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Carbon formation in combustion

CARBON FORMATION IN COMBUSTION

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INTRODUCTION

Any hydrocarbon fuel that is burned under oxygen deficient conditions will produce carbon particles, that is, soot. Soot formation is fascinating from a scientific point of view. In hydrocarbon flames, minute fuel molecules are transformed into solid soot aggregates containing hundreds and thousands of atoms. This process takes place on a time scale of milliseconds and is insufficiently understood.

METHODS

Laser ionization mass spectroscopy studies and aerosol analysis of combustion byproducts from inside of a laminar, atmospheric pressure diffusion flame burning with argon diluted methane (CH_4) are presented. Large molecules and small carbonaceous particles are found. The molecules are Polycyclic Aromatic Hydrocarbons (PAHs), with molecular masses up to 800 amu, as measured with a Time-of-Flight mass spectrometer (Siegmann and Sattler, 2000). The diameters of the particles range between 2 and 50 nm (Hepp and Siegmann, 1998).

In Figure 1, the flame is drawn schematically. Because the flame is laminar, the height above burner is also a reaction time scale. Low heights in the flame correspond to short times spent in the combustion zone, whereas larger heights are related to longer reaction times. No species are detected above the flame, all particles and PAHs are finally oxidized. The findings on PAHs and particles in the flame are displayed in Fig. 1. On the left side particle size spectra are shown, as obtained by differential mobility analysis, specialized for very small mobility radii. The spectra are assigned to the appropriate height in the flame where the samples were extracted. On the right side the maxima in concentrations of selected PAHs are assigned to the height in the flame were they were found. It can be seen that larger PAHs are generally formed later (higher) in the flame. This is the consequence of their growth process, larger PAHs grow from smaller ones by the addition of small molecules (e.g. acetylene, C_2H_2). It is clearly seen that particles are found before the large PAHs peak. Large PAHs are formed

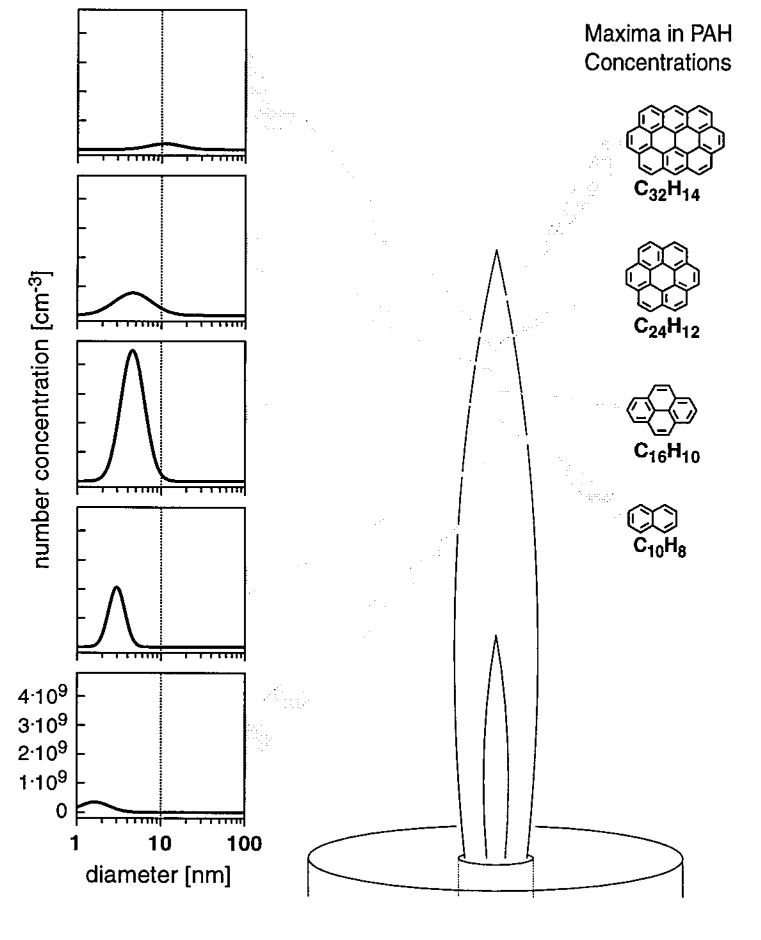

Figure 1. Schematic representation of the flame. To the left, particle size spectra are shown assigned to the height in the flame where they were measured. To the right the maxima in concentration for selected PAHs are assigned to their appropriate height in the flame.

later than soot particles. We therefore propose that particles are the precursors for PAHs; the PAHs are synthesized on the surface of the particles and evaporate into the gas phase when synthesis is completed.

CONCLUSIONS

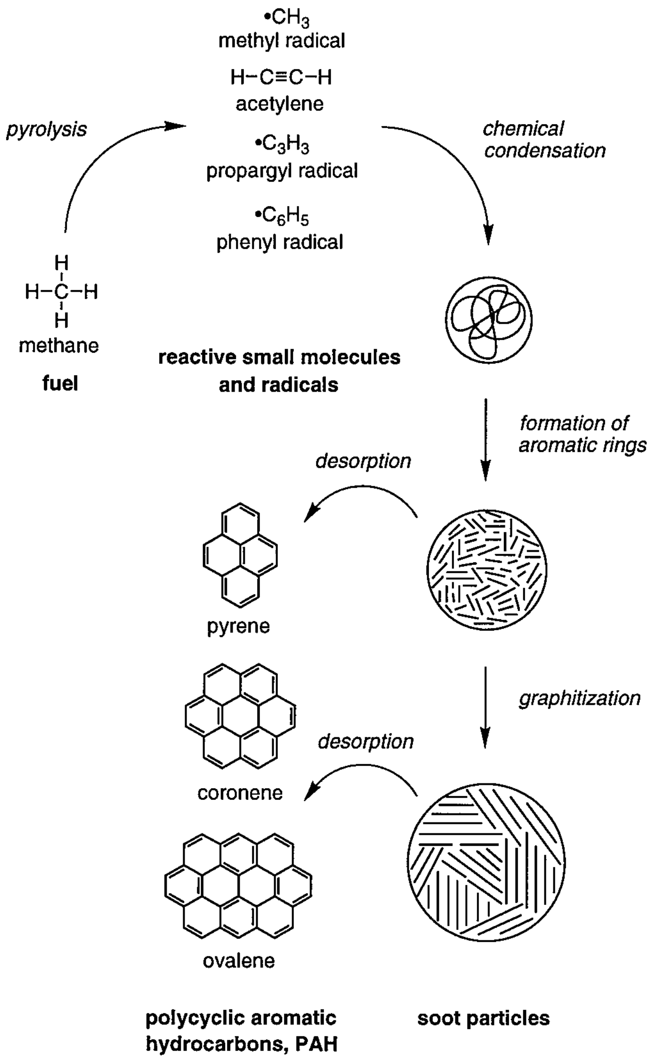

Figure 2. Proposed soot formation mechanism in diffusion flames. The straight lines drawn in the particles symbolize polyaromatic moieties (sideview).

A schematic picture of soot formation in diffusion flames shall be developed here (see Figure 2). First, a small fraction of the fuel (methane) decomposes during oxidation and heating into methyl radicals which, under fuel rich conditions, form small molecules (acetylene) and reactive radicals of various sizes. Those species add hydrocarbon radicals for growth and the growing unsaturated, radicalic hydrocarbons condense chemically to form the first particles. The primary particles consist of chainlike aggregates which are symbolized as a ball in Figure 2. The particles may be more or less liquid and they may contain small aromatic moieties, interconnected by flexible hydrocarbon chains. During heating of the particles in the flame more and more of their chainlike, aliphatic structure is converted into aromatic rings and compounds, as a consequence of the extraordinary aromatic stability. Subsequently, the polyaromatic compounds may detach from the particles when they lay at the surface and all chemical bonds are saturated. Those are the PAHs found in the gas phase. PAH synthesis therefore takes place on the particles using their surface as a template. As heating continues the particles form increasingly larger arrays of aromatic rings, becoming more and more graphitic and therefore denser (Skillas *et al.* 1999). As a consequence the PAHs which desorb into the gas phase are larger. In the same time the particles quickly coagulate and simultaneously pick up small radicals and acetylene for surface growth. The commonly observed bizarre structure of soot is due to aggregation of the primary spherical particles (In Fig. 2 the evolution of a primary soot particle is shown).

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