FORMATION AND OXIDATION OF SOOT IN DIFFUSION FLAMES

ANNUAL REPORT

(January 1990 - June 1991)

THE GAS RESEARCH INSTITUTE
8600 West Bryn Mawr Ave.
Chicago, Illinois 60631

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16. Abstract (Limit: 200 words)

This study presents the results of a unique experimental investigation on the sooting structure of methane counterflow diffusion flames where the fuel and oxidizer streams were preheated and/or diluted by products of combustion such as CO_2 and H_2O. Low strain rates were employed to spatially resolve the inner structure of these flames and detailed measurements of temperature, species, PAH, soot particle number density and volume fraction were made. A three-color (blue-yellow-orange) structure was observed. Measurable size soot particles (>5nm) were found only in the orange zone. Soot inception occurs at the diffuse interface between the yellow and the orange zones whose location depends on the local thermochemical conditions. It was found that an increase in the reactants preheating temperature (while simultaneously reducing the oxygen concentration to hold the reaction zone temperature approximately constant) led to early inception and increased soot volume fraction despite the fact that the fuel flow rates, the fuel concentration and the strain rates were essentially identical. However, addition of CO_2 and H_2O (while holding all other conditions constant) resulted in delayed soot nucleation and significant reduction in the soot volume fraction. These two observations are consistently explained by the mechanism of OH interference with soot inception. This study indicates that thermochemical conditions that favor soot nucleation substantially increase the ultimate soot loading because they control the residence time available for surface growth. A soot formation model is also derived form these measurements. This model postulates that the overall soot formation reaction follows Arrhenius kinetics. The results show that within an error bound of approximately ± 10% the overall activation energy for soot formation is 36 Kcals/mole.

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RESEARCH SUMMARY

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Objective: The objectives of this study are: (i) To quantify the formation, growth and oxidation rates of soot in counterflow diffusion flames as a function of temperature, strain rates and fuel and oxidizer concentrations of the two streams. (ii) To study the effect on the formation and oxidation rates of soot due to dilution by primary products of combustion (CO_2 & H_2O) and slight premixing of oxygen and other additives to the fuel stream. (iii) To develop a model of a radiating laminar flamelet based on the above measurements.

Perspective: In large industrial furnaces and combustors the primary mode of heat transfer is thermal radiation. This limits the use of natural gas as a fuel because only about 10% of the chemical energy is released as thermal radiation. The rest of the energy serves to increase the temperature of the burned gases. This mode of operation has two disadvantages: (i) A major portion of the chemical energy of the fuel, instead of being directly transferred to the job via radiation, must now be appropriately channeled and extracted by convective processes that require heat transfer equipment capable of handling high temperature exhaust gases. (ii) Lower flame radiation results in higher flame temperature which increases the production of pollutants such as NO_x .

To promote radiation, and hence the efficiency of heat transfer, it is necessary to increase the production rate of soot in such a way that it is completely oxidized before leaving the combustion zone. Thus, the goal of this research is to develop a quantitative understanding that will enable the control of formation and oxidation rates of soot in natural gas turbulent diffusion flames. The effects of three most important variables for controlling turbulent diffusion flames, namely temperature, composition and strain rates, and other technological possibilities such as recirculating the products of combustion and/or slightly premixing the fuel with air, are being investigated. Also, in industrial furnaces, the extinction of flamelets due to strain-out occurs at temperatures significantly higher than ambient. Such extinction may lead to incomplete combustion and/or lift-off of turbulent diffusion flames. Thus, extinction at elevated temperatures must also be investigated. The results of this work will help develop a model of turbulent diffusion flames used in industrial furnaces and combustors.

Approach: The technical approach is to conduct a detailed study on a basic unit of a turbulent diffusion flame i.e. a laminar diffusion flamelet. A unique high temperature counterflow diffusion flame burner has been constructed for this purpose. This burner is capable of preheating both the fuel and the oxidizer streams to 1500 °K (2240 °F). Thus, the temperature can be independently varied without changing the fuel or the oxidizer concentrations. This capability allows studying individual aspects of the problem separately. For example, a non-sooty blue flame can be converted into a very sooty flame as the preheat temperature is increased without altering the concentrations of the fuel and the oxidizer streams; thus enabling the determination of soot formation and oxidation rates. Another unique feature of this burner is that the strain rate can be easily varied from very low (1.5 sec^{-1}) to reasonably high ($\approx$ 50 sec^{-1}). The lower limit of the strain rates is particularly important because it provides long residence times for fuel particles to pyrolyze and produce soot. Also, low strain rates are necessary for providing a good spatial resolution for measurements. The higher limit of strain rates is important because it permits studying the extinction phenomenon. Thus, it is possible to span the entire history of the diffusion flame from extinction (blue flame) to a very sooty flame (yellow-orange-red) by changing only the strain rates or by changing only the preheat temperatures.

Results: During the last year, a large number of experiments were conducted where the fuel and oxidizer streams were preheated and/or diluted by products of combustion such as CO_2 & H_2O. Low inlet velocities resulted in low strain rates and thus a thick reaction zone convenient for probe measurements. This was necessary to spatially resolve the inner structure of these flames. Detailed measurements of temperature, species, PAH, soot particle number density and volume fraction were made. Experiments were also conducted to study the effect of strain rates on soot formation and extinction of diffusion flames. Important results of these experiments are summarized below.

▸ Soot formation experiments show a three-color (blue-yellow-orange) structure. Measurable size soot particles (>5nm) were found only in the orange zone and soot inception was found to occur at the diffuse interface between the yellow and the orange zones. The soot inception location was also found to depend on the local thermochemical conditions.

▸ An increase in the reactants' preheating temperature (while simultaneously reducing the oxygen concentration to hold the reaction zone temperature approximately constant) led to an early inception and increased soot volume fraction despite the fact that the fuel flow rates, the fuel concentration and the strain rates were essentially identical. However, addition of CO_2 & H_2O (while holding all other conditions constant) resulted in delayed soot nucleation and significant reduction in the soot volume fraction. These two observations are consistently explained by the chemical mechanism of OH interference with soot inception. Although the precise chemical steps are unclear, it is clear that the entire variation in soot formation can not be accounted for simply by a thermal mechanism. The chemical environment plays a critical role.

▸ This study indicates that thermochemical conditions that favor soot nucleation substantially increase the ultimate soot loading because they control the residence time available for surface growth.

▸ The data from the above measurements are reduced according to a one-dimensional model for a counterflow diffusion flame. This model postulates that the overall soot formation reaction follows Arrhenius kinetics. The results show that within an error bound of approximately ± 10% the overall activation energy for soot formation is 36 Kcals/mole. The physical and chemical measurements in conjunction with numerical solution of the model also show that the primary intermediate species consists of C_2 and aromatic hydrocarbons. Also the range of temperatures over which soot formation occurs lies between 1300 °K (2372 °F) and 1700 °K (3090 °F).

Work for the Next Year:

The following set of experiments and modeling are planned for the next year:

(1) **Enhancement of Experimental Capability:** In the experiments conducted so far, chemical measurements were the most tedious. It took approximately 24 hours to measure the chemical composition for a given flame using the current gas chromatographic system. Since the measurements often need to be repeated for accuracy, completing all the measurements for a given flame took more than a week. Data reduction and analysis were equally tedious. To improve the present system, the existing GC system needs to be updated to a computer based system. Also, it will be extremely helpful to add measurement capabilities for NO_x measurements. It is proposed that the NO_x measurements be made optically (laser beam absorption) like the soot measurements because they are fast and more accurate.

(1) **Soot Formation Experiments:** Thus far we have conducted and analyzed the results of soot formation experiments for pure methane. It seems important to measure NO_x in these sooty flames; such that NO_x could be related to flame radiation. Also, some experiments must be conducted with natural gas (i.e. impure methane or a controlled known mixture of methane and ethane). This will enable us to generalize the soot formation rate model.

(2) **Soot Oxidation Experiments:** During the soot formation experiments, it became very clear that the presence of CO_2 and H_2O considerably reduces the soot formation rates. However, direct oxidation of soot by oxygen or OH radicals was not investigated. This is very important from the point-of-view of enhancing flame radiation, because most of the energy liberated during soot oxidation is directly radiated away by the diffusion flame. Soot oxidation experiments are designed such that the sooty flame lies on the fuel side of the stagnation plane. This can be easily accomplished by either increasing the O_2 concentration or partially premixing air and fuel. In this configuration soot is oxidized as it passes through the hot combustion zone. It is also possible to

increase (control) the OH concentration by adding H_2O to the fuel or the oxidizer streams to assist soot oxidation. Also, the flame radiation in this configuration is directly proportional to the amount of soot oxidized. This will be quantified along with other measurements.

(3) **Effect of Strain Rates on Soot Formation, Soot Oxidation and NO_x production:** As the strain rate is increased a sooty flame becomes less sooty, then blue and eventually is extinguished. Clearly, there is competition between the rate of transport and the rate of reaction. Here we are concerned with three different reactions: (i) the overall reaction rate that governs fuel oxidation, (ii) the fuel pyrolysis reactions responsible for soot formation, and (iii) the reactions responsible for NO_x production. Thus, disappearance of the flame (i.e. extinction) represents the limits of the fuel oxidation reaction rate, whereas, the disappearance of the yellow zone represents the limits of the reaction rate responsible for soot formation. Similarly, there may also exist a critical strain rate above (or below) which NO_x is not produced. In all cases, whatever the reaction mechanism, the rate controlling step is responsible for the change. These phenomena are very important from a practical standpoint. The first phenomenon controls lift-off of turbulent diffusion flames (which has been investigated earlier in some detail), the second controls flame radiation and the third controls NO_x production. Thus, critical strain rate will be measured as a function of fuel and oxidizer concentrations and the preheat temperature. Flame temperature profiles, stagnation plane location, soot scattering and NO_x production will be measured. For some cases the species profiles will also be measured.

Project Implications: Energy transport by thermal radiation from diffusion flames is important in industrial furnaces and combustors. Soot in furnace flames promotes radiation and hence, increases the heat transfer from the flame. The research in this contract is aimed at developing a quantitative understanding of the control of formation, growth and oxidation of soot in turbulent diffusion flames. Knowing the reaction rates is important for increasing and controlling radiation in natural gas diffusion flames. As a part of this contract an excellent counterflow diffusion flame apparatus has been built. The experimental results from this apparatus provide new, very important insight into soot kinetics. Although the precise chemical steps are unclear, these results indicate that soot formation and oxidation can be modeled using Arrhenius kinetics. Comparison of the model with the experimental data shows good agreement. Work is continuing to develop an Arrhenius model that will be useful in predicting soot quantities in turbulent diffusion flames. Work during the next year will provide the key information needed to make the model a useful tool.

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1. Introduction

The processes of soot formation and oxidation in diffusion flames are considered to involve a series of chemical and physical steps [1-4]: the conversion of parent fuel molecule to soot nuclei, the growth of incipient particles via surface reaction as well as coagulation and agglomeration and the accompanying oxidative attack on these particles in a competing reaction by oxidants such as oxygen or the hydroxyl radical. Numerous approaches to soot modeling have recently been reviewed [5-6] in light of the progress achieved in the past twenty years. However, at this stage, the most complicated mechanisms pertaining to soot formation and oxidation have not been experimentally elucidated sufficiently to yield a sophisticated model that will be capable of predicting the soot field in a laminar diffusion flame and eventually in a turbulent diffusion flame.

The present study aims to achieve a better understanding of the inherent mechanisms of soot formation and oxidation in a laminar counterflow diffusion flame and to quantify the corresponding rates. There have been several excellent studies regarding soot formation in counterflow diffusion flames (U. Vandsburger, I. Kennedy and I. Glassman [7] 1984, M. Gomez, A. Littman and I. Glassman [8] 1987, H. Hura and I. Glassman [9] 1988, R. Axelbaum, W. Flower and C.K. Law [10] 1988, D.X. Du, R. Axebaum and C.K. Law [11] 1988). However, the primary emphasis of these efforts have been to investigate the relative effects of variables such as fuel structure, inert dilution and aerodynamic straining. The present work, on the other hand, independently controls all of the above variables and quantifies the formation and oxidation rates through detailed chemical species, temperature and polycyclic aromatic hydrocarbons (PAH) measurements in counterflow diffusion flames. Our first objective was to determine soot formation rates (ideally) in the absence of oxidation. This was partially accomplished by preheating the fuel and the oxidizer streams to a high temperature (as high as 1200K (1703°F)) such that the oxygen concentration in the oxidizer stream could be greatly reduced without substantially affecting the flame temperature at the same fuel concentration. It is reasonable to assume that most previous quantitative determinations of soot formation rate suffered to varying extents from the uncontrollable oxidation effect due to OH radical. The current approach attempted to improve if not eliminate this problem. It also allows us to study the effect of preheating the fuel and the oxidizer on soot formation. Preheating is an important variable that must be considered for application of this work to turbulent diffusion flames. Our second objective was to examine the effect of primary products of combustion (i.e. CO_2 and H_2O) on soot formation. Thus inert gas in the fuel and the oxidizer streams was replaced with water vapor or carbon dioxide. This led to a considerable reduction in soot volume fraction and the eventual disappearance of previously observable orange luminosity caused by soot particles. Although the effect of CO_2 and H_2O addition on soot formation has been reported before [2,13,14]. It is unclear whether this effect is chemical or thermal. In our experiments, extreme care was exercised to hold the temperature and velocity fields identical while admitting CO_2 and H_2O. Thus it was possible to study the chemical effect of CO_2 and H_2O on particle inception and growth. Finally, after understanding the complex process of soot formation in fuel-rich counterflow diffusion flames, our third objective was to develop a simple model appropriate for use in turbulent diffusion flames. The next section describes the experiment facility that was used to independently control temperature, strain rate, fuel and oxygen concentrations and diluent addition. The results of these experiments are discussed in section 3 and finally the conclusions are presented.

2. Experimental Methodology

A counterflow diffusion flame is employed in this study because it is a fundamental "building block" for turbulent diffusion flames that are of practical interest in combustion science and because it provides a well-defined, one-dimensional system convenient for both experiments and theoretical modeling. These experiments are designed such that they represent the small scale behavior of turbulent diffusion flames.

The experimental system is illustrated in Fig.1. Two streams of gases impinge against each other to form a stable stagnation plane, which lies at the center of the burner gap. Once ignited, a flat diffusion flame is established above the stagnation plane. Measurements are taken along the axial streamline. Before leaving the burner port, the gas streams pass through a porous ceramic and a ceramic honeycomb, which are electrically heated by molybdenum disilicide elements that can sustain a maximum temperature of 2100K (3323°F) in air. Co-flowing nitrogen is introduced to eliminate oxidizer entrainment and to extinguish the flame in the outer jacket of the burner. Methane, oxygen, nitrogen, helium and carbon dioxide were obtained from cylinders and flow rates were measured using critical flow orifices. Water vapor was generated by passing a stream of inert gas (helium or nitrogen) through a distilled water saturater at a controlled temperature. The saturater was designed to ensure continuous saturation of the inert gas with water vapor. All flows quoted in this report refer to standard state (25°C and 1 atm pressure).

Figure 1 also shows the optical arrangement. An argon-ion laser beam operating at 514nm line is modulated by a mechanical chopper and then directed by a collimating lens to the central axis of the burner. This beam is used for classical light scattering and extinction measurements in the sooty flame. A photomultiplier tube and a photodiode are used to detect the scattered and transmitted signal respectively. These signals are processed by a lock-in amplifier interfaced with a microcomputer. The laser-induced broadband fluorescence measurement is realized by operating the laser at the 488nm line and detecting the fluorescence intensity at 514±10nm. In the subsequent data reduction, the soot aerosol is assumed monodispersed with the complex refractive index of 1.57-0.56i [15].

Temperatures are measured by a Pt/Pt-10%Rh thermocouple with wire diameter of 0.0762mm. The thermocouple was coated with silicon dioxide to prevent possible catalytic reaction on the platinum surface. Radiation corrections were performed by assuming a convection/radiation balance on a spherical bead [16]. The emissivity of SiO_2 coating was experimentally determined. The maximum radiation correction in a heavily sooting flame was found to be around 150K (270°F).

The chemical species concentrations in the flame are obtained by a gas chromatographic system. The sample is withdrawn by an uncooled quartz microprobe and then introduced into a gas chromatograph. A 70μm sampling probe was used for most of the analysis except in the heavily sooting flame where a larger (90μm) probe was used. This probe is positioned radially along the streamlines to minimize the disturbance. The present system has been configured to measure the concentrations of stable gases (H_2, CO_2, O_2, N_2, CH_4, CO and H_2O) and light hydrocarbons (up to C_8).

For the present axisymmetric counterflow diffusion flame, a one-dimensional model is developed to calculate the velocity field from the measured temperature and chemical species. The calculated velocity field is used in the determination of soot formation and oxidation rates. It is important to note that measurement of the velocity field in a sooty flame is very difficult even by a Laser Doppler technique because it requires seeding of the flame with particles which interfere with soot formation. Also the LDV signal is distorted by the presence of soot. Thus, only the stagnation plane was optically determined and its location was used to guide the calculation.

The experimental conditions used are summarized in Table 1. This Table shows the flow rates, the average preheating temperature of the gas streams, the concentrations of methane and oxygen and the codes used to label different flames in the subsequent presentations. Two sets of experiments were conducted. In the first set, a sooty flame (BA*flame) with high fuel concentration (65%) and low oxygen concentration (16%) was initially chosen for the investigation. This choice was based on the measurement accuracy of chemical composition. It is impossible to extract a sample using a quartz microprobe in a heavily sooting flame while the soot volume fraction and the number density are difficult to accurately measure in a barely sooting flame. This was followed by the experiments (BB* and BC*) where the gas streams were preheated to an average temperature of 900K (1163°F) and 1200K (1703°F) while simultaneously reducing the oxygen concentrations to 11% and 9.7% respectively. In the second set of experiments, Inert gas in the fuel and oxidizer streams employed in BA, BB and BC flames was partially replaced with carbon dioxide (IA*, MA*, IBF*, MBF*, IBO*, MBO* and MCF*flames) or water vapor (WAF*, WAO* and WCF* flames) to study their effect on soot formation. It should be emphasized that these experiments were designed to provide an identical thermal environment to enable quantitative comparisons.

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* Flame codes and relevant conditions are listed in Table 1. These codes are used throughout this report for simplicity, i.e., a BC flame simply means no diluent addition (B: basic condition) and at one of the three preheating temperatures (C: 1200K (1703°F)).

3. Results and Discussion

Detailed temperature, gas species concentrations, PAH and soot profiles were measured for all the flames listed in Table 1. In order to consistently and accurately interpret the flame sooting structure, the non-dimensional axial coordinate Z_n† was employed [$Z_n = (Z - Z_s)/(Z_t - Z_s)$, where Z is the axial distance from the bottom surface of the burner and Z_s and Z_t are locations of the stagnation plane and the peak flame temperature respectively]. The results described below summarize the observations and data for the sooting structure of the counterflow diffusion flame and changes in it due to preheating and water vapor or carbon dioxide addition. Analysis of these data yields the soot formation rate under various conditions.

The sooting structure

1. Luminosity and flame structure: In the experiments, a three-color-layer sooting flame is clearly observable. This flame is above the stagnation plane (i.e. from $Z_n = 0$ to $Z_n = 1.1$, about 6 to 8mm thick). Figure 2 schematically illustrates this sooting flame structure. Temperature, velocity and heat release rate profiles are presented in Fig.3 and Fig.4 where velocity and heat release rate were calculated following the method described in [4]. It shows that while traveling along the central stream line, from the oxidizer side to the fuel side, a light blue zone is encountered in which the peak flame temperature (~1900 K (2963°F)) and main combustion reactions occur; in particular the chain branching reactions ($O_2 + H = OH + O$ and $O + H_2 = OH + H$) 1500K (2243°F) to 1800K (2783°F). Between the blue and yellow zones there exist a thin dark zone whose origin is not clear. In the yellow zone, measurable scattering by soot particles does not exist, but laser-induced fluorescence is detected. Thus, it is presumed that in this zone soot precursor molecules responsible for B-G (Blue-green) fluorescence are formed. The fluorescence signal increases continuously until it reaches a maximum near the stagnation plane. In the yellow zone, the concentration of precursors is not high enough for nucleation to occur. In the past, the presence of yellow in flames was considered as an indication of the presence of soot. However, we find that the flame is yellow because of large molecular weight soot precursor

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† The non-dimensional coordinate Z_n is used in the following data analysis.

molecules. Experimentally, it is relatively easy (by controlling strain rates and fuel and oxygen concentrations) to obtain a yellow flame with negligible soot particle scattering. Between the yellow zone and the stagnation plane, a dark orange zone exists where the temperature is between 1200K (1703°F) and 1600K (2423°F). Soot particulate scattering and soot volume fraction in this zone increase until we reach the stagnation plane.

In the yellow and orange zones, abundant unsaturated hydrocarbons such as C_2H_2, C_2H_4 and C_6H_6 were found to be produced through gas phase pyrolysis of methane. This chemical process followed by dehydrogenation eventually leading to formation of soot precursors [19]. It was reported earlier [3] that soot inception occurs around the dark area of the flame in the virtual absence of oxygen but in the presence of radicals and combustion products. However, we find that precursors begin to form after the dark region of the flame and soot inception occurs at the interface of yellow and orange zones. This is rational because a certain minimum concentration of soot precursors is required prior to nucleation. The small incipient particles thus formed are driven downstream by gas convection and thermophoresis as they grow in size and emit considerable radiation causing the luminosity. Two hypotheses were proposed previously regarding the color change (from yellow to orange) in the sooting zone [19]: (i) The increased amount of condensed aromatic rings causes the wavelength of maximum emission to shift toward the red; (ii) The lower temperature of the soot particle results in red emission. Evidence obtained in this work suggests that soot particles are mainly responsible for the orange emission. Flames with CO_2 and H_2O addition were less sooty, appeared yellow and were less orange. Photographs of flames with CO_2 substitution are shown in Fig.5. Here, the dark orange zone is seen to turn to yellow as CO_2 substitution is increased to 21%. Note that the flame temperature did not change but the soot volume fraction was changed.

2. Chemical species and PAH concentrations: Profile measurements for stable gases, several intermediate hydrocarbons and large PAH are shown in Figures 6, 7 and 8. The rates of chemical reactions involving these species were calculated from the species conservation equations : [4]

$$R_i = \frac{1}{M_i}\left\{\nabla[\rho y_i(v + v_{di})]\right\}, \qquad (1)$$

where, M_i is the molecular weight, ρ is the gas density, y_i is the mass fraction of species i, v is the convective velocity and v_{di} is the net diffusion velocity of species i into the local mixture. Since R_i is related to the gradient of y_i, v and v_{di} are unaffected by a scaling of the mass fraction y_i, R_{PAH} can be interpreted usefully in a relative sense from the measured relative concentrations of PAH (presumed to be acenaphthylene [20]). The overall production and destruction rate profiles are presented in Fig.9 and Fig.10.

These figures characterize the sooting structure in a counterflow diffusion flame. It is seen that primary combustion reactions occur in a narrow blue flame zone, (Z_n = 0.9~1.1) where H_2O and CO_2 are formed and O_2 is consumed. Here, H_2 and CO are oxidized to CO_2 and H_2O. The peak destruction rate of methane, however, has shifted to the fuel side in a region spatially corresponding to the appearance of abundant C_2 and PAH species. Also the large destruction rates of C_2H_2 and PAH around Z_n = 0.3~0.8 are found to coincide with the surface growth of the soot particles. This reveals the contributions of C_2H_2 and large PAH to the surface growth of soot. Many other hydrocarbons such as C_2H_6, C_2H_4 and C_6H_6 are also being produced and depleted in the same region where soot growth occurs. The roles of these species seem to be unconnected with chemical processes which directly lead to soot inception and growth. This deserves more discussion.

The soot-forming reaction sequence in a rate-controlled diffusion flame environment is quite complicated. Analysis, thus far, has indicated that the overall process may involve two coincident chemical sequences spatially overlapping each other in a three-color sooting flame zone: first the pyrolysis of methane which eventually creates intermediate hydrocarbons and soot precursors, second the inception and surface growth of soot particles which consumes the precursor and intermediate species. The mechanism of the first sequence has been proposed in [21]:

$$CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C_4H_5 \rightarrow PAH$$

In our system, methane diffuses upward across the stagnation plane into the main reaction zone while it is continuously pyrolyzed and converted to intermediate hydrocarbons, soot precursors and eventually into soot particles. Oxidative attack on precursors occurs in the yellow zone. Once formed, these young soot particles are convected