



Effects of methyl group on aromatic hydrocarbons on the nanostructures and oxidative reactivity of combustion-generated soot



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ABSTRACT

The substituted and unsubstituted aromatic hydrocarbons, present in transportation fuels such as gasoline and diesel, are thought to be responsible for most of the soot particles produced during their combustion. However, the effects of the substituted alkyl groups on the aromatic hydrocarbons on their sooting tendencies, and on the physical and chemical properties of soot produced from them are not well understood. In this work, the effect of the presence of methyl groups on aromatic hydrocarbons on their sooting propensity, and on the oxidative reactivity, morphology, and chemical composition of soot generated from them in diffusion flames is studied using benzene, toluene, and *m*-xylene as fuels. Several experimental techniques including high resolution transmission electron microscopy and X-ray diffraction are used to identify the morphological changes in soot, whereas the elemental and thermo-gravimetric analyses, electron energy loss spectroscopy, and Fourier transform infrared spectroscopy are used to study the changes in its chemical properties and reactivity. The activation energies for soot oxidation are calculated at different conversion levels, and a trend in the reactivity of soots from benzene, toluene and *m*-xylene is reported. It is observed that the sizes of primary particles and graphene-like sheets, and the concentrations of aliphatics and oxygenated groups in soot particles decreased with the addition of methyl group(s) on the aromatic ring. The physicochemical changes in soot are found to support the oxidative reactivity trends.

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1. Introduction

The fossil-derived transportation fuels, diesel and gasoline, are complex blends of hydrocarbons that are produced in petroleum refineries by fractional distillation of crude oil [1–3]. Diesel consists mainly of alkanes (paraffins and naphthenes) and aromatic hydrocarbons, whereas gasoline contains alkanes, alkenes and aromatic hydrocarbons [4]. About 75% and 50% by weight of alkanes are present in diesel and gasoline, respectively [2,3]. Gasoline contains about 15–40% by weight of alkenes [3,4]. Aromatic hydrocarbons form a significant part of fuels, representing about 10–25% by weight in diesel, and 20–50% by weight in gasoline [4,5]. Some of the abundant aromatic hydrocarbons in these fuels are ethylbenzene, toluene, xylenes, benzene, and naphthalenes [2,3,5,6].

During the combustion of these fuels, the emission of carbon monoxide, carbon dioxide, nitrogen oxides, sulfur oxides, volatile organic compounds, and soot takes place [7], which contribute to air pollution and global warming [8]. With the ever-increasing demand for fuels, the level of pollutants in the atmosphere is rising as well [9,10]. Soot emission to the environment reduces air quality, affects the climate, and can cause health problems such as asthma, lung cancer, and cardiovascular diseases [8,11,12]. For these reasons, government agencies around the world have implemented strict regulations on soot emission during fuel combustion [13,14]. To meet the emission regulations, it is important to understand the mechanism of soot formation and the effect of fuel properties on their sooting tendencies and soot characteristics, and to find novel methods to reduce pollutant emissions.

In this direction, several studies have been conducted in the literature on the emission and characterization of soot particles from aliphatic and aromatic fuels [15–19]. Soot, a product of pyrolysis or incomplete combustion of fuels [20,21], consists of near-spherical

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primary particles that are joined together via fragile networks and bonded by weak van-der-Waals force of attraction [22] to give rise to its aggregate structure [1,23]. The major elemental components of soot are carbon (>80 wt%), hydrogen (≈ 1 wt%, which is a relatively large amount on an atomic basis), and oxygen [24,25]. The oxygen atoms are present mainly as carbonyl, ethers, and anhydride surface groups [25,26]. The high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) [27–30] studies report that polycyclic aromatic hydrocarbons (PAHs) are present in soot [31–34], which either form nano-crystallites (PAH stacks) to give rise to their partially graphitic nature, or are randomly orientated with respect to each other to contribute to their partially amorphous character. Though many experimental and analytical works [20,35] have focused on the identification of the high molecular weight aromatic species (PAHs) present in soot particles, very limited information on them is available.

It has been highlighted in several studies that the above-mentioned soot characteristics (e.g., elemental composition and the ratio of crystalline graphite-like phase to amorphous organic carbons in soot) are highly dependent upon the operating conditions (fuel flow rate, temperature and pressure) and the fuel properties [20,27,36,37]. In general, aliphatic fuels lead to a lower degree of graphitization in soot as compared to aromatic fuels [38]. This is because, aliphatic fuels generate PAHs rich in aliphatic chains or condensable material that avoid the organization of graphitic layers [39]. In contrast, aromatic fuels, with high PAH concentration in their flames even at low flame heights, exhibit fast inception and growth of soot particles, and their dehydrogenation and aromatization in the post oxidation zone lead to graphitized structures in soot [40,41]. Santamaria et al. [27] reported that soot precursors and particles from aromatic flames have a higher degree of complexity than the samples obtained from an aliphatic flame. They observed that primary particles in benzene soot were nearly spherical, and formed well-defined chain-like aggregate structures. In [42], the morphological characteristics of soot from aliphatic and aromatic flames were studied, and it was reported that soot from aromatic flame had slightly higher degree of carbonization than that from aliphatic flames, possibly due to higher temperature in the aromatic flame. Using diffusion flames in [43], n-heptane, toluene and commercial gasoline were studied for their sooting behavior. Toluene soot appeared to have much larger and denser primary particles than heptane soot. Soot from gasoline and heptane/toluene mixture presented nearly spherical primary particles of small size. The same trend was observed in [5]. However, in [44], toluene addition to n-heptane did not exhibit any substantial effect on the size of primary particles and soot morphology. Jaramillo et al. [45] studied the morphology and reactivity of soot particles from *m*-xylene and *m*-xylene/n-dodecane mixture flames. While soot morphology did not change, soot from xylene/n-dodecane mixture exhibited a higher oxidation rate than soot from *m*-xylene. Recently, a comparative study of soots generated in a heavy-duty engine fueled with n-heptane and n-heptane/toluene mixture showed that n-heptane/toluene soot had highly curved nanostructure with higher concentration of aliphatic groups and σ/π ratio than n-heptane soot. The differences in soots from aliphatic and aromatic fuels were more visible in soots obtained from engine as compared to those from flames possibly due to different temperatures and pressures involved in them [46]. Though amorphous character is always present in soot particles, some aromatic fuels may also lead to the formation of fullerene nanostructures or curved PAHs in soot in low-pressure diffusion flames [47].

While both aliphatic and aromatic hydrocarbons are present in fossil fuels, it is known that the aromatic component is responsible for most of the soot particles originating during their combustion, presumably, because the aromatic ring may remain intact

during combustion, and provide a foundation for ring growth to form PAHs (soot precursors) [48]. For this reason, soot formation from aromatics has been a subject of interest since the second half of the last century [15–19,49]. A relationship between the sooting tendency and the molecular structure of aromatics was suggested in [50], where the addition of side chains to the aromatic ring increased the sooting tendency, and lengthening the chain decreased it. However, recent studies on branched aromatic fuels have shown that the lengthening of the chain has a promoting effect on their sooting tendency in flames [15,51]. A possible explanation to this is the decomposition of alkyl chains attached to the aromatic structure that lead to the formation of hydrocarbon radicals. These radicals along with the benzylic groups form naphthalene or higher aromatics. Significant differences in sooting tendencies have been found for alkylbenzenes because the formation and growth pathways for naphthalene and higher aromatics from primary, secondary and tertiary alkylbenzenes differ greatly from one another [51,52]. On the other hand, in the case of the methyl branch on aromatic rings the sooting tendency increased as the number of methyl groups was increased because it has a unique capacity to induce the sequential growth of a hexagonal network of sp^2 carbons [15,53]. The methyl group increases the soot formation rate because it provides three H-atoms that can be abstracted to produce a resonantly-stabilized benzylic group, which can form PAHs through the addition of a ring on the aromatic structure via a series of hydrocarbon addition, isomerization, and C–H fission reactions [15]. However, the position of the methyl group on the ring also plays a determinant role in fuel reactivity because the primary decomposition and molecular growth processes are affected [35]. When the methyl groups are not adjacent, the mono-aromatic structure is more stable, and it is harder to grow aromatic rings over it due to the presence of methyl groups. Consequently, soot is formed in small amounts [54], which indicates that the PAH and soot formation pathways in the flames of methyl-substituted hydrocarbons are fuel structure-dependent. The adjacent methyl groups on an aromatic fuel facilitate the formation of bicyclic aromatic species (e.g. naphthalene) that lead to high PAH concentrations in their flames. This can explain the high sooting tendency of *o*-xylene [55].

Along with the study of soot emissions from different fuels, it is also important to determine the characteristics of soot particles formed from them because the toxicity and the oxidative reactivity of soot particles are highly dependent on their nanostructures and composition [20,36,37]. Soot reactivity is particularly important for particulate filters that are used to capture soot from engine exhaust [56]. They are regenerated periodically by oxidizing soot to avoid pressure buildup in the exhaust system. The low reactivity of soot would mean a slow regeneration of filters and a possible requirement of high temperatures for soot burnout, thus making the filter and its catalyst prone to damage. For this reason, while reducing soot concentration (through new fuel formulation and/or blending), it is important to ensure that the oxidation kinetics of soot is not drastically hampered [45,57–62].

As mentioned before, while several studies provide information about the dependence of sooting tendency on fuel structure [15,50] the information about the variation in physical and chemical characteristics of soot (including its reactivity) with fuel structure remains scarce in the literature. Consequently, the role of alkyl groups bonded to aromatic fuels on the oxidative reactivity, chemical composition, and the morphology of soot particles generated during combustion is not well understood.

The aim of this study is to evaluate the effect of the presence of methyl groups on aromatic fuels on the physical and chemical characteristics of soot particles generated from them in diffusion flames using benzene, toluene, and *m*-xylene as model fuels. Although fossil-derived transportation fuels contain three xylene

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