Characteristics of non-premixed oxygen-enhanced combustion: I. The presence of appreciable oxygen at the location of maximum temperature

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A B S T R A C T

The presence of appreciable molecular oxygen at the location of maximum temperature has been observed in non-premixed oxygen-enhanced combustion (OEC) processes, specifically in flames having a high stoichiometric mixture fraction (Zst) produced with diluted fuel and oxygen-enrichment. For conventional fuel–air flames, key features of the flame are consistent with the flame sheet approximation (FSA). In particular, the depletion of O2 at the location of maximum temperature predicted by the FSA correlates well with the near-zero O2 concentration measured at this location for conventional fuel–air flames. In contradistinction, computational analysis with detailed kinetics demonstrates that for OEC flames at high Zst: (1) there is an appreciable concentration of O2 at the location of maximum temperature and (2) the maximum temperature is not coincident with the location of global stoichiometry, O2 depletion, or maximum heat release. We investigate these phenomena computationally in three non-premixed ethylene flames at low, moderate, and high Zst, but with equivalent adiabatic flame temperatures. Results demonstrate that the location of O2 depletion occurs in the vicinity of global stoichiometry for flames of any Zst and that the presence of appreciable O2 at the location of maximum temperature for high Zst flames is caused by a shift in the location of maximum temperature relative to the location of O2 depletion. This shifting is attributed to: (1) finite-rate multi-step chemistry resulting in exothermic heat release that is displaced from the location of O2 depletion and (2) the relative location of the heat release region with respect to the fuel and oxidizer boundaries in mixture fraction space. A method of superposition involving a variation of the flame sheet approximation with two heat sources is shown to be sufficient in explaining this phenomenon.

1. Introduction

In general, oxygen-enhanced combustion (OEC) refers to the use of elevated oxygen concentrations (>21% by volume) in the oxidizer stream. The benefits of OEC over conventional air-fired combustion include increased temperature and thermal efficiency for industrial heating and melting processes, reduced pollutant emissions, and fuel consumption, and improved flame stability [1]. Costs associated with air-separation have limited the number of industrial scale OEC systems; however, recent advances in air-separation technology, rising fuel prices, stricter government emissions standards, and the need to reduce atmospheric carbon dioxide (CO2) emissions have created an economic environment where the costs of OEC have diminished substantially relative to the anticipated benefits.

For example, Chatel-Pelage et al. [2] reported that current NOx reducing combustion modifications such as the use of overfire air and low-NOx burners will not be able to meet future NOx emissions standards without the addition of selective catalytic reduction technology. Depending on the size and age of the power plant, retrofitting a system to include selective catalytic reduction may be both expensive and difficult. Thus, novel low-NOx combustion modification technologies that would enable existing power plants to meet future government regulations are highly desirable. Several studies have demonstrated that OEC alone, and coupled with unique burner design and oxygen placement, can reduce NOx emissions beyond levels achieved by using overfire air and low-NOx burners [3–11].

Furthermore, rising atmospheric CO2 concentrations and their potential link to global climate change have generated enormous interest in the development of technologies to reduce CO2 emissions from combustion processes. Oxy-fuel combustion, which involves replacing the oxidizer air with a mixture of oxygen and externally recycled flue gases, has been identified as an enabling technology for CO2 capture from coal-fired power plants. Under conventional air-fired conditions the exhaust from a coal power plant contains 10–20 vol.% CO2, requiring expensive amine absorb-
tion techniques to capture CO$_2$; however, studies have demonstrated that oxy-coal power plants can achieve up to 95 vol.% CO$_2$ in the exhaust enabling CO$_2$ capture by more direct methods while reducing the costs associated with the cleanup of other pollutant emissions [12].

When utilizing OEC in non-premixed systems the concentrations of the inlet fuel and oxidizer can have a dramatic impact on the flame structure, i.e. the relationship between local temperature and local species concentrations [13–27]. When OEC is combined with fuel-dilution such that a constant amount of inert is present at the flame front, the adiabatic flame temperature is unchanged. Nonetheless, the flame structure is changed dramatically [16]. The extent of oxygen-enrichment and fuel-dilution can be quantified by the stoichiometric mixture fraction, $Z_{st}$, given by

$$Z_{st} = \left(1 + \sigma Y_{F, st}/Y_{O_2, st}\right)^{-1}$$  

(1)

where $\sigma = n_{O_2}W_{O_2}/n_FW_F$ and $Y_F$, $n_F$, $W_F$ represent the mass fraction, stoichiometric coefficient, and molecular weight of species $i$, respectively. The fuel stream boundary is indicated by the subscript $fu$ and the oxidizer stream boundary is indicated by the subscript $ox$. Thus, pure fuel burning in air represents a low $Z_{st}$ flame while heavily diluted fuel burning in pure oxygen represents a high $Z_{st}$ flame.

Several studies have examined the effects of varying $Z_{st}$ on the flame structure and combustion characteristics for gaseous fuels [13–27]. Many of these studies [14–22,24,26] have demonstrated that increasing $Z_{st}$ has an inhibitory effect on soot formation, while others have demonstrated improved flame strength [23,27]. Sugiyama and Chen [14] and Lin and Faeth [15] concluded that the soot inhibiting effect of oxygen-enrichment and fuel-dilution was due to hydrodynamic effects while Du and Axelbaum [16] proposed that soot formation was reduced at high $Z_{st}$ due to changes in flame structure resulting in less fuel and more oxygen in the region of high temperature. Furthermore, using a flame code with detailed chemistry Du and Axelbaum showed that increasing $Z_{st}$ in ethylene flames can result in a nearly two orders of magnitude increase in the concentration of molecular oxygen at the location of maximum temperature ($X_{max}$), with molar concentrations of $O_2$ reaching 8 vol.%. This phenomenon is referred to here as appreciable molecular oxygen at the location of maximum temperature and has been subsequently observed both numerically and experimentally by Sun et al. [19] in acetylene flames and Cheng et al. [25] in methane flames. Experimental results suggest that characteristics of the OEC-process are quite sensitive to changes in the concentration of molecular oxygen at the location of maximum temperature.

With regards to flame strength, Du and Axelbaum [13], Chen and Axelbaum [23], and Kitajima et al. [27] showed experimentally that increasing $Z_{st}$ results in a higher strain rate and scalar dissipation rate at extinction for non-premixed counterflow flames. At high $Z_{st}$ extinction scalar dissipation rates 20–40 times greater than for fuel–air flames can be obtained even when the equilibrium flame temperatures are the same. To understand their results Du and Axelbaum and Chen and Axelbaum simulated the flames using a counterflow flame code and proposed that the availability of oxygen in the high temperature region due to increased $Z_{st}$ accelerates the chain branching reaction $H + O_2 = OH + O$ resulting in improved flame strength. Furthermore, Chen and Axelbaum [23] found that at high $Z_{st}$ the flames are able to resist extinction at lower temperatures because at high $Z_{st}$ the location of radical production and $X_{max}$ are coincident, which allows the branching reaction to “make most efficient use” of the high temperature zone. On the other hand, in fuel–air flames the radical production zone is found at a lower temperature on the oxidizer side of $X_{max}$.

The increased presence of oxygen and oxidizing species in the region of high temperature for high $Z_{st}$ flames can also influence soot inception by affecting both the rate of soot precursor oxidation and the relative location of precursor oxidation to precursor formation. Sunderland et al. [22] proposed a theory suggesting that in order for soot to form in a non-premixed flame the local temperature and local carbon-to-oxygen ratio (C/O) must be above threshold values. Kumfer et al. [26] expanded this theory to include the effects of finite-rate chemistry and residence time and developed a simple model that describes the region conducive to soot inception as being confined between two boundaries: a low temperature boundary that is governed by finite-rate chemistry and can be manipulated by changing the fuel concentration, flame temperature, or characteristic residence time, and a high temperature boundary that is related to the presence of oxygen and oxidizing species and is characterized by the local C/O ratio as described in Sunderland et al. [22].

The above findings indicate that high $Z_{st}$ dramatically affects flame properties, and that one of the primary reasons for this is that high $Z_{st}$ flames have appreciable molecular oxygen at the location of maximum temperature. While the existence of appreciable molecular oxygen has been observed both numerically and experimentally [16,19,23], no explanation has been given in the literature for this phenomenon. The purpose of this work is to develop such an explanation by using a counterflow flame code with detailed chemistry in order to distinguish the key sub-mechanisms responsible for the existence of appreciable $O_2$ at $X_{max}$. Results obtained in this study will further our fundamental understanding of the effect of oxygen-enrichment and fuel-dilution (i.e. increasing $Z_{st}$) on flame structure.

2. Numerical

The counterflow flame code employed here was originally developed by Kee et al. [28] for premixed counter flow flames and was later modified for adiabatic non-premixed combustion by Lutz et al. [29]. Chemical reaction rates, transport properties, and thermodynamic properties are evaluated by the Chemkin software package. The detailed kinetic mechanism used here consists of 101 species and 544 reactions and was proposed by Wang and Frenklach [30] and modified by Appel et al. [31].

The accuracy of a mechanism similar to that used here was demonstrated by Sun et al. [19] at low and high $Z_{st}$ by comparing numerical results with temperature and species profiles obtained via spontaneous Raman spectroscopy. The slightly larger mechanism used here was validated by modeling the flame conditions of Sun et al. and verifying that temperature and species profiles were replicated.

The computational grid was initialized with 21 grid points and the fuel and oxidizer stream inlet boundaries were spaced 2 cm apart. Adaptive grid refinement was utilized resulting in approx. one-hundred and five grid points on average at convergence. The fuel and oxidizer stream exit velocities were held constant at 80 cm/s for all flames resulting in a strain-rate, $\alpha$, of 62 s$^{-1}$ for the fuel–air case (Flame A), 61 s$^{-1}$ for the $Z_{st} = 0.4$ case (Flame B), and 68 s$^{-1}$ for the $Z_{st} = 0.78$ case (Flame C). The strain rates were determined by fitting a straight line to the computed velocity profile upstream of the thermal mixing layer on the oxidizer side for Flames A and B, and on the fuel side for Flame C. Chen and Axelbaum [23] reported numerically determined extinction strain rates greater than 2400 s$^{-1}$ for ethylene counterflow flames at $T_{in} = 2370$ K, thus the flames considered in this study are far from extinction. The square of the gradient in mixture fraction ($dZ/dx^2$), which is proportional to the scalar dissipation rate, was also calculated at the location of stoichiometry for all flames. The values were found to be 0.45 cm$^{-2}$, 5.76 cm$^{-2}$, and 4.12 cm$^{-2}$ for Flames A, B, and C, respectively. To ensure that the higher scalar dissipation rates of Flames B and C were not responsible for the increasing
concentrations of \( O_2 \) at \( x_{\text{max}} \). Flames B and C were generated a second time (labeled Flames B’ and C’ with fuel and oxidizer exit velocities of 15 cm/s resulting in strain rates of approx. 8 s\(^{-1}\) and mixture fraction gradients much closer to that of Flame A. It was observed that the peak temperature shift was more pronounced in Flames B’ and C’ resulting in an even higher concentration of \( O_2 \) at the location of maximum temperature. Thus, leakage is not responsible for the presence of appreciable \( O_2 \) at \( x_{\text{max}} \) in high \( Z_s \) flames. Rather, this phenomenon is a result of changes in flame structure. The relevant flame parameters are provided in Table 1 for reference.

### 3. Preliminary analysis: comparing the detailed chemistry with the flame sheet approximation

Significant insight can be gained by comparing the basic structure of low and high \( Z_s \) flames obtained with detailed chemistry and with the traditional flame sheet approximation. For example, it is instructive to compare the case of ethylene burning in air with that of heavily-diluted ethylene burning in pure oxygen represented by the global reactions:

Flame A: \( \text{C}_2\text{H}_4 + 3(\text{O}_2 + 3.76\text{N}_2) \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 11.28\text{N}_2 \)

Flame C: \( \text{C}_2\text{H}_4 + 11.28\text{N}_2 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 11.28\text{N}_2 \)

In Flame C the stoichiometric amount of \( \text{N}_2 \) is the same as that found in air except the \( \text{N}_2 \) is placed in the fuel stream. In this way the adiabatic flame temperature is unaffected [16]; however, the flame structure changes dramatically as demonstrated in Fig. 1. The abscissa in Fig. 1 is the mixture fraction, \( Z \), defined as the local fraction of mass that originated from the fuel stream. For one-step chemistry the mixture fraction is given by

\[
Z = \frac{\sigma Y_F - Y_{O_2} + Y_{O_2,\text{at}}}{\sigma Y_{F,\text{ad}} + Y_{O_2,\text{at}}} \quad (2)
\]

where \( Y_i \) and \( \sigma \) are defined as before in Eq. (1). A more general expression based on the local mass fractions of carbon, hydrogen, and oxygen atoms is given by

\[
Z = \frac{Y_C-Y_C,\text{ad}}{Y_{C,\text{ad}}} + \frac{Y_H-Y_H,\text{ad}}{Y_{H,\text{ad}}} + \frac{Y_O-Y_O,\text{ad}}{Y_{O,\text{ad}}} \quad (2a)
\]

where \( Y_i \) and \( W_i \) are defined as before and \( m \) and \( n \) represent the number of carbon and hydrogen atoms, respectively, in the fuel \( \text{C}_m\text{H}_n \) [32,33]. Thus, \( Z = 0 \) is the oxidizer boundary and \( Z = 1 \) is the fuel boundary.

In Fig. 1, results from the flame sheet approximation are given by the solid lines while the dashed lines represent numerical results similar to those of Du and Axelbaum [16] for flames at strain rates away from their extinction strain rates. We note first that for the conventional fuel–air flame shown in Fig. 1a the numerical results agree with the flame sheet approximation in that molecular oxygen is depleted at the location of maximum temperature, \( x_{\text{max}} \), which is coincident with the location of stoichiometric composition for the global reaction, \( x_{\text{at}} \). The consistency of this result with the flame sheet approximation under fuel–air conditions may lead one to believe that \( O_2 \) will be depleted at the \( x_{\text{max}} \) for OEC as well. However, this is not the case, as demonstrated in Fig. 1b where we see that the concentration of molecular oxygen at \( x_{\text{max}} \) has increased to 8 vol.% for the high \( Z_s \) flame. Clearly, for high \( Z_s \) flames the location of oxygen depletion is not coincident with \( x_{\text{max}} \) because the location of maximum temperature has shifted toward the oxidizer side of \( x_{\text{at}} \). From this preliminary analysis, there are two key questions to consider when explaining the presence of appreciable molecular oxygen at \( x_{\text{max}} \):

1. Molecular oxygen is depleted at \( x_{\text{at}} \) for low and high \( Z_s \) flames; however, are the controlling mechanisms for molecular oxygen depletion the same at low and high \( Z_s \)?
2. Why does \( x_{\text{max}} \) shift toward the oxidizer side of \( x_{\text{at}} \) for high \( Z_s \) flames?

### 4. Results and discussion

#### 4.1. Characterizing oxygen depletion

To explain the presence of appreciable molecular oxygen at \( x_{\text{max}} \) for high \( Z_s \) flames, first we analyze the process of molecular oxygen depletion. Specifically we evaluate

(i) the characteristics of the location where \( O_2 \) is depleted;
(ii) the reaction(s) responsible for \( O_2 \) consumption in both low and high \( Z_s \) flames.

Fig. 2a–c present profiles of the \( O_2 \) mole fraction for Flames A–C and corresponding profiles of the net rate of molecular oxygen consumption and the rate of the reaction

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \quad (R1)
\]

In this figure \( x_{\text{at}} \) is indicated by the filled arrow and \( x_{\text{max}} \) is indicated by the open-faced arrow. From this figure it is clear that \( R1 \) is the dominant reaction responsible for \( O_2 \) consumption for flames of any \( Z_s \). We note that for all flames, the location of maximum net consumption of molecular oxygen is only slightly to the fuel side.

<table>
<thead>
<tr>
<th>Flame</th>
<th>( x_{\text{at}} )</th>
<th>( x_{\text{at},\text{ad}} )</th>
<th>( x_{\text{at},\text{max}} )</th>
<th>( O_2 ) at ( x_{\text{max}} ) (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0</td>
<td>0.21</td>
<td>0.45</td>
<td>0.34</td>
</tr>
<tr>
<td>B</td>
<td>0.16</td>
<td>0.33</td>
<td>5.76</td>
<td>0.93</td>
</tr>
<tr>
<td>C</td>
<td>0.08</td>
<td>1.0</td>
<td>4.12</td>
<td>8.18</td>
</tr>
<tr>
<td>B’</td>
<td>0.16</td>
<td>0.33</td>
<td>8</td>
<td>1.02</td>
</tr>
<tr>
<td>C</td>
<td>0.08</td>
<td>1.0</td>
<td>9</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 1 Flame parameters.
The basic trends of the distributions are similar for all three flames. For example, the concentration of O\(_2\) is almost identical for the three flames. For instance, the O\(_2\) mole fraction at the location of maximum O\(_2\) depletion differs significantly from Z\(_{st}\) = 0.064, Z\(_{st}\) = 0.4, and Z\(_{st}\) = 0.78 for Flame A to 8% for Flame C.

Consider the location where the rate of oxygen consumption is maximum to be the characteristic location of O\(_2\) depletion, independent of Z\(_{st}\), since the rate of O\(_2\) consumption diminishes rapidly and in a similar fashion for all flames beyond this location on the fuel side. As mentioned previously, the location of oxygen depletion differs significantly from Z\(_{st}\) for high Z\(_{st}\) flames because Z\(_{st}\) has shifted toward the oxidizer side of X\(_{st}\). Because of this shift, Fig. 2 demonstrates that the concentration of O\(_2\) at Z\(_{max}\) increases from 0.3% for Flame A to 8% for Flame C.

The location of molecular oxygen depletion, or equivalently, X\(_{st}\), can also be identified with the location of product formation (i.e., CO\(_2\) and H\(_2\)O). Fig. 3 shows the net rate of R1 with the rates of reactions

\[
\text{CO} + \text{OH} = \text{CO}_2 + \text{H} \quad \text{(R2)}
\]

and

\[
\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H} \quad \text{(R3)}
\]

for Flames A–C. The relative locations where (R1)–(R3) occur and the basic trends of the distributions are similar for all three flames.

Noting that R1 requires H radicals and both R2 and R3 produce H radicals, it can be seen that in the region where molecular oxygen is depleted, a “balancing” is observed between the oxygen consuming reaction (H + O\(_2\) = OH + O) and the reactions that produce H radicals. In this sense, we can talk about a kinetic coupling between H and OH radicals and moreover between R1 and R3, which confines the location of molecular oxygen depletion to the location of stoichiometry for flames of any Z\(_{st}\). Thus, we conclude that the mechanisms responsible for O\(_2\) depletion are unaffected by changes in Z\(_{st}\), and the presence of appreciable molecular oxygen at the location of maximum temperature is a result of the shift in maximum temperature relative to the location of O\(_2\) depletion at high Z\(_{st}\).

4.2. Maximum temperature shift at high Z\(_{st}\)

Next we investigate the shifting of Z\(_{max}\) relative to the location of O\(_2\) depletion at high Z\(_{st}\). Early investigations on the structure of non-premixed flames revealed distinct heat release “zones” within the reaction region. Pandya and Weinberg [34] and Pandya and Srivastava [35] observed two small valleys in the heat release profile on either side of the maximum heat release, suggesting a reaction region with three distinct zones. Bilger [36] proposed that the reaction region in hydrocarbon diffusion flames could be described by a double-zone structure consisting of an endothermic pyrolysis zone and an exothermic zone at the location of stoichiometry. In a more recent study, Sun et al. [19] distinguished the following three reaction zones in ethylene flames:

1. a zone of pyrolysis with a net conversion of C\(_2\)H\(_4\) to C\(_2\)H\(_2\),
2. a primary oxidation zone characterized by acetylene oxidation and CO formation,
3. a secondary oxidation zone characterized by CO\(_2\) and H\(_2\)O formation via R2 and R3, respectively.

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With respect to the total heat release rate profile Sun et al. also noted that three distinct zones could be identified and they associated the secondary exothermic heat release peak with R2 and R3 and the reactions

\[
\text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O} \quad (\text{R4})
\]

and

\[
\text{HO}_2 + \text{OH} = \text{O}_2 + \text{H}_2\text{O} \quad (\text{R5})
\]

In our flames we also see three heat release zones in the profile of the total heat release rate as demonstrated in Fig. 4. We also point out that in the low \(Z_{st}\) flame of Fig. 4a the location of peak temperature, indicated by the open-faced arrow, is coincident with the peak heat release location, while in the high \(Z_{st}\) flame the location of peak temperature has shifted to the oxidizer side (left) of the peak heat release location.

Fig. 5 demonstrates that it is actually possible to identify four overlapping, but distinct zones with respect to heat release. The reactions responsible for the majority of the heat release in each zone are provided in Table 2, and were selected such that the overall shape of the total heat release profile was maintained and approximate. 65% of the total integrated heat release was captured. In Fig. 5 each curve represents the combined heat release in each zone from the reactions listed in Table 2, e.g. \(Q_{ex}\) is the exothermic heat release from the dominant reactions identified in Zone 1. From right to left in Fig. 5, we distinguish the four zones as the

1. endothermic pyrolysis zone,
2. high heat intensity zone,
3. moderate heat intensity zone,
4. low heat intensity zone.

For low \(Z_{st}\) flames the pyrolysis zone (Zone 1) is overall endothermic; however, as \(Z_{st}\) increases the endothermicity of the pyrolysis zone decreases until it eventually becomes overall exothermic as demonstrated by the pyrolysis zone in Fig. 4c. Just as exothermic reactions may contribute significantly in the pyrolysis zone, significant endothermic reactions are found in the high heat intensity zone (Zone 2) and moderate heat intensity zone (Zone 3) (see Table 2 in detail). As in Sun et al. [19], we note that the dominant reactions in the endothermic pyrolysis zone involve the decomposition of ethylene and the vinyl radical in the formation of acetylene, while the reactions dominating the high heat intensity zone involve the oxidation of acetylene, the methyl radical, and CH by O. The moderate heat intensity zone is characterized by the formation of CO2 and H2O via CO and H2 oxidation by OH and the consumption of O2 by H radicals. Recognizing that R1 is endothermic while R2 and R3 produce substantial heat, it appears that the kinetic coupling discussed previously is further intensified by the interplay of the exo- and endothermic reactions in Zone 3. Furthermore, Fig. 6 demonstrates that the endothermicity of R1 and the exothermicity of R2 nearly mirror each other. Finally, the broad low heat intensity zone (Zone 4) is characterized by R4 and R5.

This fourth zone plays an important role in the phenomenon of appreciable molecular oxygen being present at the location of maximum temperature in high \(Z_{st}\) flames because it is displaced from the location of O2 depletion and contributes substantially to the secondary peak in the total heat release rate (Fig. 4). As noted previously, the exothermic contribution from R2 to the total heat release rate profile is counteracted by the endothermic heat release from R1. This amplifies the observed exothermic contribution from R4 and R5 and displaces the secondary exothermic zone peak far-
ther from the location of \( O_2 \) depletion. We also point out that the production of \( H_2O \) in Zone 4 differs from that of Zone 3 in that the intermediate step \( R4 \) forming \( HO_2 \) in Zone 4 requires a third body and is inversely dependent on temperature. Moreover, while oxygen is consumed in the formation of \( HO_2 \), it is produced when \( HO_2 \) forms \( H_2O \) in \( R5 \) such that the net \( O_2 \) depletion rate in Zone 4 by \( R4 \) and \( R5 \), shown in Fig. 7, is an order of magnitude less than

**Table 2**

Dominant reactions in four different heat zones.

<table>
<thead>
<tr>
<th>Q(_{\text{max}})</th>
<th>20 (cal/ccm/s)</th>
<th>10 ( \leq ) Q(_{\text{max}}) &lt; 20 (cal/ccm/s)</th>
<th>5 ( \leq ) Q(_{\text{max}}) &lt; 10 (cal/ccm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exothermic reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 1</td>
<td>( C_2H_5 + O = CH_2 + CO )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 2</td>
<td>( CH + H_2O = CH_2 + H )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 3</td>
<td>( CO + OH = CO_2 + H )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 4</td>
<td></td>
<td>10 ( \leq ) Q(_{\text{min}}) &lt; 20 (cal/ccm/s)</td>
<td></td>
</tr>
<tr>
<td>5 ( \leq ) Q(_{\text{min}}) &lt; 10 (cal/ccm/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Endothermic reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 1</td>
<td>( C_2H_5(M) = C_2H_4 + H(M) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 2</td>
<td>( HCO(M) = H + CO(M) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zone 3</td>
<td>( H + O_2 = OH + O )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Indicate energized molecule.

Fig. 6. Heat release from reactions \( R1 \) and \( R2 \) for (a) fuel/air \( Z_\text{st} = 0.064 \), (b) \( Z_\text{st} = 0.4 \), and (c) diluted-fuel/oxygen \( Z_\text{st} = 0.78 \).

Fig. 7. Rates of \( O_2 \) destruction and production by reactions \( R4 \) and \( R5 \) for (a) fuel/air \( Z_\text{st} = 0.064 \), (b) \( Z_\text{st} = 0.4 \), and (c) diluted-fuel/oxygen \( Z_\text{st} = 0.78 \).

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the peak O₂ depletion rate via the reaction H + O₂ = OH + O (compare Fig. 2). Fig. 7 also shows that R4 and R5 are broadened at high Zst and that the peak rate of R4 is reduced by a factor of approx. 3 when comparing Flame A to Flame C. Comparing the temperatures and the H, O₂, and H₂O concentrations in this zone for Flames A and C, we note that the broadening of R4 and R5 is due to the higher O₂ concentration, while the reduced peak rate of reaction R4 is predominantly due to the increased temperature observed in this zone for Flame C because of the temperature shift. Even though the lower peak rate of R4 at high Zt reduces the amplitude of the exothermic heat release in this zone, the broadening of R4 and R5 results in exothermic heat release at locations farther displaced from the location of O₂ depletion. As will be demonstrated below, the separation of the location of O₂ depletion and this secondary heat release zone contribute to the shifting of the location of maximum temperature.

To explain the shifting of the maximum temperature relative to the location of O₂ depletion at high Zₜ, a method of superposition was used to evaluate the effective increase in temperature (enthalpy) that would result from displaced point sources of heat in a diffusion controlled system. For simplicity, we perform a simple qualitative analysis for both low and high Zₜ flames to demonstrate the effect of two displaced heat release points. These points represent the primary exothermic zone where acetylene (as a product of ethylene decomposition) is oxidized and the secondary exothermic zone where the heat release from R2–R5 combines to form the secondary heat release maximum. In Fig. 8 the vertical dashed lines represent the point sources of heat release. The light-weight solid lines represent the temperature profiles, θ₁ or θ₂, which would result if only the primary heat source or secondary heat source existed, respectively. The superposition of the two independent temperature profiles, θst, is represented by the bold curve and the approximate location of stoichiometry is given by the filled arrow. We note immediately in Fig. 8b that the shifting of xₜₘₐₓ toward the oxidizer side of x₂ₜₙ, which results in the presence of appreciable O₂ at xₜₘₐₓ for the high Zₜ flame, is captured in this simple demonstration. Note also that for the low Zₜ fuel–air flame of Fig. 8a xₜₘₐₓ and x₂ₜₙ are nearly coincident, as expected.

The shifting of xₜₘₐₓ towards the oxidizer side of x₂ₜₙ can be explained by considering how the magnitude of the independent temperature profile slopes change in Fig. 8 when going from low to high Zₜ. Beginning with the low Zₜ flame of Fig. 8a and moving from left to right we see that θ₃ increases with a constant slope until the location of the heat source responsible for θ₂ is reached. At this point, the slope of θ₃ is reduced because θ₂ is decreasing; however, θ₅ continues to increase because the magnitude of the positive slope associated with θ₅ is greater than the magnitude of the negative slope associated with θ₂. Upon reaching the location of the heat source responsible for θ₁, the θ₁ curve decreases linearly since both θ₁ and θ₂ decrease after this point.

For the high Zₜ flame of Fig. 8b, moving left to right we see that θ₃ again increases linearly until we reach the location of the heat source responsible for θ₂, however, rather than continuing to increase after this point with a reduced slope as in the low Zₜ flame, θ₃ begins to decrease. This occurs because the heat release region is closer to the Zₜ = 1 boundary, which causes the magnitude of the negative slope associated with θ₂ to be greater than the positive slope associated with θ₁. Thus, at high Zₜ the exothermic contribution from reactions R2–R5 at a location displaced from the location of oxygen depletion can be considered responsible for the shifting of the maximum temperature relative to the location of global stoichiometry.

A more thorough analysis can be performed by obtaining values for the three heat source zones by integrating the total heat release profile of Fig. 4 numerically within each reaction zone. The heat sources are placed at the location in mixture fraction space where the local heat release extremum occurs for the respective reaction zone. For Flame A the fuel pyrolysis zone has a local minimum while for Flame C the fuel pyrolysis zone actually has a small local maximum. In the primary and secondary oxidation zones local maxima occur for all flames. As above, the final temperature distribution is obtained from the superposition of the independent temperature distributions resulting from the point heat sources.

In Fig. 9 the dashed curve (Tsup) represents the temperature profile from the numerical results plotted in mixture fraction space. The total heat release distribution, Tqoox, is also included as a reference. θₚyr is the temperature distribution that would result if only the heat release from the fuel pyrolysis zone were considered, Tpyr is the temperature that would result if only the exothermic heat release from the primary oxidation zone were considered, and Tsec is the resulting temperature if only the exothermic heat release from the secondary oxidation zone were considered. The bold line (Tsup) represents the superposition of these temperatures. The location of Zₜ is indicated by the filled arrow.

We first note in Fig. 9 how well this simple three step empirical correlation captures the temperature profile produced by the flame code. By including the endothermic zone as a third heat source in the low Zₜ fuel–air flame (Fig. 9a) we see how the endothermic reactions result in a narrowing of the high temperature region in mixture fraction space. In Fig. 9b we again demonstrate how the location of maximum temperature shifts to the oxidizer side of x₂ₜₙ. Furthermore, we note that the pyrolysis zone has a negligible effect on the temperature profile and the region of high temperature is broadened in mixture fraction space for the high Zₜ flame due to the secondary exothermic zone.
5. Conclusions

The presence of appreciable molecular oxygen at the location of maximum temperature in oxygen-enhanced combustion of ethylene was analyzed computationally using a detailed kinetic mechanism. Based on this analysis, it was found that:

1. The characteristic location of molecular oxygen depletion is nearly coincident with the location of stoichiometry, which can be characterized by the location of maximum CO₂ or H₂O production for both conventional and oxygen-enhanced combustion.

2. Molecular oxygen consumption is dominated by H radical attack for both conventional and oxygen-enhanced combustion, and an apparent kinetic and thermal coupling was observed between this endothermic reaction and the exothermic reactions producing CO₂, H₂O, and H radicals.

3. Four heat zones can be distinguished within the reaction region, namely a pyrolysis zone that is endothermic at low Z_s and is slightly exothermic at high Z_s, a high heat intensity zone where acetylene is oxidized by O, a moderate heat intensity zone where the majority of CO₂ and H₂O are formed, and a low heat intensity zone that broadens and extends farther into the oxygen rich region at high Z_s due to the increased O₂ concentrations.

4. The presence of appreciable molecular oxygen at the location of maximum temperature for high Z_s flames is due to a shifting of the location of maximum temperature relative to the location of molecular oxygen depletion. This shifting occurs at high Z_s due to:
   i. finite-rate reactions that release heat at a location displaced toward the oxidizer side of the location of stoichiometry, O₂ depletion, or maximum heat release and contribute substantially to a secondary peak in the total heat release rate profile,
   ii. the relative location of the heat release region with respect to the Z = 0 and Z = 1 boundaries in mixture fraction space.

Finally, the shifting of the location of maximum temperature was explained by considering the superposition of the temperature profiles that would result from two displaced heat sources.

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