Detailed investigation of soot nanostructure: effect of pressure

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Diesel and jet engines often operate at elevated pressures, thus the investigation of the effect of pressure on soot nanostructure may contribute to the understanding of real-world systems. In this paper preliminary results from the analysis of soot nanostructure as a function of oxidation pressure are presented. The analyzed soot was generated in premixed flames of liquid fuels: n-dodecane, m-xylene and n-butanol and oxidized under elevated pressures. Nanostructure is described via differentiating between the isotropic and nematic phases of soot particles. These phases are characterized by the polar and nematic order parameters. Along with the order parameters, the nematic phase is further characterized by graphene layer spacing and length. The structural parameters were measured by utilizing high-resolution electron microscopy and digital image analysis. The image analysis framework used in this paper is a recent development, that provided us with high-fidelity structural data. This refined methodology made drawing our conclusions possible. A significant effect of pressure was observed on soot nanostructure - increasing pressure reduced interlayer spacing and increased the average length of layers, along with altering the symmetries of the structure.

1 Introduction

Soot is a product of the pyrolysis of carbonaceous materials and is generally considered as amorphous carbon [1]. Despite being amorphous, in most cases soot nanostructures show some degree of crystalline order typically in the form of graphite microcrystals (mesophase crystalline units or clusters exhibiting short-range order in the form of parallel graphene layers, also called 'stacks'), partial fullerene (graphene layers in a concentrically symmetric, 'onion-like' structure) or partial graphitic (longer range parallelity of layers) order [2–5]. Soot particles are composed of amorphous and crystalline fractions. For the balance of this paper, the amorphous fraction is referred to as the 'isotropic phase' and the crystalline fraction is called 'nematic phase’. Soot nanostructure is affected by the thermal environment and combustion conditions [3] and also by the combusted fuel type - different fuels may produce different nanostructures [5–7].
The importance of soot nanostructure can be summarized as follows. Current soot models account for nucleation, growth, coagulation and oxidation processes [8–10], among which, all except the first are affected by the molecular structure of soot - either through the density and distribution of active surface sites determining the rate of chemical processes [11, 12] or via affecting van der Waals forces and therefore physical interactions [13, 14]. Experiments demonstrated [15], that the rate of surface growth is not exclusively determined by surface area, which further supports the importance of the arrangement of surface sites. Similarly, discrepancies exist between observed oxidation rates [2] and the rates predicted by the Nagle-Strickland-Constable equation [16], which is applicable to describe the high-temperature oxidation of carbon blacks - these discrepancies are possibly caused by uniqueness of soot structure.

In HRTEM images, individual graphene layers are made visible by phase-contrast imaging. Since typical HRTEM images contain hundreds of imaged graphene layers, in most practical cases, their representative and accurate characterization can only be carried out by using automated digital image analysis. Many automatic [17–19] and semi-automatic [20] algorithms are known that can extract structural information characterizing graphene lamellae and their arrangement. It was pointed out [21], that the heaviest drawback of these algorithms is the usage of subjectively set parameters in the implementations of image processing techniques and the sensitivity of the obtained results to these parameters. Recently, we addressed this issue and developed a novel image analysis framework by which the robust extraction of representative structural information is possible [22, 23]. If such robust techniques are available - despite being a two-dimensional technique [24] - HRTEM analysis can provide results that are consistent with X-ray diffractometry [25, 26].

Although practical combustion systems - either for energy generation or transportation - often operate at elevated pressures, there is a general lack of models describing the effects of elevated pressure on soot nanostructure [27]. Also, observations regarding the structure of soot as a function of the pressure of the oxidizing environment have not been reported before. In this study, we present results of HRTEM observations of the effect of pressure on soot nanostructure.

2 Materials and methods

In this section the conditions and equipment used for soot generation, oxidation and characterization are discussed. For the reader’s convenience, a brief overview is given on the recently developed image analysis framework and the meaning and significance of the extracted structural parameters.

2.1 Soot generation

A premixed burner was used to create the soot samples from different liquid fuels. The soot was generated in a flat flame, premixed burner under heavily sooting conditions and captured on a water-cooled stabilization plate which was located 50 mm above the burner surface.

The burner system consisted of a stainless steel chamber (50 mm inner diameter, Schedule 80, 127 mm long), where fuel and air were injected and mixed prior to entering the burner. The flame was stabilized over a tube bundle (1.578 mm inner diameter, 31.75 mm long) through which the mixture passed in laminar flow. A nitrogen shroud was utilized to shield the premixed flame from
atmospheric interference. Air and the liquid mixture were fed to the burner using a vaporizer coupled to a syringe pump and temperature control system. The vaporizer allowed for effective fuel vaporization before being mixed with the air.

The temperature in the vaporizer was controlled depending on the fuel used and the compositions of the fuel fed and vaporized fuel were analyzed by using gas chromatography to verify the performance of the vaporizer. The objective was to vaporize and deliver the mixture without distilling it. The vaporized fuel was trapped into a cold dichloromethane trap.

Soot was generated from n-dodecane, m-xylene and n-butanol. The soot generated was collected on the stabilization plate and then crushed into a powder. Flame temperatures were measured using a type-B thermocouple (wire diameter 0.02032 mm) at 50 mm above the burner surface, which corresponded to the distance where the soot is collected. The temperatures were corrected by radiation effects. Table 1 summarizes the conditions for each flame studied.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Equivalence ratio</th>
<th>C/O ratio</th>
<th>Velocity, cm/s</th>
<th>Flame temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>1.7</td>
<td>0.65</td>
<td>4.6</td>
<td>1705</td>
</tr>
<tr>
<td>m-xylene</td>
<td>2.15</td>
<td>0.7</td>
<td>4.6</td>
<td>1725</td>
</tr>
<tr>
<td>n-butanol</td>
<td>2.8</td>
<td>1.21</td>
<td>4.3</td>
<td>1723</td>
</tr>
</tbody>
</table>

2.2 Soot oxidation

A high-pressure thermogravimetric analyzer (HTGA), type Cahn TherMax 500, was used to oxidize soot under controlled pressurized conditions. All tests were performed isothermally. 10 mg soot was placed in a quartz crucible (18 mm diameter and 20 mm height). The crucible was suspended from a ceramic coil attached to a microbalance. The furnace and balance were purged with nitrogen prior to each experiment. An inert material (silicon-carbide beads) was used in all of the runs to minimize thermal and mass transfer effects by decreasing the stagnant atmosphere between the surface of the soot and the top of the container. Isothermal tests were performed at 575 °C. A heating rate of 10 K/min was used to reach the oxidation temperature in nitrogen. The oxidizer, a mixture of oxygen and nitrogen flowed at 1 l/min. Mass data was recorded approximately every second and the experiments were terminated when the mass loss surpassed 50%. After termination, the samples were quenched in nitrogen at 20K/min. Soot was oxidized under different pressures to study the effect of pressure on the soot nanostructure. In order to represent conditions from atmospheric pressure to environments in typical aircraft engines [27], 1 atm, 10 atm and 40 atm atmospheres were used.

2.3 HRTEM imaging

Soot was placed in vials with ethanol (200 proof). This mixture was filtered in a BHS Sonthofen pressurized filtration system. The remaining soot was then suspended in the ethanol and sonicated for 15 minutes. Upon completion one drop from a glass micropipette was placed on a coated lacey
carbon grid (Ted Pella 200-mesh Formvar). The grids were allowed to dry completely prior to being stored in the grid holder. HRTEM micrographs were produced using two FEI HRTEMs, Models Tecnai F30 and F20 EFTEM operated under 200 keV accelerating potential. The micrographs used for further quantification were produced at 500,000X magnification under slightly over-focused phase contrast conditions.

2.4 Image analysis

HRTEM images were processed by a novel image analysis framework specifically designed for analyzing HRTEM micrographs of soot. The details of the framework can be found in [22, 23]. In brief, the framework is based on filtering theory - the micrographs are filtered with special two-dimensional filters in order to extract interlayer spacing and symmetry parameters. Gabor filters [28] tuned to frequencies present in soot HRTEM micrographs were used to extract interlayer spacing distributions - in a previous study [22], we showed that the filtering method produces datasets that are two orders of magnitude more robust than datasets produced by conventional fringe analysis algorithms [17]. Nematic and polar order parameters ($S_{2N}$ and $S_{2P}$, respectively) were extracted by the orientation-filtering technique described in [23]. These parameters were first used to describe soot nanostructure by Shim et al. [19] and are defined as follows:

$$S_{2N} = 2 \left< \cos^2 (\alpha_i) \right> - 1$$
$$S_{2P} = 1 - 2 \left< \cos^2 (\alpha_i) \right>$$

where $S_{2N}$ is the nematic order parameter, $S_{2P}$ is the polar order parameter, $\alpha_i$ is the angle between the fringe orientation vector and a so-called director vector and $<>$ means mean value. The director vector is approximately the local mean orientation inside an image region in the nematic case; in the polar case, it is a vector pointing from polar symmetry poles (amorphous particle cores) to the fringe centroids. Given this, $S_{2N}$ is 1 for a perfectly ordered structure and 0 for a perfectly disordered structure, while $S_{2P}$ is 1 for perfect concentric symmetry, 0 for disordered phases and -1 for radial symmetry. For further details about $S_{2N}$, $S_{2P}$, the reader is referred to [19]. These parameters are also defined and computed in regions of specific size - the size of these regions is called the scale of the symmetry, $\sigma$. The term 'long-scale symmetry' therefore refers to cases in which a high value of either symmetry parameter is retained over long distances.

For the extraction of fringe length and fringe tortuosity, an extended version of the algorithm of Palotas et al. [17] was used. The image binarization scheme of Palotas et al. was extended by introducing locally varying thresholds values for fringe separation. After fringe detection, the extraction of geometric properties (length and tortuosity) was done as described in [20].

3 Results

In this section, results from both qualitative and quantitative structural analysis are presented. The quantitative discussion consists of four parts. First, results from conventional fringe analysis are
shown, demonstrating the differences between fringe length and tortuosity statistics between samples. High-fidelity interlayer spacing distributions are presented next, followed by the quantification of overall structural symmetry.

Figure 1: Examples of the acquired micrographs. A - n-butanol sample, oxidized at 1 atm. B - n-butanol sample, oxidized at 10 atm. C - n-butanol sample, oxidized at 40 atm. D - n-dodecane sample, oxidized at 1 atm. E - n-dodecane sample, oxidized at 10 atm. F - n-dodecane sample, oxidized at 40 atm. G - m-xylene sample, oxidized at 1 atm. H - m-xylene sample, oxidized at 10 atm. I - m-xylene sample, oxidized at 40 atm.

Between 10 and 20 micrographs were acquired from each sample in a representative manner. Examples of the micrographs are shown in Figure 1.
Increasing pressure under which the soots had been oxidized apparently affected the nanostructure of soot from all three fuel sources. However, the effect of pressure is not obvious at first sight. The micrographs shown in Figure 1 were selected subjectively for demonstration purposes, based on how well they represented the qualitative trends found in the different structures - note that the quantitative trends presented in this paper are averaged over all micrographs within the respective samples.

All samples developed structures typical to combustion-generated carbonaceous residues. Core-shell structures [5, 29] were predominantly found in the samples. Hollowed-out particles previously observed in diesel and biodiesel soot [29] and soot heated by pulsed lasers [30] were not found amongst the analyzed samples.

An interesting observation in the case of n-dodecane and m-xylene soots was the appearance of concentric rings at the boundaries of particles. These rings had diameters between 1 and 3 nanometers and were apparently single or multi-layered fullerene structures. In the case of n-dodecane oxidized under 10 atm, these small fullerene sub-structures dominated the nanostructure and caused qualitative differences between the appearance of the 10 atm sample and the 1 and 40 atm samples. The fullerene rings were observed in some particles of the soot produced in an m-xylene flame oxidized under 1 and 10 atm as well, although they were much less dominant in these structures. The 40 atm samples showed ordered structures free from small-scale fullerene sub-structures.

Fullerene carbon in soot has been a known phenomenon [31–34] - most previous studies focused on the formation of fullerenes in flames. In this study, however, the appearing of small fullerene molecules is associated with the reordering of the carbon structure induced by oxidation under moderate pressures.

Fringe length and tortuosity data were extracted from every micrograph acquired from each sample. The extracted information was averaged over the micrographs representing a particular sample. Figure 2 shows the obtained histograms and fit probability density functions (PDFs). The parameters of the skewed Gaussian PDFs were found by using non-linear optimization. After optimization, the PDFs were re-normalized and scaled for visualization purposes. Since only very slight differences were found between the distributions, in order to present a better visualization, the differences between the pressurized and atmospheric PDFs were computed and plotted in Figure 2. The slight differences observed suggest that increased oxidation pressure increases the size of graphene layers. This trend was found to be true for the n-butanol and m-xylene samples; however, soot from the n-dodecane flame behaved differently: n-dodecane soot oxidized under 10 atm contained shorter fringes than the atmospheric sample, while the soot oxidized under 40 atm contained longer ones. Tortuosity distributions followed a similar trend: in the case of n-butanol and m-xylene soots, fringes became less curved as pressure increased, while in the case of n-dodecane, they became more curved. The anomalous observations regarding soot from the n-dodecane flame are possibly caused by the appearance of small fullerenes in the structure as described above.

Figure 3 shows extracted interlayer spacing distributions. Interlayer spacing is the distance between neighboring graphene layers. As a number of previous studies has shown [29, 35], as the maturation of soot proceeds, stacked layers of graphene become more similar to graphite crystals. This similarity is expressed in terms of the length, linearity and spacing of the layers composing the microcrystals. Besides being an indicator for graphitic order, interlayer spacing supposedly
Figure 2: Extracted fringe length and fringe tortuosity histograms. The top row shows fringe length histograms with fit PDFs. The PDFs are skewed Gaussian distributions. The middle row shows the differences between the fit PDFs relative to the 1 atm cases. A negative difference means that there were less occurrences in a given length bin relative to the 1 atm case. The bottom row shows the differences in the fit tortuosity PDFs. Note that the scales of the horizontal axes of the top row are different than those of the middle and bottom rows.

affects the diffusivity of oxygen inside the microcrystals and thus the overall reactivity of soot. As Figure 3 demonstrates, the general trend is that increased oxidation pressure decreases the mode of the interlayer spacing distributions. The spacing of graphene layers in the atmospheric samples was found to be the longest and increasing pressure generally shifted spacing distributions toward

Figure 3: Extracted interlayer spacing histograms. The top row shows interlayer spacing histograms with fit PDFs. The PDFs are generalized Gaussian distributions. The bottom row shows the differences between the fit PDFs relative to the 1 atm cases. A negative difference means that there were less occurrences in a given bin relative to the 1 atm case.
the 0.335 nm value, which corresponds to the spacing of regular graphite crystals. In the case of n-dodecane soot oxidized under 10 atm, again, an anomalous distribution was found, as a slightly increasing mean spacing was observed. However, in this case, the difference between the 10 atm and 1 atm distributions was very slight and this difference was within the uncertainty limits of the algorithm used to extract spacing values. In the other cases, the measurements showed a definite shift in the interlayer spacing distributions toward shorter distances. It is worth noting at this point, that the slight compaction of the nematic phase caused by elevated pressures is most likely an indirect effect; that is to say, the uniaxial force of external compression is orders of magnitude weaker than the short-range forces acting between graphene layers. Thus, the compaction is more likely caused by changes in the chemical structure induced by increased pressure - these changes may include the removal of 5- and 7-membered rings and intercalations.

Besides fringe statistics and interlayer spacing distributions, symmetries in graphene layer arrangement can be measured and used to describe soot nanostructure. The term ‘symmetry’ refers to regularities in the relative position and orientation of fringes in HRTEM micrographs. Symmetry can be characterized by order parameters - the two used here is the polar \( S_{2P} \) and nematic order parameter \( S_{2N} \) introduced by Shim et al. (see [19]). Maps of the symmetry parameters were computed by the algorithm described in [23]. The extracted maps of \( S_{2N} \) and \( S_{2P} \) were integrated over the analyzed areas to obtain an aggregate measure of symmetry strength in the samples. The results are shown in Figure 4. Figure 4 visualizes the overall symmetry present at particular scales - certain scales are characteristic to certain structural primitives, e.g., strong polar symmetry at short scales represents small fullerenes. The symmetry-scale distributions shown in Figure 4 can therefore be interpreted as indicators that show the relative frequency of occurrences of particular structural primitives in the nanostructure.

![Figure 4](image)

**Figure 4:** Overall polar and nematic symmetry of the analyzed structures. The top row shows overall polar symmetry strength versus scale. The bottom row shows overall nematic symmetry strength versus scale. Insets show magnified portions of the graphs at the shortest scale. Inset axes have the same scales.

The polar symmetry distributions of all samples were found to be bimodal. The first peak appeared below a scale of 2 nm. This peak indicates the presence of small fullerenic rings - as the insets show, the overall symmetry at this scale was the highest in the n-dodecane soot oxidized under 10 atm.
atm, which is consistent with the observation regarding small fullerenic rings. The second peak was found at varying scales above 6 nm - this peak represents the larger onion-like fullerenes or core-shell structures. Peak locations at this scale roughly correspond to the average size of the onion fullerenes. Large-scale polar symmetry generally got more dominant as pressure was increased - again, soots from the n-dodecane flame were exceptions. In the case of n-butanol, the structure became more symmetric at higher oxidation pressures, with the peak shifting slightly towards lower values. This shift was found in the case of n-dodecane soot as well, although the symmetry became weaker. M-xylene soot showed a consistent increase in both symmetry strength and dominant scale with pressure. Nematic symmetry distributions are indicative to the distribution of stacked graphene layers, namely, the number of graphene sheets in each identified microcrystal. Consistent with the results of [18], nematic symmetry distributions that decreased with symmetry scale were observed. The smallest scale for the extraction of nematic symmetry was chosen to be approximately 0.4 nm, which is the scale of 2-membered graphene stacks. Monotonically decreasing profiles indicate that the relative frequency of the occurrence of stacked layers is inversely proportional to the number of graphene layers in them. All samples developed similar monotonically decreasing nematic symmetry distributions. Generally, elevated pressures increased the nematic symmetry strength of the samples, with the exception of the 10 atm n-dodecane sample. M-xylene soot showed the most significant ordering with pressure.

Figure 5: Derived properties from structural parameters extracted by HRTEM image analysis. Molecular weight was estimated by assuming a circular catenation mechanism for carbon atoms. Density was estimated by assuming graphite lattice structure. The apparent crystalline fraction is the fraction of the nematic phase in the nanostructure. All material properties pertain to the nematic phase. Circles denote mean values.

Figure 5 shows material properties derived from HRTEM structural data. The results shown in Figure 5 refer to the nematic phase only. The nematic phase was located by setting a threshold on the nematic order parameter and identifying image regions that fell over the threshold. The threshold limit was the theoretical limit set by the Maier-Saupe theory, \( S_{2N} \approx 0.43 \) [36, 37]. This threshold was varied over a ±10% range and along with the standard deviation of the structural parameters, the uncertainty resulting from the threshold variation was included in the error bars in Figure 5. The molecular weight of the nematic phase was estimated by assuming a circular catenation mechanism of carbon atoms as described in [38]. Assuming circular catenation, fringe length is directly proportional to the diameter of circular graphene layers, which, with some uncertainty, can be converted to molecular weight. The density of the nematic phase was estimated by assuming the geometry of a graphite lattice with slightly variable interlayer spacing. The density is then given...
by \( \rho = \frac{4m_C}{(2a^2d_{002} \sin 120^\circ)} \), where \( m_C \) is the mass of a carbon atom, \( a = 0.142 \) nm and \( d_{002} \) is the interlayer spacing in nm. The apparent crystallinity was defined as the volume fraction of the nematic phase in the soot structure. The three-dimensional volume fraction was approximated with the two-dimensional area fraction [24].

Both the mean molecular weight and apparent crystallinity of n-butanol and m-xylene samples increased at elevated oxidation pressures. The anomalous behavior of the 10 atm n-dodecane sample was possibly caused by the factors described above. The mean density values were affected by the mean interlayer spacing. Note that although the distributions and modes of the interlayer spacing showed clear trends with pressure, density did not. It is safe to state that within the uncertainties of the estimations, the density values did not show any significant trends or differences. Mean values and uncertainty ranges of the derived properties are shown in Figure 5.

4 Conclusion

In this study we investigated the effects of elevated oxidation pressure on soot nanostructure. Soot from the flames of three surrogate liquid fuels, n-butanol, n-dodecane and m-xylene were oxidized in controlled, high-pressure environments. HRTEM images were acquired of the obtained soot samples. The lattice structure of soot was investigated by utilizing state-of-the-art automated image analysis. Elevated oxidation pressure had an effect on the fringe length distribution and thus molecular weight of the analyzed soot - higher pressures were found to produce structures consisting of larger graphene layers. Elevated oxidation pressure also reduced the spacing between graphene sheets. Pressure significantly affected the symmetry of soot nanostructure.

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References


