



Soot surface reactivity during surface growth and oxidation in laminar diffusion flames



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ABSTRACT

Soot surface reactivity is numerically studied in laminar ethylene/air and methane/air coflow diffusion flames. Surface reactions are found to be important for many processes involved in soot formation, including surface growth and oxidation which contribute significantly to soot yield. It has recently been shown that soot particle reactivity changes as particles age during both surface growth (Veshkini et al., 2014) and oxidation (Khosousi and Dworkin, 2015). A newly developed surface character model simultaneously accounts for soot surface reactivity in surface growth and oxidation by considering soot ageing and its effects on the particle surface, reconciling the aforementioned works. This new development eliminates tuning from case to case of one parameter used in soot numerical simulations, α , the portion of soot surface sites available for reaction, which is implemented as a function of temperature and residence time (particle history). Thus, the new model reconciles the quantification of the evolving soot surface character for both growth and oxidation. The model is shown to be uniquely capable of predicting soot concentrations and smoke emissions within experimental uncertainty in a wide range of laminar diffusion sooting flames, without any variation of model parameters.

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1. Introduction

Soot emissions pose a potent threat to human health and should be avoided in combustion systems [1]. Soot is a leading contributor to the darkening of cityscapes and air pollution in the urban environment [1]. Environmental and health issues lead combustion device designers to attempt to reduce combustion-generated soot emissions; however, this challenge requires a comprehensive understanding of the physics of combustion, especially that of soot formation, which is particularly complex and remains poorly understood today. A complete understanding of this phenomenon is crucial to meet the required demands of reduced pollution. Since soot is a major health hazard in the urban environment, its pre-emission consumption in combustion is extremely important. Soot particle formation is a highly complex multi-physics phenomenon that includes fluid mechanics, heat transfer, thermodynamics, and multiphase flows [2]. Much progress has been made in the numerical modelling of combustion and soot formation in recent years [3–11]. Numerical modelling of soot formation and oxidation is very challenging in that it involves complex processes including those contributing to the formation and growth of soot particles, such

as inception, condensation, surface growth, and coagulation, and those contributing to the destruction of soot particles, such as oxidation and fragmentation. Therefore, an accurate model which predicts soot formation in flames requires precise models for these processes.

The precision of soot particle dynamics models strongly depends on the accuracy of the predictions for species and PAH concentrations, which are used in the sectional particle dynamics submodels to compute soot growth and oxidation rates. Therefore, for accurate prediction capabilities of the numerical modelling of soot formation, detailed chemical kinetic mechanisms for gas-phase reactions are required. The widely used mechanism developed by [3] attributes the growth of PAH soot precursors and also the growth of soot surfaces to hydrogen-abstraction-carbon-addition (HACA). This mechanism has been effectively used in various numerical studies to model soot formation [4–6,12,13], representing a major step towards quantitative prediction. Slavinskaya and Frank [7] presented a more comprehensive PAH growth mechanism, which introduced additional reaction pathways for PAH formation and allowed for abstraction and growth in the HACA mechanism by additional species. This mechanism that has been widely validated for a variety of flames and conditions [8,9,14–16] permits the use of more physical assumptions about the number of active sites on the soot particle and is used in the present study. The use of this mechanism has been shown to produce more accurate predictions of aromatic and soot concentrations on the

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Table 1
HACA-based soot surface growth and oxidation reactions [3], $k = AT^b e^{-E_a/RT}$.

No.	Reaction	A (cm ³ /mol s)	b	E _a (kcal/mol)
S1	C _{soot} -H + H ⇌ C _{soot} + H ₂	4.2 × 10 ¹³	0.0	13.0
S2	C _{soot} -H + OH ⇌ C _{soot} + H ₂ O	1.0 × 10 ¹⁰	0.73	1.43
S3	C _{soot} + H → C _{soot} -H	2.0 × 10 ¹³	0.0	0.0
S4	C _{soot} + C ₂ H ₂ → C _{soot} -H + H	8.0 × 10 ⁷	1.56	3.8
S5	C _{soot} + O ₂ → 2CO + product	2.2 × 10 ¹²	0.0	7.5
S6	C _{soot} -H + OH → CO + product		γ _{OH} = 0.13	

centreline, providing a better foundation to study the surface reactivity of soot.

2. Soot surface reactivity

The primary processes contributing to formation and growth of soot particles are inception, condensation, and surface growth. The surface reactivity of soot particles is an important factor in soot formation as surface growth is a significant contributor to soot yield and in some systems, it dominates [17]. Polycyclic aromatic hydrocarbons (PAHs), which are known to be the precursors to soot formation, collide and dimerize to form PAH clusters, which further combine or grow, leading to inception of soot particles. These incipient soot particles condense, aggregate, and grow through surface reactions, forming larger soot particles. Surface growth has been found to have a major impact on soot formation on the wings of the coflow diffusion flames [18].

In order to study the surface reactivity of soot, it is crucial to understand how surface reactions of soot and other species such as H₂, H₂O, H, C₂H₂, or O₂ could lead to soot growth/decay. Hydrogen-abstraction-carbon-addition (HACA) is known to be the main mechanism accountable for soot surface growth, while oxidation contributes to the decay of soot. Abstraction of an H atom from an arm-chair site on the soot particle provides a soot particle with an active (dehydrogenated) site which can react with H₂, H₂O, H, C₂H₂, or O₂. The reaction of this active site with acetylene (C₂H₂) leads to addition of two carbon atoms to the soot particle and formation of an additional aromatic ring at the active site, thus contributing to its surface growth. The reaction of the active site with O₂, however, leads to removal of carbon from the soot particle, translating into its decay. The rate expressions for HACA-based soot surface growth and oxidation, adopted from [3], are provided in Table 1.

It is known that the surface growth of the soot particles is a major contributor to soot mass yield. The surface of the soot particles reacts with the gaseous species when exposed to high temperatures. Reactivity of the soot surface, however, depends on the number of active/dehydrogenated sites which are available to react with stable gaseous species. The number of active sites per unit surface area is correlated to the concentration of C–H sites. It has been observed that the concentration of C–H sites decreases as soot matures, which confirms the experimental observations suggesting that the reactivity of surface sites changes with particle ageing [19–22]. It has been observed that the C/H ratio of a soot particle increases with particle residence time [23,24], resulting in the reduction of C–H sites and consequently reduced soot surface reactivity.

Frenklach and Wang [20] introduced the parameter α , which is based on the number of surface sites available for a given reaction, to account for particle orientation/collision probabilities and soot surface ageing. This parameter is used in numerical works to reconcile the inaccuracies associated with treating the sites on the soot surface like those on the corresponding PAH. The surface ageing effects were taken into account using α for calculation of reaction rates. Therefore, the rate of HACA surface growth (reaction S4) is calculated by

$$R_4 = \alpha k_4 [C_2H_2] [C_{soot}] \quad (1)$$

where k_4 is the per-site rate coefficient for C₂H₂ addition (for reaction S4), [C₂H₂] is the concentration of acetylene, and [C_{soot}] is the concentration of dehydrogenated sites given by

$$[C_{soot}] = \frac{A_s}{A_v} \chi_{C_{soot}} \quad (2)$$

in which A_s (cm²/cc) is the surface density of soot particles, A_v is Avogadro's number, and $\chi_{C_{soot}}$ is the number of dehydrogenated sites per unit soot surface area.

How best to implement α in the numerical models has been the subject of various studies [8,18,20]. It has been shown in the literature that treating α as a single, unchanged constant inhibits broad model applicability [18]. As a result, there have been many works suggesting that α varies with different flame properties. Much attention has been given to investigate the correlation between α and flame temperature, particle residence time, and particle size. A constant α has effectively been used in many numerical works to model HACA surface growth and soot formation [8,9,20,25], which provides sufficient accuracy to capture the correct trend of soot formation within different flame configurations. However, the value for α often needs to be adjusted as flame conditions vary. Using a constant value for α decreases the accuracy of soot modelling and adds a tunable modelling parameter as the peak soot is matched to the experimental values. It has been shown in [18] how the accuracy of using a constant α decreases as the dilution levels of the fuel increases. Referring to the importance of α to model surface growth using the HACA mechanism in soot formation, it is suggested that accurately predicting soot volume fraction in different flames requires using a non-constant (functional form) α . The use of a function for α is found to be crucial to capture the correct soot volume fraction on the wings of coflow flames due to the fact that surface growth is the primary process contributing to soot formation in this region. Different functions for α have been proposed in the literature, summarized in [18]. The initial focus of most works was on temperature-dependent functions. However, it soon became apparent that incipient soot particles, usually comprising small PAHs, are covered with more dense active sites. Therefore, the use of a function, dependent only on local temperature, results in unphysically low values of α for the young soot particles, suggesting that α should be a function of more than just local flame temperature. Furthermore, considering only local temperature in determining α ignores the relatively long characteristic times of soot growth, and the importance of particle history.

Veshkini et al. [18] studied various flame properties and their impact on α in surface growth regions. Their work showed that it is impossible to find a function for α based on either flame peak temperature or local temperature at the location of peak soot, which was also observed previously in the work of Singh et al. [26]. Veshkini et al. [18] further studied other flame properties and based their work on experimental observations suggesting that the age of a soot particle is a significant contributor to soot surface reactivity [27,28]. They combined the effects of temperature and the age of a soot particle, into one parameter, thermal age, defined as the integral of the temperature that a soot particle experiences over its residence time, $T_a = \int T dt$. This parameter accommodates the effects of both temperature and residence time. This definition implies that a soot particle

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