



# Effect of nanostructure, oxidative pressure and extent of oxidation on model carbon reactivity



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## ARTICLE INFO

### Article history:

Received 5 November 2014

Received in revised form 9 December 2014

Accepted 9 December 2014

Available online 10 January 2015

### Keywords:

Soot nanostructure

Carbon black

HRTEM

TGA oxidation kinetics

Soot reactivity

## ABSTRACT

Oxidation kinetics and fringe analysis studies of three “model” carbons, ranging from fullerene to onion-like nanostructures and a reference diesel soot were performed in a thermogravimetric analyzer. The samples were oxidized isothermally at temperatures ranging from 575 to 775 °C in air. Multiple tests were performed to obtain the most favorable operating conditions to minimize mass-transfer diffusion limitations in the experiments.

First-order reaction kinetics and an Arrhenius-type equation were used to extract the rate constants at each temperature. The activation energies for the oxidation of the carbon samples ranges from 124 to 204 kJ/mol, and it was approximately 140 kJ/mol for the reference diesel soot sample. The onion-like structure exhibited a slower kinetic rate compared to the other carbons. Similar kinetic parameters were found for “intermediate structure” model carbon and reference diesel soot.

Fringe analysis explained the differences in the kinetic parameters between carbon samples studied. The onion-like carbon “nascent” sample had a broader range of lamellae length with smaller tortuosity distribution, suggesting stacking; the “nascent” fullerene carbon had much shorter mean lamella length distribution and broader tortuosity, suggesting more curvature. Nanostructure metrics of the reference diesel soot and intermediate model carbon were between the other two carbons. Results confirm a structure–property relationship between oxidative reactivity with carbon nanostructure.

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## 1. Introduction

Soot particles emitted by diesel engines have been implicated in adverse health and environmental consequences [1,2]. The reduction of soot emissions from diesel engines has been studied through enhancement of fuel formulations, engine designs, and more effective emission-control technology. While soot formation and growth are important, the oxidative reactivity of particles and the conditions under which the particles are generated is tightly coupled to the design of efficient combustion devices for benefiting mitigation [3–12].

Many studies have been performed on soot oxidation with reviews summarizing methods to conduct surface chemistry and extract surface kinetic rates [13,14]. For example, Kennedy [13] summarized the modeling approaches of soot formation,

accounting for nucleation, growth, coagulation and oxidation processes. Higgins et al. [14] proposed and demonstrated a method based on the change in particle size to extract soot oxidation rates. Vander Wal et al. [15] uncovered alternative burning modes and showed the presence of densification of primary diesel soot particles caused by partial oxidation in the TGA.

The importance of soot nanostructure and its impact on oxidation rate has also been recognized [9,16]. Vander Wal et al. [16] showed that the presence of small curved structures in soot particles is assumed to enhance oxidation rates. Yehliu and coworkers [9] focused on the impact of fuel composition on soot reactivity and nanostructure. Other studies followed the rate variation over time suggestive of changes in nanostructure during the course of oxidation [17,18]. In addition, the effects of type of fuel on soot oxidation were investigated for oxygenated fuel blends in this case n-dodecane/n-butanol [19]. These separate studies laid a logical foundation for relating soot oxidation rates to nanostructure.

For example, Seong and Boehman [20] related soot reactivity to adiabatic flame temperature and inception time/rate, using a laminar diffusion flame burner and varied fuels. Increased flame temperature and/or earlier inception time led to less reactive soot, as

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measured by TGA profile. Crystallite height ( $L_c$ ) showed a good correlation with the reactivity, but crystallite width ( $L_a$ ) was not well-correlated with the reactivity. Arnal et al. [21] compared the reactivity of soots obtained under different combustion conditions (diesel, Printex-U and lab scale production) toward  $O_2$  and  $NO$ . The combination of transmission electron microscopy (TEM), Raman, BET illustrated that the soot with highest surface area and H content was the most reactive, but organization itself, based on Raman analysis was not strictly related to reactivity. A similar result was presented by Lapuerta et al. [22] who found by Raman analysis that biodiesel produced soot displayed more graphite-like structures and lower amorphous carbon concentration – at odds with the higher reactivity observed for the biodiesel-derived soot.

Atribak et al. [23] reported the uncatalyzed and catalyzed combustion of two commercial carbon blacks and three diesel soot samples and related the physico-chemical properties of these carbon materials. Model soot samples were less reactive than real soot samples, which was mainly attributed to a lower proportion in heteroatoms and a higher graphitic order for the case of one of the carbon blacks. Among the diesel soot samples tested, differences in volatile matter/fixed carbon were directly related to the engine operating conditions (idle or loaded) and the use of an oxidation catalyst.

Other studies have noted the impact of formation conditions upon reactivity, with structure as the link. As Rodriguez-Fernandez et al. [24] noted from their study, the oxidation profiles of diesel and biodiesel soot were different probably in response to the differences in soot structure, but other techniques should be applied for examining this structure and its changes during the oxidation process. Although only small differences were found in the reaction activation, the biodiesel reacted at lower temperature. In contrast, Happonen et al. [25] performed a comparison of particle oxidation and surface area of diesel soots from fossil and renewable fuels. Despite the different fuels, high-resolution TEM and electron energy loss spectroscopy (EELS) showed similar structure between the soots, consistent with similar oxidation properties.

On the basis of measured rate constant, Yezerets et al. [26] investigated diesel soot reactivity produced from different engines and duty cycles. They observed significant differences in reactivity between the soot samples, understanding that the reactivity of a diesel soot particle is related to the combustion conditions under which it was formed. Meanwhile Su et al. [27] also highlighted the importance of soot origin on its physico-chemical properties, which in turn influences the oxidative reactivity of the soot. Complementary observations were also made by Lee et al. [28] where soots under different diesel engine loads varied in structure.

Illustrating the profound impact of nanostructure upon oxidation process, Al-Qurashi and Boehman [29] found that EGR exerted a strong influence on the physical properties of the soot which led to enhanced oxidation rate. HRTEM images showed a dramatic difference between the burning modes of the soot generated under 0% and 20% EGR. The soot produced under 0% EGR strictly followed an external burning mode with no evidence of internal burning. In contrast, soot generated under 20% EGR exhibited dual burning modes: slow external burning and rapid internal burning. Fang and Lance [30] studied the oxidation behavior of diesel soot during the regeneration process of a DPF. They found that the reactivity of soot decreased as the regeneration time increased. The authors argued that during the regeneration process the soot underwent a transformation from amorphous structure to more orderly graphitic structure which exhibited resistance to soot oxidation. Heckman and Harling [31] studied the oxidation behavior of carbon black and graphitized carbon black. The non-graphitized carbon black was oxidized in 50%  $O_2$  at 450 °C and exhibited internal burning forming capsules whereas the graphitized carbon burned from the outside inwards.

These studies interpreting rates as reflecting structure provide the impetus to develop broader relationships between (nano)structure and oxidative reactivity. As illustration, Rouzaud and Christian [32] sought to understand the influence of textural, chemical, and structural properties on the reactivity of activated carbons toward air, using thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC). The HRTEM observation coupled with sophisticated image analysis tools provided useful information about the structural organization of different carbon materials. This was completed with the measurement of chemical and textural characteristics. The influence of the physical and chemical characteristics of the carbon materials on their reactivity with air was quantitatively analyzed by establishing linear relationships. These authors reported that the graphitic layer length and the oxygen over carbon ratio were directly tied to the oxidation parameter. No correlations were found with textural parameters such as the macro-mesoporous volume and the specific surface area.

Schmid et al. [33] performed multi-wavelength Raman microspectroscopy (MWRM) analysis for characterization of soot structure and reactivity. This method is based on the dispersive character of carbon D mode in Raman spectra (i.e., red shift and increase in intensity at higher excitation wavelength,  $\lambda_0$ ). The approach was proven by investigating various diesel soot samples and related carbonaceous materials at different wavelengths (785, 633, 532, and 514 nm). To obtain the relation between structure and reactivity of soot, MWRM analysis was combined with temperature-programmed oxidation (TPO). The comparison of MWRM (viz., the observed Raman difference integrals) and TPO data revealed a linear correlation between soot structure and oxidation reactivity. Lapuerta et al. [34] identified and suggested a set of optimized Raman parameters for analyzing and comparing soot samples from different fuels. This work showed indicators that confirm the higher reactivity of biodiesel soot with respect to diesel soot. Pahalagedara et al. [35] performed a comprehensive investigation of structure and – reactivity relationships for a diesel engine soot sample (Corning) and 10 commercially – available carbon black samples. Various structural parameters including particle size, specific surface area, degree of organization and average crystallite stacking height were correlated with TGA oxidation reactivity. A fairly linear relationship ( $R=0.64$  with all points, whereas  $R=0.65$  after excluding the outlier Printex-XE2B) was found, indicating a dependence of the oxidation activity upon the degree of organization of the carbonaceous material. Though establishing correlations between structure and reactivity, each prior study used different materials and experimental methodology. A set of materials offering a broad range of nanostructures could serve as a model set by which to bracket oxidation rates. This may also aid development of structure–property relationships relevant to oxidation.

These previous studies have not investigated the effect of pressure on kinetics, a key consideration in relation to engines. In a recent work, Jaramillo et al. [36], the oxidation kinetics of soot samples produced in flames were compared to commercial carbon black samples, using a high-pressure TGA. Lamella length and tortuosity, extracted from HRTEM images, correlated with soot reactivity. However, due to the similarity in the initial nanostructure of some of the samples, it was not possible to establish a clear relation between HRTEM image analysis and the reactivity reflecting initial structure at pressurized conditions.

In the context of these prior studies the intent of this study was to expand structure–property relationships for soot oxidation kinetic data using model carbon materials with vastly different nanostructures. In addition, soot nanostructure for “nascent” (raw soot), and partially oxidized (extent 50%) samples at 1 and 10 atm was studied by HRTEM. The lamella length and tortuosity

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