyrolysis processes and aromatic buildup reactions as their counterparts in the biofuel.

The main difference between Jet-A and biofuel is in the aromatic content. Petroleum based jet fuels contain 18 – 23 wt.% aromatics (per ASTM D1655, DEF STAN 91–91, Specification Standards for Aviation Turbine Fuels) with the balance consisting of normal, iso- and cyclic paraffins. Plant oil derived biofuels offer no aromatic content. Dependent upon the catalytic process these hydrogenated (and deoxygenated) biofuels consist of a mixture of branched and linear paraffins. Blends of the two fuel types dilute the aromatic content proportionately.

Fuel-carried aromatics bypass the soot inception processes as well as the molecular growth stages, and directly form soot nuclei. Their replacement with paraffins kinetically delays formation of a sufficient concentration while turbulence-induced mixing contributes by lowering the fuel concentration in soot forming regions. While temperature will increase as a result of mixing and accelerate reactions, the observations as shown can be rationalized by the postulated competition between kinetic pyrolysis and turbulence dilution/mixing timescales.

In the very high turbulent flows found inside a jet engine combustor, fuel-air mixing competes with the kinetic timescales for fuel pyrolysis.^{61–67} Jet-A with aromatic content can form soot once a favorable temperature level is reached but biofuel and its blends with Jet-A are restricted by the kinetic delay for pyrolysis reactions to produce sufficient aromatics for primary particle nucleation – allowing turbulence to dilute the fuel-rich, soot-forming

regions, lowering their local equivalence ratio. The implications and consequences of this hypothesis are discussed below for specific results.

3.2 Aggregate Size and Morphology

Representative HRTEM images of non-volatile particulate matter (nvPM) emitted from J-85 turbojet with Jet-A and blends with Camelina biofuel at 100% thrust are shown in Figure 3. As illustrated, aggregate size decreases with decreasing fuel aromatic content. With lower aromatic concentration, an increasing need is placed on fuel pyrolysis to reach a critical level for inception and growth. The aforementioned time delay allows greater fuel-air mixing to occur, lowering the fuel-air equivalence ratio in the soot forming regions.

As a consequence of turbulence-induced mixing the aromatic concentrations sourced from fuel and produced by pyrolysis of paraffinic components are lower, as are the overall hydrocarbon concentrations in these soot forming regions. Primary particle inception occurs in a local environment with diluted aromatic concentration with result that their number concentration is lower. Additionally, growth species' concentrations are also reduced leading to smaller primary particles. In turn the smaller primary number concentration alters the aerosol dynamics of coalescence to produce smaller aggregates.

There is also a significant difference in the aggregate morphology of particulate matter produced from the three fuels, as shown in Figure 3. For Jet-A fuel, particle inception and growth occur in regions of higher equivalence ratio, ϕ producing a large number concentration of primary particles, favoring reaction-limited cluster growth, resulting in a larger, more compact aggregates.⁶⁸⁻⁶⁹ By contrast, particle inception and growth occur in leaner regions for biofuel-blended Jet-A fuel, producing a smaller number concentration of primary particles, favoring diffusion-limited cluster growth, and producing smaller, dendritic aggregates.⁶⁸⁻⁶⁹ However, as aggregate size becomes smaller the observable difference between compact versus dendritic diminishes because of the few primary particles being insufficient to define the fractal structure of the collected aggregates.

The variation of aggregate size as a function of engine thrust is shown in Figure 4a. The aggregates size increases linearly with engine thrust level for the given fuel. The correlation coefficient is >0.98 for all linear fits, indicating a strong linear correlation of aggregate size with power. The obtained slopes are 0.45, 0.28 and 0.09 for Jet-A, 30% and 70% Camelina blends fuel respectively. Aggregate size changes most rapidly as a function of power for Jet-A fuel followed by 30% and 70% Camelina blends. This reflects the aromatic contribution to particulate formation. At higher power, temperature increases which accelerates pyrolysis reactions and formation of aromatic intermediates – but this is the same for all fuels across power levels. Higher fuel-sourced aromatic concentrations respond rapidly to higher temperature by primary particle nucleation, compared to paraffinic contents which first require pyrolysis and aromatic growth reactions. A higher rate of primary particle nucleation results in a larger number concentration and commensurately, larger aggregates as a result of increased primary particle coalescence.

Overall, aggregate size depends less upon power with decreasing fuel aromatic levels. Fuel-carried aromatics lead to high power sensitivity (i.e. steeper slope) for aggregate size

because of turbulence fuel-air mixing (or relative lack thereof). With decreasing fuel aromatic levels, the aromatics required for particle nucleation (and as species contributing to particle growth) must form via pyrolysis reactions.⁷⁰ Higher power levels increase temperature but also enhance turbulence which in turn decreases the average equivalence ratio (ϕ) of fuel-rich regions while shortening their lifetime. This balance of competing effects is manifested by lowered dependence of aggregate size upon power level, as quantified by the indicated correlations. And, given the higher H/C ratio for biofuel compared to Jet-A, aggregate size decreases for any given power level with blend level.

3.3 Primary Particle Size

Primary particle size increases with increasing aggregate size for each fuel across engine thrust levels as shown in Figure 4b. This trend reflects an encompassing trend and unifying conditions connecting primary particle and aggregate size to fuel composition and equivalence ratio (ϕ). Aromatics serve both as precursors for particle nucleation and as growth species. As aromatic concentration increases, primary particle number concentration increases while they become larger. Hence, for any given thrust, (with equivalent temperature and turbulence levels), primary particle size would be expected to be proportional to aromatic fuel content if this were the governing factor for growth. As observed, primary particle sizes are highest for Jet-A, followed by the 30% and 70% blends respectively, as illustrated in Figure 4a. The increasing size with increasing power levels reflects a combination of factors: higher fuel flow, higher temperatures and increased turbulence. The positive trend for each fuel suggests that the first two factors dominate the third which would act to reduce growth species concentrations.

3.4 Elemental Carbon Concentrations

This higher growth species' concentration and longer duration by virtue of early particle inception is supported by elemental carbon emission indices, measured as EC. A higher EC concentration is obtained for Jet-A fuel compared to the Camelina blends, as shown in Figure S11 in the supporting information. For any given power, EC is lower for fuel blends with a higher proportion of biofuel. With increasing power, EC increases, suggesting fuel flow supersedes turbulent mixing resulting in either higher number of soot forming regions and/or higher local ϕ associated with such regions forming more soot. Notably, the dependence of EC on engine thrust is weakest for the maximum biofuel blend – demonstrating sensitivity of soot formation to fuel composition. Observed by several studies, this is also supported by McEnally and Pfefferle's work which shows that the soot formation depends strongly on the molecular structure of the fuel.^{71–73} The yield sooting index (YSI) was found to increase with increasing the aromatics content of the fuel.⁷⁴ While empirically this can be cast in terms of H/C ratio, the determining factor is rooted into the chemical kinetics; the weaker dependence on power for biofuel blends indicates the increasing reliance on fuel pyrolysis for aromatic production.

3.5 Nanostructure Dependence upon Biofuel Blend Level

Aromatic concentration drives primary particle number concentration which in turn drives aggregate size. The high-resolution of HRTEM enables looking into the nanostructure of soot primary particles. Dependent upon formation chemistry and combustion environment, it

is quantified by image fringe analysis, observed here is that with increasing biofuel content, tortuosity increases while lamellae length decreases as summarized in Figure 5. The change in tortuosity with fuel chemistry indicates the dependence of inception and particle growth on local fuel-air ratio as dependent upon fuel aromatic content. Because Jet-A has a large aromatic content, soot formation processes follow a different pathway compared to the Camelina based fuels, as described earlier in this manuscript. As postulated, the required pyrolysis reactions also delay soot inception in blended fuels, allowing greater partial premixing resulting the formation of C_5H_5 containing species such as cyclopentadienyl radical (and related aromatics) which is responsible for highly tortuous lamellae.^{36, 70} (The ratio of C_5H_5/C_6H_6 determines curvature degree). To quantify these differences, digital image processing has been performed using custom algorithms.^{49, 51} The results of such analysis are summarized in Figure 6a. Figure 6b shows a skeletonized image illustrating the fringe tortuosity. Boehman and co-workers also reported the comparison of soot nanostructures for the diesel and its blend with biofuel. The soot nanostructure was found to be more curved and disordered for the biofuel blend compared to the diesel soot which are regular having a core-shell structure.^{38, 75}

3.6 CHEMKIN Comparisons

Figure 7 is a schematic representation of the possible fuel-rich pockets developing during the pyrolysis of Jet-A and biofuel in a gas turbine engine. Larger and higher fuel-rich pockets represented in black are produced in pyrolysis of Jet-A fuel, while smaller and lower fuel-rich pockets represented in gray are produced in pyrolysis of biofuel. The local ϕ in these soot forming regions affects their chemistry. Partial premixing introduces C_5H_5 , the cyclopentadienyl radical. As detailed elsewhere a dominant formation path $C_2 + C_3$ recombination to produce C_5H_5 . As known from fullerenes, C_5H_5 is necessary for lamellae curvature. To support this conjecture, chemical kinetic simulations using a commercial software package (CHEMKIN) were carried out. The simulations used a perfectly stirred–plug flow reactor to explore the pyrolysis reactions for aromatic or alkane hydrocarbons, as represented in the model by m-xylene and n-dodecane, respectively. Together these components have been widely used in surrogates for jet fuel, capturing the relevant thermophysical properties in this context.^{76–77} As the CHEMKIN calculation results in Figure 8 show, the representative aromatic m-xylene exhibits low C5/C6 ratios over the range of ϕ between 2 – 8 while n-dodecane shows higher ratios, with a maximum at an equivalence ratio of 5.

With increasing biofuel content, particle inception and growth are slowed down by the reduced aromatic content. The longer kinetic delay allows greater turbulent mixing, lowering the local ϕ . As shown in Figure 8, curvature increases with biofuel blend level – suggesting that particle formation occurs within the range of ϕ wherein the benzene required for C_5H_5 formation arises by n-dodecane pyrolysis. These calculations support the formation of C_5H_5 based on paraffinic content and partial premixing as fostered by turbulence lowering ϕ in the soot forming regions.

4.0 Conclusion

A systematic characterization of black carbon produced by a gas turbine engine at various engine thrust and fuel conditions is presented. The HRTEM images are analyzed to study the variation of aggregate size, morphology, and nanostructures with engine thrust and fuel composition. Aggregate size increases with power, the dependence is lower for fuel blends with higher biofuel content and for any given power aggregate size decreases with increasing biofuel (paraffinic) content. The size of the primary particle and aggregate scale correlate for all fuels. The HRTEM results also show that the fringe tortuosity increases with increasing biofuel content. The common thread rationalizing these observations is the competition between particle nucleation and growth – dominated by fuel-carried aromatics and turbulence-induced mixing – acting to decrease local ϕ . Aggregate morphology, primary particle size, and nanostructure are dependent upon biofuel blend levels, mediated by the combustion dynamics, specifically the soot formation processes. At present these findings highlight important considerations of using biofuel over the conventional fuel in aircraft to minimize the emission of soot benefitting human health and the environment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
HRTEM image of an aggregate showing primary particle and nanostructure.

Figure 2. Schematic representation of soot formation process highlighting the effect of aromatic content in Jet-A fuel in combustion kinetics compared to biofuel having primarily paraffinic molecules.

Figure 3.

Representative HRTEM images of soot emitted from J-85 turbojet with Jet-A and blends with Camelina biofuel at 100% thrust. The aggregate size decreases with decreasing fuel aromatic content. (a) Jet-A (b) 30% camelina blend, and (c) 70% camelina blend.

Figure 4.

(a) Variation of aggregate size as a function of engine thrust for Jet-A, 30% and 70% camelina blend fuels and (b) correlation between primary particle size and aggregate size irrespective of fuel and thrust.

Figure 5. High resolution TEM images showing nanostructures of soot particles formed at 100% thrust from three different fuels; (a) Jet-A, (b) 30% camelina blend and (c) 70% camelina blend.

Figure 6.

(a) Variation of fringe tortuosity of soot particles emitted at 100% thrust from three different fuels; Jet-A, 30% camelina blend and 70% camelina blend, and (b) skeletonized image of corresponding HRTEM image for Jet-A fuel illustrating fringe tortuosity.

Figure 7.

Schematic representation of fuel-rich pockets with time and fuel type. Darker and larger region indicate a fuel-rich pocket with higher fuel-air equivalence ratio (ϕ). With turbulence, the fuel content of rich regions is reduced as is the corresponding growth species concentration – slowing particle inception and rate of surface mass addition.

Figure 8.
Mole ratio plot of C5/C6 as a function of ϕ at 1600 K