A Review of Recent Research Results on Soot: The Formation of a Kind of Carbon-Based Material in Flames

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As a product generated from incomplete combustion, soot is harmful to people’s health and the environment. In recent decades, much attention has been paid to the control of soot generation in combustion systems. Efforts to reduce soot emissions depend on a basic understanding of the physical and chemical pathways from fuel to soot particles in flames. At the same time, flame synthesis method has become an alternative method for the preparation of carbon nanomaterials because of its advantages of low cost and mass production. Carbon-based materials can be synthesized within the sooting zones in flames. The research of soot formation mechanism in flames can provide support for the synthesis of carbon nanomaterials. In this paper, the effects of additives, temperature, and fuel type on soot formation characteristics and soot nanostructure in diffusion flames are reviewed. The deficiencies and prospects are put forward for future research.

Keywords: soot, nanostructure, formation characteristics, diffusion flame, carbon nanomaterials

INTRODUCTION

Soot generated from the burning of hydrocarbon fuel is a known pollutant. The emission of fine soot particles brings severe environmental problems. As shown in Figure 1, the physical and chemical processes of soot formation are very complex, including the formation of precursors, soot nucleation, soot surface growth and agglomeration, and soot oxidation (Richter and Howard, 2000). With carbon as the main component, soot is also a kind of carbon material. Carbon nanomaterials (CNM) are widely used in various fields including storage of hydrogen and natural gas (Mykhailiv et al., 2017), electronics (Olariu et al., 2017), and manufacture of batteries, fuel cell devices, hyperlubricants and sensors due to exceptional mechanical, thermal and electrical properties of CNM. The synthesis of CNM requires three inputs: a heat source, a carbon source and a catalyst. Recently flame synthesis method is generally accepted for the preparation of CNM (Merchan-Merchan et al., 2010). Flame synthesis method has the advantages of high energy efficiency and low cost, and can produce CNM rapidly in large quantities. It provides an effective way for the commercial production of carbon nanomaterials.

So far, many researches have been carried out on soot morphology and formation mechanism in flames. The formation of soot in flames has a lot in common with the synthesis of carbon nanomaterials by flame method. The growth of single-wall carbon nanotubes in the post-flame gases can be described by the formation of small discrete particles with a progression toward carbon nanotubes inception and growth in the upper region of the flame (Merchan-Merchan et al., 2010). This formation pathway is very similar to that encountered in soot formation. In flames carbon-based materials and related nanostructures can be synthesized within the sooting zones. Understanding the formation mechanism of soot is not only helpful for reducing the emission of soot particles but also critical for soot nanostructure design and control.
of soot and its adverse effects on human health and environment, but also good for producing carbon-based products under controlled conditions.

In this review, the latest research progress on the effects of additives, fuel type and flame temperature on the morphology evolution and nanostructure of soot in diffusion flames is introduced. The formation mechanism of soot in diffusion flames is also discussed.

EFFECT OF ADDITIVES

Additives affect soot formation mainly through dilution effect, thermal effect and chemical effect. Studies over the past few decades have provided important information on the effect of H₂ and CO addition (Dearden and Long, 1968; Du et al., 1995; Gülder et al., 1996; Guo et al., 2006, Guo et al., 2009). However, most of the previous studies did not take account of soot nanostructure. In recent years, much attention has been paid on the nanostructure of soot. Dai et al. (Dai et al., 2020) studied the effect of CO addition in the ethylene diffusion flame. The results indicated that CO chemically promoted soot formation and the dilution effect of CO addition monotonically reduced soot formation. Lin et al. (Lin et al., 2020) investigated soot formation in laminar co-flow ethylene diffusion flames with different H₂ addition ratios by Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM). The results show that the addition of H₂ promotes the formation and growth of soot precursors. A distinct and dense fine fiber network structure of soot was found at the upper part of the ethylene flame, demonstrating that the oxidation of soot in the hydrogen-doped ethylene flame was enhanced with abundant soot branches oxidized and more straight chain soot produced. Li et al. (Li et al., 2021) used the method of thermophoretic sampling and transmission electron microscopy (TEM) to study the effect of CO/H₂/N₂ addition on the morphological evolutions and nanostructures of soot in ethylene diffusion flames. Compared with N₂ addition, the addition of CO/H₂ caused greater fringe length, smaller fringe tortuosity and inter-fringe spacing for soot particles, resulting in more orderly and compact lattice structure. CO addition promoted the production of the key intermediate of acetylene. On the other hand, CO addition enriched H radical dominantly through CO + OH = CO₂ + H, promoting the formation and surface growth of soot. Besides, the soot nanoparticles were more graphitized in the H₂-doped flame with the enhancement of C₂H₂ production and the increase of pyrene concentration. In the flame tip region, the enhancement of oxidation contributed to the decrease of the fringe lengths of the particles.

In addition to the above common additives, the effects of some special additives on soot formation are also studied. Ying et al. (Ying and Liu, 2018) suggested that the soot particles in n-butanol-doped ethylene inverse diffusion flames with the dilution of CO₂ possessed larger fringe tortuosity, shorter fringe length, and higher oxidation reactivity. Before too long, Ying et al. (Ying and Liu, 2019) studied soot properties in ethylene inverse diffusion flames added with water. Results illustrated that soot nanostructure had an increased carbonization degree resulting from larger fringe length, lower fringe tortuosity and smaller interlayer spacing of soot when H₂O is doped. Alrefaai et al. (Alrefaai et al., 2018) investigated the characteristics of soot in diesel flames doped with dicyclopentadiene. It was found that the addition of dicyclopentadiene caused the increase of the content of hydrogen, oxygen and aliphatic groups, the enhancement of the reactivity, and the diminishment of the content of aromatic groups for soot particles. A similar phenomenon was found by Botero et al. (Botero et al., 2019). Salamanca et al. (Salamanca et al., 2020) studied the impact of three cyclic fuels, namely cyclohexene (C₆H₁₀), cyclopentene (C₅H₈), and methylcyclohexane (C₇H₁₄), on the nanostructure of soot in n-heptane (C₇H₁₆) diffusion flames. The fringe tortuosity of
soot was increased in n-heptane flames with cyclopentene addition, indicating that cyclopentene could be used to incorporate curvature in different carbonaceous structures to modify their properties. The formation of soot nanoparticles was enhanced with the addition of cyclic fuels because the addition of cyclic fuels results in quicker formation of the first aromatic ring than in pure aliphatic flames. The double-bond in the cyclic fuels had a more significant effect than the methyl substitution. The five-membered rings played a crucial role in the formation of incipient carbon nanoparticles. Earlier, Wang et al. (Wang et al., 2013) found that the relative content of aliphatic C-H groups was an important factor affecting the soot oxidation reactivity, and its importance was higher than that of C-OH and C=O groups. The addition of oxygenated compounds yields more curved and disordered nanostructures of soot (Abboud et al., 2018). In sum, the additives can change the concentration of intermediate species and radicals (e.g., H, OH, benzene) important for soot generation. These intermediate species and radicals are closely related to the nanostructure of soot (e.g., fringe length, interlayer spacing, fringe tortuosity). The above results are helpful for the modification of the structure of carbon nanomaterials produced in flames.

**EFFECT OF TEMPERATURE**

Temperature is an important factor not only for the nucleation and growth of soot particles, but also for the production of carbon nanomaterials. Understanding the effect of temperature on soot formation is beneficial for the development of the technology (flame method) of carbon nanomaterials production.

The high pyrolysis rate of fuel and the rapid formation of polycyclic aromatic hydrocarbons (PAHs) are mainly caused by high initial temperature (Xu et al., 2018). High initial temperature also promotes the nucleation process of soot (Mahmoud et al., 2019). The effect of gas preheat temperature on soot formation was investigated by Qi et al. (Qi et al., 2021). The soot temperature increased with higher gas preheat temperature, leading to more violent soot formation and oxidation. Chu et al. (Chu et al., 2020) investigated the effects of different reactant temperatures on soot nanostructure. Three temperatures (300, 473, and 673 K) were applied. The results showed that increasing the temperature promoted soot aggregation and generated more mature primary particles. When the reactant temperature was relatively high (673 K), soot had more curved nanostructures. The deceleration of soot surface growth could be explained by surface aging, which was characterized by the increase in curved nanostructures. In addition, the dehydrogenation process, which contributes to soot maturity and graphitic shell formation, is sensitive to flame temperature (Kholghy et al., 2016). More than 100 polycyclic aromatic hydrocarbons (PAHs) cluster together to form liquid-like particles in flames with temperatures greater than 1,350 K (Dobbins, 2002). To improve the understanding of soot formation process, much attention has been paid to soot morphology and internal nanostructure by utilizing advanced measurement methods in recent years. Improving the accuracy of measurement is very important. For example, the acquisition of Raman spectrum for sample characterization can be interfered by the fluorescence of PAHs contained in volatile organic fraction (VOF). VOF refers to the organic fractions (PAHs or saturated/unsaturated hydrocarbons), which are prone to be volatile when heated under inert atmosphere, loosely attached to the surface of soot. Liu et al. (Liu et al., 2021) revealed that VOF could be effectively removed from the soot surface when the devolatilization temperature was 650°C.

In general, adjusting the amount and type of diluents in streams is the main method to change the temperature of diffusion flames. As a result, the effect of dilution is likely to interfere with the effect of temperature (Wang and Chung, 2019). The relative influence of temperature and dilution has been identified in earlier research (Guo et al., 2002). Since CO and N₂ have similar thermal and transport properties, the addition of them has similar thermal and dilution effects (Guo et al., 2009). Higher flame temperature promotes the carbonization of soot particles and the formation of PAHs with higher planarity which reduces steric hindrance and allows the PAHs to stack (Martin et al., 2019). Raj et al. (Raj, 2019) suggested that the conversion of a planar PAH to a curved one through ring addition at an armchair site had a rapid rate at temperatures below 2,000 K. The temperature effect on soot formation in laminar diffusion flames was investigated by Davis et al. (Davis et al., 2020). The curvatures of the PAHs were reduced with the increase in flame temperature. The layer stacking of PAHs was more efficient with higher content of stacked fringes so that the PAHs became more polarizable and geometrically uniform. The curved PAHs that form young soot particles converted to graphitic structures forming mature soot aggregates. In low temperature flames, large amorphous particles with short fringe length and high fringe tortuosity were produced. In high temperature flames, soot aggregates with long fringe length and low fringe tortuosity were produced. Chu et al. (Chu et al., 2019) studied the properties of soot particles in coflow diffusion flames with different oxygen concentrations. The results showed that soot particles along the flame centerline were oxidized into dense flocculent and fibrous mesh structures when the flame temperature was increased. The flame temperature increased sharply with the increase in flame heights, leading to the soot aggregates being oxidized to loose chain-like agglomerates. Mao et al. (Mao et al., 2017) conducted a series of ReaxFF molecular dynamics simulations and the results suggested that the PAHs developed into incipient soot particles by physical nucleation at 400 K and the chemical nucleation dominated when the temperature was 2,500 K.

All in all, temperature is an important parameter for entire soot formation process. High initial temperature results in high pyrolysis rate of fuel. Thermal effects of the additives change the flame temperature which influences the formation of PAHs and the nanostructure of soot particles. Yet further study remains to be conducted for the functional relationship between temperature and soot morphology parameters.
EFFECT OF FUEL TYPE

The significant amount of CO with the existence of H₂ is a prerequisite factor for the growth of carbon nanomaterials (Hall et al., 2011). Different pyrolysis products generated from different fuels can affect soot nanostructures. In general, acetylene and aromatics make soot more graphitic. The influence of oxygen-containing functional groups on soot morphology depends on their locations in the molecules (Westbrook et al., 2006; Barrientos et al., 2013; Das et al., 2015). The effect of nitrogen-containing compounds on soot formation was investigated by Montgomery et al. (Montgomery et al., 2021). Amines had lower sooting tendencies than the structurally analogous hydrocarbons and oxygenates.

Xu et al. (Xu et al., 2020) found that cyclopentane, with a five-membered ring in the molecule, generated more soot than cyclohexane in counterflow diffusion flames because more odd carbon radicals (cyclopentadienyl and allyl, which are efficient aromatic precursors) were produced in cyclopentane flames. The aliphatic bond between the aromatic sub-units enhances the clustering of PAHs and decreases the dissociation effect due to increasing temperature (Iavarone et al., 2017). Influence of oxygenated compounds concentration on sooting propensity was studied by Abboud et al. (Abboud et al., 2017). The light extinction measurement (LEM) was used to measure the soot volume fraction. Compared with biodiesel, soot derived from surrogate diesel flames displayed less ordered graphite-like structure and contained more amorphous carbon. It was also found that adding oxygenated compounds to a diesel surrogate fuel reduced the tendency of soot production. In another study, similar sooting tendency was found in diesel flames with the addition of oxygenated compounds by Wei et al. (Wei et al., 2020). Barrientos et al. (Barrientos et al., 2015) found that shorter alkyl chain length suppressed the formation of soot and promoted the generation of less ordered soot structure. Botero et al. (Botero et al., 2016) studied the characteristics of soot particles generated from different fuels including heptane, toluene, the mixture of heptane and toluene and a commercial gasoline in laminar diffusion flames. It was found that the primary soot particles generated from the heptane flame were the smallest and the soot produced from the toluene flame showed longer, less curved fringes and more stacked layers. The properties of soot particles generated in n-decane and RP-3 kerosene flames were compared by Abdalla et al. (Abdalla et al., 2020). The results showed that soot generated from RP-3 kerosene had smaller inter-planar spacing and fewer layers. Fuels with lower decomposition temperatures can more easily generate enough local heat to complete the reactions in the synthesis process and create materials of high porosity and good crystallinity, and also prevent particle agglomeration (Parauha et al., 2021).

Thus, fuel molecular structures such as the length of the carbon chain, H/C ratio, the fuel unsaturation and the cyclic ring structure play a vital role to the sooting tendency and soot nanostructure of a combustion system. Also, the role of fuel type is important for the flame synthesis of carbon nanomaterials. In the design of combustion-based synthesis systems, the presence of suitable hydrocarbons must be taken into account to ensure the quality and repeatability of the resulting products. The results of the effect of fuel type on soot formation is valuable for the choice of the appropriate fuel to produce carbon-based materials.

CONCLUSION AND PERSPECTIVES

In this review, the effects of additives, temperature and fuel type on the evolution of soot nanostructure and morphology are introduced. The formation of soot is a complex physical and chemical process. Although a lot of research progress has been made in the field of soot formation, there are still some unsolved problems and challenges. Further research is needed to deeply clarify the formation mechanism of soot, which can not only achieve reduction of combustion emissions, but also provide theoretical support for regulating and controlling the production of carbon nanomaterials since soot formation in flames is very similar to the synthesis of carbon nanomaterials by flame method. More effort should be made to develop the modeling capabilities of soot formation and carbon nanomaterials production. Effective measurement techniques and sampling methods need to be further developed so that more detailed information and parameters of soot particles can be obtained accurately, which is beneficial to the precise control of carbon nanomaterials synthesis in flames.

AUTHOR CONTRIBUTIONS

JX proposed the conception of the study and edited the article. GY drafted the manuscript. JC and ZG checked the article.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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