EXPERIMENTAL DETERMINATION OF COAGULATION EFFICIENCY OF COMBUSTION GENERATED NANOPARTICLES

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Abstract
Coagulation is a key issue for the determination of the size distribution function of the combustion-generated particles. D'Alessio and coworkers studied the coagulation process in high temperature environment, finding a very low efficiency for particle as small as 2nm. These studies evidenced that as the diameter increase and particles become as large as 7-10nm the coagulation coefficient becomes almost unitary. However temperature dependence has been not extensively investigated. In this work the temperature effect on coagulation efficiency for combustion-generated nanoparticles is investigated.
In order to systematically study this phenomenon, ad hoc experimental equipment has been set up. A rich premixed ethylene/air flame has been used to produce a determined particle size distribution function. This particle size distribution function (PSDF) has been analyzed by using a differential mobility analyzer (DMA). A horizontal probe is positioned at fixed height above the burner. Sampling of the material from the flame occurs through a small pinhole present on the probe and it is opportunely regulated by tuning the sucking pressure. After sampling, material is immediately diluted with nitrogen at room temperature and sent to the DMA. The flow conditions allow to have dilution ratios of the order of 10^4. This strong dilution prevents further undesired reactions in the probe. A short sampling time is used in order to avoid further coagulation within the sampling line. The residence time is generally of the order of 0.1s.
In order to study the coagulation in controlled environment, in this study the sampling line has been made longer enough to achieve a residence time as large as 1.5s. Moreover, to evidence the effect of temperature the nitrogen has been sent to the system from room temperature, i.e. 300K, up to 700K. After that, temperature has been kept constant along all the sampling line through ceramic resistance. PSDF measured in absence of coagulation in sampling line shows a unimodal distribution peaked at 2nm with a shoulder around 4nm. For long residence times in the sampling line time at room temperature, particles coagulate and the peak is shifted around 10nm. Increasing the temperature of the nitrogen flow, particles exhibit smaller coagulation efficiency. PSDF measured at higher temperature progressively approach the original one. This suggests a strong effect of

temperature on coagulation efficiency also at temperature significant lower than those found in flame conditions.

Introduction

Particles emitted from real combustion systems can be strongly different from those produced close to the flame front or within combustion chamber. This is due to secondary transformations that can occur both in the atmosphere and in the late time of combustion process. In these zones, temperature conditions are usually considerably lower than in combustion chamber and large part of the chemical reactions which act on particles are slowed down. On the other hand, physical interactions between compounds are enhanced.

Coagulation phenomenon is an important phenomenon since fundamental changes can be induce in particle size distribution. Coagulation efficiency has been evaluated for small nanoparticle and for larger soot aggregates at flame temperatures [1]. Experiments have shown that nanoparticles as small as 2nm exhibit a very low coagulation efficiency for temperature as high as 1500K. On the other hand, as particle size increases, coagulation efficiency reaches the unity also at this high temperatures. This phenomenon controls particle size distribution in flames and it is mainly responsible for the long lifetimes of small nanoparticles. Particle coagulation efficiency has been also numerically evaluated. D'Alessio and coworkers [2] studied this phenomenon on the basis of physical interaction between particles driven by van der Waal interactions. Modelling this effect has been related to the ratio between interaction forces and thermal rebounds, linked to the kinetic energy of the particles. This means that as temperature decreases particle coagulation becomes more effective also for small nanoparticles. However, a systematic study of nanoparticles in low and medium temperature regime has been not conducted, although these temperature regimes result more similar to real combustion system conditions. This study has the aim to fill this gap. Particles produced from a premixed ethylene/air flame, previously investigated, have been fed to a plug flow reactor with controlled temperature. Temperature regimes from ambient up to 700K have been investigated.

Experimental set up

In order to systematic study the coagulation of small nanoparticles produced in combustion an ad hoc experimental equipment has been set up.

Particles of a fixed size distribution function are produced by using an atmospheric pressure laminar premixed ethylene/ethanol-air flame. The equivalence ratio is keeping constant, Φ=2.01, along with the mass flow rates, such that the velocity of the cold gases at room conditions is fixed at 10 cm/s. The flame is stabilized on a porous bronze McKenna burner by a stainless steel plate (located at 30 mm above the burner surface). Burner temperature is also controlled by recirculation of cooling water with a flow rate of 1l/min. High purity air and ethylene (>99.96%) are supplied by using Brooks mass flow controllers. Premixed gases are sent at room temperature.

Particles are sampled with a stainless steel probe place horizontally above the burner at a fixed height above the burner (HAB) of 10mm.
To get the particle size distribution present in flame, a sampling similar to those used before is set up. In this set up, the probe (ID = 8 mm), wall thickness of 0.5 mm, has a pinhole diameter of 0.3 mm, which is the same one used by Sgro et al. [3] in a previous study. The sampling gas enters the probe through the orifice and it is immediately diluted by a nitrogen flow before being measured on line with a differential mobility analyzer (DMA). In the operating conditions, the sampling system allows to have a dilution ratio on the order of 10^4. The probe is 80cm long, cooled down with recirculating water. The residence time in these conditions is of the order of 0.1s. For the size distribution measurements a nano-DMA (Vienna Type Model 3085) was used, in which particles are separated according to their electrical mobility. The classified particles are counted by an Electrometer Faraday Cup. The particles size distribution function obtained by DMA is successively corrected for losses in the pinhole and in the probe following the procedure of Gormeley and Kennedy [4], and Alonso et al. [5]. Once the particle size distribution is analyzed, a different probe line has been set up. Coagulation phenomenon is enhanced by using a longer probe, 13m, used to increase the residence time and let the coagulation significantly modify particle size distribution. However, in this conditions the diffusion losses become more effective and thus the correction become more important. Similarly, the pinhole has been enlarged to 0.8mm in order to get more material, increasing the concentration within the probe, again making the coagulation more effective. At room temperature the dilution has been evaluated to be of the order of 1,000, which is one order of magnitude lower than that used for evaluating the unperturbed PSD.

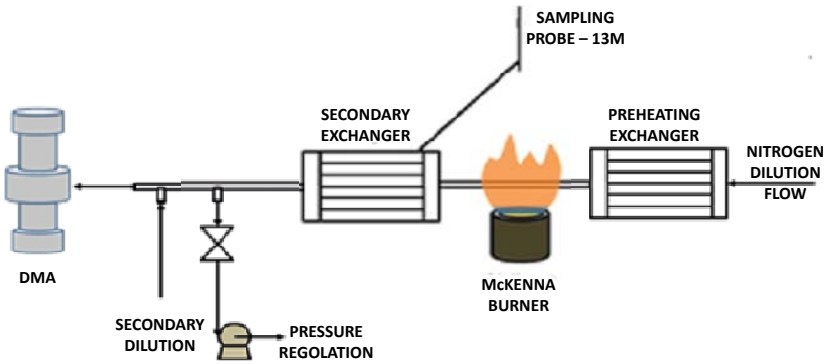

Figure 1. Sketch of experimental set up used for studying the effect of temperature on coagulation efficiency

Nitrogen dilution flow is sent in the probe at different temperatures, preheating it from ambient up to 700K. After sampling, the 13m-long probe and the nitrogen

flow therein are kept at same temperature of preheating set up by using ceramic shell resistances. Finally, a secondary dilution before entering the DMA is operated in order to immediately reduce the concentration within the limit of the detection and cool down the temperature avoiding damages to the instrument. Fig.1 reports a sketch of the experimental set up used in the present study.
Changing the temperature of the nitrogen flow can affect the dilution ratio. If a constant mass flow rate is used, the thermal expansion changes the volumetric flow rate in dependence of preheating temperature. Instead, in this work the mass flow rate of dilution flow has been changed in order of maintain a constant volumetric flow rate. It changes the molar dilution ratio in the probe but allows to isolate the effect of temperature on coagulation kinetic constant. Moreover, it allows to have the same residence time in all investigated conditions.
Details on calculation used to set the parameters are reported in formulas below:

$$Mass_{N2}^{T} = Mass_{N2}^{300}\ \frac{300}{T} \tag{1}$$

$$y_P = \frac{S}{Mass_{N2}^{300}}\ \frac{T}{300} \tag{2}$$

$$R_{COAG} = K_{COAG}(T)\ {y_P}^2 \frac{P^2}{(RT)^2} = K_{COAG}(T)\ \left(\frac{S}{Mass_{N2}^{300}}\ \frac{T}{300}\right)^2 \frac{P^2}{(RT)^2} = K_{COAG}(T)\ \left(\frac{S}{Mass_{N2}^{300}}\ \frac{P}{300\,R}\right)^2 \tag{3}$$

where $Mass_{N2}$ is the mass flow rate of nitrogen at reference (300K and set temperature), S is the mass flow rate of sampling trough the pinhole - assumed constant, y_P is the molar fraction of particles, $K_{COAG}(T)$ is the kinetic constant of coagulation which is temperature dependent. It is possible to note that particles coagulation rate shows temperature dependence only within the kinetic constant, which is the focus of this study.

Results and discussion

Results for different set up temperature of the nitrogen flow are reported in Fig.2. Results have been reported making a correction which takes into account only the secondary dilution and the diffusion losses along the probe. The primary dilution, which is constant in all the examined conditions, is not taken into account to avoid further manipulation of the data.
Figure 2 shows that the unperturbed particle size distribution, blue dots in the figure, presents a quasi-unimodal distribution with a peak at 2nm and a shoulder around 4nm; moreover, particles have all sizes smaller than 10nm. This is in agreement with experimental data obtained on similar flames.

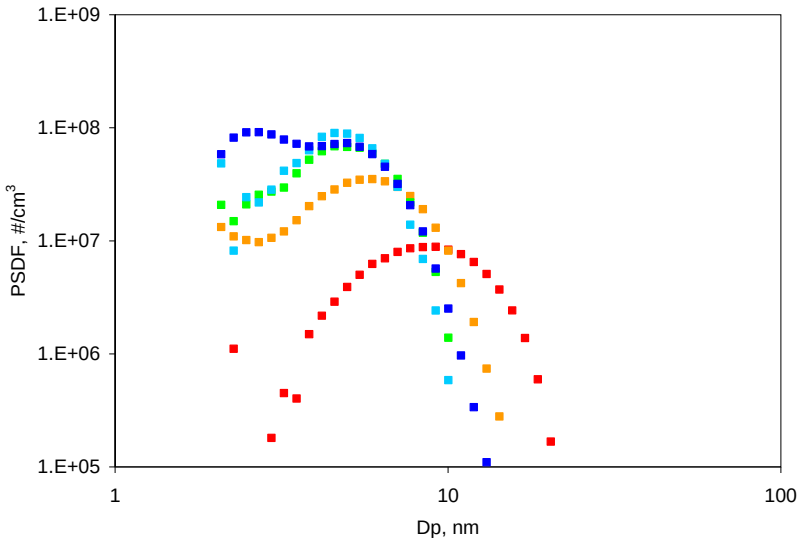

Figure 2. Evolution of particle size distribution at different temperatures (red dots – 300K; orange dots – 500K; green dots – 600K; light blue dots- 700K) for a residence time of 1.5s. Unperturbed PSD is also reported (blue dots).

Particle size distributions measured when the long probe is used exhibit a peak remarkably shifted toward large diameter evidencing that particle coagulation is quite effective. Particles coagulated at room temperature, 300K, red dots in the figure, are peaked around 10nm and particle as small as 2nm are almost absent. In the same figure, particle size distributions evaluated for higher temperature are also reported. For a temperature within the probe line of 500K, orange dots in the figure, a significant less coagulation rate can be evaluated and particle size distribution is peaked at size around 7nm. However, a change with respect to the unperturbed size distribution is still evident. Looking at PSD evolved in higher temperature environment the situation is somewhat different. In fact the evolution of PSD and the change with respect to the unperturbed situation is less evident. For a temperature in the probe of 600Kand 700K, green and light blue dots respectively in the figure, particle size distribution are peaked around 4nm and particle with smaller diameter are present although in lower numerical concentration. However, giving a general evaluation of particle size distribution it seems that coagulation became less effective, i.e. particles are not able to form larger primary particle or aggregates with sizes larger than 10nm. However, the relative decrease of the particle as small as 2nm can have different explanations. The first one relies in a wrong correction to the measured particle size distribution for taking into account diffusion losses. This correction is size dependent; for this long residence time the losses of 2nm particles can be as high as 90% of the sampled ones. This high correction factor can easily induce an underestimation of the small nanoparticle

concentration. Another possible explanation is related to the secondary dilution. Since this dilution is necessary to reduce the number of large particles it also reduces the signal of 2nm particles close to the bottom detection limit of the instrument, enlarging the uncertainty of the measure. Finally a change in particle arrangement that leads to a different coagulation efficiency should not be neglected. Such change can affect the final concentration of very small particles.

Conclusions

A systematic study of the temperature effect on size distribution of particles produced in combustion has been conducted. In particular, coagulation phenomenon has been evaluated at different temperatures. An ad hoc experimental set up which allows to study the evolution of particle size distribution has been set up.

A premixed flame of ethylene/air has been used to produce a unimodal size distribution peaked at 2nm, fed to a plug flow reactor, which can be operated at different temperatures up to 700K. Particles exhibit different coagulation efficiency for different operating temperature. In particular at room temperature particles coagulate forming particle as large as 10-20nm, whereas for 700K particles size distribution seems to not change with respect to the unperturbed on previously measured.

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