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

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Abstract

Oxidation kinetics and fringe analysis studies of three “model” carbons, ranging from fullerenic 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” fullerenic 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 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) towards 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 [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% O₂ 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 micro-spectroscopy (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, λ_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 measures were found relevant to correlating nanostructure and soot reactivity.

2. EXPERIMENTAL METHODS AND PROCEDURES

2.1 Soot Samples

Three commercial carbon blacks, Monarch 1300 (Cabot), Regal 250 (Cabot), custom onion-like carbon (OLC), obtained from a high temperature process, and a reference diesel soot were used in this study. The reference diesel soot is a NIST standard material (SRM 2975), collected from an industrial diesel powered forklift. The reference material experiments were included to understand the properties such as morphology, nanostructure and reactivity, of diesel soot produced from an engine under controlled conditions.

2.2 Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer (TGA- SDT Q600) was used for the oxidation experiments. The samples were pretreated in an inert gas until the desired oxidation temperature to drive off volatile matter with a ramp rate of 10 °C/min. The inert gas (N₂) was then switched to air at a volumetric flow rate of 500 ml/min. The mass loss curve was obtained as oxidation proceeded isothermally followed by a cooling down to room temperature.

Experiments were conducted with approximately 5 mg for Monarch 1300 (M1300), 10 mg for onion-like carbon (OLC), 8 mg for Regal 250 (R250) and 3 mg for diesel soot. The sample was placed in a quartz crucible (3.92 mm diameter and 4.35 mm height). Isothermal tests were performed at temperatures from 550 to 700 °C for M1300 and R 250, in increments of 25 °C. For the OLC, tests were performed from 575 to 775 °C. The mass loss data was recorded approximately every half second.

In addition, a high-pressure thermogravimetric analyzer (HP-TGA), Cahn TherMax 500, was used to create partially-oxidized samples at 10 atm.

2.3 BET surface area (SA)

Internal surface area of the samples was measured by isothermal gas adsorption using a surface area and porosimetry analyzer (Micromeritics, Tristar II 3020) with N₂ as adsorptive gas at 77 K (liquid nitrogen bath). Before analysis each sample was degassed under 250 °C with a N₂ gas flow for 2h to remove the moisture and any other adsorbed gas. The total surface area was obtained by analyzing the isotherms using the Brunauer–Emmett–Teller (BET) method.

2.4 HRTEM characterization and Lattice fringe analysis

The morphology and nanostructure analyses were performed in a 200- kV field emission TEM (JEOL® EM-2010F) instrument. The partially-oxidized samples were collected after

reaching about 50% weight loss in a TGA. All samples (“nascent” and partially-oxidized samples) were suspended in ethanol (200 proof) and sonicated for 15 minutes, followed by dropping the sample using a glass micropipette, onto a lacey C/Cu TEM grid (Ted Pella 300-mesh Formvar). The main purpose for using ethanol was to disperse the sample uniformly and to avoid sample agglomeration that can interfere during the TEM image acquisition. The grids were allowed to dry completely prior to being stored in the grid holder. The applied magnification was set at 40,000x for morphology investigation, and 500,000x for nanostructure analysis. All images were acquired in a Gatan® DigitalMicrograph with a slow scan CCD camera using a condenser aperture size of 70 μm and an exposure time of 0.5~1s. The average primary particle size was determined using TEM images obtained under 40,000x magnification, by measuring the diameter of more than 200 particles for each sample, using the image processing and analysis software ImageJ®. To minimize the measurement error, particles with unclear boundaries or overlapping were excluded. The binned data was plotted as histograms (fitted to lognormal distribution) from which average particle size was extracted.

Imaging analysis was performed on “nascent” and partially oxidized samples using algorithms written in-house. Quantification of the HRTEM images by lattice fringe analysis provided several statistical metrics describing the nanostructure order [37]. Fringe length is a measure of the physical extent of lamellae, whereas fringe tortuosity is a measure of their curvature of their as observed in the HRTEM images. Digital images were processed using custom separate algorithms to extract nanostructure parameters, namely length and tortuosity [38]. Histograms summarizing the distributions were fit to a 2-parameter lognormal distribution function. As for all our analyses, ~5 images are analyzed to test statistical similarity, with results co-added to measure the median fringe length and fringe tortuosity.

3. RESULTS AND DISCUSSION

3.1 Particle size distributions and surface area measurements

Representative TEM images showing the aggregate structure of the three carbon blacks and the diesel soot are illustrated in Fig. 1. Only the R250 carbon black appears to be in close resemblance to that of the “nascent” diesel soot with open, branched structures. The primary particle diameters ranged between 8 and 78 nm and the distributions are presented in Fig. 2. The mean particle size (d_p) (Table 1) ranged from 13 to 51 nm. M1300 presents the lowest particle sizes, while R250 and OLC had the largest particle size. The specific surface area of the samples (Table 1) ranged between 45 and 432 m^2/g , with M1300 showing the highest value and OLC the lowest value. Table 1. Shows these parameters in order of decreasing surface area.

3.2 Optimization of variables affecting TGA experiments

Under certain operating conditions (oxidizer flow rate, initial sample mass and type of crucible), the soot oxidation kinetics inside the TGA furnace could be a partially diffusion–

controlled reaction [39, 40]. In this case, the kinetic parameters cannot be directly obtained from TGA plots, and a combination of diffusive and kinetic models is necessary [39, 40]. To ensure that the TGA results reported in this study were not affected by diffusion limitations, multiple experiments were performed to find the most favorable conditions to estimate the kinetic parameters.

To study the effect of initial mass sample in the TGA results, a set of runs were carried out at 600°C and 500 ml/min of oxidizer gas (air) with initial mass loadings ranging from 2 to 10 mg for M1300 carbon, 5 to 16 mg for OLC, R250 carbon and 2-8 mg for diesel soot. The oxidation rates were slow when large loading masses were used indicating mass-transfer resistances through the sample layer. Low loading masses were discarded due to low reproducibility. Initial loading masses of 8-10 mg were selected as the optimal for R250 and OLC; 5 mg was used for M1300 carbon and 3 mg for diesel soot. To evaluate the effect of oxidizer gas flow rates in the mass-based oxidation profiles, combustion of 5 mg of M1300 carbon sample was carried out at 650°C at five oxidizer gas (air) flow rates ranging between 100 and 500 ml/min. The oxidation rate at a gas flow rate of 100 ml/min was lower than the 200 ml/min and 300 ml/min, but constant for gas flow rates of 400 ml/min or higher. To avoid oxygen diffusion limitations, the gas flow rate used in these experiments was 500 ml/min.

Based on previous results which showed no pressure effects on the kinetic parameters, only data from atmospheric pressure runs was utilized [36].

3.3 Oxidation Kinetics

The TGA mass loss curves were obtained under isothermal conditions and used to determine the oxidation kinetic parameters. An Arrhenius-type equation and first-order reaction kinetics was used to extract the kinetic parameters. The Arrhenius plots for the samples are presented in Fig. 3. The apparent kinetic parameters and the rate constants estimated for a fractional oxidation (α , based on mass) range up to 0.6 and are presented in Tables 2 and 3. The activation energies for the oxidation of the carbon samples ranged from 126 to 202 kJ/mol. M1300 had the lowest activation energy value while OLC had the highest. The activation energy and pre-exponential factor values for R250 and diesel soot were similar. The activation energies obtained for the samples studied were in accordance with data reported in the literature for carbon blacks and diesel soot samples [4, 14, 41-43]. Figure 4 shows the rates of oxidation, based on kinetic parameters, at 600 °C. The OLC exhibited a slower kinetic rate with a pre-exponential factor three orders of magnitude higher than for the other samples.

The reactivity of the samples can be related to the size and surface area of the particles. M1300, with the smallest size and largest surface area, showed the highest reactivity. The OLC sample with a large particle size and lowest surface area, exhibited lowest reactivity. These results are consistent with the results obtained by Sharman et. al [44].

3.4 Soot nanostructure and fringe analysis

Figure 5 illustrates the HRTEM images of the three carbon blacks and the diesel soot (each representative of nearly 50 images). In these bright-field images, the graphene layer segments are observed edge-on, via electron beam interference, hence the term “fringe” as reference. At higher magnifications, the three carbon blacks exhibit different nanostructure in their “nascent” form. M1300 exhibits mostly partially and completely closed shells whose diameter is roughly a few nanometers. In most cases the shells are not spherical but distorted, with the interior of these shells appearing to be a void. The OLC exhibited extended carbon lamella, many with ordered stacking. This organization is characteristic of a graphite structure. In contrast, R250 has short, disconnected, planar crystallites comprising several polyaromatic hydrocarbon (PAH) layers that are oriented in a concentric fashion. The particle interior exhibits more spatially disorganized carbon. Dissimilar to the carbon blacks, the reference diesel soot showed a core shell structure [45]. The outer shell is composed of several crystallites that are oriented parallel to each other, whereas the inner core is composed of several fine particles that are covered by several carbon layers with a distorted structure [46]. The values for activation energy can be related to these structures. Activation energy increased as the structure of the carbon became more ordered, as suggested by Neeft et al. [4]

Upon partial oxidation (extent 50%), HRTEM was performed to examine the nanostructural changes relative to the “nascent” material, and also to study the pressure dependence. As shown in Fig. 6, visually M1300 still consists of partially formed shells, but many have transformed to extended lamellae with some apparent loss of voids. Both pressure conditions showed roughened surfaces, indicative of oxidation. In contrast, R250 carbon black exhibited noticeably different nanostructure compared to the “nascent” nanostructure as shown in Fig. 7. Especially at atmospheric pressure, internal burning mode with little to no change of the outer shell was observed in the images. These hollow, shell-like particles appeared throughout aggregates. Internal structure and content were largely absent and visualization of lamellae was only clearly resolved along the particle perimeters. The lamella on the particle perimeters were not highly ordered, but were more undulated. This different burning mechanism was earlier reported for a few diesel soots, but is a unique observation for R250 carbon [15, 29, 45]. This same internal burning mode was not observed when R250 carbon was oxidized at a higher pressure (10 atm).

With increasing oxidative pressure, OLC exhibited a decrease in graphitic structure and increase in curvature primarily because of outer surface breakup (Fig.8). It could be understood that the oxygen might be only penetrating within the outer portions of the particles and causing breakup of the initial graphene segments, especially at higher TGA pressure. Similar to the R250, the diesel soot also showed different burning modes at the two oxidative pressures studied. As seen in Fig.9, at atmospheric pressure, oxidized diesel soot showed numerous hollow interiors with graphitized shells. Though difficult to quantify, qualitatively this soot possessed more uniform shell like structures than the R250 sample (as shown in the lower magnification images in supplemental section). At higher oxidation pressure, visually the outer surface appears to be dismantled.

Quantification of the HRTEM images describes nanostructure order; this can be achieved by lattice fringe analysis, which provides several physical metrics of the nanostructure. For the hollow shell nanostructures angle tilt studies confirmed that the inner core (hollow) region lacked any structure, so only the peripheral lamellae were analyzed. The median fringe length and tortuosity values are summarized in Fig. 10, for the three carbon blacks and diesel soot, “nascent” and after oxidation at the two pressure conditions. Consistent with the visual representations, the R250 lamellae became slightly longer with less tortuosity; those of the OLC broke up, while for the M1300 they became flatter, as a result of oxidation.

Fringe analyses do not convey the different burning modes for R250, as it only measures the physical dimensions of individual lamella. As observed in the initial nanostructure, the interior core had disorganized carbon, which preferentially burned out faster than the concentrically oriented outer lamellae at atmospheric pressure. At higher pressure, oxidation occurred faster at the particle surface by virtue of higher O₂ concentration. Therefore, internal burnout does not compete, and the faster burnout (i.e. higher rate of activation) appeared to facilitate realignment of the peripheral lamellae, as indicated by a small increase in fringe length (Fig. 10).

For M1300, the nanostructure was locked-in by the surrounding matrix, preventing lamella reorientation or extension. Neighboring lamellae with concentric curvature likely inhibited relaxation to a less-strained configuration suggesting a small increase in fringe length with oxidation. In contrast a highly ordered carbon such as the OLC exhibits an opposite trend. Lattice fringe analysis of OLC showed a decrease in nanostructure order, in agreement with the visual representations where external burning occurred led to breakup of outer surface lamellae.

By comparison the diesel soot has little change in fringe length and tortuosity. A slight decrease in fringe length was observed with increase in pressure. This suggests that the external structure of diesel soot might contain more reactive components that would preferentially burnout first.

3.5 Comparison of soot nanostructure and reactivity

Fringe analysis parameters, fringe length, and fringe tortuosity, for the different model carbons and reference diesel soot, are plotted against the activation energy values, in order to establish a structure-property relation between physical nanostructure, extracted from the HRTEM results and the oxidative reactivity. Figure 11 shows that as the activation energy value increased, fringe length increased and fringe tortuosity decreased. Previous studies have similarly shown correlation between these nanostructure metrics and oxidation rate [10, 17]. This is consistent with the interpretation of increasing reactivity as reflecting a lower relative fraction of edge site carbon atoms. Another consideration is less C-C bond strain (reflecting lower lamella curvature), effectively increasing the activation energy and decreasing the oxidation rate.

4. SUMMARY AND CONCLUSIONS

In this study, isothermal oxidation experiments were conducted for three carbon blacks and one reference diesel sample. The activation energies for the oxidation of the carbon samples ranged from 124 to 204 kJ/mol, and it was approximately 140 kJ/mol for the diesel soot. The onion-like structure exhibited a slower kinetic rate compared to the fullerenic M1300. Similar kinetic parameters were found for R250 and reference diesel soot samples.

HRTEM images visually revealed that the three uniform model carbons offered a broad set of nanostructures. M1300 carbon possesses highly-curved lamella, appearing as partial and closed, elongated and otherwise distorted shells. OLC carbon shows extended graphitic lamellae. R250 carbon had short, disconnected, individual lamella segments that appeared concentrically oriented about a disorganized inner core. Dissimilar to the model carbons, the reference NIST diesel soot (SRM 2975) showed a nanostructure commonly referred to as core-shell structure, which is characteristic of the majority of soot nanostructure from real diesel engines.

HRTEM images with increasing oxidative pressure showed a significant change in nanostructure relative to the “nascent” structure. Both the “nascent” material nanostructure and pressure played a role in the observed changes. However, the mass transfer diffusion resistances were previously observed from the TGA data under higher pressure conditions [36]. These mass transfer limitations are difficult to uncouple from the high pressure conditions; as such, the mass transfer resistances could have also contributed to changes in nanostructure.

The fringe analysis explained the differences in the kinetic parameters between the carbon samples studied. OLC “nascent” sample had a longer range of lamellae lengths with lower tortuosity, suggesting generally flatter structure; the “nascent” M1300, had somewhat shorter lamellae with broader tortuosity, indicative of greater curvature. The nanostructure parameters for the “nascent” R250 and diesel sample were between the other two carbons. Due to the similarity of initial nanostructure between the diesel and R250, oxidation rates should be similar, as indeed observed by very comparable activation energies.

The significance of this study was the high correlation between the activation energy and nanostructure. With increasing lamella length, reflecting a larger basal-to-edge carbon atom fraction, activation energy increases. However, curvature, inducing bond strain decreases the activation energy for oxidative attack. These results illustrate a key structure-property relationship for carbon, illustrated here by the oxidative reactivity dependence upon nanostructure.

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REFERENCES

- [1] A.D.H. Clague, J.B. Donnet, T.K. Wang, J.C.M. Peng, *Carbon* 37 (1999) 1553–1565.
- [2] F.J. Miller, D.E. Gardner, J.A. Graham, R.E. Lee Jr, W.E. Wilson, J.D. Bachmann, *J. Air Pollut. Control Assoc.* 29 (1979) 610–615.
- [3] G.A. Stratakis, A.M. Stamatelos, *Combust. Flame* 132 (2003) 157–169.
- [4] J.P.A. Neeft, T.X. Nijhuis, E. Smakman, M. Makkee, J.A. Moulijn, *Fuel* 76 (1997) 1129–1136.
- [5] A.L. Boehman, J. Song, M. Alam, *Energy & Fuels* 19 (2005) 1857–1864.
- [6] R. López-Fonseca, U. Elizundia, I. Landa, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, *Appl. Catal. B Environ.* 61 (2005) 150–158.
- [7] J.P.A. Neeft, M. Makkee, J.A. Moulijn, *Fuel Process. Technol.* 47 (1996) 1–69.
- [8] A. Liati, E.D. Eggenschwiler, D. Schreiber, V. Zelenay, M. Ammann, *Combust. Flame* 160 (2013) 671–681.
- [9] K. Yehliu, R.L. Vander Wal, O. Armas, A.L. Boehman, *Combust. Flame* 159 (2012) 3597–3606.
- [10] J. Song, M. Alam, A.L. Boehman, U. Kim, *Combust. Flame* 146 (2006) 589–604.
- [11] K. Yamamoto, K. Yamauchi, *Proc. Combust. Inst.* 34 (2013) 3083–3090.
- [12] X. Cheng, L. Chen, G. Hong F. Yan, S. Dong, *Applied Thermal Engineering* 62 (2014) 303–312 (2014).
- [13] I.M. Kennedy, *Prog. Energy Combust. Sci.* 23 (1997) 95–132.
- [14] K.J. Higgins, H. Jung, D.B. Kittelson, J.T. Roberts, M.R. Zachariah, *J. Phys. Chem. A* 106 (2002) 96–103.
- [15] R.L. Vander Wal, A. Yezerets, N.W. Currier, D.H. Kim, C.M. Wang, *Carbon* 45 (2007) 70–77.
- [16] R.L. Vander Wal, A.J. Tomasek, *Combust. Flame* 134 (1–2) (2003) 1–9.
- [17] A. Strzelec, T.J. Toops, C.S. Daw, D. Foster, *SAE Technical Paper* 2010-01-2127 (2010).

- [18] R.L. Vander Wal, A. Strzelec, T.J. Toops, C.S. Daw, C.L. Genzale, *Fuel* 113 (2013) 522-526.
- [19] H. Ghiassi, P. Toth, J.S. Lighty, *Combust. Flame* 161 (2014) 671-679.
- [20] H.J. Seong, A.L. Boehman, *Energy & fuels* 25 (2011) 602–616.
- [21] C. Arnal, C. Esarte, M. Abian, A. Millera, R. Bilbao, M.U. Alzueta, *Chemical Engineering Transactions* 22 (2010) 251-256.
- [22] M. Lapuerta, F. Oliva, J.R. Agudelo, A.L. Boehman, *Combust. Flame* 159 (2012) 844-853.
- [23] I. Atribak, A. Bueno-Lopez, A. Garcia-Garcia, , *Combust. Flame* 157 (2010) 2086-2094.
- [24] J. Rodríguez-Fernández, F. Oliva, R. A. Vázquez, *Energy & Fuels* 25 (2011) 2039–2048.
- [25] M. Happonen, T. Lahde, M.E. Messing, T. Sarjovaara, M. Larimi, L.R. Wallenberg, A. Virtanen, J. Keskin, *Fuel* 89 (2010) 4008-4013.
- [26] A. Yezerets, N.W. Currier, H.A. Eadler, A. Suresh, P. F. Madden, M.A. Branigin, *Catalysis Today* 88 (2003) 17–25
- [27] D.S. Su, J.O. Müller, R.E. Jentoft, D. Rothe, E. Jacob, R. Schlögl, *Top. Catal.* 30/31 (2004) 241-245.
- [28] K.O. Lee, R. Cole, R. Sekar, M.Y. Choi, J.S. Kang, C.S. Bae, *Proc. Combust. Inst.* 29 (2002) 647–653.
- [29] K. Al-Qurashi, A.L. Boehman, *Combust. Flame* 155 (2008) 675–695.
- [30] H.L. Fang, M.J. Lance, *SAE Paper No. 2004-01-3043* (2004).
- [31] F.A. Heckman, D.F. Harling, *The American Chemical Society Meeting, Miami Beach, FL, (1965)* 1–13.
- [32] J.N. Rouzaud, C. Christian, *Carbon* 77-78 (2002) 229-235
- [33] J. Schmid, B. Crob, R. Niessner, N.P. Ivleva, *Anal. Chem.* 83 (2011) 1173-1179.
- [34] M. Lapuerta, F. Oliva, J.R. Agudelo, J.P. Stitt, *Combust. Sci. and Tech.* 183 (2011) 1203-1220.
- [35] L. Pahalagedara, H. Sharma, C-H. Kuo, S. Dharmarathna, A. Joshi, S.L. Suib, A.B. Mhadeshwar, *Energy & Fuels* 26 (2012) 6557-6764.

- [36] I.C. Jaramillo, C.K. Gaddam, R.L. Vander Wal, C.-H. Huang, J.D. Levinthal, J.S. Lighty, *Combust. Flame* 161 (2014) 2951–2965.
- [37] R.L. Vander Wal, A.J. Tomasek, M.I. Pamphlet, C.D. Taylor, W.K. Thompson, J. *Nanoparticle Res.* 6 (2004) 555–568.
- [38] K. Yehliu, R.L. Vander Wal, A.L. Boehman, *Combust. Flame* 158 (2011) 1837–1851.
- [39] J. Song, C-H. Jeon, A.L. Boehman, *Energy & Fuels* 24 (2010) 2418–2428.
- [40] Q. Song, B. He, Q. Yao, Z. Meng, C. Chen, *Energy & fuels* 20 (2006) 1895–1900.
- [41] B.R. Stanmore, J. Brilhac, P. Gilot, *Carbon* 39 (2001) 2247–2268.
- [42] B. Stanmore, P. Gilot, G. Prado, *Thermochim. Acta* 240 (1994) 79–89.
- [43] K.J. Higgins, H. Jung, D.B. Kittelson, J.T. Roberts, M.R. Zachariah, *Environ. Sci. Technol* 37 (2003) 1949–1954.
- [44] H.N. Sharma, L. Pahalagedara, A. Joshi, S.L. Suib, A.B. Mhadeshwar, *Energy & Fuels* 26 (2012) 5613–5625.
- [45] T. Ishiguro, Y. Takatori, K. Akihama, *Combust. Flame* 108 (1997) 231–234.
- [46] T. Ishiguro, N. Suzuki, Y. Fujitani, H. Morimoto, *Combust. Flame* 85 (1991) 1–6.

Figure 1. Typical TEM images of the model carbons a) M1300, b) R250, c) OLC, and d) diesel soot.

Figure 2. Primary particle size distributions (d_p) of the model carbons and diesel soot. The mean diameters are: M1300 – 13 nm; R250 – 50 nm; OLC – 43 nm; and Diesel Soot – 28 nm.

Figure 3. Arrhenius plots for M1300, Diesel, R250 and Onion.

Figure 4. Mass-based oxidation rate for three different carbon black samples and diesel sample, at 600 °C and air.

Figure 5. HRTEM images of different “nascent” samples, a) M1300, b) R 250, c) OLC, and d) diesel soot.

Figure 6. Representative HRTEM images of partially oxidized (50%) M1300, a) 1 atm and b) 10 atm

Figure 7. Representative HRTEM images of partially oxidized (50%) R250, a) 1 atm and b) 10 atm [white arrows mark internal void(s), black arrow indicates lamellae on the particle perimeter]

Figure 8. Representative HRTEM images of partially oxidized (50%) OLC, a) 1 atm and b) 10 atm [arrow indicates external breakup]

Figure 9. Representative HRTEM images of partially oxidized (50%) diesel, a) 1 atm and b) 10 atm. [arrow indicates external breakup]

Figure 10. Comparison of the median a) fringe length and b) tortuosity extracted from the lognormal distribution plots by lattice fringe analysis.

Figure 11. Comparison of the activation energy ratio for different samples versus a) mean fringe Length, b) mean, fringe tortuosity

Table 1. Particulate size and surface area values

Sample	Median Particle Size dp (nm)	BET surface area (m ² /g)
M1300	13	432
Diesel	28	91
R250	50	54
OLC	43	45

Table 2. Apparent kinetic constants extracted from Arrhenius plots from isothermal experiments. Parameters are given for fractional conversion, α , range of 0.1-0.6.

sample	$k_{575\text{ C}}$ (Pa ⁻¹ min ⁻¹)	$k_{600\text{ C}}$ (Pa ⁻¹ min ⁻¹)	$k_{625\text{ C}}$ (Pa ⁻¹ min ⁻¹)	$k_{650\text{ C}}$ (Pa ⁻¹ min ⁻¹)	$k_{700\text{ C}}$ (Pa ⁻¹ min ⁻¹)
M1300	2.05E-05	3.04E-05	6.20E-05	7.95E-05	1.70E-04
Diesel	2.21E-06	3.58E-06	9.09E-06	9.50E-06	1.80E-05
R250	1.77E-06	3.13E-06	7.60E-06	1.29E-05	1.98E-05
OLC	2.38E-07	1.71E-07	2.54E-07	6.69E-07	2.76E-06

Table 3. Apparent kinetic parameters extracted from Arrhenius plots from isothermal experiments

sample	α (fractional conversion)	Temperature range (°C)	E (kJ/mol)	A (pa ⁻¹ min ⁻¹)	R ²
M1300	0.2-0.6	575-650	126	9.92E+02	0.97
Diesel	0.2-0.6	575-650	141	8.56E+02	0.95
R250	0.2-0.7	575-700	140	8.34E+02	0.94
OLC	0.1-0.6	600-700	202	1.85E+05	0.98

Figure1

Figure 1. Typical low magnification TEM images of the model carbons (a) M1300, (b) R250, (c) OLC, and (d) diesel soot.

Figure2

Figure 2. Primary particle size distributions (d_p) of the model carbons and diesel soot. The mean diameters are: M1300 – 13 nm; R250 – 50 nm; OLC – 43 nm; and Diesel Soot – 28 nm.

Figure3

Figure 3. Arrhenius plots for M1300, Diesel, R250 and Onion.

Figure4

Figure 4. Mass-based oxidation rate for three different carbon black samples and diesel sample, at 600 °C and air. [Note: different X-axis scale lengths]

Figure 5. HRTEM images of the “nascent” model carbons: (a) M1300, (b) R 250, (c) OLC, and (d) diesel soot.

Figure6

Figure 6. Representative HRTEM images of partially oxidized (50%) M1300 at oxidation pressures of: (a) 1 atm and (b) 10 atm

Figure7

Figure 7. Representative HRTEM images of partially oxidized (50%) R250 at oxidation pressures of: (a) 1 atm and (b) 10 atm [white arrows mark internal void(s), black arrows indicate lamellae on the particle perimeter]

Figure8

Figure 8. Representative HRTEM images of partially oxidized (50%) OLC at oxidation pressures of: (a) 1 atm and (b) 10 atm [arrow indicates external breakup]

Figure9

Figure 9. Representative HRTEM images of partially oxidized (50%) diesel soot at oxidation pressures of: (a) 1 atm and (b) 10 atm. [white arrows mark internal void(s), black arrow indicates lamellae on the particle perimeter]

Figure10

Figure 10. Comparison of the median (a) fringe length and (b) fringe tortuosity, extracted from the lognormal distributions by lattice fringe analysis.

Figure11

Figure 11. Comparison of the activation energy for different carbons versus (a) fringe length, and (b) fringe tortuosity