



The effect of oxidation pressure on the equilibrium nanostructure of soot particles



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ABSTRACT

The notion of equilibrium soot nanostructure was introduced by Hurt et al., who argued that the peculiar turbostratic carbon structure is an equilibrium arrangement of lamellar, graphene-like molecules. It was proposed that the typical, onion-like internal structure of primary soot particles can be satisfactorily described by thermodynamic principles. There are two main objectives of this paper. First, the effects of oxidation pressures above atmospheric pressure on soot nanostructure are investigated experimentally. The analyzed soot was generated in premixed flames of liquid fuels: n-dodecane, m-xylene and n-butanol and further oxidized in a thermogravimetric analyzer under atmospheric, 10 atm and 40 atm pressures. Nanostructure is described by utilizing high-resolution transmission electron microscopy and recently developed image analysis techniques. Second, empirical observations are compared against behavior that is semi-quantitatively predicted by the thermodynamic model. The utilization of the novel analysis technique made direct comparison between observed and computed properties possible. Reasonable consistency was found between experimental and computational results. The results suggest that the known thermodynamic model can be used to predict equilibrium structure even when soot is oxidized under pressurized conditions. Since diesel and jet engines operate at elevated pressures, the conclusions drawn in this paper may find their use in predicting soot nanostructure in the limiting case of equilibrium conditions.

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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 nanostructure shows some degree of crystalline order typically in the form of graphite microcrystals (mesophasic crystalline units or clusters exhibiting short-range order in the form of parallel graphene layers, also called ‘stacks’), partial fullerenic (graphene layers in a concentrically symmetric, ‘onion-like’ structure) or partial graphitic (longer range parallelism 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 chemical and thermal environment [3,6,7] and also

by the combusted fuel type – different fuels may produce different nanostructures [5,8–11].

The importance of soot nanostructure can be summarized as follows. Current soot models account for nucleation, growth, coagulation and oxidation processes [12–14], 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 [15,16] or via affecting van der Waals forces and therefore physical interactions [17,18]. Experiments demonstrated [19], 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 [20], which is applicable to describe the high-temperature oxidation of carbon blacks – these discrepancies are possibly caused by peculiarities of soot structure. The dependence of soot oxidation kinetics upon nanostructure was shown [21,22].

Hurt et al. showed, that soot nanostructure can be qualitatively modeled by thermodynamic principles [23]. Their model described

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the typical core–shell nanostructure [5] as an equilibrium arrangement between the competing isotropic–nematic transformation and the free energy contribution of the splay deformation of graphene layers. They argued that the core–shell structure is a configuration that is simultaneously optimal for layer growth and aromatization and the Van der Waals forces acting between layers. According to their model, the equilibrium diameter of the isotropic core is affected by the splay deformation constant, the free energy change of the isotropic–nematic transformation and properties of the nematic phase – molecular weight and density.

The quantities of interest in the model of Hurt et al. can be estimated by analyzing the high-resolution electron micrographs (HRTEM) of soot. 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 [24–26] and semi-automatic [27] algorithms are known that can extract structural information characterizing graphene lamellae and their arrangement. It was shown that – despite being a two-dimensional technique [28] – HRTEM analysis can provide results that are consistent with X-ray diffractometry [29,30].

Although practical combustion systems for transportation operate at elevated (higher than atmospheric) pressures, there is a general lack of models describing the effects of elevated pressure on soot nanostructure [31]. This paper is a follow-up of a previous study regarding pressure-dependent soot structure and reaction kinetics [21]. Soot was generated in an atmospheric flat flame and then oxidized in a high-pressure thermogravimetric analyzer (HTGA). HRTEM data are processed by means of a sophisticated image processing framework [32,33]. The extracted information includes interlayer spacing measurements and higher-order symmetry quantification. An attempt is made to explain the observed structural changes in the nanostructure by directly coupling processed HRTEM data with the thermodynamic model of Hurt et al. [23]. If successful, a thermodynamic model that can predict equilibrium soot nanostructure under pressurized conditions may provide useful practical information about the limiting case of fast reactions or long residence times.

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 an atmospheric, premixed, flat flame, 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 commercial vaporizer (Mesoscopic Devices Inc.) 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 vaporized fuel were analyzed by using gas chromatography to verify the performance of the vaporizer. The vaporized fuel was trapped into a cold dichloromethane trap.

Soot was generated from n-dodecane, m-xylene and n-butanol. Several studies reported that the fuel type affects the nanostructure of the generated soot [5,8–11], thus different fuels were tested – this particular choice of fuels represented paraffinic, aromatic and oxygenated fuels, respectively. 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. The radiation correction for the temperature was similar to that of McEnally et al. [34].

The combustion conditions for generating the samples were set in an attempt to simultaneously satisfy requirements regarding flame stability, the amount of soot generated and comparable temperature histories of the soot. Table 1 summarizes the conditions for each flame studied.

2.2. Soot oxidation

A high-pressure thermogravimetric analyzer, 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 entrance 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. Nitrogen flowed at 0.55 l/min through the microbalance to protect it. 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 20 K/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 [31], 1 atm, 10 atm and 40 atm atmospheres were used.

It is important to point out that the analyzed soot was not generated in a pressurized flame, but oxidized in a HTGA. Hurt et al. [23] suggested that the structure of real soot (i.e., soot not oxidized in a controlled environment) may be satisfactorily estimated by using thermodynamic principles. Even though the soot was oxidized up to an arbitrary 50% mass loss, it is hypothesized here that the conditions in the HTGA (low temperature and long residence time) approximate equilibrium, such that the structure corresponding to a given mass loss is a quasi-steady state

Table 1
Experimental conditions for soot generation.

Fuel	Equivalence ratio	C/O ratio	Velocity, cm/s	Flame temperature, K
n-dodecane	1.7	0.65	4.6	1705
m-xylene	2.15	0.7	4.6	1725
n-butanol	2.8	1.21	4.3	1723

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