

Open issues in soot modeling

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Abstract

This report presents a summary of efforts to critically assess the current state of soot modeling with fire dynamics simulation as the focus to evolve a strategy for developing predictive models. A literature survey clearly indicated that both semi-empirical (two-equation) and detailed models, collectively termed '*bottom-up models*', require a certain calibration of parameters to match measurements. Also since the bottom-up models are invariably applied to experiments performed as a part of each modeling effort, no clear pattern can be discerned from the values of the parameters used and hence the role of different controlling mechanisms remain unresolved. In contrast with this, Lautenberger et al. [1] developed an approach, classified here as a '*top-down model*', based on the experimentally established universality in the scaling of flame radiation with '*smoke point*'. This model utilizes the experimentally determined smoke point for various fuels to arrive at simple expressions for soot formation and oxidation as a function of scaled mixture fraction, with the smoke-point height itself as the scaling parameter. This approach is considered very encouraging but the validity of this model to general fire problems is yet to be established. Current work concludes that the missing link between these two approaches, namely, the bottom-up and top-down, is the lack of a robust model capable of predicting smoke-point heights. It is proposed to build such a model using the bottom-up approach and extend the same to fire dynamics simulations. This is expected to clarify the fundamental connections between the two approaches.

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1 Introduction

Prediction of soot emissions from flames is a problem that has been studied extensively. Research in this area is primarily driven by the need to control and minimize emission of this harmful pollutant in all combustion devices in general, diesel engines and gas turbines (where it also can potentially damage the turbine blades) in particular. Sometimes, soot is also a desired component in combustion products due to its role in enhancing radiative heat transfer, like in furnaces. Soot is a result of a number of interconnected complex chemical and physical processes occurring in the fuel rich zones and hence a strong function of the structure of the fuel molecule and temperature. The strong kinetic control of reactions under fuel rich conditions, as opposed to lean mixtures which can be considered close to equilibrium, is a major contributor to the complexity of soot modeling. These considerations clearly show that processes associated with the formation and destruction of soot is different in premixed and diffusion flames. For example, with increase in overall adiabatic flame temperatures, soot fraction is known to decrease in premixed flames while it increases in diffusion flames. This can be explained as follows - in premixed flames, with increase in temperature and concentration of OH radicals, the increase in the rate of soot oxidation (due to OH radicals) is more than that of the soot formation leading to a decrease in the soot emission (see Millikan [2]). While in diffusion flames, due to the physical separation of fuel from the oxidizer, with increase in temperature the OH concentration is not affected to the extent that it can nullify the increase in the rate of soot formation reactions. This is the reason for the differences between the sooting propensity ranking of fuels in premixed and diffusion flame configurations (see Glassman [3]). A particularly important fuel to take note of is acetylene, as it is considered an important soot precursor. It is a heavily sooting fuel in diffusion flame configurations, placed just below aromatics (the most sooting compounds), while it is the least sooting in premixed configurations (placed below olefins). This is directly related to the distinctly higher flame temperature of acetylene compared to other hydrocarbons. Therefore for premixed flames the sooting tendency ranking for fuels is given in terms of equivalence ratio at fixed temperature (2200 K) at which luminous emission starts. This data correlates very well with the number of C-C bonds in the fuel for a wide range of hydrocarbons except acetylene (see Fig. 13, p370 in Glassman [3]). At 2200 K acetylene flames turn luminous at a lower equivalence ratio compared to fuels with same number of C-C bonds

(propene, butane and 2-methylpropane). Because of this acetylene is pushed up the hierarchy of propensity to sooting. This is related to the fact that the experiments are conducted with compositions of fixed adiabatic flame temperature value of 2200 K which corresponds to most hydrocarbons burning in air except for acetylene (2723 K) and hence the enhanced role of soot oxidation at higher temperatures is suppressed resulting in a luminous acetylene flame at a lower equivalence ratio compared to fuels with same number of C-C bonds.

For diffusion flame configurations, fuels are ranked based on '*laminar smoke point*', which is measured as the fuel mass flow rate at which the soot breaks through the top in an over-ventilated laminar jet diffusion flame. Though, in an overall sense the diffusion flame smoke point can be considered a result of the balance between soot formation and destruction, it must be noted that these processes are relatively physically separated as compared to a premixed flame. This is the reason why acetylene is one of the most sooting fuels in diffusion flame configurations as its role as a soot precursor overrides the temperature effects on soot oxidation. Any modeling effort should capture this crucial difference between behavior of acetylene in premixed and diffusion flames.

Notwithstanding these differences between premixed and diffusion flames, the properties of the soot formed are similar for different fuels (see [3]), indicating the universality of formation and destruction reactions. Therefore the observed difference in soot volume fraction in a given configuration for different fuels can be explained by the differences in conditions like temperature, composition and velocity (or residence time) along streamlines. It is known that the structure of soot formed is strongly dependent on the nature of the reaction - homogeneous vs heterogeneous. Given that the properties of soot formed in both premixed and diffusion flames are very similar indicates that the soot formation process is predominantly controlled by one of the two processes, either homogeneous or heterogeneous.

1.1 Soot models

A number of mechanisms and models for predicting soot in flames have been developed and they are generally classified into three categories - empirical, semi-empirical and detailed. An extensive review of these models is given in Kennedy [4]. Models employing extrapolation of correlations for total soot emissions from experiments have limited validity in general situations and hence clearly belong to the 'empirical' category. Most of the soot models used in diesel engine and

gas turbine design belong to this category.

On the other hand, in the semi-empirical approach, one generally solves differential equations for the soot volume fraction and the number density (bins or moments). A common feature of semi-empirical models is the assumption of acetylene and/or benzene to be the precursor molecules and the soot inception/nucleation rate is taken as proportional to the concentration of acetylene/benzene produced by fuel pyrolysis. The major difference between models arise from the soot growth point of view depending on whether the process is assumed heterogeneous or homogeneous. In heterogeneous growth models the soot growth rate is taken to be proportional to the surface area and hence varies linearly as the product, $n^{1/3} f_v^{2/3}$, where f_v is the soot volume fraction and n is the soot number density. Homogeneous models take soot growth rate to be proportional to the number density (n). Lots of contradicting statements can be found in literature about the role of inception and growth in determining the soot fraction. Several statements pertaining to the nature of the growth processes, whether it is heterogeneous or homogeneous, can also be found. Kennedy [4] has clearly brought out in his review that it is difficult to draw general conclusions since in almost all efforts the models are applied to different candidate flames and invariably certain calibration of parameters is required to explain the observed results. Hence it is not possible to know the general validity of these models. But there is some evidence, for moderate to heavy sooting diffusion flames, to favor the homogeneous growth rate as the controlling mechanism in determining the soot fraction compared to heterogeneous and inception steps.

With respect to detailed models, it suffices to state that while the claim is accurate incorporation of the complex pathways for inception/nucleation and surface growth leading to soot, equal or more number of parameter calibration is required compared to semi-empirical models to explain the experimental results. Also these models have so far been applied only to premixed flames and shock tube studies. With unresolved fundamental questions pertaining to the uncertainty in precisely identifying inception species (Colket and Hall vs Frenklach school of thoughts) we are very far from a robust detailed soot model with no adjustable parameters. Given that a certain level of calibration is required for both semi-empirical and detailed models, it is perhaps better to refer to the semi-empirical model as two-equation models. Since both approaches attempt to predict soot distribution from first principles, these are categorized as belonging to '*bottom-up*' approach.

As to the question of soot oxidation models, both two equation and detailed

models use the Nagel and Strickland-Constable (O_2 only) oxidation parameters or that of Lee et al (both OH and O_2) or a combination of the two. Here again there are uncertainties associated with the frequency factor of OH reaction and hence adjusted to fit measurements. It is to be noted that accurate description of oxidation is as crucial as formation steps for the development of predictive models.

It is surprising that though critical sooting equivalence ratio for premixed flames and smoke point height for diffusion flames are recognized as fundamental indicators of sooting tendency with excellent experimental repeatability, none (except that of Markatou et al. [5] which reports attempts to predict the critical equivalence ratio of premixed flames) out of about twenty five papers reviewed in Kennedy [4] address the problem of predicting the critical equivalence ratio or the smoke point height of diffusion flames. This includes the series of papers by Smooke and group ([6], [7], [8]) and some very recent efforts reported in Nmira et al. [9] on laminar diffusion flames. To the best of the author's knowledge the issue still remains open.

1.2 Fire dynamics and soot

While attempts to develop accurate mechanisms which can capture the inception, nucleation, surface growth etc. continue, motivated by the need for a reliable tool for prediction of radiation from flames in fire dynamics simulations, Lautenberger et al. [1] developed a simple soot model utilizing a scaling law obtained from experiments on laminar diffusion flames, *that at the smoke point the radiative heat loss from the flame approaches 30% of the total heat release for moderate to heavy sooting fuels*. This result obtained by Markstein [10] for ethylene, propylene, isobutene and 1,3-butadiene along with several other correlations relating radiant emission from diffusion flames with peak soot volume fraction and soot formation growth rates is used to construct a model where the soot formation and oxidation rates are calculated as analytic functions of temperature and mixture fraction scaled appropriately by smoke point height to account for fuel effects. This approach is termed '*top-down*'. The smoke point heights for different fuels are taken as inputs. No crossovers in the sooting propensity rankings of various fuels obtained from these correlations is taken as sufficient justification for this approach. In their model both soot formation and oxidation processes are assumed to be homogeneous and the inability of the model arising out of this approximation to predict the behavior of lightly

sooting flames like methane is considered unimportant for fire situations. Predictions obtained for axial variation of radially integrated soot volume fraction for ethylene, propylene and propane candle like flames are considered encouraging. The paper concludes with an appeal for future work to evolve a robust model using the framework.

1.3 The missing link

As brought out earlier, between the models aimed at accurately capturing several soot formation and oxidation steps and that of Lautenberger et al. [1] which uses the measured smoke point heights as input, the missing link is lack of attempts to evolve a modeling strategy to capture the smoke point height of different fuels. Since this transition from non-smoking to smoking is dependent on all the critical mechanisms, namely, soot formation/oxidation, fluid dynamics, gas phase chemistry and radiative heat transfer, a physics based model capable of capturing the smoke point height will be applicable to a variety of non-premixed flame modeling. A feature intimately connected to the smoke point height is the near constancy of measured temperatures (~ 1300 K from Kent and Wagner [11]) at the tip of a flame at smoke point (taken as the location where the soot volume fraction becomes constant) for different fuels. In Markstein and De Ris [12] a different temperature (1600 K) is reported as the temperature at flame tip at smoke-point. It is pointed out by Kent (see the comments section in [12]) that this difference is due to use of a different criteria for identifying flame tip and application of the criteria used in Kent and Wagner [11] results in a temperature of 1350-1450 K, confirming the earlier measurements. Combining this experimental result with the fact that at smoke point height the soot oxidation rates are balanced by formation rates indicate that the kinetics of soot oxidation, which has received very little attention compared to formation processes, should be examined in detail. Perhaps, the smoke point height corresponds to the point of extinction of soot particles which is around 1300 K, with the balance between soot formation, oxidation and radiation loss determining the distance from the nozzle required for the temperature to drop to this critical limiting value. Kennedy [4] also has pointed out the need for a careful analysis of the soot oxidation models.

1.3.1 Flame height

Another aspect of diffusion flames connected to soot is the problem of flame height. The ratio of measured heights to the height of the flame sheet (vertical distance corresponding to $Z = Z_{st}$) in laminar diffusion flames varies from 0.9 - 1.8 (see [13]). For non-luminous flames the ratio is close to 1 and it increases as the flame turns luminous. But in both these regimes the linear relationship between the normalized flame height with Reynolds number is maintained, indicating that the flame height, even in the presence of soot is controlled by an overall convection-diffusion balance. Lin et al. [13], by correlating the measured heights of non-buoyant flames with Reynolds number has shown that the constant of proportionality is about 0.5 for blue flames (non-luminous) and 1.1 for luminous flames. It is interesting to note that the same constant correlates heights of both non-smoking and smoking flames. It can be inferred that this transition in the behavior of flame height from non-luminous to luminous condition, termed '*flame height jump*' is connected to the stronger dependence of diffusivity on temperature compared to density ([15]). Therefore the temperature decrease brought about by radiative heat loss from soot causes an increase in flame height. Radiation effects are neglected in Lin et al. [13]. Based on the suggestion in [15], the data on flame height of non-luminous and luminous flames can be correlated with a single constant by suitably accounting for the change in diffusivity with temperature. This requires an appropriate estimate for the average flame temperature in the presence of radiative heat loss. Chemistry effects are negligible since even in luminous flames the normalized flame height is proportional to the Reynolds number. Another interesting observation from Saito et al. [14] is that the position of onset of luminous radiation measured from visual observations compared to that from a deposition probe starts diverging at a Peclet number of about 1 and the ratio of probe to visual height reaches a value of 2 at a Peclet number of 2. An explanation for this phenomenon is not sought in [14].

2 Current approach

It is proposed to take a fresh look at the problem of modeling sooting laminar jet diffusion flames with the principal aim of capturing the smoke point heights of different fuels. The approach will follow the two equation model and must include -

1. A simple yet robust soot formation model with preferably no more than three steps. Acetylene and benzene can be the immediate precursor to soot with one or two steps to model fuel pyrolysis to form acetylene. The simplifying assumption that the soot formation processes in the fuel rich zones of diffusion flames is dominated by homogeneous reactions (Lautenberger et al. [1]) must be effectively utilized to simplify the mechanism of soot growth by taking the rate of the growth process as proportional to the soot number density.
2. Soot oxidation due to O_2 and OH to identify relative roles in determining smoke-point height.
3. Two different gas phase chemistry models, equilibrium and reduced kinetics, to examine the role of super-equilibrium OH in soot oxidation.

3 Expected outcomes

A simple yet robust soot model for predicting the smoke point heights of moderate to heavy sooting fuels (C_2 onwards) with a single set of input parameters. The model is expected to predict the '*flame height jump*' phenomena as well, which is indicative of the accuracy of the radiation model. Following this, the possibility of incorporating this model within a fire dynamics simulation framework for accurate prediction of radiative heat transfer will be explored.

Acknowledgements

This report was written during a stay at The University of Queensland. Discussions with Prof. Jose L Torero were most helpful in preparation of the report. The author acknowledges the inputs from discussions with Prof. H S Mukunda (IISc, Bangalore). Financial support provided by Prof. Jose L Torero is gratefully acknowledged.

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