

MODELLING THE OXIDATION AND FRAGMENTATION OF SOOT PARTICLES IN FLAMES

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Abstract

Modeling of oxidation process of soot particles in flame has been attempted by using an advanced detailed kinetic model. Oxidation-induced fragmentation has been proven to be a determinant step for correct determination of the final soot particles both in terms of abundance and of particle size distribution function. Soot is generally found in large aggregates; however in some conditions it can be totally or partially oxidized. Recent experimental results by the Sarofim group have shown that a considerable number of particles below 10nm can be formed during oxidation of these aggregates. Surface oxidation is not able to explain the increase of small particles whereas fragmentation does. Fragmentation has to be taken into account to correctly predict the number concentration of the particle emitted from combustion systems. Kinetic rates for the fragmentation process are proposed and used to simulate experimental results on soot oxidation. Model has been tested to predict the evolution of particles in a two stage burner configuration. In particular soot was produced in rich condition in the first stage and successively oxidized in the second stage in lean conditions. Soot start from a unimodal size distribution peaked at 80nm and evolves into bimodal size distribution in which a first mode peaked at 2-5 nm is evident. These small particles have to come from fragmentation process. Kinetic expressions for fragmentation process proposed in this paper are able to predict the evolution of particle size distribution function along the flame.

Introduction

Emitted particles from real combustion devices are the result of processes as formation and oxidation. Both of them contribute to the final characteristics of the particles in terms of concentration, morphology and chemical composition. Formation and growth are surely the more studied aspects due to intrinsic possibility to isolate these processes from oxidation, e.g. in premixed rich flame. In fact nowadays formation and growth are known with great details due to large number of experimental techniques set up for particle characterization in situ and extra situ. Moreover models have given new tools for understanding kinetic pathway of formation and discriminate particle in terms of amount size distribution and chemical characteristic. However in real combustion systems, oxidation is strictly coupled with formation process, resulting determinant for final emissions [1]. In fact soot oxidation can affect soot emissions not just in terms of total mass but also in terms of chemical characteristics and morphology. On the contrary new combustion environments could form soot particles with different reactivity and, finally, different capability to be oxidized.

In order to isolate oxidation effects on soot particles new experiments have been set up through years. However few experiments have been implemented to systematically study high-temperature soot oxidation [2-5] whereas many effort has been devoted to the study of catalytic oxidation of soot due to industrial needs [6-8]. Due to this lack of experimental data, models have furnished in this sense few information and kinetic rate for soot oxidation implemented are usually semi-empirical [9-14]. However general considerations on soot

oxidation have been carried out and can be used as starting point for new numerical model able to predict soot evolution in oxidative environments.

Combustion environment is fundamental to individuate the soot oxidizing species. In fact soot is generally oxidized by OH radicals [2-3, 9-10] and molecular oxygen [4-5,11-14]; however the importance of these two different processes is depending on combustion environment.

OH radical has been considered as the most important species for oxidation in fuel rich condition, due to its abundance. On the contrary, oxygen plays a key role in lean conditions due to its large amount, temperature conditions and soot radical concentration. The two oxidizing mechanisms are often coupled in real combustion systems. In laminar coflowing diffusion flames OH results much more determining in the formation zone of the flame whereas oxygen is relevant in the top of the flame when burn out occurs. These two oxidizing species have a deeply different way to oxidize soot particles. In fact, OH is able to oxidize a stable species, whereas for O₂ oxidation the presence of radicals on the particles results to be fundamental. These mechanisms generally refer to surface oxidation but deeper penetration of oxidizing species can be possible in some conditions and can lead to different process.

Fragmentation of particles during oxidation is now generally accepted by the scientific community, although rate and modality are far from being understood. However from simple considerations it is possible to find out that fragmentation cannot be any longer neglected in numerical models. This process is changing soot particles not only in terms of shape but also in terms of number concentration, strongly affecting the total burnout rate. This problem is particular important in diesel particulate filter regeneration. In fact, oxidation in these devices induces the formation of a large number of very small particles affecting the environmental performance of the engine. Moreover, oxidation-induced fragmentation could change the chemical characteristics of the particles emitted in the atmosphere affecting the role of particulate on the human health and the climate change.

Recent studies on soot oxidation have furnished a clear demonstration that fragmentation occurs in certain conditions and strongly modifies the particle size distribution function (PSDF) [2-4]. These experiments are up to now the most direct way to compare numerical model of oxidation which include fragmentation process.

In this work, starting from a detailed mechanism for soot formation and growth, oxidation process has been modelled. In particular both surface oxidation and fragmentation have been considered. Model has been tested comparing the PSDF predicted with those measured by Echavarria et al. [4] in condition in which fragmentation occurs.

Model description

Soot formation and growth mechanisms

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 [15]. 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 [16-17]. This allows to follow not only the mass of the formed particles, but also their hydrogen content and internal structure.

The model is a first approach to follow the chemical evolution and internal structure of particles formed and oxidized in flames, 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 [18].

Morphological studies conducted on particles collected from flames have revealed that ordered and disordered carbons coexist in incipient soot particles. The order arises due to

stacking of planar polycyclic aromatic hydrocarbons (PAHs) to form parallel atomic layers; the disordered part is due to the presence of randomly oriented and/or non-planar PAHs. The combustion environment in which particles are formed determines their final concentration as well as their organization at atomic scale. PAH molecules have an important role as a soot precursor: their chemical structure and the combustion environment in which they are formed may control the nature of the particles.

Two broad classes of aromatic molecules have been considered: aromatics in which only π -bonds among C atoms exist (pericondensed aromatic hydrocarbons - PCAH) and aromatics having both σ - and π -bonds between C atoms consisting of incompletely-condensed oligomers of PCAH. Formation of PCAH is modeled by the H-Abstraction-Acetylene Addition mechanism. The molecular growth process is initiated by an H atom loss and continues by addition of acetylene. Their H/C ratio decreases to very low values as the molecular size increases; the largest of these compounds is a graphene sheet. When an aromatic compound, or its radical add to the radical site instead of acetylene, incompletely-condensed oligomers of aromatics are formed. The H/C ratio of the oligomers remains comparable to those of the aromatic molecules involved in the addition reactions and it remains quite unchanged as the molecular weight of the oligomers increases. Due to the less rigid structure of the σ -bond connecting the aromatic molecules, oligomers usually assume a non-planar structure. Both pericondensed and incompletely-condensed aromatics can grow indefinitely forming extremely large molecules. The molecular growth process competes with molecule oxidation by hydroxyl radical and O_2 molecules. Whereas PCAH can only add acetylene or other gaseous hydrocarbons (if an aromatic molecule is added an incompletely-condensed aromatic is formed), an incompletely-condensed aromatic can also undergo dehydrogenation reactions forming pericondensed molecules and they migrate in PCAH class.

Simultaneously with the chemical growth reactions, physical process of coagulation of PAHs to form particle nuclei is considered. The clustering process is due to van der Waals interaction among large condensed aromatics. Binding energies which form these clusters depend on the dimensions of the aromatic molecules and on the degree of condensation of the aromatic cycles.

PCAH have an intrinsic planar structure due to the absence of σ -bonds. The disposition of layers of molecules within these clusters follows the rule of minimum free energy. If the molecules arrange in parallel stacks, an ordered particle grows (crystallite). Structures which contain σ -bonds tend to assume a non-planar structure. The steric conformation of these molecules hinders π -electrons of the molecules to reach an interaction distance. This conformation is responsible for lower binding energies which result in less ordered particles (disordered). Dehydrogenation of molecules leads to a more pericondensed structure. As a result, dehydrogenation of particles induces planarity in the molecules included in the particle and increases the level of stacking. Interaction between aromatics belonging to non-planar structures can lead to the formation of multi-stacks connected by σ -bonds (cross-linking).

Particle nuclei can continue to add molecules to increase their sizes or they can coagulate with other particles maintaining invariant total mass. Two different kinds of coagulation can be considered: coalescence and agglomeration. Coalescence occurs when a molecule from the gas-phase or a small particle collides with a particle and the formed entity tends to reduce free surface to minimize free energy. This results in the inclusion of the colliding molecules or small particles in the larger ones. In larger particles, the timescale of the molecule or small particle inclusion into the particle is larger than the timescale of the coagulation process. In that case the colliding entities maintain their own structure and they aggregate to form agglomerate of particles.

More details on the hypothesis beyond the proposed kinetic model and on its features can be found in recent publications [15-16].

Soot oxidation and fragmentation

With respect to previous version of the model oxidation-induced fragmentation of the particles is now taken into account parallel to the growth and surface oxidation mechanisms. Since hydroxyl radical and molecular oxygen have been identified to be the dominant oxidizing species of soot in flames, oxidation has been generally modeled on the base of kinetic expression for these species. In principle both surface oxidation and oxidation induced fragmentation involve the same process. In fact, in both cases the event can be generally schematized as a carbon extraction from soot particles. The main difference relies in the fact that during fragmentation the carbon extraction is in such way critic and strongly affects the internal structure of soot species. This leads to a breaking up of the particle producing smaller fragments. The activation energy of the oxidation by OH is estimated from similar reactions for benzene and PAHs and the collision frequency accounts for the size of the particles involved. Oxidation by O₂ molecules uses the rate constant of naphthyl + O₂ accounting for the increase of collision frequencies of Xu et al [19]. These expression and in particular values for activation energy are considered equal in both surface oxidation and fragmentation whereas different collision frequency factor and other parameters have been considered.

Since fragmentation was not taken into account in the previous version of the model, some considerations have led to the definition of fragmentation process in terms of reaction rates. In particular criticism of carbon extraction in fragmentation process is here described.

Particles are held together in form of aggregates or single primary particles by physical interactions of the aromatic compounds within structures and by internal cross-linking. A reduction of the dimension of the aromatic edges (responsible for physical interaction) or the destruction of the internal cross-linking for effect of the oxidation process can weaken the structure and aggregates or single particles can break apart.

Since the model separately accounts for aggregates and primary particles different fragmentation processes have to be considered.

Fragmentation is considered forming two new entities of equal mass. This process will involve aggregates with large sizes able to contain a large number of primary particles. However, successive splitting up of large aggregates can lead to small aggregates formed only by two primary particles. In this case an eventual fragmentation will form primary particles. Fragmentation can involve also primary particles. In this case internal burning leads to fragment single particle into smaller clusters. This process can continue producing very small fragments.

These simple considerations describe all the fragmentation process. Schematic sketch reported in Fig.1 can help to figure out the processes described. It is worth to note that growth and fragmentation appear as different direction in the same evolution path.

Since fragmentation is related to an internal burning of soot, molecular oxygen is considered to be less reactive than OH and hence the only species able to not react on the surface and diffuse towards the points of contact of the primary particles. Larger aggregates have an higher number of contact points and their oxidation-induced fragmentation is considered to be more likely as the size increases. A linear dependence with size of aggregates is considered in this paper.

Aggregates composed by two primary particles are hard to be found, especially with sizes less than 20nm. This suggests that the capability of these aggregates to maintain their shape is weaker with decreasing size. In other words, aggregates of very small sizes are considered to have an high capability to undergo fragmentation process and produce primary particles.

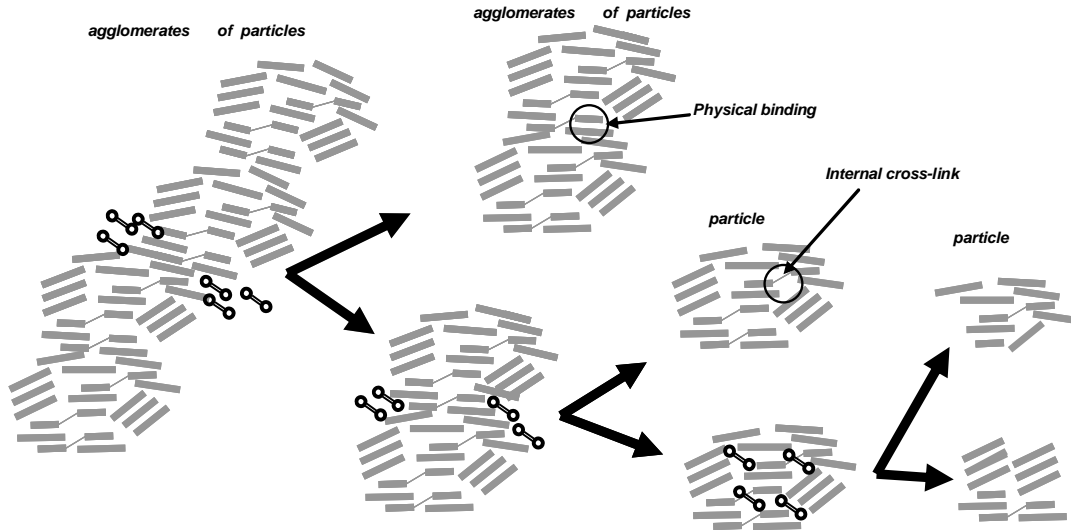


Figure1: Schematic sketch of soot fragmentation; Oxygen molecules are reported in black

As stated before, fragmentation of primary particles is related to the weakening of internal forces, mainly constitute by physical interaction and cross-linking. The strength necessary to maintain together the particle increases as the size of the particle increases. As a consequence, primary particle fragmentation has been considered to linearly increase with particle size itself.

The kinetic expressions used for fragmentation are reported in equations 1-3 as a function of the O₂ oxidation rate:

$$K_{\text{Frag A} \Rightarrow \text{A}} = K_{\text{Oxy}} \gamma_{0 \text{ A} \Rightarrow \text{A}} N_{\text{C}}; \quad \gamma_{0 \text{ A} \Rightarrow \text{A}} = 1\text{E-}13 \quad (1)$$

$$K_{\text{Frag A} \Rightarrow \text{P}} = K_{\text{Oxy}} \gamma_{0 \text{ A} \Rightarrow \text{P}} N_{\text{C}}^{-1}; \quad \gamma_{0 \text{ A} \Rightarrow \text{P}} = 1 \quad (2)$$

$$K_{\text{Frag P} \Rightarrow \text{P}} = K_{\text{Oxy}} \gamma_{0 \text{ P} \Rightarrow \text{P}} N_{\text{C}}; \quad \gamma_{0 \text{ P} \Rightarrow \text{P}} = 1\text{E-}4 \quad (3)$$

Size dependence is accounted for through the number of C atoms (N_{C}) in the expression of the kinetic constants

Fragmentation model is generally based on morphological consideration on the processes involved. The rate constants used in the equations 1-3 are not coming directly from gas kinetic considerations and can be affected by uncertainties. However, even if the absolute value can strongly affect the total soot burnout rate, the effect on particle size distribution function is determined just by the ratio between different fragmentation processes

Typical values of the oxidation rate with respect to fragmentation for selected numbers of C atoms in the aggregates/particles are reported in table 1.

Table 1. Ratio between oxidation rate by O₂ and different fragmentation rates; N_{c} is the number of carbon atoms.

N_{c}	D, nm	$\frac{K_{\text{Oxy}}}{K_{\text{FragA} \Rightarrow \text{A}}}$	$\frac{K_{\text{Oxy}}}{K_{\text{FragA} \Rightarrow \text{P}}}$	$\frac{K_{\text{Oxy}}}{K_{\text{FragP} \Rightarrow \text{P}}}$
10^4	7	1.E+09	1.E+04	5.E-01
10^6	40	1.E+07	1.E+06	5.E-03
10^8	160	1.E+05	1.E+08	5.E-05

Model validation

Model has been tested by following the evolution of the particle size distribution functions in oxidative environment. Data are taken from Echavarria et al. experimental set up [4] which has been previously used by Neoh et al. [2-3] to study soot oxidation. The experimental apparatus consists in a two stage burner: soot is produced in a first stage burner by a rich premixed flame and successively sent together with an excess of air to a second stage burner in which it is oxidized. This particular set up allow us to investigate several conditions of soot oxidation. In particular it is possible to tune the overall and the second stage equivalent ratio in order to increase the relative abundance of O₂ and OH and hence the relative importance of oxidation and fragmentation mechanisms.

In the present work only lean was analysed condition which exhibits more clearly the fragmentation process.

Particles were collected with a horizontal probe and analysed by an SMPS which allows to obtain PSDF down to 3nm. Experimental data reported in Fig.2 clearly show that the size distribution function evolves in the second burner producing particles as small as 3 nm which were not present in the initial PSDF (that coming from the first stage burner) and most likely come from fragmentation. Basically most part of the initial PSDF is constituted of very large particles that can be generally considered aggregates of primary particles. The initial PSDF is used as input to the model and it is reported in comparison with experimental data in the figure (HAB=0mm). Evolution of the PSDF at different heights above the second stage burner is reported in the same figure. It is possible to see how small fragments are formed quite soon by fragmentation of primary particles. Moreover fragmentation of large aggregates into smaller aggregates reduces the mean dimension and peak position. Model is able to reproduce quite well both the total burn out rate and the change in shape of PSDF.

Figure 2 also shows the evolution of the PSDF when fragmentation is not considered. It is worth to note that the oxidation rate alone is not able to reproduce the total burnout rate and the change in the shape of the PSDF. In particular production of very small particles is not clearly evidenced. Model results were shifted by 2.5 mm in order to compensate the cooling down of temperature due to the presence of the probe. This shift has been operated several times when model results are compared with experimental data taken from SMPS.

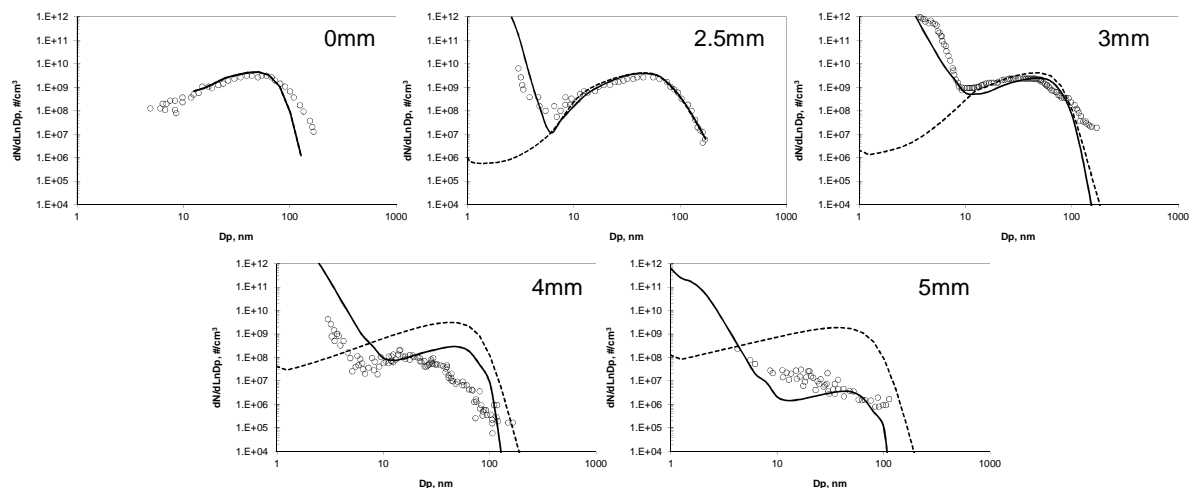


Figure 2: Particle size distribution functions at different height above the burner in lean conditions. Previous oxidation model as dashed line, model which contains fragmentation as continuous line Data (dots) are taken by [4]

To better evidence the agreement with experimental data in Fig.3 cumulative PSDF are reported. Particles larger and smaller than 10nm are separately grouped to show fragmentation process. From Fig.3 it appears that fragmentation strongly affects total number of small particles whereas large particles do not exhibit an increase in number. After a fast fragmentation process, burn out involves both large and small particles reducing the number concentration by orders of magnitude. The model is able to reproduce quite well the effect.

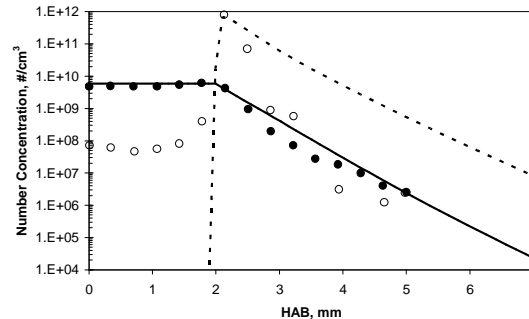


Figure 3: Number concentration of particles as function of height above the burner. Particles larger than 10nm (●, —) and particles from 3nm to 10nm (○, - -) are reported. Experimental data (dots) are taken by [4].

Principal gaseous by-products were also collected. Looking at gas profile in Fig.4 the cooling down appears evident looking at oxygen concentration that starts to decrease after 2.5mm. Moreover general good agreement between gas phase data and model prediction is found. This can be further support to some final considerations on soot oxidation and fragmentation. Looking at oxygen concentration it is possible to note that it remains quite constant up to 3mm and then suddenly decreases. This behaviour suggests that probe affects the flame temperature, cooling down the system and avoiding oxidation takes place. This is in accordance also with modelled and experimental evolution of particles size distribution functions described above.

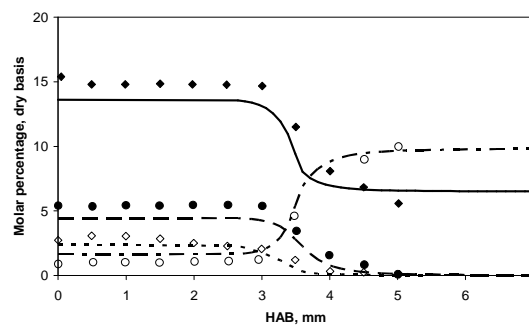


Figure 4: Modelled and experimental gas profile of O₂ (◆, —) H₂(◇, - -) CO(●, —) and CO₂ (○, - -). Data are taken by [4]

Conclusions

An enhanced model to predict oxidation induced fragmentation has been proposed. Model starts from a detailed kinetic model based on sectional approach which allows to account for particles size distribution function, hydrogen content and state of aggregation of particles. Starting from morphological considerations kinetic expression for fragmentation rate has been carried out. Fragmentation is mainly linked with oxidation by O₂ and it is related to the dimension of particles. Two pathways for fragmentation process were individuated: large

aggregates can fragment forming smaller aggregates or primary particles; primary particles can break up producing smaller clusters down to few nanometers.

Model was tested against particles size distribution functions sampled in a second stage burner set up for oxidation studies. Particles fed to this burner are larger than 10nm. Evolution of PSDF exhibits a mode peaked at 3nm during oxidation process. These particles come from fragmentation. Model is able to reproduce quite well both total burn out rate and change in shape of PSDF. Comparison with oxidation rate not considering fragmentation shows underestimation of total oxidation rate and small particle production.

Oxidation-induced fragmentation results of fundamental importance for the correct prediction of final emitted PSDF. Moreover it can affect also the chemical characteristic of the emitted particles. This appears even more important for real combustion systems such as diesel engine or turbines which operate with large amount of oxygen and relatively high temperatures.

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