In-situ Study of the Early Stages of Soot Formation and Growth in a Live Flame

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A better understanding of the structural physics and chemistry of the dynamic processes of soot nucleation in the steady-state combustion of gas or liquid aerosol fuels will aid the design of industrial and domestic burners with improved energy economy and reduced pollution characteristics. However, little is known about the early stages of soot formation from naked flames [1]. From microscopy it is clear that nanoparticles are formed at first [2,3] and that, dependent on the conditions in the flame, these grow and agglomerate in the reaction zone developing into particles approaching microns in size [4]. Following soot formation dynamically requires scattering techniques. The soot volume fraction in hydrocarbon flames, however, is typically 10^{-7} which makes *in situ* measurements extremely difficult. Light scattering techniques have traditionally been used in an attempt to follow the condensation of soot [5] but visible wavelengths necessarily restrict the measurement to the later stages of growth above the flame where the particle density is high, rather than the initial processes of nucleation in the flame where particles may well have much lower densities, as is the case in the formation of fullerines [6]. We have therefore turned to X-ray scattering facilities at the ESRF in order to probe soot formation in the nanoparticle regime within a live flame by utilising the high spatial resolution and intensity available.

The experimental arrangement involves inserting a 5kW gas slot burner on a vertical travel in the sample zone of BM26B. A burner from Loughborough whose combustion characteristics were already characterised was adapted at Aberystwyth by boxing in to comply with ESRF Safety recommendations and inserting a vertical slot at flame height to accommodate the incident and scattered X-ray beams. The burner was mounted on a vertical travel with controls for remotely aligning the flame with the X-ray beam. Separate fuel and air supplies were included and a metal grid surrounded the flame to ensure the continuous flow of reactants and exhaust products and to maximise a turbulent-free region for the experiment. The burner slot was 10cm in length and placed longitudinally to ensure sufficient path length for adequate SAXS statistics for a volume fraction of ~ 10^{-7} soot particles. The vertical narrowness of the X-ray beam provided sufficient spatial resolution within the flame to explore different regions as well as adequate angular resolution at the detector. With laminar and steady conditions established, soot particles travel uniformly through the combustion zone and so their structural evolution could be traced spatially by lowering the burner in stages, starting with the X-ray beam in reaction zone working up through the flame. By employing a slight positive pressure prevented agglomerated particles from final stages of soot formation from falling back into the reaction zone.

SAXS profiles measured at different heights in a steady methane flame are plotted in Fig. 1. From extrapolated I_0 values these indicate that the electron density contrast ($\Delta\rho^2$) close to the reaction zone is low but then increases as soot formation advances vertically through the flame. Complementary to this trend the q dependence of the SAXS intensities point to Guinier radii of around 10 nm which at first fall to ~ 3nm before beginning to rise again as $\Delta\rho^2$ increases. The evidence so far points to the initial stage of soot formation in methane flames progressing from expanded nuclei to higher density smaller particles which then begin to agglomerate as the process advances through the reaction zone.

In our initial experiments we overcame the not inconsiderable safety conditions required to run a combustion chamber in an ESRF hutch as well the physical requirements of achieving laminar flow throughout the flame height for the duration of each measurement. However, in this preliminary run we experienced some collimation and normalisation difficulties. In particular, adjustments now need to be made to the beam line vacuum system and to the box surrounding the burner. These will enable the experiment to be located optimally for the SAXS camera with the X-ray beam passing freely through the flame region without interference from the vertical slot. These alterations will also lower the parasitic scatter by reducing the air path either side of the flame. We also wish to install a facility for replacing the flame with laminar hot air of similar temperature to assist in normalisation of the scatter from the soot particles.

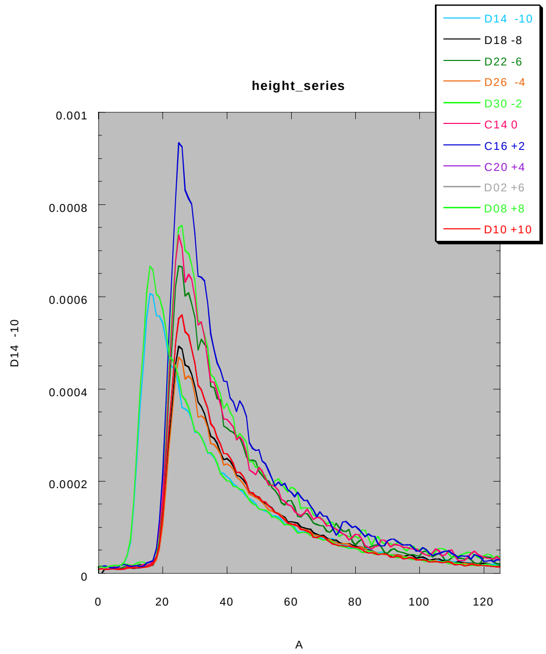

Fig. 1 Preliminary *in situ* SAXS profiles obtained for soot formation at different flame heights in a methane flame using a purpose-built gas slot burner on BM26B.

Although light scattering techniques have been used for some time to examine the final stages of soot formation [5], we believe that these *in situ* SAXS experiments on a naked flame represent the first high resolution attempt to employ scattering methods to follow the nanostructure of soot during nucleation. With the mechanical alterations described above, we expect to improve quantitative measurement of the size and density of soot particles. We then plan to explore soot nucleation for different flame conditions and different fuels. If inter-particle interactions are present in the initial stages of soot formation, indirect Fourier transformation [7] and regularisation [8] techniques can be applied. These will allow model-independent determinations of particle size distributions to be made which will be advantageous if the surfaces and interfaces are fractal or diffuse rather than smooth, as may be the case close to the flame centre. We have already observed surface roughening with *in situ* SAXS in the initial nucleation of nanoparticles in matrices and in powders [9,10,11].

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