Combustion-Induced Rapid Phase Transition of CH_4/O_2/Inert Mixtures

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Oxy-combustion is an important step towards zero-emission. However, over-adiabatic pressure shocks have been found when igniting oxygen-enriched lean or rich fuel mixtures in non-adiabatic reactors. This phenomenon has been demonstrated to be linked to the Rapid Phase Transition of water produced by the combustion reaction and, thus, it has been named "combustion-induced Rapid Phase Transition" (cRPT).
In this work, we present further results of explosion tests in a non-adiabatic 5 dm^3 cylindrical vessel. In particular, we focused the attention on the role of nucleation sites on the occurrence of cRPT. To this aim, we sprinkled talc (fine powder) over the internal surface of the vessel, thus providing nucleation sites.
Results show that cRPT may be prevented if nucleation sites are present at the vessel walls, thus favoring the evaporation kinetics and preventing the water super-heating.

1. Introduction

The use of pure oxygen or oxygen-enriched atmosphere in the combustion of fuel mixtures containing methane is an important step towards zero-emission technologies. However, when oxygen-enriched fuel mixtures are adopted, an anomalous explosion behaviour may occur: over-adiabatic pressure peaks up to 400 bar have been found in non-adiabatic reactors with very severe consequences for equipment, auxiliary systems, instrumentation and mitigation systems (Di Benedetto et al., 2011; 2012a-d; Salzano et al., 2012).

This phenomenon has been demonstrated to be related to the Rapid Phase Transition of water produced by the combustion reaction (and, thus, it has been named "combustion-induced Rapid Phase Transition", cRPT), which condenses at the vessel walls and explosively re-evaporates.

When a liquid reaches its boiling point in the absence of nucleation sites, the boiling process may be delayed so that the liquid reaches superheated conditions. If a limit temperature is reached, homogeneous spontaneous nucleation may induce the liquid to boil in an explosive manner (Rapid Phase Transition, RPT) (Corradini et al., 1988; Reid, 1976; 1983; Nedelka et al., 2003). More specifically, the rapid production of high-pressure vapor exerts sudden pressure on the surrounding fluid, thus leading to the formation of strong shock waves. Eventually, we have attributed the cRPT phenomenon to the occurrence of cycles of condensation/evaporation of the water produced by combustion at the walls of the explosion vessel, followed by superheating of the liquid film due to radiative heat transfer from the flame.

After the discovery of this novel phenomenon, we deeply investigated the conditions at which it occurs, by identifying the range of vessel wall temperatures (Di Benedetto et al., 2012b), the effect of inert concentration (Di Benedetto et al., 2012a), and the effect of the surface to volume ratio (Di Benedetto et al., 2012c) for several fuel mixtures and inert gases.

In this work, we present further results of explosion tests in a non-adiabatic 5 dm^3 cylindrical vessel. More specifically, we have investigated the role of nucleation sites on the occurrence of such phenomenon. To this aim, we sprinkled talc (fine powder) over the internal surface of the vessel, thus providing nucleation sites.

2. Experimental section

The reactor consists of a closed cylindrical vessel made of 5-cm-thick AISI 316 SS steel. The vessel volume is 5 cm^3. Figure 1 shows the scheme of the experimental rig. Further details of the experimental apparatus are given elsewhere (Di Benedetto et al., 2009).
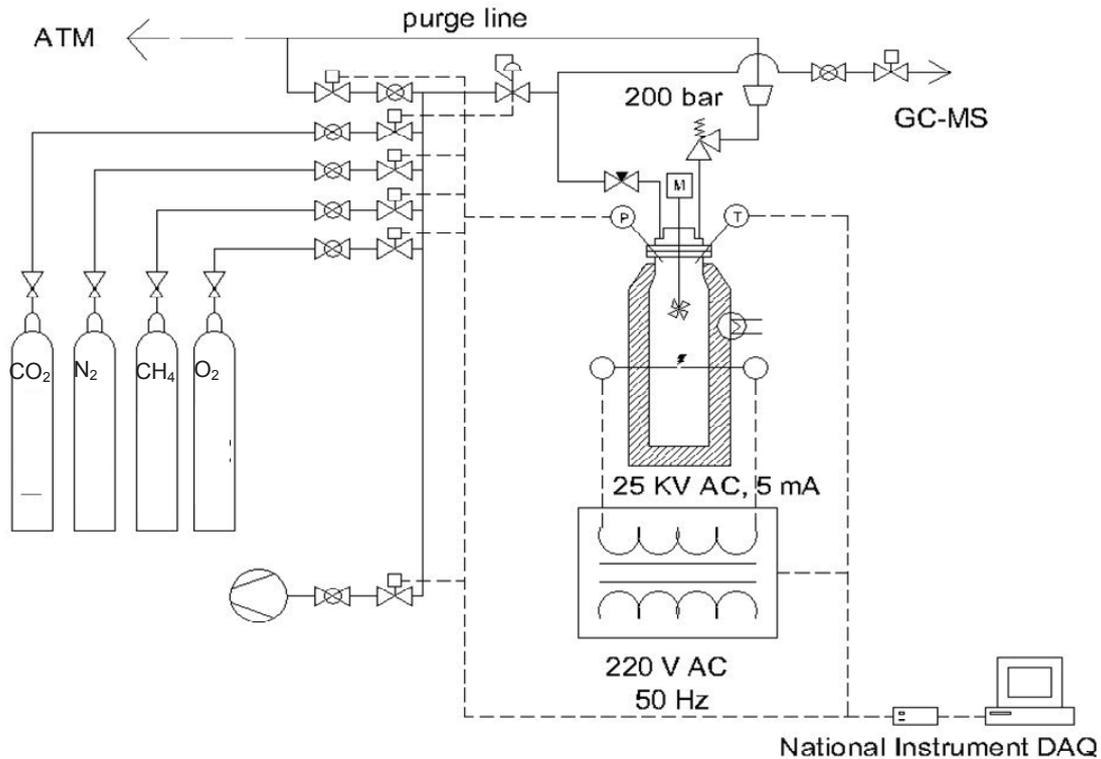

Figure 1: The experimental rig adopted in this study

The $CH_4/O_2/N_2/CO_2$ mixtures tested were obtained by using the partial pressure methodology. After the pure components (purity above 99.9 % by volume) entered the vessel, they were premixed by mechanical stirring (rotating shaft velocity equal to 200 rpm). The mixture composition was monitored by a Gas Chromatograph/Mass Spectrometer (GC/MS) system (Finnigan FOCUS DSQ by Thermo Electron Corporation). The premixed gases were allowed to settle for around 30 s and then ignited by a 25 kV (30 mA) electric spark positioned at the center of the vessel.

The pressure time histories were registered at a rate of 1.25 Mega sample/s by using a Kulite pressure transducer (ETS-1A-375M) and a National Instrument (USB-6251) acquisition system. For all tests, the initial pressure was P = 1 bar.

Table 1: Composition of the fuel mixtures investigated in this work. Adiabatic temperature (T_{ad}) and pressure (P_{ad}) and partial pressure of water (P_{H2O}) have been calculated by GASEQ (2012). The experimental value of P_{cRPT} is shown when observed

	RUN1	RUN2
CH_4 (%)	13.8	18.5
O_2 (%)	27.6	36.9
N_2 (%)	18.5	24.6
CO_2 (%)	40	20
P_{ad} (bar)	8.9	10.7
T_{ad} (K)	2579	2962
% H2O v/v at adiabatic conditions	25.7	30.8
P_{H2O} (bar) in burned gases	2.3	3.3

The compositions of the mixtures investigated are given in Table 1. In the same table, the adiabatic pressure and temperature and the partial pressure of the water produced by the combustion reaction, as calculated by using the GASEQ (2012) code, have been reported for the sake of discussion.

The tests have been repeated at least two times. The results have high reproducibility when combustion peak pressures are considered (±1 %). When cRPT peak pressure are observed, experimental data have larger error (up to ± 20 %), due to the partial stochastic behaviour with respect to the maximum value.

3. Results

Figure 2 shows the pressure time history as measured for RUN1 (Table 1). The value of adiabatic pressure is also reported in this plot (dashed horizontal line).
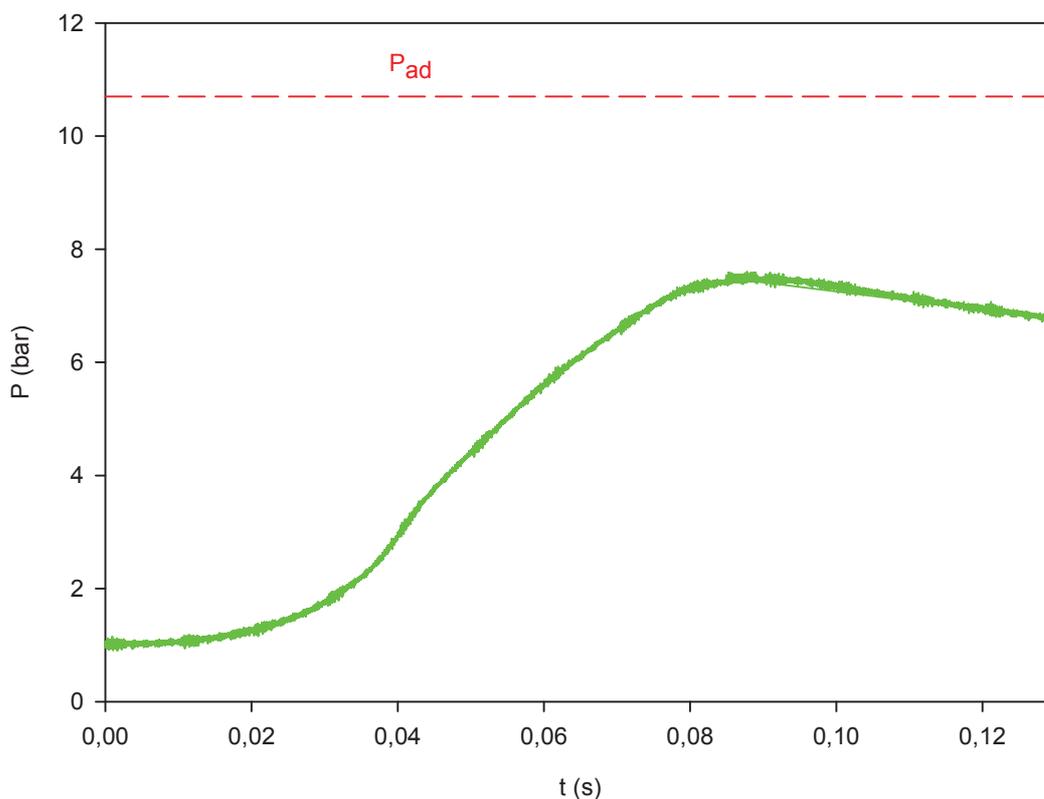

Figure 2. Pressure vs. time, RUN1

The maximum pressure achieved with RUN1, $P_{max} \sim 7.5$ bar, is lower than the corresponding adiabatic value, $P_{ad} = 8.9$ bar. At the end of the run, a significant amount of liquid water is found inside the vessel: the water produced by methane combustion condenses at the cold walls of the vessel (the measured wall temperature is equal to about 283 K). The total pressure reduction in the gas phase due to water condensation and heat losses causes the maximum pressure being lower than the adiabatic pressure.

When the CO_2 amount is decreased (from 40 % to 20 %, RUN2), a transition to a different behaviour for the pressure development can be observed: after a value close to the adiabatic pressure has been reached, a spike in the pressure signal is found (Figure 3). Quite unexpectedly, the peak pressure corresponding to the spike is much higher than the adiabatic pressure (27 bar vs. 10.7 bar). It is worth saying that such peak pressure was able to destroy the rupture disk of the vessel, which was set to 200 bar.
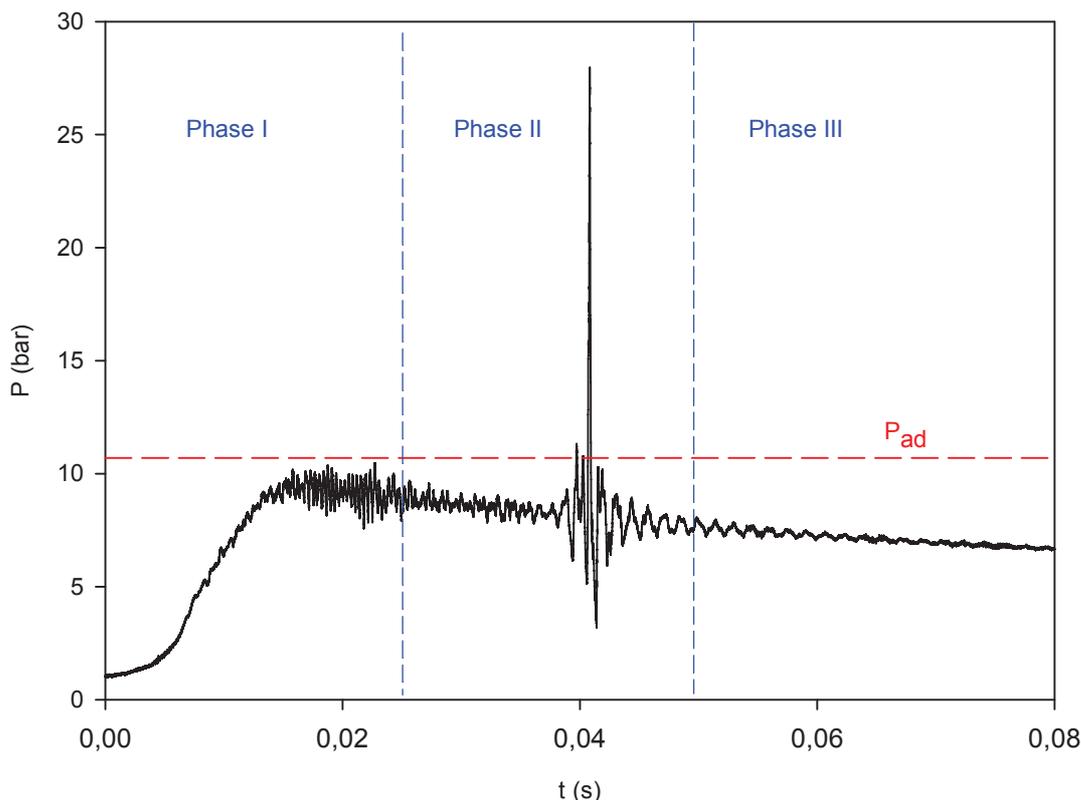
Figure 3. Pressure vs. time, RUN2

We have conceptually divided the pressure time trend into three parts (Figure 3), which correspond to different phases. Phase I is characterized by an oscillating signal whose average value increases with time up to reach the adiabatic value (P_{ad} ~ 10.7 bar) when combustion has come to an end. We have attributed the oscillating nature of the signal to the coupling between the reaction time and the water condensation time. Water condensation occurs at the vessel walls since the water partial pressure in the burned gases (P_{H2O} = 3.3 bar) is much higher than the water vapor pressure at the boundary layer adjacent to the vessel walls (T_{wall} = 283 K; $P°_{H2O}$ = 0.022 bar). During phase II, the over-adiabatic peak pressure is observed and the oscillation period is synchronized with the time of water condensation and the time of water evaporation at the vessel walls triggered by radiation. Finally, the oscillation period for phase III has been found to be related to the time required for pressure waves travelling along the vessel.

As stated previously, the over-adiabatic pressure peak has been attributed to the occurrence of the water rapid phase transition. Indeed, when the combustion reaction has completed, the hot burned gases start heating the liquid water film accumulated in the boundary layer close to the vessel walls. Such liquid water does not contain nucleation sites, which allow the water evaporation. Hence, the water produced by methane combustion can be super-heated up to a temperature higher than the evaporation temperature (i.e., the so-called "super-heating temperature"), remaining in a meta-stable condition.

When the liquid water temperature reaches the super-heating temperature (~ 450 K), the liquid film at the walls of the vessel evaporates in an explosive manner (Rapid Phase Transition), with the production of shock waves which may coalesce, giving rise to the severe pressure peak measured.

In order to provide further evidence for our explanation of the observed phenomenon, we have performed an additional run with the same mixture composition as RUN2, but sprinkling a small amount of common talc powder (< 1 g, $Mg_3Si_4O_{10}(OH)_2$, ultra-fine powder) (Piniazkiewicz et al., 1994) over the internal surface of the vessel, thus providing nucleation sites for the film of liquid water formed after condensation. If confirmed, this modality should prevent the water liquid film from reaching the super-heating temperature, thus allowing water evaporation at the thermodynamic temperature.

Figure 4 shows the pressure time history as measured in the presence of talc powder on the vessel walls. Quite clearly, the presence of talc powder reduces significantly the peak pressure, which decreases to about 12 bar. This result suggests that the presence of talc favors the kinetics of water evaporation, thus preventing the water super-heating and eventually the RPT explosion.
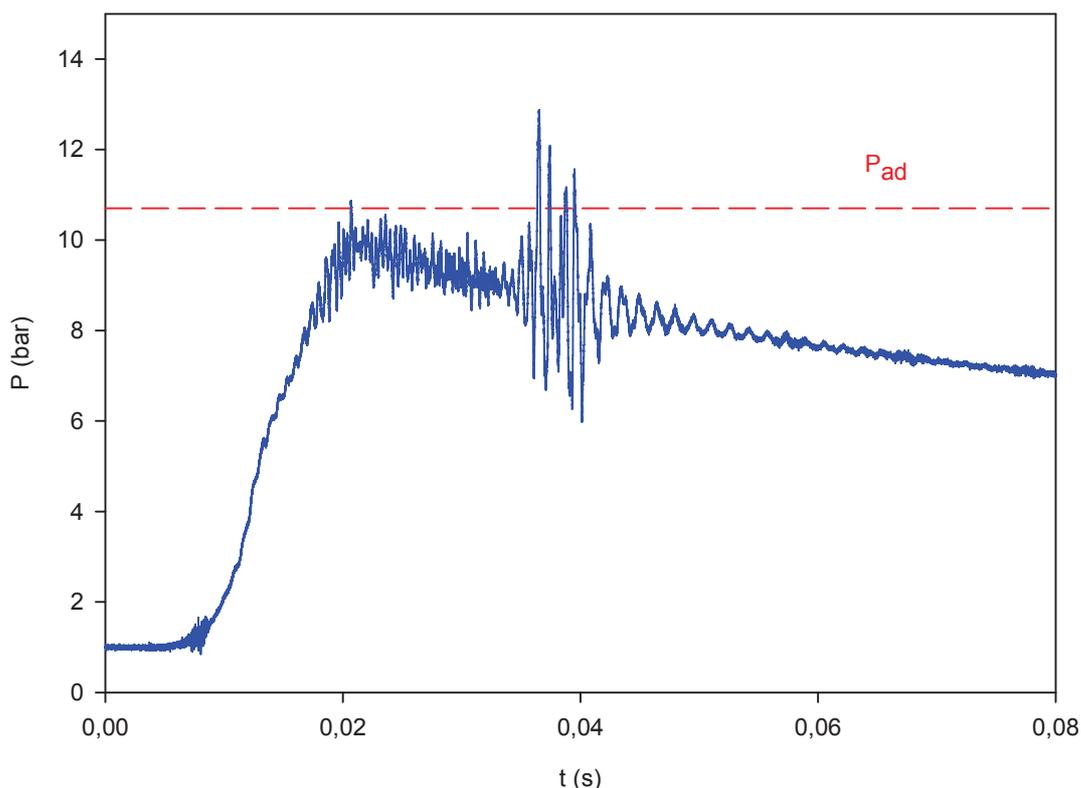
Figure 4. Pressure history in the presence of talc powder on vessel walls (the composition is the same as RUN2).

4. Conclusions

The severe phenomenon which we have demonstrated to occur during the deflagrative combustion of $CH_4/O_2/N_2/CO_2$ mixtures should be taken into account in the safety criteria for design and operation of chemical plants that process and storage flammable gas mixtures.

The results here presented partially explain the occurrence of severe explosions (often attributed to detonation) of low reactivity mixtures, which cannot be explained by means of classical theories (Oran and Williams, 2012).

The combustion-induced Rapid Phase Transition (cRPT) may be prevented if nucleation sites are present (e.g., on the vessel walls), thus favoring the evaporation kinetics and preventing the water super-heating.

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