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PAH structure analysis of soot in a non-premixed flame using high-resolution transmission electron microscopy and optical band gap analysis

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ABSTRACT

Soot particles formed in a system of non-premixed liquid fuel flames supported on a wick-fed, smoke point test burner (ASTM D1322-08) were characterized by in-situ visible light extinction and thermophoretically-sampled high-resolution transmission electron microscopy measurements, HRTEM. The fuels studied were heptane, toluene and their iso-volumetric mixture (H50T50), given their relevance as surrogate fuels. Extinction measurements were used to calculate the soot volume fraction, F_v, and determine the optical band gap (OBG) as a function of flame position. The OBG was derived from the near-edge absorption feature using Tauc/Davis-Mott analysis. A direct band gap ($r = 0.5$) was selected for this analysis assuming that the electronic properties of soot are dominated by the molecular structure of the PAHs. For the HRTEM analysis, soot samples were collected at different locations in the flame using thermophoretic sampling and a fast-insertion technique. The images were then analyzed using a ‘lattice-fringe’ algorithm, to determine important parameters such as the fringe length. Polycyclic aromatic hydrocarbon (PAH) sizes were estimated from conjugation lengths obtained from OBG measurements and fringe lengths from HRTEM measurements. Across all studied flames, the peak F_v ranged from 3.4 ppm in the heptane flame to 17.6 ppm in the toluene flame. Despite this wide range, the average OBG across the different flames only varied from 2.05 eV in the H50T50 to 2.10 eV in the toluene flames, which is consistent with molecule lengths of between 0.96 nm and 0.99 nm. Lattice fringe analysis yielded slightly lower average fringe lengths between 0.91 and 0.99 nm throughout the different flames. Results of in-situ and ex-situ characterization of soot suggests that flames of different fuel nature and sooting stage undergo the transition from chemical to physical growth at a similar size, about the size of circumpyrene.

1. Introduction

The high complexity of petroleum-based fuels has encouraged the search for mixtures of limited components to ease the development of new combustion technologies through computational tools, and to generate insight and understanding of underlying fundamental processes. Commercial fuels are mixtures of hundreds of hydrocarbons. The primary chemical classes of hydrocarbons in fuels are paraffins, olefins and aromatics [1,2]. The soot particles formed by the combustion of these fuels are widely regarded as pollutants, and are increasingly regulated both in terms of number and mass of particulate matter emitted from on-road vehicles.

Sooting limits are defined to assess the sooting propensity of a fuel. In co-flow diffusion flames a common target is the smoke point – the greatest flame height without smoke emission under laminar diffusion combustion [3]. A lower smoke point indicates a higher sooting tendency. In the 1950s the first studies trying to relate the molecular structure of hydrocarbons with smoke point were published [4,5]. The results indicated that the rate at which hydrocarbons produced soot increased as follows: paraffins $<$ isoparaffins $<$ mono-olefins $<$ naphthenes $<$ alkynes $<$ aromatics. Comparing molecules with the same number of carbons, the more compact the structure, the greater the tendency to soot. Furthermore, several studies have observed that a high percentage of fuel carbon in aromatic structures is converted into soot [6]. Therefore branched or cyclic structures present lower smoke points, although the effect is

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small compared with the increase in sooting tendency derived from the increase of aromatic character [7].

The formation of soot during combustion has been the subject of extensive research. The last century has seen significant efforts to explain model, and predict the hundreds of chemical and physical changes that take place in combustion processes [8–15]. A widely accepted interpretation is that the pathway begins with the formation of molecular precursors such as polyacetylenes and polycyclic aromatic hydrocarbons (PAHs) from the fuel source [10]. There is some agreement that the rate limiting reaction is the formation of the first aromatic ring, for which various mechanisms have been proposed [16,17]. The mechanism for particle inception is debated, but there is significant proof suggesting PAHs play an important role [18,19]. As the molecular mass of PAHs increases a collision between two such molecules becomes more likely to result in the formation of a dimer [10]. Therefore polymerization occurs at an increasing rate, forming larger molecules until the inception of a solid nucleus occurs. Another model for particle inception states that changes in temperature and pressure along the space result in condensation of PAHs, followed by formation of liquid nuclei, which then proceed to form solid particles [10,17]. Once primary particles are formed, these nascent soot particles undergo surface growth (and in some systems, competing oxidation reactions), and the small particles agglomerate into larger fractal structures [8,10,20].

Experimental studies of soot morphology revealed that the crystallinity in mature soot particles arises due to stacking of planar PAHs to form parallel atomic layers and their alignment along the periphery of soot particles [21–24]. It is clear from these studies that PAH molecules act as a soot precursor, and their relative orientations reveals the degree of crystallinity of soot particles. The variations in the structure of the PAHs, their sizes and their orientations in soot particles has also been found to depend heavily on the type of the fuel producing it, fuel flow rate and the temperature [25,26]. The presence of PAH stacks and clusters revealed by HRTEM images of soot particles, indicates that the coagulation of PAHs may be responsible for soot nucleation. Furthermore, through Raman spectroscopy, crystallite sizes between 1.0 and 1.2 nm were estimated in a diffusion flame, corresponding to PAHs with 4–5 aromatic rings across (approximately the size of circumcoronene) [27].

In soot models it is often assumed that pyrene dimerization is the critical soot particle formation step [28,29]. However, there are a number of recent studies that challenge this view [16,30–33]. For example, the PAH growth mechanism presented by Violi [34] models large, non-planar PAH sheets in a flame-like environment. A large set of reactions describe the growth of a PAH molecule using a kinetic Monte Carlo (KMC) algorithm and Molecular dynamics (MD) techniques. They found that molecular size was the largest factor with the onset of dimerization possibly beginning with PAHs the size of ovalene ($C_{38}H_{14}$) [34,35]. Similar results were found by Kraft's group at Cambridge employing a population balance PAH-PP (polyaromatic hydrocarbon-primary particle) model [36–38] coupled with KMC-ARS (kinetic Monte-Carlo-aromatic site). For the physical binding of PAHs based on van der Waals interactions large PAH molecules of the order of 50 carbon atoms were found to be required [36,39]. Using conventional molecular dynamics (MD) simulations with the isoPAHAP potential (isotropic potential for the PAH interactions), the melting points of clusters of ovalene, hexabenzocoronene and circumcoronene were estimated. It was concluded that at 1500 K a critical size of peri-condensed PAH for a nascent soot particle is $C_{71}H_{21}$ and for a mature particle is $C_{54}H_{18}$ (circumcoronene) [40].

The purpose of this paper is to estimate the size of aggregating[1] aromatics in soot particles. A combination of two techniques is used to find characteristic lengths of PAHs: an optical band gap (OBG) determination from Tauc/Davis-Mott analysis [42] to estimate the conjugation length, and 'lattice-fringe' analysis from HRTEM images to estimate fringe lengths. We compare the results of the two techniques from soot formed in a wick-fed diffusion flame burning different liquid fuels. The fuels studied were heptane, toluene and their iso-volumetric mixture (H50T50), given their relevance as surrogate fuels. Extinction measurements were used to calculate the soot volume fraction, F_v, and determine the OBG. Soot was thermophoretically sampled from the flames and imaged with HRTEM.

2. Methods

2.1. Burner

In this study, the smoke point test burner [3] was used as simple, known and standardized way to test different liquid fuels in terms of their combustion at atmospheric conditions. This wick-fed burner (inset Fig. 1), that has been previously described [43,44], was used to generate a laminar diffusion flame of liquid fuel. The burner consists of a cylindrical reservoir, with an inner concentric hole where the wick is placed, and a 7 mm i.d nozzle. The flame height is adjusted by rotating a threaded fitting and increasing the wick exposure (i.e, increasing the fuel flow rate).

The fuels tested are heptane, toluene and their mixture of 50/50% by volume (H50T50). Flame heights close to the smoke point were selected: 4 cm, 0.7 cm and 1.1 cm respectively. In the case of heptane the selected flame height was much lower than its smoke point (7.3 cm) due to experimental limitations [44].

2.2. Extinction measurements and Tauc analysis

The experiment schematic is shown in Fig. 1. Full details of this set-up can be found in a previous manuscript [42]. In summary, the collimated beam from a broadband super continuum light source (NKT Photonics EXB-4) was expanded and focused onto the entrance slit of a monochromator, McPherson Model 2035 with 1200 g/mm gratings blazed at 500 nm (providing 2 nm resolution in the experimental configuration). The beam was then split into two channels, the extinction channel, which provided line of sight measurements through the flame and a power metering channel, which bypasses the flame allowing for power fluctuation monitoring. The transmitted light channel was periscoped into the flame and then focused into the center of the flame, at the focal point the beam diameter was 0.47 mm. Downstream of the flame, the beam was collimated and focused onto a photodiode detector with a mounted diffuser facilitating detection. A pair of lock-in amplifiers, referencing a chopper at 400 Hz, were used to collect and digitize the signal.

The flame was scanned horizontally over the range −1.0 cm–1.0 cm in 0.05 cm increments, at each wavelength. After completing the scan, the positioner would return to the starting position and the monochromator would move 2 nm to the next wavelength. The procedure was repeated until the entire spectral range, 440 nm–740 nm, was covered. The spectral range between 540 nm and 740 nm was covered with steps of 10 nm. The height above the burner (HAB) was measured from the burner rim. Heptane flame was mapped from an HAB of 0.5 cm in 0.5 cm increments until the tip (4 cm). H50T50 and toluene flames were mapped from 0.3 cm HAB, in increments of 0.2 cm until the flame tip (1.1 cm and 0.7 cm respectively).

Given that the flame is axi-symmetric, the line of sight extinction will be a combination of contributions from the different radial positions. The radially distributed extinction was tomographically reconstructed using an Abel inversion technique. In this paper, the extinction spectra as a function of wavelength are fit to a power function

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[1] Aggregates are defined as assemblages of PAHs including primary particles. Agglomerates are defined as assemblages of primary particles into fractal structures [41]