

COMBINING SMALL ANGLE AND WIDE ANGLE X-RAY SCATTERING TECHNIQUES FOR *IN-SITU* STUDIES OF PARTICLE FORMATION PROCESSES IN REACTIVE SYSTEMS USING A NEW DETECTOR PROTOTYPE

¹Frederik Ossler, ¹Linda Vallengag, ²Sophie. E. Canton,
²Peter Sondhauss

¹Division of Combustion Physics, Lund University, LUND, Sweden; ²Max-lab, Lund University, LUND, Sweden

Introduction

To date there are still many unknowns on how particles are formed from gas phase reactive systems such as combustion. It is possible to study particles *in-situ* using X-ray scattering techniques: Separate applications have shown that the size distribution of soot particle can be measured using Small-Angle X-ray Scattering (SAXS) [1-4] and particle structure with Wide-Angle X-ray Scattering (WAXS) [5,6]. Combining SAXS and WAXS would be the best choice for studying particle formation processes, because that allows one to understand how size and structure are coupled during the chain of events from the earliest steps of molecular clustering/growth to fully mature nanoparticles and soot. In recent work SAXS and WAXS detectors, containing one and 6 channels, respectively, were combined and operated synchronously [7]. Last year a new SAXS detector containing 20 channels was constructed and tested on the same type of flame systems. In this work we describe the latest results from these combined SAXS and WAXS measurements.

Experimental

The experimental set-up used for the combined SAXS and WAXS measurements using the new detector at MAX-lab, beamline D611 is shown in Fig.1.

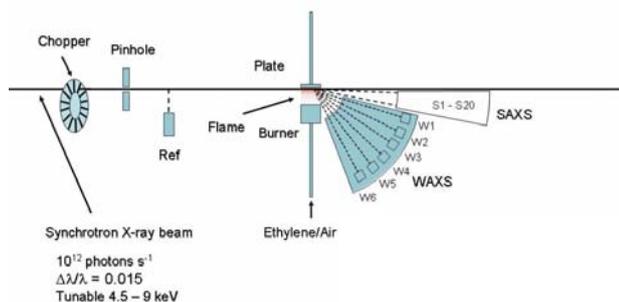


Fig.1 The experimental set-up.

X-ray radiation with a relative bandwidth of 0.015 was tunable between 4.5 and 9 keV. The maximum flux of the radiation, 10^{12} photons s^{-1} , was obtained at 6.5 keV. Most of the experiments were performed between 5 keV and 6 keV.

The beam was modulated by a mechanical chopper, operating at frequency slightly above 1 kHz. The focus of the beam was placed close to a pinhole of 0.5 mm diameter. A reference detector (scintillator/photomultiplier) recorded the scattered photons from the beam before it passed through the flame circa 18 mm above the surface of the burner and 2 mm below a metal plate (steel or copper), which worked as cooler and a flame stabilizer. The diameter of the burner was 20 mm. It had a porous bronze plug, through which pure ethylene was fed at atmospheric pressure. Typical flow velocities were 1.2 cm/s – 1.7 cm/s. Scattered photons were collected at 20 different angles typically between 0.5° and 10° , with a separation of 0.5° with the SAXS detector and 6 different angles between 17.5° and 60° , with a separation of 8.5° for the WAXS detector. The outputs from the channel detectors were sent through preamplifiers and then to sampling and A/D converter with high dynamic range and a rate of better than 200 k samples s^{-1} .

The sampled signals were averaged to reduce effects of noise induced by limited photon statistics. Typical average times were 1 s or 10 s. Signals from chopper reference, signal reference, SAXS/WAXS, and thermocouples were sampled synchronously at the maximum sampling rate. Specially designed software was used for on-line background reduction (pseudo lock-in reducing contributions from background radiation and leakages of ambient light into the detectors) and signal averaging.

Figure 2 shows a picture of the experimental set-up while the experiments is running



Fig.2 Picture of the experimental set-up while an experiment is running.

Results and Discussion

When the flame was turned on the temperature of the burner surface increased and the chemistry and nanoparticle production in the flame region speeded up until it ca 1000 s after ignition. In this period of time only relatively small amounts of nanoparticles/soot had condensed on the metal plate. The temperature under stabilized conditions was 800 K close to the burner surface. As the carbon layer grew on the surface heat transfer from the gas to the plate increased

causing a drop of temperature in the measured volume. As the layer continued to increase and entered the probed volume strong enhancement of the scattering intensity was observed for the WAXS.

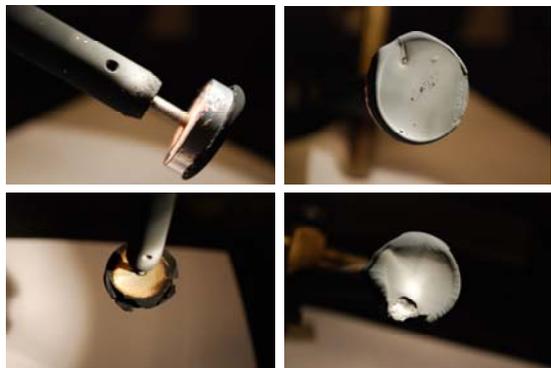


Fig.3 Nanoparticles/soot condensed on copper (upper) and steel (lower) plates (diameter = 20 mm).

Figure 3 shows pictures of condensed nanoparticles/soot on two different metal plates (steel and copper). The carbon materials present an amazingly ordered structure despite the considerable layer thickness. Fine structures of the carbon materials surfaces follow the roughness structures of the supporting metal plates.

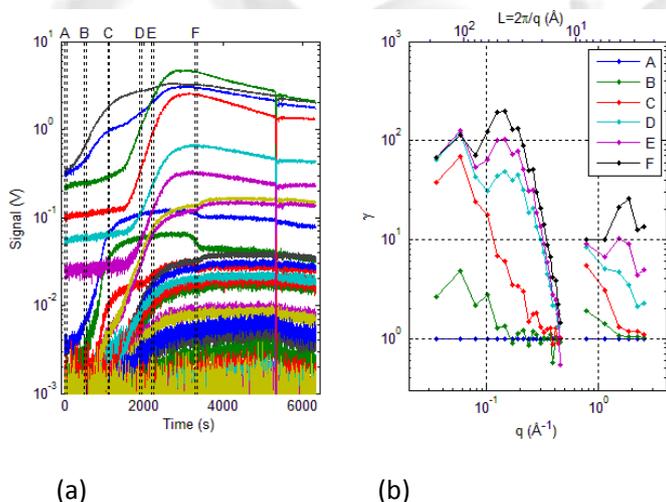


Fig.4 (a) The raw traces and (b) scattering patterns corresponding to specific times during the experiments.

Fig.4 presents an example of results from an experimental run using a steel plate. (a) shows the raw signal traces and (b) the corresponding ratios of scattering intensities, γ , between the actually and initially measured data during the experiment. The data was averaged for 51 s before γ (q) was calculated. $q = 4\pi \sin(\theta) / \lambda$, was the momentum exchange parameter and θ and λ , were the scattering angle and wavelength of the

radiation, respectively. The top axis of the graph in (b) gives the characteristic length scale $L = 2\pi / q$, obtained as the Fourier transform of the q scale. The results show that there are significant changes on the intensities and profiles of the SAXS and WAXS patterns over time.

During the first 1000 s the intensity in the small angle ($q < 0.4 \text{ \AA}^{-1}$) region increased as well as that for the lowest angles of the WAXS channels. Although the intensity in the SAXS region changed drastically the main shape of the profile was maintained, indicating that there was a raise in the concentration of nanoparticles while the mean size, estimated to be $\sim 5 \text{ nm}$, changed weakly. In the overlap region, $0.45 \text{ \AA}^{-1} < q < 0.75 \text{ \AA}^{-1}$, extending into the WAXS region the data indicated considerable enhancement in the intensity for scattering caused by an average length scale close to 10 \AA . Slightly before 2000 s an increase in the scattering sets in in the region $0.06 \text{ \AA}^{-1} < q < 0.45 \text{ \AA}^{-1}$ ($8 \text{ \AA} < L < 100 \text{ \AA}$), with a maximum present around $q = 0.15 \text{ \AA}^{-1}$ ($L = 40 \text{ \AA}$). After 2000 s the scattering intensities at the two smallest angles ($q < 0.06 \text{ \AA}^{-1}$; $L > 100 \text{ \AA}$) hardly changed, whereas the intensities continued to grow for $0.06 \text{ \AA}^{-1} < q < 0.45 \text{ \AA}^{-1}$. There was an increase in intensity and change in the shape of the scattering intensity profile in the WAXS regions $0.75 \text{ \AA}^{-1} < q < 2.5 \text{ \AA}^{-1}$ ($2.5 \text{ \AA} < L < 80 \text{ \AA}$), which would correspond to stacking and graphite formation appearing late when the intensity at the smallest angles change very little or hardly at all.

Conclusion

A new multichannel combined SAXS/WAXS detector has been tested on a dynamic flame system. The results demonstrate the potential of the detector for in-situ studies on particle formation and phase transition dynamics in low density and hostile environment.

References

- [1] England, WA. An In situ X-Ray Small-Angle Scattering Study of Soot Morphology in Flames. *Combust. Sci. Technol.* 1986;46 (1-2):83-93.
- [2] Hessler JP, Seifert S, Winans RE. Spatially Resolved Small-Angle X-Ray Scattering Studies of Soot Inception and Growth, *Proceedings of the Combustion Institute* 2002;29:2743-2748.
- [3] di Stasio S, Mitchell JBA, LeGarrec JL, Biennier L, Wulff M. Synchrotron SAXS (In Situ) Identification of Three Different Size Modes for Soot Nanoparticles in a Diffusion Flame. *Carbon* 2006;44(7):1267-1279.
- [4] Sztucki M, Narayanan T, Beaucage G. In situ Study of Aggregation of Soot Particles in an Acetylene Flame by Small-Angle X-ray Scattering. *J. Appl. Phys.* 2007;101(11):114304.
- [5] Ossler F, Larsson J. Exploring the Formation of Carbon-Based Molecules, Clusters and Particles by In Situ Detection of Scattered Radiation. *Chem. Phys. Letters* 2004; 387(4-6), 367-371.
- [6] Ossler F., Larsson J. Measurements of the Structures of Nanoparticles in Flames by In Situ Detection of Scattered X-Ray Radiation. *J. Appl. Phys.* 2005;98(11):114317..
- [7] Ossler F., Canton S.E, Larsson J. X-ray scattering studies of the generation of carbon nanoparticles in flames and their transition from gas phase to condensed phase". *Carbon*, 47, 3498-3507 (2009).