

# ON THE PHENOMENON OF COMBUSTION-INDUCED RAPID PHASE TRANSITION OF WATER

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## Abstract

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). More specifically, the rapid production of high-pressure vapour exerts sudden pressure on the surrounding fluid, thus leading to the formation of strong shock waves.

In a previous paper, we have shown that the RPT phenomenon can be observed when igniting  $\text{CH}_4/\text{O}_2/\text{N}_2$  mixtures with high oxygen contents. Indeed, the measured pressure time histories displayed interesting and unexpected behaviour in that very high pressure peaks ( $\sim 240$  bar) were recorded. We have attributed such anomalous behaviour (named Combustion-induced Rapid Phase Transition, CRPT) 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, hence culminating in the Rapid Phase Transition.

In this work, we further verify our thesis by performing explosion experiments in the presence of nucleation sites, thus promoting the heterogeneous boiling mode and hindering the water explosion due to RPT. To this end, we added talc (fine powder) on the vessel walls. The results show that, in the presence of nucleation sites, the pressure peak is significantly reduced to a value close to the adiabatic value.

## Introduction

In nature, two kinds of explosion phenomena can occur: chemical explosion and physical explosion. Chemical explosions generally involve fast exothermic reactions, such as combustion reactions. Physical explosions do not involve chemical reactions, but they include the Rapid Phase Transition (RPT) phenomenon. RPT explosions occur when a liquid is rapidly super-heated in the absence of nucleation sites, e.g., by mixing with another fluid at a temperature beyond its boiling point [1-9]. The consequent violent production of high-pressure vapour exerts sudden pressure on the surrounding fluid, thus leading to the formation of strong shock waves [10]. Super-heated liquid explosions are well known and have been observed in the concomitance to vessel rupture [11], steam explosions, as in nuclear reactors [12], foundry accidents [13,14], and also in natural events as volcano eruptions [15].

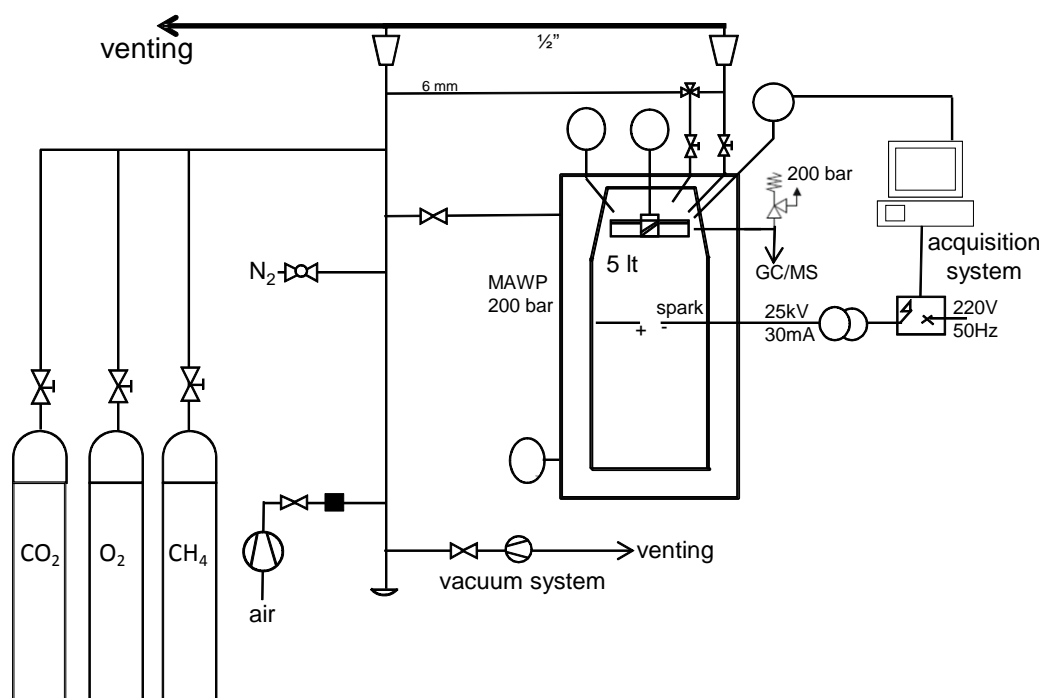
Chemical and physical explosions have always been considered separate and independent phenomena. However, in a previous paper, we have shown that physical steam explosions can occur during chemical explosions [16]. Indeed, when exploding  $\text{CH}_4/\text{O}_2/\text{N}_2$  mixtures in a non-adiabatic closed vessel, the pressure time histories exhibit oscillations and several peak pressures much higher than the adiabatic values ( $> 200$  bar), which cannot be addressed to chemical phenomena. Hence, we have attributed the occurrence of such phenomenon to the water super-heating and the subsequent RPT. More precisely, we have shown that the water produced by the combustion reaction condenses and accumulates at the cold walls of the

vessel, forming a liquid film. The contact between the hot burnt gases and the liquid water generates a super-heated liquid film whose rapid evaporation causes a super-adiabatic pressure peak.

In this work, we revise the Combustion-induced Rapid Phase Transition (CRPT) phenomenon to the end of investigating the role of nucleation sites on the occurrence of such phenomenon. To this aim, we added talc (fine powder) on the internal surface of the vessel, thus providing nucleation sites for preventing water super-heating and favouring water evaporation.

### Experimental apparatus and conditions

Our experimental system has been described recently [16-18] and is just briefly mentioned here. The reactor consists of a closed cylindrical vessel made of 5-cm-thick AISI 316 SS steel. The vessel volume is 5 lt. Fig.1 shows the scheme of the experimental rig.



**Figure 1.** Scheme of the experimental rig

The  $\text{CH}_4/\text{O}_2/\text{N}_2/\text{CO}_2$  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.

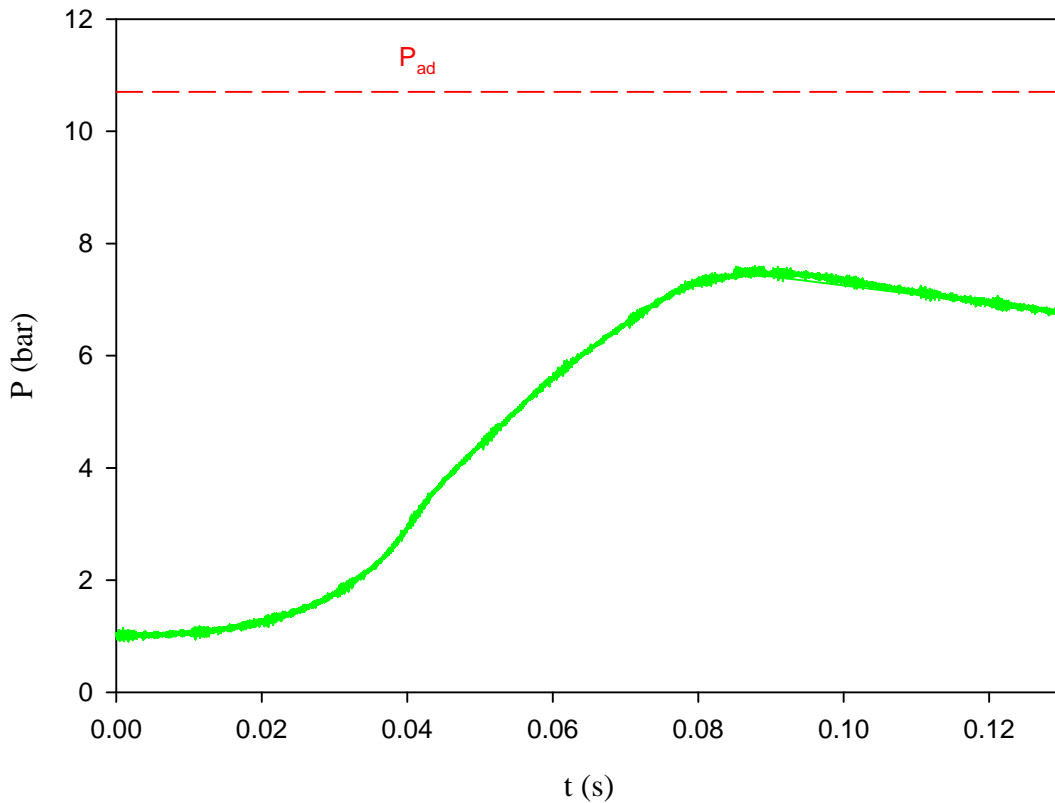
Table 1 shows the compositions of the mixtures investigated in this work. The theoretical values of adiabatic pressure and temperature reached after the explosion in closed vessel are also reported in the table, along with the water content and the corresponding value of partial pressure at adiabatic conditions. We tested the explosion behaviour of two mixtures characterized by the same  $\text{O}_2 / \text{CH}_4$  ratio ( $= 2$ ), but different  $\text{CO}_2$  contents (20 % and 40 %).

**Table 1.** Compositions and adiabatic pressure and temperature of the mixtures investigated

	RUN1	RUN2
CH <sub>4</sub> (%)	13.8	18.5
O <sub>2</sub> (%)	27.6	36.9
N <sub>2</sub> (%)	18.5	24.6
CO <sub>2</sub> (%)	40	20
P <sub>ad</sub> (bar)	8.9	10.7
T <sub>ad</sub> (K)	2579	2962
% H <sub>2</sub> O v/v at adiabatic conditions	25.7	30.8
P <sub>H2O</sub> (bar) in burned gases	2.3	3.3

## Results

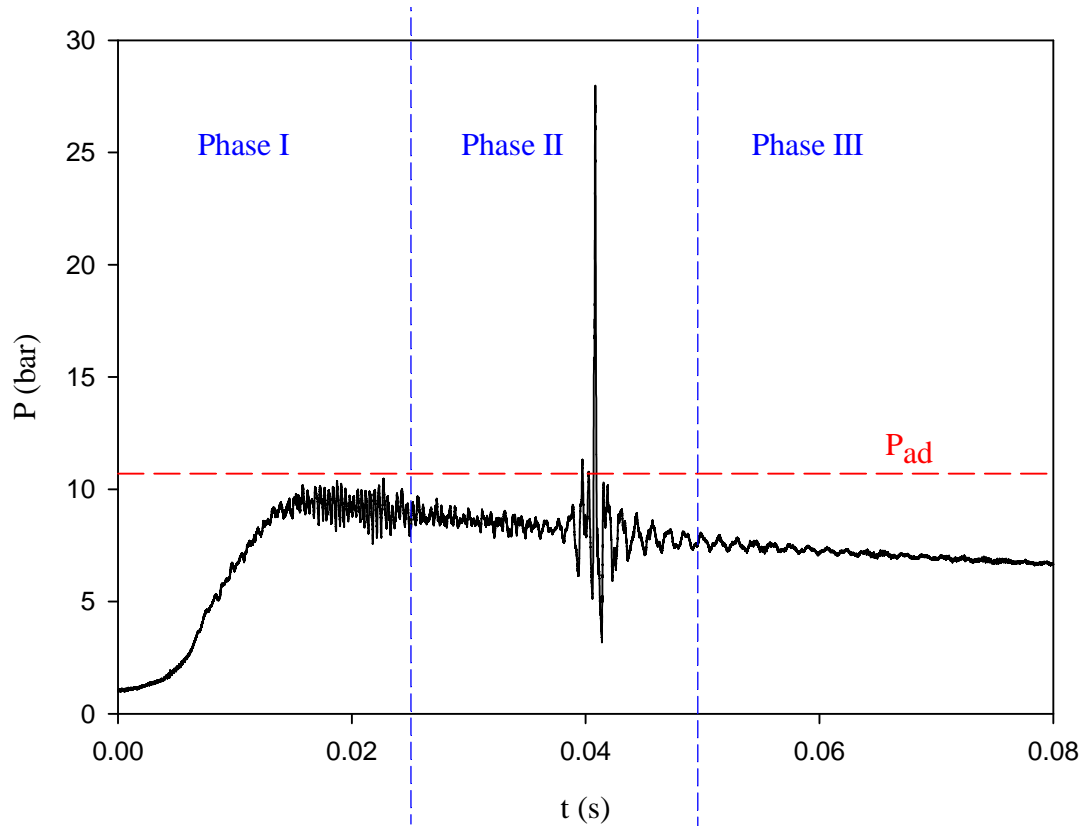
Figure 2 shows the pressure time history as measured for RUN1 (Table 1). The value of adiabatic pressure is also reported in this plot (dashed horizontal line).



**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,  $P_{\text{ad}} = 8.9$  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<sub>2</sub> 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.

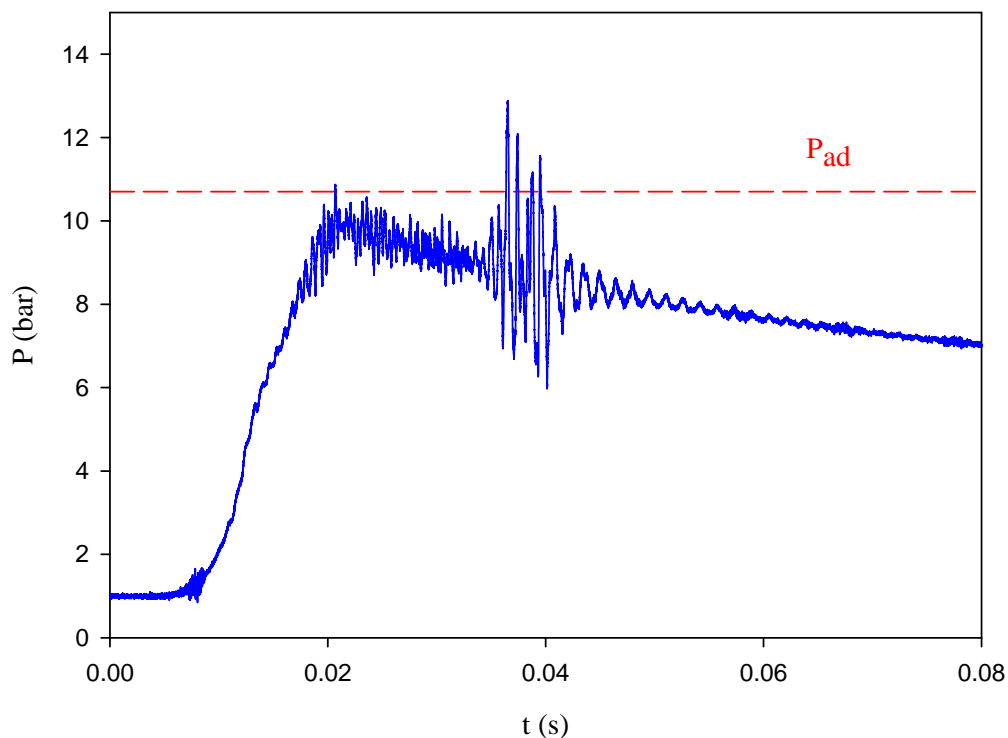
In a previous paper, we have conceptually divided the pressure time trend into three parts (Figure 3), which correspond to different phases [16]. Phase I is characterized by an oscillating signal whose average value increases with time up to reach the adiabatic value ( $P_{ad} \sim 10.7$  bar) when combustion has come to an end. We have addressed 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 ( $P_{H_2O} = 3.3$  bar) is much higher than the water vapour pressure at the boundary layer adjacent to the vessel walls ( $T_{wall} = 283$  K;  $P_{H_2O}^{\circ} = 0.022$  bar). In 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 occurrence of 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 ( $\sim 450$  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 introducing a small amount of common talc powder ( $< 1$  g,  $Mg_3Si_4O_{10}(OH)_2$ , ultra-fine powder [19]) over the internal surfaces of the vessel walls, 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 favours the kinetic 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).

## 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 Combustion-induced Rapid Phase Transition (CRPT) may be prevented if nucleation sites are present (e.g., on the vessel walls), thus favouring the evaporation kinetic and preventing the water super-heating.

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