

# **Ultrafine particle emission from combustion devices burning natural gas**

Patrizia Minutolo<sup>1</sup>, LeeAnn Sgro<sup>2</sup>, Maria Antonietta Costagliola<sup>3</sup>, Maria Vittoria Prati<sup>3</sup>,  
Mariano Sirignano<sup>2</sup>, Andrea D'Anna<sup>2</sup>

<sup>1</sup>Istituto di Ricerche sulla Combustione, CNR, P.le Tecchio 80, 80125, Napoli, Italy

<sup>2</sup>Department of Chemical Engineering, University of Naples Federico II, P.le Tecchio  
80, 80125, Naples, Italy

<sup>3</sup>Istituto Motori, CNR, V.le Marconi, 1, 80125, Naples, Italy

New challenge in combustion is the extended use of “clean” fuels, such as methane, in “particle free” combustion devices. Although large efforts have been made, actual combustion systems burning methane are still source of particulate that might be emitted in the atmosphere. In this paper measurements of ultrafine particle emission from premixed laboratory flames and several practical combustion systems including domestic heaters and I.C. engines, all burning methane or natural gas are presented.

A new diagnostic tool based on particle sampling and mobility size measurements has been used in order to evaluate total particulate concentrations and size distribution functions. The measuring apparatus, in the utilized configuration, allows detecting particle down to 2nm. An electrical low pressure impactor, much more sensible for particles larger than 20 nm, is instead used for the measurement of the larger particles.

For all devices examined, experiments have shown that methane and natural gas combustion, even when it is conducted in overall lean premixed conditions, can produce particles with a mean size of 2-3nm and a very high number concentration, clearly higher than the ambient air background.

## **1. Introduction**

It is increasingly recognized that ultrafine particles (UFP), those with sizes down to few nanometers, may cause or exacerbate human health problems (Bräuner et al., 2007, 2008; Oberdörster, Oberdörster, and Oberdörster, 2005; Stölzel et al., 2007) and may contribute to photochemical smog (Seinfeld and Pandis, 2006). Combustion systems are indicated to be the main sources of UFP, particularly motor vehicle exhaust. However, due to instrument limitations, previous studies of sources of UFP have measured particles >10 nm in diameter, although the smallest fraction of the particle size distribution plays a particularly important role in health and environment. These particles indeed dominate size distributions in terms of number concentration and have unique chemical composition and morphology since they maintain molecular

characteristics in terms of chemical reactivity, but at the same time exhibit transport and surface related phenomena typical of particles (D'Anna, 2009)

New diagnostics for particles, which allow analysis on a molecular level, have been developed in the last years, or borrowed from molecule-based natural sciences. Their use has improved our knowledge about the physical and chemical properties of combustion-formed nanoparticles and also about the kinetics of particle formation in combustion. These new technologies have made it possible to extend the range of UFP measurements down to about 2 nm (Chen et al., 1998), revealing the presence of particles in combustion technologies, such as blue flames of natural gas (Minutolo et al., 2008, Wallace et al., 2008), which have been considered up to now particle-free. These combustion systems are widely used and they represent the most diffused indoor combustion technologies thus contributing to most of the UFP we are exposed (Wallace et al., 2009). Therefore this work is focused on UFP in the range of 2 nm to 100 nm produced by blue flames of methane and natural gas in some commonly used combustion systems. The objective is to characterize the emission rates and number concentrations of UFP produced by these sources. First of all, an analysis of laboratory premixed flames of methane has been performed changing the fuel/air fed conditions in order to find the threshold of equivalence ratio for particle formation. Thereafter a typical domestic stove-top and a boiler, which are the main sources of indoor particles, has been analyzed. Finally the combustion of natural gas in a motor vehicle has been investigated.

## **2. Experimental**

Experiments were carried out burning both high purity level methane (IP 3.5) and natural gas from domestic pipeline. The gross analysis of the latter is: 84% methane, 8% ethane, 2% propane, 5% nitrogen and lower concentrations of larger hydrocarbons.

Laminar premixed flames of methane were stabilized on a water cooled porous bronze burner (60 mm o.d.). Experiments were performed at different equivalence ratios from the stoichiometric value up to the first visible flame emission, keeping constant the cold gas flow velocity at 4.74cm/s.

Experiments on a cook top burner were performed with a CF Parker 5327M burner fuelled with methane. The burner is representative of domestic cooking appliances mainly used in the early '90s but still largely employed today by the lower class population living in urban areas and it is the most diffused in rural regions. The combustion was partially premixed. The methane flow rate was varied in the flow range 2.25 - 9 L/min; the resulting flames were generally blue colored and the changes in the fuel flow rate simply produced a slight change in the flame shape and some strikes of fair yellow luminosity. A stainless steel cylinder was placed above the burner to reduce flame perturbation. A small hole was drilled into the wall of the cylinder to allow particle sampling. The presence of the cylinder favored a higher stability of the flame, and, as a consequence, a higher repeatability in the measurements.

The home heating burner consisted of a knitted metal fiber head which is normally housed in a commercial boiler for water heating. The combustion head is manufactured into a unique "sock," that allows its application around the support without any welded seams. Air-gas mixing takes place within the aspiration circuit from the air intake. From

the gas train the fuel flows inside the aspiration air vent and through a special mixer. Mixing begins and finally ends within the burner spiral. Natural gas from the domestic pipeline was used. The burner was tested in free atmosphere. Some measurements were also performed with the burner mounted inside the boiler.

A Fiat Punto 60 Natural Power 1242cc 38kW vehicle was tested over driving cycles executed on chassis-dynamometer. Constant speed tests (30, 70 and 120 km/h) were performed. The vehicle was approved according to Euro 4 legislative standard. It was equipped with a bi-fuel gasoline/natural gas (CNG) engine.

Two different instruments were employed to determine particle size distributions: an Electrical Mobility Spectrometer (EMS – Model Tapcon 3/150) with high sensitivity in the 1-100nm range and an electrostatic classifier, a nano- Differential Mobility Analyzer (nano-DMA) and a alcohol-based condensation particle counter (Model 3936, TSI) with sensitivity in the 3-100nm range. These diagnostic techniques are both based on the measure of the differential mobility of charged particles. An Electrical Low Pressure Impactor (ELPI) was also used to extend the range of the number distribution function up to 10micron. The ELPI was positioned downstream of a double-stage partial sampling system (Dekati FPS) which worked with a sampling flow rate of 6 liter/min, a dilution factor of about 17 and 150°C as primary dilution temperature.

The combustion-generated aerosol formed in laboratory flames was diluted and transported to the analysis system via sampling devices which were designed to minimize effects on the sampled aerosol to avoid sampling artifacts. For the measurements performed in practical combustion systems, where the number concentration of particle is much lower than the flame, ejectors with variable dilution ratios were used. The dilution ratio was fixed at 10,000 for the laboratory flames, 3.55 for the cook top-burner and the boiler and 17 for the engine measurements. These values were chosen to avoid particle nucleation in the probe and in the sampling line.

### 3. Results and discussion

Rich premixed flames of methane with varying quantities of fed fuel were investigated. Figure 1 reports the particle size distribution (PSD) functions measured at 10mm above the burner, i.e. far downstream of the main oxidation region of the flame, in a zone characterized by an almost constant concentration of both oxidation and pyrolysis products. PSD functions were measured for equivalence ratios ranging from 1.72 to 2.00, i.e. in fuel rich conditions below the appearance of a yellow luminosity.

The PSD functions cover a wide range of sizes between 1 and 100nm. In the less rich flame, the PSD function is unimodal with a mean size of about 2.5nm and a maximum number concentration of  $1E11$  particle/cm<sup>3</sup>. As the equivalence ratio is increased the number of particles also increases and shifts toward larger size particles. At an equivalence ratio of 1.88 a shoulder in the larger size region is evident which develops in a bimodal PSD function, with a first peak at 3.5nm and a second at around 15nm, at  $\Phi=2.00$ . For  $\Phi < 2.00$ , the flames appear blue colored and a fair yellow luminosity is observed for the  $\Phi=2.00$  flame. The total number concentration of particles has been evaluated from the measured PSD functions and it is reported in Fig.2 as a function of the equivalence ratio. In the same figure the contributions of the first and the second mode particles are also reported. Particle number concentration increases by an order of

magnitude moving from  $\Phi=1.72$  to  $\Phi=1.88$  and the totality of the particles produced were  $<10$  nm. By contrast, about 25% of the particles produced at  $\Phi=2.00$  (i.e. when the flame shows a fair yellow luminosity) were  $>10$  nm (Figure 2).

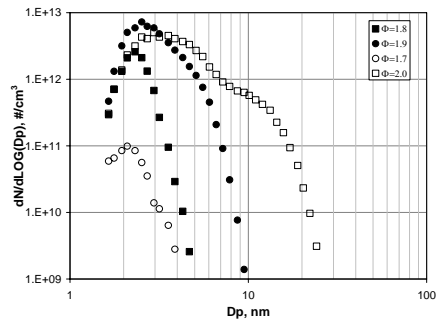


Figure 1 Size distribution functions of ultrafine particle generated by the methane flames with equivalence ratios ranging from 1.72 to 2.00.

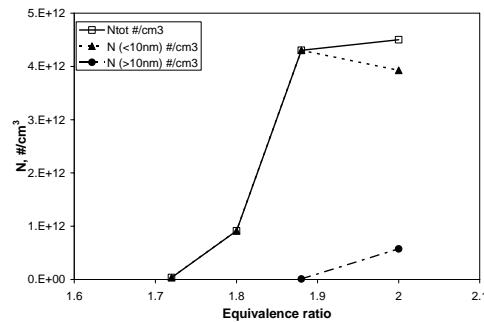


Figure 2 Number concentrations of total particles, the first and second mode of the PSD functions as a function of the equivalence ratio.

It is worth to note that premixed blue flames of methane produce UFP in a relatively low mass concentration of the order of 10-50ppb but in a huge number concentration. The formation of these particles is due to condensation reactions of aromatic compounds formed as soon as the oxygen availability for hydrocarbon oxidation is reduced (D'Anna, 2009). It means that if the molecular mixing is not perfect and local rich conditions are reached, UFP can be formed also in practical combustion systems characterized by blue flame luminosity.

To explore the possibility that commercial combustion devices burning methane or natural gas with blue flames can emit UFP, we have measured PSD functions near a cook-top and a boiler burner. Figures 3 and 4 report the measured PSD functions.

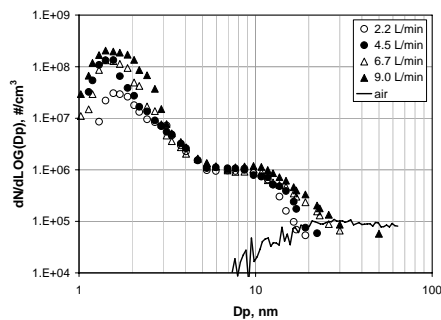


Figure 3 Size distribution functions of ultrafine particle generated by a cook-top burner with different amount of fed methane. Line is air contribution to UFP.

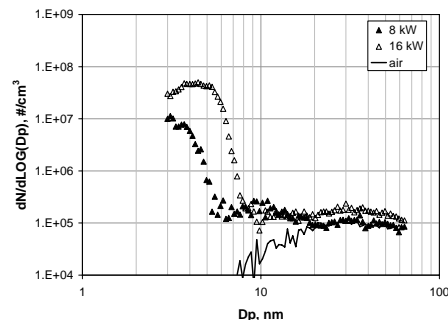


Figure 4 Size distribution functions of ultrafine particle generated by a boiler burning natural gas at 8 and 16kW. Line is air contribution to UFP.

The cook-top was fuelled with increasing amounts of methane from 2.2 to 9.0 L/min. In all the examined conditions a bimodal PSD function was measured. The first mode is located at about 1.5-2nm whereas the second one is at around 10-15nm. The number concentrations of the two particle modes increase at increasing fuel flow rate with the formation of larger particles up to 50nm in the higher fuel rate condition. It is important

to underline that the number concentration of the larger particles is of the same order of magnitude of ambient air particles also reported in the figures. Particles present in the combustion air reach concentrations of the order of  $1E5 \text{ \#/cm}^3$  in the 10-100nm range and are practically negligible for sizes  $<10\text{nm}$ . The cook-top burner showed a blue luminosity in all the examined conditions except some strikes of yellow luminosity more abundant at higher fuel flow rates. Partially premixing probably causes local rich mixture which promotes UFP formation.

PSD functions measured in the boiler burners have been obtained with a DMA which measuring range was limited down to 3nm. The PSD functions have been measured at two loads, namely 8 and 16kW burning natural gas in overall fuel-lean conditions (10% excess air). The PSD functions show a bimodal behavior, however the large size particle mode is due to the contribution of combustion air particles. The nanometer-size mode is located at about 3-4nm depending on the boiler power. The number concentration of the first mode particles is again very large of the order of  $1E8 \text{ \#/cm}^3$  showing that although the combustion process occurs in overall fuel-lean conditions there are some regions where the mixing at molecular level is not sufficient to overcome particle formation. The overall mass emissions of UFP in the two systems is however very low of the order of 1ppb.

Last set of measurements were performed at the exhaust of a vehicle powered with natural gas. Figure 5 reports the PSD functions measured at steady state at 30 and 120km/h. PSD functions obtained by DMA are compared with those obtained by ELPI but in a wider range of dimensions.

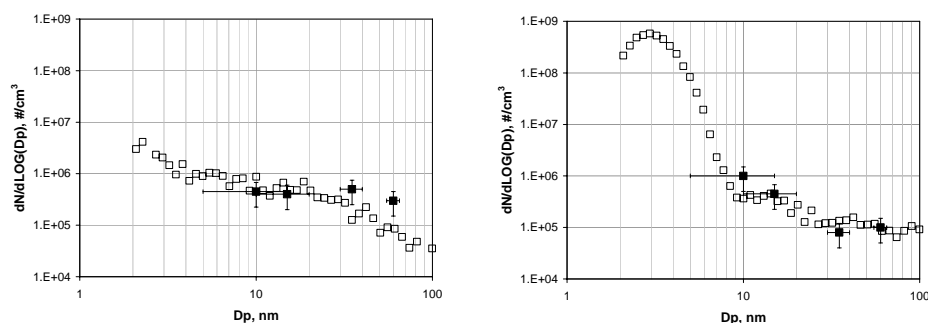


Figure 5 Size distribution functions of ultrafine particle generated by a motor vehicle at steady-state conditions: left side 30 km/h; right side 120 km/h

It is interesting to notice that also at the exhausts of a vehicle engine powered by methane a bimodal size distribution is observed. The first nanometric mode is strongly increased at high engine speed indicating that in this condition a less efficient mixing process occurs inside the cylinder causing the formation of UFP. As for the other practical combustion systems, the emission of  $>10 \text{ nm}$  particles is partially due particles already present in the combustion air or might be due to the occurrence of much richer fuel conditions.

A preliminary characterization of the UFP collected from the cook-top burner and the domestic heater (Minutolo et al., 2008) have shown that these particles are clusters of high-molecular-mass aromatic compounds, both pericondensed and incompletely

condensed structures formed at local slightly fuel-rich conditions and not oxidized in the post-oxidation zones of the systems.

#### 4. Conclusion

Ultrafine particle emission from premixed laboratory flames and several practical combustion systems including domestic heaters and I.C. engines, all burning methane or natural gas have been measured. A new diagnostic tool based on particle sampling and mobility particle size measurements have been used. The measuring apparatus, in the utilized configuration, allows detecting particle down to 2nm.

For all devices examined, experiments has shown that methane and natural gas combustion, even when it is conducted in overall lean premixed conditions, can produce particles with a mean size of 2-3nm and a very high number concentrations, clearly higher than the ambient air background. These particles are clusters of high-molecular-mass aromatic compounds, both pericondensed and incompletely condensed structures formed at local slightly fuel-rich conditions and not oxidized in the post-oxidation zones of the systems.

#### References

- Bräuner, E.V., Forchhammer, L., Møller, P., Barregard, L., Gunnarsen, L., Afshari, A., Wählin, P., Glasius, M., Dragsted, L. O., Basu, S., Raaschou-Nielsen, O., Loft, S., Exposure to ultrafine particles from ambient air and oxidative stress-induced DNA damage. *Environ. Health Perspect.* 2007, 115, 1177-1182.
- Bräuner, E.V., Forchhammer, L., Møller, P., Simonsen, J., Glasius, M., Wählin, P., Raaschou-Nielsen, O., Loft, S., Indoor particles affect vascular function in the aged: An air filtration-based intervention study. *Am. J. Resp. Crit. Care Med.* 2007, 177, 419-25.
- Chen, D., Pui, D.Y.H., Hummes, D., Fissan, H., Quant, F.R., Sem, G.J., Design and evaluation of a nanometer aerosol differential mobility analyzer (nano-DMA). *J. Aerosol Sci.* 1998, 29, 497-509
- D'Anna, A., Combustion-formed Nanoparticles. *Proc. Combust. Inst.* 2009, 32:593-613
- Minutolo, P., D'Anna, A., Commodo, M., Pagliara, R., Toniato, G., Accordini, C., Emission of fine particles from natural gas domestic burners. *Environmental Engineering Science* 2008, 25(10), 1357-1363
- Oberdorster, G., Oberdorster, E. and Oberdorster, J., Nanotoxicology: An emerging discipline evolving from studies of Ultrafine particles. *J. Environ. Health Perspectives* 2005, 113, 823-839.
- Seinfeld, J.H., Pandis, S.N., *Atmospheric Chemistry and Physics - From Air Pollution to Climate Change.* John Wiley & Sons, New York, 2006
- Stölzel, M., Breitner, S., Cyrus, J., Pitz, M., Wölke, G., Kreyling, W., Heinrich, J., Wichmann, H.-E., Peters, A., Daily mortality and particulate matter in different size classes in Erfurt, Germany. *J. Exposure Sci. Environ. Epidemiol.* 2007, 17, 458-467.
- Wallace, L., Wang, F., Howard-Reed, C., Persily, A., Contribution of Gas and Electric Stoves to Residential Ultrafine Particle Concentrations between 2 and 64 nm: Size Distributions and Emission and Coagulation Rates. *Environ. Sci. Technol.*, 2008, 42 (23), 8641-8647.