

MODELLING THE GROWTH OF POLYNUCLEAR AROMATIC HYDROCARBONS IN DIFFUSION FLAMES

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Abstract

It has been noted for some years that the concentrations of many species in laminar hydrocarbon diffusion flames correlate with mixture fraction, or alternatively, local equivalence ratio. Therefore, once the spatial profile for the mixture fraction is established, it is possible to approximate both the concentration and net chemical rate profiles for a great many flame species. However, some species exhibit concentration gradients along contours of constant mixture fraction in a flame. The results of our past work show that most of the species along the chemical pathway leading to soot particle formation in diffusion flames, including all of the Polynuclear Aromatic Hydrocarbons, exhibit this type of behaviour. For these species, it is necessary to consider not only the chemistry of the growth environment, which may be adequately described by the mixture fraction, but also the residence time within the growth region. This paper will describe how such a model could be expressed, and present some initial comparisons with laboratory flame data.

Introduction

The earliest mathematical treatment of diffusion flame structure was that of Burke and Schumann [1]. Although incremental improvements to the Burke-Schumann model have been made over the years, it was not until recently that a new and more realistic approach to thinking about diffusion flame structure could be formulated. This can be traced to two improvements: the evolution of powerful computers and the development of the conserved scalar description of flame structure. The former has provided the capacity for the calculation of the two-dimensional structure, including up to C_2 chemistry, for laminar diffusion flames. The latter provides a framework for the development of simplification schemes for flame structure calculations.

In general, to compute the structure of a laminar diffusion flame requires the simultaneous solution of the energy, momentum, and species conservation equations. The latter can be written in the Shvab-Zeldovich form as [2]:

$$L(Y_i) \equiv \rho u_k \cdot \left(\frac{\partial Y_i}{\partial x_k} \right) - \frac{\partial \left(\rho D_i \left(\frac{\partial Y_i}{\partial x_k} \right) \right)}{\partial x_k} = w_i \quad (1)$$

where Y_i is the mass fraction of species i , w_i is its chemical production rate of species i , ρ is the gas density and u_k is the component of velocity in the x_k coordinate.

Chemical elements (such as C, H, and O) are conserved during chemical reaction ($L(Z_i) = 0$) and linear combinations of elemental abundances, such as the mixture fraction, ξ , will also be conserved [3].

It has been noted that the concentrations of many flame species are only a function of mixture fraction, $Y_i = f(\xi)$ [2]. For these species, since

$$\rho u_k \cdot \left(\frac{\partial \xi}{\partial x_k} \right) - \frac{\partial \left(\rho D_i \left(\frac{\partial \xi}{\partial x_k} \right) \right)}{\partial x_k} = 0 \quad (2)$$

it follows that the chemical rate is given by

$$w_i = - \left(\frac{1}{2} \right) \rho \chi \cdot \left(\frac{d^2 Y_i}{d\xi^2} \right) \quad (3)$$

with the instantaneous scalar dissipation rate, χ , defined as:

$$\chi = 2D \cdot \left(\frac{\partial \xi}{\partial x_k} \right)^2 \quad (4)$$

What if a species concentration is not a function of only mixture fraction? In particular, what if the chemistry is slow enough that transport might occur before a reaction proceeds? This is the case for the species along the chemical pathway leading to soot particle formation in diffusion flames, including all of the Polynuclear Aromatic Hydrocarbons, which exhibit concentration gradients along lines of constant mixture fraction [4]. For these species, it is necessary to consider not only the chemistry of the growth environment, which might be adequately described by the mixture fraction, but also the residence time within the growth region.

If this residence time dependence is included, a more complicated version of Eq. 3 can be derived which has two simple limits. The first would be if the time dependence was zero. In that case the equation would reduce to the result of Eq. 3. The other limit would hold if the diffusion coefficient for the species under consideration were zero, or at least small enough that terms which include it were small with respect to the residence time dependent terms. This would be almost exactly true for soot particles. Even small aromatics have diffusive velocities which are small with

respect to their convective velocities [4]. In this latter limit, the change in a species concentration would be simply given by integration over the residence time. We adopt this simple view in formulating the model presented in the next section.

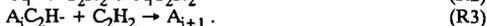
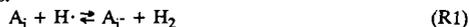
A Model for PAH Chemistry in Laminar Diffusion Flames

We describe below a model which describes the physical and chemical processes that affect PAH and soot concentrations along a stream line in a laminar methane/air diffusion flame. The development is similar in spirit to that presented in a recent paper by Kennedy et al. [5]. In both models, soot processes are divided into three broad categories: inception, chemical growth, physical growth (agglomeration), and oxidation. Both assume that the rate of the soot processes depends on local temperature and the concentrations of major species, and these are fully determined by mixture fraction. In our model, we attempt to rationalize the choice of rates based on a knowledge of the fundamental chemical processes which are occurring in the flame combined with detailed measurements of species concentrations.

Growth

The growth chemistry in our model is based on the work of Frenklach et al. who proposed a model for ring growth based on the successive addition of acetylene to a growing aromatic radical core [6]. This model, in various forms, has been applied to studies of PAH and soot formation in shock tubes and premixed flames [6-10]. Frenklach developed a simplified version of his model to identify key parameters controlling PAH growth in combustion environments [10]. We used this simplification to demonstrate the important role of agglomeration in PAH growth [11].

In Frenklach's simplified mechanism parent PAH, A_i , are converted into a phenyl-like radical, A_i^- , by hydrogen abstraction. The resulting radical reacts with acetylene to form a radical addition product $A_iC_2H_2^-$. A subsequent acetylene addition irreversibly forms the next largest parent PAH. This reaction sequence is illustrated as:



In this reaction scheme, steady-state estimates for the concentrations of A_i^- and $A_iC_2H_2^-$ can be derived. The rate of formation of the A_{i+1} PAH can therefore be written as

$$\frac{d[A_{i+1}]}{dt} = k_{eff} [A_i], \quad (5)$$

where k_{eff} is dependent upon the concentrations of C_2H_2 , H_2 , and H .

In our prior work, we found that agglomeration only becomes important when the reduced mass of the colliding pair is suitably large: greater than 400 amu. Following the lead of this earlier work, we here assume that an agglomeration reaction can be written as



where the rate constant of this process will be 0 for collisions of lighter PAH and close to the gas kinetic limit for collisions among the heavier PAH.

Inception

As seen above the aromatic growth is treated as an irreversible sequence of acetylenic addition steps to a growing aromatic core whose source is benzene, A_1 . There are a number of

models for the chemistry of the formation process of benzene which involve either reactions of C_2 with C_4 species [6] or the reaction of two C_3 species [15]. It is conceivable that a simplified expression for this process using steady state arguments (analogous to Frenklach's approach for ring growth) might be derived. If successful, such an approach would be expected to result in an expression for the A_1 inception rate which depends only on mixture fraction. However, given the current active debate on the mechanisms for the formation of benzene in flames, such a simplification may be premature.

Fortunately, there may be another approach to deriving an inception rate. Over the past few years we have collected an extensive data base for species concentrations and temperature in a laminar methane/air diffusion flame. This data has included measurements of the concentration of stable species such as acetylene and molecular hydrogen [12] and has been recently extended to include profile measurements of radicals species [13,14]. With this data base, we have demonstrated how the overall rates for a species chemistry may be calculated [13]. For the initial work presented here, we will assume that the benzene formation rate dependence on mixture fraction is given by our previous results for the Wolfhard-Parker diffusion flame [13].

Oxidation

In his dissertation work, McKinnon developed a comprehensive soot model which explicitly included a soot oxidation step [9]. Based on the work of Brezinsky [17], McKinnon assumed that successive reaction of carbons on the PAH or soot with hydroxyl radical results in a decrease of one ring number for the PAH and the formation of carbon monoxide. McKinnon found that inclusion of the Nagle and Strickland-Constable expression for soot oxidation by molecular oxygen overpredicted the soot oxidation rate, and he omitted this pathway from his final model. In the initial steps of the current research, we will also only include oxidation of PAH and soot by hydroxyl radical.

If it is assumed that (1) the concentrations of C_2H_2 , H_2 , H , and OH are only functions of mixture fraction (i.e. their concentrations will not be affected by the aromatic growth chemistry) and (2) aromatic species will not diffuse then the progress of aromatic growth may be followed by integrating aromatic concentrations along a stream line using mixture fraction correlation data from our data base. The derivation of this flame field is discussed in the next section.

Flame Field Calculations

We have modelled the structure of a methane/air diffusion flame which has been studied by Santoro et al. [18]. Velocity, density, and mixture fraction fields throughout the flame are obtained using a computer code which has been described previously [19-21]. In this model, it is assumed that (a) major species concentrations are only a function of mixture fraction (and their concentrations can be found upon solution of the transport equation for mixture fraction, Eq. 2), (b) the rates of chemical reactions that determine major species concentrations are large with respect to transport rates, and (c) all species diffusivities are the same.

The transport equations for mixture fraction and momentum are solved for axisymmetric flow using a streamline coordinate transformation. The flow is parabolic and the boundary layer assumptions are made that the transverse pressure gradient and longitudinal diffusion fluxes are negligible. Buoyancy forces are included in the momentum equation. Diffusivity and viscosity were calculated from the local temperature using the Sandia transport property data [22]. The temperature vs. mixture fraction correlation was obtained from our analysis of a methane/air diffusion flame

supported on a Wolfhard-Parker burner [12]. The predicted mixture fraction field and streamlines are shown in Figure 1.

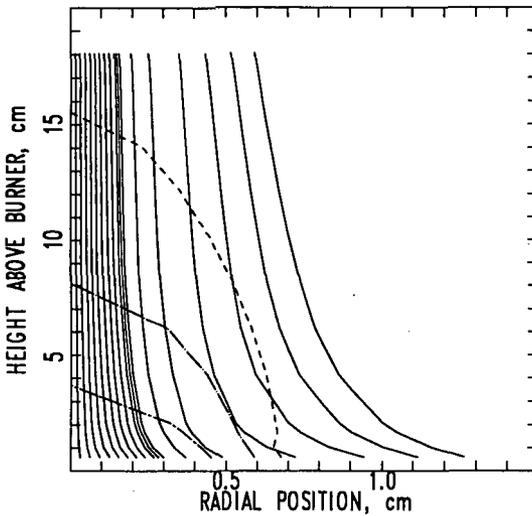


Figure 1 Streamlines and contours of mixture fraction in calculated axisymmetric methane/air diffusion flame. The stoichiometric contour ($\xi = 0.055$), and two fuel-rich contours ($\xi = 0.1$ and 0.2)

Results and Discussion

The concentrations of polynuclear aromatic hydrocarbons have been calculated along a series of streamlines in the flame shown in Figure 1. The model was first run using the expression for the effective rate constant for chemical growth derived from local temperature, and the concentrations of C_2H_2 , H_2 , and $H\cdot$ correlated against mixture fraction from the Wolfhard-Parker flame data. It should be noted that a H -atom plays a critical role in this chemistry: abstraction of ring hydrogens from the PAH is responsible for "activating" the surface for further growth. Unfortunately, in the

flame region that growth is likely to occur, there are no reliable measurements of H-atom concentration [14]. In these flame regions we have calculated [H·] assuming total local equilibrium. There has been much written about the importance of super-equilibrium concentrations of radicals in combustion processes in general [19] and aromatic growth in particular [10]. Although it is well known that super-equilibrium exists near the high temperature reaction zone of hydrocarbon diffusion flames [13], calculations also suggest that super-equilibrium extends well into the fuel rich flame regions where growth may occur [19]. Therefore, assumption of total equilibrium may grossly underpredict the concentration of hydrogen atoms and, consequently, the rate of ring growth. Our model calculations bear this out: unless an enhancement factor for chemical growth was included, no appreciable build-up of PAH occurs. To reach a volume fraction of soot approaching that which has been observed experimentally [18], this factor must be on the order of 500, which implies hydrogen atom concentrations in the growth region on the order of a few hundred parts per million. With current measurement strategies for hydrogen atom, this is a value near the detection limit in fuel rich regions of a diffusion flame [23].

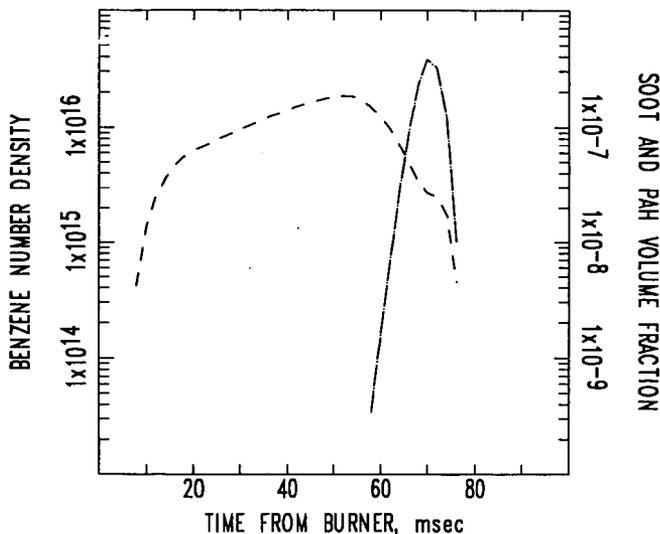


Figure 2 Concentrations of benzene (—) and heavy PAH and soot (---) as a function of time from burner surface for the streamline of peak soot loading (the fifth from the right streamline in Figure 1).

Figure 2 shows the concentrations of benzene and the soot volume fraction along a streamline which exhibited maximum PAH growth rates. Soot volume fraction is defined as the volume occupied by all species larger than coronene (A_7) in the model assuming that they all have the same density as soot. As expected, large concentrations of benzene precede the formation of larger PAHs in the

flame and that the volume fractions in this flame are small enough that total oxidation of the PAH occurs near the flame tip. (The oxidation of larger PAH leads to the shoulder on the benzene profile at 70 msec.)

Figure 3 shows a contour plot for soot concentrations in the flame calculated with the factor of 500 used for the enhancement of chemical growth rates. This picture looks qualitatively similar to comparable pictures derived from laser light scattering and extinction measurements [18] and to other model calculations of soot formation and oxidation in diffusion flames [5].

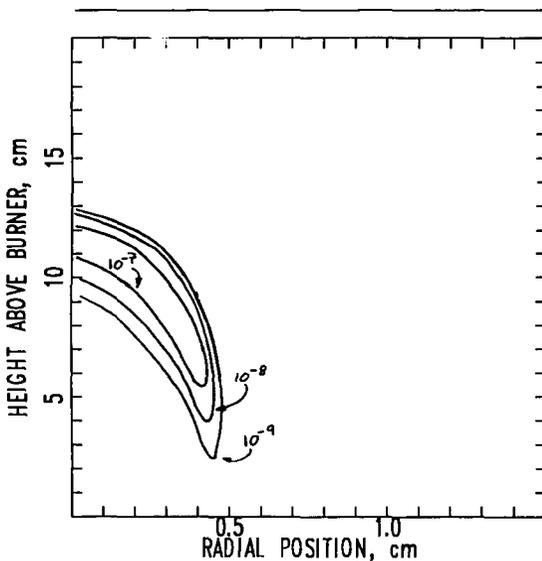


Figure 3 Contours of soot volume fraction in methane/air diffusion flame.

Conclusions

These model calculations provide an initial attempt to combine simplified aromatic growth chemistry with the conserved scalar description of diffusion flame structure. Although preliminary, the results suggest the important role that super-equilibrium hydrogen atom concentrations play in the growth chemistry. Future model improvement will hinge on the development of a more quantitative understanding of this factor.

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