

Gas-Phase Detonations in Pipes: the 8 Possible Different Pressure Scenarios and their Static Equivalent Pressures Determined by the Pipe Wall Deformation Method (part 1)

Hans-Peter Schildberg

BASF SE, D-67056 Ludwigshafen, Germany
hans-peter.schildberg@basf.com

Explosive gas mixtures which are prone to undergo the transition from deflagrative to detonative explosion can occur in chemical process plants. In this case explosion pressure resistant design is the only viable safety concept. Whereas such a design is straightforward to realize for deflagrative explosions, which can be treated as static loads, there is worldwide not yet any accepted procedure for constructing pipes and vessels to be pressure proof against the dynamic loads brought about by gas-phase detonations. In particular, there is still a huge lack of the fundamental information on the peak height and peak width of the different conceivable detonative pressure scenarios, not to mention of how to evaluate the interaction of these pressure peaks with the walls of the enclosures.

In this paper the focus is on detonations in pipes. For the first time ever a systematic classification of the different detonative pressure scenarios is established. To do so, it is proposed to define two different pipe types and to distinguish between 8 different detonative pressure scenarios. In a next step the pipe wall deformation method is proposed which allows to assign to each of the 8 detonative, highly dynamic pressure scenarios an equivalent static pressure which can then be used in the formulae of by the established pressure vessel guidelines, which can only cope with static loads, to determine the desired detonation pressure proof pipe design. Based on the large number of experiments done so far, a proposal is presented which allows to predict in good quantitative approximation all short pipe scenarios on the basis of two long pipe scenarios, which substantially reduces the experimental effort. The expected variation of the static equivalent pressures with variation of initial temperature, initial pressure and the mixture composition is discussed.

1. Introduction

In explosive gas mixtures the self-sustaining flame front, which is usually the result of an oxidation reaction or a decomposition reaction, can either propagate in a deflagrative (flame speed is less than the speed of sound of the unreacted gas mixture, which is in most cases close to the speed of sound in air) or in a detonative (flame speed is larger than the speed of sound) manner through the entire volume filled with gas mixture. For ternary mixtures of type combustible/O₂/N₂ figure 1 gives examples for the composition ranges where the flame front always propagates in deflagrative manner and where the transition from the deflagrative to the detonative propagation ("DDT" = deflagration to detonation transition) is in principle possible. Whether the DDT actually occurs still depends on the geometry of the enclosure, the type of the ignition source and the composition of the mixture.

In chemical process plants potentially detonative mixture compositions can occur during deviations from normal operating conditions. For some processes (e.g. partial oxidation reactions) the use of such mixtures under normal operating conditions would even be of economic interest since these mixtures often allow for higher space/time yields. Since the presence of effective ignition sources can usually never be ruled out in process plants with absolute certainty, the only viable safety concept in the case that detonable gas mixtures are present is detonation pressure proof design of the enclosures (usually pipes and vessels). Note that explosion pressure

relief does not work with gas-phase detonations because the reaction front propagates at speeds larger than the speed of sound in the hot reaction products and therefore the pressure relief happens only after the walls of the enclosures have been exposed to the detonative pressure.

Gas-phase deflagrations in closed structures (vessels, pipes) exhibit explosion pressure ratios (maximum pressure developed during the course of the explosion divided by p_{initial} which denotes the pressure in the closed structure at the moment of ignition) in the range of 8 to 10 (values for stoichiometric combustible/air mixtures at $T_{\text{initial}} = 20\text{ }^{\circ}\text{C}$). The pressure load can be regarded as quasi-static, i.e. the time period during which the pressure rises from its initial value to the maximum value is some orders of magnitude larger than the cycle times of the fundamental radial oscillation modes of the pipes and vessels affected by the deflagrative explosion. An explosion pressure resistant design of plant components is state-of-the-art and can be done according to well established standards (for example: DIN EN 13445, part 1-6 and DIN EN 13480, part 1-6), which exclusively deal with static loads.

Gas-phase detonations bring about pressure/time profiles with an infinite slope of the leading edge and a width at half maximum as short as $10\text{ }\mu\text{s}$ and up to some milliseconds. The explosion pressure ratio (maximum value p_{det} of the detonative pressure peak divided by p_{initial}) can be much higher than for deflagrations. Since these peaks represent highly dynamic loads, a methodology capable of reliably predicting the structural response of plant components exposed to this type of load would have to account for aspects like eigenfrequencies of longitudinal and transversal oscillation modes, mode coupling and strain rate hardening. Hitherto, there are worldwide no guidelines available for an explosion pressure resistant design of pipes and vessels against the pressure load of gas-phase detonations.

From the perspective of process engineering there is an ever increasing demand for a guideline on detonation pressure proof design of pipes and vessels, since admitting potentially detonable gas mixtures on a routine basis would widen the admissible range of process parameters in many cases and thereby increase the process efficiency.

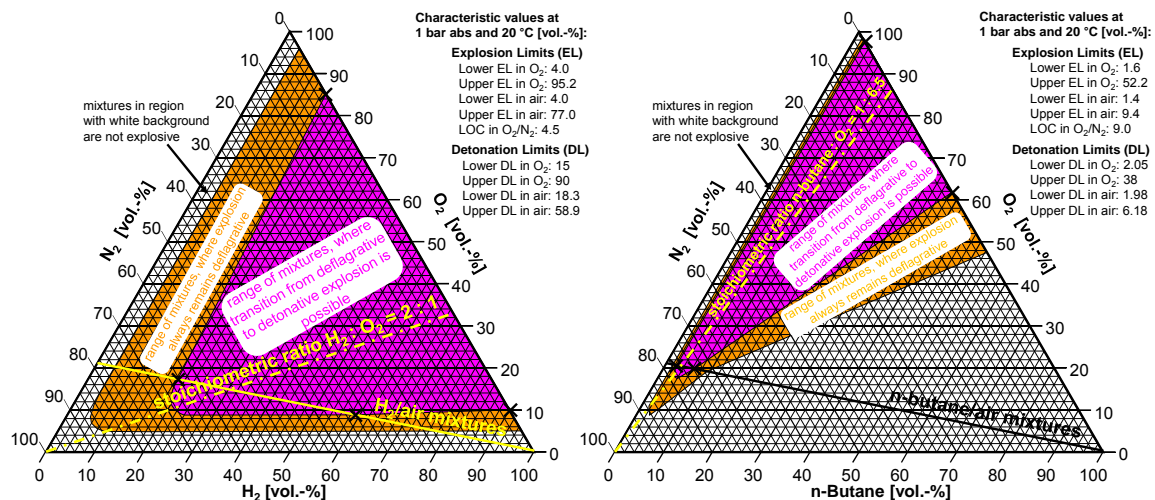


Figure 1: Explosion diagrams (Molnarne, 2008) of $\text{H}_2/\text{O}_2/\text{N}_2$ and $n\text{-Butane}/\text{O}_2/\text{N}_2$ at $p_{\text{initial}} = 1\text{ bar abs}$ and $T_{\text{initial}} = 20\text{ }^{\circ}\text{C}$. The detonation limits at 1 bar abs and 20 °C, which are indicated by black crosses in the diagrams, are taken from Nettleton (1987). The curve connecting the crosses is an interpolation of the author. The region enclosed by this curve represents the subset of the explosive range where mixtures can undergo a transition from deflagrative to detonative explosion.

2. State of knowledge concerning the pressure load associated with gas-phase detonations

The worldwide knowledge base in this respect is as such:

- 1: Detonative explosions of gaseous mixtures in long pipes (length is much larger than the predetonation distance) had been investigated to a reasonable extent in the past, mainly between 1960 and 1990. The focus of the work was on the behavior of the detonable mixture itself, but not on the interaction between the associated detonative pressure peaks and the wall of the pipes. For process safety the knowledge of the latter topic is paramount.

- 2: Short pipes (length is between between 1 and about 1.5 times the predetonation distance), in which much higher pressures than in long pipes can occur due to precompression effects, were hardly investigated. Therefore, in contrast to long pipes, there has not even evolved a clear perception of the different detonative pressure scenarios possible in this type of pipe, not to mention information about effective loads on the wall.
- 3: Gas-phase detonations in vessels have hardly ever been matter of research.
- 4: The investigated mixtures were only of the type combustible/air with but a few exceptions. However, in chemical process plants a much wider spectrum of combustible/oxidant/inertgas mixtures is relevant.
- 5: In the past 15 years publications emerged in which people tried to predict the structural response of a pipe wall on the detonative load by FE calculations (Karnesky 2013, Duffey 2011, Shepherd 2009, Smeulers 2010, Smeulers 2012). In principle FE calculations, provided they include the strain rate hardening of the wall material and both the elastic and the plastic structural response, do have the potential to predict the effective load brought about by gas-phase detonations on the pipe wall. The fundamental input required by any FE calculation is the detonative pressure/space/time profile. These profiles are theoretically understood only for the two most simple detonative pressure scenarios “stable detonation” and “reflected stable detonation”. However, for the remaining 6 scenarios all related to the transition from deflagration to detonation (DDT) these profiles are unknown, and the attempts to predict them by simulating the extremely complex process of flame acceleration up to the occurrence of the DDT by reactive computational fluid dynamics have not yet reached a level in reliability high enough to be accepted as a basis for evaluating process safety issues (and the question is whether they ever will).

In conclusion it can be stated that there is not yet any methodology available on which the design of detonation pressure proof pipes, not to mention detonation pressure proof vessels, could be based.

3. Background information on the transition from deflagration to detonation

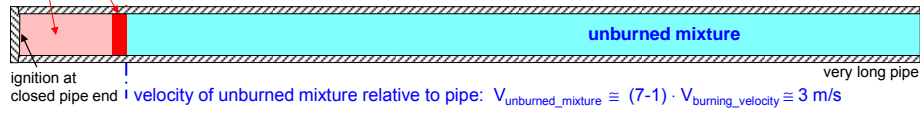
The most important aspects related to the run-up from deflagration to detonation in a pipe are compiled in figure 2. Note that all quantitative values in this figure are roughly what can be expected for common stoichiometric hydrocarbon/air mixtures. After the flame front was established by the local release of ignition energy, it permanently converts unreacted mixture into hot reaction gases which, due to their temperature being about 2000 K to 3000 K higher, expand correspondingly (note that there is usually not a big change in the mole number) and act like a moving piston on the yet unreacted and initially quiescent mixture ahead of the flame front. This results in a pressure distribution in the pipe as illustrated by the curve t_1 in figure 3: a pressure front bringing about a pressure rise by a factor of approximately 2 propagates into the quiescent unreacted mixture at a speed slightly larger than its speed of sound (typically about 330 m/s for most stoichiometric hydrocarbon/air mixtures). The unreacted gas between the flame front (=head of the piston) and the initial pressure front moves in direction of flame propagation (i.e. to the right side in the figure) with about 200 to 250 m/s.

As the flame accelerates due to the positive feedback loop explained in figure 2, the piston represented by the expanding reaction gases also accelerates. As soon as its speed relative to the moving gas ahead of it becomes larger than the speed of sound in the moving unreacted mixture (i.e. the piston moves with about 500 to 600 m/s relative to the pipe), unreacted mixture is compressed directly ahead of the flame front, such that a bump emerges in the pressure signal (curve t_2 in figure 3). Furthermore, the compression of unburned mixture ahead of the accelerating piston is also caused by its inertia and by restrictions to flow in the pipe. In figure 3 the pressure distribution between the bump of unburned mixture and the initial pressure front is slightly simplified as a plateau whereas in reality the pressure level rises slightly as one moves from the initial pressure front backwards to the pronounced bump of compressed gas directly ahead of the flame front as consequence of small shock waves being generated at the location of the flame (here the gas expands) during the entire process of flame acceleration. At the very last stage of flame acceleration (i.e. before the DDT occurs) the flame moves at 1000 to 1300 m/s relative to the pipe and the acceleration is typically about 1000000 m/s^2 (see example in figure 4). The corresponding values of the “piston” can be expected to be about 10 to 20 % less.

The transition to detonation occurs as soon as the temperature in the precompressed unburned mixture directly ahead of the flame front has risen by adiabatic compression to values so far beyond its autoignition temperature that the ignition delay time has fallen to values of a few microseconds. Since the time interval between compressing the unburned mixture and burning it in a deflagrative flame is extremely short, the ignition delay time must become that small to enable autoignition before the mixture is “eaten up” by the deflagrative flame front. Figure 4 presents single frames of a high speed video giving evidence of this autoignition event in the precompressed mixture ahead of the flame front. Once this autoignition event happens, the detonative mode of burning is established (sudden expansion of the autoignited gas causes a powerful shock wave into the cold gas upstream and the next adjacent “layer” is brought to such a high temperature that it also autoignites and so on).

1st stage: directly after ignition, flame propagates into the initially quiescent unburned mixture

hot reaction gases | velocity of flame relative to unburned mixture: $V_{burning_velocity} = V_{laminar_burning_velocity} \cong 0.5 \text{ m/s}$
 flame-front | expansion ratio of reaction gases for isobaric combustion: $\cong 7$
 | velocity of flame relative to pipe: $V_{flame_speed} \cong 7 \cdot V_{burning_velocity} \cong 3.5 \text{ m/s}$



Example for Reynolds number of unburned mixture directly after ignition

speed of unburned gas $v = 3.0 \text{ m/s}$; inner pipe diameter $d = 50 \text{ mm}$; dynamic viscosity $\eta = 8.15 \mu\text{Pa}\cdot\text{s}$ for pure propane; $\eta = 18.2 \mu\text{Pa}\cdot\text{s}$ for pure air; density $\rho = 1.4 \text{ kg/m}^3$ for a hydrocarbon/air mixture (for a stoichiometric propane/air-mixture, which contains 4.03 vol.-% propane, we assume the same dynamic viscosity as for pure air)
 $R_e = (v \cdot d) / (\eta / \rho) = 11538$. This value is much larger than the threshold of 2400 for transition to turbulent flow!!

2nd stage: flow of unburned mixture has become turbulent, flame propagates in turbulent mixture

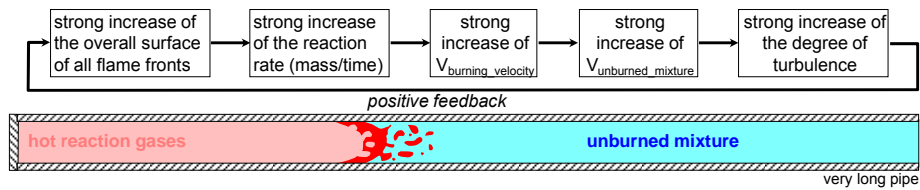


Figure 2: Illustration of the flame acceleration process in a hydrocarbon/air mixture. The expanding reaction gases act like a moving piston on the unburned mixture, which starts to flow in turbulent manner shortly after ignition (see example for Reynolds number). Then, in the second stage, a positive feedback loop further increases the flame speed.

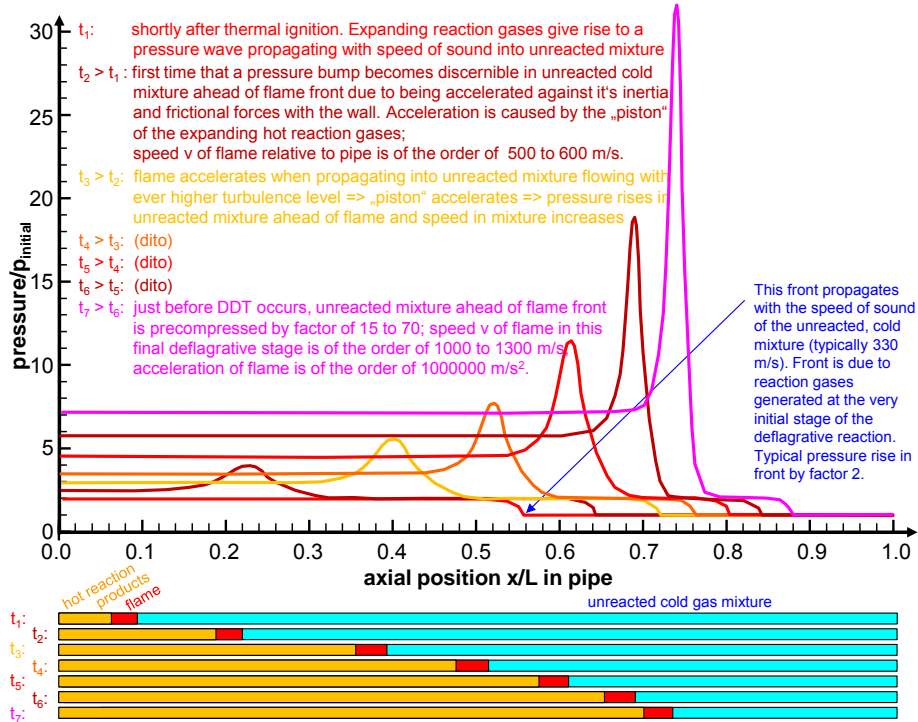


Figure 3: Qualitative sketch of the pressure distribution in a pipe as resulting from a flame acceleration process as illustrated by figure 2 at consecutive instants during run-up to detonation.

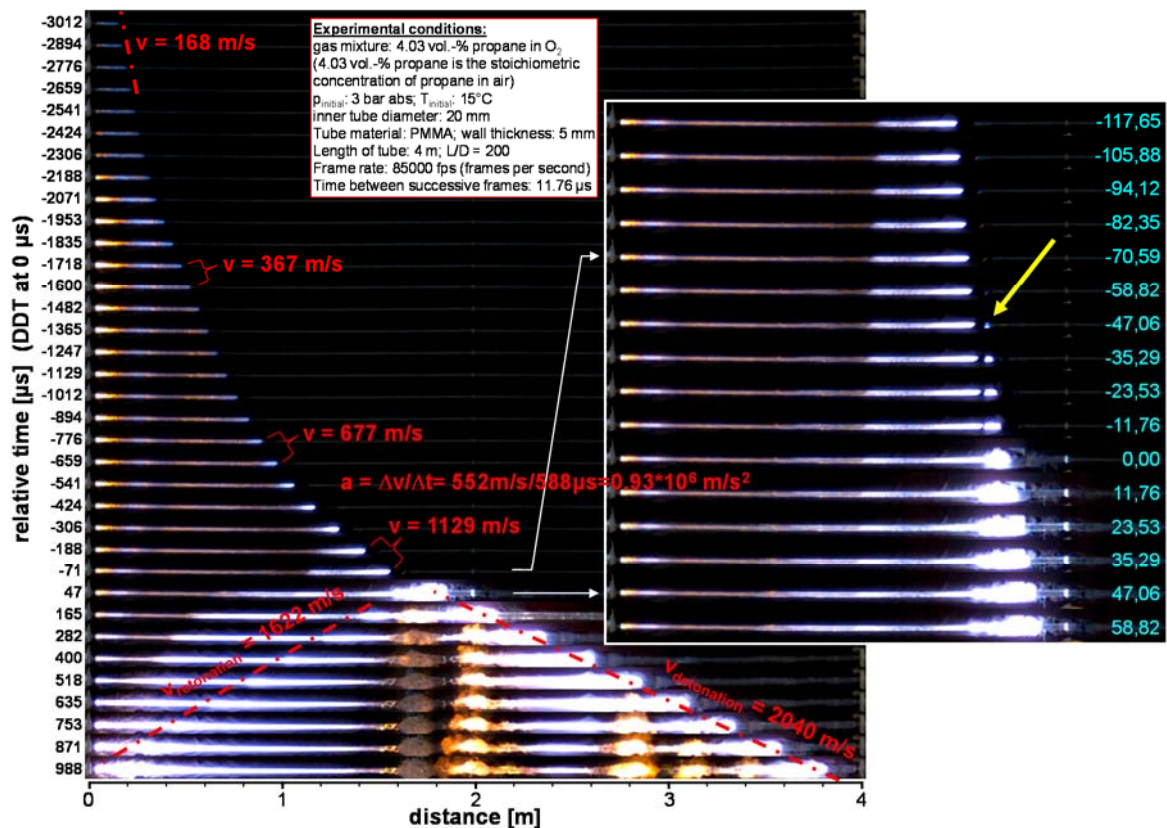


Figure 4: Sequence of consecutive frames of a high speed video illustrating the transition from a deflagrative to a detonative explosion. Clearly visible is the ignition by adiabatic compression in the bump of precompressed gas ahead of the flame front at $-47.6 \mu\text{s}$ (see yellow arrow). Note that the pipe ruptured a several locations after the DDT occurred, so flames escaping from the pipe are visible in the frames at relative times $\geq 282 \mu\text{s}$ and at distances $\geq 1.7 \text{ m}$. The video was recorded at BASF.

4. Approach proposed by BASF to develop a guideline for detonation pressure proof design of pipes exposed to internal gas-phase detonations

At BASF in Ludwigshafen a comprehensive research project was carried through during the last 4 years to quantify the effective load experienced by pipes when exposed to internal gas-phase detonations. Intermediate results were published as the work progressed (Schildberg 2013, 2014, 2015, 2016). Now, at the end of the project a rather clear perception of the involved effects has emerged. The effective load of gas-phase detonations in vessel-like geometry has not yet been investigated.

4.1 Proposal for classifying the detonative pressure scenarios into 8 different types and the pipes into two different types

Based on the pressure/distance plots shown for the predetonation stage in figure 3, figure 5a displays pressure-distance profiles at different time instants in the course of the transition from deflagration to detonation in a long pipe and figure 6a displays the analogue for short pipes. Quantitatively the pressure ratios given in both figures roughly correspond to what can be observed for stoichiometric hydrocarbon/air mixtures at 20°C .

For the ease of illustration and for to enable coarse quantitative estimates discussed later, we have drawn these figures with the “plateau approximation” introduced in chapter 2, i.e. the pressure between the bump of unburned mixture and the initial pressure front is assumed constant. Quantitatively, this pressure front raises the pressure in the unreacted mixture by about a factor of 2. Also, as soon as the initial pressure front gets reflected and propagates backwards in the direction of the location of the ignition source, we assume a constant pressure in the region affected by the reflected wave. Quantitatively, the reflected wave raises the pressure by a factor of approximately 1.5.

Note that the pressures in both figures 5a and 6a are meant to be the maximum values of the pressures that would be measured at a certain axial position by an ideal piezoelectric pressure transducer (very fast response

characteristic and very small diameter of the pressure sensitive membrane) and not the static equivalent pressures defined later in chapter 4.2.

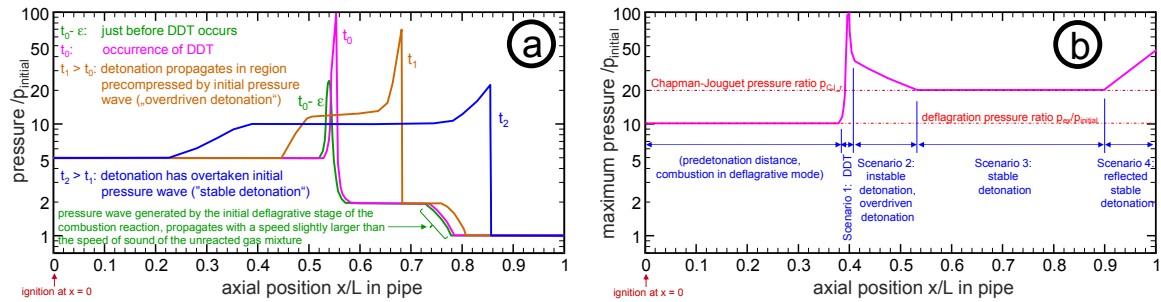


Figure 5: a) Schematic illustration of the pressure/distance profiles in a long pipe at different time instances close to the point of time of DDT-occurrence. The peak in the curve labelled $t_0 - \epsilon$ represents the highly precompressed unreacted gas immediately ahead of the flame front, generated by the ever faster expanding "piston" formed by the hot reaction gases. b) Maximum pressure ratios found in a long pipe during the course of an explosion with transition from deflagration to detonation in dependence on the axial position (schematic).

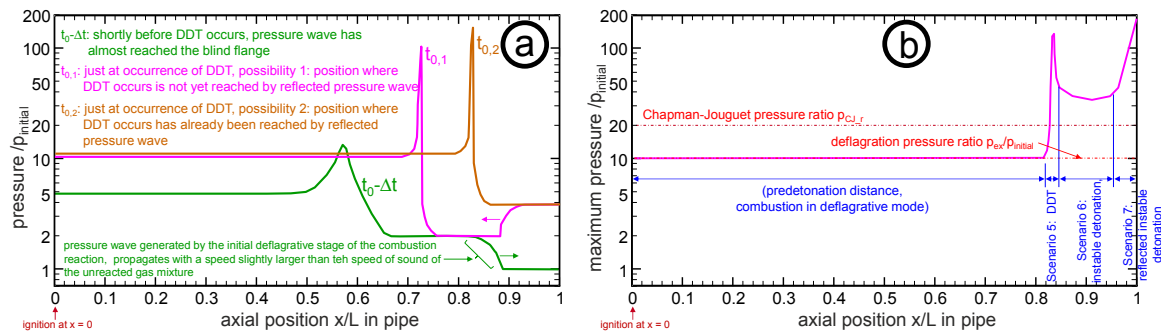


Figure 6: a) Schematic illustration of the pressure/distance profiles in a short pipe at different time instances close to the point of time of DDT-occurrence. b) Maximum pressure ratios found in a short pipe during the course of an explosion with transition from deflagration to detonation in dependence on the axial position (schematic). Scenario 8, which is not displayed in the above sketch, is generated by coalescence of 5 and 7 under omission of 6, i.e. the DDT occurs directly ahead of the blind flange.

References

- Duffey T.A., 2011, "Plastic Instabilities in Spherical Vessels for static and Dynamic Loading", Journal of Pressure Vessel Technology, Vol. 133, 051210-1-051210-6
- Karnesky J., Damazo J., Chow-Yee K., Rusinek A., Shepherd J. E., 2013, "Plastic deformation due to reflected detonation", International Journal of Solids and Structures, 50 (1), pp. 97-110
- Molnare M., T. Schendler and V. Schröder, 2008, *Safety Characteristic Data Volume 3: Explosion Regions of Gas Mixtures*, Wirtschaftsverlag NW, Bremerhaven; ISBN 978-3-86509-856-6
- Nettleton M.A., 1987, *Gaseous Detonations*, p. 76, Chapman and Hall Ltd., New York; ISBN 0-412-27040-4
- Shepherd J.E., 2009, "Structural Response of Piping to Internal Gas Detonation", Journal of Pressure Vessel Technology, Vol. 131, Issue 3, doi: 10.1115/1.3089497
- Smeulders J.P.M, Pape G., 2010, "Design rules for pipe systems subject to internal explosions-Part 1", Proceedings of ASME 2010 Pressure Vessels and Piping Conference (Paper No. PVP2010-25695)
- Smeulders J.P.M, Pape G., 2010, "Design rules for pipe systems subject to internal explosions-Part 2", Proceedings of ASME 2010 Pressure Vessels and Piping Conference (Paper No. PVP2010-26177)
- Smeulders J.P.M, Pape G., Ligterink N.E., 2012, "Modelling the effect of plasticity on the response of pipe systems to internal explosions", Proceedings of ASME 2012 Pressure Vessels and Piping Conference (Paper No. PVP2012-78482)