



Evolution of size distribution and morphology of carbon nanoparticles during ethylene pyrolysis



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ABSTRACT

The effects of furnace temperature and residence time on particle size distributions (PSDs) of carbon black, which is a type of carbon nanoparticle, were studied with a scanning mobility particle sizer. Particles were classified according to their mobility diameters by a differential mobility analyzer, followed by thermophoretic sampling by scanning electron microscopy to investigate their carbon black morphologies. PSDs were power-law distributions at short residence times and log-normal distributions at long residence times; these distributions indicate that agglomeration increases with increasing residence time. In addition, few 2.5-nm-sized particles existed above 1540 ± 40 K, while the critical size was 3 nm at 1350 ± 40 K. This finding indicates that the critical size of nuclei changes with temperature. At high temperatures of 1776 and 1676 K, the 100 and 180-nm-sized particles, whose primary particles kept their shape, had very complex morphologies. In contrast, at low temperature at 1570 K, the morphologies of 100 and 180-nm-sized aggregates are relatively simple, and primary particles nearly fused together in those aggregates. These observations indicate that the nucleation rate and fusing behavior change with temperature.

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1. Introduction

Carbon black, a carbon nanoparticle, is a type of soot that is produced industrially by the partial combustion or thermal decomposition of hydrocarbons; it is used as a filler in composite materials such as tires and the electrode materials of batteries. Although the smallest individual units of carbon black are aggregates, transmission electron microscopy (TEM) images of carbon black show that the aggregates appear to be formed by spherical particles fused together [1]. In general, morphology is one factor that determines the properties of composite materials. Although production of carbon black is via a well-established route on an industrial scale, the techniques used to control morphology are based on trial-and-error and the fundamentals of the production process are not well understood. The process is complicated because chemical reactions occur rapidly with heat and mass transfer; therefore, it is difficult to control the shape of the resulting aggregates. Hence, the aggregation mechanism of carbon black is not yet completely understood [2]. Trial-and-error control of aggregate morphology has inherent limitations; thus, a theoretical solution is required.

While there have been few reports on the morphology of carbon black and the production process [3–5], including our own study [6–10], numerous investigations of soot, which is equivalent to carbon black, have been reported [6,7,10–17]. Recent scanning mobility particle sizer (SMPS) analyses contain much information on particle size-distributions (PSDs) and provide a coagulation mechanism for soot and formation mechanisms for incipient soot [18–31]. Those PSDs indicate bimodal distributions at larger heights above the burner surface, and the distribution remains bimodal throughout the flame [19,21,22]. In an ethylene flame, the behavior of the PSD changes at a maximum flame temperature of around 1850 K [18,23]. Furthermore, any changes in the bimodal nature of PSDs were found in ethylene flames doped with benzene [20,27] and in *n*- and *i*-butanol flames [29]. SMPS analyses of a well-stirred reactor (WSR) and subsequently of a plug flow reactor (PFR) [25,26,32] and tubular reactor [24] showed the sensitivity of the sooting process and size distribution. In modeling studies, detailed PSDs of soot formed in laminar premixed flames have been predicted using the Galerkin method [33]; those PSDs have been investigated using a sectional approach by applying detailed chemical reaction kinetics [34–38]. These studies showed evidence of bimodal soot PSDs in some flames.

Monte Carlo simulations coupled with detailed chemical kinetics of soot formation and stochastic numerical methods have been used to capture the evolution of PSDs along with full structural details

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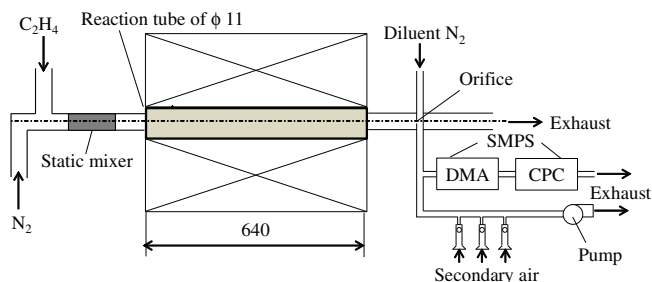


Fig. 1. Schematic of the experimental setup. Units of numerical values are mm (ϕ means diameter).

of the particles [11,39]. Recently, a polycyclic aromatic hydrocarbon-primary particle (PAH-PP) model was developed that described soot particles by their aromatic structures, including their functional site descriptions and detailed surface chemistry mechanisms [13–16]. However, little is known experimentally about the relationship between PSDs and the morphology of soot. Our recent experimental studies have revealed that morphology changes with temperature, residence time, and feedstock composition [8,9]. Our recent detailed kinetic analysis for those experimental conditions indicates that nuclei concentration and nucleation rate strongly affect the morphology of carbon black [6, 7].

While it has been shown that nucleation behavior affects morphology [7], the details of the nucleation mechanism are still not understood. Several studies of the nucleation mechanism have been performed both experimentally and by modeling.

The theory that incipient soot is produced by the formation of dimers of pyrene is mainly supported [40]. However, there are recent reports that nuclei consist of larger PAHs in models [41,42]. Results from an inclusive analysis of atomic force microscopy (AFM), TEM, helium-ion microscopy (HIM), and an infrared spectrometer coupled to a microscope (micro-FTIR) suggest that particles are liquid-like at the time of impact on a substrate surface and that significant amounts of aliphatic compounds are present in the nascent soot formed by an ethylene–argon–oxygen flame [18,20,28,43,44]. Although an SMPS, including nano-differential mobility analysis (DMA), revealed nano-sized PSDs, the growth behavior of nascent soot is still being discussed. In addition, The PSDs and morphology of soot produced at the condition similar to industry in tube reactors under an inert atmosphere have not been so much discussed because numerous studies of soot have used flames.

In this study, we clearly determined the evolution of the size distributions and morphologies of carbon nanoparticles in ethylene pyrolysis in an isothermal laminar-flow reactor. The evolution of PSDs was measured at selected temperatures, and a collection of particles classified by DMA enabled their morphologies to be evaluated in detail. In particular, the effects of temperature on critical diameter and complexity of aggregation are addressed here.

2. Experimental

The experimental setup (Fig. 1) shows a laminar-flow reactor equipped with an electric furnace. Carbon black was generated by the thermal pyrolysis of ethylene in an alumina tube (inner diameter = 11 mm, length = 640 mm) heated by the furnace. The temperature at the outer wall of the alumina tube was in the range from 1350 to 1800 K. In a preliminary experiment, the axial temperature of the gas in the reaction tube was measured using an R-type thermocouple. The axial temperature profiles are showed in Fig. 2. The average temperature zone was defined as the area in which the axial temperature was within 10% of the maximum, and the residence time was defined as the time required for the feedstock gas to pass through this zone. Changes in flow velocity resulting from temperature changes were

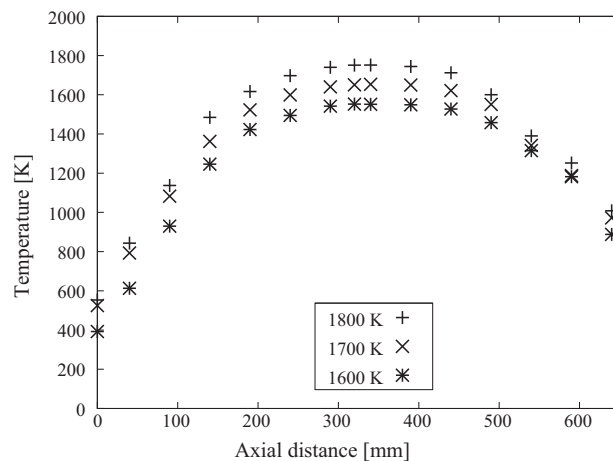


Fig. 2. The axial temperature profiles along the central axis of the reactor at a flow rate of 3 L/min.

Table 1

The residence times and maximum temperatures in the reactor at each flow rate.

Flow rate [NL/min]	Residence time [ms]	Maximum temperature [K]
2	75	1775.9
3	50	1763.2
4	37	1741.1
5	30	1728.1
6	25	1710.0
7	21	1687.1
2	79	1675.9
2.5	63	1670.0
3	53	1663.2
4	40	1641.1
5	32	1614.3
9	17	1640.0
2	84	1575.9
2.5	67	1570.0
3	56	1563.2
4	42	1541.1
5	33	1514.3
2	91	1350.0
3	61	1350.0

considered. Ethylene was diluted with nitrogen to a concentration of 1.00 vol%, and the mixture was introduced via an alumina tube at a flow rate of 2.00–9.00 NL/min. The pressure in the reaction tube is atmosphere pressure because the downstream of the one is exposed to atmosphere. The residence times and maximum temperatures in the reactor at each flow rate are showed in Table 1.

Particle-laden gas was drawn into a sampling probe connected vertically at the end of the reactor in a manner similar to that used by Zhao et al. [21–23]. The probe was made of a ¼ inch (OD) stainless steel tube (0.89 mm thickness) connected vertically to a ½ inch (OD) stainless steel tube. The sample gas entered the probe through a 1.0-mm-diameter orifice and was immediately diluted by a cold nitrogen flow at 10–30 NL/min. Dilution was necessary to quench the chemical reactions and prevent coagulation and the diffusive loss of particle in the sampling system.

The dilution ratio to modify the number concentration obtained by the SMPS analysis was determined from the concentration of CO₂ because the thermophysical properties of CO₂ are similar to those of nitrogen. The CO₂ flow rate was set to be identical to that of the feedstock. The CO₂ was supplied to the reaction tube under the same conditions as those in the pyrolysis experiment, and the dilution ratio was determined from the CO₂ concentration after it was diluted by nitrogen. This concentration was determined by using a Varian 490 gas chromatograph equipped with a thermal

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