Ultrafine particles from combustion sources: sampling and measurement

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Air quality issues related to the presence and emission levels of particulate matter have been recently addressed towards ultrafine and nanoparticles size fractions, with typical dimensions included in the range from 0,1 µm down to few nm. Particular attention has been paid to their emissions from combustion activities, although the large majority of investigations in this field are dedicated to traffic sources, with rather limited studies for stationary energy production systems. Following a general review of available data on ultrafine particle emissions from various stationary combustion systems and different fuels, present work describes a dedicated particulate matter stack sampling line which combines a dilution system and an electrical low pressure impactor for evaluating number concentrations and size distributions of the condensible fraction arising from dilution and cooling of flue gases with atmospheric air. Preliminary results obtained with the system for residential heating boilers fed with different fuels (wood pellets, fuel oil, natural gas) are reported and analyzed in terms of their dependence with fuel type, boiler operating regime and sampling conditions (dilution ratios, hot and cold sampling).

1. Introduction

It is widely known that particulate matter emitted from combustion processes varies greatly in size and composition. Whereas a general agreement about the definition of the ultrafine fraction (UFP) has still to be reached, the atmospheric sciences community currently adopts the term for indicating the size fraction of particles under 0.1 µm. UFP particles are mainly constituted by carbonaceous agglomerates and of some of the inorganic components of the fuels. Although main concerns of UFP were originally related to the potential new class of environmental hazards arising from the development of nanotechnologies, with most of the research studies oriented to indoor exposure in the industrial sector, attention has been recently also addressed to their emissions from combustion activities (Biswas and Wu, 2005): however, the large majority of investigations in this field are dedicated to traffic emissions (e.g., diesel vehicles), with rather limited studies for stationary combustion sources.
The research project "ULTRAPART", conducted by Politecnico di Milano at Laboratory for Energy and Environment (LEAP) in Piacenza, in cooperation with

Parma and Brescia Universities, was recently established with the main task of giving a contribution to fill the gap in this latter sector. The paper outlines its main scientific contents, with particular reference to the most relevant aspects of the measurement approach adopted and to the first results obtained on residential heating boilers.

Emission of UFP from stationary combustion sources

Literature data on UFP number concentration levels in flue gas from combustion systems are included, on average, between 10^6 - 10^8 cm^{-3}, except for waste to energy plants and natural gas turbines, with reported values in the range 10^5 - 10^6 cm^{-3} (Gomez-Moreno et al., 2003; VEOLIA, 2007) and 10^3 cm^{-3} (Klippel et al., 2004), respectively. Highest emissions are reported for fuel oil and biomass boilers, whilst natural gas systems present variable emission levels, depending on combustion technology and operating heat load. Bag filters applied in coal fueled power plants are able to achieve concentration reductions of about 3 orders of magnitude in the 0.03-10 µm size range (Yi et al., 2006).

However, currently lacking standard measurement procedures, the comparison between different plants is largely indicative because the emissions are strongly influenced by fuel type, combustion technology, particulate matter removal system, operating conditions and, lastly, by sampling and counting devices adopted. The measurement system is very important, particularly for the number of particles but also for the mass concentration in case of some fuels. The results may differ significantly depending on whether the measurement is performed with conventional hot stack gas methods or by dilution cooling of the gas, simulating thus the effects of atmospheric dilution on particle nucleation and/or condensation effects arising from semivolatile flue gas components. The effects of dilution depend basically on the primary particulate matter concentration and the semivolatile compounds content of the emissions. Dilution can trigger new particle formation by nucleation (homogeneous condensation) of condensable gases in two ways: by cooling the gas, decreasing thus the vapor pressure of the semivolatile species which then tend to condensate, and by decreasing the primary particulate matter concentration in the emissions which otherwise would serve as a surface for heterogeneous condensation process, thus reducing the possibility of nucleation. Nucleation thus increases the particle number concentration while it has almost no observable effect on mass concentration, with the size distribution peaking in the smallest diameters. On the other hand, heterogeneous condensation may increase the mass concentration and shifts the particle diameters towards larger values: the number concentration might thus decrease as the particles with the smaller diameters grow (condensational growth) or coagulate with each others.

2. Methods

Several particulate matter measurement and sampling methods and devices have been developed for responding to the great variety of measurement conditions (ambient, stack, combustion chamber) and measured quantities (mass concentration, number concentration, size distribution). For measurements oriented to the evaluation of mass concentration and chemical characterization, the difficulties with UFP arise from the negligible flue gas content of material, hence the requirement of long sampling times, whilst for size distribution determinations dynamic changes undergone by the particles with nucleation, volatilization, condensation and coagulation processes, strongly influenced by sampling conditions, might lead to rather unstable results. In view of these difficulties and of their inherent uncertainty, the development of standard measurement protocols is a difficult task.

The principal techniques applied for the identification and quantification of UFP in ambient air as well as in flue gas emissions from combustion sources are based on diffusion of light, inertial separation, electric mobility or on the diffusive motion of particles. The very small dimensions of the particles require some modifications of conventional measurement systems such as the condensational growth of particles prior to their detection with optical methods or the utilization of low pressure flows with inertial separators.

The sampling assembly utilized in the ULTRAPART project, developed in cooperation with Stazione Sperimentale per i Combustibili. The line includes a dilution system in series with the particulate matter measurement device. The sample is extracted from the stack, through a nozzle which keeps the flow near isokinetic conditions: the dilution procedure, which follows the EPA CTM-039 (US EPA, 2004), is conducted in a sampling and dilution apparatus composed of PM_{10} and $PM_{2.5}$ cyclones in line with a residence chamber preceded by a mixing zone where the dilution occurs. A controllable dilution ratio (DR) is applied to the flue gas stream. A 142mm filter at the exit of the residence chamber captures the primary particulate matter present in the stack gas and the particulate matter condensed and/or formed during the dilution and cooling of the sampled gas in the chamber. The system is provided with temperature and relative humidity sensors to control the required sampling conditions. In order to prevent condensation of the semivolatiles, cyclones and venturi are maintained at 5°C above the stack gas temperature with a heating system. Real time measurements of number concentrations and size distributions are obtained with an electrical low pressure impactor (ELPI - Dekati Ltd., Finland) connected at the end of the residence chamber prior to the filter. The instrument measures the number concentration and determines the particle size distribution in the size range 0.007-10 µm with 12 channels and a final filter stage. The impactor is equipped also with an external heating system to regulate the instrument's temperature in case of hot stack sampling without dilution. Stack gas dilution is applied for simulating the behavior of the emissions under atmospheric dispersion, dilution and cooling conditions. Although the actual dispersion in the atmosphere will be stronger than the effect created with the dilution ratios applicable with the sampling device, the study might give an insight of the behavior of the particles immediately after stack emission.

Measurements were conducted in a laboratory test bench on a 100 kW wood pellet boiler, equipped with an axial cyclone for particulates removal, and on a 150 kW boiler with no particulate control device, fired with light fuel oil and with natural gas. Boilers were exercised at two different operating conditions: due to the different regulation characteristics, the wood pellet unit was effectively operated at full as well as minimum load values (30% of heat output at full load), whilst for fuel oil experiments the boiler operation at partial load conditions was simulated by simply reducing the air/fuel ratio; for natural gas full load only was tested. Measurements were performed with and without diluting the stack gas. Hot tests without dilution were carried with a heated sampling probe equipped with a $PM_{2.5}$ cyclone, with the ELPI impactor connected in line downstream the cyclone: the impactor was utilized for number concentration measurements whilst total particulate mass was evaluated through a conventional stack hot filter method. Number concentrations and corresponding size distribution were obtained through ELPI readings whereas the mass measurements were performed gravimetrically on the properly conditioned 142mm filter at the end of the diluter or on the conventional hot filter in case of no dilution. For calculation purposes the UFP are considered to be the sum of the last 4 stages of the ELPI impactor, the upper stage having a cut diameter of 0.157 µm and a geometric mean diameter of 0.121 µm.

3. Results and discussion

Preliminary results obtained for the different boilers investigated during dilution sampling measurements are reported in Table 1 and plotted in Figure 1 in terms of the main parameters of interest (number concentrations and size distributions), with typical size distributions illustrated in Figure 2. For all tests average temperatures measured in the dilution chamber at final filter ranged between 24-33 ºC, for dilution ratios (DR) applied included between 15 and 50.

Number concentrations measured for the pellet boiler range between $2{\cdot}10^7$ and $6.7{\cdot}10^7$ cm^{-3}, with an average value of $4{\cdot}10^7$ cm^{-3}. The mode diameter is located around 0.072 µm, with the fraction of UFP accounting on average for nearly 90% of the total concentration given by all ELPI stages. Variation of applied DR, particularly over values higher than 20, is seen to have minor effects on concentrations and size distributions. During boiler operation at minimum heat load, a slight decrease in number concentrations is registered, with the minimum value detected for all the tests ($2{\cdot}10^7$ cm^{-3}) and with a corresponding size distribution shifted towards larger particles (mode diameter 0.204 µm, UFP fraction of 40%). Boiler exercise at non nominal conditions seems thus to generate less UFP, probably for the significant presence of primary coarser particles arising from non optimized combustion conditions and able to act as condensation nuclei. This is at least partially confirmed by the total mass of fine particulate emitted ($PM_{2.5}$ + condensable fraction), showing an increase from nearly 11 mg m^{-3} measured at nominal heat load, without any appreciable effect from varying DR, up to 48 mg m^{-3} at non-nominal operating conditions. Also on a mass basis, the fine fraction constitutes on average 90% of the total particulate matter in both operating conditions. Hot measurement tests (i.e. without dilution) result in number concentrations exceeding the detection limits of the ELPI impactor. UFP emission levels measured from light fuel oil boiler show a rather clear dependence with dilution. Increase in number concentrations from a minimum of nearly $3.3{\cdot}10^6$ cm^{-3} at the higher dilution ratios (DR=30-50) up to $1.1{\cdot}10^8$ cm^{-3} for the lower ratio (DR=15) were observed, with the latter conditions resulting thus in values comparable with wood pellet measurements. Despite this, no measurable variations were detected in particle size distributions, with very similar results in the whole range of dilutions applied and without any apparent shift in the mode diameters, located around 0.021 µm.

At non-nominal operating conditions, achieved by reducing the oxygen content of the exhaust gas from 3% to 1.5%, no significant effect is registered on the number of particles measured regardless the dilution ratio applied, with concentrations fairly stable around an average value of $1.3 \cdot 10^7$ cm^{-3}. On the other hand, the mode diameter is located around 0.072 µm, indicating the emission of coarser particles with respect to the operation at nominal conditions. The fraction of UFP accounts, on average, for more than 99% of the total number concentration during the operation with all dilution ratios at full load, with a slight decrease to 94% for reduced load operation. Mass concentrations detected increase from about 4 mg m^{-3} at full load up to nearly 18 mg m^{-3} at reduced oxygen, still without any significant variation with dilution ratios applied. Hot sampling results in lower number of particles with respect to dilution measurements, with values around $1.3 \cdot 10^6$ cm^{-3} and $6 \cdot 10^6$ cm^{-3} at full and reduced load conditions, respectively: UFP concentration levels appear thus affected by measurable contributions from condensation processes. Results obtained for natural gas fired boiler are included, as expected, in the lower range of values detected for all the experiments. Number concentrations range between $4.3 \cdot 10^3$ and $6.3 \cdot 10^3$ cm^{-3}, with an average value of about $5 \cdot 10^3$ cm^{-3} when operating at a dilution ratio of 15 and with no detectable results at higher dilutions. Resulting concentration levels are almost an order of magnitude lower than background values measured in combustion air, included in the range $2{,}5\text{-}3{,}5 \cdot 10^4$ cm^{-3}. As for diesel oil boiler at full load, the mode diameter is located around 0.021 µm**.** Due to the very low UFP emissions measured with dilution sampling, no hot tests were further conducted.

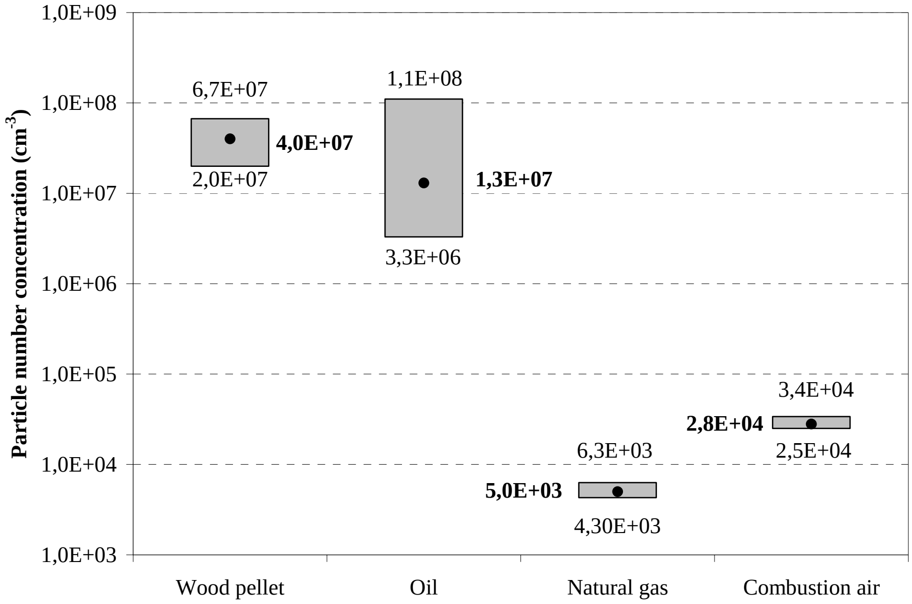

Figure 1 – Measured range and average particle number concentration for considered fuels and combustion air.

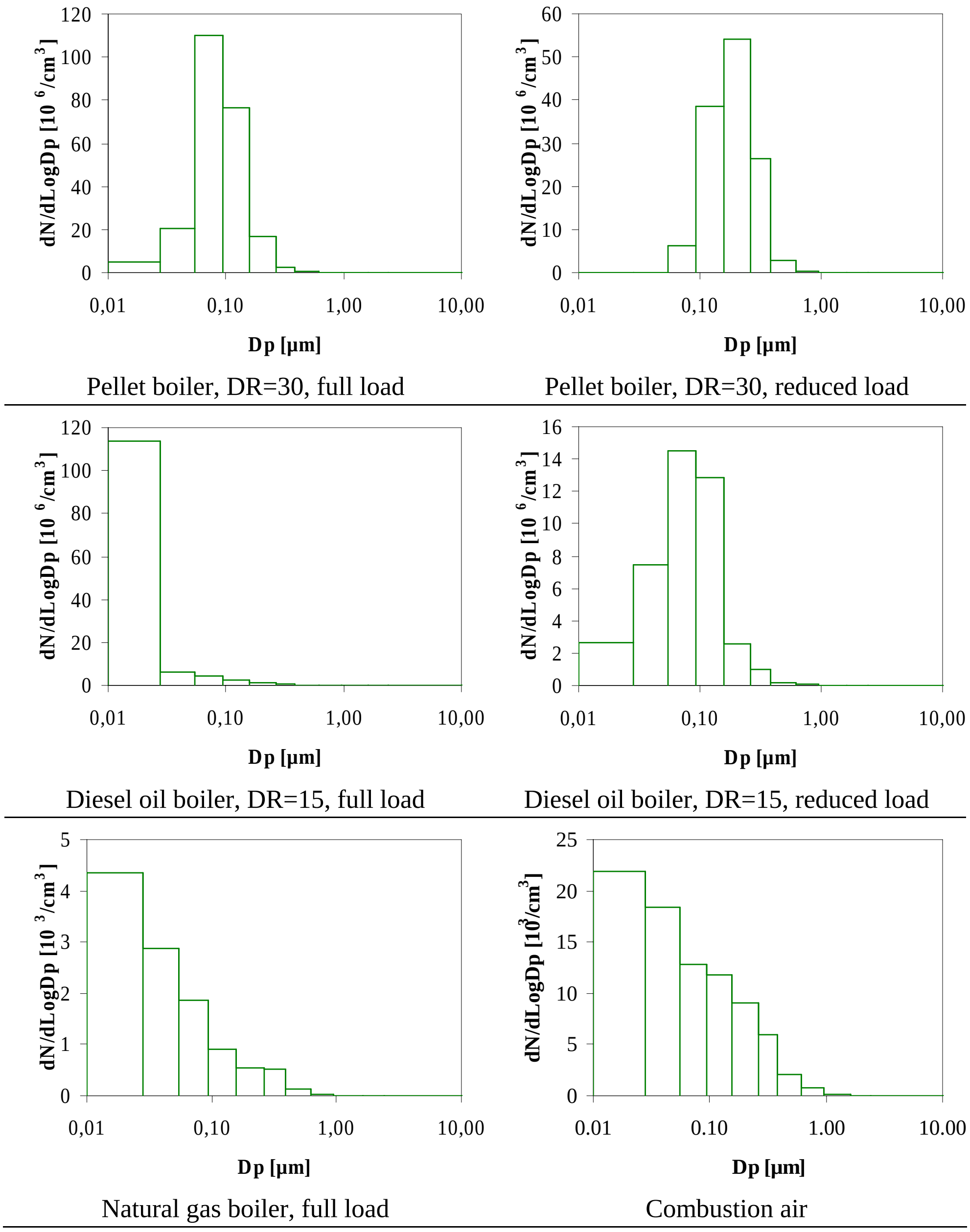

Figure 1 – Measured number size distributions of particles for wood pellet, Diesel fuel oil and natural gas fired boilers and for combustion air.

Table 1 - UFP emissions concentration measured during experimental tests.

Boiler type	**Concentration (cm^{-3})**	**Fraction < 0.1 μm (%)**	**Mode diameter (μm)**
Wood pellet	$2 \cdot 10^7$-$6.7 \cdot 10^7$	92 (nominal load) 40 (reduced load)	0.072 (nominal load) 0.204 (reduced load)
Light fuel oil	$3.3 \cdot 10^6$-$1.1 \cdot 10^8$	>99 (nominal load) 94 (non nominal load)	0.021 (nominal load) 0.072 (non nominal load)
Natural gas	$4.3 \cdot 10^3$-$6.3 \cdot 10^3$	89	0.021
Combustion air	$2.5 \cdot 10^4$-$3.4 \cdot 10^4$	78	0.021

Conclusions

UFP emissions for residential heating boilers were measured with a sampling device setup for evaluating primary and condensable fractions. Number concentrations and size distributions detected result mainly dependent, as expected, with the type of fuel burned. Natural gas results in the lowest generation of ultrafine fractions, with values comparable or even lower to background air contents and non detectable number concentration levels for increasing dilution ratios over the minimum value. Wood pellet boiler generates the highest values, with minor changes detected from variations in the dilution ratios applied during sampling, probably arising from the significant flue gas content of primary particles and the absence of favorable conditions for enhanced nucleation or condensational growth with increasing dilution ratios. On the other hand, dilution appears to have some influence for light fuel oil boiler where, due to the lower primary particles concentrations, a slight increase in UFP concentrations is observed for the minimum dilutions applied. Both for wood pellet and diesel oil boilers, operation at reduced heat load result in measurable variations in UFP emissions, with lower number concentrations and coarser size distributions that, together with increasing total mass concentrations, indicate poorer combustion performance with respect to nominal conditions.

The sampling device setup developed within ULTRAPART research project demonstrated good flexibility and measuring capabilities during the whole ensemble of test runs performed for all the range of dilution ratios applicable. Further planned campaigns will be dedicated to the characterization of UFP emissions from full scale stationary sources, particularly waste to energy plants.

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