CHEMICAL ENGINEERING TRANSACTIONS, Volume 16, 2008
Guest Editor Eliseo Ranzi
 ISBN 978-88-95608-03-7 ISSN 1974-9791

Particulate Emission from Internal Combustion Engines

Di Iorio, S., Merola, S.S., Vaglieco, B.M.
Istituto Motori – CNR, Via G. Marconi – 80125 Napoli – ITALY

D'Anna, A.
Dipartimento Ingegneria Chimica – Università "Federico II", P.le V. Tecchio, 80 – 80125 Napoli - ITALY

Minutolo, P.
Istituto Ricerche Combustione – CNR, P.le V. Tecchio, 80 – 80125 Napoli – ITALY

In this work, number concentration and size distribution at the exhaust of a Port Fuel Injection (PFI) Spark Ignition (SI) engine downstream a three-way catalyst and a Direct Injection Common Rail Diesel engine have been measured with two particle size instruments. The gas exhaust is first diluted, a nano DMA is used to obtain the particles size distribution function in the 3-60 nm range, in parallel, an electrical low pressure impactor (ELPI) is used to investigate a wider size range of 7 nm up to 10 μm. The two sizing techniques furnishes complementary information, in particular, DMA resolution is necessary to obtain the true distribution of the smaller particles. The measurements show that the Spark Ignition engine emit a large number of particles in all the investigated conditions. The maximum of the particles size distribution is measured at about 4nm. At the exhausts of a Diesel engine small particles are less abundant and difficult to detect.

1. Introduction

Traffic-related particle emission is of great concern because of the hazards to health and the environment. Consecutive series of more stringent regulations have oriented technology projects devoted to the understanding of particle formation in engine combustion in order to reduce particle formation. Technology improvements, including direct injection, common rail, turbocharging, multi-pulse fuel injections, and controllable valve timing have been found to be controlling ways of cutting particulate emissions from engines.

Diesel engine is considered, among the internal combustion engine systems, to be major cause of particulate matter emission. Exhaust particulate matter is a complex mixture that depends on engine operation, fuel composition, lube oil, after-treatment technology, and exhaust procedures. The diffusion controlled character of engine combustion produces carbonaceous particles with sizes between 1 and 300 nm. Ash from trace metals, or cerium and iron fuel additives used to catalyze diesel particulate filter (DPF) regeneration, usually becomes incorporated into the carbonaceous particles. Together these constitute the emitted particulate matter. Emitted small nanoparticles are often considered not to be directly connected with combustion process, but rather thought to nucleate during dilution and cooling of the exhausts. Indeed, as exhaust cools

Please cite this article as: Di Iorio S., Merola S.S., Vaglieco B.M., D'Anna A. and Minutolo P., (2008), Particulate emission from internal combustion engines, Chemical Engineering Transactions, 16, 251-258

semivolatile materials can nucleate to produce a nanometric diameter mode. Sulfate plays an important role, but is very sensitive to dilution ratio and humidity. Lube oil might be also responsible depending on the mechanical characteristics of the engine. Exhaust after-treatment complicates the picture by removing condensable organic material from the exhausted particulate matter but, by oxidizing SO_2 to SO_3 it can also increase the propensity for nucleation by sulfate.

The question still remains if nuclei particles emitted from an engine are carbonaceous ultrafine particles nucleating from the gas-phase in the high temperature environment containing trace metals deriving from the fuel or are low volatile organic compounds and sulfur condensed on organic nanoparticles as exhaust exits the engine and cools.

Nanoparticles are present in low mass concentration, but surprisingly high number concentrations due to their very low sizes. The emission of these particles into the atmosphere constitutes a serious concern for health and for their contribution to photochemical smog. The smallest particles play a particularly important role in health since they are able to penetrate deeper than larger particles into the respiratory system. They may also affect the radiation balance of the atmosphere by serving as condensation nuclei for cloud formation and for contrails in the upper atmosphere. For these reasons, the role of combustion-formed nanoparticles is of central interest in the field of atmospheric chemistry. These particles may account for a large part of the organic carbon in urban atmospheres and they might also explain the phenomenon of "nucleation burst" after agglomeration in rain.

Recent work shows that a nuclei mode of nonvolatile particles is also found in hydrocarbon-rich laboratory flames. These are characterized as 2-5 nm spherical particles transparent to visible radiation, with relatively low C/H ratio. Engine exhaust and flame nanoparticles have recently been compared [Sgro et al. 2008], via UV extinction and size distribution measurement at the exhausts of diesel and gasoline engines. The similarity of the chemical properties and the size distribution functions of the emitted particles with those found in laboratory flames suggested that combustion-formed nanoparticles can escape the combustion process and be emitted into the atmosphere. Thus combustion, as well as the fuel, may have a dominant role in determining the type and amount of particles emitted.

Our objective here is to present particle emission data from two modern vehicles equipped with a light duty diesel engine and a fuel port injection gasoline engine. We examine size distribution functions with different detection systems including a Scanning Mobility Particle Sizes and an Electric Low Pressure Impactor in addition to conventional measurements for emitted gaseous products and total particulate matter. Effect of engine speed and load are analyzed as well as temperature of the exhausted material. Finally, to address potential environmental impact, we investigate the effectiveness of diesel exhaust after-treatment to reduce nuclei particle emissions.

2. Experimental System

2.1 Engines

Two commercial engines were tested on a dynamometer: a four-stroke Port Fuel Injection (PFI) Spark Ignition engine and a Direct Injection Common Rail Diesel engine.

The spark ignition engine has four in-line cylinders, 16 valves, a displacement of 1.2 litres and a compression ratio of 10.6:1. The engine has a multipoint electronic injection system and it is equipped with a three - way catalyst and two lambda meters. The first one was located upstream the catalyst in order to control the Air-Fuel ratio; the second one was placed downstream the catalyst in order to check the catalyst operation. All the measurements were made using low sulphur commercial gasoline fuel and lubricating oil.

The compression ignition engine is a Unijet Common Rail with four cylinders,16 valves and a displacement of 1.9 litres. A commercial diesel fuel with less than 10 ppm sulphur was used in the tests.

Specific sensors for temperature were installed upstream, downstream and on the exhaust pipe of both engines. The measurements consisted of different constant speed driving conditions (1000, 2000 and 3000 rpm for the gasoline engine and 1500 and 2000n rpm for the diesel engine) at low and medium load (50% and 100%). The driving parameters were recorded by standard measurement devices. Each engine test point was maintained for 10 minutes in order to have a high statistics of the data. The measurements were carried out in the exhaust where temperature was higher than 500K.

2.2 Measurements

<u>DMA system</u>

Differential Mobility Analysis (DMA) is becoming a widely accepted tool for the determination of the size distribution of particle formed in combustion environments.

DMA measurements require a high dilution sampling system to reduce the sample temperature and concentration and to avoid further reactions and particle coagulation in the sampling line. Particles are charged and separated in an electrostatic classifier based on their electrical mobility. A mobility, or size distribution is determined by counting the charged particles which exit the classifier, varying the applied voltage. When state of the art instrumentation is used, a size distribution from 1-100 nm can be measured [Sgro et al. 2007]. The accuracy of the measurement relies on the correct evaluation of the dilution ratio required to suppress particle coagulation in the sampling line, charging efficiency and particle losses through the sampling lines/instrument. This is particularly problematic for particles down to 10nm [Minutolo et al. 2008]. Diffusion losses and the interpretation of particle mobility in terms of size are critical points.

Sampled gas entered the probe through the orifice and was immediately diluted in two steps by Fine Particle Sampler which allows to control dilution ratio and temperature. Primary dilution temperature was set around 250°C and the second one around ambient temperature. Since the dilution ratio is a function of sample pressure and temperature, these values are constantly monitored and the dilution ratio is determined on-line. The dilution ratio was 90:1 and the temperature was around 37°C.

Diluted samples were measured on-line with a nanoDMA system (TSI SMPS 3936 nano). In the SMPS used in this work the aerosol sample is charged by passing through a bipolar ion neutralizer (Model 3077 Aerosol Neutralizer: Kr-85). The charged and neutral aerosol particles then enter a Differential Mobility Analyzer (nanoDMA 3085) in which particles are separated according to their electrical mobility. The classified particles which exit the DMA are counted by a CPC (3025A), which measures the particle concentration. The SMPS was operated in high flow mode (10 l/min sheath flow and 1.5 l/min aerosol flow) and dual blower mode was used to boost sheath flow, reducing transport time and minimizing the diffusion particles losses inside the instrument. TSI Aerosol Instrument Manager software (AIM) was used to determine the particles size distribution function. A recent upgrade of the original software, which accounts also for the particle losses inside the instrument by diffusion to the walls, was also used [Minutolo et al, 2008]. Because of the very low detection efficiency of CPC for small particles, the low cut off limit for the size distribution function reported by the software is at the mobility diameter of 3nm.

ELPI System

Size distribution and number concentration of particles were measured by Electrical Low Pressure Impactor (ELPI). ELPI classifies particles considering their aerodynamic diameter. It combines the principles of electrical detection with size classification by impaction. A corona-wire diffusion charger is used to unipolarly charge the incoming particles. Next, the aerosol stream is introduced to a low-pressure cascade impactor where the particles are collected in 12 different stages depending on their aerodynamic diameter. In the first stage large PM particles with large quantity of kinetic energy collide into the first collecting plate and are trapped. Smaller PM particles have less inertia and are swept around the collecting plates to the next stage. In this way PM particles should be trapped in the impactor according to their size. Each impactor stage contains a sensitive electrometer that measures the current flow associated with the impacting particles. This current can then be measured in real-time. Combining the current readings from every impaction stage, the size distribution of the aerosol sample is obtained.

Before entering the ELPI the emission gases were diluted in two steps by the fine particle sampler with the same procedures as used for the DMA measurements.

Conventional Analysis

HC were measured by IR analyzer and NOx by UV chemiluminescence analyzer. The particulate mass concentration was obtained by opacimeter.

The measurements have been repeated in order to evaluate the evolution of the exhaust temperature.

3. Results and Discussion

Particle emissions are measured from two commercial engines run on a dynamometer at low and medium load (50 and 100%) using commercial ultra-low sulphur fuels.

Particle size from a gasoline engine

Particle size distributions are recorded with the DMA and ELPI systems in four speed conditions and two loads. Table 1 reports details of engine conditions.

Table1. Operative conditions

Speed, rpm	Load, %
1000	50
1500	50
1500	100
2000	50
2000	100
3000	50

Figure 1 compares the particle size distributions measured at low load in two temperature conditions of the exhaust. Both measuring techniques shows the presence of a large number of very low particles with sizes down to 3nm.
The two measurements are in good agreement for particle sizes of the order of 30-60 nm whereas the DMA shows a larger number concentration in the range 7-30nm (the smallest size range which can be measured by ELPI). Disagreement could be related to the large bin size of the ELPI and to the very low charging efficiency of the instrument for particles with sizes below 10nm.
DMA clearly shows a nucleation mode at about 5nm. The formation of this mode is still controversial. It might be constituted of semivolatile material condensed in the exhaust line. However measurements performed maintaining the sampling line at temperatures higher than 250°C show that the nucleation mode still survive showing the non-volatile nature of this mode.

Particle size from a diesel engine

Table 2 reports experimental conditions for the diesel engine.

Table2. Operative conditions

Speed, rpm	Torque, Nm
1500	30
1500	76
2000	30
2000	76

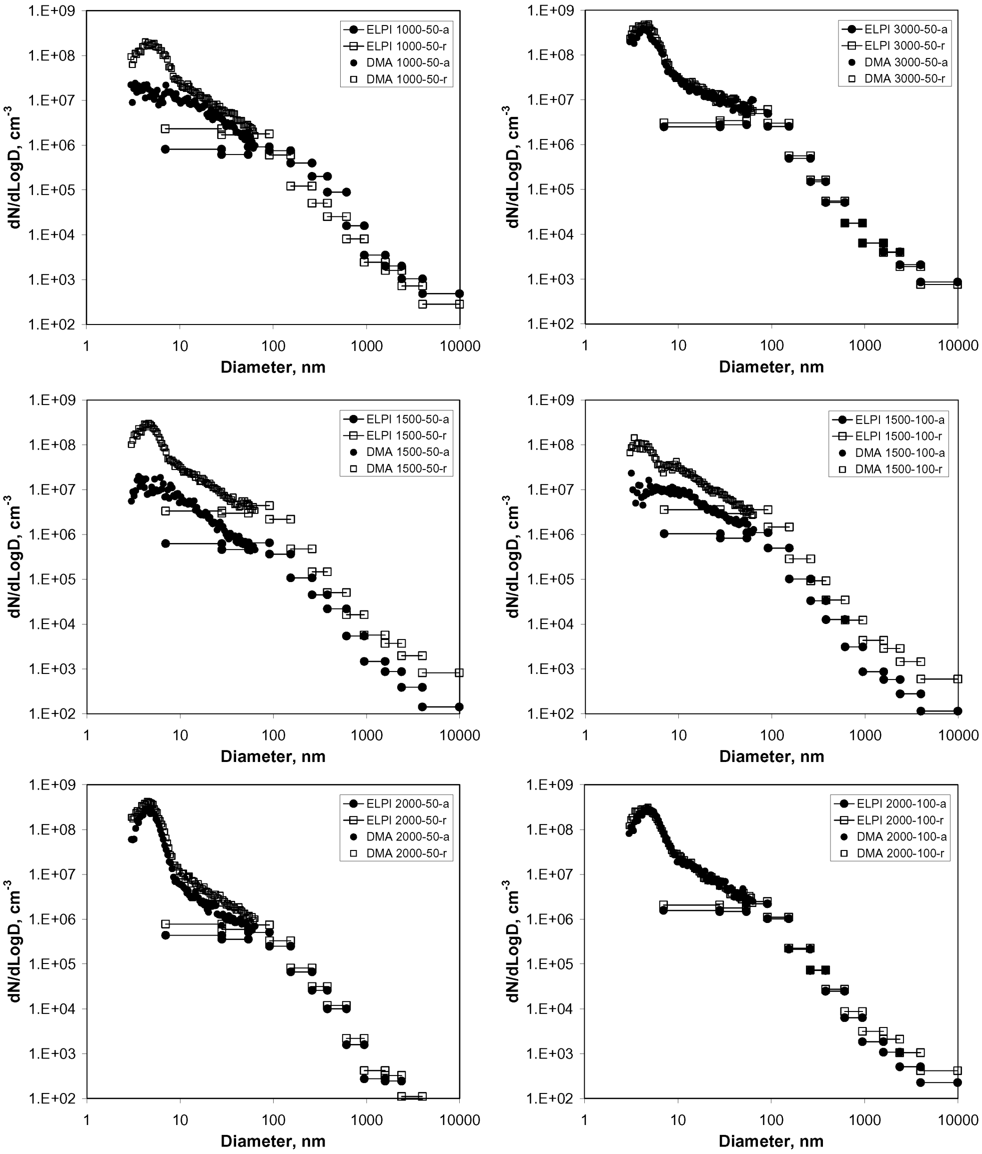

Fig.1. Particle size distribution measured in the exhaust of a gasoline engine for various operative conditions with a DMA and an ELPI system. Squares and circles report repeated measurements.

Figure 2 reports the comparison of particle size distributions at the various engine speeds and two loads in two temperature conditions of the exhaust. The particle size distributions are quite different from that measured at the exhaust of the gasoline engine. They are still unimodal, the maximum in the size distribution function is around 60 nm. Unlike the measurements made at the exhaust of the gasoline engine, in these measurements a good agreement between DMA and ELPI are found. For Diesel engine the nucleation mode, i.e. particles below 10nm is rarely detected. Only in the low speed, high load conditions a distinct increase of the nucleation mode particles is detected.
It is worth noting that optical measurements made in the exhaust of the engine indicated that the nucleation mode is combustion-formed [Merola et al. 2006].
While ELPI system detects a larger number of particles in the case of Diesel engine respect to the gasoline one, the high sensitivity of DMA for detecting very small particles down to 3 nm allows to evidence the presence of an higher number of particles in the nucleation mode for the gasoline engine.

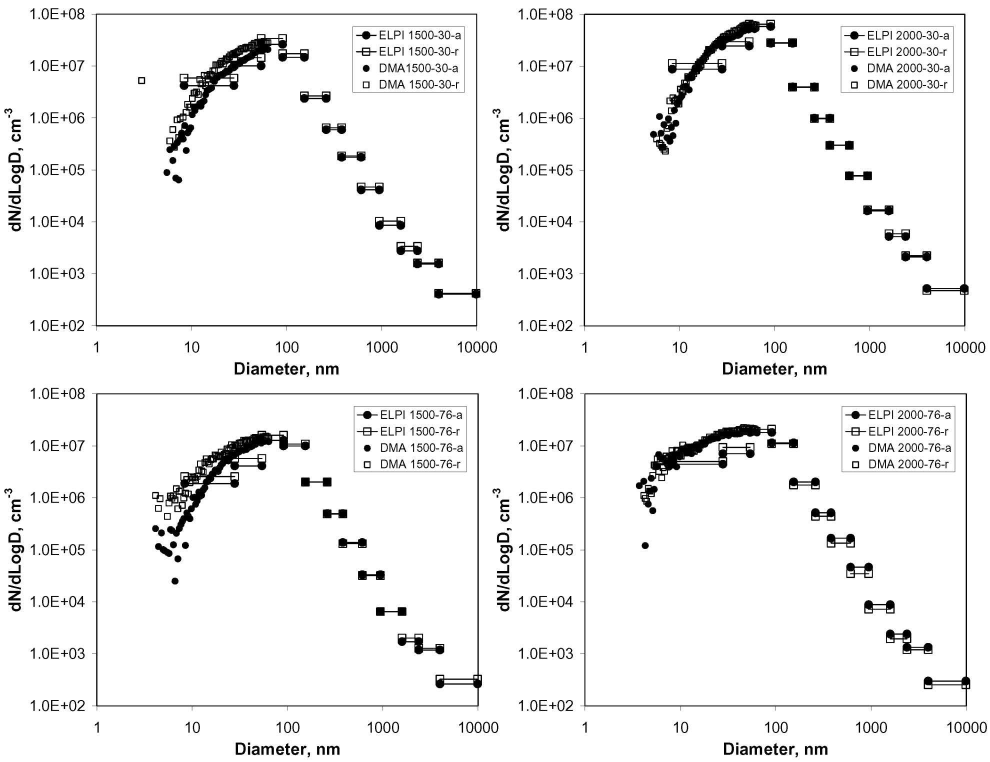

Fig.2. Particle size distribution measured in the exhaust of a diesel engine for various operative conditions with a DMA and an ELPI system. Squares and circles report repeated measurements.

4. Conclusions

The main environmental problem of combustion systems is related to the formation of particles with sizes down to 2nm more than to larger soot aggregates. Smaller NOC particles are formed quite soon in the main reaction zone and their concentration is a strong function of the local (and instantaneous) C/O ratio, while soot formation is a slower process due to the coagulation of NOC, when their concentration exceeds a critical value. Therefore modern combustion systems, which tend to eliminate the formation of soot by better mixing and less rich mixtures with modest improvements of the present technology, are faced with more serious challenge with regard to the suppression of NOC, whose formation is much faster and strictly connected with the time resolved structure of the reaction zones.

An interesting result is that the mass concentration of NOC is comparable with that of soot in modern combustion systems and therefore their number concentration is extremely high. Nevertheless, we were able to trace back consistent quantities of NOC in the exhaust of engines and in the atmosphere and this happens because the coagulation of NOC is orders of magnitude slower than the value predicted by the gas kinetic theory. In other terms, NOC particles are so small that they preferentially rebound on the other particle, or any other surface instead of adhere to it. Clearly, this effect reduces drastically the efficiency of conventional filtering systems or traps, which are designed for the larger soot particles, whose sticking efficiency is almost equal to one.

The subsequent fate of NOC in the atmosphere is a very interesting field of investigation, but the progress so far have been limited by the absence of commercial instruments, which can measure size and number concentration of nanoparticles smaller than 3nm (Kulmala et al., 2004).

6. References

Kulmala M., Vehkam.aki, H., Pet.aj.a, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., McMurry, P.H. (2004) Formation and growth rates of ultrafine atmospheric particles: a review of observations, J Aerosol Science 35 143–176.

Merola S.S., Vaglieco B.M., Tornatore C.,(2006) Characterization of Nanoparticles Emitted During the Regeneration of Catalysed Diesel Particulate Filter, Chemical Engineering Transactions vol. 10 pp. 507-513.

Minutolo, P., D'Anna A., D'Alessio A., (2008) On detection of nanoparticles below the sooting threshold, Combustion and Flame 152 287–292.

Sgro, L.A., A. De Filippo, G. Lanzuolo, A. D'Alessio, (2007) Characterization of nanoparticles of organic carbon (NOC) produced in rich premixed flames by differential mobility analysis, Proc. Comb. Inst. 31 631-638.

Sgro , L.A., Borghese , A., Speranza , L., Barone , A., Minutolo , P., Bruno A., D'Anna, A., D'Alessio, A., (2008) Measurements of Nanoparticles of Organic Carbon and Soot in Flames and Vehicle Exhausts, Environ. Sci. Technol., 42, 859–863.