



# Influence of aliphatic side chains of aromatic hydrocarbons on soot formation: Experimental and numerical investigation

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## ABSTRACT

The effect of aliphatic side chains in the feedstock on soot formation was studied with experimental and numerical simulation. Feedstocks of ethylbenzene, xylene, toluene, and benzene were pyrolyzed at different residence times and temperatures, and the particle size distribution (PSD) of the formed soot was measured. The initial nucleation rates of soot during ethylbenzene or toluene pyrolysis was high. However, after a long residence time, the amount of soot produced from benzene pyrolysis became higher than for these feedstocks. This result suggests that at long residence times, the growth rate of soot from benzene is higher than those of ethylbenzene and toluene. Numerical simulation for the pyrolysis of ethylbenzene, toluene, and benzene was conducted with the KAUST PAH Mechanism 2 (KM2) model, and the prediction accuracy was improved by adding some new reactions. The simulations were performed at two conditions similar to the experimental ones: The production rate of polycyclic aromatic hydrocarbons (PAHs) was very high at the beginning of reactions of ethylbenzene and toluene, indicating high rates of soot nuclei generation. In benzene pyrolysis, modification of the KM2 model led to a higher predicted PAH concentration than that with the original KM2. Most of the reactions we added to the KM2 model are those of PAH growth by phenyl addition (PA). Therefore, the PA mechanism would be an important reaction pathway for PAH growth in the pyrolysis of benzene.

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## 1. Introduction

During the combustion of fossil fuels, large amounts of substances are generated and emitted into the atmosphere to cause serious pollution. A main pollutant among them is soot, a carbon-based particulate matter. Because soot floats in the atmosphere, absorbing sunlight at an extraordinarily high rate and emitting a large amount of heat, it is thought to be partially responsible for global warming [1,2]. Also, soot particles can deeply penetrate the human body and harm the respiratory system [3,4]. For these reasons, it is important to understand the mechanism of soot formation to minimize its negative impacts. On the other hand, soot in the form of carbon black (CB) is an important ingredient in tires, ink, rechargeable batteries, and many other products. It has the aggregated morphology composed of many primary particles with diameters of 10–100 nm. When used as a reinforcement material in tires, the morphology of CB strongly affects the energy loss and wear resistance of the tire. However, only trial-and-error methods

have been developed to control the microstructure of CB. In this regard, understanding the mechanism of CB generation will elucidate factors that control its formation *a priori*, allowing the flexible design of CB morphology.

Several recent studies have examined the formation and characteristics of soot [5–7]. Ono et al. compared numerical results about the soot nucleation behavior obtained with the sectional method with experimental data of soot formation during the pyrolysis of benzene using image analysis [8]. The formation of soot particle nuclei was found to affect the final morphology of soot [9]. Furthermore, Dewa et al. observed the formation of soot nuclei by the soot particle size distribution, and evaluated its formation from secondary electron images [10]. Their results also indicated that the formation of the soot nuclei affected the final soot. Therefore, to understand soot formation, it is particularly important to clarify factors that affect the formation of soot particle nuclei.

Two kinds of models have been suggested as mechanisms for the formation of soot nuclei and CB. In the first model, the nuclei were formed through the addition of low-grade hydrocarbons to polycyclic aromatic hydrocarbons (PAHs) formed from the burning of fossil fuels, as well as from the reaction of identical PAHs [11–14]. In the second model that has been supported by many

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recent studies, polymers were formed and transformed into soot particle nuclei when several PAH molecules physically interact with one another [15–21]. Since both models assume PAHs as the precursor to soot, it is key to understand factors governing the formation of PAHs. Among relevant studies, Shukla et al. pyrolyzed various feedstocks and analyzed the chemical species with time-of-flight mass spectrometry (TOF-MS). Hydrogen-abstraction-carbon-addition (HACA), phenyl addition/cyclization (PAC), and methyl addition/cyclization (MAC) were suggested as important reaction mechanisms in the generation and growth of PAHs [22–25]. By measuring the particle size distribution (PSD) of soot produced from pyrolyzing a mixture of benzene and PAHs with 2–7 rings, Ono et al. pointed out the importance of the PAH-addition cyclization mechanism for generating PAHs with high molecular weights [26]. Despite these experimental investigations of PAH formation mechanism, however, the actual process involves a very large number of chemical species and many reaction pathways, making it difficult to evaluate the effect of a single reaction pathway. By considering some elementary reactions, detailed chemical reaction mechanisms were constructed, and the influence of specific reaction pathways could be evaluated. Wang and Frenklach constructed a pioneering model [27] of PAH generation and growth through the HACA mechanism in hydrocarbon combustion and pyrolysis. Using this model, they analyzed acetylene and ethylene flames and pointed out that the HACA mechanism is important in the formation of the first aromatic ring. Afterwards, more and more chemical species and reaction pathways were taken into account to produce more accurate models. Norinaga et al. [28] and Kousoku et al. [29] reported some important reaction pathways when benzene is used as the feedstock. The recent USC Mech Version II model [30] can predict the amount of benzene production with high accuracy when using low-grade hydrocarbons as feedstock. Meanwhile, the KM1 model [31] accurately predicts the amount of PAH generation using hydrocarbons. The USC Mech Version II and KM1 models were combined in the KM2 model [32], which allows accurate quantitative prediction of PAH formation for a wide variety of feedstocks. Nevertheless, even in cases where KM2 is accurate about the formation of PAHs, the predicted soot formation differs from the experimental observations [21].

As well as the PAH formation process, the coagulation process strongly has an effect on soot formation. Lindstedt and Waldheim reported that coagulation efficiency with PAHs would be larger with the molecular size of PAHs [33]. Sirignano and D'Anna suggested that the soot particles produced different feedstocks and reaction temperatures exhibit different behaviors of coagulation as a function of their size [34]. They reported small soot particles showed low coagulation rate. These studies do not focus on the dependence of coagulation process on various feedstocks.

The PSD of soot can consist of power distribution (showing the generation of particle nuclei) and log-normal distribution (showing the production of aggregates) [35,36]. Accordingly, many researchers have measured the PSDs of soot [5,6,37–44]. For example, Zhao et al. tested soot formed from ethylene flames, and reported that both the flame temperature and residence time influence the formation of particle nuclei and aggregates in soot [38]. Focusing on the feedstocks, Echavarria et al. compared the PSDs of soot generated from benzene and ethylene flames, and found that particles are generated in higher numbers and grow faster in the former [41]. Camacho et al. found that particle nuclei production in *i*-butanol flames is faster than in *n*-butanol ones [42]. Furthermore, Berero et al. formed soot in flames using toluene, heptane, and their mixtures as the feedstock, and reported that the smoke point dropped and the rate of particle growth accelerated as the ratio of toluene rose [43]. Since the feedstocks influence the reactivity as well as the reaction pathways [22–24], their effect on the rate and amount of soot nuclei production should be considered.

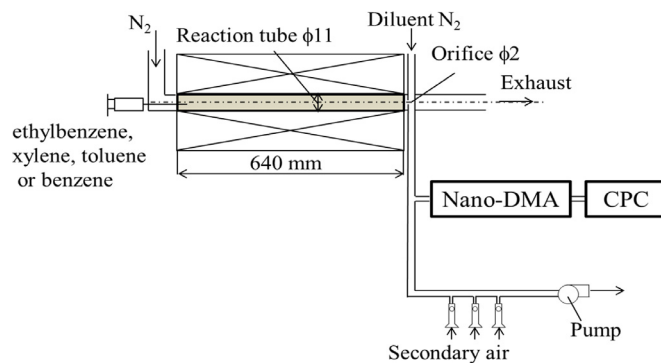


Fig. 1. Schematic of experimental apparatus ( $\phi$  means diameter).

Therefore research is advancing on various feedstocks, with recent studies concentrating especially on feedstocks with aliphatic side chains.

Because aliphatic side chains of aromatic hydrocarbons critically affect the feedstock reactivity and reaction pathways [45,46], they are considered to strongly influence the generation of soot. In one study, Conturso et al. examined the effect of aliphatic side chains on the volume fraction of soot in flames of ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, or toluene blended with ethylene. It was found that for xylenes, a closer distance between the two methyl groups corresponds to a larger soot volume fraction [47]. Furthermore, Guerrero et al. found that, among *m*-xylene, toluene, and benzene flames, the smoke point was lower when the feedstock has methyl groups [48]. However, these studies have not examined the effects of aliphatic side chains on the soot particle nuclei production, or their aggregation as measured by the PSD. Furthermore, the maximum temperature and temperature distribution in flames vary according to the feedstocks, making it difficult to isolate the effect of environmental temperature.

In this study, we measured PSDs of soot produced in the pyrolysis of ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, toluene, or benzene in an inert atmosphere with an electric furnace. In addition, under two different maximum temperatures, we examined the effect of the aliphatic side chains on the rate of soot nucleation. The KM2 model [32] was used to provide the detailed chemical reaction mechanisms, and the reaction dynamics were simulated focusing on the ethylbenzene, toluene, and benzene feedstocks. By qualitatively comparing the productions of PAHs and soot, we studied factors that affect the formation of soot nuclei. Furthermore, we tried to improve the accuracy of PAH production from the model, by adding PA mechanism to the PAH growth pathways in KM2.

## 2. Experimental and analytical methods

The experimental setup (Fig. 1) is similar to that described by Dewa et al. [10]

The liquid feedstock was fed into a reaction tube of alumina (Nikato) using a syringe pump, diluted by nitrogen, and then pyrolyzed with the use of an electric furnace (Siliconit). As a preliminary experiment, a R type thermocouple was inserted into the reaction furnace and was located on the central axis. Only nitrogen was supplied to the furnace, and the temperature distribution in the reaction tube was measured. After confirming that the temperature of the reaction tube reached steady, temperature measurement was carried out for a total of 15 points. Figure 2 shows the temperature profile in the reaction tube for each experimental condition. The temperature downstream of the orifice is seen in the supplemental material. The residence time and maximum temperature at each flow rate are listed in Table 1.

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