ON THE EFFECT OF INITIAL PRESSURE ON THE c-RPT PHENOMENON OF CH$_4$/O$_2$/N$_2$/CO$_2$ MIXTURES


basco@irc.cnr.it

* Istituto di Ricerche sulla Combustione, CNR, Via Diocleziano 328, 80124, Napoli, IT
** Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università “Federico II”, Napoli, IT

Abstract
The effect of initial pressure on the explosion behaviour of a stoichiometric CH$_4$/O$_2$/N$_2$/CO$_2$ mixture under oxy-combustion conditions was studied. The increase of initial pressure was demonstrated to significantly affect the explosion features. In particular, as the initial pressure increases, a transition was found from a deflagration mode to an explosion mode dominated by the severe combustion-induced Rapid Phase Transition (c-RPT) phenomenon. In particular, when increasing the initial pressure from 1 bar to 3 bar, the peak pressure was found to increase from 12.5 bar to 200 bar.

Introduction
In previous papers, we have studied the explosion behavior of CH$_4$/O$_2$/N$_2$/CO$_2$, H$_2$/O$_2$/N$_2$/CO$_2$ and CO/H$_2$/O$_2$/N$_2$ mixtures under oxy-combustion conditions, at initial atmospheric temperature and pressure [1; 2]. An anomalous behavior has been observed for mixtures with high content of hydrogen and oxygen, but low concentration of CO$_2$. Indeed, peak pressures up to ten times the adiabatic combustion pressure have been found. The observed phenomenon cannot be connected to any classical theory for detonation or deflagration-to-detonation transition (e.g., the Shock Wave Amplification by Coherent Energy Release (SWACER) mechanism [3]) or pre-compression effects. Hence, we have demonstrated that the observed over-adiabatic spikes are due to the water produced by the combustion reaction, which condenses and accumulates on the vessel walls. To be more specific, the contact among the hot burnt gases and the liquid water may generate vapor in an explosive manner, if the liquid is super-heated. Such phenomenon has been recently explained and named “combustion-induced Rapid Phase Transition” (c-RPT) [4-7]. The aim of the present study is the analysis of the effects of initial pressure on the reactivity and explosion behavior of CH$_4$/CO$_2$ mixtures in oxygen-enriched air.
Experimental
The experimental set-up adopted in this study is shown in Fig. 1. The main reactor is an AISI 316 SS steel (MAWP=400 bar) cylindrical vessel (5 lt) with wall thickness of 5 cm. The mixture composition was obtained by the partial pressure method. Gases were ignited by an electric spark (25 kV, 30 mA) positioned at the center of the vessel. Each test was performed 3 times. Pressure histories were recorded by KULITE ETS-IA-375 (M) series transducers powered by a chemical battery (12 VDC/7 Ah) in order to minimize any disturbance on the output supply, which was recorded by means of a National Instrument USB-6251 data acquisition system (1.25 Msamples/sec). Further details can be found elsewhere [4-7].

Figure 1. The experimental set-up adopted for this study.

In this work, the reactivity and the explosion behavior of a stoichiometric CH\textsubscript{4}/O\textsubscript{2}/N\textsubscript{2} mixture in the presence of CO\textsubscript{2} (20% v/v) were analyzed by varying the initial pressure, P\textsubscript{i}. The oxygen-enrichment factor, E, is defined as:

\[ E = \frac{O_2}{O_2 + N_2} \]  

(1)

Oxy-combustion conditions were reproduced at a value of E = 0.6. Table 1 reports the values of adiabatic temperature (T\textsubscript{ad}) and pressure (P\textsubscript{ad}) at constant volume, as computed using the GASEQ code [8]. The laminar burning velocity was obtained from the pressure history recorded in the closed vessel. In particular, we used the equations of Dahoe et al. [9] that link the flame radius, r\textsubscript{f}, and the laminar burning velocity, S\textsubscript{l}, to the pressure time history. The flame radius was calculated by using the following correlation:

\[ r_f = \left( \frac{3V}{4\pi} \right)^{\frac{1}{3}} \left[ I - \left( \frac{P^o}{P} \right)^\frac{1}{2} \left( \frac{P_{max} - P}{P_{max} - P^o} \right) \right]^{\frac{1}{3}} \]  

(2)
where \( P_{\text{max}} \) is the maximum measured pressure, \( P^0 \) is the initial pressure, and \( V \) is the vessel volume.

The (un-stretched) laminar burning velocity, \( S_l \), was then calculated according to:

\[
S_l = \lim_{r_f \rightarrow 0} \left[ \frac{d}{dr} \frac{r_f}{\Delta r_f} \right]
\]

(3)

where \( r(t) \) is the best fit function in the range \( \Delta r_f = (r_f - r_{\text{f,o}}) \) that refers to the range of the flame radius for which either ignition or wall and vessel shape effects on the flame propagation can be neglected.

**Table 1.** \( P_i \) (initial pressure); molar fraction of CH\(_4\) and O\(_2\); \( T_{\text{ad}} \) (adiabatic temperature) and \( P_{\text{ad}} \) (adiabatic pressure) as calculated using GASEQ [9]. Oxygen-enrichment factor \( E = 0.6 \); CO\(_2\) = 20% v/v

<table>
<thead>
<tr>
<th>Test #</th>
<th>( P_i ), bar</th>
<th>( Y_{\text{CH}_4} )</th>
<th>( Y_{\text{O}_2} )</th>
<th>( T_{\text{ad}}, \text{K} )</th>
<th>( P_{\text{ad}}, \text{bar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>0.185</td>
<td>0.369</td>
<td>2962.0</td>
<td>10.69</td>
</tr>
<tr>
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<td>1.50</td>
<td>0.185</td>
<td>0.369</td>
<td>3000.2</td>
<td>16.19</td>
</tr>
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<td>0.185</td>
<td>0.369</td>
<td>3027.4</td>
<td>21.73</td>
</tr>
<tr>
<td>4</td>
<td>2.50</td>
<td>0.185</td>
<td>0.369</td>
<td>3048.4</td>
<td>27.31</td>
</tr>
<tr>
<td>5</td>
<td>2.75</td>
<td>0.185</td>
<td>0.369</td>
<td>3057.4</td>
<td>30.11</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>0.185</td>
<td>0.369</td>
<td>3065.6</td>
<td>32.91</td>
</tr>
</tbody>
</table>

**Results**

Table 2 gives the values of the laminar burning velocity of the analyzed mixture, obtained from the experimental pressure history by using Eqs (2-3). As expected, the laminar burning velocity decreases with increasing pressure [10].

**Table 2.** Laminar burning velocity, \( S_l \), calculated from the experimental pressure histories for the composition reported in Table 1

<table>
<thead>
<tr>
<th>( P_i ), bar</th>
<th>( S_l ), cm s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.78±0.01</td>
</tr>
<tr>
<td>1.50</td>
<td>0.57±0.01</td>
</tr>
<tr>
<td>2.00</td>
<td>0.42±0.04</td>
</tr>
<tr>
<td>2.50</td>
<td>0.38±0.03</td>
</tr>
<tr>
<td>2.75</td>
<td>0.35±0.04</td>
</tr>
<tr>
<td>3.00</td>
<td>0.31±0.03</td>
</tr>
</tbody>
</table>

Fig. 2 shows some of the recorded pressure histories. In the plot, the presence of c-RPT spikes is clear. As the initial pressure increases, the spike becomes much more higher than the adiabatic pressure.
Figure 2. Pressure time histories for tests with $P_i = 1; 1.5; 2.5; 3$ bar.

In Table 3, the intensity of the c-RPT phenomenon, in terms of peak overpressure ($P_{\text{peak c-RPT}}$) and deflagration index ($K_{\text{c-RPT}}$), and its characteristic time ratios ($\theta_1$ and $\theta_2$) are reported for different initial pressures, together with the partial pressure of water in the given explosion conditions ($P_{\text{H}_2\text{O}}$) (calculated using GASEQ [9]).

Table 3. Partial pressure of water in the given explosion conditions ($P_{\text{H}_2\text{O}}$), peak overpressure ($P_{\text{peak c-RPT}}$), deflagration index ($K_{\text{c-RPT}}$), characteristic time ratios ($\theta_1$ and $\theta_2$)

<table>
<thead>
<tr>
<th>Test #</th>
<th>$P_i$, bar</th>
<th>$P_{\text{H}_2\text{O}}$, bar</th>
<th>$P_{\text{peak c-RPT}}$, bar</th>
<th>$K_{\text{c-RPT}}$, bar/m s</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>3.26</td>
<td>12.53 ± 0.00</td>
<td>58415</td>
<td>1.71</td>
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<tr>
<td>2</td>
<td>1.50</td>
<td>4.98</td>
<td>24.79 ± 7.14</td>
<td>147629</td>
<td>2.36</td>
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<tr>
<td>3</td>
<td>2.00</td>
<td>6.73</td>
<td>41.44 ± 8.87</td>
<td>93261</td>
<td>3.06</td>
<td>0.99</td>
</tr>
<tr>
<td>4</td>
<td>2.50</td>
<td>8.49</td>
<td>56 ±12.13</td>
<td>240264</td>
<td>3.70</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>2.75</td>
<td>9.38</td>
<td>57.29 ± 3.36</td>
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<td>3.94</td>
<td>1.08</td>
</tr>
<tr>
<td>6</td>
<td>3.00</td>
<td>10.27</td>
<td>203.72 ± 19.74</td>
<td>175053</td>
<td>4.09</td>
<td>1.07</td>
</tr>
</tbody>
</table>

From Table 2, it is clear that, as the initial pressure increases, the partial pressure of water in the gaseous products increases and the explosion phenomenon becomes more severe. This is consistent with our explanation of the phenomenon (see [4-7]), which considers the partial pressure of water as the main issue for the occurrence of the c-RPT spike.

The occurrence and severity of the c-RPT phenomenon can also be explained through the analysis of the characteristic times: the time required by the flame to travel along the radial direction of the vessel, $\tau_{\text{reac}}$; the time for water cooling and condensation at the walls, $\tau_{\text{cond}}$; the time of heat exchange between flame and walls by radiation, $\tau_{\text{rad}}$.

In Table 3, the ratio between the condensation time and the reaction time ($\theta_1 = \tau_{\text{cond}}/\tau_{\text{reac}}$) and the ratio between the condensation time and radiation time
\( \theta_2 = \tau_{\text{cond}}/\tau_{\text{rad}} \) are given. Fig. 3 shows the severity of the observed c-RPT phenomenon in terms of \( P_{\text{peak c-RPT}} \) as a function of \( \theta_1 \). As \( \theta_1 \) increases, \( P_{\text{peak c-RPT}} \) increases.

![Figure 3. \( P_{\text{peak c-RPT}} \) as a function of \( \theta_1 \).](image)

The severity of the c-RPT phenomenon was also evaluated in terms of deflagration index, \( K_{c-RPT} \), calculated according to:

\[
K_{c-RPT} = \left[ \frac{\Delta P_{\text{peak c-RPT}}}{\Delta t_{\text{peak c-RPT}} / 2} \right]^{1/3} \cdot V^{1/3}
\]

(4)

where \( \Delta t_{\text{peak c-RPT}} \) is the time interval of peak duration and \( V \) is the vessel volume. Fig. 4 shows \( K_{c-RPT} \) as a function of \( \theta_2 \). As \( \theta_2 \) increases, the c-RPT phenomenon becomes more severe (even if large data dispersion is found).

![Figure 4. \( K_{c-RPT} \) as a function of \( \theta_2 \).](image)
Conclusions
The reactivity (i.e., the laminar burning velocity, $S_l$) of the analyzed mixture decreases with increasing initial pressure. The c-RPT phenomenon has been observed in all tests. The corresponding peak pressure and the deflagration index ($K_{cRPT}$) increase with pressure. These trends are not in contrast with the trend of the laminar burning velocity, because c-RPT is a phenomenon which appears after the end of chemical reaction and is driven by the presence of water in the reaction products and by the heat transport between the flame and the vessel walls.

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References