EXPERIMENTAL AND NUMERICAL ANALYSIS OF THE INFLUENCE OF OXYGEN ON SOOT FORMATION IN LAMINAR COUNTERFLOW FLAMES OF ACETYLENE

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Axisymmetric counterflow flames at atmospheric pressure are used to investigate the influence of oxygen on soot formation. An acetylene/nitrogen mixture is blown against the hot postflame gases of a lean premixed flame stabilized on a sinter metal plate, thereby preheating the oxidizer. Oxygen is then added separately to the fuel and oxidizer side. Measured temperature, species concentration and soot volume fraction profiles are compared with calculations. The latter are performed using a detailed kinetic reaction mechanism with 452 reactions and a detailed soot model describing particle nucleation, coagulation, polycyclic aromatic hydrocarbon (PAH) condensation, surface growth, and surface oxidation. It is found that oxygen addition increased the maximum soot concentration in both cases. The model predicts the same trends, and satisfactory agreement between measured and calculated values for all investigated parameters is observed. To distinguish between chemical influences of oxygen addition and thermal and dilution effects, further numerical studies are carried out following a procedure similar to the one proposed by Axelbaum et al. [1]. For fuel side addition of oxygen, the increased soot volume fraction is attributed to a catalytic effect triggering the production of benzene via C_3 and C_4 species. For the case of O_2 addition to the oxidizer stream, it is found that the higher flame temperature was the main cause for the increased soot concentration.

Introduction

The influence of gaseous additives on soot formation has been investigated extensively in the past [1–11]. In these efforts, oxygen addition has played a key role. On the one hand, this is due to the complexity of the combined thermal, dilution, and chemical effects which result through addition. On the other hand, O_2 is considered a candidate for soot suppression through enhanced oxidation. Early work was focused on premixed combustion [2,3], in which both suppressive interaction and catalytic interaction of oxygen were identified. The main effects in the latter case were an enhancement of fuel decomposition and precursor formation and an increase in production of atomic hydrogen promoting aromatic growth. As several studies revealed, also in diffusion flames soot concentration can rise with the addition of oxygen. When added to the fuel side, this was found mainly for alkene fuels and was explained by direct chemical interaction [4,5,6]. This phenomenon is also expected for alkynes [6]. For alkanes, contradictory results stating both promotive and suppressive effects of O_2 have been published [4,8,9]. Oxygen-enriched oxidizer led also to an enhanced soot production in ethylene diffusion flames, which was considered to be mainly a thermal effect [4].

To distinguish the influences of temperature, dilution, and chemistry, several proposals for experimental work were made in the literature. Axelbaum and coworkers [1] introduced the concept of maintaining the flame temperature constant while varying dilution through partial replacement of nitrogen by argon. In the work of Gülder [8], a constant flame temperature was achieved by adapting the initial temperature of the reactants. Glassman [9] pointed at the importance of the entire temperature field for the soot growth process. He postulated that soot concentration can be correlated to the time a particle is convected through a zone where temperatures are high enough for particle inception to occur. In that context, Glassman [9] and Du et al. [10] underlined the significance of thermal diffusivity variations introduced by additives.

In this paper, experimental and numerical investigations are combined to isolate the effects of temperature, dilution, and chemistry introduced through the addition of oxygen to the fuel and oxidizer side of an acetylene counterflow diffusion flame. This study is part of a larger project investigating flames with preheated oxidizer. The preheating was achieved through a lean premixed flame stabilized at the oxidizer nozzle. Thus, the oxidizer consisted of the hot combustion products of that.
Summary for all investigated flames: boundary conditions, strain rate, calculated location of stagnation plane (distance from the fuel nozzle), possible effects of addition, calculated temperatures, and normalized soot volume fractions

<table>
<thead>
<tr>
<th>Flame</th>
<th>1</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
<th>3a</th>
<th>3b</th>
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<tbody>
<tr>
<td>Oxidizer side</td>
<td>(\Phi)</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.62</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>(\chi_{\text{inert}})</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>% Argon in inert</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>4.5</td>
<td>0</td>
</tr>
<tr>
<td>Fuel side</td>
<td>(X_{\text{CH}_2})</td>
<td>0.506</td>
<td>0.479</td>
<td>0.479</td>
<td>0.506</td>
<td>0.506</td>
</tr>
<tr>
<td></td>
<td>(X_{\text{N}_2})</td>
<td>0.494</td>
<td>0.496</td>
<td>0.496</td>
<td>0.494</td>
<td>0.494</td>
</tr>
<tr>
<td></td>
<td>(X_{\text{add}})</td>
<td>0</td>
<td>0.025</td>
<td>0</td>
<td>0.025</td>
<td>0</td>
</tr>
<tr>
<td>Strain rate</td>
<td>(K) (1/s)</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Stagnation plane</td>
<td>(h) (mm)</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>Possible effects</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>Dilution</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chemistry</td>
<td>+</td>
<td>+</td>
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<td>Temperatures</td>
<td>(T_{\text{max}}) (K)</td>
<td>1897</td>
<td>1904</td>
<td>1904</td>
<td>1904</td>
<td>2004</td>
</tr>
<tr>
<td></td>
<td>(T_{\text{soot inc}}) (K)</td>
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<td>1862</td>
<td>1867</td>
<td>1866</td>
<td>1928</td>
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<tr>
<td></td>
<td>(T_{f,\text{soot}}) (K)</td>
<td>1068</td>
<td>1106</td>
<td>1065</td>
<td>1063</td>
<td>1126</td>
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<tr>
<td>Normalized soot volume fractions</td>
<td>(f_{v,\text{max}})</td>
<td>1</td>
<td>1.3</td>
<td>0.96</td>
<td>1.05</td>
<td>1.4</td>
</tr>
</tbody>
</table>

**Experimental**

Figure 1 displays the counterflow configuration used. The premixed oxidizer is stabilized on a cooled sinter metal plate at the upper nozzle (diameter 50 mm). The fuel side nozzle is located at a distance of 16 mm and has the same geometry. A nitrogen shroud flow keeps outside air from penetrating into the counterflow zone. All gas flows are controlled by thermal mass flow controllers, with an accuracy of 1%. High-purity gases are used. The usual aceton impurity in acetylene was limited to 2% and taken into account in the calculations. The boundary conditions of the investigated flames are summarized in Table 1. For all flames, the total mass flow rates were 0.165 g/s for the oxidizer and 0.082 g/s for the fuel premixed flame. As a reference case (flame 1 in Table 1), a diffusion flame without further \(O_2\) addition using an acetylene/nitrogen mixture as fuel was considered. In flame 2a, \(O_2\) was added to the fuel stream. The addition to the oxidizer was realized through a leaner gas mixture of the premixed flame (flame 3a).

After a brief description of the experimental setup and the detailed kinetic model used for the calculations, experimental and modeling results are compared. Further calculations following a procedure similar to that of Axelbaum et al. [1] are used for the isolation of the effects discussed. For the case of \(O_2\) addition to fuel, in flame 2b chemical influences are suppressed by replacing oxygen with nitrogen. The maximum flame temperature and inert dilution occurring in case 2a were maintained by replacing a portion of the nitrogen in the oxidizer stream with argon. In flame 2c, only the maximum temperature was conserved with reference fuel concentration. For the case of increased \(O_2\) concentration in the oxidizer (flame 3a), dilution effects can be neglected since changes in the oxygen mole fraction in the combustion products of the premixed flame were below 1% compared with the reference case. The contribution of higher flame temperature is isolated by comparison with flame 3b, where the maximum temperature of flame 3a is retained while chemical concentrations of inerts and reactants are those of the reference case.
stream. The strain rate was calculated using the formulation of Puri and Seshadri \[12\]. For flame 3b, the replacement of nitrogen by argon resulted in a significant strain rate variation. Both experimental observations and numerical results revealed, however, that this variation affected the soot concentration by less than 5%.

The experimental methodology is similar to that reported previously \[13\]. Along the axis of symmetry, gas was sampled through a heated quartz glass probe with an opening diameter of 100 \( \mu \text{m} \). The position of the probe was controlled optically with a cathetometer. A stainless steel tube connected the probe to a 1 \( \text{cm}^3 \) sample loop of a gas chromatograph equipped with a thermal conductivity and flame ionization detector. All tubing was kept at temperatures above 400 K to prevent any condensation. Detected species were \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CO, CO}_2 \), and hydrocarbons consisting of up to six \( \text{C} \) atoms.

The soot volume fraction on the axis of symmetry was measured by laser light extinction using an argon-ion laser at \( \lambda = 488 \text{ nm} \). Although all flames have a one-dimensional structure, a slight curvature which is most likely caused by buoyancy effects was observed. Therefore, the line-of-sight integrated transmittance signal had to be corrected. This was achieved with a discrete “onion peeling” technique \[14\]. It was found that the local centerline extinction coefficient, \( k_{\text{ext}} \), differed from the mean value by a factor of up to 2, with the largest deviations being observed close to the point of maximum soot concentration. The soot volume fraction, \( f_{\text{c}} \), was calculated from

\[
f_{\text{c}} = \frac{\lambda k_{\text{ext}}}{6\pi\text{Im}(m^2 - 1)} \frac{m^2 - 1}{m^2 + 2}
\]

with a complex refractive index of \( m = 1.95 - 0.66i \). All data presented in Figs. 5 and 6 are corrected as described above.

Temperature measurements were performed with a Pt/PtRh thermocouple (type B) with a bead diameter of 100 \( \mu \text{m} \). The position was also controlled optically. Results were corrected for heat loss through radiation, assuming a cylindrical shape of the bead. The values for the temperature-dependent emissivity of Pt/PtRh surfaces were interpolated using data from Ref. \[15\]. Since thermocouple measurements in sooting flames may be influenced by soot depositions, an additional pyrometer method \[16,17\] was employed for further temperature measurements in this zone. For this technique, light emission from the sooting region of the flames at 488 nm was detected with a 12 bit charge-coupled device (CCD) camera equipped with a 10 nm half-bandwidth interference filter. Comparing the flame emission with a calibrated black body light source (tungsten light), a corresponding black body temperature, \( T_b \), is obtained. The line-of-sight averaged soot temperature, assumed to be reasonably close to the average gas-phase temperature, was calculated from equation 2. The constant \( c_2 = 0.01438 \text{ km} \) is taken from Wien’s law, and \( \tau_{\text{j}} \) is the integrated transmission signal at 488 nm evaluated by the extinction measurements.

\[
\frac{1}{T} = \frac{1}{T_b} + \frac{\lambda}{c_2} \ln (1 - \tau_{\text{j}}) \quad (2)
\]

### Numerical Simulation

Soot formation in the counterflow configuration is simulated by integrating a soot model into the numerical formulation of the counterflow problem. A similarity solution allows the latter to be written as one-dimensional conservation equations of mass, transverse momentum, species, and energy \[18\]. The formulation of the soot model is essentially taken from Ref. \[19\]. Following the work of Frenklach and Harris \[20\], additional transport equations for statistical moments of soot are derived:

\[
\rho c dM_j/r_{\text{p},i} - d/dy \left( \rho D_{i,1} d/dy \left( \frac{(M_{j,-2/3})}{\rho} \right) \right) - d/dy \left( 0.55 \sqrt{\frac{T}{\tau}} \frac{1}{\tau} \frac{d\tau}{dy} M_j \right) - M_j = 0 \quad (3)
\]

In equation 3, \( \rho \) denotes the density, \( y \) the coordinate in axial direction, \( c \) the corresponding velocity, \( D_i \) the diffusion coefficient for the smallest soot particles, and \( \tau \) the kinematic viscosity. For the derivation of equation 3, it is assumed that the diffusion coefficient for soot particles, \( D_{\text{p},i} \), varies with \( d^{-2} \) and can be expressed through

\[
D_{\text{p},i} = i^{-2/3} D_{\text{p},1} \quad (4)
\]

The definition of the statistical moments is given by

\[
M_i = \sum_{i=1}^{\infty} i^i N_i \quad (5)
\]

where \( N_i \) is the number density of particles of size \( i \), with \( i \) representing the number of \( \text{C}_2 \) molecules for that size class. For the present paper, the first two statistical moments were solved, representing the total particle number density and the total soot concentration. The source term, \( M_i \), in equation 3 is the sum of contributions from particle inception due to polycyclic aromatic hydrocarbon (PAH) coagulation, PAH condensation on soot, particle coagulation, surface growth, and oxidation. The first three processes are described with Smoluchowski’s coagulation equation:

\[
\dot{N}_i = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{ij} N_j N_{i-j} - \sum_{j=1}^{\infty} \beta_{ij} N_i N_j \quad (6)
\]

In equation 6, \( \beta_{ij} \) is the frequency coefficient for
SOOT FORMATION AND DESTRUCTION

Further growth of PAH is assumed to be a fast polymerization process through HACA. The introduction of a steady-state assumption for PAH allows this to be modeled with algebraic equations. The calculations were performed with the code FlameMaster developed at the Institut für Technische Mechanik [23].

Results and Discussion

Figures 2 through 5 display the comparison between measured (solid symbols) and calculated (lines) data of important parameters for flames 1, 2a, and 3a. The flame structure of the counterflow configuration can best be explained by means of the temperature profile in Fig. 2. At the oxidizer side (16 mm), there is a sharp increase in temperature due to the stabilized premixed flame. The maximum temperature is found in the center (8 mm), which marks the position of the diffusion flame. These profiles are well reproduced by the model, including the increased peak temperature for flame 3a. In the sooting zone between 4 and 6 mm, the thermocouple data are below calculated values for all cases. This is most likely caused by soot depositions on the thermocouple, since data obtained by optical measurements are higher. The reasonable agreement in the CO profiles (Fig. 3) substantiates that the overall flame structure of the configuration can be predicted with the reaction mechanism used.

Important stable intermediates for soot are C₃H₄ and benzene, which are displayed in Fig. 4. For both species, an enhanced production can be found for the case of oxygen addition to fuel (flame 2a). Although a quantitative deviation has to be noted, this trend is clearly reproduced by the calculations. Similar characteristics can be found for C₄H₈ isomers, with the maximum concentration being increased by a factor of 4 (calculated: factor of 2) in flame 2a as compared with flames 1 and 3a (not shown in figures). The only species for which O₂ addition to the oxidizer results in higher intermediate concentrations is diacetylene (not shown in figures). In flame 3a, the peak value of that intermediate is 60% higher (calculated: 40% higher) than in the other flames. The remaining hydrocarbon species investigated did not display any significant changes in their profiles for the three flames.

The profiles of soot concentration expressed as soot volume fraction are displayed in Fig. 5. For both cases of oxygen addition, a considerable enhancement of soot is found in both the experiment and the calculations. For all flames, the maximum soot load is overpredicted by the model, but the trends are again well reproduced. These results agree well with findings for ethylene flames [4,7] and match the expectations formulated by Hura and Glassman [6].

From the satisfactory agreement between experimental and simulated data, we conclude that the reaction mechanism can be used for further numerical analysis.

collisions between non-interacting particles in the free molecular regime. The last two processes listed above involve chemical reactions and are modeled after a modified H abstraction and C₂H₂ addition (HACA) mechanism [21,22].

The reaction mechanism modeling the gas-phase chemistry for species up to five-ring aromatics is taken from Ref. [19]. The kinetic data may be obtained on request. A modification for the kinetic data of the 1,3-butadienyl (C₄H₅) oxidation was introduced to avoid stronger overprediction of benzene production in flame 2a. In the reaction mechanism, benzene is produced either through recombination of C₃H₃ or via acetylene addition to C₄H₂ species.
In the remaining part of this paper, we discuss the results from the calculations. The calculated soot volume fraction profiles using an approach similar to that of Axelbaum et al. [1], as discussed in the introduction, are presented in Fig. 6. While temperature and dilution only lead to small changes in soot concentration, there is a large difference between flames 2a and 2b and between flames 3a and 3b. For both cases, one could therefore be tempted to conclude that the increased soot concentration is exclusively due to chemistry. The results from the species profiles above would, however, justify the assumption of modified chemistry only for flame 2a. With that in mind, it is worthwhile to take a closer look at the temperature distribution of the flames. For that reason, Table 1 lists temperatures of flame positions corresponding to the beginning of particle inception \(T_{\text{soot inc}}\) and maximum soot volume fraction \(T_{\text{fv,max}}\). These two locations characterize the temperature distribution across the zone where soot is formed. For both cases in flame a, there is a higher temperature at the location of maximum soot concentration than in flames b. Therefore, increased soot growth has to be assumed, although the maximum flame temperature is kept constant in flames a and b. This result clearly supports Glassman’s findings [9]. It may not suffice to maintain maximum flame temperature to isolate the chemical effects of additives. This leads to the question of what causes the variations of the temperature fields. For flame 2a compared with flame 1, the change can be attributed to a modified heat release due to chemistry, which is displayed on the left side of Fig. 7. The additions of oxygen and argon are quite small, so that major changes in thermodiffusivity are not introduced. For flame 3a compared with 3b, modified thermal diffusivity is to be expected because of the large argon concentration. The right part of Fig. 7 shows the center of the temperature profile for these flames.
and a clear shift of the profile is obvious, whereas the location of maximum soot concentration is not shifted at all (Fig. 6). This leads to the conclusion that the increase in soot concentration in flame 3a compared with 3b cannot be attributed to modified chemistry but rather to the shifted temperature field. Considering the species profiles of flames 1 and 3a, one can conclude that oxygen addition to the oxidizer increases the soot load through a thermal effect.

To further characterize the modified chemistry in flame 2a, data of a reaction flux analysis were used. It was found that benzene formation is enhanced via both the C3 and the C4 path. In Ref. [6], it was postulated that O2 addition to thermally stable fuels such as ethylene and acetylene would lead to an extensive increase in the radical pool. In the present case, the most important radicals were identified to be vinyl (C2H3) and propargyl (C3H3). The first reagents with acetylene through reaction 7, triggering the C4 path, and the second directly forms benzene through recombination.

\[
C_2H_3 + C_2H_2 \rightarrow C_6H_6
\]  
(7)

All radical species including the H radical had only slightly higher (less than 3%) maximum concentrations in flame 2a compared with the reference. However, the profiles were shifted to lower temperatures. This supports Frenklach et al.’s early findings [2, 3] on the catalytic effect of oxygen in the acetylene fuel stream and explains the higher production rates of benzene.

**Summary**

Experimental and numerical investigations are used to characterize the influence of separate O2 addition to the fuel and oxidizer stream of a counterflow diffusion flame. Satisfactory agreement between measured and calculated data was observed. For both cases, the soot concentration was increased compared with the reference flame. Oxygen addition to fuel has a catalytic effect. By radical production at lower temperatures, it triggers pyrolytic reactions. The consequences are slightly increased heat release, enhanced benzene formation via the C3 and C4 path, and increased soot formation. For the case of oxidizer side addition, higher soot concentrations are due to thermal effects.

**Acknowledgments**

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**REFERENCES**

COMMENTS

Ariel Dvorjetski, Technion—Israel Institute of Technology, Israel. Concerning the influence of dilution, could you specify the quantitative effect on the oxidant Lewis number in the examined flames versus the reference value of oxidant Lewis number?

Author’s Reply. The dilution influence was only relevant for the O2-addition to the fuel side. Significant changes in the oxygen Lewis number were observed only for flame 2a in the zone near the stagnation plane. While the value for the reference flame was in the order of 0.88, it increased in flame 2a by up to 3.5% in that zone.

Daniel Rosner, Yale University, USA. When the gas stagnation plane is not far from the diffusion flame [1], then axial species mass transport driven by the local temperature gradient will be important, and one should take into account the fact that the dimensionless thermophoretic diffusivity for the “smaller” PAHs will fall noticeably below 0.55 (the “heavy particle” [Waldman-] limit value). Rational estimates of the molecular weight dependence of the thermophoretic (Ludwig-Soret) diffusivity of the PAHs below 300 amu have recently been made [2] and could readily be incorporated in the next level of flame-soot modeling.

REFERENCES


Author’s Reply. In this study, thermophoretic transport was in fact neglected for small PAH. The mass of an average soot particle is at least one order of magnitude larger than that of small PAH. Therefore, the particle-limit asymptote for the dimensionless thermophoretic diffusivity was used in equation 3. Analysis of the terms in this equation showed that thermophoretic transport played a minor role for all flames studied. Hence, uncertainties in this term do not affect the conclusions of this work.