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Deflagration, Detonation and Combustion-induced Rapid Phase Transition

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The paramount of the explosion classification should take into account a new explosion mode, called combustion-induced Rapid Phase Transition (cRPT), which occurs when the water produced by a deflagration condenses at the reactor wall and starts cycles of evaporation/condensation driven by the heat transferred from the flame to the water (by radiation), eventually culminating in a severe phenomenon of rapid phase transition.
Some evidences of this phenomenon are present in the literature, but they are often considered as detonation or meta-stable or thermal explosion, without further explanation. In this work, we review those literature results in the light of the novel cRPT phenomenon.

1. Introduction

Oxy-combustion of methane, hydrogen and carbon monoxide at initial atmospheric conditions of temperature and pressure has shown the presence of intense pressure peaks, up to ten times the adiabatic value (Di Benedetto et al., 2009; 2011; 2012a; Salzano et al., 2012; Basco et al., 2013).
In the above cited papers, we have attributed the observed over-adiabatic pressure peaks to the rapid phase transition of super-heated liquid water produced by the combustion reaction and condensed at the vessel walls. Such complex phenomenon has been named combustion-induced Rapid Phase Transition (cRPT). It is the result of a coupling between deflagration and physical explosion, similarly to LNG explosion (Di Benedetto et al., 2012c; Bubbico and Salzano, 2009).
In the literature, explosions of methane in oxygen-enriched air do not show this behaviour, probably due to the use of low-rate acquisition systems, which average the pressure history. In other cases, the observed over-adiabatic peaks have been attributed to detonation or deflagration-to-detonation transition, e.g., the Shock Wave Amplification by Coherent Energy Release - SWACER mechanism - (Lee et al., 2008) or pre-compression effects (Kuznetsov et al., 2005).
Recently, the BASF researchers, in the framework of the FP7 SAFEKINEX project (SAFEKINEX, 2009), have identified a range of methane/oxygen/nitrogen compositions in which a similar phenomenon was found. They recognized this explosion mode as different from detonation and deflagration modes, and called it meta-stable or thermal explosion.
In this work, we compare BASF results to our results in order to test their nature in the light of the cRPT phenomenon.

2. The cRPT phenomenon

Figure 1 shows a typical pressure time history where the cRPT was observed. The plot regards the explosion of $CH_4/O_2/N_2/CO_2$ (CH_4: 22.9 %; O_2: 45.7 %; N_2: 11.4 %; CO_2: 20 %) mixture in a cylindrical AISI 316 stainless-steel vessel. The wall thickness is 5 cm, the diameter is equal to 14 cm, and the vertical length is 40 cm. The reactor is equipped with rupture disks able to withstand 200 bar. The pressure recording is performed by means of Kulite ETS-IA-375 (M) series pressure transducers with a natural frequency of 150 kHz. These transducers are specifically designed for high-pressure, high shock environments and blast analysis. They were fed by a chemical battery (12 VDC/7 AH) to minimize any disturbance on the output supply, which was recorded by means of a National Instrument USB-6251 data acquisition system (16 bit, 1.25 × 106 samples/s) with a frequency up to 600 kHz. More details on the experimental apparatus are given in our previous paper (Di Benedetto et al., 2012b).

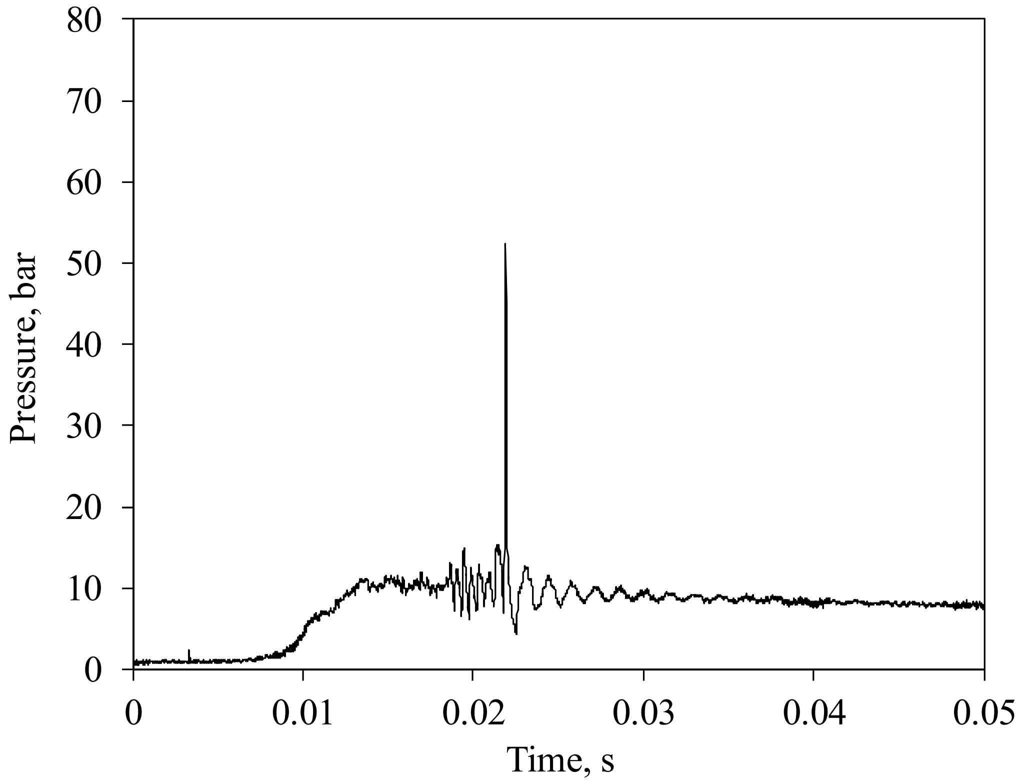

Figure 1: The occurrence of cRPT as observed in the case of $CH_4/O_2/N_2/CO_2$ mixture ($E=O_2/(O_2+N_2)=0.80$ and CO_2=20 %v/v).

The spark ignition is provided by electric arc at any desired energy by means of high voltage power generator (Spellman SL1200, DC up to 30 kV) or high voltage power generator (25 KV AC and 5 mA). The use of high-voltage capacitor (we normally adopt 590 pF) is adopted in order to control the spark energy and time by RC circuit. Spark gap may be regulated (1 mm for the measurement reported in this document to the standard 6.4 mm as for flammability limits).

The pressure signal oscillates in time culminating in a over-adiabatic pressure peak after the propagating flame has reached the vessel walls (time equal to 0.02 s), hence after the end of the combustion reaction. We attributed this behaviour to cycles of water production by reaction-water condensation at the vessel walls-water super-heating-water rapid phase transition.

Up to now, the only recognized chemical explosion mode able to give rise to over-adiabatic pressure peak is detonation.

The reasons for ruling out the detonation mode as the cause of such phenomenon are discussed below.

i) Following Lee (2008), for a deflagration- to-detonation transition (DDT) to occur, the deflagration must first accelerate to its maximum CJ deflagration velocity, which is about 0.5 the sound speed of the products. That is not observed if analyzing the pressure history, which is consistent with a burning velocity in the laminar or wrinkled regime.

ii) The cRPT phenomenon was observed in our equipment with length L to diameter D ratio very small (L/D varies between 1 and 3, Di Benedetto et al., 2012b). The occurrence of detonation in accidental explosions is relatively rare unless in relatively long tubes (see, e.g., the works by Ciccarelli and Dorofeev (2008) and Kessler et al. (2010) for natural gas DDT in smooth tubes).

iii) In hydrogen/air mixtures, the increase in pressure is typically about 20 times the initial pressure; these values are consistently lower than the observed cRPT peaks. We found peak pressure up to 50 times the adiabatic value (Di Benedetto et al., 2009).
iv) We have found the disappearing of the cRPT phenomenon by sprinkling ultra-fine $Mg_3Si_4O_{10}(OH)_2$ powder over the vessel walls which prevents explosive water evaporation providing nucleation sites (Salzano et al., 2013).
v) We have found that, when heating the reactor walls at temperatures higher than the water condensation temperature, cRPT does not occur (Di Benedetto et al., 2011).
vi) Ignition intensity has been demonstrated as not affecting the occurrence of cRPT. This effect can be seen in Figure 2. Even with very low energetic spark, the cRPT phenomenon can be observed with negligible variation in the pressure history (and peak).

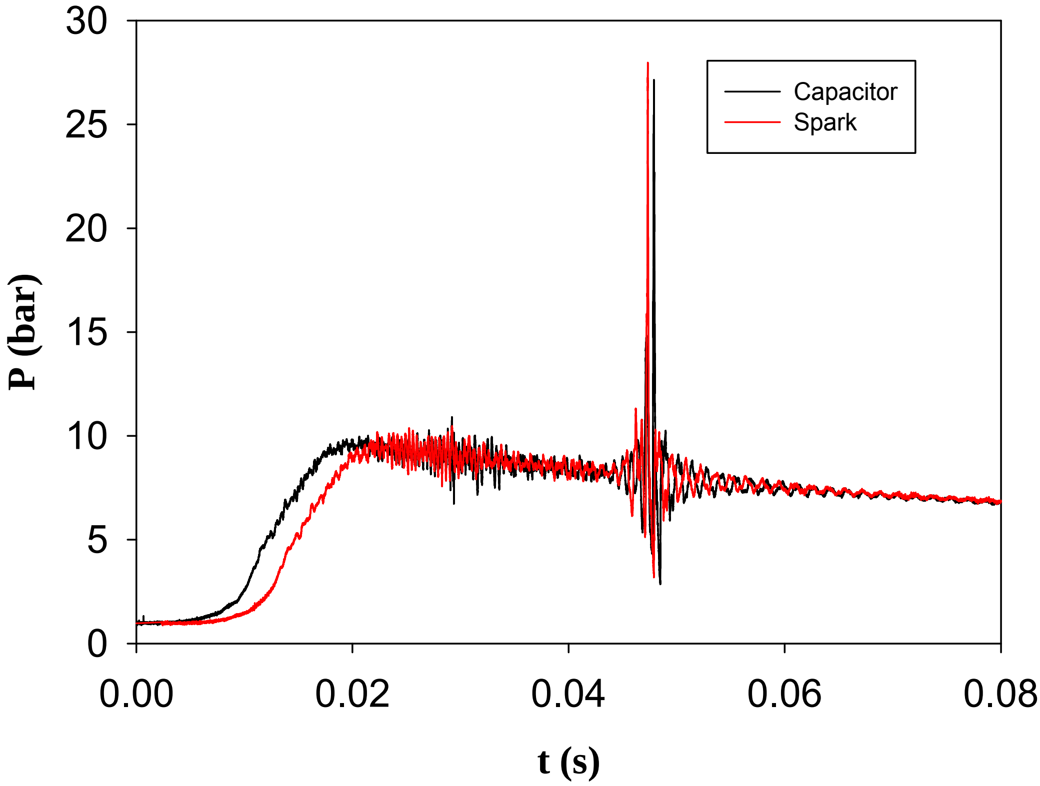

Figure 2: Ignition effect on the occurrence of cRPT for the explosion of methane/oxygen-enriched air with CO_2 (CH_4: 18.5%; CO_2: 20.0%; O_2: 36.9%; N_2: 24.6%). The capacitive spark (7 kV, 40 pF, E ≈ 1 mJ) signal and the 25 kV spark signal almost overlap.

3. Criterion of existence of the cRPT phenomenon

In our previous papers, we developed a criterion for identifying the occurrence of c-RPT. The criterion is based on the evaluation of a dimensionless number (θ_1) which is the ratio between the water condensation time (τ_{cond}) and the reaction time (τ_{reac}):

$$\theta_1 = \frac{\tau_{cond}}{\tau_{reac}} \tag{1}$$

The time τ_{reac} is the time required by the flame to travel along the radial direction of the vessel:

$$\tau_{reac} = \frac{d}{2} S_F \tag{2}$$

where d is the reactor diameter, and S_F is the flame speed calculated as a function of the laminar burning velocity, S_l, and the expansion factor (i.e., the adiabatic pressure, P_{ad}, to initial pressure, P_o, ratio):

$$S_F = S_l \cdot \left(\frac{P_{ad}}{P_o}\right) \tag{3}$$

τ_{cond} is the time for water condensation at the vessel walls:

$$\tau_{cond} = \frac{\rho c_p V}{h_c A} \tag{4}$$

where ρ and c_p are the density and the specific heat of the gas mixture, respectively. V and A are the volume and lateral surface of the vessel, and h_c is the heat transfer coefficient due to condensation.

From the analysis of all the experimental results reported in the cited literature, we have obtained the following general criterion for the occurrence of the cRPT phenomenon:

$\theta_1 < 1$ deflagration mode
$\theta_1 \geq 1$ cRPT mode

4. Evaluation of literature results

Schildberg and Holtappels (2010) have tested the explosion behaviour of $CH_4/O_2/N_2$ mixtures with different compositions in a spherical vessel (D = 340 mm).
The explosion pressure was recorded by piezoelectric pressure sensors with 500 kHz and sampling frequencies of up to 100 ks/s. They found three modes of explosions: deflagration, detonation and heat explosion. The pressure time history measured during heat explosion was significantly different from that of a detonation. It exhibited an over-adiabatic peak and also an oscillating behaviour. In Table 2, the compositions at which heat explosion was found are shown.

Table 2: The occurrence of heat explosion as observed in Shildberg and Holtappels (2010)

$E = O_2/(O_2+N_2)$	CH_4 % v/v	P_0 bar	P_{ad} bar	P_{max} bar	Explosion mode	θ_1
0.79	6.00	1.00	6.6	-	Deflagration	0.11
0.78	10.0	1.00	8.9	-	Heat explosion	1.14
0.75	20.0	1.00	12	-	Heat explosion	4.29
0.63	46.0	1.00	11	-	Deflagration	0.50
0.64	44.0	1.00	12	-	Deflagration	0.72
0.60	50.0	1.00	8.1	-	Deflagration	0.21
0.35	15.0	5.00	55	90	Heat explosion	30.5
0.50	20.0	5.00	62	65	Heat explosion	61.0
0.67	25.0	5.00	68.5	140	Detonation	95.7
1.00	7.00	5.00	36.8	34	Deflagration	0.46
1.00	10.0	5.00	45.6	140	Heat explosion	3.41
1.00	12.0	5.00	50.1	210	Heat explosion	6.52
1.00	14.0	5.00	53.8	480	Heat explosion	9.98
1.00	15.0	5.00	55.5	505	Heat explosion	11.79
1.00	17.5	5.00	59.4	240	Heat explosion	16.42
1.00	20.0	5.00	62.9	470	Detonation	101.29
1.00	25.0	5.00	69.2	503	Detonation	133.29
1.00	35.0	5.00	80.1	310	Detonation	155.01
1.00	40.0	5.00	84	500	Detonation	135.34
1.00	45.0	5.00	85	920	Detonation	90.77
1.00	50.0	5.00	81.8	500	Detonation	51.84

The heat explosion was considered to be induced by the temperature increase due to the adiabatic compression of the fresh gas ahead of the flame and the passing by of the induction time, after which the explosion takes place. The latter could take place locally, e.g., near the bottom where the centrally ignited deflagration flame due to buoyancy arrives last and it could result in an intense pressure wave (Holtappels

and Pasman, 2007). Oran and Gamezo, as cited in the Safekinex report (2009), have characterized this peak as a failed detonation or an unsuccessful hot spot to produce a shock and a detached flame.
An alternative explanation given by the same authors is the SWACER mechanism (Lee, 2008). The flame front itself with heat transfer and radical species diffusion ahead of the flame will favor the occurrence of gradients. This mechanism could explain the single peak as well as the full detonation cases.
For each composition, we computed the dimensionless number θ_1. We found that at the conditions under which heat explosion is observed, $\theta_1 > 1$, suggesting that the cRPT phenomenon occurs. Conversely, during deflagration, θ_1 was found lower than 1.

5. Conclusions

In the literature, novel explosion modes have been found when using ultra high frequency pressure transducers. Such novel explosion modes are characterized by over-adiabatic pressure peaks and oscillating pressure signals, but they cannot be addressed to detonation. When applying the criterion of the existence of the cRPT phenomenon to these literature data, it turns out that they are the result of cRPT. According to all these results, we may affirm that a new explosion mode has to be included in the general explosion classification which is due to the synergic coupling between a physical explosion (rapid phase transition) and a chemical explosion (deflagration), as shown in Figure 3.

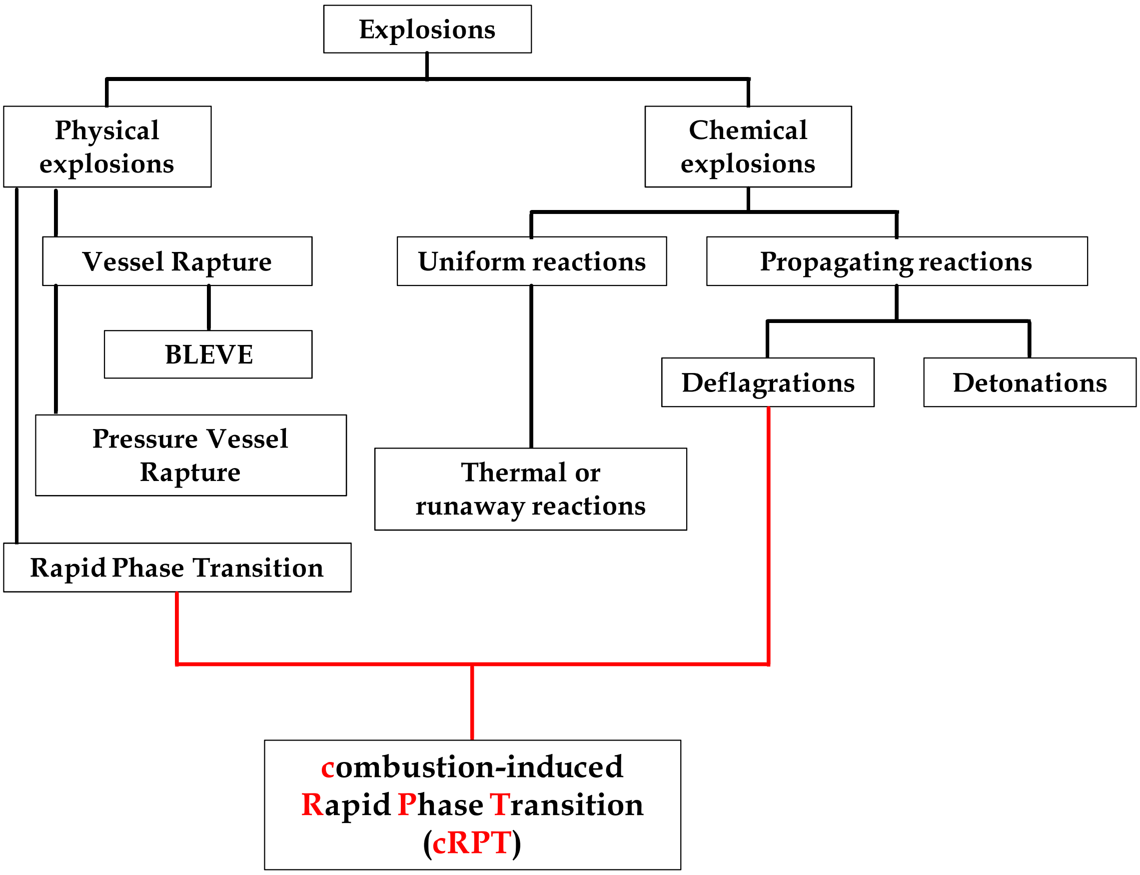

Figure 3: Explosion classification with the inclusion of the new explosion modality (in red)

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