Assessment of a reference aerosol generated by a propane diffusion flame (CAST) in the sub-23 nm range

E. Daskalos[1], A. Melas[1], D. Deloglou[1], A. Zygogianni[1], E. Papaioannou[1,2], 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

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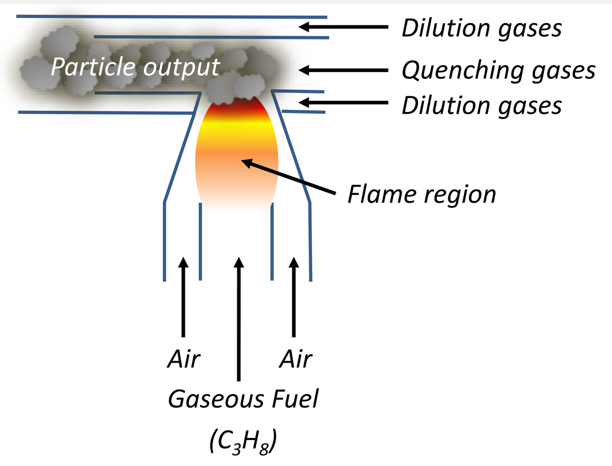
INTRODUCTION

Particulate number (PN) emissions regulations from contemporary light duty direct injection (DI) internal combustion (IC) engines (Diesel and Gasoline) are currently limited to a cutoff limit of 23nm due to the Particle Measurement Programme (PMP) that constitutes the standard method for certification. The cut-off limit is applied to avoid measurement uncertainties (artefacts, particle losses and gaps in basic understanding of the nature of the various particles) that appear in the realm below 23 nm. However, in various cases, the fraction of particles omitted by PMP can represent up to 50% in terms of total concentration. Thus, understanding the mechanisms, the nature and managing to measure nanoparticles down to 10 nm (free of conditioning related artefacts), is the next challenge for the scientific community and the regulatory authorities of EU to further protect the health of its citizens. In this study, we examine the suitability of Combustion Aerosol Standard (CAST) to serve as a reference sub-23nm particle generator for the measurement devices and procedures of the near future. To investigate this capability, the conducted experiments evaluate the generated aerosol in terms of size distribution, concentration, nature and composition. Furthermore, the aerosol is thermally treated through a PMP compatible setup, alternatively incorporating an in-house Catalytic Stripper (CS) as a substitute of the more common Evaporation Tube (ET). Finally, particle losses across the conditioning system were quantified by incorporating numerical calculations based on thermophoresis and diffusion which consist the main known mechanisms of this size range.

CHARACTERIZATION OF CUSTOM CAST AEROSOLS

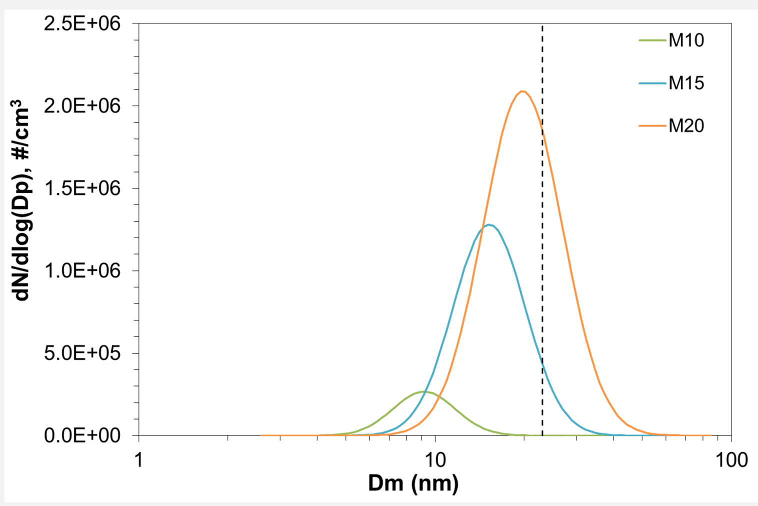
Production of reference, custom sub-23nm aerosols



Schematic of CAST operating principle

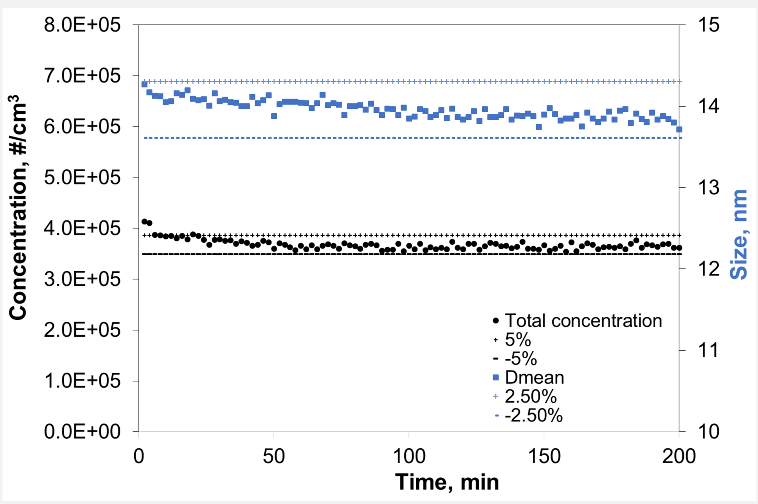
CAST is capable of producing aerosols with both standard and user tailored size, concentration and volatile fraction characteristics by simply fine tuning the flow rates of the gas mix that takes part in the oxidation/quenching processes.

Size



Produced custom Sub-23nm CAST distributions

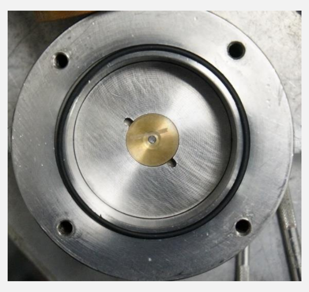
Stability

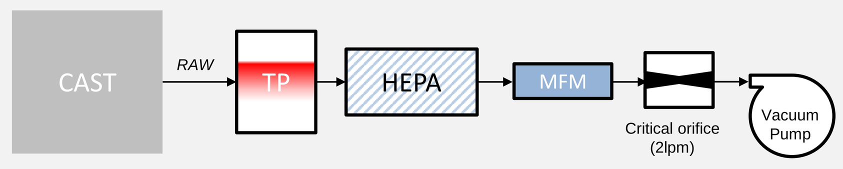


Stability of the custom aerosol over a period of 200mins

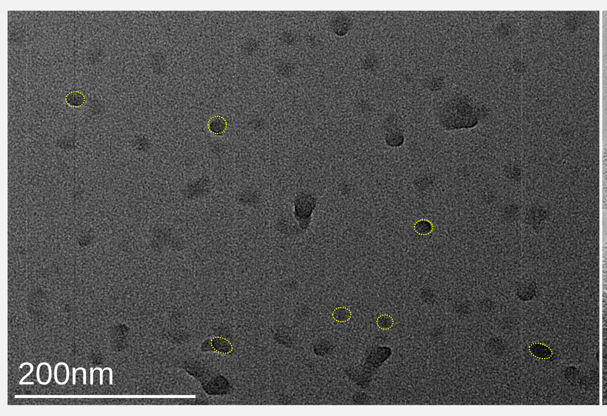
TEM Analysis

For TEM analysis, raw M15 aerosol was sampled on EMS® Holey/Carbon Film copper grids (300 mesh) for 50mins with a flowrate of 1,95lpm by means of an in-house thermophoretic (TP) sampler [1] and loaded on a JEOL® JEM 2010 TEM microscope. ΔT across the sampling gap (400μm) was kept constant at 85°C resulting to a thermophoretic gradient of 2.11x10⁵ °C/m.

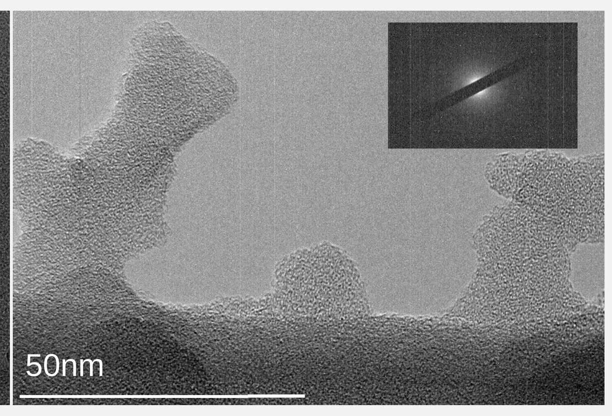

TEM grid positioning on the in-house TP



TEM sampling setup



Low magnification TEM of M15



HR TEM of M15

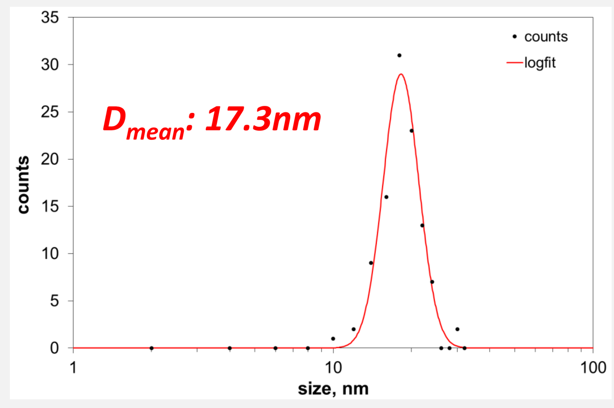
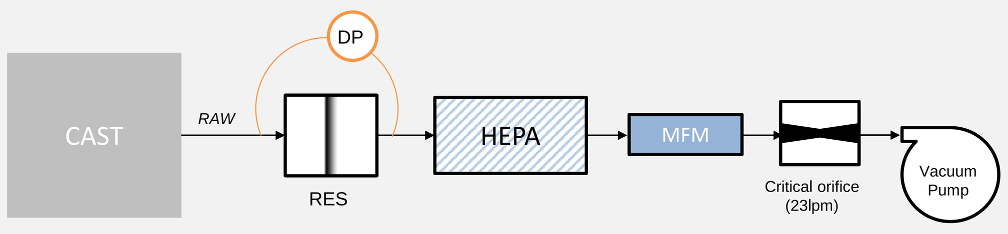


Image analysis based size distribution of M15 aerosol

TEM revealed that M15 particles were amorphous, lacking a well defined perimeter, exhibiting a semi-solid nature of elliptical/spherical shape. Furthermore, analysis of TEM images with ImageJ® revealed that particle sizes lie in the range of 10-30nm, with a mean value of 17.3nm.

RAMAN – Thermogravimetric analysis

For RAMAN/TGA analysis, samples were collected on Φ47mm Tissuquartz PALL® filters, thermally pretreated at 850°C for 1h. For comparison, samples were collected also for the standard CAST modes MP1 (190nm) and MP7 (40nm). Sampling flow was kept constant to 23.5lpm by means of a critical orifice. RAMAN analysis was performed on a Renishaw® inVia Raman-FTIR microscope equipped with an Ag laser (514.5nm), while TGA on a Pyris® 6 Thermogravimetric analyzer.

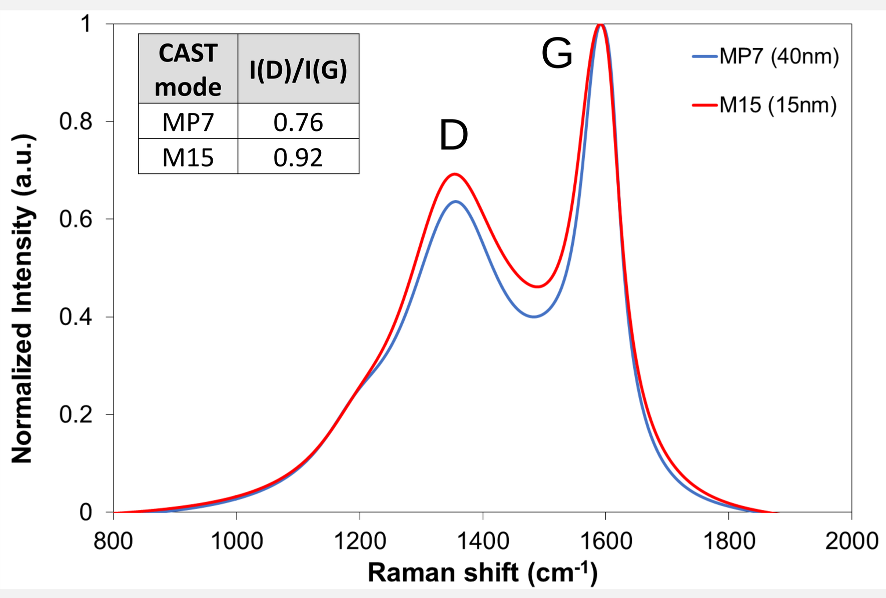


RES sampling setup

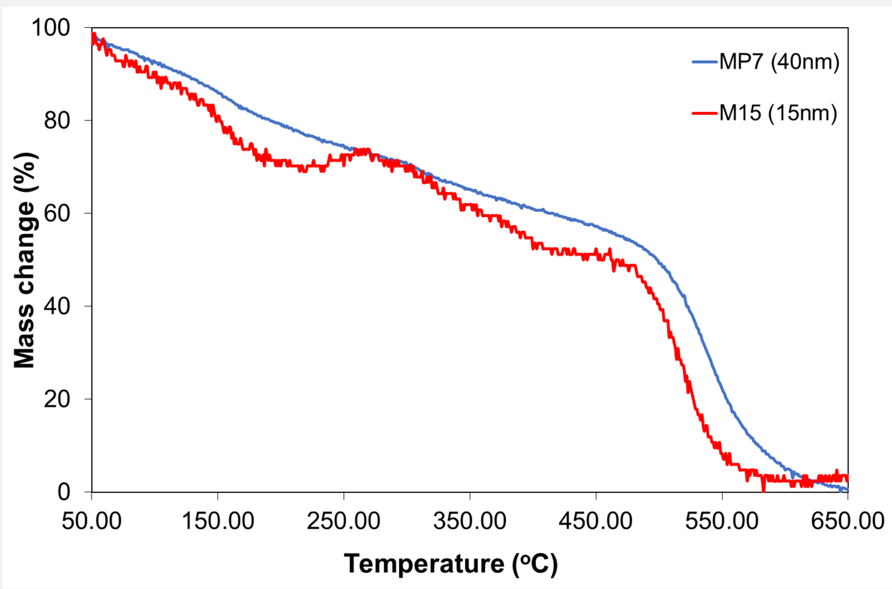

M15 RES sample

CAST mode	Sampling time (min)	DP (mbar)
MP1	3	300
MP7	32	300
M15	190	5.4

Sampling conditions



Raman spectra of fuel-rich CAST aerosols



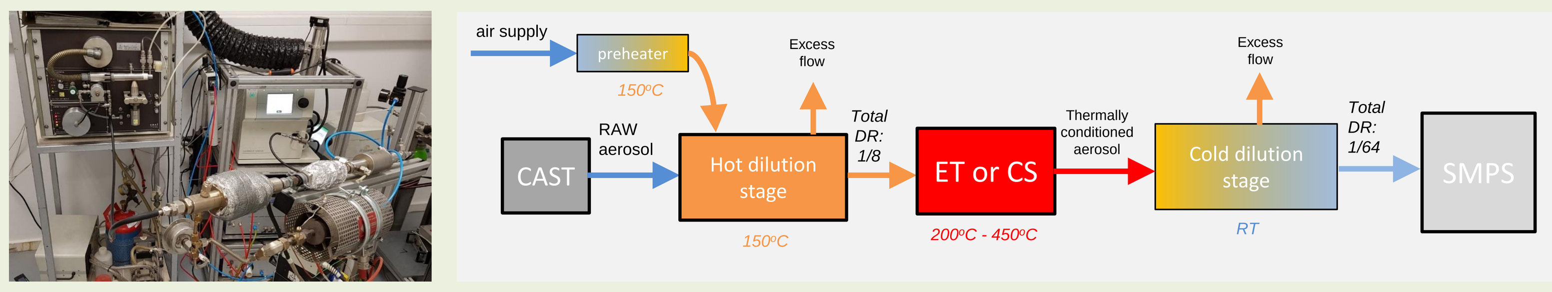
Thermogravimetric spectra of fuel-rich CAST aerosols

RAMAN analysis was based on the de-convolution approach [2]. D peak @1350cm^{-1} arises from defect structures, while G peak @1600cm^{-1} from ordered structures. I(D)/I(G) ratio is indicative of the OC fraction, decreasing for more ordered structures. The shoulder @ 1200cm^{-1} represents C-O groups, or stretching vibration modes of C-C and C=C or sp²-sp³ bonds, while the area between the two peaks (~1500cm^{-1}) represent amorphous carbon. Also, an increase of D width indicates higher OC fraction.

Thermogravimetric analysis reveals the enhanced volatile nature of M15, estimating the OC fraction up to ~52% in comparison to 45% of MP7. Furthermore, carbon oxidation occurs at slightly lower temperature (~480°C) compared to MP7 (~500°C).

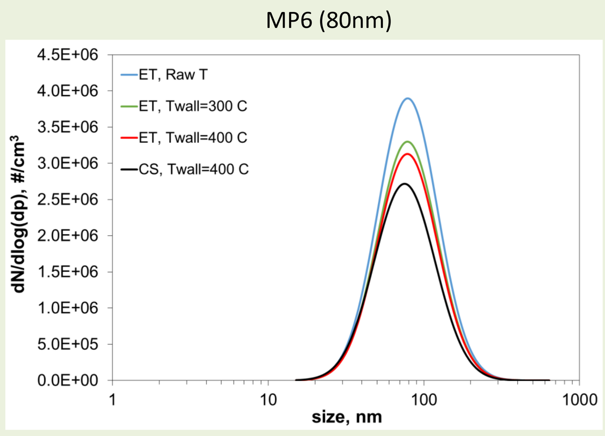
EFFECTS OF PMP TREATMENT ON THE AEROSOL CHARACTERISTICS

Standard and custom CAST modes underwent a PMP-like thermal treatment in order to assess their artefact generation potential. For the removal of volatiles ET and CS were used alternatively. The penetration fraction (P) of the treated particles were also theoretically estimated by employing a theoretical framework [3] and compared to experimental findings.



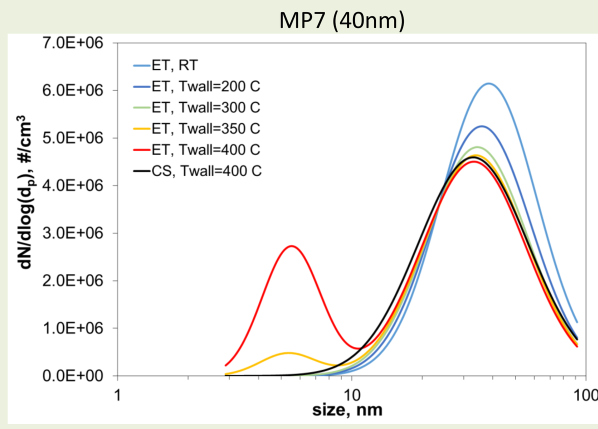
Experimental setup and schematic of the PMP compatible system

MP6 (80nm)



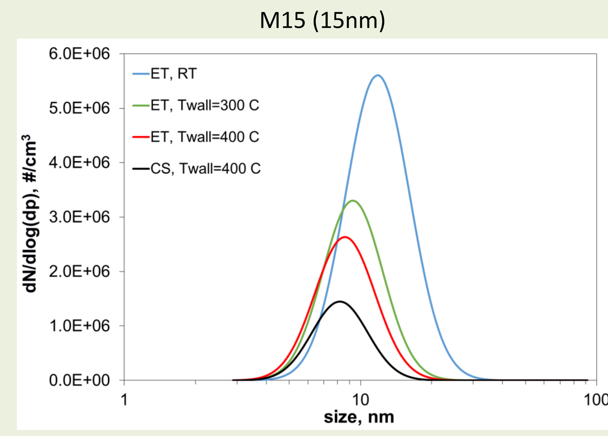
PMP status	P_{tot}	$<d_m>$
ET, RT	-	83.8
ET, T_{wall}=300 °C	0.85	83.4
ET, T_{wall}=400 °C	0.81	83.4
CS, T_{wall}=400 °C	0.79	80.8

MP7 (40nm)



PMP status	P_{tot}	$<d_{m,1}>$	$<d_{m,2}>$
ET, RT	-	40.7	-
ET, T_{wall}=300 °C	0.82	37.3	-
ET, T_{wall}=400 °C	0.78	36.5	5.9
CS, T_{wall}=400 °C	0.67	36.1	-

M15 (15nm)



PMP status	P_{tot}	$<d_m>$
ET, RT	-	11.9
ET, T_{wall}=300 °C	0.55	9.4
ET, T_{wall}=400 °C	0.44	8.7
CS, T_{wall}=400 °C	0.33	8.3

For both setups, penetration values of mode MP6 seem rather stable and fairly independent of any thermal effects. In the case of MP7 penetration is similar to those of MP6 only for the ET setup, while a nucleation mode occurs at ~6nm for T_{wall}>350°C as an artefact due to recondensation of evaporated species. This mode disappears under the catalytic action of CS. Custom mode M15 exhibits the strongest dependency to thermal conditions, manifesting a 30-45% deviation from theoretical estimations of P (0.85) due to evaporation of volatile species. Finally, for all modes, subtle (MP6, MP7) to profound (M15) particle shrinkage was observed attributed to evaporation of the organic fraction.

CONCLUSIONS / FUTURE WORK

- CAST is capable of producing nanoparticles in the sub-23nm range exhibiting flexibility, stability and repeatability as required by a reference device
- Sub-23 nm aerosols are populated by amorphous, “semi-solid”, non-fractal, near spherical particles with high organic fraction (>50%)
- Thermal treatment of CAST aerosols through the more common PMP setup (with ET) may produce artefacts that may constitute 27-50% of the total concentration depending on operation temperature
- Substitution of the ET sub-unit by a CS leads to a more effective removal of artefacts

1. Real time RAMAN/FTIR measurements under oxidative atmosphere, at various thermal levels is expected to reveal more about the dynamic nature of such “semi-solid” particles
2. Development of a more efficient particle sampling system, specialized for the sub-23nm size range

References

[1] E. Daskalos, N. Vlachos, A. G. Konstandopoulos, *The microstructure of soot aggregates produced by the Combustion Aerosol Standard (CAST) generator*, ETH, 2011

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[3] B. Giechaskiel, M. Arndt, W. Schindler, A. Bergmann, W. Silvis, Y. Drossinos, SAE Int. J. Engines, 5, 2012

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Contact: Emmanouil Daskalos ● Tel: +30 2310 498247 ● Fax: +30 2310 498190 ● e-mail: emdaskal@cperi.certh.gr ● Web: http://apt.cperi.certh.gr