



FT-IR and ^1H NMR characterization of the products of an ethylene inverse diffusion flame

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Received 26 August 2005; received in revised form 25 March 2006; accepted 4 April 2006

Available online 30 May 2006

Abstract

Knowledge of the chemical structure of young soot and its precursors is very useful in the understanding of the paths leading to soot particle inception. This paper presents analyses of the chemical functional groups, based on FT-IR and ^1H NMR spectroscopy of the products obtained in an ethylene inverse diffusion flame. The trends in the data indicate that the soluble fraction of the soot becomes progressively more aromatic and less aliphatic as the height above the burner increases. Results from ^1H NMR spectra of the chloroform-soluble soot samples taken at different heights above the burner corroborate the infrared results based on proton chemical shifts (H_α , H_β , and H_γ). The results indicate that the aliphatic β and γ hydrogens suffered the most drastic reduction, while the aromatic character increased considerably with height, particularly in the first half of the flame.

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Keywords: Soot; FT-IR; ^1H NMR; Inverse diffusion flame

1. Introduction

The intensive use of fossil fuels, mainly in combustion processes, leads to the generation of a carbonaceous material known as soot. Due to its high polyaromatic hydrocarbon content, this material even at low concentrations has serious consequences for human health, especially when the particulate matter is in the nanometer-sized range [1]. The health risks are not only mutagenic, but also potentially carcino-

genic [1–4]. As a result, government agencies have introduced strict control measures that regulate the release of soot into the environment. Measures like these have encouraged research and development of environmentally friendly technologies [5–8].

The formation of soot is a very complex phenomenon that involves homogeneous and heterogeneous processes and continuous competition between reactions [9–12]. Although the process of soot evolution has been investigated experimentally and theoretically in many studies [8–44], there is still some information lacking on the chemical structure of the different compounds formed in the flame that lead to soot formation, especially during the early stages of soot

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inception. The acquisition of material with young soot characteristics represents an experimental challenge due to the fast oxidation and pyrolysis transformations that take place in the flame, especially in typical combustion systems [12,13,23,24]. To study the early period of soot formation, several types of diffusion flames have been used extensively, and one of these is the coflow normal diffusion flame (NDF) [8,12,18–21,33–35]. In the NDF, the fuel is introduced through the central tube of the burner while the oxidizer is introduced in an annular ring. An alternate approach is the inverse diffusion flame (IDF), which is basically obtained by inverting the air and fuel positions relative to a NDF configuration; that is, the oxidizer goes through the central tube and the fuel is in the annular space [22–32,35].

Up to now, most of the studies that involve the early period of soot formation have been carried out in normal diffusion flames due to their simplicity. Unfortunately, one of the disadvantages that this type of configuration presents is that soot particles and condensed intermediate hydrocarbons are transported toward the centerline of the flame due to thermophoretic forces. Because these particles are formed on the inner or fuel-rich side of the reaction zone, they must pass through the main reaction zone prior to exiting the flame, thus exposing them to significant oxidation and carbonization processes [12,23,33]. Therefore, obtaining young soot from this configuration requires intrusive sampling into the center of the flame, which results in disturbance of the system. Needless to say, the amount of sample obtained under these conditions is often minimal.

Studies carried out by Dobbins and colleagues in a NDF identified for the first time the presence of young soot in combustion systems, using thermophoretic particle deposition on a cooled target [19–21,33]. However, the results of this study were limited to transmission electron microscopy analysis due to the small amount of sample that could be collected. In another study using an underventilated normal diffusion flame configuration (U-NDF), a detailed analysis of young soot was obtained. Unfortunately, this type of configuration is somewhat difficult to operate in a reliable manner due to stability problems, which resulted in the flame being confined within the walls of a tube [34].

Although numerous investigations have been carried out on NDF configurations, very few have been done on an IDF. One of the first studies related to this type of configuration was published in 1955 by Arthur and Napier, who pointed out that the soot produced in an IDF was stickier and more viscous than the soot produced in a NDF [32]. However, it was only in 2002 that Blevins et al. confirmed that the soot generated in an IDF is chemically and morphologically similar

to the young soot found in a U-NDF, with the characteristic that it is 50% soluble in dichloromethane, allowing direct chemical analysis [22,23].

Another advantage of the IDF configuration compared with NDF is that it provides a better separation of pyrolysis and oxidation processes. In addition, soot and intermediate products from these processes are transported away from the main reaction zone by thermophoretic forces, and since these products are formed on the outer or fuel-rich side of the flame, they do not pass through the main reaction zone and thus avoid significant oxidation or carbonization. This configuration provides an opportunity to gather large samples of young soot from the surroundings without need to invade the flame with the sampling probe. This approach opens the possibility of studying the early stages of soot formation in a direct way [22,23, 25,27,28].

Although many experimental and theoretical investigations support the hypothesis that soot inception occurs through coagulation reactions of polycyclic aromatic hydrocarbons (PAHs) [10,13–17], which are formed quickly in the region of the flame just ahead of the nucleation zone (commonly defined as the onset of the yellow luminosity in a flame), very little is known about the molecular structure of these compounds. In particular, information on the variation of the content of oxygen and alkyl groups in PAH along the flame is missing and few studies in this direction have been carried out [36–39].

Recently, Öktem et al. [39] used photoionization aerosol mass spectrometry (PIAMS) to characterize semivolatile material present on soot particles deposited on an aluminum probe. The sample was collected at the soot inception region of a premixed ethylene flame. They found that at lower heights above the burner (below the soot inception point), the soot chemical composition was dominated by polycyclic aromatic hydrocarbons, whereas aliphatic compounds made a noticeable contribution to soot growth after the soot inception point, where the particles become older. Similar results were obtained by Ciajolo et al. [37,38] using FT-IR and UV-vis analyses. They found that the condensable material of soot collected in an ethylene premixed flame has a significant contribution of aliphatic hydrogens just after the soot inception point due to CH_2 and CH_3 groups. Although these studies were carried out on premixed flames, it should be noted that the current work reflects results from a diffusion flame.

One of the causes for the lack of structural information is that the spectroscopic characterization of these materials becomes difficult due to their low solubility in solvents, and the amount of sample, which that is often minimal. Therefore, much of the information available for premixed and diffusion flames

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