Temperature and oxygen effects on oxidation-induced fragmentation of soot particles

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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.

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1. Introduction

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

Particle formation is not the only mechanism that contributes to the determination of the final particle emissions. In real com-

bustion devices, the oxidation processes play a determinant role for particle emissions. In fact, most of the emitted particles could be those escaping oxidation, usually during the last part of the combustion process within combustion devices or in the after-treatment system [16–19]. As a result of soot oxidation mechanism studies, semi-empirical reaction rates are used in a large number of models [20–23]. It is accepted that soot can be oxidized when it reacts with molecular oxygen (O_2) and hydroxyl radical (OH). Two kinetic expressions to account for the soot oxidation via O_2 and OH have been proposed by Nagle-Strickland-Constable (NSC) [24] and Neoh et al. [25], respectively. Although these reaction rates have been widely used, and result in fair agreement with experimental data, a deeper comprehension of the oxidation phenomena of combustion-generated particles is needed.

1.1. Phenomenology of oxidation-induced fragmentation

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 [27–31] conducted on a two-stage burner similar to Sarofim and Neoh, 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, CO_2, and H_2O, 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, O_2, 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 – O_2, plays a determinant role in fuel lean conditions. In fact, under these conditions, O_2 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 O_2 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] supported a similar mechanism for soot particles, finding in their experiments the appearance of a considerable number of sub-10 nm particles during particle oxidation. These sub-10 nm 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 ($\varnothing_{overall}$) 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