

NUMERICAL CALCULATION OF SOOT FORMATION IN PREMIXED HYDROCARBON FLAMES

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Keywords: Soot formation, numerical simulation, hydrocarbon flames

Abstract

Numerical calculations including a chemical model for soot formation have been performed for premixed burner stabilized ethene-air flames at 0.1 and 1.0 MPa that have been investigated experimentally by Wagner et al. The maximum temperatures in the flames have been varied in the experiments by changing the mass flow rates of the mixture. In accordance with the experimental data the numerical calculations predict a bell shaped dependence of the final soot volume fraction on the maximum flame temperature.

The dependence of the final soot volume fraction on pressure between 0.1 and 1.0 MPa is calculated to be proportional $p^{1.5}$ to p^2 . This is slightly weaker than found experimentally in the experiments of Wagner et al. It is concluded that the pressure dependence of some gasphase reaction rates, in particular that for the formation of benzene and the PAH growth has to be validated.

Introduction

In sooting hydrocarbon flames fuel molecules are converted within few milliseconds into carbonaceous particles containing millions of carbon atoms. It is known that the formation of soot is mainly determined by particle inception, by coagulation of primary soot particles to larger aggregates, and by heterogeneous reactions of soot particles with the surrounding gasphase. Much progress has been made in understanding these processes, however, a number of problems are yet unsolved [1-4].

Phenomenologically, the final soot volume fraction f_v^∞ in premixed flames—that is the soot volume fraction attained shortly after the reaction zone—depends for a given fuel on pressure, mixture, composition and temperature. From numerous experimental work, e.g. [5-9] it is known that in a pressure range from 0.1 to 1.0 MPa the final soot volume fraction varies with the square of pressure. The temperature dependence of the final soot volume fraction reveals a bell shaped form, whereas the dependence on mixture composition may be given as $f_v^\infty \sim [(C/O) - (C/O)_{\text{sooting limit}}]^n$ with $2.5 \leq n \leq 3$, cf. [8].

The formation of soot in premixed flames is dominated by heterogeneous surface growth reactions, see e.g. [10,11]. Ethyne has been found to be the most likely chemical "growth specie", because ethyne is the most abundant hydrocarbon species in the soot forming region of premixed flames.

A mechanistic interpretation of surface growth reactions has been introduced by Frenklach [12]. Analogously to the planar growth of polycyclic aromatic hydrocarbons, surface growth of soot particles is, on the per-site basis, explained by a radical hydrogen abstraction carbon addition (HACA) mechanism. In addition oxidation of soot particles by OH and O₂ has been taken into account.

In the following the over-all temperature and pressure dependence of the final soot volume fraction is explained in terms of chemical reactions between gasphase compounds and the soot surface. This concept basically contains the competing processes in soot formation by surface reactions: carbon addition by adding ethyne and oxidation by oxygen and OH. Presuming a different temperature dependence of the three processes, the picture of the temperature dependence of the soot volume fraction is—in principle—understandable.

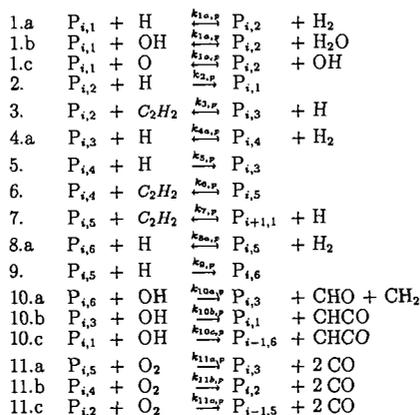
Model for soot formation

The model for soot formation that has been integrated into a numerical code for one-dimensional flat premixed flames, cf. [14], has been developed from the one discussed above. The PAH growth has been formulated with the help of fast polymerisation reactions [14] reducing the number of equations to be solved and the numerical effort. It should be emphasized that detailed models of the kind below depend essentially upon the quality of kinetic parameters and the knowledge of the reaction channels for the reactions of the species involved. Furthermore, it should be mentioned that these models reproduce only phenomena connected with the formation of the bulk of soot. Many phenomena, e.g. the formation of high molecular tarry structures that are observed in an early stage of soot formation or the "fine structure" of soot are not covered by these models.

The model is essentially subdivided into three parts — gas phase chemistry, polymerisation of PAH and formation and growth of soot particles.

The gas phase chemistry up to the first aromatic ring is calculated with the help of a detailed mechanism provided by Warnatz [15], consisting of about 250 elementary reactions between 52 chemical species. The first aromatic ring, viz. benzene, is formed via the reaction $C_3H_3 + C_3H_3 \rightleftharpoons c - C_6H_6$. The calculation of the growth reactions of benzene to small PAH follows the mechanism suggested by Frenklach and Warnatz [16]. Following Frenklach [17], the further growth of PAH is assumed to be a polymerisation process.

Within each polymerisation stage two aromatic rings are added to a given PAH. Each step from PAH to PAH involves several chemical reactions. The detailed growth and oxidation mechanism used for the calculations presented here is given below.



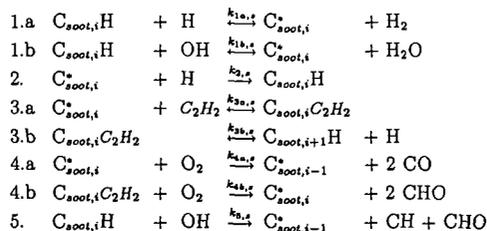
The growth mechanism is initiated by an H-abstraction step due to the attack of H, O and OH via reactions 1a-1c. The radicalic site of $P_{i,2}$ may be deactivated by the H-addition (reaction 2) or by the revers of reactions 1a-1c. Ethyne is taken up at the radicalic site of $P_{i,2}$ via reaction 3. The repetition of this reaction sequence (reactions 4-6) leads to the closure of an aromatic ring. Because $P_{i,5}$ has a radicalic site, ethyne may be added again and an other ring closure occurs (reaction 7). This second ring closure leads to the next polymerisation stage, where the reaction sequence is repeated. In analogy to the radical sites of $P_{i,2}$ and $P_{i,4}$ the radical site of $P_{i,5}$ can be deactivated by H-addition (reaction 9) or by the revers of reactions 8a-8c. PAH may be oxidized by reactions with OH (10.a-c) and t PAH with a radicalic site may be oxidized by reactions with O_2 (11.a-c).

The formulated reaction sequence is one possible reaction sequences leading to PAH-growth involving six-membered rings. Five-membered rings can be included by similar reaction sequences involving a larger number of intermediates without affecting, however, the basic ideas of the following approach.

Differently from the approach of Frenklach the growth of the PAH is assumed to be a fast polymerisation process. It follows that each PAH is in quasi steady state and that the concentrations of PAH can be calculated from an algebraic system of equations. Details of this analysis are given in [14].

The pathways to soot from PAH are particle inception and condensation of PAH on the surface of the soot particles. Both pathways are assumed to follow Smolouchowski's coagulation equations in the free molecular regime [12,18]. The equations are also used to calculate the coagulation of soot particles.

The heterogeneous surface growth and oxidation of soot particles follow the mechanism given below:



The mechanism is modified compared with the one introduced by Frenklach [12]. The reverse of reaction 1.b accounts for the radicalic site consuming influence of H_2O . Reaction 3 consists of two reactions—carbon addition, ring closure—, because it has been found recently that the reverse of reaction 3 accounts for the limitation of surface growth at high temperatures [19]. The more detailed analysis here shows, that the reverse of reaction 3.a is responsible for this effect, while reaction 3.b is approximately irreversible. If—in analogy to Frenklach's formulation and the planar PAH growth— $\chi(C_{soot,i}^*)$ and $\chi(C_{soot,i}C_2H_2)$ are replaced by the assumption of quasi stationarity, the appearance rate of soot can be expressed as follows. We first introduce a factor accounting for the progress of soot growth.

$$f3a = \frac{k_{3b,f}}{k_{3b,f} + k_{3a,b} + k_{4b}[O_2]} \quad (1)$$

If the ring closure via reaction $k_{3b,f}$ is fast compared with the radicalic site consuming and oxidation reactions then $f3a = 1$. If the radicalic site consuming and oxidation reactions are fast then $f3a = 0$. With this definition we write

$$\chi(C_{soot,i}^*) = \frac{k_{1a,f}[H] + k_{1b,f}[OH] + k_{3b,b}[H](1 - f3a)}{k_{1a,b}[H_2] + k_{1b,b}[H_2O] + k_2[H] + k_{3a,f}[C_2H_2]f3a} \cdot \chi(C_{soot,i}) \quad (2)$$

$$\chi(C_{soot,i}C_2H_2) = \frac{k_{3a,f}[C_2H_2]}{k_{3b,f} + k_{3a,b} + k_{4b}[O_2]} \cdot \chi(C_{soot,i}^*) + \frac{k_{3b,b}[H]}{k_{3b,f} + k_{3a,b} + k_{4b}[O_2]} \cdot \chi(C_{soot,i}) \quad (3)$$

$$\frac{df_s}{dt} = (k_{3a,f}[C_2H_2]f3a \cdot \chi(C_{soot,i}^*) - (k_{3b,b}[H](1 - f3a) + [OH]k_5) \cdot \chi(C_{soot,i})) \cdot S \quad (4)$$

In the soot forming limit ($f3a = 1$). In the radicalic site consuming limit, $f3a = 0$ the growth of soot is limited at high temperature because of the high activation energy of reaction $k_{3a,b}$.

The algebraic formulation of this model leads to an infinite number of partial differential equations for the number density of soot particles which is reduced to a limited number by using the method of moments (method 2 in [18]). Thermophoretical transport and size dependent diffusion of soot particles has been considered. The system of equations is solved numerically employing a Newton Method

Results and Discussion

Burner stabilized flat premixed ethene-air flames ($C/O = 0.72$) that have been investigated experimentally by Wagner et al. [8,20] have been numerically simulated at 0.1 and 1.0 MPa. The maximum flame temperature in the experiment has been varied by varying the mass flow rate of the unburnt mixture.

The temperature and soot volume fraction profiles of an ethene-air flame ($C/O = 0.72$) with a cold gas flow velocity of 4.5 cm/s are given in Fig.1. The soot volume fraction (cm^3_{soot}/cm^3_{gas}) is density related. Therefore, we have normalized the profile to a temperature of 1400 K. This is also demonstrated in Fig.1. It is obvious from this figure, that the final soot volume fraction is attained at a height of 35 mm above the burner. At larger heights the soot volume fraction increases with decreasing temperature and the normalized soot volume fraction remains constant. The agreement between calculated and measured data is reasonably good.

The calculated final soot volume fractions of all investigated flames at 0.1 MPa are shown in Fig. 2 in dependence on the flame temperature at 10 mm height above the burner. The final soot volume fraction: is given in the the normalized form. We prefer the normalized soot volume fraction, because this definition is not dependent on the shape of the temperature profile. The comparison of the model prediction with experimental data from Refs.[8,20] reveal that the calculations reproduce the soot volume fraction quite well at high flame temperatures. At lower flame temperatures the agreement between measured and calculated soot volume fractions is reasonable. In summary, the over-all dependence of soot formation on flame temperature can be understood with the help of the detailed chemistry soot model.

Most of the rate coefficients of reactions concerning the formation and growth of PAH or soot are unknown and have to be estimated from comparable gasphase reactions by analogy. However, the above discussed results clearly point out that within the framework of the presently available information the soot volume fraction can be predicted reasonably in terms of chemical reactions between gasphase compounds and the soot surface.

In addition to the calculations above the temperature dependence of soot formation in ethene/air flames at 1.0 MPa has been calculated. This is shown in Fig.3. It can be seen, that the model again predicts a bell shaped dependence of the soot volume fraction on flame temperature. However, the pressure dependence of the prediction as well as the temperature dependence at the higher pressure is weaker than found in the experiment [8]. The pressure

dependence of the final soot volume fraction is calculated to be proportional to p^2 at high flame temperatures. With decreasing flame temperature the pressure dependence reduces to proportional to $p^{1.6}$. A similar weak pressure dependence has been found experimentally [9] at pressures larger than 1.0 MPa where the final soot volume fraction varies linearly with pressure. We conclude that the decreasing pressure dependence of the soot volume fraction with increasing pressure is overestimated by the model used in this investigation. We note that the linear increase of the density related soot volume fraction just refers to the linear increase of the density with pressure. An analysis of the numerical results indicates, that the increasing partial pressure of H_2 is responsible for the limited rate of soot formation at high pressure. The increasing partial pressure of H_2 reduces the number of radicalic sites on the surface of the soot particles via the reverse of reaction (1.a.s).

Conclusions

A model that encompasses two pathways to soot from PAH, particle inception and condensation of PAH on the surface of the soot particles and that describes surface growth of soot similarly to the planar growth of PAH is employed to predict temperature and pressure dependence of soot formation in premixed ethene-air flames.

Within the framework of this model the experimentally measured final soot volume fraction and its temperature and pressure dependence are well reproduced.

Acknowledgement

This research was partially supported by the commission of the European Communities, the Swedish National Board for Technical Development (STU) and the Joint Research Committee of European car manufacturer (Fiat, Peugeot SA, Renault, Volkswagen and Volvo) within the IDEA programs.

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