1
2
3 **Temperature and oxygen effects on oxidation-induced fragmentation of**
4 **soot particles**

5
6 Mariano Sirignano^a, Hossein Ghiassi^{b,*}, Andrea D'Anna^a, JoAnn S. Lighty^b
7

8
9 ^a Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università
10 degli Studi di Napoli Federico II, Italy

11
12 ^b Department of Chemical Engineering, University of Utah, Salt Lake City, UT, USA
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

40 *** Corresponding Author.** Address: Department of Chemical Engineering, University of Utah,
41 Salt Lake City, UT, USA. Fax: +1 801-585-9291.

42 E-mail address: HosseinGhiassi@yahoo.com

ABSTRACT

In this work soot oxidation induced-fragmentation is modeled by using a Multi-Sectional approach. The model has been developed previously and applied successfully, confirming the role of oxidation-induced fragmentation in soot burnout under different combustion conditions. The Multi-Sectional model was used without further modification to understand the mechanism governing the oxidation-induced fragmentation of soot aggregates and particles by modeling particle size distributions (PSDs) previously measured in a two-stage burner under a wide range of temperature and in both fuel-lean and fuel-rich overall conditions. The model was able to reproduce the experimental data in all the investigated conditions both in terms of PSDs and total mass of oxidized particles.

An analysis of model results suggested that when temperature decreased, small particles produced by oxidation-induced fragmentation could not be completely oxidized and, thus, could be emitted; on the other hand, when temperature increased, the global oxidation process was more effective and small particles were oxidized and reduced in number concentration.

When studying fuel rich conditions, the model predicted that the local presence of a relevant oxygen concentration caused the oxidation-induced fragmentation mechanism, producing small particles, which could eventually be emitted.

Finally, a sensitivity analysis was conducted on oxidation-induced fragmentation indicating that aggregate fragmentation controlled soot burnout whereas particle fragmentation was responsible for small particle formation. However, the sensitivity analysis also suggested that both mechanisms were needed for the correct prediction of the evolution of PSDs.

67 KEYWORDS

68 Multi-Sectional method, oxidation-induced fragmentation, soot, particle size distribution, two-

69 stage burner

70

70

71 **1. Introduction**

72 Over the years, soot emission mechanisms have been extensively studied to improve
73 combustion processes [1–5] and, thus, reduce their impact on human health [6,7] as well as on
74 the environment [8]. Most studies have been devoted to the understanding of soot inception, i.e.,
75 the process which leads from gas-phase, high molecular mass species, such as PAHs, to the
76 formation of the first particle or condensed phase compound [9–13]. Despite these efforts,
77 inception remains the least understood mechanism in combustion-derived particle formation,
78 whereas there is a larger convergence in the combustion community on the surface growth
79 mechanism and the dynamics of particles and large aggregates [14,15].

80 Particle formation is not the only mechanism that contributes to the determination of the final
81 particle emissions. In real combustion devices, the oxidation processes play a determinant role
82 for particle emissions. In fact, most of the emitted particles could be those escaping oxidation,
83 usually during the last part of the combustion process within combustion devices or in the after-
84 treatment system [16–19]. As a result of soot oxidation mechanism studies, semi-empirical
85 reaction rates are used in a large number of models [20–23]. It is accepted that soot can be
86 oxidized when it reacts with molecular oxygen (O_2) and hydroxyl radical (OH). Two kinetic
87 expressions to account for the soot oxidation via O_2 and OH have been proposed by Nagle-
88 Strickland-Constable (NSC) [24] and Neoh et al. [25], respectively. Although these reaction rates
89 have been widely used, and result in fair agreement with experimental data, a deeper
90 comprehension of the oxidation phenomena of combustion-generated particles is needed.

91 *1.1. Phenomenology of oxidation-induced fragmentation*

92 While oxidation is responsible for the soot burn-out, particle aggregates can be attacked by

oxidant species such that the structure weakens and the aggregates subsequently break apart. This process, oxidation-induced fragmentation, has been noted in the study of Neoh, Howard and Sarofim [26]. However, despite the novelty and possible impact on soot emission in combustion, oxidation-induced fragmentation has not been fully incorporated into soot models, with some exceptions. Recently, due to new studies conducted on a two-stage burner similar to Sarofim and Neoh's [27–31], and due to the increased number of details now possible in soot combustion models, oxidation-induced fragmentation can be taken into account [32–34].

The study of the oxidation process and, in particular, of oxidation-induced fragmentation is difficult since oxidation is usually competing with formation and growth of soot particles. This overlapping of effects does not allow a straightforward approach to the study of the oxidation. The two-stage burner proposed by Sarofim and Neoh [26] and this group [27–31,35] isolates oxidation from formation, allowing more complex and hidden phenomena to be studied, such as oxidation-induced fragmentation. Further details of the two-stage burner can be found in previous experimental work [35].

Experimental investigations, mainly conducted on a two-stage burner, have shown that during the oxidation of soot particles in high-temperature environments, fragmentation of aggregates and even fragmentation of primary particles may occur [27,30,31]. The evolution of particle size distributions (PSDs) obtained with two-stage burner setup has constituted a benchmark for the modelers to approach the problem and the agreement of model predictions with results produced in the two-stage burner represents an achievement.

Several research groups have proposed phenomenological and numerical models to describe oxidation-induced fragmentation using different approaches [32–34,36,37]. Starting from experimental evidence of the internal structure of soot particles as well as appropriate

experiments to isolate the contribution of oxidation and indeed of oxidation-induced fragmentation, a general sketch of the processes taking place can be drawn. The brief discussion below serves as an introduction to the phenomenological model of oxidation-induced fragmentation.

Particles can be attacked by several oxidant species, depending on the flame conditions. Since other species, i.e., O, CO, CO₂, and H₂O, usually have a negligible contribution to oxidation under most combustion conditions present in real and lab-scale devices and particularly in the investigated conditions [25,38,39], only OH and molecular oxygen, O₂, are studied here. The two oxidants differ regarding reactivity and of relative abundance in the combustion environment, again depending on the combustion conditions. Under fuel rich conditions, due to its relatively high abundance, OH is considered the most important species contributing to the oxidation process in competition with the formation and growth pathways. On the other hand, molecular oxygen - O₂, plays a determinant role in fuel lean conditions. In fact, under these conditions, O₂ is abundant, up to the order of percentages in mole fraction, before and after the flame front, and its contribution to the global oxidation rate becomes important [40]. In fuel lean conditions, particle formation does not start, and thus no soot particles are formed; however, due to gas recirculation, typical of turbulent and diffusion-controlled combustion, soot particles can be formed in fuel-rich conditions and pass through fuel lean conditions where they can be eventually oxidized [41,42].

Oxidation by OH and O₂ are considered surface processes able to subtract carbon atoms from the particles. Oxidation-induced fragmentation of particles can occur if the oxidizing species penetrate the aggregates or even the particles and remove C atoms from a weak point causing the break-up of the large aggregates and particles into smaller aggregates and smaller particles

[30,31].

In addition, stepwise splitting up of large aggregates because of oxidation-induced fragmentation can lead to smaller aggregates formed by a limited number of primary particles. Fragmentation can also involve primary particles where internal burning fragments a single particle into smaller particles. The process can continue producing very small molecular clusters.

Oxidation-induced fragmentation can be distinguished into two mechanisms: aggregate fragmentation and single particle fragmentation. The fragmentation of aggregates occurs if the carbonaceous material at the contact points of the primary particles is oxidized destroying the “bridges” holding together the primary particles. Recently, our group has shown that these “bridges” are more reactive as compared to the rest of particle surface [30,31].

In the fragmentation of single particles, particles fragment into smaller particles. Previous work on coal has shown that as internal structure is destroyed, and porosity increases, the particle will eventually break apart [43,44]. Neoh et al. [26] and Echavarria et al. [27,28] support a similar mechanism for soot particles, finding in their experiments the appearance of a considerable number of sub-10nm particles during particle oxidation. These sub-10nm particles have been linked with oxidation-induced fragmentation since a particle shrinking model could not explain their formation.

Oxidation-induced fragmentation as described above has recently been incorporated into a Multi-Sectional model [33,45–48] for particle evolution in flames which discretizes the combustion aerosol on the basis of the number of C and H-atoms and the morphology: single molecules, molecular clusters and primary particles, and particle aggregates. In contrast to other modeling approaches [49], the Multi-Sectional model is the only one that may account for both aggregate and primary particle fragmentation. The model has been tuned using the experimental

data produced by Echavarria et al. [27,28] on the two stage burner and has been used to simulate diffusion flames of ethylene increasing the predictions of particle volume fractions and sizes with respect to previous models in which oxidation induced fragmentation was not included [20–24,49–57].

The results produced by Echavarria et al. in the two-stage burner were limited [27,28] in terms of temperature and mixing conditions. More recently this group, using the same experimental setup, has published a set of data which cover the evolution of PSDs during the oxidation process over a wide range of temperatures and both fuel-rich and fuel lean overall conditions [30,31,35]. In the present work, the Multi-Sectional model was used without any further adjustment to reproduce the evolution of size distribution and give insight into the role and the relative importance of oxidation-induced fragmentation.

2. Experimental methods

The data used for this study was previously generated, but a brief overview of the experimental apparatus follows. A two-stage burner designed after the apparatus of Neoh [58] was used to generate soot in a fuel-rich premixed flame, which served as the first stage. The soot was then burned in a secondary, premixed burner. Details are given in Ghiassi, et al. [59]. In the first-stage burner, air and fuel (ethylene > 99.99 %) were added to the bottom of a 5-cm ID stainless steel chamber under $U_1 = 3.77$ cm/s. Complete mixing occurred over a thick bed of glass beads, and the flame was stabilized over a tube bundle through which the mixture passed in laminar flow. The overall equivalence ratio (ϕ) is defined by the ratio of fuel to total oxygen (oxygen injected into the bottom and top burners) fed into the burner over the stoichiometric ratio.

Different diluents in the oxygen stream were used to achieve various temperature conditions in the second-stage burner. Nitrogen (N_2), argon (Ar) and helium (He) were used to produce fuel lean flames on the top burner. Argon and helium were chosen to achieve higher and lower temperature than nitrogen, respectively, which was the reference case. In order to achieve different oxygen enrichment, on the top burner, a flame with a fuel-rich equivalence ratio was also investigated. Values of the first burner and overall equivalence ratios, for all the conditions, are reported in Table 1.

Temperature profiles were measured using a 0.02032 cm diameter, type-B thermocouple. The radiation correction for the temperature was similar to that of McEnally et al. [60]. A Scanning Mobility Particle Sizer (SMPS), which consisted of a TSI 3080 classifier and a 3025 ultrafine condensation particle counter, was used with a 3085 nano-DMA (differential mobility analyzers) to measure particle size distributions (PSDs) in the size range from 3 to 140 nm. The SMPS sampling system was similar to that of Zhao et al. [61,62] with some minor changes in probe size (OD = 1.1cm) and pinhole diameter (0.024 cm). Dilution ratios were in the range of 10^3 to 10^4 which minimized particles losses and coagulation in the sampling system. Corrections for diffusion losses and coagulation along the sampling line were carried out following the procedure presented by Minutolo et al. [63]. H_2 , O_2 , CO, and CO_2 were sampled using a water-cooled probe (0.2-cm ID) and analyzed by online gas chromatography (VARIAN, CP-4900 Micro GC).

3. Chemical kinetic modeling

3.1. Multi Sectional model

The kinetic mechanism of molecular growth and oxidation was based on the lumping of

high-molecular-mass species by their number of C and H atoms and by their state of aggregation, i.e., single molecules, clusters of molecules (primary particles) and aggregates of primary particles, described in detail in previous publications [33,34]. The lumped scheme was coupled with a mechanism of oxidation and pyrolysis of the hydrocarbon fuels which was extensively validated in premixed and diffusion flame [33,34,46–48].

Starting from pyrene, all of the compounds with larger molecular masses were considered as lumped species. The reactions accounting for molecular weight growth and oxidation were treated on the basis of similarity with gas-phase reactions involving PAHs. Lumped molecular species in their stable and radical form were accounted for. The collision frequency of the chemical reactions was evaluated by kinetic theory. Although the reactions for the lumped species cannot be considered as elementary reactions, this approximation was the primary foundation of the sectional approach and it was applied to all the particle phase reactions.

3.2. Oxidation-induced fragmentation: reaction rate calculations

Model details of oxidation and particularly oxidation-induced-fragmentation processes have been extensively published through the years [33,34,46–48]; however, for the sake of completeness of the discussion, the key features, how they have been designed and specifically treated by the Multi-Sectional model, are detailed below.

In the Multi-Sectional model, all the lumped species can be oxidized in their stable and radical form by OH and O₂, respectively, in similarity with the PAH oxidation for which some studies are present in literature. Both OH and O₂ oxidation were considered in the subtraction of carbon atoms from the lumped species, reducing their total amount. Since these processes, similar to the growth process, were considered as surface processes, they were modeled taking into account the collision rate based on the size of the lumped species. The determined reaction

rates have been tested in premixed and laminar diffusion flames, giving fair agreement in fuel-rich premixed conditions but failing to match the complete burnout in a non-smoking diffusion flame [57]. In addition, the consideration of oxidation as only a surface reaction was not able to reproduce the evolution of particle size distributions during the soot oxidation measured in the two-stage burner [33]. To improve mechanism predictions and to implement the phenomenological model, oxidation-induced fragmentation was introduced.

Fragmentation of aggregates into smaller aggregates, and eventually into single particles, and the breaking apart of a single particle forming smaller ones were considered. As described in the introduction, aggregates can fragment if oxidation occurs at the contact points of the primary particles. Oxidation of interstitial material is still a surface reaction, directed toward a selected zone of the aggregate. However, gas-phase oxidant species have to access to the bridge between the particle which might be “hidden” by the fractal structure and thus not immediately accessible. Hence, in the version of the Multi-Sectional model used in the present work, molecular oxygen, O_2 , was considered the only species able to fragment the aggregates. OH is also likely to be oxidizing the bridge sites, concurrently with the surfaces. However, since the reaction is so fast, it is difficult to ascertain the contributions of OH and further study is needed.

Starting from these considerations about aggregate fragmentation, the reaction rate of oxidation-induced fragmentation of aggregates was related to the total O_2 oxidation rate. A fragmentation event was modeled to occur after the removal of a fraction δ of C-atoms from the particles close to the point of contact between particles. The number of contact points in the aggregates can be estimated by dividing the total mass of the aggregates by the average mass of the primary particles. It was considered that there were more than two C-atoms holding the aggregate together. Given this, the fraction δ of C-atoms that must be removed to cause

fragmentation is expressed as

$$\delta C = \alpha * n_C^P \quad (1)$$

where n_C^P is the total number of carbon atoms per primary particles and α is the fraction of the total number of C-atoms constituting the primary particles to be removed.

Of course, not all the oxidation events occur on the contact points. The probability that the oxidation by O_2 occurred at a weak link between two particles is equal to the inverse of the number of active sites for O_2 oxidation on the particle surface:

$$n_{active\ sites} = \chi \pi d_p^2 \quad (2)$$

where $\chi = 1.7 \times 10^{19} \text{ m}^{-2}$ [64] is the number of sites per unit area and πd_p^2 is the primary particle surface area. Each oxidation event removed two carbon atoms. The fragmentation rate of aggregates is then given by:

$$k_f = k_{O_2} * (n_P - 1) / ((\chi * \pi * d_p^2) * \delta C) \quad (3)$$

where d_p is the size of the primary particles and n_P is the number of primary particles in the aggregate which can be calculated as $n_P = n_C^A / n_C^P$. n_C^A is the number of C-atoms in the aggregate. In the model d_p is considered to be 20nm. This choice has been used in prior studies [65–67]; however, it does not imply that all the primary particles are 20nm or that the model can be applied under only these conditions. A primary particle with d_p of 20nm, and the corresponding number of C-atoms was used to estimate the number of contact points in an aggregate and resulted in a manageable expression for the reaction rate of the oxidation induced fragmentation (Eq. 3).

Experimental evidence of the internal structure of particles was used for consideration of the fragmentation of a single particle. HR-TEM images of young soot particles suggest that clusters of aromatic compounds appear to be the major constituents of primary particles [12]. An average size of less than 1nm can be retrieved from HR-TEM images and these structures are often referred as Basic Structure Units (BSUs). Although an overall compact structure could be hypothesized for these particles, HR-TEM images suggest that single particles prefer to arrange in more loose structures in which these BSUs are randomly organized and are separated from each other by “pores” having a length of the same order of magnitude of the BSU [12]. Some oxidant species may diffuse into these pores. In fact, oxidant can erode a particle on its surface, but it can also penetrate the pores internally to oxidize the particle. The possibility that the reaction takes place only on the surface versus consideration of both surface and internal reaction was linked with the ratio between the reaction time and the diffusion time of the oxidant species through the pore. Once again, molecular oxygen would likely play this role and penetrate the particles burning internally due to its slower burning rate. To correctly evaluate the reaction rate relatively of molecular oxygen in comparison with its diffusion into the pores of the structure, some assumptions on particle structure were made. The length of the aromatic island visible in the HR-TEM images is 1 nm on average, i.e., an aromatic compound constituted by 20-25 C-atoms. The number of aromatics in well-organized structures was always on the order of 4-5 stacked planes at a distance of about 0.35 nm. To evaluate the size of the pores and oxygen diffusion, a length of the same order of magnitude as the BSU (1nm) and a width of about 0.5 nm were considered. Although larger pores can be found in the particles, these conservative values were more typical of aged soot. Knudsen diffusion of molecular oxygen in the pores was derived from the kinetic theory of gases by replacing the path length with the pore diameter and

the rate of the surface oxidation by O₂ for a range of particles. By comparing the characteristic diffusion time with the characteristic reaction time of surface oxidation with O₂ at a flame temperature of 1500K and with the geometrical characteristics of the pores reported above, the process is in the reaction limited regime, leading to the hypothesis that diffusivity of O₂ is not the controlling step in the internal oxidation of particles. On the other hand, because of the faster reactivity of OH, it does not penetrate the pores but oxidizes the particle on its surface. This evaluation was not dramatically affected by particle structure assumptions, i.e. fringe length or pore size. As long as these parameters do not change by orders of magnitude, molecular oxygen diffusion into the pores of primary particles is faster than reaction rate.

When oxidation by O₂ occurs in the depth of the pores, the particle can fragment into two parts by again considering the removal of a fraction δ of C-atoms within the particles after the penetration within the pore. This number of carbon atoms is given here by

$$\delta C_{\text{pores}} = \beta * n_C^P \quad (4)$$

where again n_C^P is the total number of carbon atoms per primary particles and β represents the fraction of C-atoms in the particle that must be removed to cause fragmentation of the particle.

The number of pores present in the structure, n_{pores} , can be evaluated from the volume of a single pore relative to the particle volume. It can be considered that for each BSU one pore of similar dimension exists. The number of BSUs constituting a particle, n^{BSU} , is obtained by dividing the number of C-atoms in the particle by the number of C-atoms constituting the BSU. The number of C-atoms in the BSU, n_C^{BSU} , is obtained from the above reported HR-TEM images; the BSU is estimated to contain four aromatic molecules each of 25 C-atoms. Hence,

$$n^{BSU} = n_{pores} = n_C^P / n_C^{BSU}. \quad (5)$$

Finally, just a fraction of the entire pore surface was considered to be a weak point for the oxidation-induced fragmentation, namely, the area at the bottom of the pore, $A^{pores\ active}$. For cylindrical pores with a depth L , of the same order of magnitude of the BSU (1 nm) and diameter, w , of about 0.5nm, the internal surface area of the pores was obtained:

$$A^{pores\ active} = (\pi w^2/4 / (\pi wL + \pi w^2/4)). \quad (6)$$

The fragmentation rate for the particles is then:

$$k_f = k_{O_2} * (\pi w^2/4 / (\pi wL + \pi w^2/4)) * n_{pores} / (\delta C_{pores}) \quad (7)$$

The model presented relies on two parameters, namely α , i.e., the fraction of the total number of C-atoms constituting the primary particles to be removed to cause aggregate fragmentation, and β , i.e., the fraction of C-atoms in the particle that must be removed to cause fragmentation of the particle.

α and β , were not assigned a priori, but were retrieved from a sensitivity analysis of the model predictions against the experimental data of Echavarria et al. [27,28]. Using values of $\alpha = 0.01$ (1% of the total number of C-atoms in the primary particle) and $\beta = 0.05$ (5% of the total number of C-atoms in the particle) the model was able to reproduce both the total burn out rate and the change in shape of PSDs quite well for an overall equivalence ratio of 0.8. The model predicted the oxidation-induced fragmentation and these values were not changed in this work.

3.3. Multi-Sectional Model Inputs

The model used the experimental temperature profile, the gas chromatograph (GC) results at the exit of the top burner, and the initial PSDs as input. These inputs were used to avoid initial

discrepancy between the model and the experimental data, which could lead to misinterpretation of the results. Particles larger than 20nm, based on experimental PSDs, were considered aggregates of primary particles whereas particles smaller than 10nm were considered single particles. Particles of an intermediate size were hypothesized to be a mixture both particles and aggregates; a linear interpolation was used to determine the number of aggregates and the number of single particles to input to the model. This assumption was made in agreement with experimental findings from a different experimental setup [65,66] as well as results obtained in two-stage burner experiments [25–28,30,31]. The fraction of particles below 20nm was relatively small in terms of mass and number concentration. Hence, the choice of considering these two classes of particles (20nm and 10nm) as single particles or as aggregates did not significantly influence the results. A sensitivity analysis, not reported in this paper, confirms this assumption. In the present model, aggregates formed by particles with sizes on the order of 2-4 nm were not considered. Discussion on this point is reported in [33,44–46] where the model is explained in detail. It is worth mentioning that experimental data suggest that particle sizes as large as 7-10nm are needed to form aggregates [17,68,69].

The SMPS does not distinguish between particles and aggregates as it measures only the mobility diameter. In this regard, the choice regarding the first part of PSDs has less importance. In the future, and for better comparison, the use of an auxiliary technique, such as HR-TEM, would help explain this point further.

4. Results and discussion

In this section both experimental results and model predictions are presented: first, those regarding the effect of temperature on oxidation-induced fragmentation in a fuel-lean

environment; and, second a fuel-rich case was explored. These results are compared with those obtained in fuel-lean conditions to show similarities and differences. Finally, the model was used to distinguish between the relative contributions of different reaction pathways of oxidation-induced fragmentation to the global soot burnout and the change in PSDs. While some of the experimental data have been published elsewhere [30], the PSDs have not. Modeling attempted to shed light on the role of oxidation-induced fragmentation in total burn out and on the formation of sub-10nm particles during soot oxidation. This latter aspect has been clearly seen experimentally; however, a definitive explanation has not been achieved.

4.1. The effect of temperature on fragmentation(experiments with He, Ar, and N₂)

To investigate the effect of the temperature on oxidation-induced fragmentation, the oxidant stream fed to the second (top) burner was diluted with different species. In particular, as shown in Table 1, nitrogen (N₂) argon (Ar) and helium (He) were chosen to dilute the oxygen (O₂), to obtain a fixed diluent/oxidant molar ratio of 79/21, similar to air and also similar to other cases previously investigated [27,28,30]. Since the number of moles in the second burner has been kept constant, the velocity of cold gas was constant. The flame obtained by using N₂ as a diluent is presented as a reference case for two reasons. First, the use of N₂ effectively results in a flame with a temperature intermediate between those produced with Ar (higher temperature) and He (lower temperature). Second, N₂ has been used in previous works. For all the investigated cases, the conditions of the flame in the first burner was kept constant (see details in Table 1), as the first burner was used to “feed” a determined particle size distribution to the top burner.

Temperature profiles for the three different diluents are shown in Figure 1 [30]. As seen in the figure, peak temperature differs by only approximately 100K between the cases; in contrast, quite remarkably, oxidation-induced fragmentation is significantly different as reported below. In

addition, the position of the flame front shifts within 1.5mm in the three cases: this difference has been found to be of a minor effect, as discussed further below.

Measurements of the major constituent gas-phase concentrations, by using on-line GC analysis, are reported in Fig. 2 versus the residence time in the flame. The residence time was calculated by taking into account the thermal expansion due to temperature and the variation in the number of moles. In fact, although the cold gas velocity in the second burner was kept constant, the differences in temperature profiles caused slight changes in the effective velocity profiles along the flame and in the residence time in each flame. The use of residence time instead of the height above the burner takes these small differences into account, allowing a better comparison.

Figure 2 also reports the model predictions for the different cases investigated. The inputs for the model were both the initial gas composition and the temperature profiles. However, due to the perturbation of the probe used to sample the gas from the flame, the modeled profiles were shifted 2.5mm away from the burner to match the experimental gas profiles. This procedure was necessary since the probe locally cools down the flame, slowing down the chemical reactions and thus moving the reaction zone downstream. The shift occurred before the conversion from the height above the burner to the residence time. The shift was found to be the same for all the flames and was kept constant. This procedure was applied several times in previous studies where gas concentration, as well as experimental PSDs, was compared to model predictions [70]. Figure 2 shows that, due to overall lean conditions, the O_2 concentration after the first reaction zone, decreased, approaching a final value between 6 and 8%. More important, in all the investigated conditions, the gas concentration profiles were quite similar, suggesting that the effect of their differences on the oxidation-induced fragmentation was negligible and that

temperature played a dominant role. Model results, also reported in the figure, were in fair agreement with experimental data.

In Fig. 3 the experimental particle size distributions (PSDs) collected in the second burner are reported together with model predictions. The predicted PSDs matched fairly well with the experimental data. Again, the model parameters, i.e., the fraction of the total number of C-atoms constituting the primary particles to be removed to cause aggregate fragmentation, and the fraction of C-atoms in the particle that must be removed to cause fragmentation of the particle, were been changed from those based on different conditions, but the same experimental set up. The ability of the model to predict PSD evolution at different temperature conditions validates its use for other combustion conditions.

Experimental data suggest that the temperature had a major effect on oxidation-induced fragmentation. Looking at the reference case, N_2 (center column in Fig 2), the initial PSD was centered around 40nm with a small number of particles below 10nm, and the complete absence of particles with diameters below 4nm. When the temperature and, correspondingly, the oxidation rate, increased, an increase in the number concentration of particles smaller than 5nm was observed (2.4mm). At the same time, a decrease of large particles (probably aggregates), both in concentration and size, was observed. The burning of large and/or small structures continued until they were fully oxidized at the end of the flame (4.8mm), and were no longer detected due to limits of the experimental apparatus. Note that the measured PSDs started at 3nm, whereas the model indicated the presence of particles as small as 2nm in relevant number concentration. These particles, although negligible in mass, were dominant in the PSDs.

By increasing the temperature, the Ar case (left column in Fig. 2), all reaction rates were faster, and the evolution of PSDs was harder to follow. In fact, since oxidation-induced fragmentation

can be seen as a particular event of the global oxidation, an increase in temperature increased the reaction rates of both processes. Accordingly, in the Ar case, a rise in number concentration of particles smaller than 5nm was clearly visible at 2.4mm, with hints of this rise just before and after this location. The shorter appearance of the peak of these small particles produced by oxidation-induced fragmentation was mainly because they were oxidized too fast to appear clearly and persist in the flame, as compared with the N₂ case. Similarly, the reduction in size and concentration of the larger particles was quicker in the Ar case, and a complete burn-out was reached at the end of the flame.

Interestingly, the He case (right column in Fig. 2) showed an opposite behavior; the temperature decrease resulted in incomplete oxidation of small and large particles. In fact, particles smaller than 5nm produced by oxidation-induced fragmentation persisted all along the flame, and complete burnout was not reached. This result shows how the global oxidation rate was sensitive to the oxidation-induced fragmentation and how, in certain conditions, smaller fragments were produced from larger particles which cannot be completely oxidized.

Some considerations on the nature of the small particles can be extrapolated from this analysis. The small particles, less than 10 nm, were formed from the break-up of primary particles meaning that their features, i.e., the internal structure down to the atomic level, could be more likely associable to a “*nano-soot*” rather than a large aromatic structure similar to an ensemble of PAHs with loose interconnections, which is typically found during the formation process. These differences could result in a different reactivity toward human health and/or toward after-treatment systems. Further studies on these particles will be needed to investigate more deeply their nature.

In order to better show the effect of oxidation-induced fragmentation on the number

concentration, Fig. 4 (left panel) shows the integrated particle number as a function of residence time for particles between 3 and 10 nm. The highest temperature case, Ar, showed the smallest rise in number concentration, followed by N_2 and, finally, He - the lowest temperature case. This again is evidence on the competition between oxidation-induced fragmentation, producing small particles in high number concentration, and global oxidation process that reduces their amount.

Since the diluents have different thermo-fluid dynamic characteristics, there were also slight differences in the combustion environment and initial PSDs. Fig. 4 (right panel) illustrates the model results for the integrated number concentration where the experimental temperature profiles from Fig. 4a were used, but N_2 replaced Ar and He, and identical initial PSDs - namely the one measured in the N_2 case, were used. This numerical investigation strengthens the important role of temperature in oxidation-induced fragmentation.

4.2. The effect of fuel lean and fuel rich condition

Previous studies showed the importance of fragmentation in fuel-lean conditions where molecular oxygen plays a key role. In this section results from a fuel-rich second burner are presented to understand the role of oxidation-induced fragmentation under this condition. The results are compared with the reference case, fuel-lean, N_2 as diluent.

Changing the equivalence ratio in the second burner resulted in changing the concentration of O_2 which directly affects the temperature and combustion chemistry. In the previous section, it was found that oxidation-induced fragmentation was strongly dependent on the temperature while the gas species profiles were kept similar for all the flames. The temperature profile measured in the fuel-rich case is reported in the Fig. 5 together with the reference case. The temperature in the rich flame was lower than in lean N_2 case, namely, 50 K less than the reference case, and the location of maximum temperature was shifted toward the burner. Also, the fuel-rich

case temperature was higher than the He case previously presented (about 30 K).

In Fig. 6, the measured and predicted gas profiles for the fuel-rich case (left panel) are reported against residence time. For the sake of clarity, the reference case gas profiles are reported as well (right panel). The modeled profiles were shifted away from the burner by 2.5mm as previously described. Gas concentration profiles show that O_2 concentration was initially higher for the lean case than for the rich case, the latter exhibiting an oxygen concentration of 2-4% in the main reaction zone.

In Fig. 7, measured and modeled PSDs for the lean N_2 case and fuel-rich case are reported. The model predictions were in good agreement with experimental data, especially in matching when the oxidation-induced fragmentation became effective. In the fuel-rich case (right), the initial PSD was similar to the one measured in lean cases: the PSD was centered on 40nm, and there were no particles smaller than 4nm mobility diameter. The increase in number concentration of the small particles in the rich case was present at 1.6 and 2.4mm and persisted along the flame. Finally, the particle concentration was reduced, but a complete burnout was not reached. The rise in the number concentration of the small particles was a net effect of the competition between oxidation-induced fragmentation and global oxidation. Due to overall rich conditions, global oxidation was slower, and molecular oxygen contributed at lower flame heights where it was present. As the flame front was passed, the oxidation was mainly due to OH radical, since molecular oxygen was present in negligible concentrations. In the fuel-rich case, small particles reached higher concentrations as compared to the lean N_2 case where they were continuously oxidized.

4.3. Sensitivity analysis

A sensitivity analysis is presented to understand the role of the different pathways in the

oxidation-induced fragmentation process. The lean N_2 case was chosen due to the apparent presence of the rise in the number concentration of small particles as well as the presence of complete burn out at the end of the flame. The two different mechanisms of oxidation-induced fragmentation, namely aggregate fragmentation and single-particle fragmentation were alternatively removed from the model to investigate their role.

In Fig. 8, modeled PSDs obtained with the complete model (continuous line), as well as those obtained from “switching off” the oxidation-induced fragmentation mechanisms are reported and compared with experimental PSDs. It is possible to see that the switching off the different mechanisms of oxidation-induced fragmentation resulted in different PSD trends. In particular, just accounting for the aggregate fragmentation cannot explain the rise in the particles smaller than 5nm. These small particles must come from single particle fragmentation. In Fig. 8 the modeled PSDs produced with aggregates fragmentation only (dashed line, center panels) followed the complete model for the large particles earlier in the flame— up to 2.4 mm HAB - but it produced a unimodal distribution. Also, the size of the larger particles decreased overall, but the modeled PSDs failed to match the experimental data. These findings are in accordance with a similar sensitivity analysis previously conducted [33].

On the other hand, when accounting solely for single particle fragmentation (dotted line, left panels), the first increase in number concentration (between 1.6mm and 2.4mm in the Fig. 8) was predicted. However, once all these particles were consumed (at 3.2mm in the Fig. 8), the number concentration suddenly decreased, not matching the complete model and the experimental data. Moreover, this model completely failed to match the change in the size of the large particles and burnout.

Finally, when both mechanisms of oxidation-induced fragmentation were switched off (long

dashed line, right panels), the model which accounts for the single particle fragmentation and the model without any fragmentation collapsed for larger particles at higher heights above the burner. These results suggest that the complete model cannot be considered as just the sum of the two mechanisms since a synergistic effect was present. Aggregate fragmentation gradually produced smaller aggregates, and eventually single particles, which were, in turn, fragmented, producing smaller particles. In addition, global oxidation was taking place, competing with the fragmentation mechanisms and contributing to particle burn out.

5. Conclusions

A systematic study of the effect of temperature and oxygen mixing on oxidation-induced fragmentation of soot aggregates and particles has been conducted. Soot particle size distributions, measured during the oxidation process in a two-stage burner [30], were modeled with a Multi-Sectional method that accounts for oxidation-induced fragmentation. The model parameters had been previously tested in premixed and diffusion flames. Without changing any parameters, the model reproduced the evolution of PSD over a wide range of temperature and oxygen-mixing conditions quite closely.

Overall the model suggests that oxidation-induced fragmentation processes and the oxidation rates were very sensitive to the temperature. A decrease in temperature can induce a global slowdown of the oxidation process. As a net result, oxidation-induced fragmentation produced a large number of small particles, not completely oxidized. On the contrary, an increase of temperature can enhance the global oxidation process and small particles produced by oxidation-induced fragmentation were quickly oxidized. Fuel-rich and fuel-lean results suggest that in the presence of relevant oxygen concentration, even for a short time, e.g., in the preheating zone of

the investigated fuel-rich flame, oxidation-induced fragmentation took place. Small particles can then be emitted if the complete oxidation is not reached. These local conditions can be likely found in turbulent flames where there is a continuous mixing between the combustion by-products and the fresh fuel/air mixture.

Finally, the sensitivity analysis conducted with the Multi-Sectional method indicated that aggregate fragmentation dominates the process of mass reduction whereas particle fragmentation was responsible for the increase of small particle number concentration. However, both mechanisms were needed for the correct prediction of the evolution of particle size distribution.

The understanding of oxidation-induced fragmentation was aided by the use of the Multi-Sectional model. In particular, the need for considering both aggregate and particle fragmentation to follow the evolution of PSD during soot oxidation was clearly verified. Both these process strongly influence the total burn out and the size of emitted particles and, as such, should be included in models for soot prediction.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. 1133480 while Dr. Lighty served at the National Science Foundation. Any opinions, findings, and conclusions expressed in this publication are those of the authors and do not necessarily reflect the views of the National Science Foundation.

MS and AD'A acknowledge the financial support of Accordo di Programma MSE/CNR PAR 2013-2014 "Miglioramento dell'efficienza energetica dei sistemi di conversione locale di energia".

573 **References**

- [1] H. Jander, H.G. Wagner, Soot formation in combustion, in: Int. Round Table Discuss. (Vandenhoeck Ruprecht, Gottingen), 1990.
- [2] H.E. (Ed) Bockhorn, Soot Formation in Combustion (Mechanisms and Models), 1994.
- [3] H. Bockhorn, A. D’Anna, A.F. Sarofim, H. Wang, (EDs.), Combustion Generated Fine Carbonaceous Particles, KIT Scientific Publishing, 2009. <https://books.google.com/books?id=8-Dk399oJwUC>.
- [4] A. D’Anna, Combustion-formed nanoparticles, Proc. Combust. Inst. 32 (2009) 593–613.
- [5] H. Wang, Formation of nascent soot and other condensed-phase materials in flames, Proc. Combust. Inst. 33 (2011) 41–67.
- [6] P. Pedata, N. Bergamasco, A. D’Anna, P. Minutolo, L. Servillo, N. Sannolo, et al., Apoptotic and proinflammatory effect of combustion-generated organic nanoparticles in endothelial cells., Toxicol. Lett. 219 (2013) 307–314.
- [7] P. Pedata, T. Stoeger, R. Zimmermann, R. Zimmermann, A. Peters, G. Oberdorster, et al., “Are we forgetting the smallest, sub 10 nm combustion generated particles?,” Part. Fibre Toxicol. 12 (2015) 34.
- [8] J.H. Seinfeld, S.N. Pandis, Editors., Atmospheric chemistry and physics: from air pollution to climate change, 2nd Edition., Wiley, 2006.
- [9] A. D’Anna, M. Sirignano, M. Commodo, R. Pagliara, P. Minutolo, An Experimental and Modelling Study of Particulate Formation in Premixed Flames Burning Methane, Combust. Sci. Technol. 180 (2008) 950–958.
- [10] M. Sirignano, A. Collina, M. Commodo, P. Minutolo, A. D’Anna, Detection of aromatic hydrocarbons and incipient particles in an opposed-flow flame of ethylene by spectral and time-resolved laser induced emission spectroscopy, Combust. Flame. 159 (2012) 1663–1669.
- [11] M. Alfè, B. Apicella, R. Barbella, A. Tregrossi, A. Ciajolo, Distribution of Soot Molecular Weight/Size along Premixed Flames as Inferred by Size Exclusion Chromatography, Energy & Fuels. 21 (2007) 136–140.
- [12] M. Alfè, B. Apicella, R. Barbella, J.N. Rouzaud, A. Tregrossi, A. Ciajolo, et al., Structure–property relationship in nanostructures of young and mature soot in premixed flames, Proc. Combust. Inst. 32 (2009) 697–704.
- [13] A. D’Alessio, A.C. Barone, R. Cau, A. D’Anna, P. Minutolo, Surface deposition and coagulation efficiency of combustion generated nanoparticles in the size range from 1 to 100 nm, J. Aerosol Sci. 100 (2016) 1–12.

606 10 nm, *Proc. Combust. Inst.* 30 (2005) 2595–2603.

607 [14] A. D'Alessio, A. D'Anna, P. Minutolo, L.A. Sgro, A. Violi, On the relevance of surface
608 growth in soot formation in premixed flames., *Proc. Combust. Inst.* 28 (2000) 2547–2554.

609 [15] M.D. Smooke, M.B. Long, B.C. Connelly, M.B. Colket, R.J. Hall, Soot formation in
610 laminar diffusion flames., *Combust. Flame.* 143 (2005) 613–628.

611 [16] M.M. Maricq, N. Xu, The effective density and fractal dimension of soot particles from
612 premixed flames and motor vehicle exhaust, *J. Aerosol Sci.* 35 (2004) 1251–1274.

613 [17] L.A. Sgro, A. Borghese, L. Speranza, A.C. Barone, P. Minutolo, A. Bruno, et al.,
614 Measurements of Nanoparticles of Organic Carbon and Soot in Flames and Vehicle
615 Exhausts., *Environ. Sci. Technol.* 42 (2008) 859–863.

616 [18] J.S. Lighty, J.M. Veranth, A.F. Sarofim, Combustion Aerosols: Factors Governing Their
617 Size and Composition and Implications to Human Health, *J Air Waste Manag Assoc.* 50
618 (2000) 1565–1622.

619 [19] B.R. Stanmore, J.F. Brillhac, P. Gilot, The oxidation of soot: a review of experiments,
620 mechanisms and models, *Carbon N. Y.* 39 (2001) 2247–2268.

621 [20] A. Veshkini, S.B. Dworkin, M.J. Thomson, A soot particle surface reactivity model
622 applied to a wide range of laminar ethylene/air flames., *Combust. Flame.* 161 (2014)
623 3191–3200.

624 [21] M. Frenklach, Reaction mechanism of soot formation in flames, *Phys. Chem. Chem. Phys.*
625 4 (2002) 2028–2037.

626 [22] N. Morgan, M. Kraft, M. Balthasar, D. Wong, M. Frenklach, P. Mitchell, Numerical
627 simulations of soot aggregation in premixed laminar flames, *Proc. Combust. Inst.* 31
628 (2007) 693–700.

629 [23] M.S. Celnik, M. Sander, A. Raj, R.H. West, M. Kraft, Modelling soot formation in a
630 premixed flame using an aromatic-site soot model and an improved oxidation rate, *Proc.*
631 *Combust. Inst.* 32 (2009) 639–646.

632 [24] J. Nagle, R.F. Strickland-Constable, Oxidation of carbon between 1000 and 2000°C, in:
633 *Proc. Conf. Carbon*, 5th, 1961: pp. 154–164.

634 [25] K.G. Neoh, J.B. Howard, A.F. Sarofim, Soot oxidation in flames., in: *Proceeding*
635 *Combust. Inst.*, Plenum, 1981: pp. 261–282.

636 [26] K.G. Neoh, J.B. Howard, A.F. Sarofim, Effect of Oxidation on the Physical Structure of
637 Soot, in: *Proceeding Combust. Inst.*, 1985: pp. 951–957.

- 638 [27] C.A. Echavarria, I.C. Jaramillo, A.F. Sarofim, J.S. Lighty, Burnout of soot particles in a
639 two-stage burner with a JP-8 surrogate fuel, *Combust. Flame.* 159 (2012) 2441–2448.
- 640 [28] C.A. Echavarria, I.C. Jaramillo, A.F. Sarofim, J.S. Lighty, Studies of soot oxidation and
641 fragmentation in a two-stage burner under fuel-lean and fuel-rich conditions, *Proc.*
642 *Combust. Inst.* 33 (2011) 659–666.
- 643 [29] H. Ghiassi, P. Toth, J.S. Lighty, Sooting Behaviors of n-Butanol and n-Dodecane Blends,
644 *Combust. Flame.* 161 (2013) 671–679.
- 645 [30] H. Ghiassi, P. Toth, I.C. Jaramillo, J.S. Lighty, Soot oxidation-induced fragmentation:
646 Part 2: Experimental investigation of the mechanism of fragmentation, *Combust. Flame.*
647 163 (2015) 170–178.
- 648 [31] H. Ghiassi, P. Toth, I.C. Jaramillo, J.S. Lighty, Soot oxidation-induced fragmentation:
649 Part 1: The relationship between soot nanostructure and oxidation-induced fragmentation,
650 *Combust. Flame.* 163 (2015) 179–187.
- 651 [32] M.E. Mueller, G. Blanquart, H. Pitsch, Modeling the oxidation-induced fragmentation of
652 soot aggregates in laminar flames, *Proc. Combust. Inst.* 33 (2011) 667–674.
- 653 [33] M. Sirignano, J. Kent, A. D’Anna, Modeling formation and oxidation of soot in
654 nonpremixed flames, *Energy & Fuels.* 27 (2013) 2303–2315.
- 655 [34] M. Sirignano, J. Kent, A. D’Anna, Further experimental and modelling evidences of soot
656 fragmentation in flames, *Proc. Combust. Inst.* 35 (2015) 1779–1786.
- 657 [35] H. Ghiassi, I.C. Jaramillo, J.S. Lighty, Kinetics of soot oxidation by molecular oxygen in a
658 premixed flame, *Energy & Fuels.* (2016).
- 659 [36] S.J. Harris, M.M. Maricq, The role of fragmentation in defining the signature size
660 distribution of diesel soot, *J. Aerosol Sci.* 33 (2002) 935–942.
- 661 [37] Q. Zhang, M.J. Thomson, F. Guo, H.; Liu, G.J. Smallwood, Modeling of Oxidation-
662 Driven Soot Aggregate Fragmentation in a Laminar Coflow Diffusion Flame, *Combust.*
663 *Sci. Technol.* 182 (2010) 491–504.
- 664 [38] R. Puri, T.F. Richardson, R.J. Santoro, R.A. Dobbins, Aerosol dynamic processes of soot
665 aggregates in a laminar ethene diffusion flame, *Combust. Flame.* 92 (1993) 320–323.
- 666 [39] F. Xu, A.M. El-Leathy, C.H. Kim, G.M. Faeth, Soot surface oxidation in hydrocarbon/air
667 diffusion flames at atmospheric pressure, *Combust. Flame.* 132 (2003) 43–57.
- 668 [40] C.P. Fenimore, G.W. Jones, Oxidation of soot by hydroxyl radicals, *J. Phys. Chem. A.* 71
669 (1967) 593–597.

- 670 [41] M.E. Mueller, Q.N. Chan, N.H. Qamar, B.B. Dally, H. Pitsch, Z.T. Alwahabi, et al.,
671 Experimental and computational study of soot evolution in a turbulent nonpremixed bluff
672 body ethylene flame., *Combust. Flame.* 160 (2013) 1298–1309.
- 673 [42] A. Attili, F. Bisetti, M.E. Mueller, H. Pitsch, Formation, growth, and transport of soot in a
674 three-dimensional turbulent non-premixed jet flame., *Combust. Flame.* 161 (2014) 1849–
675 1865.
- 676 [43] A.R. Kerstein, B.F. Edwards, Percolation model for simulation of char oxidation and
677 fragmentation time-histories., *Chem. Eng. Sci.* 42 (1987) 1629–1634.
- 678 [44] R. Chirone, L. Massimilla, P. Salatino, Comminution of carbons in fluidized bed
679 combustion, *Prog. Energy Combust. Sci.* 17 (1991) 297–326.
- 680 [45] M. Sirignano, J. Kent, A. D’Anna, Detailed modeling of size distribution functions and
681 hydrogen content in combustion-formed particles, *Combust. Flame.* 157 (2010) 1211–
682 1219.
- 683 [46] A. D’Anna, M. Sirignano, J. Kent, A model of particle nucleation in premixed ethylene
684 flames, *Combust. Flame.* 157 (2010) 2106–2115.
- 685 [47] M. Sirignano, M. Alfè, A. Tregrossi, A. Ciajolo, A. D’Anna, Experimental and modeling
686 study on the molecular weight distribution and properties of carbon particles in premixed
687 sooting flames, *Proc. Combust. Inst.* 33 (2011) 633–640.
- 688 [48] M. Sirignano, M. Conturso, A. D’Anna, Effect of furans on particle formation in diffusion
689 flames: An experimental and modeling study, *Proc. Combust. Inst.* 35 (2015) 525–532.
- 690 [49] G. Blanquart, H. Pitsch, Analyzing the effects of temperature on soot formation with a
691 joint volume-surface-hydrogen model, *Combust. Flame.* 156 (2009) 1614–1626.
- 692 [50] S. Mosbach, M.S. Celnik, A. Raj, M. Kraft, H.R. Zhang, S. Kubo, et al., Towards a
693 detailed soot model for internal combustion engines, *Combust. Flame.* 156 (2009) 1156–
694 1165.
- 695 [51] S.B. Dworkin, Q. Zhang, M.J. Thomson, N.A. Slavinskaya, U. Riedel, Application of an
696 enhanced PAH growth model to soot formation in a laminar coflow ethylene/air diffusion
697 flame, *Combust. Flame.* 158 (2011) 1682–1695.
- 698 [52] A. Raj, M. Celnik, R. Shirley, M. Sander, R. Patterson, R. West, et al., A statistical
699 approach to develop a detailed soot growth model using PAH characteristics, *Combust.*
700 *Flame.* 156 (2009) 896–913.
- 701 [53] A. Raj, M. Sander, V. Janardhanan, M. Kraft, A study on the coagulation of polycyclic
702 aromatic hydrocarbon clusters to determine their collision efficiency, *Combust. Flame.*
703 157 (2010) 523–534.

- 704 [54] M. Sander, R.I.A. Patterson, A. Braumann, A. Raj, M. Kraft, Developing the PAH-PP
705 soot particle model using process informatics and uncertainty propagation, *Proc. Combust.*
706 *Inst.* 33 (2011) 675–683.
- 707 [55] T.S. Totton, D. Chakrabarti, A.J. Misquitta, M. Sander, D.J. Wales, M. Kraft, Modelling
708 the internal structure of nascent soot particles, *Combust. Flame.* 157 (2010) 909–914.
- 709 [56] A. D’Anna, A. Violi, Detailed Modeling of the Molecular Growth Process in Aromatic
710 and Aliphatic Premixed Flames, *Energy & Fuels.* 19 (2005) 79–86.
- 711 [57] A. D’Anna, Detailed Kinetic Modeling of Particulate Formation in Rich Premixed Flames
712 of Ethylene, *Energy & Fuels.* 22 (2008) 1610–1619.
- 713 [58] K.G. Neoh, Soot burnout in flames, Massachusetts Institute of Technology, 1980.
714 <http://hdl.handle.net/1721.1/15866>.
- 715 [59] H. Ghiassi, Soot oxidation and the mechanisms of oxidation-induced fragmentation in a
716 two-stage burner for ethylene and surrogate fuels, Utah, 2015.
- 717 [60] C. McEnally, Ü. Köylü, L.D. Pfefferle, D.E. Rosner, D.C.S. McEnally, U.O. Koylu, et al.,
718 Soot volume fraction and temperature measurements in laminar non-premixed flames
719 using thermocouples, *Combust. Flame.* 109 (1997) 701–720.
- 720 [61] B. Zhao, Z. Yang, J. Wang, M. V. Johnston, H. Wang, Analysis of soot nanoparticles in a
721 laminar premixed ethylene flame by scanning mobility particle sizer, *Aerosol Sci.*
722 *Technol.* 37 (2003) 611–620.
- 723 [62] B. Zhao, Z. Yang, M. V Johnston, H. Wang, A.S. Wexler, M. Balthasar, et al.,
724 Measurement and numerical simulation of soot particle size distribution functions in a
725 laminar premixed ethylene-oxygen-argon flame, *Combust. Flame.* 133 (2003) 173–188.
- 726 [63] P. Minutolo, A. D’Anna, M. Commodo, R. Pagliara, G. Toniato, C. Accordino, Emission
727 of fine particles from natural gas domestic burners, *Environ. Eng. Sci.* 25 (2008) 1357–
728 1363.
- 729 [64] A. Kazakov, M. Frenklach, Dynamic Modeling of Soot Particle Coagulation and
730 Aggregation: Implementation With the Method of Moments and Application to High-
731 Pressure Laminar Premixed Flames, *Combust. Flame.* 114 (1998) 484–501.
- 732 [65] R.A. Dobbins, C.M. Megaridis, Morphology of flame-generated soot as determined by
733 thermophoretic sampling, *Langmuir.* 3 (1987) 254–259.
- 734 [66] S. Will, S. Schraml, K. Bader, A. Leipertz, Performance characteristics of soot primary
735 particle size measurements by time-resolved laser-induced incandescence., *Appl. Opt.* 37
736 (1998) 5647–5658.

- 737 [67] M. Lapuerta, F.J. Martos, J.M. Herreros, Effect of engine operating conditions on the size
738 of primary particles composing diesel soot agglomerates., *J. Aerosol Sci.* 38 (2007) 455–
739 466.
- 740 [68] M. Commодо, L.A. Sgro, P. Minutolo, A. D’Anna, Characterization of Combustion-
741 Generated Carbonaceous Nanoparticles by Size-Dependent Ultraviolet Laser
742 Photoionization., *J. Phys. Chem. A.* 117 (2013) 3980–3989.
- 743 [69] M. Commодо, G. De Falco, A. Bruno, C. Borriello, P. Minutolo, A. D’Anna,
744 Physicochemical evolution of nascent soot particles in a laminar premixed flame: from
745 nucleation to early growth., *Combust. Flame.* 162 (2015) 3854–3863.
- 746 [70] C.A. Echavarria, A.F. Sarofim, J.S. Lighty, A. D’Anna, Evolution of soot size distribution
747 in premixed ethylene/air and ethylene/benzene/air flames: Experimental and modeling
748 study, *Combust. Flame.* 158 (2011) 98–104.

749

750

Table 1

Table 1. Experimental conditions.

	ϕ_1^a	ϕ_{Overall}^b	ϑ^c	Secondary oxidizer composition
Lean N ₂ diluent (base case)	1.98	0.9	3.77	21% O ₂ –79% N ₂
Lean Ar diluent	1.98	0.9	3.77	21% O ₂ –79% Ar
Lean He diluent	1.98	0.9	3.77	21% O ₂ –79% He
Rich N ₂ diluent	1.98	1.15	3.77	21% O ₂ –79% N ₂

^a Equivalence ratio in the first burner

^b Overall Equivalence ratio

^c Cold gas velocity, cm/s (STP)

Figure 1

Fig. 1. Top burner temperature profiles as a function of HAB for the three different cases investigated: Ar diluent – highest flame temperature, N₂ diluent – medium flame temperature, He diluent - lowest flame temperature. Adapted from [30].

Figure 2

Fig. 2. Species concentration profiles measured at different residence time in the top burner for the three different case investigated [30]: Ar diluent – highest flame temperature (left), N₂ diluent – medium flame temperature (center), He diluent - lowest flame temperature (right). Model predictions are reported as continuous lines.

Figure 3

Fig. 3. PSDs measured at different heights above the top burner (from the bottom: 0, 0.8, 1.6, 2.4, 3.2, 4.0 and 4.8mm HAB) for the three different case investigated: Ar diluent – highest flame temperature (green - left), N₂ diluent – medium flame temperature (blue - center), He diluent - lowest flame temperature (red - right). Model predictions are reported as continuous lines.

Figure 4

Fig. 4. Modeled integrated number concentration of particles between 3nm and 10nm at different residence time in the top burner for the three different case investigated [30]: Ar diluent – highest flame temperature (continuous line green), N₂ diluent – medium flame temperature (continuous line blue), He diluent - lowest flame temperature (continuous line red) compared with experimental data (symbols); left. Right, model predictions using the same temperature profiles as the results on the left, but N₂ as diluent and same initial PSD for all cases.

Figure 5

Fig. 5. Top burner temperature profiles as a function of HAB for the rich and lean (N_2 as diluent) case investigated. Adapted from [30].

Figure 6

Fig. 6. Species concentration profiles measured at different residence time in the top burner for the rich (right) and lean (N2 as diluent, left) case investigated [30]. Model predictions are reported as continuous lines.

Figure 7

Fig. 7. PSDs measured at different heights above the top burner (from the bottom: 0, 0.8, 1.6, 2.4, 3.2, 4.0 and 4.8mm HAB) for the lean (N_2 as diluent, left [30]) and rich (right) cases investigated. Model predictions are reported as continuous lines.

Fig. 8. PSDs measured at different heights above the top burner (from the bottom: 0, 0.8, 1.6, 2.4, 3.2, 4.0 and 4.8mm HAB) for the lean case using N_2 as diluent [30]. Model predictions obtained with different fragmentation models are reported: complete model (continuous line); only particle fragmentation (dotted line – left column); only aggregate fragmentation (dashed line – center column) no fragmentation (long dashed line – right column).