Classification of a Graphitized Anthracene Soot Sample via Image Analysis

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Abstract

Carbonous soot has abundant negative environmental impacts, both on human health and on climate change. Studies have already established that black soot produced during combustion of fossil fuels and biomass results in a number of diseases and mutagenic defects, while also being the second largest contributor to man-made climate change. These studies have resulted in the implementation of a number of soot reduction methods and further research on these topics. The formation mechanisms and the effects of combustion variables on soot nanostructures have been thoroughly studied; however, the health effects of different soot nanostructures have yet to be studied. A HRTEM image of a graphitized anthracene soot particle was studied using image analysis to place the soot into one of the three soot categories: amorphous, highly curved, or graphitic. The distribution of the structural element orientation angles was shown to congregate around 90°, meaning that the elements are mostly parallel to each other. The predominantly parallel structural elements of the graphitized anthracene soot indicate that the sample is a graphitic soot. These findings are consistent with previously hypothesized soot formation mechanisms. These insights can contribute towards the current knowledge of how soot forms in combustion applications like engines, and how these engines can be improved to reduce soot formation. It is recommended that soot like the one observed in this study be reduced in engines to reduce their effect on climate change. It is also recommended that further research be done to determine whether different soot nanostructures, like the graphitic nanostructure observed here, result in different health effects.

Introduction

The carbon-rich black soot present in diesel exhaust due to incomplete combustion\textsuperscript{1,2} is of interest for two reasons: climate change and health concerns. Black soot particles make their way into the upper atmosphere where they can have a significant effect on the overall balance between reflected and absorbed electromagnetic radiation from the sun.\textsuperscript{3–5} Carbonous soot, being black\textsuperscript{6}, absorbs electromagnetic radiation of all frequencies, and is hypothesized by some to be the second largest contributor to global warming after carbon dioxide.\textsuperscript{4} Furthermore, after an average residence time of ten days in the atmosphere,\textsuperscript{3,5} black soot often returns to the earth in precipitation where it can affect ecological water cycles\textsuperscript{4,5} and reduce the reflectance of snow and ice,\textsuperscript{3,4} leading to snow, ice, and glacial melting.\textsuperscript{4}

It is known that different combustion variables influence the nanostructure of soot,\textsuperscript{1,2} but it is less known whether or not the different nanostructures have different effects on health. The very small particle sizes of black soot allow for deep penetration into the small cavities of the lungs. As a result, a large group of lung diseases and cancers is thought to arise from black soot.\textsuperscript{3,7,8} It is
known that certain polyaromatic species present in soot are carcinogenic and mutagenic, including those with five-membered rings. These species can be harmful to both the affected organism and their offspring. A number of adverse health effects can result from prenatal exposure to polyaromatic hydrocarbons that may be present in soot. Studies have purported that physical abnormalities, lung infections and asthma, slower mental and behavioral development and development of psychological coditions, and childhood obesity can result from prenatal exposure to polyaromatic hydrocarbons.

To control black carbon soot emissions from diesel engines, modern diesel cars and trucks are fitted with a diesel particulate filter (DPF). With nearly complete integration into the diesel automobile/truck fleet in the last few decades due to regulations, diesel particulate filters achieve the desired effect of removing black soot from diesel exhaust via a catalyst, and then burned off with a small amount of fuel to allow for catalyst regereration. In addition to DPFs, the combustion characteristics of diesel fuel can be controlled to effect soot production. In particular, colder combustion environments of fossil fuels, which may exist upon startup before the engine is warmed up, or near the cylinder walls, may produce more black soot than under normal conditions. Careful planning, research, and tweaks to engine structure to control the combustion environment of diesel fuel may result in reductions of black soot production in diesel engines.

**Theory**

It is generally acknowledged that the nanostructures present in soot begin forming around a single nucleation point and grow during combustion by deposition of carbonous nanoparticles. The pyrolysis-like conditions in certain flames induce the formation of these species due to insufficient oxygen; these conditions exist in diffusion flames, for example. These nanoparticles can be flat polyaromatic hydrocarbons, or curved polyaromatic hydrocarbons with five-membered rings. The reactive intermediary pathways and kinetics present with equivalence ratios conducive for soot formation result in the formation of these carbonous nanoparticles. The most stable of these soot precursor species survive the high combustion temperatures and go on to form soot. The nanostructure of soot is dependent upon multiple variables. Generally speaking, soot structure falls in to three categories: (1) amorphous structure, (2) highly curved structure with shells and capsules due to the presence of five-membered rings in the polyaromatic hydrocarbons, and (3) graphitic structure with parallel structural elements. The variables that are known to influence the structure of black soot include temperature of formation, flow rate, and fuel structure. Some variables dominate over other variables in influencing the structure of soot. It has been found that at low temperatures, all soot is amorphous regardless of the fuel. At high temperatures, studies have found that high flow rates result in a highly curved soot nanostructure structure, while low flow rates result in a graphitic structure. This has been found to be true for many fuel structures including unsaturated, aromatic, and aromatic with five-membered rings; however, oxygenated fuels like ethanol result in highly curved nanostructures regardless of the flow rate. The principal conclusion is that the flow rate alters the species that adds mass to the growing soot particle during combustion.

The microscopy technique used to capture the image of the soot particle analyzed here is high-resolution transmission electron microscopy (HRTEM). HRTEM is a powerful imaging
microscopy technique which uses a beam of electrons aimed at the subject (in contrast to photons present in optical microscopy) to generate an image. HRTEM can attain images of very small objects; even individual atoms can be observed with HRTEM. HRTEM achieves a greater resolution than optical microscopy due to the very physical constants that govern the laws of light and quantum mechanics; optical microscopes are limited by the size of the wavelengths of optical light, while HRTEM is limited by the much smaller wavelength of the electrons beam – the de Broglie wavelength – which is small enough to observe the parallel structural elements of the soot observed here. Imaging analysis can be a powerful tool in the analysis of soot structure by determine the angles of these structures – soot structures that are generally parallel to each other indicate a graphitic soot, while soot structures that appear random or highly variable indicate a curved structure or amorphous structure.

Methods

The 8-bit structural element pattern, shown in Figure 2, was extracted from the HRTEM generated image of a graphitized anthracene soot sample, shown in Figure 1. The structural elements were analyzed as particles in the U.S. National Institute of Health’s ImageJ image analysis software to determine the Feret angle of each particle. The Feret angles of the 365 particles were placed into a distribution from 5° to 180°. The distribution was then shifted so that the peak orientation angle of the structural elements was aligned with 90°.

Results and Discussion

The orientation angle distribution of the graphitized anthracene soot sample was determined via image analysis of the Feret angle of the structural elements using the ImageJ software. The ImageJ software gave a Feret angle distribution with a peak around 30°; however, the distribution was shifted 60° such that the statistical mean of the orientation of all structural elements was 90°. This
meant that the reference axis was shifted to the normal of the average orientation angle. Figure 3 shows this distribution of structural element orientations in degrees clockwise from the reference axis.

![Structural Element Orientation Distribution for Graphitized Anthracene Soot](image)

Figure 3: Graphitized Anthracene Soot Structural Element Orientation Distribution

The aggregation of structural element orientations around the 90° angle indicates that many of the structural elements lie parallel to each other along the same plane. This suggests that the graphitized anthracene soot sample in Figure 1 is a graphitic soot (in contrast to an amorphous or highly curved soot). This supports the conclusion that certain variables discussed in Theory can influence the soot structure such that a graphitic soot can result. Other studies have examined the soot formation from anthracene and observed similar results, while other fuels have been observed to produce soots with different nanostructures. It is known that the soot observed here has the effects on global climate that were discussed earlier; it is recommended that measures be taken to reduce the production of the soot observed here and other soots. These reduction methods include the continued adoption of diesel particulate filters (DPFs) and implementation of other researched methods of soot reduction in engines. As discussed earlier, the health effects of soot, and the polyaromatic hydrocarbons present in soot, are known, but it is unknown whether different nanostructures affect human health differently. Therefore, it is recommended that further studies be done to examine how different soots, like the graphitic soot observed here, affect human health.

Conclusions

Carbonous soot has numerous negative environmental impacts, both on human health and on climate change. Studies that have already demonstrated that black soot produced during combustion of fossil fuels and biomass results in a number of diseases and genetic defects, while also being the second largest contributor to anthropogenic climate change, have resulted in the implementation of a number of soot reduction methods and further research. The formation mechanisms and the effects of combustion variables on soot nanostructures have been thoroughly studied; however, the health effects of different nanostructures have yet to be studied. A HRTEM
image of a graphitized anthracene soot particle was analyzed using image analysis to classify the soot into one of the three soot categories: amorphous, highly curved, or graphitic. The distribution of the structural element orientation angles was shown to convene around 90°, meaning the elements are mostly parallel to each other. The predominantly parallel structural elements of the graphitized anthracene soot indicate that the sample is a graphitic soot. These findings are consistent with previously hypothesized soot formation mechanisms. These insights can contribute towards the understanding of how soot forms in combustion scenarios like engines, and how these engines can be improved to reduce soot formation. It is recommended that soot like the one observed in this study be reduced in engines to reduce their effect on climate change. It is also recommended that further research be done to determine whether different soot nanostructures, like the graphitic nanostructure observed here, result in different health effects.
References


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