Oxidative Fragmentation of Soot Aggregates

A. D. Melas[1,2], P. Baltzopoulou[1], M. Kostoglou[3], E. Daskalos[1], Y. Drossinos[4], A. G. Konstandopoulos[1,2]

[1]Aerosol & Particle Technology Laboratory, CPERI/CERTH, P.O. Box 60361, 57001, Thessaloniki, Greece
[2]Department of Chemical Engineering, Aristotle University, P.O. Box 1517, 54006, Thessaloniki, Greece
[3]Div. Of Chemical Technology, Dept. of Chemistry, Aristotle University, 54124, Thessaloniki, Greece
[4]European Commission, Joint Research Centre, I-21027, Ispra (VA), Italy

INTRODUCTION

Over the last years, legislation on particulate matter emissions of diesel cars focuses on ultrafine particles (smaller than 100nm) which are claimed to be responsible for climate change and irreversible health effects. In Euro 5b, a particle number limit was introduced in addition to the already existing particulate mass limit. Particle number and size distribution are unstable and depend on internal processes like coagulation and fragmentation[1]. While the coagulation kernel has been extensively studied in the literature[2], there is still lack of understanding about the fragmentation mechanism.

Harris and Maricq[3] found that soot particle size distributions from various types of diesel engines have a lognormal shape which may be predicted from the solution of the fragmentation-aggregation equation with Brownian coagulation in the continuum regime. Kostoglou and Konstandopoulos[4] introduced a more-physically based fragmentation mechanism where fragmentation of the soot aggregates is assumed to occur due to surface oxidation of the solid contacts between the primary particles, the so-called “necks”.

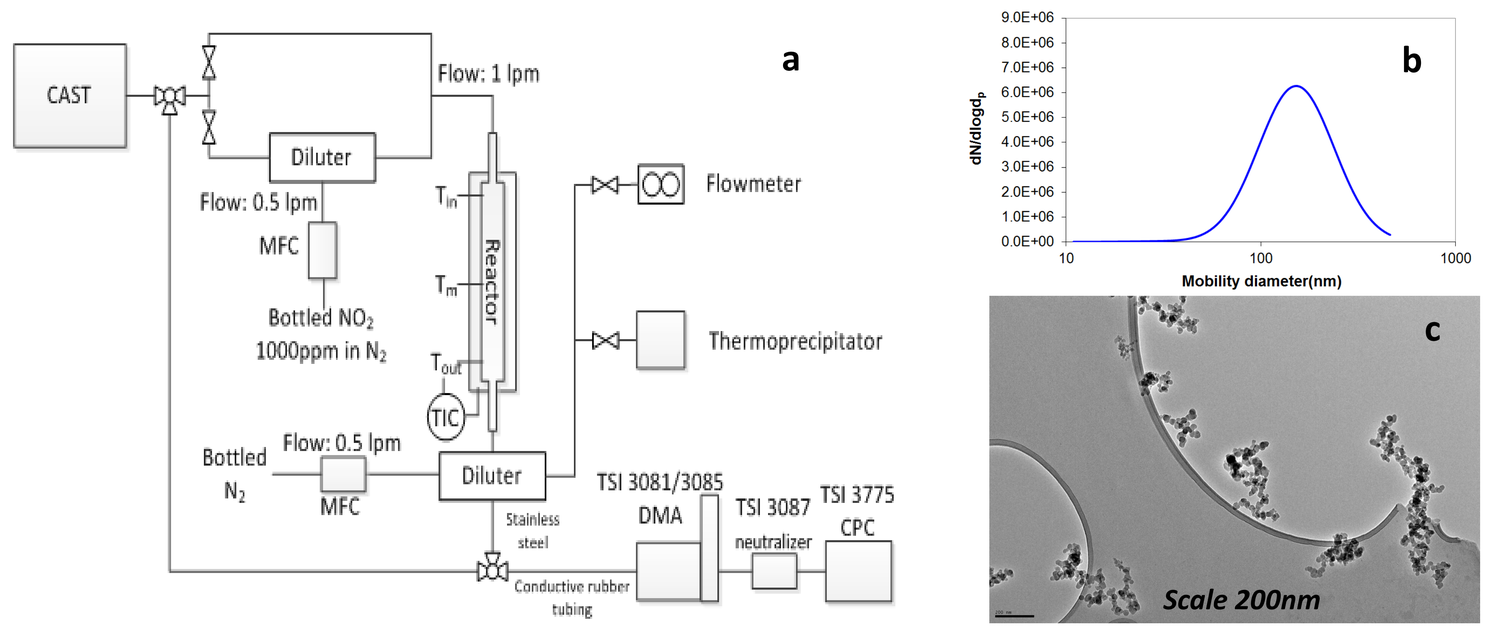

Figure 1: a- Schematic diagram of the experimental setup, b- mobility particle size distribution of the CAST-generated soot, c- TEM image of CAST-generated soot particles

EXPERIMENTAL SETUP

Figure 1a shows the experimental setup. Soot aggregates generation is done with a Combustion Aerosol Standard (CAST 2, Matter Engineering). Its main advantage is that it generates soot aggregates similar to the diesel engine emitted, but with a monomodal, stable, and repeatable mobility size distribution (Fig. 1b). Soot aggregates were driven to a heated reactor, where the temperature effect is studied with the presence of two different oxidants; oxA: O_2 (21%), and oxB: O_2 (10.5%)-NO_2 (500ppm). A Scanning Mobility Particle Sizer (SMPS) was employed to measure the particle size distribution (PSD). In parallel with the SMPS a custom-made thermoprecipitator[5] operated, which was used to collect soot particles for TEM analysis.

RESULTS

Particle size concentration

The PSD remained monomodal and similar to the upstream measurement for temperatures up to T=1000K for both oxA (Fig. 2a) and oxB (Fig. 2b). As the temperature increased further, a second and a third peak appeared for both oxidants at d~25nm and d~10nm respectively. For oxB, the phenomenon occurred at lower T due to the NO_2 presence.

Number Concentration and mass balance

The total number concentration (C_{tot}) initially decreased as the temperature increased (Fig. 3a). When the distribution became trimodal, C_{tot} started increasing overcoming even the upstream measurement. This is a strong indication that oxidative fragmentation occurs. The total mass (Fig. 3b) was calculated by the number concentration following a method presented in [6]. The reaction rate was calculated by the mass loss at the different residence times. The pre-exponential prefactor was found to be larger for oxB, showing the impact of NO_2 at soot oxidation.

TEM images

TEM images (Fig. 4) confirmed the SMPS measurements. For both oxidants, at T>1000K, we observed particles with d~25nm and d~10nm that correspond to the second and the third peaks respectively.

Algorithmic study

The fragmentation algorithm, assumed uniform neck distribution and random neck breakage. Our approach was based on graph theory where a cluster is a set of connected bound monomers expressed via the adjacency matrix. The random breakage of a neck was equivalent to the replacement of a randomly selected element of the adjacency matrix that equals one with zero. Finally, we used the sparse matrix to calculate the number of clusters that the new adjacency matrix contained. Figure 5 shows the fragment mass fraction distribution which is 'U'-shaped (mainly primary particles break), independently of the aggregate’s structure, in agreement with the experimental findings.

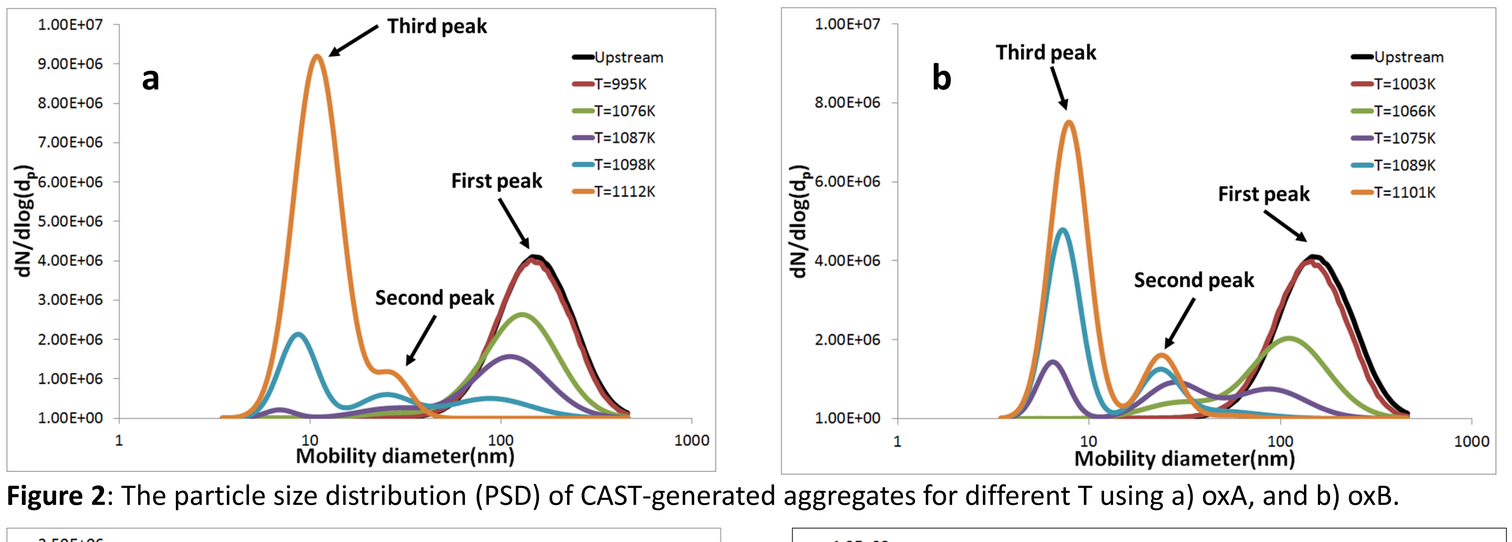

Figure 2: The particle size distribution (PSD) of CAST-generated aggregates for different T using a) oxA, and b) oxB.

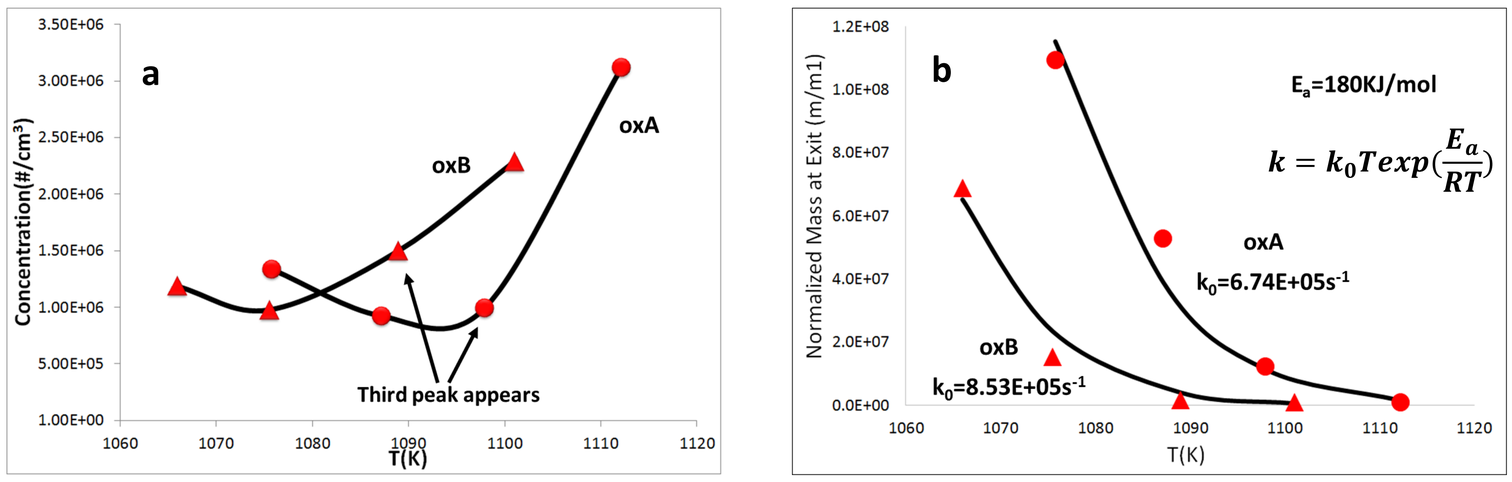

Figure 3: The total number concentration (a) and the total mass (b) at different temperatures.

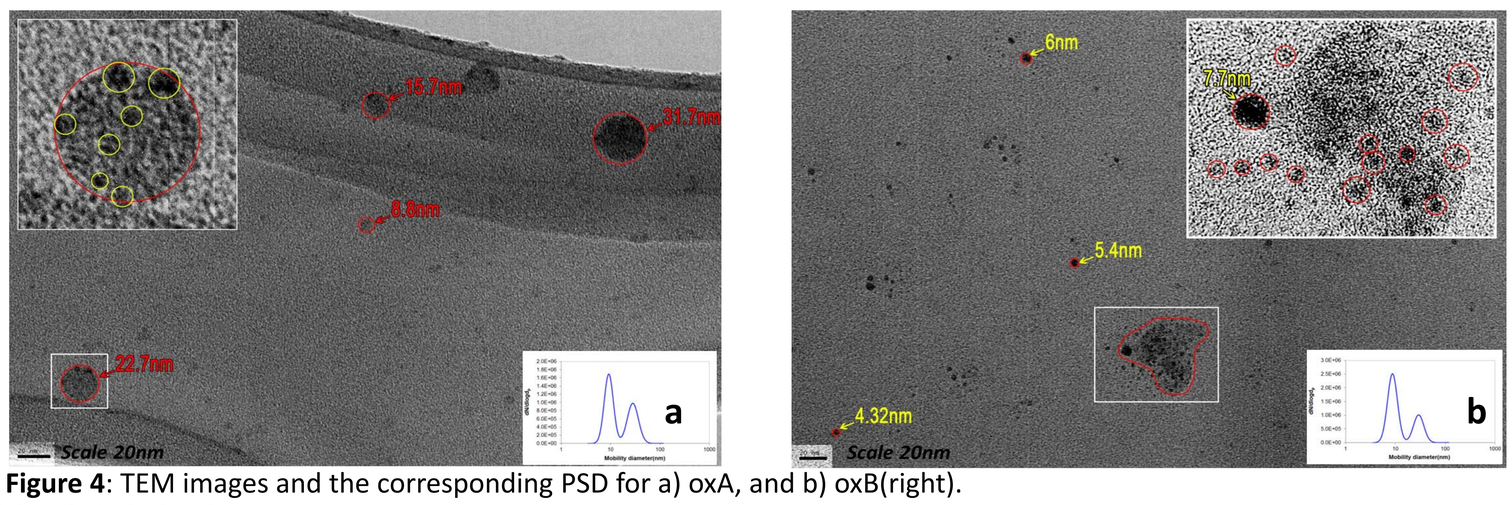

Figure 4: TEM images and the corresponding PSD for a) oxA, and b) oxB(right).

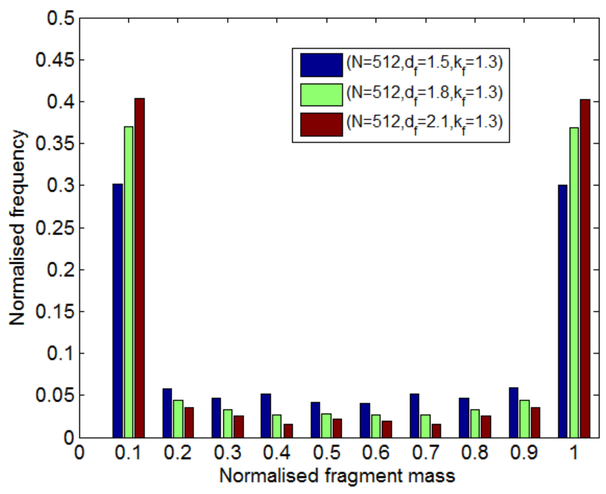

Figure 5: The normalized frequency of the aggregates mass fraction after a single-neck breakage, divided in 10 bins.

CONCLUSIONS

- At T>1000K, a second and a third peak appeared at the particle size distribution, while the particle number increased. This is a strong indication that fragmentation due to oxidation occurs.
- The pre-exponential factor is larger for oxB showing the impact of NO_2 at soot oxidation.
- TEM images confirmed the existence of small particles in the outflow at T>1000K.
- The algorithmic study gives a ‘U’-shaped fragment distribution in agreement with the experimental findings.

REFERENCES

1. S.K. Friedlander, ”Smoke, Dust and Haze”, Oxford University Press, New York, 2000.
2. M. Kostoglou and A.G. Konstandopoulos, *J. Aerosol Sci.*, **32**, 1399 (2001).
3. S.J. Harris and M.M. Maricq, *J. Aerosol Sci.*, **33**, 935 (2002).
4. M. Kostoglou and A.G. Konstandopoulos, *J. Aerosol Sci.*, **34**, S1061-S1062 (2003).
5. E. Daskalos and A.G. Konstandopoulos, *European Aerosol Conference EAC 2008*, August 24-29, Thessaloniki, Greece
6. A.D. Melas, L. Isella, A.G. Konstandopoulos, Y. Drossinos, Aerosol *Sci. Technol.*, **48**, 1320 (2014).

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Contact: Anastasios Melas ● Tel: +30 2310 498246 ● Fax: +30 2310 498190 ● e-mail: amelas@cperi.certh.gr ● Web: http://apt.cperi.certh.gr