MODELING EVALUATION OF THE EFFECT OF SAMPLING PROBE ON PARTICLE SIZE DISTRIBUTION FUNCTIONS IN PREMIXED FLAME

M. Sirignano and A. D'Anna

Università Federico II di Napoli – Piazzale Tecchio 80, 80125 Napoli - Italy

Abstract

Different sampling systems have been proposed to collect particulates from flame reactors. All of these sampling systems induce perturbations mostly on the temperature and the velocity field inside the flame. Generally to avoid artifact due to velocity field perturbation the sampling system is set up to obtain isokinetic probing. On the other hand, the higher is the difference between the combustion temperature and the probe, the higher is the perturbation. Since the cooling down of the sampling system is necessary to quench the reactivity of the collected samples, it is not possible to completely avoid temperature perturbation on the flame. A change of the temperature for effect of the probe might influence the reactivity of the system and the chemical and morphological properties of the collected particles.

In the present work a detailed kinetic model for particle formation in flame is used to predict the effect of temperature perturbation induced by the sampling probe on the chemical characteristics and morphology of the particles formed in a premixed rich ethylene flame. Model accounts both for chemical reactions with gas phase, particle-to-particle interactions and condensation of gas phase PAHs on particles.

Temperature profiles of pristine and perturbed flames have been taken from literature. Moreover a sensitivity analysis to temperature decrease due to the presence of the probe has been performed to take into account the uncertainty of measurements. Model evidences that the cooling down of the flame locally enhances coagulation process leading to formation of particles with larger sizes and more hydrogenated structures.

Introduction

The impact of particles emitted from combustion systems strongly depends on their physical and chemical characteristics. Recent studies have demonstrated that health effect of combustion-generated particles is strictly linked with their chemical composition and morphological features [1,2]. Moreover, to better understand the role of precursors and the pathways of particle formation, large efforts have been spent to fill the gap between gas phase by-products and large aggregates. These nanoparticles have been individuated as the intermediate stage of particle formation; however in some conditions they can be emitted and contribute to the total emission of the combustion systems [3-5].

New techniques have been developed to characterize these compounds not only in terms of total amount but also of chemical composition and size distribution. These can be generally divided into in-situ and ex-situ techniques. Although the in-situ techniques allow to minimize the perturbation of the system and give more reliable results, they do not give a definitive representation of particle formation and features. In particular, with optical techniques it is possible to obtain some information on chemical characteristics and total amount of species produced in combustion but fewer details are given about size and morphology of particles [6-9]. In order to completely characterize these particles and obtain insights on their formation pathway, size distribution functions (PSDF) are a fundamental issue to cover with experimental and modelling investigation. To obtain this information mobility analyser are

the most used and reliable instruments. These instruments work on the effective mobility of nanoparticles in an imposed force field, e.g. an electrical field [10-13]. The accuracy of these tools allows to detect particles as small as 1nm with high reliability. A great effort has been made in avoiding artefacts in the sampling and measuring system. However, the impact that the insertion of a sampling probe inside the combustion system has not been analysed in detail. From this point of view it appears of great relevance the understanding of the properties of particles formed in perturbed systems and how the collected material can be correlated with the particles really formed in the flame without probe insertion.

To conduct this analysis a detailed kinetic model has been implemented to model the induced perturbation of the probe into combustion. Model results are compared with literature data for size distribution functions of the particles. Finally a quantification of the error linked to flame perturbation is given and guide lines for further experiments are presented.

Model description

A sectional method is used for the modelling of aromatic growth and particle inception. It is based on a previously developed kinetic mechanism of particle formation with a double discretization of the particle phase in terms of C and H atom number [14]. The present model also distinguishes between different particle structures based on their state of aggregation, i.e. high molecular mass aromatic molecules, clusters of molecules and aggregates of cluster of molecules (here defined particles) and agglomerates of particles [15-16]. This allows to follow not only the mass of the formed particles, but also their hydrogen content and internal structure.

The model is fully coupled with the main pyrolysis and oxidation of the fuel. It is based on the recent experimental evidences on the mechanism of particle nucleation and the internal structure of the particles in high temperature environments [17].

Briefly, H/C ratio allows to follow different class of aromatic compounds: pericondensed aromatic hydrocarbons, generally having a H/C ration below 0.5 and oligomers of polycyclic aromatic hydrocarbons. Both of these can chemically growth through addition of acetylene or other PAHs. Moreover a polymerization process is also considered and leads to formation on internal cross-linked structure. Dehydrogenation is taken into account for modeling the evolution of structures toward more graphitized ones. All these compounds belong to "molecules" compounds in terms of aggregation state since they have undergone only chemical growth. If a physical stacking or coalescent coagulation occurs a dimer is formed and a new state of aggregation is considered. These compounds are here called "clusters" and can range from a small dimer to a single primary soot particle with sizes of tens of nanometer. Also these compounds can growth through chemical addition in similar way to molecules. Whenever particles coagulate forming chain like structure and keeping their identity, a new state of aggregation is considered and "aggregates" are formed. Also these compounds can undergo chemical growth and other processes similarly to the others. All the sectional species can undergo oxidation. OH radical and molecular oxygen are considered to be the main oxidizing species and kinetic rate are evaluated on the base of experimental data for soot oxidation. This simple sketch of classes of compounds considered is more widely described and details on kinetic expression and rates are given in other recent papers [14-15].

Experimental conditions investigated

In order to have information on particle size distribution function several type of differential analyzer are adopted. They generally work with on-line apparatus in order to sample particles from combustion systems. Sampling systems are different both in terms of perturbation of the combustion system and of possible artifacts along the sampling line such as coagulation of particles. In particular, Kasper and Zhao [18] proposed a simple system in

which an horizontal probe was put in the flame to collect particles. The probe was constituted by a steel tube on which a small pinhole was made. This pinhole represents the effective part of the probe system and sampled material passes through it. To control the suction through the pinhole, a vacuum pump generates an underpressure into the pipeline of the order of some mm of H_2O. Nitrogen is fed into the tube such that the sampled material is immediately diluted and cooled. In these conditions it is possible in principle to avoid coagulation of particles, undesired reactions and, thus, artifacts along the sampling line. This sampling system has been widely adopted by different research groups all over the world [10-13] and it is accepted as one the most efficient experimental set up to collect particle from flames. Recently Wang has proposed a new system for collecting particles [19]. It is based on same principles of the previous one described above. However in this new set up a tubular probe was embedded in a circular aluminium plate. The pinhole was made in a similar way and the plate was moved along the flame axis to provide sampling at different height above the burner. This approach allows to have a stagnation plane in proximity of the probe-plate and this configuration can be modelled with as an opposed-flow diffusion flame. However this different set up leads to a stronger perturbation in terms of temperature.

Several studies have shown that in the case of the tubular probe the perturbation of the flame is limited to 2-3 mm from probe position and the flame temperature was downed at 800-1000K whereas in the case of the plate-probe the temperature close to the stagnation was as low as 400-500K [19-21]. These perturbations affect particle size distribution functions before entering into the pinhole. Moreover, even if the particle size distribution function could exhibit small differences, the condensation of small amount of gas phase material on soot particles can strongly affect surface properties and the chemical nature of these latter.

Model has been used to predict particle formation, concentration, size distribution functions and physical and chemical structure, in a laminar premixed ethylene-oxygen-argon flame with an equivalence ratio of 2.07 and a cold gas velocity of 8cm/s at standard conditions. The burner was water cooled and shrouded by a nitrogen flow. Further details of the flame can be found in literature [13]. The flame was slightly sooting and it was characterized by temperature and PSDF measurements. Temperature measurements were used as input for the model. In particular both free flame and flame perturbed by probe were analyzed. For correct evaluation of the effect of the probe along the flame axis, several simulations were performed with different temperature profiles investigating the different positions of the probe in the flame. The model adopted in this work was the same adopted form premixed flames in other publications [14-15].

Results and Discussion

Figure 1 reports the temperature profile of the pristine flame and those measured when a sampling probe is inserted at different heights along the burner axis, namely 6, 8, 10, 12 and 15 mm. The temperature profiles have been measured by the Wang's group by inserting the probe in a premixed rich ethylene flame with equivalence ratio across the soot threshold limit. Perturbation of the temperature profiles is of the order of 3 to 5 mm upstream of the sampling probe location. Moreover the temperature drops dramatically close to the probe reaching very low value around 400-500 K. It is worth to note that for very low heights of probe insertion, namely 6mm above the burner, also the main flame zone is perturbed.
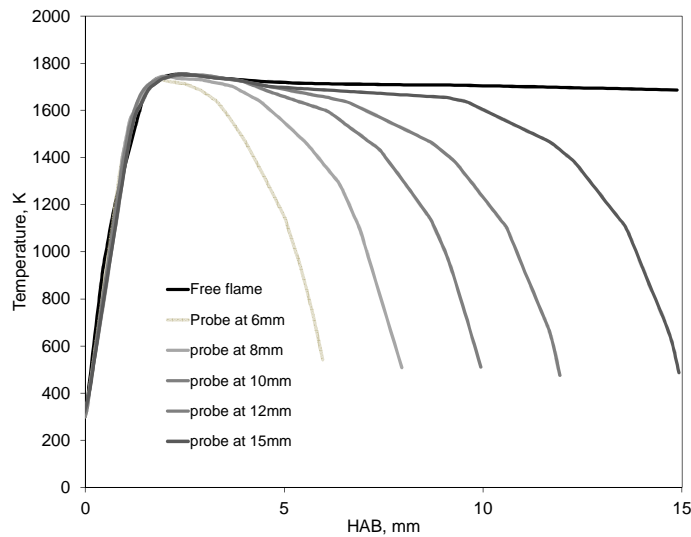
Figure 1. Experimental temperature profile for the free ethylene flame and for the flame with the probe positioned at different heights above the burner. Data are taken from [13].

The decrease of the temperature for effect of probe insertion might affect both the main oxidation mechanism (when the probe is inserted al low heights) and the particle inception mechanisms. Figure 2 shows modeled concentration profiles of total particulate matter and of the different classes of compounds belonging to particulate, i.e. high molecular mass molecules, clusters of molecules and aggregates of clusters of molecules, following their definition reported in the modeling section. Concentration data are scaled at ambient temperature in order to take into account the change of the temperature along the flame for effect of probe insertion. Continuous line is the result of the modeling when the pristine flame temperature profile is used. Lines at different colors represent the modeling results when the flame temperature is decreased for effect of probe insertion. Modelling stops at probe location.
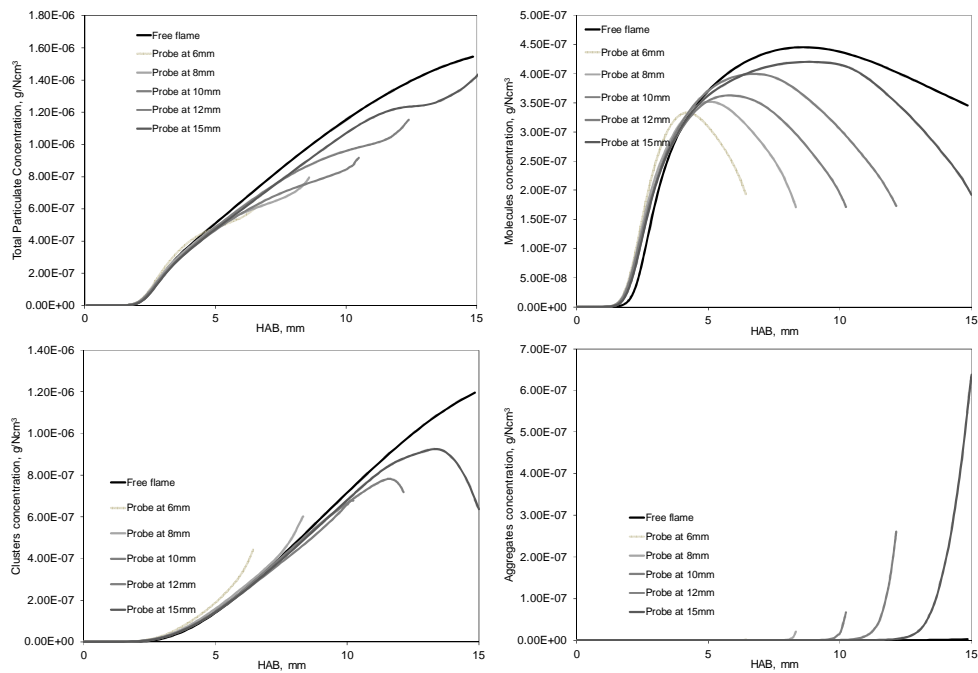

Figure 2. Modeled concentration profile of total particulate matter (top left), molecule (top right), clusters of molecules (bottom left), aggregates of clusters of molecules (bottom right) for free flame and for the flame with the probe positioned at different heights above the burner.

In the pristine flame, total particulate concentration increases with a high formation rate in the inception region around 3mm thereafter the formation rate decreases approaching very low values at the end of the flame as shown by a quite constant value of the concentration of particulate at the end of the flame. High mass molecules contribute to the total particulate in the inception region (between 3 and 5mm) thereafter their concentration decreases and clusters of high mass molecules are formed. The formation of aggregates of clusters is not evident in the unperturbed flame.

Probe insertion and subsequent temperature decrease in correspondence of the probe cause a change in the profile of the total particulate matter and the species contributing to particulate formation. As shown by the colored lines reported in Fig.2, the insertion of the probe decreases the rate of particulate formation approaching the probe, for effect of temperature decrease. This effect is clearly shown by the constant values of the concentration of particulate a few millimeters above the probe. However, just very close to the probe location particulate concentration increases again. This is the region where temperature drops to values of the order of 400-500K. The analysis of the concentration profiles of the different components to the total particulate shows that probe insertion increases the formation of clusters of high mass molecules in the initial regions of the flame and of aggregates of clusters at higher heights. For effect of higher concentrations of clusters and aggregates, the concentration of high mass molecules is strongly reduced.

In order to gain more information on the effect of the probe in the flame, Fig. 3 reports the PSDF predicted by the model with and without probe. Figure 3 reports also the experimental data taken from [13]. Experimental data are reported in the literature as normalized data such that is not possible a quick comparison on the absolute values whereas it is possible to have indication about the shape and the mean diameters of the PSDF.

Model results obtained with the temperature profile of the unperturbed flame do not reproduce the experimental data at higher heights above the burner but just at the first measured height (dashed lines in Fig.3). Probe perturbation, essentially the decrease of the temperature for effect of probe insertion, strongly influences the shape of the PSDFs and makes the predicted PSDFs more similar to the experimental ones as shown by the continuous lines reported in the figure. Indeed, particles stop their growth at lower size in the pristine flame, whereas with probe insertion, particle sizes arise up to 20 nm in agreement with experimental data. The change in the mean size is linked to coagulation. This phenomenon is generally found to be important within the sampling probe if the critical dilution is not reached. The comparison showed in Fig.3 evidences that this effect can be not completely avoided even if the critical dilution ratio is reached due to the decrease of the temperature for effect of probe presence.

It is worth noting that the comparison with experimental data show a good agreement in terms of mode diameters when the probe is considered, whereas the results obtained in the free flame are not able to reproduce the experimental PSDFs.

The analysis of the modeled H/C ratios of total particulate and of the different classes might help in the understanding the effect of the probe on the chemical composition of the particulate matter produced in flame. Moreover, it gives general information on the pathways of particle formation involved. Figure 4 reports the H/C ratio for total particulate matter, molecules, clusters and aggregates. For clearness for the flames with the probe perturbation only the final values of H/C are reported, whereas for the free flame the evolution along the axis of H/C ratio is plotted. For all three classes of compounds and, thus, also for total particulate matter, the H/C ratio when the probe is present results much higher than those modeled for the pristine flame.
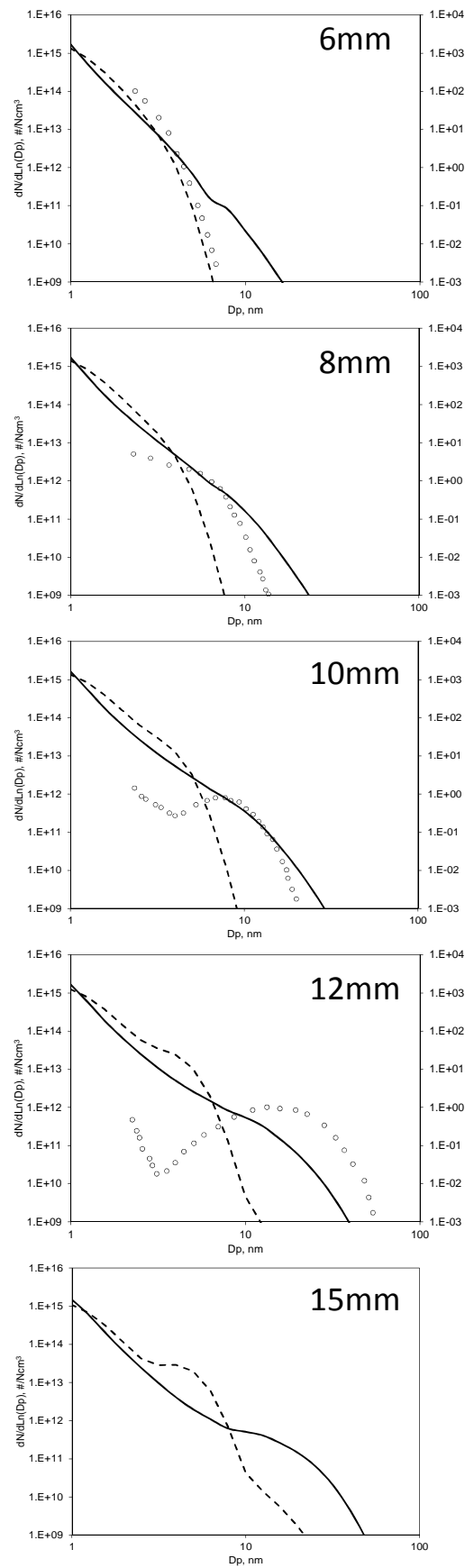
Figure 3. Modeled particle size distributions are reported at different heights above the burner representative of different probe positions. Free flame is reported as dashed line, perturbed flames are reported as solid line. Normalized data (dots) taken from [13] are reported on the secondary axis.

H/C ratio in the pristine flame (dashed lines) decreases along the flame axis due to a molecular growth and dehydrogenation processes. On the contrary, in the flames affected by probe perturbation H/C ratios approach values typical of the gas-phase PAHs and remain quite constant along the axis. A slow decrease of the H/C is observed just for the aggregates of clusters. This suggests that when the probe cools down the flame, particulate matter is not formed through a chemical process of molecular growth and dehydrogenation, but instead small species such as gas-phase PAHs are constantly added to the incipient particles substantially contributing to the final concentration of particulate.
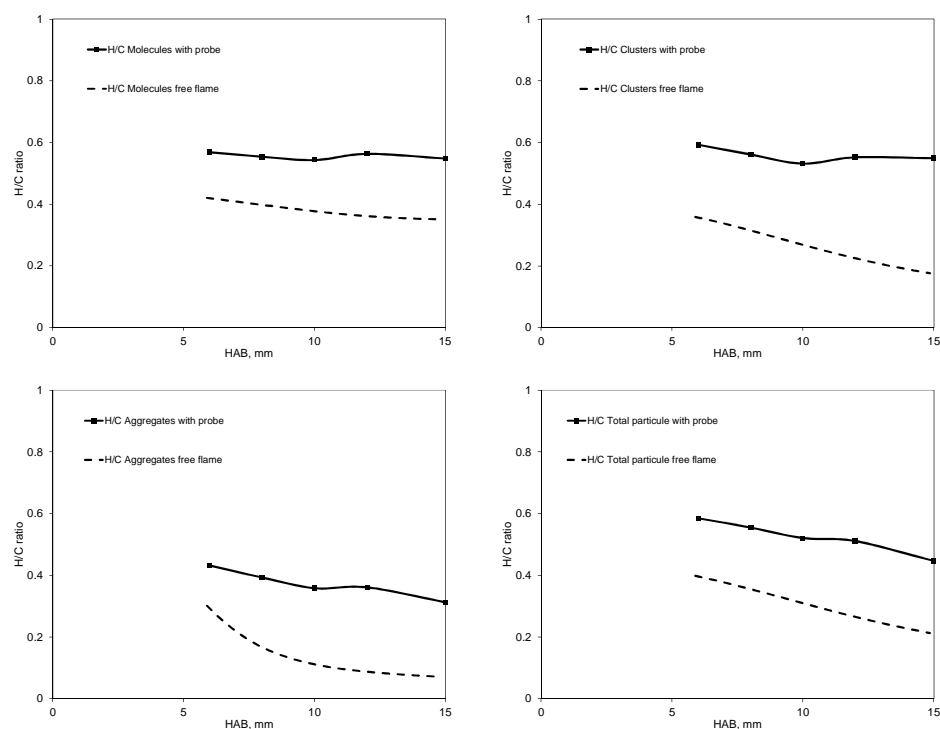

Figure 4. Modeled H/C ratio of total particulate matter (top left), molecule (top right), clusters of molecules (bottom left), aggregates of clusters of molecules (bottom right). Data for free flame are reported as dashed line. For the flame with the probe positioned at different heights above the burner only the values at probe position are reported (dots).

Model allows to make a reaction analysis that can be useful to better understand the effect of the probe. In particular this analysis allows to evidence which pathways of reaction are enhanced or suppressed by the cooling of the flame due to the presence of the probe. Figure 5 reports the main reaction pathways that change the total volume fraction and the size distribution of particles. In particular two pathways of nucleation are considered, the chemical growth through radical-molecule mechanism and dimerization process both involving gas-phase PAHs. Growth through acetylene and chemical addition of gas phase PAHs are considered together with physical condensation of PAHs on existing particles. Finally chemical interaction between two existing particles to form new ones and physical coagulation are reported.

Nucleation and addition of material from gas-phase affect the total volume fraction whereas the polymerization process and coagulation act on the size distribution. Figure 5 reports only the reaction analysis for the free flame at the higher position of the probe, namely 15mm above the burner. Very similar considerations can be done for all the other positions. The reaction rates are scaled for the density effect due to temperature variation.

Figure 5 evidences that all the pathways linked with chemical routes are inhibited by the cooling of the probe. This result is somewhat predictable, however the drop here is quantified to be several orders of magnitude lower. On the other hand, physical interactions are strongly enhanced by temperature drop. Physical pathways are linked to van der Wall forces which become relatively stronger and dominant if the kinetic energy of the particles drops (temperature decreases). Chemical addition of material from gas phase and physical condensation are almost balanced since the total volume fraction is not dramatically changed by the presence of the probe (see Fig 2). In the same way polymerization rate decays in the zone of the cooling whereas coagulation strongly increases. This two pathways are far from being in balance since coagulation is much more effective also in the free flame and thus its variation are more significant for the final PSDF.
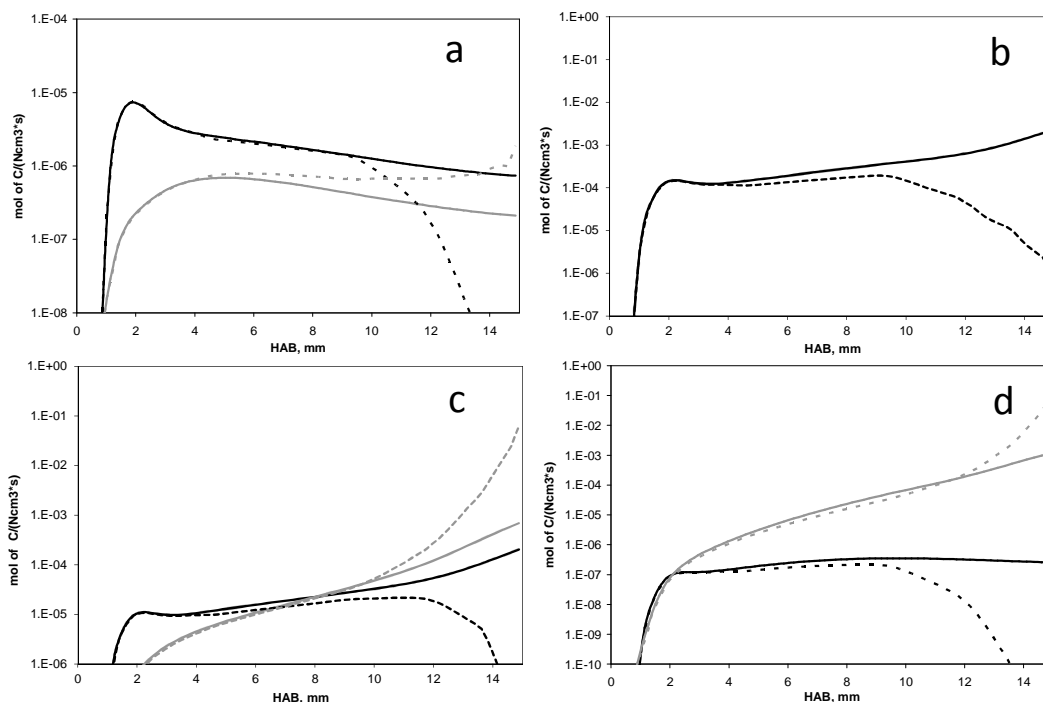

Figure 5. Modeled reaction rates are reported: a) nucleation via chemical pathway (black), nucleation via physical pathway (grey); b) acetylene addition (black); c) chemical addition of gas-phase PAHs (black), physical condensation of gas-phase PAHs (grey); d) radical-molecule particle interaction (black), particle-particle coagulation (grey). Data for the free flame are reported as solid lines. Data for the flame with probe at 15mm above the burner are reported as dashed lines.

Conclusions

An advanced kinetic model has been used in order to evaluate the effect of the probe in the analysis of particles produced in premixed flames. The cooling down of the system has been already experimentally studied and temperature profiles have been taken as input for the model. An ethylene premixed flame has been investigated. For this flame particle size distribution functions have been experimentally obtained.

Model shows that the presence of the probe changes the profile of total particulate concentration. Moreover model allows to discern that large aggregates are formed only when probe is present and are absent in the free flame investigated. The H/C ratio obtained from the model suggests that particles produced with the presence of the probe are more similar to gas phase PAHs and dehydrogenation is not effective. Analysis of PSDF evidences that the cooling due to the probe enhances coagulation and leads to larger mean sizes for the particles. In particular the large particles with sizes up to 20 nm experimentally found are not predict by

the model if the probe is not considered. Finally the reaction analysis clarify that the presence of the probe, reducing flame temperature, inhibits chemical pathways such as chemical addition from gas phase and radical-molecule reactions. The probe has an opposite effect on the physical interactions: in particular both condensation of PAHs and coagulation rate increase of orders of magnitude becoming the predominant pathways and strongly affect the nature of the particle produced.

References

1. Alföldy, B., Giechaskiel, B., Hofmann, W., Drossinos, Y. Size distribution dependent lung deposition of diesel exhaust particles. Aerosol. Sci. Tech. 40: 652–663 (2009).
2. Franck, U., Herbarth, O., Röder, S., Schlink, U., Borte, M., Diez, U., Krämer, U., Lehmann, I. Respiratory effects of indoor particles in young children are size dependent. Sci. Total Environ. 409: 1621–1631 (2011).
3. D'Anna, A. Combustion formed nanoparticles. P. Combust. Inst. 32: 593–613(2009)
4. Bockhorn, H., D'Anna, A., Sarofim, A.F., Wang H., (Eds), Combustion Generated Fine Carbonaceous Particles, Karlsruhe University Press, Karlsruhe (2009).
5. Wang H., Formation of nascent soot and other condensed-phase materials in flames. Proc. Combust. Inst. 33: 41-67 (2011).
6. D'Alessio, A., D'Anna, A., D'Orsi, A., Minutolo, P., Barbella, R., Ciajolo, A. Precursor formation and soot inception in premixed ethylene flames. Proc. Combust. Inst. 24: 973-980 (1992).
7. D'Anna, A., Commodo, M., Violi, S., Allouis, C., Kent, J. Nano organic carbon and soot in turbulent non-premixed ethylene flames. Proc. Combust. Inst. 31: 621-629 (2007).
8. Commodo, M., Diagnostic for the characterization of nanometric structures in high temperature reactive systems, PhD Thesis
9. D'Anna, A., Commodo, M., Sirignano, M., Minutolo, P., Pagliara, R. Particle formation in opposed-flow diffusion flames of ethylene: An experimental and numerical study. Proc. Combust. Inst. 32: 793-801 (2009).
10. Sgro, L.A., Basile, G., Barone, A.C., D'Anna, A., Minutolo, P., Borghese, A., D'Alessio, A. Detection of combustion formed nanoparticles. Chemosphere 51: 1079–1090 (2003).
11. Maricq, M.M., A comparison of soot size and charge distributions from ethane, ethylene, acetylene, and benzene/ethylene premixed flames. Combust Flame. 144: 730–743 (2006).
12. Echavarria, C. A., Sarofim, A. F., Lighty, J. S., D'Anna, A., Evolution of soot size distribution in premixed ethylene/air and ethylene/benzene/air flames: Experimental and modeling study. Combust. Flame. 158: 98–104 (2011).
13. Abid, A.D., Heinz N., Tolmachoff, E.D., Phares, D.J., Campbell, C.S., Wang, H., On evolution of particle size distribution functions of incipient soot in premixed ethylene–oxygen–argon flames Combust. Flame 154: 775–788 (2008).
14. Sirignano M., Kent J.H., D'Anna A. Detailed modeling of size distribution functions and hydrogen content in combustion-formed particles Combust. Flame, 157:1211 (2010)
15. D'Anna A., Sirignano M., Kent J.H., A model of particle nucleation in premixed ethylene flames Combust. Flame, 157 (2010).
16. Sirignano M., Alfè M., Tregrossi A. Ciajolo A. D'Anna A., Experimental and modeling study on the molecular weight distribution and properties of carbon particles in premixed sooting flames Proc. Comb. Inst, 33 (2011).
17. Ciajolo A. In: H. Bockhorn, A. D'Anna, A.F. Sarofim and H. Wang (Eds), Combustion Generated Fine Carbonaceous Particles, Karlsruhe University Press, Karlsruhe (2009), 333–344.

18. Kasper, M., Siegmann, K., Sattler, K. Evaluation of an in situ sampling probe for its accuracy in determing particle size distributions from flames. Aerosol Sci. 28(8): 1569-1578 (1997).
19. Abid, A.D., Camacho, J., Shee, D.A., Wang, H. Quantitative measurement of soot particle size distribution in premixed flames – The burner-stabilized stagnation flame approach Combust. Flame 156: 1862–1870 (2009).
20. De Filippo, A., Sgro, L.A., Lanzuolo, G., D'Alessio, A. Probe measurements and numerical model predictions of evolving size distributions in premixed flames. Combust. Flame 156: 1744-1754 (2009).
21. De Filippo, A., Characterization of carbonaceous nanoparticle size distributions (1-10 nm) emitted from laboratory flames, diesel engines and gas appliances. PhD Thesis, Università di Napoli "Federico II", 2009.