7.2 Detonations and explosions

7.2.1 Introduction

From an operative point of view, we can define an explosion as a release of energy into the atmosphere in a small enough volume and in a short enough time to generate a pressure wave of finite amplitude travelling away from the explosion source, which can be heard. Clearly, also different definitions can be given, but the aforementioned one has the advantage of including all the explosions that are of some interest for industrial process plant safety. This definition considers only explosions in air, which are the only explosions of some interest in this context. The energy released can be stored, before being released, in various forms, such as: nuclear, chemical, pressure, etc.

The pressure wave generated by the explosion is the main phenomenon to focus on when damage to people or goods are concerned. However, it is worthwhile stressing that the main damage, as far as accidental explosions in a process plant are concerned, does not stem from the pressure wave itself, but from some indirect effect generated by the pressure wave. In particular, the main injuries to people are usually caused by fragments that may form missiles, and by structure collapse. Moreover, the damage caused to the process units by the blast wave are not usually very large, but large enough to cause a dispersion into the environment of the chemical stored in the unit. When such a chemical is toxic or flammable, much more serious accidents can be triggered, such as large fires or the dispersion of large clouds of toxic chemicals into the atmosphere, through what is usually called a domino effect.

A diagram of the accidents involving explosions in a process plant is shown in Fig. 1. From such a diagram, we can see that any major accident in the process industry originates from a loss of containment from a process unit (e.g. tank, reactor, apparatus, pipe, etc.), leading to a release of chemicals in the environment.

This loss of containment can be catastrophic following the collapse of an apparatus. When the chemical in the apparatus is a compressed gas, it will expand from the bursting pressure of the apparatus up to the atmospheric value. Since the characteristic time of such an expansion is very short, the energy released from the expansion generates an explosion. The gas released will form a cloud that will be dispersed and diluted into the atmosphere by mixing with air. When no ignition sources are present (or even when the gas is not flammable), no more energy can be released and, consequently, no more explosions can follow. However, when the gas is flammable and ignition sources are present close to the release point, the small amount of flammable gas mixed with air (that is, with larger concentration than the upper flammability limit) in a diffusive flame. In this case, the characteristic time for the combustion energy release is determined by the fuel and air transport rate towards the flame, and it is consequently too large to generate any explosion. When the ignition is delayed, the cloud of flammable gas can mix with air, thus creating a large amount of fuel-air mixture with concentration inside the flammability range. In this case, following the ignition, the characteristic time for the combustion energy release is determined by the velocity of the flame that propagates into the flammable mixture, and it can be short enough to generate an explosion, usually called UVCE (Unconfined Vapour Cloud Explosion).

When the collapsing apparatus also contains some liquid at room temperature, we can have two different situations depending on the value of the normal boiling point \( T_{b} \) of the liquid compared to the room temperature.

When the liquid temperature, which is equal to the ambient one, is lower than its normal boiling temperature, then the liquid is subcooled; so the characteristic time for its evaporation, and consequently for the energy release related to the expansion from the liquid to the vapour volume, is quite long and no explosion can occur. The vapours from the slow evaporation of the liquid pool will be dispersed in the atmosphere, which could lead to the aforementioned phenomena.

When the liquid temperature is higher than its normal boiling temperature, then the liquid is overheated (and consequently in a non-equilibrium condition) and the characteristic time for its complete or partial evaporation is quite short; such a fast evaporation can cause a flash or an explosion called BLEVE (Boiling Liquid Expanding Vapour Explosion). The vapours from the fast liquid evaporation...
will be dispersed in the atmosphere and they could lead to the aforementioned phenomena.

A process fluid can also be released through a non-catastrophic failure of the apparatus, such as a loss from a flange or from a pipe breakage. In this case, the released chemical, that can be either gas, liquid or two-phase mixture, will be dispersed into the atmosphere (maybe after evaporation) and may result in the aforementioned phenomena.

The collapse of the apparatus can also be caused by an internal explosion. In this case, apart from the aforementioned phenomena, the blast wave will travel from inside to outside the apparatus. Such an explosion can be caused by various situations, such as the explosive decomposition of an unstable compound, the deflagration of a flammable mixture of gas or dust, an exothermic chemical reaction out of control (i.e. a runaway reaction).

Below, the main characteristics of the various kinds of explosion, as well as the models available that estimate the consequences of different explosions will be discussed.

### 7.2.2 Decomposition of unstable compounds: ideal explosions

The more common explosions are related to the decomposition of unstable chemical compounds, such as the condensed phase explosives.

A chemical compound is said to be thermodynamically unstable when the free energy change of its decomposition reaction is negative, $\Delta G^\circ(T)<0$. Since $\Delta G^\circ$ is the Gibbs free energy change related to the complete transformation, in the reference state, of a stoichiometric amount of reactants in the products, a negative value of $\Delta G^\circ$ means that the products of the decomposition reactions have a lower free energy than the original compound. This means that the equilibrium constant of the decomposition reaction is larger than unity, $K(T)>1$, from the well known relation $K=\Pi a_i^\gamma=\exp(-\Delta G^\circ/RT)$, where $a_i$ is the activity of the species $i$, $\gamma$ is the stoichiometric coefficient of the same species (taken as positive for the reaction products and negative for the reactants), $R$ is the ideal gas constant and $T$ the temperature. In practice, from these relations it follows that a system kept at constant temperature and initially containing all the species (reactants and products) with unity activity, evolves spontaneously towards the products. In other words, at the given temperature, the considered products are more stable than the reactants.

Quite often, unstable compounds contain some oxygen atoms in the molecule, with the consequent formation of some oxides (which are usually very stable species, in particular CO$_2$) among the decomposition products. A typical example refers to TNT (TriNitroToluene, one of the most common explosives), whose chemical formula is C$_7$H$_5$O$_6$N$_3$.

Not all the thermodynamically unstable compounds can explode. To do that, firstly it is necessary to provide the compound with an amount of energy (such as a collision, a spark, a hot surface, etc.) large enough to start the decomposition reaction; secondly, the decomposition reaction must be fast and exothermic enough, i.e. it must release enough energy in a short time.

Although the explosive potential of a compound must always be verified experimentally, there are some preliminary analytical criteria that can determine, at least as a first approximation, the explosive potential of a compound. A first criterion is based on the analysis of the functional groups which are present in the molecule of the compound.

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**Fig. 1.** Flow diagram for explosion generation following an industrial process plant accident.
The presence of some of the groups in Table 1 is a clear indicator that the compound may be unstable. More analytical criteria require the evaluation of some parameters, basically related to the decomposition and combustion enthalpies as well as the stoichiometry of the complete decomposition or combustion reaction. The most well-known of such criteria are used in the software CHETAH (CHEmical Termodynamic And Hazard evaluation, originally developed by ASTM, American Society for Testing and Materials, Seaton et al., 1974) that evaluates the decomposition of a compound formed by carbon, hydrogen, oxygen and nitrogen to give CO₂, H₂O, N₂, CH₄, C, H₂, and O₂ into the proportions leading to the largest decomposition (or combustion) enthalpy. The lower the decomposition enthalpy (i.e. the larger in absolute value while negative, since it is related to an exothermic reaction), the larger the explosive potential, because more energy is released by the decomposition reaction. Moreover, the closer the decomposition and combustion enthalpies are, the larger the explosive potential is, since this means that the largest part of the oxygen required for the complete oxidation is already contained in the molecule of the compound. Similar information is provided by the oxygen balance that indicates the amount of oxygen (in grams) required for the complete oxidation of 100g of the compound. The closer to zero this indicator is, the larger the explosive potential is; in fact, similar to the combustion and decomposition enthalpies, this means that the largest part of the oxygen required for the complete oxidation is already contained in the molecule of the compound. For each indicator, some empirical semi-quantitative scales are defined giving the explosive potential of the compound. The criteria used in the CHETAH software are summarized as an example in Table 2.

The decomposition of an unstable compound leads to the instantaneous transformation of the solid compound into its high temperature decomposition products that expand in a very short time. Such an expansion is the easiest way to generate a blast wave (which is, as previously mentioned, the essential feature of an explosion) and can be described by the movement of a plug accelerating inside a cylinder. The pressure waves created by the accelerating plug propagate into the atmosphere in front of the plug at the speed of sound which is, for an ideal gas, equal to $c = \sqrt{RT/M}$, where $\gamma$ is the ratio of the specific heat at constant pressure and volume, and $M$ is the molecular weight. The pressure waves generated later propagate into an atmosphere at higher pressure, since the previous pressure waves have already travelled through it, and at higher temperature because the compression of the atmosphere is adiabatic. It follows that the pressure waves generated later travel at a higher speed than those generated previously and consequently superimpose them. The sharp change in all the state variables (e.g. pressure and temperature that change sharply across the pressure wave) becomes larger and larger, and finally results in a shock wave propagating from the explosion source. These explosions can be defined ideal since the explosion source can be regarded as a point, and the energy release from such a point can be regarded as instantaneous – in other words, the energy is released in a negligible volume and over a negligible time.

The shock wave generated by an ideal explosion propagates from the explosion epicentre at an increasing speed up to a limit value. The qualitative behaviour of the pressure vs. time at a given distance from the explosion epicentre is shown in Fig. 2: pressure rises almost instantaneously up to a maximum value, $P^o$, and

### Table 1. Functional groups which are typical of unstable compounds

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Functional group</th>
<th>Functional group</th>
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<tbody>
<tr>
<td>$\equiv C \equiv C$</td>
<td>$\equiv C \equiv N\equiv O \equiv Me$</td>
<td>$N^+\equiv HZ^-$</td>
</tr>
<tr>
<td>$\equiv C \equiv C \equiv Me$</td>
<td>$N\equiv N\equiv N\equiv O$</td>
<td>$N^+\equiv OHZ^-$</td>
</tr>
<tr>
<td>$\equiv C \equiv C \equiv X$</td>
<td>$N\equiv NO_2$</td>
<td>$N\equiv O$</td>
</tr>
<tr>
<td>$\equiv CN_2$</td>
<td>$N\equiv NO_2$</td>
<td>$C\equiv C\equiv O$</td>
</tr>
<tr>
<td>$\equiv C\equiv N\equiv O$</td>
<td>$C\equiv N\equiv N\equiv O\equiv C$</td>
<td>$N\equiv Me$</td>
</tr>
<tr>
<td>$\equiv C\equiv NO_2$</td>
<td>$C\equiv N\equiv N\equiv S\equiv C$</td>
<td>$C\equiv O\equiv O\equiv H$</td>
</tr>
<tr>
<td>$\equiv C\equiv O\equiv N\equiv O$</td>
<td>$C\equiv N\equiv N\equiv N\equiv C$</td>
<td>$[N\equiv Me]^+Z^-$</td>
</tr>
<tr>
<td>$\equiv C\equiv O\equiv NO_2$</td>
<td>$N\equiv N\equiv N\equiv N\equiv N$</td>
<td>$C\equiv O\equiv C$</td>
</tr>
<tr>
<td>$\equiv C\equiv Me$</td>
<td>$Hg\equiv N^+\equiv HgX^-$</td>
<td>$O\equiv O\equiv Me$</td>
</tr>
<tr>
<td>$\equiv A^+\equiv Me \equiv X$</td>
<td></td>
<td>$O\equiv O\equiv O$</td>
</tr>
<tr>
<td>$\equiv O \equiv X$</td>
<td></td>
<td>$N_3$</td>
</tr>
</tbody>
</table>
then falls down gradually as the shock goes away. In this phase, the overpressure can be also negative, i.e. absolute pressure can become lower than the atmospheric value. These negative overpressure values are usually quite small and rarely exceed 30 kPa. In order to estimate the consequences on people and structures, shape and intensity of a blast wave are usually characterized through several parameters; among them, the maximum side-on overpressure and the corresponding positive impulse. The side-on overpressure is defined as the overpressure (with respect to the atmospheric value) occurring at the side of a structure hit by the blast wave, as shown by the $P_0$ value in Fig. 2. The local behaviour of the side-on overpressure vs. time $t$ during the positive overpressure phase is usually represented through the general relation

$$P = P^0 \left[1 - \frac{t}{t_D} \right] \exp \left(-\alpha \frac{t}{t_D}\right)$$

where $\alpha$ is a decay parameter and the time starts when the shock wave of finite amplitude $P^0$ arrives.

The positive overpressure impulse, $i_P$, is defined as

$$i_P = \int_0^t P \, dt = P^0 \alpha \left[1 - \frac{1}{\alpha} \left(1 - \exp(-\alpha)\right)\right]$$

As the blast wave travels away from the explosion epicentre, side-on overpressure decreases.

Damage to people and structures due to the blast wave depend on several factors, characteristic of both the shock wave and the structure or person hit. In practice, four threshold values can be used to estimate the expected damage to structures. The complete destruction of structures that cannot be repaired is expected for side-on overpressure larger than 83 kPa. Heavy damage to the structures, that is, partial destruction of the structure due to the collapse of some structural element, is expected for side-on overpressure between 83 and 35 kPa. Moderate damage to the structures involving heavy but repairable damage to some component (such as walls collapsing) is expected for side-on overpressure between 35 and 17 kPa. Minor damage, such as shattering of windows and doors or cracks in walls, and roofing and tiling, is expected for side-on overpressure between 17 and 3.5 kPa.

### 7.2.3 Physical explosions

The term physical explosions means explosions that do not involve any chemical reaction in the energy release mechanism, such as those occurring due to the rapid expansion of a compressed gas or the vapour produced by a Rapid Phase Transition (RPT). The shock wave formation mechanism can always be depicted as an accelerating plug, similar to the aforementioned ideal explosions. The main difference is that both the volume from which the energy is released and the time necessary for its release are no longer practically zero as for ideal explosions. For instance, when a pressurized vessel containing only gas collapses, the gas rapidly expands from the bursting pressure to the atmospheric one generating an explosion. Not all the energy stored in the compressed gas is used to generate the shock wave. A significant amount of this energy is

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**Table 2.** Semi-quantitative scales used by CHETAH software for defining the explosive potential of a $C_xH_yO_z$ compound with $n$ atoms

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta h_D$</td>
<td>$&gt;-1.25$</td>
<td>$&lt;-2.92\text{ to } -1.25$</td>
<td>$&lt;-2.92$</td>
</tr>
<tr>
<td>$\Delta h_C - \Delta h_D$</td>
<td>$&lt; -20.93$</td>
<td>$&lt;0$</td>
<td>$&gt;-20.93$</td>
</tr>
<tr>
<td>$\frac{16(2x+y/2-z)}{M}$</td>
<td>$-240\text{ to } -160$</td>
<td>$-160\text{ to } -80$</td>
<td>$120\text{ to } 240$</td>
</tr>
<tr>
<td>$\frac{10(\Delta h_D)^2}{M}$</td>
<td>$&lt;30$</td>
<td>$30\text{ to } 110$</td>
<td>$&gt;110$</td>
</tr>
</tbody>
</table>
dissipated through various phenomena, such as plastic deformation before a vessel bursts or kinetic energy transferred to the fragments. As a rough estimation, about 30% of the energy stored in the compressed gas is transferred into the shock wave; about 40% provides kinetic energy to the fragments that can consequently be propelled over great distances, while the remaining 30% is dissipated.

When the vessel that collapses also contains a liquid phase, we can distinguish two different situations, as a function of the normal boiling point value compared to the room temperature, as previously discussed. When liquid temperature (which is assumed equal to the ambient one) is lower than its normal boiling point, the liquid is subcooled and it has no tendency to flash (the fast evaporation of an overheated liquid is usually referred to as a flash). However, when liquid temperature is higher than its normal boiling point, the liquid is overheated (i.e. it is in a non-equilibrium condition) and it has a strong tendency to flash. This leads to more vapour, whose expansion usually results in a minor explosion (since the characteristic time of a flash is not usually short enough), apart from when the liquid conditions trigger the BLEVE phenomenon. In this case, the characteristic time of the phase transition is very short (of the order of some ms) and a serious explosion can occur. The classic BLEVE theory explains the increase of the evaporation rate as a consequence of the homogeneous nucleation triggering, i.e. the formation of bubbles in the fluid bulk without any nucleation centre that are usually provided by the vessel surface roughness. Homogeneous nucleation leads to a much faster flash and, consequently, to a much stronger shock wave. Moreover, when the vessel does not collapse completely but simply breaks (as is the usual case), resulting in fast depressurization, the rapid evaporation due to the homogeneous nucleation does not allow the vapours to exit without pressurizing the vessel, which consequently collapse propelling their fragments around.

Homogeneous nucleation can only happen when the liquid is sufficiently overheated. It is not enough for the liquid temperature to be higher than its normal boiling point, but it must also be higher than another limit value, which characterizes each compound. As a consequence, in order to have a BLEVE, as a first necessary condition the liquid must be overheated, i.e. rapidly lead to a non-equilibrium condition characterized by a temperature value much higher than its normal boiling point. The short time for overheating the liquid is a necessary condition in order to avoid a slow evaporation of the liquid. In this case, the liquid would reach equilibrium conditions not instantaneously (i.e. with a short characteristic time necessary to cause an explosion) but gradually (i.e. with a long characteristic time not suitable for generating an explosion). The fast overheating of a liquid can be due to a fast depressurization of a gas liquefied by compression (e.g. following the collapse of an LPG, Liquidified Petroleum Gas, tank), but also following the contact of a low-volatile hot liquid with a more volatile cold one. Typical examples are the accidental contact of water with melting metals or salts, or of LNG (Liquified Natural Gas) with water. For the first two cases, water is the more volatile cold liquid that can vaporize producing an explosion, while in the latter case it is LNG.

The second necessary condition to have a BLEVE is to overheat the liquid enough, i.e. the liquid temperature must be higher than the threshold value for the homogeneous nucleation triggering. This means that when two liquids come into contact, the temperature of the hotter liquid must be higher than the critical temperature for homogeneous nucleation triggering when depressurization starts. The critical temperature value for homogeneous nucleation triggering, \( T_{cl} \), as a function of pressure can be estimated for hydrocarbons as \( T_{cl} = \frac{1}{T_{sl}} (0.11 P + 0.89) \) where \( T_{cl} \) is the critical temperature in K and \( P \) the reduced pressure, i.e. the ratio of pressure to critical pressure. At atmospheric pressure, the previous relation is well approximated by \( T_{cl} = 0.85 T_{cl} \). For hydrocarbon mixtures, the value of \( T_{cl} \) can be approximated by a weighted average on the mole fractions of the pure species critical temperature values for homogeneous nucleation triggering.

The second condition, i.e. sufficient overheating, is shown in Fig. 3 for an accident involving the heating of a vessel containing a liquefied gas. In the figure, the vapour pressure and the threshold overheating for triggering the homogeneous nucleation are shown. Let’s assume that the liquefied gas in the vessel is characterized by point 1 which lies on the vapour pressure line since the liquid is in equilibrium with its vapour at room temperature, \( T_A \), at a temperature value equal to its vapour pressure at that temperature, \( P^v(T_A) \). In this case, an accidental heating of the vessel can lead the liquid conditions (represented by a point on the vapour pressure line, since vapour-liquid equilibrium conditions prevail inside the vessel) up to point 2. If the vessel collapses under these conditions, the pressure suddenly drops to the atmospheric value, \( P_A \), represented by point 3. Liquid is then in a non-equilibrium condition since its temperature is higher than its normal boiling point, and consequently it will flash. The homogeneous nucleation phenomena cannot be triggered since the liquid overheating is not enough. However, if the vessel collapses when the liquid temperature (and pressure) has reached point 4, the rapid depressurization leads the liquid to point 5, farther than the homogeneous nucleation boundary. In this case, a BLEVE is possible.

\[ \text{Fig. 3. Vapour pressure and critical overheating for homogeneous nucleation lines.} \]
7.2.4 Gas or dust explosions

Gas or dust explosions (note that when the diameter of the particles is small enough, dusts behave like gas) are explosions involving a combustion chemical reaction in the energy release mechanism, such as Unconfined Vapour Cloud Explosions (UVCE) or confined deflagrations inside buildings, pipelines, or process units.

In order for a cloud of vapours to explode, a large amount of flammable vapours must be dispersed into the atmosphere before finding an ignition source. In this case, the vapour cloud can create a significant amount of fuel-air mixture with concentration inside the flammability range. The reason why it is necessary that a significant amount of fuel should be inside the flammability range (making it impossible for small flammable gas releases, say lower than 1,000 kg, apart from very reactive compounds such as hydrogen, acetylene or ethylene oxide to explode, as well as for clouds ignited immediately after the release) can be explained by considering how the flame propagation inside a flammable mixture (in the following, such a flame will also be referred to as a combustion wave) can generate a pressure wave. Such a mechanism is similar again to an accelerating plug. Let us consider the analogy between a pipe filled with a flammable mixture ignited at one end and the plug movement previously discussed, as shown in Fig. 4. When the pipe is open on both the sides, the burned gases (that are at a much higher temperature than the unburned ones and consequently have a much lower density) expand and exit from the pipe end close to the ignition point. The flame (i.e. the combustion wave) propagates inside the still unburned gases with a velocity which is characteristic of this flammable mixture. However, when the pipe is closed at the end near the ignition point, the expanding burned gases cannot exit the pipe from this end and, consequently, they move towards the unburned gases pushing them. The burned gas expansion acts as a plug pushing the unburned gases and generates a pressure wave. A cloud of flammable vapours ignited at the centre acts similarly, with the only difference being that the unburned gas expansion acts as a plug pushing the unburned gases away from the flame front. Flame propagates with a well defined velocity which is characteristic of the flammable mixture in front of the flame are laminar, the flame front velocity compared to the unburned gases not only consequently they push the unburned gases away from the flame front. Flame propagates with a velocity compared to the burned gases, which is always equal to the burning velocity, but since the burned gases move in relation to a fixed observer, the flame front velocity in relation to such an observer is larger than the burning velocity. This velocity is called flame speed. If the fluid dynamic conditions of the flammable mixture in front of the flame are laminar, the velocity of the flame only depends on the physical and chemical characteristics of the flammable mixture and is called laminar flame velocity. The burning velocity, $S_b$, and the laminar flame velocity, $S_f$, are related to each other by the expansion factor, $E$, defined as the ratio of the burned to unburned gas velocities.

When the unburned mixture is motionless, the flame front velocity compared to the unburned gases not only depends on the physical and chemical characteristics of the flammable mixture, but also the composition, ambient pressure and room temperature. Flame front propagation inside a flammable mixture is, in fact, determined by the heat and radical species transport from the high temperature burned gases to the low temperature unburned ones, as shown in Fig. 5. When the flame propagates into a motionless mixture, the mass and heat transport phenomena are determined by the effective transport coefficients (mass and heat diffusivity) according to the Fick and Fourier laws. Consequently, the flame propagates with a well defined speed that is usually of the order of 0.5 m/s for a hydrocarbon-air mixture slightly richer in fuel compared to the stoichiometry. Some of these velocity values, usually referred to as burning velocity, are summarized in Table 3, from which it is evident that the more relevant exceptions to the aforementioned typical value refer to very reactive compounds, such as hydrogen or acetylene. These velocity values, as previously mentioned, are relative to the unburned gases in front of the flame. For motionless gases, such velocity values correspond to the flame front velocity in relation to a fixed observer; this situation is depicted in the diagram of Fig. 4, referring to a pipe with both ends open. In this case, the unburned gases do not move and the flame propagates with a velocity, in relation to an observer united with the pipe, equal to the burning velocity.

When the pipe is closed at one end, or the ignition source is inside the cloud, the burned gases cannot discharge and consequently they push the unburned gases away from the flame front. Flame propagates with a velocity compared to the unburned gases, which is always equal to the burning velocity, but since the unburned gases move in relation to a fixed observer, the flame front velocity in relation to such an observer is larger than the burning velocity. This velocity is called flame speed. If the fluid dynamic conditions of the flammable mixture in front of the flame are laminar, the velocity of the flame only depends on the physical and chemical characteristics of the flammable mixture and is called laminar flame velocity. The burning velocity, $S_b$, and the laminar flame velocity, $S_f$, are related to each other by the expansion factor, $E$, defined as the ratio of the burned to unburned gas velocities.

**Fig. 4.** Combustion wave propagation in a duct ($v_p$ is the velocity of the piston; $v_{pw}$ is the velocity of the pressure wave; $v_{cw}$ is the velocity of the combustion wave).
Fig. 5. Diagram of a flame front propagating in a flammable mixture.

the unburned volume, \( E = V_f/V_1 \), which is roughly equal to 8 for hydrocarbon – air mixtures:

\[ S_f = ES_0 \]

This relation holds true as far as the flammable mixture is initially still, fluid dynamic conditions are laminar, flame surface is regular and burned gases are trapped inside the flame front.

Even in laminar conditions, the velocity of the flame front can be larger than that predicted by the previous

Table 3. Maximum burning velocity, \( S_0 \), and maximum laminar flame velocity, \( S_f \), for some flammable gases

<table>
<thead>
<tr>
<th>FUEL</th>
<th>( S_0 ) (m s(^{-1}))</th>
<th>( S_f ) (m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.58</td>
<td>14.2</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.62</td>
<td>4.9</td>
</tr>
<tr>
<td>Butane</td>
<td>0.50</td>
<td>3.7</td>
</tr>
<tr>
<td>Butene</td>
<td>0.57</td>
<td>4.3</td>
</tr>
<tr>
<td>Ciclohexane</td>
<td>0.52</td>
<td>4.1</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.52</td>
<td>4.0</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.52</td>
<td>4.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.53</td>
<td>4.0</td>
</tr>
<tr>
<td>Ethene</td>
<td>0.83</td>
<td>6.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.50</td>
<td>28.0</td>
</tr>
<tr>
<td>Methane</td>
<td>0.45</td>
<td>3.5</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.52</td>
<td>4.0</td>
</tr>
<tr>
<td>Propane</td>
<td>0.52</td>
<td>4.0</td>
</tr>
<tr>
<td>Propene</td>
<td>0.66</td>
<td>5.1</td>
</tr>
</tbody>
</table>

relation due to the presence of flame wrinkling that increases the flame front surface, generated by both flame front instabilities and by the flame front passing over some obstacles. Since the burned gas production rate is proportional to the flame front area, the flame speed increases and can be evaluated as:

\[ S_f = ES_0 \frac{A_f}{A_0} \]

where \( A_f \) is the real flame front area and \( A_0 \) the regular shaped flame front area (e.g, planar or hemispherical).

In turbulent conditions (with reference to unburned gases), the velocity of the flame front not only depends on the physical and chemical characteristics of the flammable mixture, but also on the fluid dynamics that defines the turbulence level of the flammable mixture where the flame propagates. In the case of flames that propagate, thereby pushing the unburned gases in front of them, increasing the unburned gases velocity inevitably leads to an increase in their turbulence level. The presence of obstacles in the unburned flow creates wakes that in turn further increase turbulence. The effect of the unburned turbulent flow is twofold: the larger vortexes induce a flame wrinkling, thus increasing the flame front area and, consequently, leading to a flame velocity increase through the aforementioned mechanism, while the smaller vortexes induce an increase of the mass and heat transport rates from the flame to the unburned gases. The value of the effective heat and mass transfer coefficients (turbulent mass and heat diffusivity) is in fact much larger than the analogous molecular value. This increase of the mass and heat transport rate results in a similar increase of the flame velocity, which in turn leads to a further increase of the unburned gases velocity, their turbulence level and, through a feedback mechanism, a further increase of the flame front acceleration and, finally, the generation of larger pressure waves.

In conclusion, as previously mentioned, in order for a gas or dust explosion to generate significant overpressure, a substantial flame front acceleration is required. For this to happen, on one side there must be some obstacles to increase the unburned turbulence level, and on the other side, the cloud must be large enough so that the mechanisms for flame front acceleration can become effective. If the flame front acceleration becomes really strong, the shock wave generated can heat the unburned gases so much that it ignites them. In this case, the combustion wave, through the accelerating plug mechanism, no longer generates the pressure wave propagating in front of it, but it is the shock wave that ignites the flammable unburned mixture generating the combustion wave. The energy released by the combustion allows the shock wave to sustain itself.

These two phenomena are markedly different. In the first case (combustion wave that generates the pressure wave), the two waves (the pressure and the combustion one) are separated and the combustion wave velocity is subsonic (of the order of some m/s) compared to the unburned gas conditions in front of the flame. The overpressure values across the pressure wave are quite small (lower than a few bar, 1 bar being the maximum for UVCE), and pressure and density reduces through the combustion wave. This phenomenon is called deflagration and the related phenomenology is illustrated in Fig. 6. Also the pressure peak shape experienced by a target at a given distance from the
vapour cloud centre is different from that previously discussed for ideal explosions and illustrated in fig. 2. In particular, the pressure gradient is less sharp, as shown in Fig. 7.

In the second case (pressure wave that generates the combustion wave), the two waves (the pressure and the combustion one) are coupled and their velocity is supersonic (in the order of some thousands of m/s) compared to the unburned gas conditions in front of the flame. The overpressure values across the pressure wave are quite high (a few tens of bar), and pressure and density increase through the coupled pressure and combustion wave. This phenomenon is called detonation and the related phenomenology is illustrated in Fig. 8. Detonations of vapour clouds are not common and they require, for common fuels, the ignition by a detonator, i.e. by the blast wave generated by a condensed phase explosion.

The difference between the two phenomena (deflagration and detonation) will be discussed further below. It is interesting to note that the existence of two different kinds of combustion wave can be easily deduced from the mass and energy balance equations across a combustion wave using a reference system united with the flame front, as shown in figure Fig. 9. Here, a one dimensional flat combustion wave moving through a constant section duct is illustrated. With reference to a coordinate system united with the duct, the combustion wave moves towards the right (that is, into the still unburned gases) at a constant velocity equal to \( u_1 \); whereas in the case of a reference system united with the flame front itself is still and the unburned gases move towards it with a velocity equal to \( u_2 \). Using such a reference system and labelling it with the subscript:

\[
P_2 - P_1 = \left(\frac{\alpha_1 u_1}{1 - \frac{\alpha_1}{\alpha_2}}\right)^2 \alpha_2 \alpha_1 > 0
\]

From relation [7] (usually referred to as the Rayleigh line, since it represents the equation of a straight line on the plane \( P_2 vs. 1/\alpha_2 \), as will be discussed in section 7.2.5), the following inequality can be deduced:

\[
\frac{P_2 - P_1}{u_2 - u_1} = \left(\frac{\alpha_1 u_1}{1 - \frac{\alpha_1}{\alpha_2}}\right)^2 \alpha_2 \alpha_1 > 0
\]

from which we can see that pressure and density change in the same direction through the flame front. From relation [8], it follows that when the pressure increases, velocity decreases. A first kind of combustion wave is thus characterized by an increase of both pressure and density through the flame front: these compression waves are called detonations. In this case, the burned gas velocity in relation to the flame front is lower than the unburned gases. The second kind of combustion wave is characterized by a decrease of both pressure and density through the flame front: these are expansion waves called deflagrations. The burned gas velocity in relation to the flame front, in this case, is larger than the unburned gases. As previously discussed, in the case of detonations, combustion and shock waves are coupled, and through them pressure increases. In the case of deflagrations, the two waves (combustion and shock waves) are uncoupled: pressure increases through the shock wave, whereas it decreases.
through the combustion wave. The pressure decrease through the flame front is usually very small: the ratio of the burned to unburned gas pressure for hydrocarbons-air mixtures is usually close to 0.98.

Transition from deflagration to detonation (DDT, Deflagration to Detonation Transition) requires a very high acceleration of the flame front that is not usually reached in free field explosions (UVCE). On the other hand, this phenomenon can arise in duct explosions, due to the large turbulence generated by the unburned flow in ducts.

The mechanism leading to the pressure rise when a flammable gas or dust mixture is ignited in a confined environment is completely different from that previously discussed for unconfined explosions. For unconfined explosions, the combustion proceeds at almost constant pressure. Due to the higher temperature of the burned gases compared to the unburned ones (about 8 times higher for stoichiometric hydrocarbon-air mixtures), the burned gas volume increases (about 8 times for stoichiometric hydrocarbon-air mixtures, from the ideal gas law) and a pressure wave can be generated through the accelerating plug mechanism.

When the deflagration is completely confined, the combustion proceeds at constant volume and the temperature increase inevitably results in a pressure increase (about 8 times for stoichiometric hydrocarbon-air mixtures, from the ideal gas law). In this case, the characteristic time of the phenomenon (i.e. the flame front velocity) does not play any role in the maximum pressure value, which is determined by the constant volume constraint.

If the plant unit where deflagration occurs is not fitted with emergency release systems (explosion panels or rupture disks), the pressure increase can lead to the collapse of the unit with consequences similar to those previously discussed. On the contrary, if the explosion panels are correctly designed and the unit is designed to sustain the deflagration, the unit will not collapse and the burned and unburned gases will be discharged through the explosion panels. Obviously, rupture disks or explosion panels are effective (when correctly designed) only for protecting an apparatus from deflagrations since in a detonation the shock wave travels at supersonic speed; it consequently reaches the vessel walls before the information that pressure in the vessel is increasing, which propagates at the speed of sound, can reach the emergency system.

### 7.2.5 Hugoniot relation

The mass [5] and momentum [6] balance equations can be complemented by the steady state energy balance equation (referring to the reference system illustrated in Fig. 9):

\[ C_r T_r + \frac{1}{2} u_r^2 = C_r T_1 + \frac{1}{2} u_1^2 + q \]

and by an equation of state for the burned gases, that for ideal gas is

\[ P = \rho RT/M \]

where \( \rho \) is the molar density. In these relations, \( M \) is the molecular weight, \( C_r \) is the specific heat at constant pressure, while \( q \) is the massive enthalpy difference between unburned and burned gases, i.e. the heat released. If the thermodynamic conditions of the unburned gases \( (T_1, P_1, \rho_1) \) are known, the unknown variables involved in the four equations [5], [6], [10] and [11] are the burned gas state variables \( (T_2, P_2, \rho_2) \) and the burned and unburned gas velocity in relation to the combustion wave \( (u_1, u_2) \). In total, there are 5 unknown variables in 4 equations and the system cannot be solved without giving the value of one unknown.

The four equations in five unknown ones can be recast in one equation with two unknown ones, \( P_2 \) and \( \rho_2 \), with the Rankine-Hugoniot relation:

\[ \frac{P_2}{\rho_2} = \frac{P_1}{\rho_1} - \frac{1}{2} \left( \frac{P_2 - P_1}{\rho_2 - \rho_1} \right) \frac{1}{\rho_2} = \frac{1}{\rho_1} \]

The curve representing this relation for a given value of \( q \) on a \( P_2 \) vs. \( 1/\rho_2 \) diagram (or, since the values of \( P_1 \) and \( \rho_1 \) are given, on a \( P_2/P_1 \) vs. \( q/\rho_2 \) diagram) is called the Hugoniot curve and is shown in Fig. 10.

In this figure, two curves are shown: the first one for \( q=0 \) refers to adiabatic shock waves (Rankine-Hugoniot curve), while the second one for \( q \neq 0 \) belongs to a family characterized by different \( q \) values (Hugoniot curves) Hugoniot curves are the locus of all the possible values of \( P_2 \) and \( 1/\rho_2 \) for given values of \( P_1 \) and \( 1/\rho_1 \) and a given value of \( q \). The point \( (P_1, 1/\rho_1) \), characteristic of unburned gases, is usually called the origin of the Hugoniot diagram and it is indicated in the figure with the symbol \( O \). From this point, all the Rayleigh lines [7] pass, which represent a condition that must be fulfilled by the burned gases state variables. The burned gases state will consequently be represented by the crossing of one Hugoniot curve with one Rayleigh line. The figure shows two Rayleigh lines that are tangent to the Hugoniot curve shown on the diagram. The two tangent points are usually called the Chapman-Jouquet (C-J) points, upper (labelled U in the figure) and lower (labelled L in the figure) for that tangent to the upper or the lower branch of the Hugoniot curve. The intersections of the Hugoniot curve with the horizontal and vertical straight lines through the origin identify two other important points, labelled X and Y in the figure. These four points identify five significant regions on the Hugoniot curve, labelled in the figure with the Roman numbers from I to V. In the following, only some properties of the different branches of Hugoniot curves (of some practical relevance) will be discussed; more mathematical details can be found in the relevant literature.

The Hugoniot curve represents all the possible solutions of the Hugoniot relation; however, not all of these solutions have a physical meaning. In fact, on the V branch it is required that \( P_2 \geq P_1 \) and \( 1/\rho_2 \geq 1/\rho_1 \), which violates the constraint enforced by the Rayleigh line [7]. This region represents solutions without any physical meaning. Branches I and II represent compression waves where \( P_2 \geq P_1 \); these are detonation waves. Branches III and IV represent expansion waves where \( P_2 \leq P_1 \); these are deflagration waves. It can be proved that in both the C-J points, the Mach number (defined as the ratio of the velocity and the sound velocity) in the burned gas conditions is equal to one, \( M_2 = 1 \), i.e. the burned gas velocity compared to the combustion wave is equal to the sound speed in the burned gas conditions, \( u_2 = c_2 \). Combining relations [7] and [8] results in:

\[ \frac{u_2 - u_1}{1/\rho_2 - 1/\rho_1} = \rho_2 u_1 \]

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Since $1/v_{c2}<1/v_{c1}$ on branches I and II, related to detonations, it follows that $u_c<u_i$. In a reference system united with the duct where the detonation wave propagates (shown in Fig. 11 for the same combustion wave in Fig. 9, where the positive directions for velocities are also indicated), the unburned still gas velocity is equal to zero, while that of the burned gases is equal to $v_2=v_{pp}-u_i$, where $v_{pp}=u_i$ is the detonation wave velocity compared to a reference system united with the duct. From these relations it follows that $v_2=v_{pp}-u_i-u_{c2}>0$; this means that the burned gases behind the detonation wave move in the same direction as the detonation wave. Depending on the value of $v_2$ compared to $v_{pp}$, the burned gases may or may not reach the detonation wave.

At the C-J point $u_c=c_2$, and therefore

$$v_{pp}=u_i+v_2=c_1+v_2>c_2$$

the detonation wave at this point travels at supersonic velocity. Moreover, although the burned gases travel in the same direction as the detonation wave, they cannot reach it since $v_{pp}>v_2$.

Branch I is called the strong detonations branch where pressure and density are higher than in the C-J point. Passing through the detonation wave, the gas velocity compared to the detonation wave decreases drastically from supersonic values to subsonic ones (it can be proved that $M_2<1$). In practice, it is quite difficult to generate a strong detonation wave even in controlled laboratory conditions and, consequently, this branch is of no significant practical interest.

Branch II is the weak detonation one where pressure and density of the burned gases are lower than that of the C-J point. Passing through the detonation wave, the gas velocity compared to the detonation wave decreases but still remains supersonic (it can be proved that $M_2>1$). In practice, it is quite difficult to generate a weak detonation wave since it requires very reactive gases and, consequently, this branch is of limited practical interest.

Point X, which is characteristic of constant volume detonations ($1/Q_2=1/Q_1$), would require a detonation wave velocity (with respect to a fixed reference system) equal to infinity, as deduced from the Rayleigh line together with the previous relations. Since such a velocity cannot be achieved, point X also represents a meaningless physical system state.

In conclusion, most of the detonation waves lie on the C-J point, while branches I and II represent meaningless regions from a practical point of view. This allows the value $u_c=c_2$ to be assigned to one of the five variables of the problem. The system of 4 equations [5], [6], [10] and [11] can therefore be solved giving the values of the 4 variables: $T_2, P_2, Q_2$ and $u_1$. It should be stressed that in this case, the problem can be solved without any information on the chemical reaction rates that transform, in the flame front following the detonation wave, unburned gases into burned ones providing the energy required by the detonation wave to be sustained. This is a consequence of the supersonic speed of the detonation wave, which cannot obtain information from the flame front that follows it.

Branch IV is known as strong deflagration. While passing through the deflagration wave, the unburned gas velocity compared to the deflagration wave must drastically accelerate from subsonic to supersonic values (it can be proved that $M_2>1$). It can also be proved that this is not possible in constant section ducts, and therefore a strong deflagration wave (including the C-J point) has never been observed in practice.

Branch III is known as weak deflagration. In this region, $P_1>P_2>P_1$ and $1/Q_2<1/Q_1$. The burned gas velocity compared to the deflagration wave increases, $u_c>u_i$, but it is still subsonic. In this case, using a reference system united with the duct and following the same procedure used for the detonation waves, seeing as the unburned gases are motionless and the velocity of the deflagration wave is equal to $v_{pp}=u_i$, it can be proved that $v_2=v_{pp}-u_i-u_{c2}<0$; this means that the burned gases behind the deflagration wave move in the

![Fig. 10. Rankine-Hugoniot diagram.](image)
opposite direction compared to the deflagration wave itself, which is another important difference between deflagration and detonation waves. Deflagration waves lying in region III are often observed in practice. However, in this case, there is no condition like the C-J one for deflagration waves that allows the last degree of freedom in equations [5], [6], [10] and [11] to be saturated and therefore to solve the problem without providing any information on the flame front. The solution to the problem (or, in other words, the definition of the slope of the Rayleigh line for a given system) requires a detailed description of the flame front, which is the goal of several models developed for predicting the burning velocity. A thorough discussion of such models is outside the aim of this topic and can be found in the dedicated literature.

Point Y, which is characteristic of the constant pressure deflagrations \((P_1 = P_2)\), requires a nil deflagration wave velocity (compared to a fixed reference system), as deducible from the Rayleigh line together with the previous relations, and it is consequently meaningless from a practical point of view.

### 7.2.6 Estimation of overpressure caused by an explosion

An explosion can be in a steady state or not; a steady state (or self-sustained) explosion requires the deflagration or detonation wave to travel inside a flammable mixture, whose combustion is able to sustain the combustion wave motion making the phenomenon stationary. When the combustion wave reaches the flammable mixture boundary, the combustion wave propagates in the atmosphere and gradually dissipates the energy. Similarly, the shock wave generated by the point release of a given amount of energy is transitory, and the overpressure generated decreases by increasing the distance from the energy source point. It is therefore important to know the shock wave velocity (and thus its location after a given time) as well as how the overpressure gradually decreases as the shock wave moves away from the epicentre.

Rankine-Hugoniot relations [7], [8] and [10], together with some relations for the ideal gas as well as the mass balance [5], can be shown in the following equivalent relations:

\[
\frac{\rho_1}{\rho_2} = \frac{u_1}{u_2} = \frac{\gamma - 1}{\gamma + 1} + \frac{2}{\gamma + 1} \frac{M_1^2}{P_1}
\]

\[
\frac{P_1}{P_2} = \frac{2\gamma M_1^2}{\gamma + 1} \frac{\gamma - 1}{\gamma + 1}
\]

These relations show how the shock wave intensity (i.e. the value of the shock wave overpressure, \(P_s\)) increases with \(M_1\), i.e. with the shock wave velocity. In the limit condition for which \(M_1 \to 1\), we obtain \(P_s \to P_1\), i.e. the pressure wave vanishes. In the limit condition for which \(M_1 \to 1\) (and consequently the shock wave overpressure is much higher than the atmospheric value), the following approximate relations can be deduced:

\[
\frac{\rho_1}{\rho_2} = \frac{u_1}{u_2} = \frac{\gamma - 1}{\gamma + 1}
\]

\[
\frac{P_1}{P_2} = \frac{2\gamma M_1^2}{\gamma + 1}
\]

from which we can see that for supersonic shock waves, the ratio of the densities before and after the shock wave is of the order of unity, while that of the pressure values is much larger than unity.

Through order of magnitude considerations on the various energy terms, it is possible to derive an important relation between the energy released by an ideal explosion, \(q\), and the distance, \(R(t)\), where the shock wave generated by such a release of energy arrives after a given time \(t\). In the following relations, the superscript “ means shock wave conditions, subscript 1 means still atmosphere in front of the shock wave, and subscript 2, gas behind the shock wave.

After a given time \(t\), the energy released by the explosion will be of the same order of magnitude of the energy of the shock wave computed as internal and kinetic energy of the gases behind the shock wave. In other words, the explosion energy is used to heat and to move the still atmosphere through which the shock wave propagates. The volume behind the shock wave is of the order of \(V \approx R^3\), and therefore the mass of gas behind the shock wave (which has been heated and moved by the shock wave itself) is of the order of \(m = qR^3\). The fluid velocity behind the shock wave is of the same order of magnitude as the radial velocity of the shock wave, that is of the order of \(v = \frac{dR}{dt} \approx R^2/t\) and consequently the kinetic energy \(E_k\) of the moving gas is of the order of \(E_k = mV^2 = qR^5/t^2\). The specific internal energy \(e_i\) of an ideal gas is of the order of \(e_i = \frac{C_v}{R} = \frac{C_v}{\gamma - 1} (\gamma - 1) = C_v/\gamma\) and therefore the internal energy per unit volume of the gases behind the shock wave, also using relation [17] and the equation giving the sound speed for an ideal gas, is of the order of \(\frac{\rho_2 e_{i2}}{\rho_2} = P_2 = \rho_2 \gamma \frac{C_v}{\rho_2} = \rho_2 \gamma \frac{C_v}{\rho_2} \left(\frac{dR}{dt}\right)^2 = qR^5/t^2\). The internal energy \(E_u\) behind the shock wave is therefore of the order of \(E_u = qR^5/t^2\), which is of the same order of magnitude as the kinetic energy. The explosion energy must be of the same order of magnitude, that is

\[
q = qR^5/t^2
\]

and therefore

\[
q = k_0 R^5/t^2
\]

where \(k\) is a constant of unity order. This means that after a given time \(t\) the shock wave has reached a distance equal to

\[
R = \left(\frac{q}{k_0 t}\right)^{1/5}
\]

This relation provides two items of information: how the variables change behind the shock wave and a functional relation between the distance travelled by the shock wave, the overpressure and the explosion energy. The first item of information (known as the Sedov-Taylor solution of the shock wave) can be obtained by solving the details of the flow field behind the shock wave; this can be done by solving the partial differential equations of the radial fluid flow, which are made up of the continuity equation, the Euler equation in spherical coordinates and the energy conservation equation for an adiabatic flow, that is \(P\gamma = \text{cost}\) (assuming that the wave motion has a spherical symmetry and that the atmosphere behaves like an ideal gas with \(\gamma = \text{cost}\)). These equations can be integrated once the boundary conditions are known, which is not a trivial task for explosion problems. However, it is possible to assume
that after a given time, all the details concerning the energy release, provided it can generate a shock wave, become irrelevant. This implies that the shape of the pressure, density and velocity profiles does not depend on time, and the solution of the previous equation system is self-similar. From a mathematical point of view, this means that the pressure, density and velocity trends behind the shock wave can be computed as a characteristic value (e.g. that on the shock wave) times a universal function of a dimensionless coordinate $z = r/R(t)$. In order to compute the variable profiles behind the shock wave, further information is required: the shock wave position as a function of time, $R(t)$. More precisely, knowing the functional behaviour given by equation [19], $R = R(t)$, suffices. The differential equations system that derives from it is very complex, but can be integrated analytically.

From a practical point of view, the second item of information that can be deduced from relation [19] is more important, i.e. the functional relation between the distance travelled by the shock wave, the overpressure and the explosion energy. Inserting the time relation that derives from $P_2 = qR_2(t)$ into equation [19], it follows:

\[
R^0 = \left(\frac{q}{k_0}\right)^{1/3} R^0(\frac{q}{P_2})^{2/3} \text{ that is } R^{03}P = \text{constant}
\]

or, in other words,

\[
\ln R^0 = -3\ln \left(\frac{R^0}{q^{1/3}}\right) + \text{constant}
\]

where the more common symbol $R^0$ has been used to indicate the overpressure $P_1$ on the shock wave. This relation shows how the pressure values at a given distance from the detonation of a given amount of condensed explosive must lie on a straight line on a log-log plot that shows overpressure vs. the ratio $R^0q^{-1}$. $R^0$ being the distance from the epicentre and $q$ the amount of energy released by the explosion (or, equivalently, the mass of explosive). This justifies the Hopkinson-Cranz scaling rule used to extrapolate experimental measurements concerning condensed phase explosion to larger scales. This scaling law states that the explosion of different amounts of the same explosive, the same geometry and in the same atmosphere will produce shock waves that are similar in the same scaled distance. By similar shock waves, we mean two shock waves with the same overpressure but with an impulse scaled through a suitable factor. The most used scaling factor is that proposed by Sachs, stating that the overpressure scaled by the ambient pressure, $P = P_1/P$, and the dimensionless impulse as, $I = I_q = R^0P^{-1/3}$, are a universal function of the scaled distance. $R = R^0P^{-1/3}(q^{1/3})$. As far as the overpressure vs. distance trend is concerned, this scaling law follows the qualitative behaviour predicted by equation [21].

Changes in atmospheric pressure values (and, consequently, also in the sound speed in the atmosphere, $c_0$) are of minor relevance; thus, simpler relations are often used in practice to scale impulse and distance in which only the dependence on the amount of energy released appears, such as $I = I_q/q^{1/3}$ and $R = R^0q^{1/3}$.

Experimental data referring to overpressure generated by condensed phase explosions lie in a straight line on a log-log plot as required by this scaling law, as shown in Fig. 12 for TNT. For a given explosive, it obviously does not matter if the amount of energy released, $q$, or the amount of explosive, $W$ are used in the scaling laws, since these two values are proportional through the decomposition energy, which is equal to 4,437-4,765 kJ/kg for TNT.

**Explosion effects from condensed phase explosions**

These explosions are very similar to ideal explosions. A simple and effective method to foresee the effects of this kind of explosion assumes that different condensed phase explosions releasing the same amount of energy will produce similar effects. This allows the explosion of an equivalent amount of any condensed phase explosive to be converted, from the standpoint of released energy, into TNT with the simple relation:

\[ W_{\text{TNT}} = W_{\text{compound}} \frac{\Delta h_{\text{compound}}}{\Delta h_{\text{TNT}}} \]

Therefore, the equivalence ratio between the amount of TNT and a given compound, $\alpha$, is simply given by the ratio between the decomposition enthalpies of the two compounds:

\[ \alpha = \frac{W_{\text{TNT}}}{W_{\text{compound}}} = \frac{\Delta h_{\text{compound}}}{\Delta h_{\text{TNT}}} \]

The expected consequences can be estimated using the equivalent amount of TNT together with the information shown in the diagrams of Fig. 12.

The main uncertainty factor regarding the decomposition of unstable compounds accidentally accumulated in a process plant is the estimation of the amount of unstable compound that participates in the shock wave formation: the total amount present does not always decompose so quickly as to fully contribute to the explosion.

**Explosion effects from unconfined vapour cloud explosions (UVCE)**

Estimating the overpressure generated by a UVCE requires the knowledge of some key parameters; among them, the mass of flammable gas involved in the explosion and the ignition point. To estimate the mass of flammable gas involved in the explosion, atmospheric dispersion models can be used which give the amount of flammable gas in the cloud with concentration inside the flammability range. A short cut method assumes that about 10% of the mass released lies in the flammable region; the effect of such an approximation is obviously quite different depending on the meteorological and release conditions. On the other hand, although the influence of the ignition point can be relevant, it is not usually considered in the simulation models since it is practically unpredictable.

**TNT equivalent model.** This method approximates the gas cloud deflagration effects to those of an ideal TNT detonation. As previously discussed, the two phenomena are markedly different. On the other hand, how to estimate the effects of the detonation of a given amount of TNT is well known and supported by much experimental evidence; consequently, the use of this simple approach as a first approximation is quite common.

The application of this method to UVCE requires the evaluation of the amount of TNT which is equivalent, from the amount of energy released standpoint, to the mass of gas
in the cloud. This estimate can be made with a relation similar to equation [23]:

$$\alpha = \frac{W_{\text{TNT}}}{W_{\text{gas}}} \frac{\Delta h_{\text{gas}}}{\Delta h_{\text{TNT}}} \varepsilon$$

In this case, the equivalence ratio between the amount of TNT and flammable gas, $\alpha$, is no longer equal but simply proportional, through the parameter $\varepsilon$ (i.e. an explosion efficiency), to the ratio of the gas combustion enthalpy to the TNT decomposition enthalpy. The ratio between the energy released by burning 1 kg of flammable gas and that released by the decomposition of 1 kg of TNT is equal to about 10 for many hydrocarbons.

The uncertainties related to the use of this method are not so much linked to the amount of flammable gas in the cloud, but mainly to the estimation of the parameter $\varepsilon$: this summarizes all the differences between an ideal TNT and UVCE explosion, and can only be estimated by analyzing the consequences of past real accidents. For such accidents, the amount of gas inside the flammability range when the cloud was ignited is not usually known, and consequently the explosion efficiency is usually estimated based on the whole mass of gas released. Unfortunately, the efficiency value is affected by many parameters which are characteristic of the single accident (meteorological or release conditions, etc.), resulting in a wide variability of the explosion efficiency. This is shown in Fig. 13 which gives the values of the equivalence ratio, $\alpha$, estimated assuming an explosion ratio equal to 10.

It should be noted that the central value of the distribution is equal to about 0.3 (an explosion efficiency equal to $\varepsilon=0.03$), even if some higher values have occasionally been recorded. However, 97% of the data show a value lower than 1. Instead of considering the whole mass of gas released, let's look at an atmospheric dispersion computation carried out to estimate the real amount of gas inside the flammability range. From such an amount, you can obtain an equivalent amount of TNT multiplying it by 3 instead of 0.3 on the basis of the rough assumption that about 10% of the gas released is inside the flammability range.

This method cannot be used close to the centre of the explosive cloud since it would result in unrealistic high overpressure values. A common modification limits the maximum overpressure value for a UVCE to 1 bar and consequently modifies the TNT curve as shown in Fig. 14, where the amount of explosive refers to the gas released. Assuming there is an explosion efficiency equal to 10% and a ratio between the gas and TNT enthalpies equal to 10, the amount of gas released and equivalent TNT are obviously the same (in other words, the equivalence factor, $\alpha$, is equal to 1); whereas if there is a lower efficiency (say 3%, as shown in the figure), the curve will be moved to the left.

**Wiekema model.** This method assumes that the unconfined vapour cloud deflagration is similar to an expanding hemispherical plug moving at a given average velocity which is defined, with reference to Fig. 13, as the ratio of the burned gas cloud radius to the deflagration time. High average deflagration velocities characterize high reactive compounds or compounds whose flame velocity is very sensitive to turbulence induced accelerations (for instance, ethylene oxide), while the opposite is true for low values of the average deflagration velocity (for instance, methane).

Solving the mathematical model simulating an accelerating hemispherical plug with different average velocities, various correlations (one for each average velocity) can be obtained between the relative dimensionless overpressure (compared to the atmospheric value, $[P/P_a] - 1$) and the dimensionless ratio of the distance to the cubic root of energy in the cloud, $R/L_0 = R/V_{I} \Delta h_{C}/P_{I}$. In this relation, $V_{I}$ is the gas volume which is initially inside the flammability range, while $\Delta h_{C} = 3.5 \times 10^{6} \text{ J/m}^3$ is an average value of the energy released by the combustion of one cubic metre of a stoichiometric hydrocarbon-air mixture.

According to the previous discussion concerning ideal explosions, Fig. 15 gives an almost linear behaviour on a log-log plot of the overpressure vs. the ratio of the distance to the cubic root of the explosion energy, which is represented by $V_{I} \Delta h_{C}$.
This method gives four curves delimiting three ranges, each of which is characteristic of a given range of average deflagration velocity. The main novelty introduced by this method compared to the equivalent TNT one is the classification of several flammable compounds as a function of their reactivity and tendency to accelerate their flame front into three reactivity categories: low, medium, and high. This method associates a range of overpressure as a function of the distance (in Fig. 15) with each reactivity class.

In other words, this method recognizes that the energy of the cloud is not the only relevant parameter that defines the overpressure generated by a UVCE, since the flame front acceleration is the real mechanism able to generate a shock wave. From a different point of view, this method solves the problem beforehand of choosing the explosion efficiency in the equivalent TNT method, which is the parameter that summarizes all the differences between a TNT detonation and a gas cloud deflagration. More precisely, it reduces the variability range of such a parameter. The method actually gives a range of overpressure for a given distance for each reactivity class, and thus for each flammable compound. The width of such a range represents the influence of the presence of some obstacles, and consequently of the turbulence induced acceleration of the flame front, on the overpressure value. The lower value refers to deflagrations in a low congested area, while the upper one to deflagrations in high congested regions. This results in a value of the ratio between the distances estimated with the upper and lower limits equal to about 2-3. Such an uncertainty is quite similar to that found in the choice of the efficiency value with the equivalent TNT method. A classification of some compounds as a function of their reactivity for this method is summarized in Table 4.

Multi-Energy model. This method further develops the idea of the Wiekeima method for which a flammable gas cloud can result in a UVCE only when it is ignited in a sufficiently congested area so that the flame front velocity can significantly increase. As a consequence, not only doesn’t all the released gas participate in the explosion, but neither does all the gas inside the flammability range. Only the flammable mixture inside congested areas (or in high turbulence regions, such as those close to high velocity releases of a flammable gas) contributes to a UVCE. The strength of the explosion depends on the kind of gas as well as the degree of congestion of the area. It follows that the
gas cloud usually results in more than one explosion, located in the various congested area of the plant, whose effects must be considered separately.

The effect of various explosions can be estimated through a similar approach to Wiekeema, using 10 different average deflagration velocities, as shown in Fig. 16. The full lines refer to detonations, whereas the dashed lines refer to deflagrations. The parameter values on both the axes are dimensionless as in the previous Wiekeema method.

Although this approach tries to represent the UVCE phenomena more precisely, it also requires an arbitrary choice of some parameters that have, in the final analysis, the same physical meaning as the explosion efficiency in the equivalent TNT method. In particular, it is necessary to define which regions of a plant should be considered congested or not, at which distance two congested areas generate two separate explosions (25 m is a common but arbitrary suggestion) and finally the explosion class, ranging from 1 to 10.

While the identification of the congested area can be intuitive, the choice of the explosion class is more problematic. The value of 10 gives results similar to the equivalent TNT method (obviously limited to the gas present in a given congested region) with an equivalence factor equal to 20% (which is close to the 30% value referred to the mass of gas inside the flammable region previously discussed for the equivalent TNT method). The value equal to 7 seems to be reasonable for many practical situations; values of 6 and 7 provide similar results if the overpressure is lower than 0.1 bar and the maximum pressure is equal to 1 bar. For non congested areas and a still atmosphere, a value equal to 1 seems adequate, whereas for non congested areas and a moving atmosphere, a value equal to 3 may be more adequate.

**CFD models.** The availability of more powerful computers as well as more efficient numerical methods enables us to deal with the problem of solving the Navier-Stokes equations for turbulent flows in complex geometries within the context of CFD (Computational Fluid Dynamics).

Theoretically, these models could be considered really predictive since they solve the local balance equations of mass, momentum and energy with suitable boundary conditions defining the problem to be solved. On the other hand, the main problem of CFD models (apart from the large amount of resources required, both in terms of operator experience and CPU performance, which limits the application of this approach to relatively simple problems) is the representation of the interaction between turbulence and combustion chemical reactions. This is an important research field where no consolidated and general results have been obtained yet. The various approaches developed are often limited to a single kind of problem and the predictions’ reliability of this approach needs to be assessed by comparing it with experimental data. An agreement with a given set of experimental data is often obtained by introducing one or more adjustable parameters, whose value is defined by the experimental data in consideration. This makes the model no longer completely predictive and limits its use to semi-quantitatively predicting the influence of the change in some parameters (such as the geometric ones) on the overpressure generated by the explosion.

### Table 4. Classification of some compounds according to the Wiekema method

<table>
<thead>
<tr>
<th>Reactivity</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>ammonia, 1,3-dichloropropene, epichlorhydrine, methane, carbon monoxide, tetra ethyl lead</td>
</tr>
<tr>
<td>Medium</td>
<td>acetaldehyde, acetonitrile, formic acid, acrylonitrile, 1,3-butadiene, n-butane, 1-butene, vinylchloride, diethylamine, dimethylamine, ethane, ethene, propane, propene</td>
</tr>
<tr>
<td>High</td>
<td>ethylene oxide, acetylene</td>
</tr>
</tbody>
</table>

**Physical explosion effects**

As previously discussed, this definition summarizes all the explosions generated by the rapid expansion of a liquid or vapour compound without involving any chemical reaction in the formation of the shock wave, such as the combustion reactions involved in UVCE. A chemical reaction could be involved during a vessel pressurization, such as in the case of a confined deflagration able to increase the internal pressure up to vessel failure. Typically, physical explosions follow a vessel collapse, with the consequent release into the atmosphere of both mass and internal energy previously contained in the vessel. The difference between the internal energy of the compound in the vessel and in the atmosphere represents the maximum energy amount available for generating the explosion.

The shock wave is generated by the partial transformation of the internal fluid energy into mechanical energy. The fluid internal energy available for the formation of a shock wave depends on the thermodynamic state of the fluid, which in turn depends on the kind of fluid and on the bursting conditions. The estimation of the internal energy of the fluid when the vessel collapses can be done in different ways depending on the assumed scenario: ideal or real gas expansion, liquid evaporation (flash or BLEVE), confined deflagration, etc.

As previously discussed for UVCE, the more common methods are variations of the equivalent TNT method. Also in this case, the predictions are less accurate in the region close to the vessel (up to about 10-20 vessel diameters), whereas they are reasonable at larger distances.

The use of the equivalent TNT method (or other similar methods, providing some corrections for the region near the vessel) requires an estimation of the
energy used for generating the explosion. Not all the available energy can be used for generating the shock wave: part of it is transformed into fragment kinetic energy, that can be thrown at large distances; part of it can be used to strain the vessel before failure; and part of it is dissipated.

The last part of the internal energy can be used to expand the fluid and, consequently, to form a shock wave whose characteristics depend on the expansion velocity: the larger the phenomenon velocity, the more similar the characteristics of the generated shock wave are to those of an ideal explosion. It is difficult to quantify the amount of energy used to generate the shock wave. Brittle fractures of a vessel give larger values than ductile ones. A conservative approach (reasonable since the overpressure values generated by a vessel collapse are not usually so large as to produce disastrous effects at large distances) needs to consider that all the available energy is used to generate the shock wave.

If the vessel content can be assimilated to an ideal gas, the difference of internal energy between the initial state before vessel collapse and the final one at ambient conditions can be computed as:

\[ q = \frac{(P_0 - P_f)V_f}{\gamma_0 - 1} \]

where the subscript 0 refers to the initial conditions in the vessel before failure, \( P_f \) is the ambient pressure, \( V \) the volume and \( \gamma \) the specific heats ratio.

When the vessel also contains some liquid, flash or BLEVE possibility should be checked by comparing room temperature value with the normal boiling point and the critical temperature for homogeneous nucleation. If the liquid cannot flash, there is only some vapour expansion. If it can produce a BLEVE, the expansion of the evaporated liquid also contributes to the shock wave, whereas if it flashes, the expansion of the evaporated liquid can contribute (not necessarily) to the shock wave. In this case, a conservative approach is to also consider the evaporated liquid for computing the available energy.

In all the cases, the internal energy change can be computed using a thermodynamic state diagram for the fluid being tested or performing an adiabatic flash computation. From a state diagram, the values of the specific enthalpy, \( h \), and specific volume, \( \nu \), at the bursting vessel temperature and pressure are readily available. Following an isentropic line, the same diagram gives the values of these variables at ambient pressure. The specific internal energy in the two states can then be computed as \( e_q = h - P \nu \). When the final state involves a mixture of saturated liquid and vapour, the specific state variables can be computed as

\[ m = \frac{1}{1 - x} m_l + x m_v. \]

In this relation, \( m \) is a specific variable, \( L \) and \( V \) refer to saturated liquid and vapour, respectively, while \( x \) is the vapour quality, which is usually provided by the same state diagram.

**Bibliography**


**References**


**List of symbols**

- \( A_0 \) — smooth surface area of the flame front
- \( A_f \) — real surface area of the flame front
- \( a_i \) — \( i \)-th species activity
- \( c \) — sound speed
- \( C_p \) — constant pressure specific heat
- \( E \) — expansion factor
- \( e_u \) — specific internal energy
- \( h \) — specific enthalpy
- \( I \) — scaled impulse
\( i_p \) positive impulse
\( K \) equilibrium constant
\( m \) variable
\( M \) Mach number
\( M \) molecular weight
\( n \) number of atoms
\( n \) parameter defining the symmetry
\( p \) pressure
\( p^o \) maximum overpressure
\( P_c \) critical pressure
\( P_r \) reduced pressure
\( P_v \) vapour pressure
\( q \) combustion heat
\( r \) spatial coordinate
\( R \) ideal gas constant
\( R \) distance
\( R \) scaled distance
\( R_j \) distance travelled by the shock wave at time \( t_j \)
\( S_0 \) burning velocity
\( S_f \) flame velocity
\( T \) thermodynamic temperature
\( t \) time
\( t_A \) shock wave arrival time
\( T_C \) critical temperature
\( t_D \) positive impulse duration
\( T_{SL} \) critical temperature for triggering the homogeneous nucleation
\( u \) velocity in relation to the flame front
\( v \) velocity in relation to a fixed observer
\( V \) volume
\( v \) specific volume
\( W \) amount of explosive
\( x \) vapour quality

**Greek letters**

\( \alpha \) decay parameter
\( \alpha \) equivalence ratio of the amount of explosive to that of TNT
\( \gamma \) ratio of specific heats at constant pressure and volume
\( \Delta G^\circ \) free Gibbs energy change of reaction
\( \Delta h_c \) combustion enthalpy
\( \Delta h_d \) decomposition enthalpy
\( \epsilon \) explosion efficiency
\( \nu_i \) stoichiometric coefficient of species \( i \)
\( \xi \) dimensionless coordinate
\( \rho \) density

**Superscripts**

\( o \) of the shock wave

**Subscripts**

1 unburned gases or atmosphere in front of the shock wave
2 burned gases or atmosphere behind the shock wave
\( o \) of the vessel before collapse
\( A \) ambient
\( CW \) combustion wave
\( L \) lower C-J point
\( P \) plug
\( PW \) pressure wave
\( U \) upper C-J point

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