CHEMICAL ENGINEERING TRANSACTIONS

VOL. 26, 2012

Guest Editors: Valerio Cozzani, Eddy De Rademaeker

ISBN 978-88-95608-17-4; ISSN 1974-9791

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1226059

The cRPT Phenomenon: Theoretical Evaluations

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We have recently showed that when exploding hydrocarbon fuels in highly oxygen-enriched air, the pressure-time history may display unexpected and anomalous behaviour in that oscillating signals and pressure peaks much higher than the adiabatic values (up to about 300 bar) were recorded. We addressed this anomalous behaviour, named combustion-induced Rapid Phase Transition, cRPT, to the occurrence of cycles of condensation/evaporation of water vapour on the walls of the vessel, followed by superheating of the liquid film due to radiation heat transfer from the flame, culminating in the water rapid phase transition. In this work we analyse this phenomenon by means of theoretical calculations of the characteristic times for the occurrence and intensity of such phenomenon.

1. Introduction

Two explosion phenomena may exist: chemical explosion, which generally requires fast exothermic reaction thus including the classical combustion reaction, the point-source, solid or liquid explosives or nuclear explosions, and physical explosion, which may include over-pressurisation explosion or Rapid Phase Transition explosion (RPT). This last phenomenon occurs when liquid mixes with another fluid characterised by temperature higher than its boiling point, in the absence of nucleation sites: the liquid superheats and the rapid production of high-pressure vapour exerts sudden pressure on surrounding fluid, thus leading to the formation of strong shock waves.
Superheated liquid-vapour explosions have been observed to occur in the presence of vessel rupture from years, as in the case of the Boiling Liquid Expanding Vapour Explosion (BLEVE) phenomenon (Reid, 1979, 1983), steam explosion as in nuclear reactors (Corradini et al., 1981, 1988) or even foundry accidents (Hess, 1969; Epstein et al., 2000) or volcanic eruptions (Freundt, 2003). However, in recent papers, we have showed experimentally that the chemical explosion of CH_4/O_2/inert mixtures in non-adiabatic vessel can drive sever steam explosion with the production of significant shock waves with over-adiabatic peak pressure up to 400 bar (Di Benedetto et al., 2011a;b).
In our opinion Holtappels and Pasman, (2007) also found the same phenomenon however defining it as a kind of transition state between the deflagration mode and the detonation mode. Also, the phenomenon cannot be explicated by classical theory for detonation or deflagration to detonation transition as e.g. Shock Wave Amplification by Coherent Energy Release (SWACER mechanism) (Lee and Moen, 1980; Lee et al., 1984) 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 forming a film. The contact between the hot burnt gases and the liquid water eventually generates a super-heated liquid film leading in turn to an

Please cite this article as: Di Benedetto A., Cammarota F., Di Sarli V., Salzano E. and Russo G., 2012, The crpt phenomenon: theoretical evaluations, Chemical Engineering Transactions, 26, 351-356 DOI: 10.3303/CET1226059

explosive rate of vapour production. Eventually, we have named such anomalous behaviour after RPT as combustion-induced Rapid Phase Transition, cRPT.

In the following, for an extended set of mixtures, we have analysed the occurrence probability and the intensity of over-adiabatic cRPT-derived pressure peak by means of classical thermo-chemical and fluid-dynamic analysis.

2. Experimental

All experimental tests have been conducted in a AISI 316 SS steel, cylindrical vessel (5 dm^3), wall thickness of 5 cm (Figure 1). Maximum allowable working pressure is 400 bar. Mixture compositions have been obtained by partial pressure method, starting from vacuum conditions. The mixtures were stirred few seconds before ignition in order to produce homogeneous mixtures. Each run was performed three times and the average value was taken. Pressure histories were recorded by KULITE ETS-IA-375 (M) series transducers. They were fed by a chemical battery (DC 12 V / 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 (16 bit, $1.25 \cdot 10^6$ samples s^{-1}) with a frequency up to 600 kHz. No manipulations were performed on the analog signal output from the transducer or on the digital data recorded. For all tests, the initial pressure was set to 1 bar and the initial temperature to 298 K.

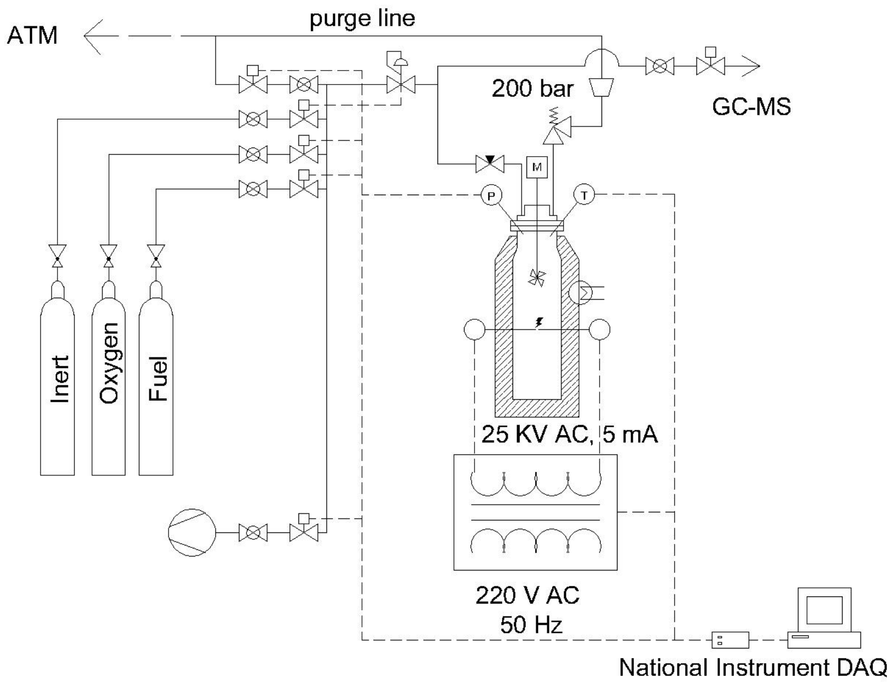

Figure 1: Equipment adopted for the experimental tests.

A typical pressure history with the occurrence of c-RPT spike quite after the maximum adiabatic pressure is reached, is shown in Figure 2 for the methane explosion in oxygen-enriched oxidant (CH_4 18.5 % v/v; CO_2 20.0 % v/v; O_2 36.9 % v/v; N_2 24.6 % v/v).

3. Results and discussion

Figure 3 shows the over-adiabatic c-RPT peak pressure as obtained in the experimental equipment described above, with respect to the partial pressure of water P_{H2O} as calculated by using an equilibrium code (GASEQ, 2011) at the final explosion conditions (constant internal energy, constant volume), i.e. in the combustion products at the adiabatic pressure, for a large range of experimental tests (Di Benedetto et al., 2011 a, b). The plot shows that the relevant cRPT peak pressures occur if P_{H2O} is higher than 2 bar.

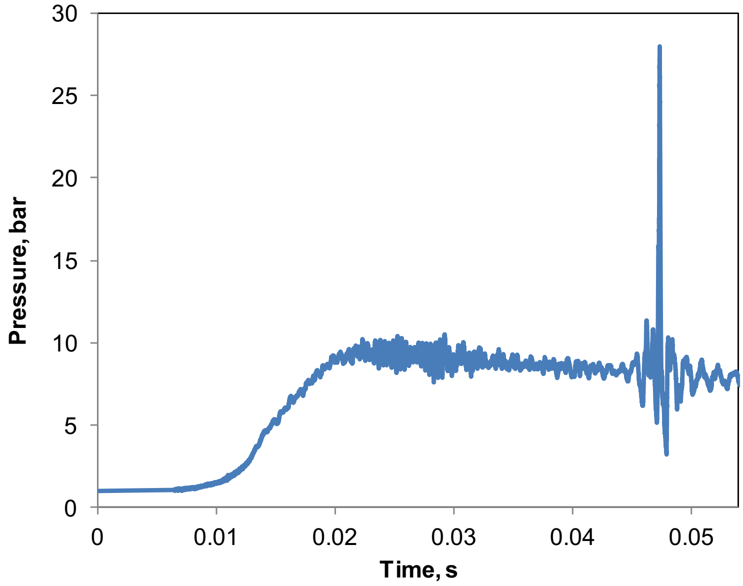

Figure 2: Pressure history in the case of c-RPT occurrence. Fuel composition: CH_4 18.5 % v/v; CO_2 20.0 %; O_2 36.9 %; N_2 24.6 %.

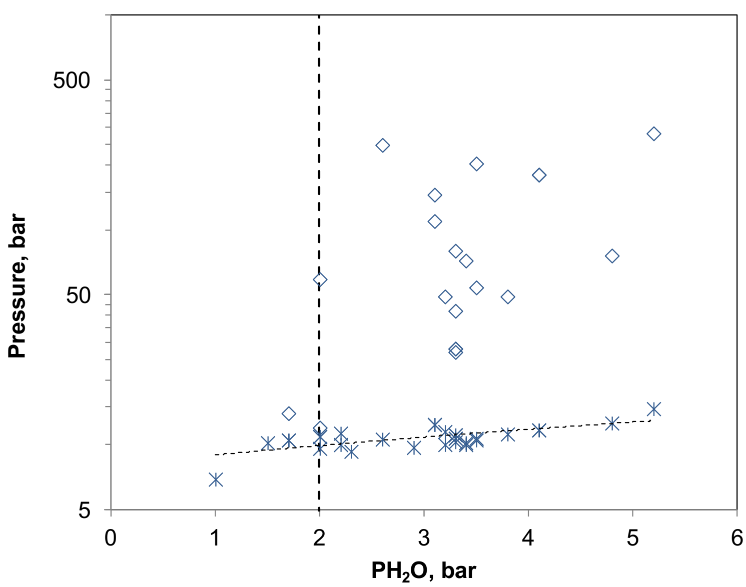

Figure 3: Experimental c-RPT peak pressures with respect to the partial pressure of water after explosion in closed vessel. Stars are maximum pressures observed, excluding c-RPT spikes.

On the basis of our experimental and theoretical evaluations, we have also ascertained that the ratio θ_1 between the time for radial flame propagation (τ_{reac}) and the time for water condensation (τ_{cond}) is the leading parameter for the likelihood of the cRPT phenomenon:

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

More precisely, we found that if the radial flame propagation rate is lower than the condensation rate (hence $\theta_1 < 1$), the water produced by the combustion reaction may condensate at the walls as soon as it is formed and super-heating conditions are possible.
Furthermore, we have evidenced that the severity of the cRPT phenomenon is correlated to the ratio between the condensation time (τ_{cond}) and the flame radiation time (τ_{rad}), θ_2:

$$\theta_2 = \frac{\tau_{cond}}{\tau_{reac}} \tag{2}$$

In Eqs.(1,2), the reaction time, τ_{reac}, was calculated by considering the time required by the flame to travel along the radial direction of the vessel:

$$\tau_{reac} = \frac{0.5d}{S_f} \tag{3}$$

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):

$$S_f = S_l E = S_l \left(\frac{P_{ad}}{P^\circ} \right) \tag{4}$$

In Eq. (4), the expansion factor was evaluated assuming all gas as burned and at the maximum theoretical pressure (P_{ad}).
The explosion phenomenon is unsteady and dominated by the thermal inertia of the vessel walls. It is then interesting to evaluate the heating/cooling time of the vessel walls, τ_{hcw}:

$$\tau_{hcw} = \frac{\delta_w^2}{\alpha_w} \tag{5}$$

where δ_w is the wall thickness (0.05 m) and α_w is the wall thermal diffusivity (4.54 10^{-5} m^2/s). τ_{hcw} is equal to about 55 s for the experiments in our reactor. This time is much higher than the explosion time (≈ 100 ms). As a consequence, during the unsteady pressure increase due to explosion, the vessel walls behave as isothermal walls with $T_w \approx 10$ °C.
Notwithstanding, the combustion process is not adiabatic. Besides heat losses by natural convection, the flame exchanges heat with the vessel walls through radiation. The time of heat exchange between flame and walls by radiation, τ_{rad}, was computed through the following formula:

$$\tau_{rad} = \frac{\rho C_p V \left(T_F - T_w\right)}{\sigma \varepsilon A \left(T_F^4 - T_w^4\right)} \tag{6}$$

where ρ and Cp are the gas density and specific heat capacity, V the vessel volume, T_F the flame temperature (adiabatic temperature), σ the Stefan-Boltzmann constant, ε the emissivity, and A the surface area enclosing the radiating gas volume (assumed as equal to the surface area of the vessel walls).

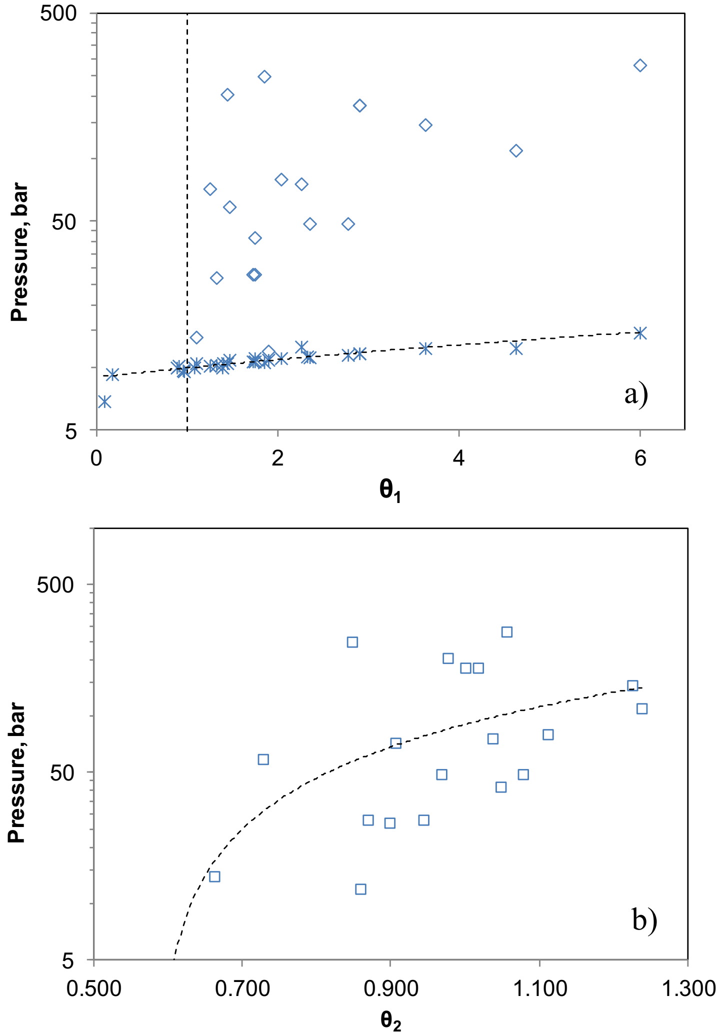

Figure 4: c-RPT peak pressure with respect to θ_1 (a) and θ_2 (b). In the case of θ_1, the maximum pressures (stars) reached in the vessel, excluding c-RPT spikes, are showed.

The combustion reaction produces water whose adiabatic partial pressure is given in Table 1. Depending on the relative values of the water partial pressure and the water vapor pressure at 10 °C (temperature of the vessel walls), which is equal to 0.02 bar, condensation may occur at the walls. The condensation time, τ_{cond}, was then calculated as:

$$\tau_{cond} = \frac{\rho C_p V}{h_c A} \tag{7}$$

where h_c is the coefficient of heat transfer due to condensation at the walls evaluated according to the formula reported in Incropera and DeWitt (1996).

Figure 5 reports the values of θ_1 and θ_2 for a large set of experimental data reported in our previous papers (Di Benedetto et al., 2011a;b) for stoichiometric methane explosion with oxygen, by varying the concentration of fuel, the oxygen enrichment and the type and concentration of inert. In the same plot, the maximum flame pressure (excluding the cRPT spike) reached in the vessel is also showed for the sake of comparison.

The occurrence of cRPT is observed only for $\theta_1 > 1$. On the other hand, the θ_2 value shows a clear indication on the trend of cRPT peak: on increasing θ_2 the over-adiabatic peak increases.

4. Conclusions

The occurrence of c-RPT and its severity (intensity) has been proved to be predicted by the evaluation of characteristic time for condensation, reaction and radiation. Further experimental and theoretical development are needed for the analysis of scale effects and surface over volume ratio.

Aknowledgments

The authors gratefully acknowledge the financial funding provided by MiSE (Ministero per lo Sviluppo Economico) within the framework of the project “Carbone pulito”.

References

Corradini M.L., Kim B.J., Oh M.D., 1988, Vapor explosions in light water reactors: A review of theory and modeling. Progress in Nuclear Energy, 22, 1-117.

Corradini M.L., Swenson D. V., Woodfin R.L., Voelker L.E., 1981, An analysis of containment failure by a steam explosion following a postulated core meltdown in a light water reactor. Nuclear Engineering and Design, 66, 287-298.

Di Benedetto A., Salzano E., Russo G., 2011a. Anomalous behaviour during explosions of CH4/O2/N2/CO2 mixtures, Combustion and Flame, 158, 2214-2219.

Di Benedetto A., Salzano E., Russo G., 2011b, Effect of diluents on rapid phase transition of water induced by combustion, AIChE Journal, DOI: 10.1002/aic.12778.

Epstein M., Fauske H. K., Theofanous T.G., 2000, On the mechanism of aluminum ignition in steam explosions. Nuclear Engineering and Design, 201, 71-82.

Freundt A., 2003, Entrance of hot pyroclastic flows into the sea: Experimental observations. Bulletin of Volcanology, 65, 144-164.

GASEQ, 2011. A Chemical Equilibrium Program for Windows. Available at: <www.c.morley.dsl.pipex.com> Accessed 30.11.2011.

Hess P.D., Brondyke K.J. 1969, Causes of molten aluminum-water explosions and their prevention. Metal Progress, 95, 93-100.

Holtappels K., Pasman H.J., 2007, Interpretation of gas explosion tests; extremes in explosion severity, Deliverable No. 10, SAFEKINEX: SAFe and Efficient hydrocarbon oxidation processes by KINetics and Explosion eXpertise, FP7 Programme “Energy, Environment and Sustainable Development” Contract No. EVG1-CT-2002-00072.

Incropera F.P., DeWitt D.P., 1996, Fundamentals of Heat and Mass Transfer. John Wiley & Sons Inc., 4th edition, New York, United States.

Lee J.H.S., Knystautas R., Freiman A., 1984, High speed turbulent deflagrations and transition to detonation in H_2-air mixtures. Combust. Flame, 56, 227–239.

Lee J.H.S., Moen I.O, 1980, The mechanism of transition from deflagration to detonation in vapor cloud explosions. Prog. Energy Combust. Sci., 6, 359–377.

Reid R. C, 1979, Possible mechanism for pressurized-liquid tank explosion or BLEVE's. Science, 203, 1263-1265.

Reid R. C., 1983, Rapid phase transitions from liquid to vapor. Advances in Chemical Engineering, 12, 105-208.