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Full Length Article

The evolution of soot morphology and nanostructure in laminar diffusion flame of surrogate fuels for diesel

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ABSTRACT

The morphology and nanostructure of soot particles in laminar diffusion flame has been investigated in this work. The fuels considered were diesel surrogate fuels, including n-heptane, n-butanol and the volumetric mixture 50% n-heptane/50% n-butanol (H50B50). Thermophoretic sampling and TEM (transmission electron microscopy) analysis were utilized to study the morphology and nanostructure of soot particles at different points on the centerline inside the flames. The soot morphological characteristics include primary particle diameter, projected area of aggregate, and fractal dimension. The nanostructure is quantitatively described by fringe length, tortuosity and inter-fringe spacing.

Overall, n-butanol flame produced smaller primary particles and aggregates, followed by H50B50, and n-heptane flames. The primary particle diameter shows a trend of increasing first and then decreasing due to soot growth and oxidation respectively. The fractal dimension of aggregates almost keeps increasing along the centerline, indicating more and more compact soot structure. As the particles travel along the flame, a graphitic ‘onion-like’ structure develops where the core remains amorphous and the outer shell graphitises. In the process of soot growth, the fringes become shorter and less curved, meanwhile inter-fringe spacing increases due to electron repulsion between the adjacent carbon layers. Subsequently, the degree of graphitization would increase, concretely, fringe length increases, while tortuosity and inter-fringe spacing decrease. At the flame tip, most microcrystalline carbon layers in the outer shell are oxidized, which causes a sharp increase in the tortuosity, but does not have obvious effect on the other two parameters. In addition, for mature soot near the flame tips, particles in n-butanol flame has the maximum fringe length and tortuosity while the minimum inter-fringe spacing.

1. Introduction

The negative impact of submicrometer airborne particulate matter (PM) on human health and the environment has aroused great public attention [1]. Therefore, it is extremely important to control soot formation in combustion devices such as engines and their emissions to the environment [2]. Soot formation and evolution include the following physical and chemical processes: fuel pyrolysis, polycyclic aromatic hydrocarbon (PAH) formation, particle inception, coagulation, particle coalescence, surface growth, carbonization, agglomeration, and oxidation [3–5].

Recent years, a lot of scholars have studied the soot morphology and nanostructure for diesel engine with the help of TEM analysis [6–11]. These studies investigated the influence of a variety of factors on soot characteristics produced by different diesel engines, such as operating condition and fuel property. Soot particles in diesel engine exhaust overall become more chain-like along the exhaust pipe, while these particles become more spherical in shape with increasing engine speed/load conditions at any locations [6]. The primary particle sizes tended to decrease with the increasing exhaust temperature, mainly because of particle oxidation at high temperatures [7]. Song et al. [8] studied fuel property impacts on diesel particulate morphology and nanostructures. The results showed that both aromatics and sulfur contents affected particle growth (in size) most significantly, while aromatics and naphthene did the total yield of PM emissions (in mass) most significantly. Soewono et al. [9] investigated the morphological properties of the engine-emitted soot by means of TEM analysis. Their results suggested that the fractal dimensions are independent of fuel type, while engine load conditions had slight influence on D_f. Miyashita et al. [10] sampled soot particles from the exhaust of a GDI engine operated with three different fuel injection timings. The aggregates size and the primary particles diameter both decreased depending on the fuel injection timing, in the order from advanced, normal and retarded, due to the difference in residence time for soot particles in the in-cylinder

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regions with temperatures suitable for soot formation and growth. Zhang et al. [11] conducted an experimental investigation of in-flame soot and wall deposited soot morphology in a diesel engine. It was found the vast majority of in-flame soot particles have stretched chain-like aggregate structures comprised of many small primary particles while wall-deposited soot particles show more simple and compact cluster-like structure.

However, the soot particles in most of these studies were sampled in the engine exhaust. Although some researches sampled the soot in engine cylinder successfully, it was quite difficult to achieve. Therefore, studying the soot produced by diesel engine can hardly reveal the whole evolution process of soot particles.

Soot has very variable nanostructure, which ranges from amorphous to graphitic to fullerenic [12]. Laminar coflow diffusion flame is very suitable for studying the soot evolution process. This is because 1) They represent a simpler version of complex practical flames [13], 2) Have all of the physical and chemical processes that affect soot [14], 3) Co-flow flames are multi-dimensional, and 4) Are relatively simple to model numerically [14,15]. Therefore, numerous studies were carried out to investigate soot morphology or nanostructure based on laminar diffusion flame. Kholghy et al. [16] studied the morphology evolution of soot sampled on the centerline and an outer streamline of laminar co-flow diffusion flame of a surrogate for Jet A-1. They observed the solid soot particle inception and transition from liquid PAH to solid soot particles (carbonization) which happens very fast. Botero et al. [17] studied the evolution of soot particles in liquid-fuelled diffusion flames. Their results showed evidence of PAH coagulation in the inception region. And as the particles travel through the flame, a graphitic order developed where the core remained amorphous and the outer shell graphitised. Vander Wal et al. [18] studied soot generated in wick-fed diffusion flames of a commercial diesel and biodiesel. It was found that soot particles produced by different fuels have distinct nanostructures. Soot in biodiesel flame has a more curved ‘onion-like’ structure compared to that in diesel flame. Apicella et al. [19] applied HRTEM fringe analysis to soot sampled along the axis of sooting premixed benzene and ethylene flames. It was found the percentage of fringes with high tortuosity and the percentage of nearly-straight fragments decreased and increased, respectively, throughout the soot formation region. The nanostructure of soot has a great relationship with fuel composition. Alfè et al. [20] investigated the effect of fuel structure on soot nanostructure based on premixed flame. Their results showed that soot produced by cyclic paraffins and aromatics has a more organized structure than straight paraffins and ethylene. The effects of unsaturation and the ester moiety in the fuel molecule on the soot morphology were studied by Lapuerta et al. [21] in a laminar diffusion flame. The fuels include 1-decene, 5-decene and n-decane and a biodiesel surrogate. Their results indicated that the average primary particle diameter and the size of the agglomerates increase along the flame length to around two thirds of the flame length and then decrease as a consequence of oxidation becoming dominant over soot nucleation and growth. The lowest fractal dimensions are observed for the oxygenated fuel and the highest ones for the unsaturated fuels.

The fuels investigated in this study are n-heptane, n-butanol and the volumetric mixture 50% n-heptane/50% n-butanol (H50B50). The reason why selecting n-butanol is based on the actual application background that adding oxygenated compound to liquid fossil fuel can reduce the exhaust emissions. Butanol is a fuel that can potentially be produced from all sorts of feed stocks with the help of advanced fermentation techniques [22]. As a kind of oxygenated fuel, n-butanol has its own properties. Its heating value is much higher compared to methanol and ethanol. Moreover, it has a higher cetane number than other alcohols and its heat of vaporization is less than half of that of ethanol, which could improve the ignition performance of engine at cold start or low load conditions [23]. Therefore, lots of investigations have been conducted related to n-butanol combustion. It is significant to study the characteristics of soot produced by n-butanol combustion and the effect of n-butanol addition on soot formation of fossil fuels or their surrogate fuels, such as n-heptane.

The aim of this study is to investigate the evolution of soot morphology and nanostructure in laminar diffusion flames of n-heptane, H50B50 and n-butanol. Concretely, the detailed evolution process of soot in n-heptane diffusion flame was investigated by multi point sampling followed by TEM and HRTEM analysis. Different stages of soot particles were observed, meanwhile their morphology and nanostructure were studied, which could reflect the features of soot in different stages. On the other hand, the effect of n-butanol addition on soot evolution and characteristic was also studied by comparing soot particles in n-heptane, H50B50 and n-butanol flames. The morphology features that this study focuses on include soot particle shape, primary particle diameter, projected area of aggregate, fractal dimension, etc. The nanostructure parameters include fringe length, tortuosity and inter-fringe spacing, which were obtained by lattice-fringe analysis using a self-developed algorithm in Matlab.

2. Experimental methods

2.1. Burner setup and flame description

The experimental system for this study is shown in Fig. 1, which mainly consists of co-annular burner, Bronkhorst Vapor Delivery Module (VDM), pressurized fuel tank, air compressor, air dryer, air heater, heating elements, sampling probe and computer. The co-annular burner is utilized to produce a laminar, co-flow diffusion flame. It consists of a 10.9 mm inner diameter milled steel fuel tube with a wall thickness of 0.9 mm and a concentric 90 mm inner diameter air annulus. It is a significant challenge to vaporize the heavy liquid fuels. To solve this problem, VDM was used to quickly transform the liquid fuel to gaseous. As shown in Fig. 1, the liquid fuel is stored in a pressurized fuel tank, and can be pressed into VDM by high-pressure N2. Meanwhile, another high-pressure N2 is used as carrier gas to carry the vaporized gaseous fuel out of VDM. The flow rate of carrier gas N2 for the three flames was 0.35 L/min. The vaporization temperature was settled as 423 K for the fuels used in this experiment. The flow rates of carrier gas and liquid fuel were both controlled by MFC (Mass Flow Controller) respectively. The function of air compressor, air dryer and air heater is to provide hot air without water vapor. In this experiment, the air flow rate was settled as 150 L/min to provide enough oxidant for the flame and prevent it from the environmental influence. The small glass beadings are used to make the co-flow air well-distributed. To prevent a significant temperature drop and condensation in the fuel tube inside the burner, the co-flow air was heated to 453 K.

The fuels considered in this study are diesel surrogate fuels, including n-heptane, n-butanol and the volumetric mixture 50% n-heptane/50% n-butanol (H50B50). In order to ensure the same carbon mass content for the three fuels, their mass flow rates were set as different values as shown in Table 1. Therefore, the flame heights were also different. N-heptane flame was the highest, followed by H50B50 and n-butanol flames.

2.2. Thermophoretic sampling and sampling points

To obtain information of the morphology and nanostructure of soot particles, thermophoretic sampling was utilized followed by processing and analysis of the images of the soot samples, which were captured by lacey C/Cu TEM a transmission electron microscope (TEM). The sampling probe shown in Fig. 1 was utilized to sample soot particles in flame, namely thermophoretic sampling. It was fixed on a toothed belt type electric cylinder, which can precisely control the probe to the designated location in flame and then withdraw it rapidly. The residence time in flame can be controlled in tens of milliseconds. A C/Cu TEM grid with 230 mesh, 3 mm in diameter, is held by the probe, and when it travels into flame, the soot particles would be deposited on the